PHASE TRANSITION STUDIES OF LIQUID CRYSTAL COLLOIDS

WITH SOLVENTS AND NANO-SOLIDS

by

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A Dissertation Submitted to the Faculty of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the Degree of Doctor of Philosophy

> in Physics

> > by

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April 15, 2011

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Abstract

This Dissertation presents a series of studies of dilution and different form of disorder effect on liquid crystal (LC) phase transitions. We have used high-resolution AC-calorimetry, dielectric spectroscopy as well as polarizing microscopy to characterize the effects of solvent such as hexane, acetone, decane, and nanomaterials such as multiwall carbon nanotubes and ferroelectric nanoparticles on the phase transitions of several liquid crystals. The liquid crystals of interest are: pentylcyanobiphenyl (5CB), octylcyanobiphenyl (8CB), and decylcyanobiphenyl (10CB). Studies have been carried out as a function of solvent, nanotube, and nanoparticles concentration and temperature spanning the isotropic to nematic (*I-N*), nematic to smectic-A (*N*-SmA), and isotropic to smectic-A (*I*-SmA) phase transitions.

The effect of dilution by a nonmesogenic, low molecular weight, miscible, and compatible solvent (n-hexane) on the isotropic-nematic (I-N) and the nematicsmectic-A (N-SmA) phase transition in the liquid crystal (LC) octylcyanobiphenyl (8CB) as a function of n-hexane concentration is reported. The heating and cooling temperature scans were performed without continuous mixing for all samples of n-hexane mole fraction ranging from 0.02 to 0.12 including the bulk 8CB. Generally, the *I-N* specific heat peaks shift towards lower temperature nonlinearly while becoming broader but retain the same first-order character as the bulk with increasing hexane concentration. The N-SmA heat capacity peak shifts nonmonotonically to lower temperature and evolves in shape, with a reproducible hysteresis, as x_{hex} increases. The N-SmA imaginary part of heat capacity remains zero up to $x_{hex}^{TCP} \simeq 0.07$ above which the distinct peak is observed, corresponding to a jump in both the real and imaginary enthalpy. A simple power-law analysis reveals an effective exponent that increases smoothly from 0.30 to 0.50 with an amplitude ratio $A^-/A^+ \to 1$ as $x_{hex} \to x_{hex}^{TCP}$. This observed crossover towards the N-SmA tricritical point driven by solvent concentration is consistent with previous results and can be understood as weakening of the liquid crystal intermolecular potential promoting increased nematic fluctuations. It is shown that solvent dilution

of an LC, if miscible and depending on solvent structure, can lead to a controlled altering of the intermolecular potentials responsible for mesophasic behavior.

The first-order transition from the isotropic (I) to smectic-A (SmA) phase in the liquid crystal 4-cyano-4'-decylbiphenyl (10CB) doped with the polar solvent acetone (ace) has been studied as a function of solvent concentration. Heating and cooling scans were performed for miscible 10CB+ace samples having acetone mole fractions from $x_{ace} = 0.05(1 \text{ wt.\%})$ to 0.36(10%) over a wide temperature range from 310 to 327 K. Two distinct first-order phase transition features are observed in the mixture whereas there is only one transition (I-SmA) in the pure 10CB for that particular temperature range. Both calorimetric features reproduce on repeated heating and cooling scans and evolve with increasing x_{ace} with the high temperature feature relatively stable in temperature but reduced in size while the low temperature feature shifts dramatically to lower temperature and exhibits increased dispersion. The coexistence region increases for the low-temperature feature but remains fairly constant for the high-temperature feature as function of x_{ace} . Polarizing optical microscopy supports the identification of a smectic phase below the high-temperature heat capacity signature indicating that the lowtemperature feature represents an injected smectic-smectic phase transition. These effects may be the consequence of screening the intermolecular potential of the liquid crystals by the solvent that stabilizes a weak smectic phase intermediate of the isotropic and pure smectic-A.

The study on the weakly first-order isotropic to nematic (I-N) and the continuous nematic to smectic-A (N-SmA) phase transitions of the liquid crystal octyl-cyanobiphenyl (8CB) doped with well dispersed multiwall carbon nanotubes (CNTs) as a function of CNT concentrations is reported. Thermal scans were performed for all samples having CNT weight fraction from $\phi_w = 0.0005$ to 0.0060 over a wide temperature range well above and below the two transitions in pure 8CB. Both the I-N and the N-SmA transitions evolve in character and have their transition temperatures qualitatively offset by $\sim 1.1 K$ lower as compared to that in pure 8CB for all 8CB+CNTs samples. The enthalpy change associated with each phase transition is essentially the same as that of pure 8CB and remains unchanged with increasing ϕ_w . However, there is an evidence that the thermal transport properties of the composites differ from the pure LC upon cooling below a ϕ_w dependent temperature within the nematic phase. In addition, a new C_p feature is resolved for intermediate ϕ_w samples that appears to be correlated to this onset temperature.

A combined high-resolution dielectric and calorimetric study of the isotropic (I) to nematic (N) phase transition of carbon nanotube (CNT) doped liquid crystal (LC) as a function of CNT concentration is reported. The evolution of the I-N phase transition, the temperature dependence of local nematic ordering formed by dispersed CNTs in the LC media and the transition enthalpy, were coherently

monitored. Anisotropic CNT-aggregates induce local deformation to the nematic director and form *pseudo-nematic* domains within the LC media. Results clearly indicate the dramatic impact of dispersed CNTs on both the isotropic and nematic phases of the LC+CNT hybrid system.

Finally, the weakly first-order isotropic to nematic (I-N) and the continuous nematic to smectic-A (N-SmA) phase transition study is reported on liquid crystal octylcyanibiphenyl (8CB) doped with a ferroelectric nano-particle Barium Titanate, BaTiO₃ (BT). A high-resolution ac-calorimetric study was performed as a function of temperature and BT concentration over a wide temperature range well above and below the two transitions. From the thermal scans of all samples ($\phi_m = 0.001$ to 0.014 and pure 8CB), it is revealed that both the I-N and the N-SmA transitions evolve in character and have their transition temperatures shift lower as the ϕ_m increases. Increasing hysteresis with increasing concentration is also observed at the I-N transition between heating and cooling ΔC_p peaks within the two-phase I+N coexistence region. These effects suggest that there are strong interactions between the polar LC molecules and ferroelectric BT nanoparticles.

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Acknowledgments

I would like to offer my deep and sincere gratitude to my supervisor Professor Germano S. Iannacchione, for his excellent guidance, stimulating suggestions, assistance and encouragement throughout this work. His profound knowledge and excellent experimental skill gave me an extraordinary experience. This work would never have been possible without his support and encouragement. I am deeply indebted for putting a lot of effort to teach me about experimental physics, technical writing and presentation techniques. Thank you very much.

I really appreciate a lot the help from all the members of the Physics Department at WPI, but especially that of the two secretaries, Jacqueline H. Malone and Margaret Caisse. Special thanks go to the department of Physics providing financial and moral support. I want to thank Roger Steele for his technical assistance.

I would like to express my sincere thank to Prof. P. K. Aravind for suggestions, guidelines and help throughout my stay at WPI and for serving my dissertation committee. Next, I would like to thank Prof. Georgi Georgiev from Assumption College for serving my dissertation committee.

I am also very grateful to my Dad, Mom and my daughters for their unconditional love and support. Lastly and most importantly, I thank my wife Srijana Sigdel for her support, encouragement, and understanding. Dedicated to my Dad and Mom.

Chapter

Introduction

1.1 Introduction

Liquid crystal (LC) is an anisotropic fluid which exhibits both the properties of solid and liquid. As its name suggests it is an intermediate phase of matter in between the liquid and crystal [1, 2]. The molecules in a crystal possess both positional and orientational order while the molecules in a liquid do not have any order and can move freely in random manner. The liquid crystal molecules possess orientational and partial translational order. LC can flow as a liquid and at the same time its molecules may be oriented in a certain direction like the molecules in a crystal do. LC has some crystalline properties such as magnetic, electric and optical anisotropy, periodic arrangement of molecules in one spatial direction as well as some typical properties of a liquid such as fluidity, elasticity and formation of droplets. For this reason, the LC phases are called mesophases(meaning 'in between phase') and the molecules that show mesomorphic phases are called 'mesogens'. Typically, the molecules are rod-like or disk-like. The rod like molecules or rod-like mesogens are elongated (~ 25 Å) and have anisotropic geometry which leads to preferential alignment along one spatial direction. Disclike molecules or discotic mesogens are flat and have more or less disc-shaped central core leading to two dimensional columnar ordering. A large number of wellknown compounds show liquid crystalline behavior e.g. cellulose, DNA, cholesterol esters, paraffins.

The credit for the discovery of liquid crystal goes to an Austrian botanical

physiologist Friedrich Reinitzer, even though the liquid crystalline behavior, without recognizing its nature, was observed in the past as well [3]. In 1888, Reitnizer observed two melting temperatures of cholesteryl benzoate [4, 5, 6]. At 145.5 °C it melts forming a cloudy liquid, that become clear at 178.5 °C. Reitnizer was puzzled with this peculiar feature shown by the compound and wrote to physicist Otto Lehmann seeking help from later's expertise of polarizing microscopy. After the observation of the sample gotten from Reinitzer, Lehmann realized that the cloudy liquid observed was a new state of matter and coined the name "liquid crystal", illustrating that it is something between a liquid and a solid, sharing important properties of both [7]. Today, thousands of other substances are known which have a diversity of phases between the solid and liquids. Interest in LC research increased after world war II. Development of industrial applications and basic studies of structure and phase transition of LC has promoted dramatic growth in LC research in recent years.

Liquid crystal technology has had a major effect in many areas of science and technology [8, 9]. The most common application of liquid crystal technology is liquid crystal displays which has grown to a multi-billion companies. From simple wrist watch, to an advanced computer screen LCDs have evolved into an versatile interface. LCD uses much less power than that CRTs use. Progress in understanding LC phases also helps the understanding of more complex soft materials such as cell membrane and of natural processes- e.g. certain diseases such as sickle-cell anemia.

Typically LCs are formed from organic molecules of rigid aromatic core of benzene rings and flexible end group. The molecules of the compounds which form liquid crystalline phase are often found to have following certain structural features:

(a) Anisotropic shaped molecules such as rod shaped or disc shaped having high aspect ratio which is length to breadth ratio (~ 4 for a typical liquid crystal 5CB) (b) Having flat comment as because ring

(b) Having flat segment e.g. benzene ring

(c) A fairly good rigid backbone containing double bonds defines the long axis of the molecule.

(d) The existence of easily polarizable and strong dipoles groups in the molecules.





Figure 1.1. Building Block of LCs.

A broad class of organic molecules with the general pattern as shown in Fig. 1.1 form liquid crystalline phases.

1.2 Liquid crystalline Phases

Based on the mechanism that drives the liquid crystalline self-assembly, LCs are usually classified into two broad categories: <u>Thermotropic</u> and <u>Lyotropic</u> liquid crystals. Thermotropic LCs are induced by thermal process. They show phase behavior change as a function of temperature. Thermotropic mesogens can be obtained either lowering the temperature of its isotropic phase or raising the temperature of its solid phase. The thermotropic LC which can be changed into the LC state either from lowering the temperature of a liquid or raising the temperature of a solid is called <u>enantiotropic</u> LC and the liquid crystal which reaches LC phase only upon a unidirectional change in temperature is called monotropic.

Lyotropic LCs are induced by solvent. Their phase behavior change due to the

change in concentration of solvent. The most common and conventional lyotropic LCs consist of amphiphilic (surfactant) molecules having a hydrophilic (polar) head and hydrophobic (non-polar) tail dissolved in water. When the amphiphilic molecules are dissolved in an appropriate solvent (*e.g.* water), they self-assemble in such a way that the polar heads are in contact with a polar solvent (water) and the non-polar tails are in contact with non-polar co-solvent producing small, essentially spherical aggregates (~ 5 nm in diameter) known as micelles. These micelles are formed only when the concentration of amphiphilic molecules is greater than some critical value. Below the critical concentration, the solution looks like general solvent with solute particles distributed randomly in a solvent. At higher concentrations, the molecules may arrange into planer bilayer membrane forming a lamellar phase. Lyotropic LCs are of great interest in biological studies.

LC displays varieties of intermediate thermodynamically stable phases but the most common and important are "Nematic" and "Smectic" phases. This nomenclature was provided by Friedel [10]. The brief description of each of these phases are as follows;

1.2.1 Nematic Phase

Nematic is the simplest liquid crystalline phase and derived its name from a Greek word $\nu\eta\mu\alpha$ meaning thread because of the observed thread-like defects in their structures while seen under polarizing microscope. In nematic phases (Fig. 1.2), the molecules are free to move in all directions *i.e.* there is no positional order of centers of mass but they tend to orient in a certain direction. The direction of preferred orientation can be described by a unit vector, \hat{n} , and is called nematic-director. For uniaxial nematic, the director \hat{n} is a "headless" vector *i.e.* $\hat{n} = -\hat{n}$. A nematic sample can be considered as a collection of large number of domains each of which has a single director. The directors in different domains may point in different directions and it changes smoothly from one domain to another due to the absence of real boundaries between the domains. The interface between the domains is called a topological defect.

The magnitude of local order is described by the orientational order parameter



Figure 1.2. Cartoon of nematic phase along with nematic texture observed under polarizing microscope. The scale bar is of 10 μ m.

which is the average of the second Legendre polynomial in the most useful form

$$S = \langle P_2(\cos\theta) \rangle = (1/2) \langle 3\cos^2\theta - 1 \rangle, \qquad (1.1)$$

where θ is the angle between a molecule's long axis and the director \hat{n} . The angled bracket indicates the local average over all the molecules. This quantity measures the average degree of molecular alignment with respect to the director[2]. In an isotropic phase, molecules are randomly oriented in all possible directions where $\langle \cos^2 \theta \rangle = 1/3$, so the order parameter S = 0. When the director \hat{n} is parallel to the long molecular axis (if all the molecules are oriented in one direction), $\theta = 0$ for all molecules, then $\langle \cos^2 \theta \rangle = 1$ and S = 1 and we get perfectly ordered nematic phase. If $\theta = \pi/2$, then $\langle \cos^2 \theta \rangle = 0$ making the order parameter S = -1/2. It is worth noting that S varies from -1/2 to 1 where -1/2 represents the unstable situation with all the molecules perpendicular to the director. Typically, S lies in between 0.6 - 0.8 in the deep nematic phase. Also, a simple form $\langle \cos \theta \rangle$ can not be used as an order parameter because of the fact that $\hat{n} = -\hat{n}$.

To get the information of order of molecules in a nematic phase the scalar nematic order parameter, S, is not sufficient and we need a macroscopic order parameter which is more general a symmetric and traceless second rank tensor (Q_{ij}) [2] and is established in three dimensions. For uniaxial nematic, it is given



Figure 1.3. Schematic of chiral nematic liquid crystal phase

by

$$Q_{ij} = \frac{1}{2} S \left(3\hat{n}_i \hat{n}_j - \delta_{ij} \right), \qquad (1.2)$$

where, i, j, = x, y, z are the axes of the coordinate system and δ_{ij} is the identity tensor.

When a molecule having its mirror image different from itself, called chiral molecule, is introduced in an achiral nematic system then a special type of nematic phase is formed which is known as chiral nematic (N^*) phase or cholesteric phase. In this phase, chiral packing produces the helix-like orientation of the director *i.e* \hat{n} rotates or twists along an orthogonal axis. See Fig. 1.3. This phase is characterized



Smectic-A

Figure 1.4. Cartoon of Smectic-A along with Smectic-A texture observed under polarizing microscope. The scale bar is of 10 μ m.

by pitch which is the distance over which the director makes one complete rotation in the helix and typically much larger than the molecular length and is of order of an optical wavelength. The pitch is generally temperature dependent.

1.2.2 Smectic Phase

As a thermotropic liquid crystal is cooled down from its nematic phase, a one dimensional positional ordering characterized by the formation of planer layers together with the long-range nematic orientation order develops. The phase thus formed is called smectic phase whose name is derived from a Greek word $\sigma \mu \eta \gamma \mu \alpha$ for "soap" (thick, slippery substance). Smectic phases (Fig. 1.4) have a layered structure with the molecules oriented parallel or tilted to the layer normal. In smectic-A (SmA), molecules are parallel to layer normal and in smectic-C (SmC) phase the molecules are tilted with respect to layer normal. They are characterized by absence of positional order within the layers *i.e.* molecules have some freedom to move within the layer but they are not free to move between the layers. Smectics can be considered as stacks of two dimensional fluids but they behave as crystalline across the layers. The one dimensional positional ordering in SmA or SmC may be described in terms of a density wave of the center of mass of the molecules [1, 2].

$$\rho(z) = \rho_0 \left[1 + |\psi| \cos\left(\frac{2\pi}{d}z\right) \right],\tag{1.3}$$



Figure 1.5. Cartoon of Smectic-A phase demonstrating molecular arrangement, the director orientation, and density distribution along layer normal z

where z is the coordinate parallel to the layer normal, ρ_0 is the average density, d is the layer spacing and $|\psi|$ is the amplitude of the density modulation and is a scalar smectic order parameter (the most important part of the order parameter). When $|\psi| = 0$, the density is uniform and there is no layered structure. Typically the value of $|\psi|$ is much less than one and decreases with increasing temperature. The spatial correlation of molecular positions decay algebraically to zero at long distances in contrary to a 3D solid where it decays to a finite constant. The algebraic decay of the correlation implies that the thermal fluctuations destroy the smectic order over sufficiently large length scale (Landau-Peierls instability) [11, 12]. However, in practice smectic layering is rather easily stabilized by confinement of samples between solid substrate. In the simplest smectic phase, SmA, the director \hat{n} is perpendicular to the smectic plane (Fig. 1.5). In each layer, the molecular centers of mass are arranged randomly and molecules have liquid-like freedom of translation and of rotation about their long axis[2, 13]. The SmA is optically uniaxial with the optical axis being normal to the layer plane.



Figure 1.6. Cartoon of Smectic-C phase

In SmC phase (Fig. 1.6), the molecules are arranged in layers as in SmA phase but the director is tilted at an angle θ with respect to smectic layer normal.

If the chirality is introduced in the SmC phase then a chiral smectic-C ($\text{Sm}C^*$) phase is formed. As in the chiral nematic phase, the director in $\text{Sm}C^*$ rotates from layer to layer in a helical fashion.

1.3 Review of Thermodynamics

The materials presented in this dissertation involve the characterization of thermal parameters like heat capacity, latent heat, enthalpy, entropy, free energy etc. In this section a brief review of thermodynamic parameters and basic thermodynamic relations are presented.

The word 'thermodynamics' comes from Greek origin meaning heat (therme) and energy or power (dynamics). Thermodynamics is that branch of physics which deals with the transformation of heat into mechanical work. Thermodynamics is used in many discipline such as physics, engineering, biochemistry etc. to understand physical processes and has innumerable applications. In thermodynamics, we consider macroscopic systems and never are interested in the atomic constitution of the matter.

A certain quantity of matter bounded by some closed surface is known as a system and anything outside this system which can exchange energy with it and has a direct bearing on the behavior of the system is called surroundings. The state of a system is defined by assigning values to a sufficient number of variables. The state of a system can be represented by specifying its pressure P, volume V, and temperature T provided the system is in equilibrium. These parameters describing the state of the system are called thermodynamic variables or thermodynamic coordinates. Therefore, a thermodynamic system can be described in terms of thermodynamic coordinates. A certain relation exists between these thermodynamic coordinates. The first and second law of thermodynamics provide two relations which respectively can be stated as,

$$dQ = dU + PdV, (1.4)$$

$$dQ = TdS. \tag{1.5}$$

Combining the two laws, we have

$$TdS = dU + PdV, (1.6)$$

$$dU = TdS - PdV. (1.7)$$

Here, dQ is amount of heat change, dU is change in internal energy, and dS is entropy change. For the complete description of a system these coordinates are not sufficient and we need some function which are the function of variables P, V, T, and S and are known as thermodynamic potentials or the state functions. Four important thermodynamic state functions are as follows;

1.3.1 Thermodynamic state functions

1. Internal or Intrinsic energy: The internal energy of a thermodynamic system is the energy possessed by the system by virtue of its molecular constitution and the position of the molecules and is defined by the equation,

$$dU = dQ - dW, (1.8)$$

where, dW is the external work done and may be replaced by PdV and dQ may be replaced by TdS by second law of thermodynamics. Therefore,

$$dU = TdS - PdV. (1.9)$$

When a system passes from one state to another, the change in internal energy is independent of the route followed between the two states.

2. Helmholtz free energy:

It is defined as

$$F = U - TS. \tag{1.10}$$

A small change in the Helmholtz free energy is related to change in heat and work via first law of thermodynamics:

$$dF = dU - d(TS) = dQ - dW - SdT - TdS = dQ - TdS - SdT - dW.$$
(1.11)

In reversible process

$$dF = -SdT - dW. (1.12)$$

At constant temperature

$$dF = -dW. \tag{1.13}$$

The Helmholtz free energy measures the amount of work a system can do in an isothermal reversible process. If the process is not reversible, $dQ-Tds \neq 0$ and dQ < TdS. Therefore, dF < -dW. The F at constant T is a minimum as a function of all parameters which are not fixed by external constraints.

3. Enthalpy: It is defined as

$$H = U + PV. \tag{1.14}$$

The enthalpy measures the amount of work a system can do in an adiabatic, isobaric process. This is the amount of non-mechanical work, since the pressure has to be kept constant.

4. Gibb's free energy:

It is defined as,

$$G = U - TS + PV. \tag{1.15}$$

The Gibbs potential measures the amount of work a system can do at constant temperature and pressure. The Gibbs potential measures the amount of non-mechanical work a system can do on the outside world at constant pressure and temperature.

1.3.2 Thermodynamic Response functions

Thermodynamic response functions are derivatives of one thermodynamic parameter with respect to another under specific conditions on the remaining variables.

1. Heat Capacity:

It is one of the most important response functions to measure. Measurement of heat capacity is the heart of our research in ac-calorimetry. It tells us how much heat the system will take up if we increase its temperature. These measurements can be done either at fixed pressure or volume. The specific heat at constant pressure is given by

$$C_p = \left(\frac{dH}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right).$$
(1.16)

In general, the source of a sample's heat capacity (C) are the fluctuations of the sample's energy. Thus, it is natural to consider C as a dynamic quantity. However, for most materials the characteristic relaxation time of the energy fluctuations are too short to be sensed by traditional calorimetric techniques. Nevertheless, a complex heat capacity may be defined containing a real (C')and imaginary (C'') component indicating the storage (capacitance) and loss (dispersion) of the energy in the sample analogous to a complex permittivity.

$$C^* = C' - iC''. (1.17)$$

2. Thermal expansivity:

Another important response function is thermal expansivity (or coefficient of thermal expansion) which is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p. \tag{1.18}$$

3. Isothermal compressibility:

It is defined as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$
(1.19)

1.4 General Description of Phase Transition

The sudden, dramatic change in a system's properties may occur by altering the thermodynamic variables such as temperature, pressure etc. We refer to this situation as a phase transition. Phase transitions present a challenge to statistical mechanics. By definition, at the transition point the system is expected to exhibit singular behavior.

1.4.1 Symmetry

The change in temperature of a system can cause a change in order and disorderness of a system. At the highest temperature a system will be at its most disordered state. It will have the highest symmetry possible. As the temperature is lowered, when there is a phase transition, that symmetry is frequently broken; the resultant system will have a lower symmetry.

1.4.2 Order of Phase transition

Order of a phase transition is an important tool to classify the nature of the nonanalytic behavior at the phase transition. When two phases co-exist they will each have same Gibbs free energy G.

Traditionally, phase transitions were characterized, by Paul Ehrenfest, on the basis of the nature of kink (discontinuity) in G. If n^{th} derivative of G with respect to temperature T, keeping other intensive variables constant, is discontinuous then the transition was said to be n^{th} order. Since $(\partial G/\partial T)_p = -S$, we see that the discontinuity in $(\partial G/\partial T)$ is the change in entropy between the two phases. Thus at a first order phase transition, the entropy changes discontinuously, while at second order and higher order transitions the entropy varies continuously. And since the latent heat is given by $T\Delta S$ it follows that there is latent heat involved with a first order phase transition, but not with higher orders.

Nowadays Ehrenfest classification is no longer used. According to modern classification, there are two types of transitions one being a first-order and the other second-order or continuous phase transition. First-order phase transition involves latent heat and discontinuity in thermodynamical parameters. In secondorder phase transition no discontinuity occurs; all the thermodynamic parameters vary continuously.

A first-order phase transition from a phase a to phase b can be formulated as [13]

$$G_a - G_b = 0, \qquad (1.20a)$$

$$-\left[\frac{\partial G_b}{\partial T}\right]_P + \left[\frac{\partial G_a}{\partial T}\right]_P = S_b - S_a = \Delta S = L/T, \qquad (1.20b)$$

$$\left[\frac{\partial G_b}{\partial P}\right]_T - \left[\frac{\partial G_a}{\partial P}\right]_T = V_b - V_a = \Delta V, \qquad (1.20c)$$

where, ΔS and ΔV are changes in entropy and volume respectively at the transition and L is latent heat. For the first-order transition, changes in enthalpy $\Delta H($ or $\Delta S)$ and in volume ΔV are observed.

For second-order phase transition both ΔH and ΔV are zero but second derivative of Gibbs function with respect to temperature and pressure lead to change in heat capacity, expansivity and compressibility [13].

$$G_a(T, P) = G_b(T, P), \qquad (1.21a)$$

$$-\left[\frac{\partial G_b}{\partial T}\right]_P + \left[\frac{\partial G_a}{\partial T}\right]_P = S_b - S_a = \Delta S = 0, \qquad (1.21b)$$

$$\left[\frac{\partial G_b}{\partial P}\right]_T - \left[\frac{\partial G_a}{\partial P}\right]_T = V_b - V_a = \Delta V = 0, \qquad (1.21c)$$

$$\left[\frac{\partial^2 G_b}{\partial T^2}\right]_P + \left[\frac{\partial^2 G_a}{\partial T^2}\right]_P = \frac{1}{T}[C_{p_a} - C_{p_b}] = \frac{\Delta C_p}{T},$$
(1.21d)

$$\left[\frac{\partial^2 G_b}{\partial P^2}\right]_T - \left[\frac{\partial^2 G_a}{\partial P^2}\right]_T = V[\kappa_a - \kappa_b] = V\Delta\kappa, \qquad (1.21e)$$

$$\left[\frac{\partial^2 G_b}{\partial P \partial T}\right] - \left[\frac{\partial^2 G_a}{\partial T \partial P}\right] = V[\alpha_a - \alpha_b] = V \Delta \alpha.$$
(1.21f)

1.4.3 Order Parameter

A Phase transition occurs when a new state of symmetry develops from either ordered (low temperature) or disordered (high temperature) phase. The ordered phase has a lower symmetry due to the breaking of symmetry during the transition of disordered to ordered phase. The ordered state can be characterized by introducing a parameter that describes the character and strength of the broken symmetry which is called an order parameter, ϕ . The order parameter provides the extent to which the configuration of molecules in the less symmetric (more ordered) phase differs from that in the more symmetric (less ordered) phase. In general, an order parameter describing a phase transition satisfies the following requirements:

1. $\phi = 0$, in the more symmetric (less ordered) phase, and

2. $\phi \neq 0$, in the less symmetric (more ordered) phase.

The choice of a order parameter follows in a quite natural way and depends upon the system involved but not in the unique way given by the above requirements. In the case of ferromagnetic transitions, the magnetization which is a vector with three components is an order parameter. In the case of liquid-vapor transition, the order parameter is the difference in density between liquid and vapor phases.

1.5 Theoretical Background

1.5.1 Landau Theory of Phase Transition

Phase transitions involve symmetry breaking (or developing). Generally more symmetric (disordered) phase is a high-temperature phase and lower symmetric (ordered) phase is a low-temperature phase. This symmetry breaking can be represented by order parameters. The original Landau theory is based on the fact that the thermodynamic quantities of the lower symmetry phase can be obtained by expanding the thermodynamic potential in powers of the order parameters and its spatial variation in the neighborhood of the order-disorder transition point and that sufficiently close to the transition, only the leading terms of the series are important so that the said expansion becomes a single low-power polynomial. The thermodynamic behavior of the order parameters in the more ordered phase is then determined by minimizing the thermodynamic potential.

Let us consider a macroscopic system the equilibrium state of which is characterized by a spatially invariant, dimensionless, scalar order parameter ϕ . The general form of the Landau free energy is postulated to be

$$F(P,T,\phi) = F(P,T,0) + r\phi + \frac{1}{2}A\phi^2 + \frac{1}{3}B\phi^3 + \frac{1}{4}C\phi^4 + \cdots, \qquad (1.22)$$

where, F(p,T,0) is free energy for a given pressure and temperature of the state with $\phi = 0$. The coefficients r, A, B, C are phenomenological constants and function of temperature and pressure. The equilibrium states can be obtained by minimizing F with respect to ϕ for fixed P and T *i.e.*

$$\frac{dF}{d\phi} = 0, \quad \frac{d^2F}{d\phi^2} > 0. \tag{1.23}$$

At the transition temperature these stability conditions are

$$\frac{dF}{d\phi} = r = 0, \quad \frac{d^2F}{d\phi^2} = A = 0,$$
 (1.24)

because of the coexistence of both the regions. The condition, r = 0, is derived from the fact that high temperature phase with $\phi = 0$ must give rise to an extreme value of $F(P, T, \phi)$. The second condition, $A = a(T - T_c)$ with $a = (dA/dT)_{T_c} > 0$, follows from the behavior of F at $\phi = 0$ for T above and below the transition temperature T_c . The landau theory postulates that the phase transition can be described by the expression

$$F(P,T,\phi) = F(P,T,0) + \frac{1}{2}a(T-T_c)\phi^2 - \frac{1}{3}B\phi^3 + \frac{1}{4}C\phi^4 + \cdots$$
(1.25)

The Eq. (1.25) has following solutions near the phase transition;

$$\phi = 0, \quad \phi = \frac{B \pm [B^2 - 4ac(T - T_c)]^{1/2}}{2C}.$$
 (1.26)

Here, the negative sign of B is chosen for the reason of convenience. The coefficients B and C may be treated as temperature independent coefficients. The discontinuity of ϕ at the transition requires B = 0 i.e. for low temperature ϕ reads

$$\phi = \frac{a[(T - T_c)]^{1/2}}{C}, \quad C > 0.$$
(1.27)

For a phase which remains invariant by replacing ϕ with $-\phi$, only even powers of ϕ survive. Thus in case of second order phase transition

$$F(P,T,\phi) = F(P,T,0) + \frac{1}{2}A\phi^2 + \frac{1}{4}C\phi^4 + \cdots$$
(1.28)

For spatially non-uniform system where the order parameter varies in space ($\phi = \phi(r)$), we need to add a term of the form $\gamma [\nabla \phi(r)]^2$ in free energy expansion. The equation then reads,

$$F(P,T,\phi) = F(P,T,0) + \frac{1}{2}A\phi^2 - \frac{1}{3}B\phi^3 + \frac{1}{4}C\phi^4 + \dots + \frac{1}{2}\gamma[\nabla\phi(r)]^2.$$
(1.29)

Even though the Landau theory is mainly for second order phase transition, it

can be extended to the first order phase transition. For the first order transition, B = 0, C < 0 and the third order term $B\phi^3$ must present in the free energy expansion.

The problem with this theory is that the coefficients appearing in the expansion are phenomenological and their dependence on the molecular properties are not defined. In addition, this theory does not contain any information about the molecular interactions. Despite these difficulties, Landau theory has been successfully applied to varieties of phenomena. It is simpler than mean-field (MF) theory.

1.5.1.1 Isotropic to nematic (*I*-*N*) phase transition

The nematic state is described by the symmetric traceless tensor order parameter Q. For description of the isotropic to nematic (I-N) phase transition, the free energy density (energy per unit volume) f near the transition is expanded up to fourth or sixth order in Q and all the terms must be invariant combinations of order parameter under all rotations. For uniaxial nematic, in general, the free energy density is given by [14]

$$f = f_0 + \frac{1}{2}A(\frac{2}{3}Tr(Q^2)) - \frac{1}{3}B(\frac{4}{3}Tr(Q^3)) + \frac{1}{4}C(\frac{4}{3}Tr(Q^4)) + \dots + D[\nabla Q]^2 + E(\hat{n}.\nabla Q)^2 + f_{FE} + f_{SE} + f_{EM} + \bigcirc (Q^5),$$
(1.30)

where, A, B, C, D, and E are phenomenological parameters. The terms f_{FE} , f_{SE} , and f_{EM} add the contribution of free energy due to frank elastic energy, surface elastic free energy, and electromagnetic interaction respectively. The terms containing gradient account for the spatial variation of the order parameter. The presence of cubic term ensures the first order nature of the *I-N* phase transition. Since the *I-N* transition takes place near A = 0 it is assumed that the parameter A is only temperature dependent term and the others can be regarded as temperature independent. We can write

$$A = a(T - T^*), (1.31)$$

where, a is a positive phenomenological constant and T^* is the limit of metastability of the isotropic phase.

In the simplest model and in terms of scalar nematic order parameter S, the

free energy density for the I-N phase transition can be written as

$$f = f_0 + \frac{1}{2}AS^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + \cdots$$
(1.32)

In the isotropic phase S = 0 and in the nematic phase $S \neq 0$. The constant B > 0 for uniaxial phase with positive anisotropy.

The thermodynamic quantities such as transition temperature T_{IN} , the value of order parameter, entropy and latent heat can be calculated by requiring that fbe an extremum with respect to S in equilibrium and that the free energies of the ordered and disordered phases (nematic and isotropic) be equal at the transition. The later condition implies that the nematic and the isotropic phases can coexist at the transition temperature. If other variables such as pressure, density are included in our expression, the two phase would exist along a range of temperatures rather than at a single point. The equations determining thermodynamic parameters are

$$f = \left[\frac{1}{2}a(T_{IN} - T^*) - \frac{1}{3}BS + \frac{1}{4}CS^2\right]S^2 = 0, \qquad (1.33)$$

$$\frac{\partial f}{\partial S} = [a(T_{IN} - T^*) - BS + CS^2]S = 0.$$
(1.34)

Solving these equations, we can get two possible solutions:

$$S_{IN} = 0, \quad T_{IN} = T^*;$$
 (1.35)

$$S_{IN} = \frac{2B}{3C}, \quad T_{IN} = T^* + \frac{2B^2}{9aC}.$$
 (1.36)

When $T^* < T < T_{IN}$, the minimum corresponds to a nematic phase. There exists a local minimum corresponding to a possible supercooled isotropic state.

The transition entropy density at T_{IN} is given by

$$\Delta s = -\frac{\partial (f - f_0)}{\partial T}|_{T = T_{IN}} = -\frac{1}{2}aS^2 = -\frac{2aB^2}{9C^2}.$$
(1.37)

The contributions other than included in the model always ensure the positive value of the entropy. Since the I-N is a first-order transition, there is presence of latent heat (discontinuity of enthalpy) associated with the transition. The latent
heat per unit volume is given by

$$\Delta H = T_{IN} \Delta s = \frac{2aB^2 T_{IN}}{9C^2}.$$
(1.38)

The heat capacity C_p in the nematic phase diverges close to T_{IN} as

$$C_p \sim |t|^{-0.5},$$
 (1.39)

where, $t = (T^{**} - T)/T_{IN}$, and T^{**} is the superheating temperature of the nematic phase. In the isotropic phase, $C = C_0$ is constant and at T^{**} it shows a jump.

1.5.1.2 Nematic to Smectic-A (N-SmA) phase transition

The nematic to smectic-A (N-SmA) transition in an uniaxial nematic liquid crystal involves the rearrangement of the molecules in the layered structure. Molecular centers in SmA are, on average, arranged in equidistant plane. Within these layers the molecules can move randomly remaining the director perpendicular to the smectic layers. In the thermodynamic limit, there exist no true long-range translational order in SmA phase and the N-SmA phase transition theory is a theory of one dimensional melting. At the N-SmA phase transition, the continuous translational symmetry of the nematic phase is spontaneously broken by the appearance of one dimensional density wave in the SmA phase. Mcmillan [15] and de Gennes [2] theories suggested that the N-SmA transition could be first-order or second-order changing the order at tricritical point (TCP). However HPL theory [16, 17] argued that the N-SmA transition can never be second order ruling out the possibility of TCP. Now, it is believed that the N-SmA phase transition is continuous in the absence of special circumstances [2].

The Landau-de Gennes theory for the N-SmA phase transition can be developed by defining order parameter for the SmA phase. The order parameter is $|\psi|$ and is defined as the amplitude of a one dimensional density wave where wave vector q_0 is parallel to the nematic director (the z-axis), $\rho(\vec{r}) = Re[\rho_0 + \exp(i\vec{q_0}.\vec{r})\psi(\vec{r})]$, $q_0 = 2\pi/d$ is the wave vector corresponding to the layer spacing d. The complex field $\psi(\vec{r}) = \psi_0 \exp(i\vec{q_0}.\vec{r})$ has its spatial variation on scale larger than d. Since the difference between a value of $-|\psi|$ and $|\psi|$ only amounts to the choice of the origin the expansion in terms of $|\psi|$ only contains even-power terms. The free energy density near the N-SmA transition is given by

$$f_{SmA} = \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 + \cdots, \qquad (1.40)$$

where, $\alpha = \alpha_0(T - T_0)$, α_0 , and β are constants. At temperature $T_{NA} = T_0$ and below T_0 , α vanishes and above this temperature it is positive. The coefficient β is always positive. On these consideration alone one could have second-order (continuous) N-SmA phase transition but there are number of complications that needs to be considered.

First, the coupling between smectic order parameter ψ and scalar nematic order parameter S. To account this coupling a term of the form $f_1 = -C\psi^2 \delta S$ should be added in the free energy density expression. Here, C is a positive constant and $\delta S = S - S_0$ is increase in the nematic order that comes from the fact that the value of S does not coincide with S_0 obtained in the absence of smectic order.

Second, the nematic free energy density which is minimum for $\delta S = 0$ must be added to the free energy expression (1.40). The nematic free energy density is given by

$$f_N = f_N(s_0) + \frac{1}{2\chi} \delta S^2, \qquad (1.41)$$

where, $\chi(T)$ is a response function (susceptibility), which is large but finite near the *I-N* transition T_{IN} and small for $T < T_{IN}$ because of the nearly saturation of S_0 . The total free energy density is

$$f_S = f_N(s_0) + f_1 + f_{SmA} = f_N(s_0) + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 - C\psi^2\delta S + \frac{1}{2\chi}\delta S^2 + \cdots$$
(1.42)

Minimizing f_S with respect to δS , we get $\delta S = C\psi|^2\chi$. Therefore,

$$f_S = f_N(s_0) + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta'|\psi|^4 + \cdots, \qquad (1.43)$$

with $\beta' = \beta - 2C^2 \chi$. Depending on the values of C and χ and the resulting sign of β' three different cases can be obtained:

(i) If $T_0 \sim T_{IN}$, $\chi(T_0)$ is large and β' is negative. In this case the transition is of first-order and takes place at $T_{NA} > T_0$. One must add a positive sixth order term in the free energy to ensure the stability.

(ii) If $T_0 \ll T_{IN}$, $\chi(T_0)$ is large and β' is positive. In this case the transition is of

second-order and takes place at $T_{NA} = T_0$.

(iii) When $\beta' = 0$, $\chi(T_{NA}) = 2\beta/C^2$ and one has a crossover from a continuous (second-order) to first-order transition and corresponds to a tricritical point (TCP). We also need to consider the following effects:

 \Box the director fluctuation in nematic phase [18, 19] which gives rise to a coupling term of the form $f_{\hat{n}} = -C_{\hat{n}}|\psi|^2$ and should be added to the free energy relation. \Box layer fluctuation in the smectic phases.

 \Box the coupling between the nematic order parameter tensor Q_{ij} with the smectic order parameter (may be in the form of $f_2 \sim D\psi^2 \delta Q$).

In summary, one should include all possible effects in free energy.

1.5.1.3 Isotropic to smectic-A (*I*-SmA)phase transition

The direct *I*-Sm*A* transition is observed for some liquid crystals and is of first order in nature. As in the case of the *I*-*N* and the *N*-Sm*A* phase transitions we begin by defining order parameters. The nematic order parameter is a symmetric, traceless tensor given by $Q_{ij} = (1/2)S(3\hat{n}_i\hat{n}_j - \delta_{ij})$. The smectic order parameter $\psi(\vec{r}) = \psi_0 \exp(-i\varphi)$ is a complex quantity the modulus $|\psi_0|$ of which is the amplitude of a one dimensional density wave characterized by a phase φ . The layer spacing is given by $d = (2\pi)/q_0$ with $q_0 = |\nabla \varphi|$. The total free energy density near the *I*-Sm*A* transition reads [20]

$$f = f_0 + \frac{1}{2}AS^2 - \frac{1}{4}BS^3 + \frac{9}{16}CS^4 + \frac{1}{2}\alpha\psi_0^2 + \frac{1}{4}\beta\psi_0^4 + \frac{3}{4}\lambda\psi^2S^2 + \frac{1}{2}b_1\psi_0^2q_0^2 + \frac{1}{2}b_2\psi_0^2q_0^2 + \frac{1}{2}e_1S\psi_0^2q_0^0),$$
(1.44)

where, f_0 is the free energy density of the isotropic phase, $A = a(T - T_{IN}^*)$, and $\alpha = \alpha_0(T - T_{IA}^*)$. The T_{IN}^* and T_{IA}^* are the critical temperatures for hypothetical second order transition to nematic and smectic state respectively in the absence of cross coupling. All other coefficients including α and α_0 are assumed to be constant near the transition point. The sign of the coupling coefficient λ of the direct coupling between nematic and smectic order determines the stability of a phase over the other. The negative sign of λ favors the smectic-A phase over the nematic whereas the positive λ favors the nematic phase over the smectic-A phase.

For negative λ , the transition is always the *I*-Sm*A* without a nematic phase in

between. At $T = T_{IA}$, the free energy has two minima: one at S = 0 corresponding to an isotropic phase and the other at $S \neq 0$ corresponding to a smectic-A phase. At the *I*-SmA transition, the isotropic minima at S = 0 and the smectic-A minima at $S \neq 0$ (or at S_{SmA}) have equal free energies with a barrier height separating them. To prevent the possible arrival of the *I*-N transition before the *I*-SmA transition, the T_{IA} has to be larger than the T_{IN} .

1.5.1.4 Effect of solvent on phase transitions

Phase transitions are modified in the presence of non-mesogenic, low-molecular weight solvents. Generally solvents dilute the liquid crystal and change the intermolecular potential significantly. Consequently the change in the phase transition behavior in the mixture takes place. In the presence of a non-mesogenic, low-molecular weight solvent, the Landau-de Gennes free energy density for the I-N transition takes the form [21]

$$f = f_0 + \frac{1}{2}AS^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + E(x)S^2 + \cdots, \qquad (1.45)$$

where, the term $E(x)S^2$ has been added to account for the coupling of the order parameter S and the solvent concentration x. E(x) can be expanded as a power series of x. Keeping only the leading terms and solving the equation, the new transition temperature, new order parameter etc. under the influence of the solvent can be found.

For the N-SmA phase transition, we can modify Landau-de Gennes free energy density by adding two solvent concentration dependent terms and a term related to the free energy density of the solvent itself [21]

$$f_S = f_N(s_0) + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 - C\psi^2\delta S + \frac{1}{2\chi}\delta S^2 + A\psi^2 x + D\psi^2\delta S x + ES^2 x + \cdots$$
(1.46)

Minimizing this energy with respect to δS , different thermodynamic quantities can be found.

Similarly free energy density expression for the I-SmA phase transition can be modified by adding appropriate x dependent terms in the general expression.

To fully understand the system, all the possible effects such as effect of director

fluctuations, coupling between Q (not only S) and ψ , coupling between Q, ψ , and x should be included in the free energy density relation.

1.6 Review of LC mixtures and composites

As a way of exploring the fundamental nature of the LC interactions responsible for mesogenic order, critical behavior, and the tuning of viscoelastic properties, attention has been drawn to the study of miscible mixtures of liquid crystals and non-mesogenic, low-molecular weight, solvents [21, 22, 23, 24, 25]. X-ray diffraction experiments performed on the smectic-A and smectic-C phases of thermotropic liquid crystals mixed with an organic solvent have shown that the smectic layer spacing increases with solvent content [25]. This research also demonstrated the formation of an organic lyotropic lamellar liquid crystal phase in which the solvent molecules largely intercalate between the smectic layers of the LC. It was also mentioned that from a visual inspection of octylcyanobiphenyl (8CB) and n-hexane (hex) mixtures that the solvent was not uniformly distributed throughout the host LC and minimal, non-reproducible, swelling of smectic layers occurred for solvent volume fractions ≥ 0.1 . It was then suggested that the amount of solvent that can be miscibly incorporated in an LC depends on the host LC, temperature, as well as the nature and amount of solvent; noting that the 8CB+hex mixture phase separates for a solvent to liquid crystal mole ratio ≥ 0.1 . Other studies of the effect of a biphenyl solvent on the splay and bend elastic constants and the rotational viscosity coefficient observed an anomalous behavior of the splay elastic constant K_{11} , the dielectric anisotropy $\Delta \varepsilon$, and the effective rotational viscosity coefficient γ_1^* near the N-SmA transition [26]. A theoretical study on the influence of nonmesogenic solvent on the N-SmA phase transition using Landau approach found a concentration induced tricritical point for the N-SmA transition and that the Frank elastic constants K_{11} , K_{22} , and K_{33} are modified as a function of solvent concentration near the N-SmA phase transition [23].

When carbon nanotubes (CNTs) are dispersed in a liquid crystal, they can modify the physical properties of the liquid crystal. In a well-dispersed CNT in a LC host, there is surface anchoring of the LCs on the CNT surfaces, presumably through the $\pi - \pi$ stacking of the hexagonal structure of both the biphenyl and graphene, that is strengthened by a binding energy originating from charge transfer between the LCs and CNT [27]. In recent years, the dispersion of CNTs in liquid crystal media has attracted intense interest. Research has been focused on dispersion and alignment of CNTs in thermotropic or lyotropic liquid crystals [28, 29, 30, 31, 32, 33, 34], and studies of LC+CNT composite system for improving electro-optical switching properties [35, 36, 37, 38, 39]. Some research efforts have also been made on phase behavior and phase transitions of LC+CNT mixtures [40, 41, 42]. LC+CNT binary systems were investigated using optical microscopy and DSC, finding an enhancement of the isotropic to nematic (*I-N*) phase transition temperature revealing a "chimney" type phase diagram in LC+CNT mixtures over a narrow range of ~ $0.1 - 0.2 \ wt.\%$ of CNT [40]. An *I-N* phase transition was observed in a LC+CNT suspension due to the joule heating produced by a dc-electric field that rotates the CNT out of sample plane short-circuiting the electrodes and producing a current flow through the CNT [42].

The hybrid system containing liquid crystal and ferroelectric nano-particles such as barium titanate (BaTiO₃) and tin-hypodiphosphate $(Sn_2P_2S_6)$ are interesting because of the composite system shows the new properties that are not observed in pure LC. The ferroelectric nano-particles of smaller size (around 20 nm) can influence the physical properties of liquid crystal without forming defects and disturbing the LC director [43]. It has been shown that the addition causes an increase of the isotropic to nematic phase transition temperature [44], increase in dielectric anisotropy [43, 45], higher birefringence and lower voltage and conductivity [46].

1.7 Dissertation Outline

This dissertation presents the experimental results on the effect of solvents on the liquid crystalline phase transitions using high-resolution AC-calorimetry, dielectric spectroscopy, and polarizing microscopy. It also provides the studies of the influence of nano-materials such as carbon nano-tubes (CNTs) and BaTi0₃ nano-particles, on the LC phase transitions. We emphasize the I-N, N-SmA, and I-SmA phase transitions.

Chapter 2 deals with the brief review of experimental techniques we used ac-

calorimetry, polarizing microscopy, and dielectric spectroscopy. Chapter 3 presents the result of influence of hexane (hex) on the I-N transition of octylcyanobiphenyl (8CB) in the binary mixture of 8CB+hex. Chapter 4 provides the details of the investigation of 8CB+hex system on the N-SmA phase transition. Chapter 5 presents the effect of acetone (ace) on the I-SmA phase transition in 10CB+ace system. Chapter 6 provides the effect of carbon nano-tubes on the I-N and the N-SmA phase transition of 8CB+CNT and 5CB+CNT systems. Chapter 7 provides the studies on the influence of BaTiO₃ ferroelectric nano-particles on the I-N and the N-SmA phase transition. Chapter 8 presents the conclusion of our work and the future directions.

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Chapter

Experimental Techniques

2.1 Review of AC-Calorimetry

2.1.1 Introduction

There are many successful methods to study different phase transitions of liquid crystals; some of them include calorimetry, x-ray diffraction, neutron scattering, light scattering, NMR, optical microscopy, etc. Among the different calorimetric techniques to study liquid crystals, traditional adiabatic calorimetry has high precision and can be used to determine the latent heat of strong first-order transitions. However, this method does not have enough resolution possibilities to characterize a second-order transition and requires a large sample of several grams to get reliable data [1]. Differential Scanning Calorimetry (DSC) has high sensitivity, making it a widely used method because of its ease of operation and small sample size (10 mg). Due to rapid scan rates of 1-5 K/min, the precision and absolute accuracy in enthalpy changes are modest, and the temperature resolution is poor [2]. Since its introduction into the literature during the late 1960s [3], the AC-calorimetry has developed into a very powerful, well-established and widely used technique for studying a variety of phase transitions in liquid crystals, polymers and biological systems.

AC-calorimetry, originally introduced by Sullivan and Seidel [3], and Handler et al. [4], is a semi-classical, well-established, widely used, and very reliable technique. AC technique is a versatile technique which is demonstrated by many existing studies on several different systems, such as low temperature properties of superfluid helium films adsorbed in porous glass [5] and graphite [6], superconducting films [7], melting of nitrogen on graphite [8], bulk liquid crystal [9], and free-standing liquid crystal films[10]. Some of the characteristic features of the AC-calorimetry are as follows:

- 1. Heat capacity measurements are made in quasi-equilibrium condition which is crucial because of the fact that many thermodynamic theories of phase transition are based on equilibrium considerations.
- 2. Only a small amount of sample is sufficient for high resolution measurement which is important fact for ensuring the thermal equilibrium as well as when large amount of a batch of a sample is not available.
- 3. Perfect thermal isolation of the sample from the surrounding is not required.
- 4. It can measure thermal conductivity and dynamic heat capacity $C_p(\omega)$.
- 5. Extremely high relative caloric sensitivity. Results better than 0.001% at low temperatures are typical.
- 6. Very high temperature resolution (in the μK range) and very wide temperature range, from 50 mK to above 3000 K

The calorimeter in our lab has dual mode- AC mode as well as non-adiabatic scanning mode. Non-adiabatic scanning (NAS) calorimetry allows to extract latent heat information which cannot be measured by an AC mode. Although the relative accuracy is very high, the absolute accuracy of the measured heat capacity is about 1-10%, due to the sensitivity to the internal and external thermal relaxation times.

2.1.2 Theory of Operation

The basic principle of the AC-calorimetric technique consists of heating a sample by periodically modulated sinusoidal power and monitoring the resulting temperature oscillation. The basic equation of AC-calorimetry can be roughly calculated using the definition of heat capacity as follow:

$$C_p = \left| \frac{dQ}{dT} \right| = \left| \frac{dQ/dt}{dT/dt} \right| \approx \frac{P_0}{\omega T_{ac}},$$
(2.1)

where, P_0 is the amplitude of the power oscillation, ω the power frequency, and T_{ac} the amplitude of the temperature oscillation. Application of oscillatory heating power and obtaining resulting oscillating temperature can be achieved by using heaters and thermistors attached on the surfaces of the cell. One has to take thermal coupling in a calorimetric cell into account when separate heaters and thermometers are used. Sullivan and Siedel [3] performed the thermal analysis considering a simple thermal model as shown in Fig. 2.1 which is called one lump thermal model. The model considers a heater (h) of heat capacity C_h and of temperature T_h , a sample (s) with heat capacity C_s and of temperature T_s , and a thermometer (θ) of heat capacity C_{θ} and of temperature T_{θ} interconnected by thermal conductances K_h and K_{θ} . The cell+sample+heater+thermistor system in connected to a thermal bath (b) of heat capacity C_b and temperature T_b via a thermal link of conductance K_b . This model becomes geometry independent i.e., the locations of heater, thermometer, as well as the cell geometry, are not important, as long as certain requirements are met. The model assumes the zero thermal resistance between the sample and the cell.

The heat-balance equations for the system are $(T' = \partial T / \partial t)$ [11]

$$C_h T'_h = P_0 e^{i\omega t} - K_h (T_h - T_s),$$
 (2.2a)

$$C_s T'_s = K_h (T_h - T_s) - K_b (T_s - T_b) - K_\theta (T_s - T_\theta),$$
 (2.2b)

 $C_{\theta}T'_{\theta} = K_{\theta}(T_s - T_{\theta}). \tag{2.2c}$

The steady-state solution for these equations consists of a bath temperature term, a constant term depending upon K_b and oscillating term which is inversely proportional to the heat capacity

$$T_{\theta} = T_b + T_{dc} + T_{ac}e^{i(\omega t + \Phi)}, \qquad (2.3)$$

where, $T_{dc} = P_0/K_b$ is the rms temperature raise, Φ is the absolute phase difference between power and temperature oscillations, and ω is modulation frequency.

If we make the assumptions (i) the heat capacities of the heater and of the thermometer are much smaller than that of the sample (ii) the sample, the heater, and the thermometer come to in equilibrium in a time (τ_i - internal time constant or relaxation time) much shorter than the modulation period i.e., $\omega \ll 1/\tau_i$ and



Temperature Bath

Figure 2.1. Schematic diagram of the One Lump Thermal Model used for AC Calorimetry.

(iii) the modulation period is much shorter than the sample-to-bath relaxation time $(\tau_e - \text{external time constant}) \ i.e., \ \omega \gg 1/\tau_e$, then the amplitude of the temperature oscillation can be written as;

$$T_{ac} = \frac{P_0}{\omega C} \left(1 + \frac{1}{\omega^2 \tau_e^2} + \omega^2 \tau_{ii}^2 + \frac{2}{3} \frac{K_b}{K_s} \right)^{-\frac{1}{2}}.$$
 (2.4)

And the phase difference between the temperature and power oscillations is given by

$$\Phi = -\frac{\pi}{2} + \arctan\left(\frac{1}{\omega\tau_e} - \omega\tau_i\right).$$
(2.5)

The various relaxation times (time constants) are defined as follows:

$$\tau_h = C_h / K_h, \tag{2.6a}$$

$$\tau_s = C_s/K_s, \tag{2.6b}$$

$$\tau_{\theta} = C_{\theta}/K_{\theta}, \qquad (2.6c)$$

$$\tau_e = C/K_b, \qquad (2.6d)$$

$$\tau_i = \tau_h + \tau_s + \tau_\theta, \qquad (2.6e)$$

$$\tau_{ii}^2 = \tau_h^2 + \tau_s^2 + \tau_\theta^2, \qquad (2.6f)$$

for the sample (s), heater (h), and thermometer (θ), indicating the characteristic thermal relaxation time for each element with the total heat capacity of the system $C = C_h + C_s + C_{\theta}$. Under the conditions where the above assumptions mainly,

$$\frac{1}{\tau_e} << \omega << \frac{1}{\tau_i}, \tag{2.7}$$

are well satisfied, the expression calculating heat capacity takes the form

$$C = \frac{P_0}{\omega T_{ac}} = C^*. \tag{2.8}$$

We usually use the relative phase shift φ , which doesn't carry the constant $-\pi/2$ phase difference, between the temperature and the power as:

$$\varphi = \Phi + \pi/2. \tag{2.9}$$

Therefore,

$$tan(\varphi) = \frac{1}{\omega\tau_e} - \omega\tau_i = \frac{K_e}{\omega C} - \omega \left(\frac{C_s}{K_s} - \frac{C_h + C_\theta}{K_h + K_\theta}\right).$$
(2.10)

The phase shift is related to both the heat capacity and the thermal conductance of the system.

The heat capacity is frequency dependent and can be considered as a complex quantity which can be expressed as combination of real, $C'(\omega)$, and imaginary, $C''(\omega)$, parts:

$$C'(\omega) = C'(\omega) - iC''(\omega), \qquad (2.11)$$

analogous to the complex permittivity real heat capacity representing in-phase (capacitive) part and imaginary part representing loss (dispersive) part of heat capacity. Solving Eqs. (2.4) and (2.10) for C' and C'', yields:

$$C'(\omega) = \frac{P_0}{\omega T_{ac}} \cos \varphi * f(\omega), \qquad (2.12a)$$

$$C''(\omega) = \frac{P_0}{\omega T_{ac}} \sin \varphi * g(\omega) - \frac{K_b}{\omega}, \qquad (2.12b)$$

where,

$$f(\omega) = \left[1 + \cos^2(\varphi) \left(\frac{2K_b}{3K_s} + \frac{2\tau_i}{\tau_e} - 2\tau_s\tau_c\omega^2\right)\right]^{-1/2}, \quad g(\omega) = f(\omega) \left[1 + \frac{\omega\tau_i}{\tan(\varphi)}\right] \approx 1$$
(2.13)

with τ_c the internal thermal relaxation time for the cell, τ_i and τ_e are given from Eqs. (2.6e) and (2.6d). In the limit of zero internal thermal resistance, or $\tau_i \ll \tau_e$, both $f(\omega)$ and $g(\omega)$ approach one for all ω . These corrections were applied to all samples studied here. The value of the external thermal resistance $R_e(=1/K_b)$ is typically the same for all samples, $R_e \sim 200$ K W⁻¹.

The specific heat capacity, C_p , can then be found as

$$C_p = \frac{C'(\omega) - C_{empty}}{m_s} = \frac{C^* \cos(\varphi) f(\omega) - C_{empty}}{m_s} , \qquad (2.14)$$

$$C''(\omega) = C^* \sin(\varphi) g(w) - \frac{1}{\omega R_e} , \qquad (2.15)$$

where, C_{empty} is the heat capacity of the empty cell, $C^* = P_0/(\omega T_{AC})$, m_s is the mass in grams of the liquid crystal.

Eqs. (2.14) and (2.15) are the basic equations used in the calculation of the real and imaginary heat capacities for our calorimeter. Experimentally, the amplitude of the temperature oscillations T_{ac} , and the relative phase shift φ , are measured. At the beginning of each experiment, for a set frequency ω , the amplitude of the power dissipated in the resistive heater, P_0 , as well as its phase shift, are measured.

The excess specific heat associated with a phase transition can be determined by subtracting an appropriate background C_p^{BG} from total specific heat over a wide temperature range. The excess specific heat is given by

$$\Delta C_p = C_p - C_p^{BG}.$$
(2.16)

For the N-SmA phase transition,

$$\delta C_p = C_p (N - SmA) - C_p^{BL}, \qquad (2.17)$$

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where, C_p^{BL} is the baseline or wing below N-SmA C_p phase transition peak.

The enthalpy change associated with a phase transition is defined as

$$\delta H = \int \Delta C_p dT. \tag{2.18}$$

For a second-order or continuous phase transition, the integration covers the entire δC_p peak over as a wide temperature range as possible and gives the total enthalpy change δH associated with the transition. But, for a first-order transition the situation is complicated due to the presence of a coexistence region and a latent heat ΔH . Due to partial phase conversion during a T_{ac} cycle, typical δC_p values obtained in the two-phase coexistence region are artificially high and frequency dependent, due to the dynamics of the phase conversion. The pretransitional enthalpy δH is typically obtained by integrating the linearly truncated δC_p peak between high-temperature and low-temperature limits [12]. A simple integration of the observed ΔC_p peak yields an effective enthalpy change δH^* , which includes some of the latent heat contribution. Here, $\delta H < \delta H^* < \delta H + \Delta H$. The total enthalpy change for a weakly first-order phase transition is the sum of the integrated pretransitional enthalpy and the latent heat, $\Delta H_{total} = \delta H + \Delta H$, where ΔH_{total} can be obtained from non-adiabatic scanning calorimetry[12]. The integration of the imaginary part of heat capacity given by Eq. (2.15) yields the imaginary transition enthalpy $\delta H''$ and is a measure of dispersive component of the complex enthalpy. The quantity $\delta H''$ can be used as an accurate indicator of first-order behavior. Since the fixed heating frequency ω is used in this work, the $\delta H''$ is only approximately proportional to the latent heat. Since the twophase conversion rate may be different for different samples, the proportionality between the $\delta H''$ and the latent heat changes as the sample changes and requires a detailed frequency scan for each sample to establish the accurate relation. In an AC-calorimetric technique the uncertainty in determining the enthalpy is typically 10% mainly due to the uncertainty in the baseline and background subtraction.

The phase shift contains information about the heat capacity and the internal time constant, which is directly related to the sample's thermal conductivity. Empirically, it has been observed that for a weak first order transition there is always a peak in the phase, while, for strong first order transitions, the phase might show a 1 point anomaly or a simple discontinuity. This is because the transition happens very fast and pre-transitional fluctuations are very small compared with the latent heat of the transition. For the case of the weak first order transitions, the width of the phase peak has been associated with the two-phase coexistence region where the release or absorption of the latent heat occurs. In this case, another heat source or heat sink appears which has an energy spectrum. This spectrum is generally, completely different from the one applied at the heater (delta function), which is being detected. This shows up as a peak in the imaginary heat capacity, the width of which is equal to the two-phase coexistence. In most of the other cases, i.e., outside the two-phase coexistence region, and for most of the second order phase transitions, the heat capacity is purely real and independent of ω , so $C''(\omega) \equiv 0$. This fact may be used to extract the external resistance R_e directly from the AC-technique.

The inequalities in Eq. (2.7) are the most important approximations needed to solve Eqs. (2.2). Experimentally, the approximations (2.7) should be verified for every sample and can be done by performing frequency scans. A frequency scan determines the frequency range where the heat capacity data are frequency independent. A frequency scan is done by changing the frequency maintaining the same voltage amplitude of applied power oscillation to the heater, keeping the bath temperature constant, and measuring the sample temperature oscillation for each frequency. A log-log plot of ωT_{ac} vs. ω gives a frequency independent 'plateau' in some range of frequencies which provides the range of working frequency of the calorimeter. In this range the heat capacity is frequency independent and has smallest value and neither of the thermal relaxation times, internal and external, plays a major role and can be neglected. A typical frequency scan profile is shown in Fig. 2.2. The internal and external time constants are extracted by fitting the graph 2.2 with the equation;

$$\omega T_{ac} = \frac{A}{\sqrt{1 + (\omega \tau_e)^{-2} + (\omega \tau_i)^2 + R}},$$
(2.19)

where, the fit parameter, R, is typically fixed to zero, because it is generally very small and the nonlinear least squares fit is insensitive to this parameter.

Experimentally, it is feasible to fulfil the requirements of Eq. (2.7) controlling external and internal time constants. The external time constant can be controlled by tailoring the thermal link between the bath and the sample. This is usually achieved by choosing an appropriate material, length and cross-sectional area of the electric leads for the heater and thermometer and by thermally anchoring the heater and thermometer to the temperature-controlled reservoir. The internal time constant can be adjusted by appropriately changing the sample thickness. If the sample thickness d is less than the thermal diffusion length $\lambda = \sqrt{(2K_sA)/\omega C_s}$, where A is the cross-sectional area of the sample, then, the right hand side inequality of Eq. (2.7) is satisfied. In this case, the locations of heater and thermometer on the cell are unimportant and the measurements are geometry independent.



Figure 2.2. Log - log plot of $\omega T_{ac} vs \omega$. Solid line through the data points is the fit. The dashed lines represent $1/\tau_e$ and $1/\tau_i$.



Figure 2.3. Cell design of an envelope type cell.

2.1.3 Design and Operation of the AC Calorimeter

2.1.3.1 Calorimetric Cell Design

An aluminum "envelope" heat capacity cell, 15 mm in length, 8 mm in width, and ~ 0.5 mm thick was prepared from a sheet of 99.9% pure aluminum foil purchased from Alfa Aesar [13]. The cell was cleaned in progressive applications of water, ethanol and acetone in an ultrasonic bath. For the LC+solvent studies, the sheet was folded and sealed on three sides with super-glue (cyanoacrylate) and for the nanomaterial+LC samples the folded sides are ironed (pressed). The envelope design of the cell is easy to construct, improves the sensitivity of the technique, and improves the frequency scan profile as compared to its old-fashioned cup and lid counterpart. A schematic of the envelop cell design is shown in Fig. 2.3.

Before loading the sample, we usually degas it at a high temperature, well into the isotropic phase of the LC sample, for at least 2 hours, in order to remove possible absorbed water. This procedure is the same for all samples, since we want to make sure that all samples have the same thermal history. After the sample is loaded, typically 15 - 30 mg, the fourth side of the 'envelope' is closed by folding and gluing or tightly pressing together the edges of the cell depending upon the type of sample used.

Once the cell is ready a heater was attached to one of the surfaces of the cell using acetone diluted GE varnish. A strain gauge of type FAE-25-12-S13EL that was purchased from BLH Electronics, Inc. [14], with a nominal resistance

of 120Ω was used as a heater. We trimmed the Kapton edges of the heater to match the dimensions of the cell before attaching on the cell, in order to reduce the background heat capacity of the heater.

The temperature sensor is then attached by a small drop of GE varnish at the center of the cell, on the opposite side from where the heater is attached. The sensor is an ultra-small bead, type 61A8, from YSI Temperature [15]. The bead diameter is about $0.254 \ mm$, and the leads are about $8 \ mm$ long. These beads have a time constant of about $0.5 \ s$ in still air, as specified by their manufacturer. The whole cell arrangement is allowed to dry under a lamp, for several hours, before mounting it on the calorimeter.

2.1.3.2 Calorimeter Design

The cell+sample needs a very good temperature control and a controlled environment, like vacuum, or inert gas atmosphere. Therefore, the cell holder is placed inside a massive cylindrical copper block which acts as a bath. The temperature of the bath is controlled by a Lakeshore model 340 temperature controller via a proportional-integral-derivative (PID) feedback loop [16]. At the rim of the cylinder the temperature stability is observed to be ± 1 mK while it is about 100 μ K inside the cavity of the cylinder where the cell+sample rests. The temperature scan can be achieved with different rates varying from 10 mK/hr to 5 K/hr adjusting the PID settings for slow response. This bath is placed inside a water bath. This whole arrangement is placed inside a small kitchen refrigerator.

A flexible heater from Omega Engineering, with dimensions that are closely matched to that of the bath, is glued to the outside surface of the cylinder. A platinum PT-100 resistive temperature device (RTD), refereed as platinum resistance thermometer (PRT), purchased from Lakeshore is used as a controlled thermometer. It can measure the bath temperature next to the cell very accurately. These PRTs and heater are connected to Lakeshore temperature controller.

A copper lid, with a long stainless steel tube in the middle, is mounted with bolts on top of the bath as shown in Fig. 2.4. At the end of the tube there is a copper plate which has posts for the electrical lead connections. A PRT, which is called center PRT, is anchored via a hole on the plate. This PRT is very close to the cell and the center of the bath cavity, therefore can measure the bath



Figure 2.4. Design of the *AC* Calorimeter (Old version). The sample lies inside a massive copper cylinder, whose temperature is controlled by Lakeshore temperature controller. The cylinder is place inside the water bath. The whole arrangement is place inside a refrigerator (not shown).

temperature, T_b , next to the cell, with very good accuracy. In the newer version of the calorimeter, a copper lid nicely rests on top of the copper block due to presence of a lip on the block. A copper tube one end of which has a copper plate with eight posts is inserted inside the cylinder through a hole on the bottom as shown in Fig. 2.5. The center PRT in this case is anchored on the plate and the terminals are connected to the posts. These posts has electrical lead connections which are connected to Keithley DMM. For this version, we use a DSC pan [17] as cell. A thermistor is attached on the body of the cylinder of the cell and a strain-gauze heater is connected at the bottom of the DSC pan.

The leads of heater and thermistor attached on the surfaces of the cell are connected to the post. These leads support the cell in place. At the other side of the posts are soldered permanently the wires that connect the sample's heater and thermistor to the break-out box, and from there to the Keithley DMM. However, in newer version, the wire lead connections are made directly to the Keithley DMM.

The block diagram of the AC-calorimeter which shows the outside circuit connection is shown in Fig. 2.6. The Keithley DMM, model 2002 with a multiplex



Figure 2.5. Design of the *AC* Calorimeter (New version). The sample lies inside a massive copper cylinder, whose temperature is controlled by Lakeshore temperature controller. The cylinder is place inside the water bath. The whole arrangement is place inside a refrigerator (not shown).

scan card model 2001-SCAN is used for required measurements.

The resistance measurements of the center PRT and the thermistor are configured as 4-wire, while the voltage and resistance measurements, across the heater and the standard resistor, are configured as 2-wire measurements [18]. The resistance measurements of heater and standard resistance are needed in order to accurately determine the AC power applied at the cell.

The power to heat the sample is provided by sending a sinusoidal power through the heater from a Hewlett Packard Function Generator/Arbitrary Waveform Generator, model HP 33120A [19]. The heater is connected in series with a high precision standard resistor, of resistance R_{std} . This standard resistance reduces the voltage across the strain gauge heater and it is used to measure the current through the heater accurately, since $I_h = I_{std}$ (since they are in series).

The experiment is computer-controlled. The control program was written by Prof. Germano Iannacchione and Dr. Aleksander Roshi and was written in C++, and compiled under Borland C++. The communication with the instruments is done through a PCI-GPIB interface card from National Instruments, Inc. [20].



Figure 2.6. Block diagram the calorimeter, showing all the connections to the instruments.

The data acquisition program is written in multi-threaded fashion which enables an efficient splitting of the temperature control procedure from the data collection procedure. The main thread collects the data, does the preliminary analysis and the storage and printing of the results, while the second thread controls the temperature. Both threads communicate with each other when needed. There is a configurational file, called ini file, in which the user can change the parameters such as temperature range, frequency range, voltage amplitude, frequency etc. as needed. The input configuration file is saved in the parameter output file (*.par), which stores the fit parameters.

At first, the power dissipated at the strain gauge heater is measured by measuring the heater and standard resistance. This is done by "digitizing" [21] the voltage across the standard resistor and then the heater. The amplitude of the power dissipated at the cell is calculated from the formula:

$$P_0 = I_h V_h = I_{std} V_h = \frac{V_{std}}{R_{std}} V_h, \qquad (2.20)$$

where, V_{std} , V_h are the voltage amplitudes at the heating frequency and R_{std} is the resistance of the standard resistor. From the waveform the phase of the power oscillations φ is also extracted.

Once the power measurement is over, the temperature controlling thread (TCT) is started. The data collection, starts after the TCT has signaled the main thread to start digitizing.

2.1.4 Thermometry

The accurate measurement of temperature is one of the most important part of AC-calorimetry. Two types of resistive temperature sensors were used in this work, platinum resistance thermometer (PRT), and carbon-flake thermistors. The PRTs are used to monitor the bath temperature and the carbon-flake thermistor is used to monitor the cell+sample temperature. These devices work on the principle that the resistance changes as a function of temperature. Change in resistance as a function of temperature are measured first and then these resistance values are converted into temperature using specific calibration functions. PRTs have an almost linear function with a positive temperature coefficient ($\partial R/\partial T \simeq const > 0$). They are generally very stable and very reproducible even for different thermometers; therefore they are good for calibration and control. The temperature dependence of resistance for PRT can be expressed as

$$R = R_0 \left(1 + \alpha T + \beta T^2 \right), \qquad (2.21)$$

where, R_0 , is the resistance at $0^{\circ}C$, and α , β are calibration constants. Rearranging Eq. (2.21), we get;

$$T = \frac{1}{2\beta} \left[-\alpha + \sqrt{\alpha^2 - 4\beta(1 - R/R_0)} \right].$$
 (2.22)

The bath temperature can be calculated as;

$$T_{prt} = \frac{T_b^{prt} + T_a^{prt}}{2},$$
 (2.23)

where, T_b^{prt} and T_a^{prt} are found by converting the resistances before and after

digitizing respectively.

Carbon flake thermistors are very small and very sensitive. They have highly nonlinear temperature-resistance relation with a negative temperature coefficient $(\partial R/\partial T < 0)$.

For the thermistor, the relation between temperature and resistance can be expressed as;

$$\frac{1}{T} = a_0 + a_1 \log\left(\frac{R}{R_0}\right) + a_2 \left[\log\left(\frac{R}{R_0}\right)\right]^2, \qquad (2.24)$$

where, a_0 , a_1 , a_2 are constants, and R_0 is the resistance at some temperature. We consider $R_0 = 10000 \ \Omega$ for all calculations. Since the coefficients will drift slightly with time, recalibration of the thermistor against the PRT at the end of each run is required.

Experimentally, the digitized resistance waveforms are fitted with the function;

$$X = a + bt + ct^{2} + A_{\omega}sin(\omega t) + A'_{\omega}cos(\omega t) + A_{2\omega}sin(\omega t) + A'_{2\omega}sin(\omega t), \quad (2.25)$$

where, the term $a+bt+ct^2$ represents the background term and the others represent oscillating term with the voltage frequency ω and power frequency 2ω . From the fit, the amplitude ΔR and phase ϕ for each frequency are found:

$$\Delta R_{\omega} = \sqrt{A_{\omega}^2 + (A_{\omega}')^2}, \quad \varphi_{\omega} = \tan^{-1} \left(\frac{A_{\omega}}{A_{\omega}'}\right); \quad (2.26a)$$

$$\Delta R_{2\omega} = \sqrt{A_{2\omega}^2 + (A_{2\omega}')^2}, \quad \varphi_{2\omega} = \tan^{-1}\left(\frac{A_{2\omega}}{A_{2\omega}'}\right); \quad (2.26b)$$

Therefore, the amplitude ΔR , the average thermistor resistance R_{th} , and the phase φ_R , of the resistance oscillation, are found from the fit of the digitized waveform. From Eq. (2.24), the temperature of the thermistor T_{th} , can be easily calculated. From the amplitude ΔR , since the amplitude of the oscillations is very small, we can find T_{aC} , (the corresponding amplitude of temperature oscillations), by using the relation:

$$T_{ac} \approx \left| \frac{dT}{dR} \right| \Delta R,$$
 (2.27)

 T_{ac} is needed in the calculation of C^* (see Eq. (2.8)). From Eqs. (2.24) and (2.27),

 T_{ac} is then calculated by:

$$T_{ac} = T_{th}^2 \frac{\Delta R}{R_{th}} \left[a_1 + 2a_2 \log\left(\frac{R_{th}}{R_0}\right) \right].$$

$$(2.28)$$

2.2 Polarizing Microscopy

The polarizing microscopy was originally developed for investigating structures of rocks and minerals. But this technique has become a popular tool for different field of science such as biology, medicine, polymer chemistry, physics etc.

The polarized light microscope is used to study the materials that are visible under crossed polarizers due to their optical anisotropic property. These materials have two different refractive indices for different direction of polarization which is called the properties of birefringence. The microscope must be equipped with a polarizer and an analyzer. The polarizer is positioned in the light pathway before the sample to be studied and the analyzer is placed in the pathway between the objective of the microscope and the sample. Liquid crystal textures were observed under the crossed-polarizers condition where the optical axes of the polarizer and analyzer are perpendicular to each other. In the absence of the sample, dark field of view is observed because of the action of crossed polarizer analyzer arrangement. When a sample like liquid crystal is inserted in between the crossed-polarizers, textures or patterns are observed due to the interaction of light with the sample. A simple experimental arrangement is shown in Fig. 2.7 [22]. Since liquid crystals exhibit optical anisotropy (birefringence), polarizing microscopes are popular to study liquid crystals. Peculiar optical patterns within a liquid crystal sample can be observed by using a polarizing microscope. The phases and defects can be investigated by observing these optical patterns.

Textures for different liquid crystals, LC+solvent, and LC+nanomaterial composites were observed as a function of temperature. The temperature control was achieved using a microscopic hot stage.



Figure 2.7. Design of the Polarizing Microscope[22].

2.3 Dielectric Spectroscopy

Materials which are electrical insulators but can be polarized and can store electrical energy are called dielectrics. An electric field causes the charges of a dielectric material to displace slightly from their equilibrium positions. The polarization after the application of an electric field takes a finite time to reach its maximum value. The phenomenon is generally described by a general term 'dielectric relaxation. The term 'dielectric' is connected to materials with a high polarizability and is expressed by a number called dielectric constant. Dielectric constant provides the extent to which a material can concentrate electric flux. It can be shown that under an alternating electric field the real and imaginary components of the dielectric constant are given by

$$\varepsilon' = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{1 + (w\tau)^2},\tag{2.29}$$

and

$$\varepsilon'' = \frac{\Delta\varepsilon}{1 + (w\tau)^2} (\omega\tau) \tag{2.30}$$



Figure 2.8. Design of the dielectric spectrometer [27].

where ω is sweeping frequency, τ is the relaxation time, and $\Delta \varepsilon = \varepsilon_0 - \varepsilon_\infty$ is the dielectric relaxation strength for a single relaxation process. Here, ϵ_0 , and ε_∞ are dielectric constants at infinite frequency and zero frequency (static dielectric constant) respectively. The complex dielectric constant of a material can be expressed as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega). \tag{2.31}$$

The real part represents the storage of the electric field energy and the imaginary part corresponds to the dispersion (dissipation) of energy through a relaxation process.

The dielectric constant ε^* can be measured by performing the capacitance measurement as the dielectric constant of a sample is the ratio of sample filled capacitance and empty cell capacitance. Our experimental set-up is based on the ACcapacitance bridge technique [23, 24, 25]. The experiment is started by balancing the AC-bridge at some frequency. A frequency (or voltage or temperature) scan is then performed from this point. The off-balance in-phase and out-of-phase signals are acquired by digital lock-in amplifier [26]. The off-balance signal is converted to the equivalent change in capacitance by a simple multiplicative conversion factor and converted into the dielectric constant dividing it by the empty cell capacitance. The absolute real and imaginary parts of the complex dielectric constant are determined by adding or subtracting (depending on whether the frequency is increasing or decreasing from the reference frequency) the off-balance single to that directly measured at the reference frequency. The spectrometer set-up is as shown in Fig. 2.8 [27].

2.4 Materials

2.4.1 Liquid crystals

2.4.1.1 Characteristics of 5CB

5CB is the abbreviated name of the *LC* pentylcyanobiphenyl or 4-cyano-4'-pentylbiphenyl. 5CB has a typical rod-like molecule, with a rigid biphenyl core, to which are attached an aliphatic tail and a polar cyano head group. Its molecular weight is $M_w = 249.36 \text{ g mol}^{-1}$. The molecular structure is shown in Fig. 2.9 and 2.10.



Figure 2.9. Molecular structure of the 5CB molecule.



Figure 2.10. 3D structure of the 5CB molecule.

Pure 5CB undergoes a weakly first-order isotropic to nematic phase transition, at $T_{IN}^o = 308$ K. The phase sequence (in Kelvin) for 5CB is

Crystal
$$\xrightarrow{\sim 295} N \xrightarrow{308} I$$

2.4.1.2 Characteristics of 8CB

8CB is the abbreviated name of the LC octylcyanobiphenyl or 4-cyano-4'-octylbiphenyl. It is one of the most well known and probably the most studied LC. 8CB has a typical rod-like molecule, with a rigid biphenyl core, to which are attached an aliphatic tail and a polar cyano head group. Its molecular weight is $M_w = 291.44$ g mol⁻¹. The molecular structure is shown in Fig. 2.11 and 2.12.



Figure 2.11. Molecular structure of the 8CB molecule.



Figure 2.12. 3D structure of the 8CB molecule.

Pure 8*CB* undergoes a weakly first-order isotropic to nematic transition, at T_{IN}^o = 313.98 K, and a continuous nematic to smectic-*A* transition, at T_{NA}^o = 306.97 K. Below 290 K 8*CB* crystalizes via a first order transition. The phase sequence (in Kelvin) [12, 9] for 8*CB* is

2.4.1.3 Characteristics of 10CB

10CB is the abbreviated name of the LC decylcyanobiphenyl or 4-cyano-4'-decylbiphenyl. 10CB has a typical rod-like molecule, with a rigid biphenyl core, to which are attached an aliphatic tail and a polar cyano head group. Its molecular weight is $M_w = 319.49 \text{ g mol}^{-1}$. Molecules are 2.45 nm long and 0.5 nm wide [28]. The molecular structure is shown in Fig. 2.13 and 2.14. Pure 10*CB* undergoes direct



Figure 2.13. Molecular structure of the 10CB molecule.



Figure 2.14. 3D structure of the 10CB molecule.

isotropic to smectic-A transition, at $T_{IA}^o = 323.69$ K. This transition is a first-order. This has a strongly first-order smectic-A to crystal transition at ~ 316 K [29, 30]. The phase sequence (in Kelvin) for 10CB is

$$\label{eq:crystal} \begin{array}{ccc} \sim & 316 \\ & & \\ \hline \end{array} & SmA_{\rm d} \end{array} \xrightarrow{323.7} I$$

2.4.2 Solvents

2.4.2.1 Characteristics of n-hexane

Hexane (n-hexane) is an alkane with 6 carbons with the chemical formula C_6H_{14} . Hexane is colorless liquid at room temperature with melting point 178 K (-95° C) and boiling point at 342 K(69° C). It has molecular mass of 86.18 g mol⁻¹ and a density of 0.65 g ml⁻¹. It is widely used as non-polar solvents. It is relatively safe, largely unreactive, and volatile solvents. It does not have any known mesogenic (liquid crystalline) phases. The structure is shown in Fig. 2.15.



Figure 2.15. Structure of the n-hexane molecule.

2.4.2.2 Characteristics of acetone

Acetone is an organic, colorless, flammable, and highly volatile liquid. It has chemical formula $(CH_3)_2CO$ and structure as shown in Fig. 2.16. Acetone has a molar mass of 58.08 g mol⁻¹, density 0.79 g/cm³, boiling point 56.53 ° C (330 K), and melting point -94.9° C (178 K). Acetone is highly miscible with water and acts as a very good polar aproctic solvent. This is typically a solvent of choice for cleaning purposes in the laboratory. It is a good solvent for plastics and synthetic fibers and used as a solvent in different organic reactions in the laboratory. Acetone does not have any known mesogenic (liquid crystalline) phases.

2.4.2.3 Characteristics of decane

Decane is a hydrocarbon with chemical formula $CH_3(CH_2)_8CH_3$ and the structure is shown in Fig. 2.17. It is a flammable liquid and immiscible in water. It is a non-polar solvent having molecular mass 142.29 g mol⁻¹, melting point -27.9° C (245.1 K), and boiling point 174.1° C (447.1 K)



Figure 2.16. Structure of the acetone molecule.



Figure 2.17. Molecular structure of the acetone molecule.

2.4.3 Nanomaterials

2.4.3.1 Characteristics of carbon nanotubes

Carbon nanotube (CNT) is an allotrope of carbon and is a member of the fullerene structural family. CNTs consist of tubular structure with walls made up of carbon atoms regularly arranged into a honey-comb lattice or graphene sheet. See Fig. 2.18. They have diameter on the order of nanometers and length ranging from micrometers to millimeters, even centimeters possessing an extremely high aspect ratio (diameter to length ratio). CNTs are therefore single-molecule 'string-like' particles. CNT can be metallic or semiconducting depending upon the way how the graphene sheet is rolled up.

If CNT has only one wrapped concentric cylinder, it is called a single-walled CNT, if two concentric tubes are present, it is double-walled and if it consists of


Figure 2.18. Structure of the CNT[31].

multiple concentric tubes, it is multi-walled CNT (Fig. 2.18). Due to the combination of peculiar geometry and graphitic nature of the walls, CNTs have exceptional mechanical, electrical and thermal properties [32]. Outstanding properties, small size and shape of CNTs create a unique combination appealing for many diverse applications as a single molecule or as sets.

2.4.3.2 Characteristics of BaTiO₃

Barium Titanate (BaTiO₃) is an inorganic ferroelectric oxide which undergoes a transition from a ferroelectric tetragonal phase to paraelectric cubic phase upon heating above $130^{\circ}C$. Ferroelectricity in the tetragonal BaTiO₃ is due to an average relative displacement of the Titanium atom producing permanent dipole moment. It has spontaneous polarization of 0.26 C/m^2 [33]. Ferroelectric properties and high dielectric constant make BaTiO₃ useful in different applications such as multilayer ceramic capacitor[34, 35], IR detectors[36], holographic memmory[37]. When ferroelectric BaTiO₃ is dispersed in a liquid crystal, it enhances the physical properties of the liquid crystal. In this work, we use BaTiO₃ of size 200 nm which was purchased from Nanostructured and Amorphous Materials Inc. The structure of a BT molecule is shown in Fig. 2.19.



Figure 2.19. Structure of the $BaTiO_3$ molecule.

2.5 Sample preparation

Liquid crystals 5CB, 8CB, and 10CB were purchased from Frinton laboratory [38] and used after degassing them in their isotropic phase for about 2 hours. Solvents acetone, hexane, decane etc. were purchased from Sigma-Aldrich[39] and were used without further purification. Carbon nanotubes sample were kindly provided by Dr. Sioan Sinha and used after degassing for 2 hours at 320 K temperature. Barium Titanate was used after careful degassing for about 2 hours at a temperature of 320 K.

2.5.1 Calorimetry Sample Preparation

2.5.1.1 8CB+n-hexane mixtures

When the calorimetric envelope cell mentioned earlier was thoroughly dried, the desired amount of liquid crystal followed by a relatively large amount of n-hexane (hex) were introduced to the cell. The mass of the sample and cell was monitored as the n-hexane was allowed to evaporate slowly until the desired mass of the n-hexane was achieved. At the point of the desired mass of the 8CB+hex mixture, the envelop flap was quickly folded and sealed with super-glue (cyanoacrylate). Careful massing of super-glue and sample during every stage of this process ensured the

proper amounts of materials were sealed within the cell. Extensive care was taken in handling the sample due to relatively rapid evaporative nature of n-hexane and total mass of the cell was periodically checked. Different samples having x_{hex} ranging from 0 (pure 8CB) to 0.12 were prepared. Here x_{hex} is n-hexane mole fraction, and is defined as $x_{hex} = n_{hex}/(n_{hex} + n_{LC})$, where n_{hex} and n_{LC} are the moles of hexane and liquid crystal used.

2.5.1.2 10CB+acetone mixtures

A specified amount of 10CB was transferred to a vial to which a relatively large amount of acetone (HPLC grade, 99.9+% pure acetone from Aldrich) was added and ultrasonicated to thoroughly mix. The acetone was then allowed to slowly evaporate until the desired mass of the mixture was reached.

2.5.1.3 LC+nanomaterials composites

The degassed LC, proper amount of degassed carbon nanotubes and relatively large amount of spectroscopic grade (ultra-low water content with purity of 99.9%) acetone were mixed in a vial. The mixture was then mechanically mixed in a touchmixer for about an hour and ultrasonicated in an ultrasonic bath for about 10 hours in the isotropic phase of pure 8CB. After ultrasonication the dispersion was placed over the hot plate to evaporate the acetone slowly out of the mixture and then the mixture was degassed under vacuum at 318K for about 2 hours. Different samples having ϕ_w ranging from 0.0010 to 0.0060 were prepared using same procedure. Here, $\phi_w = m_{CNT}/(m_{LC} + m_{CNT})$ is the weight fraction of CNT, where m_{CNT} and m_{LC} are masses of CNTs and LC respectively.

The degassed LC, proper amount of degassed Barium Titanate (BT) and relatively large amount of spectroscopic grade (ultra-low water content with purity of 99.9%) acetone were transferred in a vial. The mixture was then mechanically mixed in a touch-mixer for about an hour and ultrasonicated in an ultrasonic bath for about 10 hours in the isotropic phase of pure 8CB. After ultrasonication the dispersion was placed over the hot plate to evaporate the acetone slowly out of the mixture and then was degassed under vacuum at 318K for about 2 hours. Different samples having ϕ_m ranging from 0.001 to 0.014 were prepared using same procedure. Here, $\phi_m = m_{BT}/(m_{LC} + m_{BT})$ is the mass fraction of BT, where m_{BT} and m_{LC} are masses of BT and LC respectively.

2.5.2 Microscopy Sample and Cell Preparation

Same samples prepared for calorimetry were used to observe the texture in the polarizing microscope (crossed polarizer). For the LC+solvent studies microscope slides with a concave cavity were used. After putting a drop of sample it was covered by a cover slip. The cover-slip was glued over the slide using super-glue. In the case of LC+nanomaterial sample, a drop of sample was put on the plane surface of the microscope slide and was covered by a cover-slip. Thus made slides were observed under the crossed polarizer and analyzer.

2.6 Experimental procedure

This section describes the experimental procedure and provides the parameters used such as frequency, thermal scan rate etc. in the experiments.

For 8CB+hex system, the first heating scan followed by a cooling scan was performed with a thermal scan of 1 K/h. The sample was kept in isotropic phase for about 6 hours in between the heating scan and the following cooling scan. Another set of heating and cooling was done at a heating frequency of 0.03125 Hz and a final slow scanning rate of ± 0.4 K/h. All the samples experienced the same thermal history. The second set of data is presented here.

For 10CB+solvent and 8CB+BaTiO₃ systems, the first heating scan followed by a cooling scan was performed at a heating frequency of 0.196 rad/s (0.03125 Hz) and a thermal scan of 1 K/hr. The sample was kept in isotropic phase for about 6 hours in between the heating scan and the following cooling scan. Another set of heating and cooling was done at the same heating frequency and the same thermal scanning rate to see whether there is significant drift of heat capacity peaks. All the samples experienced the same thermal history. The second set of data is presented here.

For 8CB+CNT system, the first heating scan followed by a cooling scan was performed at a heating frequency of 0.196 rad/s (0.03125 Hz) and a thermal scan of 1 K/hr. The sample was kept in isotropic phase for about 6 hours in between the heating scan and the following cooling scan. Another set of heating and cooling

was done at a heating frequency of 0.03125 Hz and a thermal scanning rate of ± 0.2 K/h for -3 K $< T_{NA} < +3$ K and ± 1 K/h for other ranges of temperature. The second set of data is presented here.

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Chapter 3

Isotropic to nematic phase transition in octylcyanobiphenyl and n-hexane binary mixtures

3.1 Introduction

The effect of the disorder and impurities on condensed matter systems is an important and challenging problem to the fundamental understanding of phase ordering or self-assembly and continually attracts the attention of researchers. The disordered systems often display complex and rich phenomena, being the generalization of the pure (ideal) systems. Disorder can dramatically alter the physical properties of multi-component, composite systems. In particular, the effect of disorder on phase transitions is important as the disorder typically couples to the order parameter, which can be usefully described as a random local field that is conjugate to the order parameter. This is usually realized in systems with random inclusions in a phase ordering media, *e.g.*, a colloidal dispersion of solids in a complex fluid. Another form of disorder is presented by dilution effects, which imposes instead the random breaking or weakening of intermolecular bonds or interactions responsible for the phase ordering. Exploring a good physical system representing random dilution effects in a controlled manner offers a physical probe to unresolved problems in the understanding of mesophasic order [1].

Liquid crystals (LCs) are an attractive model system for studying mesophasic

ordering and phase transitions. The phase behavior of LC is strongly influenced by disorder and impurities, and are easily handled allowing for unique control of the important physical parameters. Examples of induced random field-like disorder through random surface interactions are silica aerosil [2, 3, 4, 5], aerogel [6, 7], controlled porous glass [8, 9, 10], and other uniform cylindrical confinements [11, 12]. The LC phase behavior can also be altered by using external electric and magnetic fields [13, 14]. Also, by employing LC+LC mixtures [15, 16, 17, 18], new phases and phase diagrams have been explored. Finally, mixture systems comprised of water, surfactant, and a nematic liquid crystal have revealed unique arrangements of spherical micelles in a microemulsion upon full phase separation either by cooling into the nematic phase or the addition of an appropriate cosurfactant [19, 20, 21].

Recently, renewed attention has been drawn to miscible mixtures of liquid crystals and non-mesogenic, low-molecular weight, solvents for furthering basic understanding of mesogenic order and tuning viscoelastic properties [22, 23, 24, 25, 26]. An x-ray study of a binary mixture of a LC and n-hexane focussing on the nematic to smectic-A phase transition indicated from visual inspection that in 8CB/nhexane mixtures (for n-hexane volume fraction 0.1 and up) the solvent is not uniformly distributed throughout the host LC, and minimal, non-reproducible swelling is observed [22]. The experimental studies on 8CB+cyclohexane [26] system that enforced uniformity by continuous mixing, revealed a linear decrease in isotropic to nematic transition temperatures, and constant latent heat during the transition with increasing solvent mole fraction.

In this work, we study the effect of a non-mesogenic, low molecular weight, solvent (n-hexane) concentration on the weakly first-order isotropic to nematic (I-N) phase transition on octylcyanobiphenyl (8CB) and n-hexane (hex) binary mixtures (8CB+hex) as a function of n-hexane concentrations. The introduction of n-hexane on 8CB causes the dramatic change in the phase transition behavior in 8CB+hex mixtures. The heat capacity peak associated with the I-N phase transition, ΔC_p , shifts towards lower temperature non-monotonically and becomes progressively smeared as the hexane concentration increases. There is significant hysteresis in the ΔC_p shape between heating and cooling, especially for higher hexane concentrations. On heating, the ΔC_p peak exhibits a broad tail where the peak temperature is significantly below the nominal transition temperature. On cooling the ΔC_p peak reveals a sharp jump reminiscent of the pure 8CB peak. The integrated ac-enthalpy remains fairly constant as a function of hexane molar fraction whereas the imaginary part of the enthalpy reveals a sharp increase at hexane mole fraction of around 0.07.

The presence of n-hexane in 8CB introduces two effects; impurity and viscoelastic softening. Both effects are in equilibrium but produce different results. The shift in transition temperature downwards, general smearing of ΔC_p , and constancy of δH_{IN}^* are consistent with an impurity effect. The non-monotonic transition temperature shift, narrowing of the nematic temperature range, hysteresis in the ΔC_p shape, and jump in $\delta H_{IN}''$ at $x_{hex} \approx 0.07$, appear to be indicative of changes in the effective viscoelastic properties of the composite. This later mechanism has a profound effect on the lower temperature nematic to smectic-A transition, which will be presented in chapter 4.

3.2 Results

3.2.1 Overview

For pure 8CB, from the same batch used for all mixture samples, the *I-N* phase transition occurs at $T_{IN}^0 = 313.20$ K while the *N*-SmA transition occurs at $T_{NA}^0 =$ 306.09 K, both are about 1 K lower than the highest values reported in the literature [31]. In addition, the effective enthalpy $\delta H_{IN}^* = 4.67 \pm 0.47$ J/g and the dispersive enthalpy $\delta H_{IN}^{"} = 0.59 \pm 0.06$ J/g for the *I-N* transition in pure 8CB, which is within 10 % of the literature value [6]. These results indicate the relative purity of the LC and are used for comparison to the mixture results for internal consistency. A summary of transition temperatures, nematic temperature ranges, and enthalpies for all samples on heating is given in Table 3.1.

The excess specific heat associated with a phase transition can be determined by subtracting an appropriate background C_p^{BG} from the total specific heat over a wide temperature range; $\Delta C_p = C_p - C_P^{BG}$. Fig. 3.1(a) illustrates this subtraction, the dash-dot line represents the background.

The resulting excess specific heat data for 8CB+hex samples on heating are shown in Fig. 3.2(a) over a 3 K temperature range about T_{IN} . Here, ΔC_p are

Table 3.1. Summary of the calorimetric results for pure 8CB and the 8CB+hex samples on heating. Shown are n-hexane molar fraction x_{hex} , I-N transition temperature T_{IN} , nematic temperature range ΔT_N , I+N co-existence region δT_{I+N} (in Kelvins), effective ac-enthalpy change δH_{IN}^* and dispersive enthalpy $\delta H_{IN}^{''}$ (in J/g).

	10	0	111	1	1		IN (10)		
x_{hex}	T_{I}	N	ΔT_{I}	V	δT_{I+N}	r	δH_{IN}^*	δF	$I_{IN}^{\prime\prime}$
0.00	313.20 :	± 0.07	$7.11\pm$	0.11	0.25 ± 0	.21	4.67 ± 0.4	7 0.59	± 0.06
0.02	309.95 :	± 0.39	$5.53 \pm$	0.59	1.08 ± 1	.17	3.99 ± 0.4	0 0.33 :	± 0.03
0.03	309.12 :	± 0.27	$5.03 \pm$	0.41	1.00 ± 0	.81	4.19 ± 0.4	2 0.40	± 0.04
0.06	309.48	± 0.33	$5.27 \pm$	0.50	1.17 ± 0	.99	3.36 ± 0.3	4 0.32 :	± 0.03
0.08	308.06 :	± 0.42	$4.46 \pm$	0.63	2.26 ± 1	.26	3.79 ± 0.3	8 1.27 :	± 0.13
0.09	305.16 :	± 0.64	$3.23\pm$	0.96	2.08 ± 1	.92	4.11 ± 0.4	1 0.97	± 0.10
0.12	303.62 :	± 0.94	$2.53 \pm$	1.41	2.65 ± 2	.82	4.09 ± 0.4	1 1.15 :	± 0.12

presented in Joule per Kelvin per gram of the sample. The ΔC_p peaks of the *I-N* transition shift towards lower temperature as well as progressively smearing with increasing x_{hex} . Also, the *I-N* ΔC_p peak on heating exhibits a broad wing, or tail, on the isotropic side of the transition. Fig. 3.2(b) shows the dispersive part of heat capacity C'' for pure 8CB and 8CB+hex samples on heating. The *I-N* transition C'' peaks are also smeared with progressively longer tail on the isotropic side as the hexane concentration increases. Interestingly, the temperature of the C'' peak does not coincide with the temperature of the ΔC_p peak on heating. Because of the mismatch between C'' and ΔC_p peaks in temperature and the long ΔC_p tail on the isotropic side, the temperature of the *I-N* transition on heating is taken as the approximate inflection point of C'' on the isotropic side.

On cooling the excess specific heats shows in Fig. 3.3(a) and imaginary heat capacities shown in Fig. 3.3(b) reveal consistent behavior. Using the jump in C''on the high-side of the transition, T_{IN} shifts to lower temperature monotonically consistent with T_{IN} from heating scan. The ΔC_p peaks of the *I-N* transition are smeared for higher hexane mole fractions but with a broad tail on nematic side of the transition. This is contrast to that seen on heating. Significant hysteresis in ΔC_p shape is observed at the *I-N* phase transitions on heating and cooling for higher hexane mole fractions. In particular, ΔC_p of the *I-N* transition on cooling appears more step-like with increasing x_{hex} . Heating and cooling ΔC_p results for various cycle for a given n-hexane concentration match each other well.



Figure 3.1. (a) The specific heat on heating as a function of temperature for the $x_{hex} = 0.06$ sample illustrating the overall background (dashed-dot) and low-temperature wing under the N-SmA peak (dashed) behavior used to determine ΔC_p and δH_{IN}^* . (b) Dispersive part of heat capacity on heating for the $x_{hex} = 0.06$ sample illustrating $\delta H_{IN}^{"}$ and the *I*-N transition temperature T_{IN} . See text for details.

3.2.2 Phase Diagram

The *I-N* and *N*-SmA phase transition temperatures as a function of n-hexane mole fraction are shown in Fig. 3.4(a) for heating and cooling scans. As previously described, the *I-N* phase transition temperature T_{IN} is defined as the high temperature limit of the *I+N* co-existence region from isotropic to nematic region, determined from C'' for heating and cooling scans. See Fig. 3.1(b), which illustrates this procedure. The *N*-SmA phase transition temperature T_{NA} was determined in two ways; for lower x_{hex} samples it is simply the *N*-SmA ΔC_p peak



Figure 3.2. (a) The excess specific heat ΔC_p on heating as a function of temperature about T_{IN} for pure 8CB and all 8CB+hex samples. See legend. (b) The dispersive part of heat capacity on heating for all samples as a function of temperature about T_{IN} . Note the broad ΔC_p and C'' wing on the high-temperature side of the peaks.

temperature, whereas for higher concentrations, where the N-SmA transition exhibits a peak in C'', T_{NA} is taken as high temperature limit of N-SmA C'' peak. The *I*-N transition temperatures for heating and cooling as function of x_{hex} are consistent with each other, but T_{IN} on cooling becomes progressively lower than on heating with increasing x_{hex} . The *I*-N ΔC_p peak temperature given by dashed line in Figure 3.4(a), becomes significantly smaller T_{IN} on heating reflects the unique smeared nature of the transition.

As the mole fraction of n-hexane increases the transition temperatures decrease non-linearly with a plateau or bump at $x_{hex} \approx 0.07$ for both T_{IN} and T_{NA} . See



Figure 3.3. (a) The excess specific heat ΔC_p on cooling as a function of temperature about T_{IN} for pure 8CB all 8CB+hex samples. See legend. (b) The dispersive part of heat on cooling for all samples as a function of temperature about T_{IN} . Note the sharp jump in ΔC_p and C" on the high-temperature side of the peaks as well as progressive step-like character of ΔC_p with increasing x_{hex} .

Figure 3.4(a). Figure 3.4(b) shows the nematic temperature range $\Delta T_N = T_{IN} - T_{NA}$ as a function of n-hexane mole fraction revealing an overall decrease in ΔT_N with a plateau similar to that seen in $T_{IN}(x_{hex})$ and $T_{NA}(x_{hex})$. The nematic range decreases from 7.11 K for pure 8CB to 2.53 K for the $x_{hex} = 0.12$ sample. The behavior of ΔT_N simply indicates the greater suppression of orientational order (nematic phase) relative to smectic ordering due to the presence of the solvent. The I + N coexistence region on heating and cooling as a function of x_{hex} is shown in Figure 3.4(c). The region increases linearly as x_{hex} increases.



Figure 3.4. (a) The *I*-*N* and *N*-Sm*A* phase transition temperatures as a function of x_{hex} on heating (\circ) and cooling (\bullet). Solid lines are guides to the eye and dashed line indicates the temperature of the ΔC_p peaks on heating.(b) The nematic temperature range ΔT_N on heating (\circ) and cooling (\bullet) as a function of x_{hex} . Dash-dot lines indicate the transition temperature shifts in 8CB+cyclohexane. See reference [26]. The vertical doted corresponds to the point where $\delta H''_{IN}$ exhibits a jump in magnitude. (c) The *I*+*N* coexistence region on heating (\circ) and cooling (\bullet) as a function of x_{hex} .

3.2.3 The *I*-*N* phase transition enthalpy

The enthalpy change associated with a phase transition is defined as

$$\delta H = \int \Delta C_p dT \tag{3.1}$$

where the integration is usually carried over as wide a temperature range as possible. For first-order phase transitions, the situation is complicated due to the presence of coexistence region as well as a latent heat ΔH . The total transition enthalpy change for weakly first-order phase transitions is the sum of the pretransitional enthalpy and latent heat associated with the transition and is given by $\Delta H_{total} = \delta H + \Delta H$. Due to partial phase conversion $N \rightleftharpoons I$ during a T_{ac} cycle, typical ΔC_p values using ac-calorimetry obtained in two phase coexistence region are frequency dependent and remarkably high. The integration of observed ΔC_p yields an effective enthalpy δH_{IN}^* , which includes some but not all of the latent heat contributions. In addition, the enthalpic contribution of a near-by phase transition must be subtracted to further isolate the appropriate ΔC_p . This typically involves defining the ΔC_p wing contribution that underlays the lower temperature transition. The integration of the imaginary part of heat capacity given by Eq. (6.6) yields the imaginary transition enthalpy $\delta H''_{IN}$, which is the dispersion of energy in the sample and an indicator of the first-order character of the transition. Fig. 3.1(a) and (b) illustrates the way how we calculate the effective ac-enthalpy change δH^*_{IN} and imaginary enthalpy $\delta H^{''}_{IN}$ respectively. The shaded regions give δH_{IN}^* and $\delta H_{IN}^{"}$. In ac-calorimetric technique the uncertainty in determining the enthalpy is typically 10 % due to the base line and background subtractions.

The effective I-N transition enthalpy δH_{IN}^* was obtained by integrating ΔC_p from 299K to 317 K for pure 8CB and all 8CB+hex samples then subtracting the N-SmA transition enthalpy contribution. See Fig. 3.1(a). The dispersive enthalpy of the I-N transition was obtained by integrating C'' just over the I-N C'' peak and then scaling by mass of the sample m_s . See Fig. 3.1(b). In this work, fixed heating frequency was used, thus $\delta H_{IN}''$ is only proportional to the transition latent heat.

The resulting δH_{IN}^* and $\delta H_{IN}''$ for heating and cooling scans as the function of hexane mole fraction for all 8CB+hex samples are shown in Fig. 3.5. The δH_{IN}^*



Figure 3.5. (a) The total integrated ΔC_p ac-enthalpy δH_{IN}^* and (b) integrated C^* enthalpy δH_{IN}^* of the *I-N* transition for heating (\circ) and cooling (\bullet) as the function of \mathbf{x}_{hex} . Solid lines are guides to the eye. The vertical dot line indicates the jump in δH_{IN}^* . The thick solid line in (b) is the mean spacing between n-hexane molecules \bar{l} and the horizontal dash line provides the point at which it crosses the vertical dotted line, $\bar{l}_{0.07} = 23$ Å.

values are all approximately shifted from that seen in pure 8CB but otherwise independent of x_{hex} and are consistent on heating and cooling. See Fig. 3.5(a). The dispersive enthalpy of the *I-N* transition, $\delta H_{IN}''$ exhibits a sudden jump from 0.32 to 1.27 J/g at $x_{hex} \approx 0.07$. This step increase in $\delta H_{IN}''$ at $x_{hex} \approx 0.07$ corresponds to the plateau region seen in Fig. 3.4 for the T_{IN} , T_{NA} , and ΔT_N as a function of x_{hex} .

3.3 Discussion and conclusions

The introduction of n-hexane to 8CB greatly affects the behavior of the I-N phase transition. The main effect of solvent is to dilute the liquid crystal, resulting in two main changes; an impurity effect and viscoelastic softening of the mixture. The impurity mechanism introduces concentration fluctuations (random local transition temperatures) and a generic truncation of the order parameter correlation length. However, the presence of solvent can screen LC molecules from one another, a dilution effect, that softens the viscoelastic properties of the mixture with respect to that of pure LC. This viscoelastic softening can substantially change the role of order fluctuation in the phase transition leading to non-linear shifts in T_c and hysteresis of the transition behavior.

T. P. Rieker [22] studied the LCs/n-hexane systems on the N-SmA phase transitions in LC/n-hexane systems and observed from visual inspection that for 8CB/n-hexane, the solvent was not uniformly distributed throughout the host LC and only a minimal, non-reproducible, swelling of the SmA layers were observed. However, these samples were of higher n-hexane concentration than ours, a reported volume fraction of 0.1. In the concentration range studied here, corresponding to a volume fraction from 0.015 to 0.060, visual inspection of sealed 8CB+hex samples over many months did not reveal any sign of de-mixing/separation. Large scale phase separation is not likely to play a major role in the results reported here.

Broader peaks and significant tails of ΔC_p in isotropic side of the transition on heating for higher hexane mole fraction indicate that the melting of the samples takes place for large temperature range. But during the cooling scans crystallization starts sharply. Therefore the melting and crystallization are driven by different dynamics which may be due to the coupling of viscoelastic properties with orientational order of the sample. Matching of heating and cooling ΔC_p results for various cycles for a given n-hexane sample indicates that the significant hysteresis observed during cooling and heating is not due to phase separation rather due to the different dynamics in heating and cooling scans. Shifting ΔC_p towards lower temperature and diminishing I- $N \Delta C_p$ peaks height indicate that the scalar order parameter S and correlation length ξ are greatly affected by n-hexane in the composites.

Non-linear transition temperature dependence on n-hexane mole fraction in 8CB+hex mixtures is unique as compared to that seen in 8CB+cyclohexane [26]. The authors showed that for 8CB+cyclohexane systems the *I-N* latent heat remains constant for all the cyclohexane concentrations. Similar behavior is observed in 8CB+hex system with a nearly constant ac-enthalpy for all n-hexane mole fractions studied. Details of the I-N heat capacity peaks were not published, so further comparison is not possible. The linear versus non-linear transition temperature behavior in 8CB+cyclohexane and 8CB+hex systems can be accounted in the following two ways: the first is the linear structure of n-hexane as compared to cyclohexane ring structure and the second is the procedure of mixing the sample during the experiment. Our experiments does not involve any stirring of the sample during the experiment where as the study of 8CB+cyclohexane was done with continuous stirring of the samples during the experiments, which may wash out this behavior. Non-stirring effect may produce nanoscale phase separation which consequently can cause two driving forces to develop in two opposite directions. These forces probably cause the increment in transition temperature showing nonlinear behavior in the phase diagram. The dash-dot lines in the phase diagram show the data from reference [26], which indicate the good agreement with our data in lower hexane concentration regime only but not for higher concentration regime.

A distinct jump in $\delta H_{IN}''$ at $x_{hex} \approx 0.07$ is observed that indicates the sudden change in dynamics of the *I-N* phase conversion. Since screening is presumably playing an important role, one measure of this effect is the mean distance between solvent molecules, \bar{l} . Assuming that the solvent molecules are uniformly distributed throughout the mixture, the value of \bar{l} may be estimated from the specific volume of the LC and that of the solvent. For 8CB and n-hexane, the specific volume (volume per particle) are $v_{8CB} = 486.14$ Å³ and $v_{hex} = 218.17$ Å³, respectively. We assume a linear variation as $v_{mix} = v_{8CB}$ at $x_{hex} = 0$ to $v_{mix} = v_{hex}$ at $x_{hex} = 1$ yielding a dependence of $v_{mix}(x_{hex}) = -267.97(x_{hex}) + 486.14$ in units of Å³ for the volume per 'average' molecule in the 8CB+hex mixtures. Considering a uniformly distributed n-hexane molecules, each centered in a spherical unit cell, the volume per molecule can be calculated as $v_{mix} = x_{hex}(\pi \bar{l}^3)/6$, the volume of the unit cell times the number of n-hexane molecules gives the total sample volume divided by the total number of molecules. Equating these two definitions of v_{mix} gives

$$\bar{l} = [(6/\pi)(v_{mix}(x_{hex}))/(x_{hex})]^{1/3}$$
(3.2)

where the linear $v_{mix}(x_{hex})$ dependence is used. For \bar{l} smaller than the length-scale for the LC interaction, approximately the LC molecular length, the screening effect on the LC interaction potential should dominant. The $\delta H'_{IN}$ jump occurs around at hexane mole fraction of ~ 0.07 where the mean distance between the hexane molecules \bar{l} is found to be approximately equal to 8CB molecular length ($\simeq 23$ Å). The functional dependence of $\bar{l}(x_{hex})$ is shown in the lower panel of Fig. 3.5.

We have undertaken a detailed ac-calorimetric study on the effect of nonmesogenic, low molecular weight solvent (n-hexane) on octylcyanobiphenyl (8CB) with an emphasis on the weakly first-order I-N phase transition. The dilution of the liquid crystal causes the decrease in liquid crystal molecular interactions and change in viscoelastic properties, which consequently gives rise the evolution of the phase transitions. The results obtained in this work reveal new aspects of the effect of non-mesogenic disorder on the mesogenic ordering. Non-mesogenic solvents like n-hexane, could be an important tool to probe and tune intermolecular potentials of liquid crystals. Continued experimental efforts are needed specifically, light scattering studies probing the nematic elastic constants as a function of solvent content and temperature would be particulary important and interesting.

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Chapter 4

Nematic to smectic-A phase transition in octylcyanobiphenyl and hexane binary mixtures

4.1 Introduction

The phase transition between the nematic and smectic-A (N-SmA) phases is interesting and important because it involves the breaking of a continuous symmetry as well as belonging to the same universality class as the superconducting transition in metals and the superfluid transition in ⁴He. The N-SmA transition has been used as a model phase transition for the study of confinement and disorder effects [1, 2, 3]. The phase transition behavior is also sensitive to an applied external electric or magnetic field [4, 5] as well as with LC+LC mixtures [6, 7, 8, 9, 10]. Even though the N-SmA transition has been extensively studied [11], there remains some unresolved issues regarding the fundamental nature of the transition.

Recently, attention has been drawn to the study of miscible mixtures of liquid crystals and non-mesogenic, low-molecular weight, solvents as a way of exploring the fundamental nature of the LC interactions responsible for mesogenic order, critical behavior, and the tuning of viscoelastic properties [12, 13, 14, 15, 16]. X-ray diffraction experiments performed on the smectic-A and smectic-C phases of thermotropic liquid crystals doped with an organic solvent have shown that the smectic layer spacing increases with solvent content [16]. This research also

demonstrated the formation of an organic lyotropic lamellar liquid crystal phase in which the solvent molecules largely intercalate between the smectic layers of the LC. It was also mentioned that from a visual inspection of octylcyanobiphenyl (8CB) and n-hexane (hex) mixtures that the solvent was not uniformly distributed throughout the host LC and minimal, non-reproducible, swelling of smectic layers occurred for solvent volume fractions ≥ 0.1 . It was then suggested that the amount of solvent that can be miscibly incorporated in an LC depends on the host LC, temperature, as well as the nature and amount of solvent; noting that the 8CB+hex mixture phase separates for a solvent to liquid crystal mole ratio $\gtrsim 0.1$. Other studies of the effect of a biphenyl solvent on the splay and bend elastic constants and the rotational viscosity coefficient observed an anomalous behavior of the splay elastic constant K_{11} , the dielectric anisotropy $\Delta \varepsilon$, and the effective rotational viscosity coefficient γ_1^* near the N-SmA transition [17]. A theoretical study on the influence of non-mesogenic solvent on the N-SmA phase transition using Landau approach found a concentration induced tricritical point for the N-SmA transition and that the Frank elastic constants K_{11} , K_{22} , and K_{33} are modified as a function of solvent concentration near the N-SmA phase transition [14].

A recent calorimetric study of the N-SmA transition in mixtures of 8CB and cyclohexane (8CB+chex) was performed under continuous stirring conditions [12]. This study found a linear decrease of the transition temperatures T_{NA} and a linear increase of critical heat capacity exponent α with increasing mole fraction of cyclohexane x_{chex} . This behavior ends at a tricritical point (TCP) where the transition becomes first-order at $x_{chex}^{TCP} = 0.046$, just below which $\alpha = 0.5$ and the nematic range $\Delta T_N = T_{IN} - T_{NA} = 4.8$ K. For $x_{chex} > x_{chex}^{TCP}$, the N-SmA latent heat smoothly increases non-linearly from zero [12]. This work also presented a theoretical effort to understand the linear transition temperature shift along the same lines as Ref [14].

To review the relevant concepts, the N-SmA phase transition is a non-trivial member of the 3D-XY universality class due to the anisotropy of its critical fluctuations parallel and perpendicular to the director [11, 18, 19]. The N-SmA critical behavior is strongly effected by the coupling between the smectic order parameter $\psi(\vec{r}) = \psi_0 \exp(i\vec{q_0}.\vec{r})$ and the nematic order parameter $Q_{ij} = (1/2)S(3\hat{n}_i\hat{n}_j - \delta_{ij})$. Here, the ψ is the amplitude of the one-dimensional density wave, $\rho(\vec{r}) = Re[\rho_0 +$ $\exp(i\vec{q_0}.\vec{r})\psi(\vec{r})$], $q_0 = 2\pi/d$ is the wave vector corresponding to the layer spacing d, S is a scalar parameter measuring the magnitude of orientational order on short length scales, and \hat{n} is the nematic director describing spatial orientation of the orientational axis on longer length scales. The δS and $\delta \hat{n}$ couplings introduce two more terms in free energy expression as compared to the usual standard form. One term is of the form $\psi^2 S$, which is nematic-smectic order parameter coupling [20, 21] and the other is smectic order-nematic director fluctuation coupling $\psi^2 \delta \hat{n}$ [22, 23]. The former coupling reveals the effects of the elasticity of the nematic order prior to the onset of the smectic order and can drive the N-SmA transition from XY like to tricritical to weakly first-order [24]. The coupling $\psi^2 \delta \hat{n}$ causes the anisotropic elastic deformations in the smectic. The strength of this coupling depends on the magnitude of the splay elastic constant K_{11} , which is directly proportional to S^2 . Since it is expected that a low-molecular weight solvent miscible in an LC would affect both δS and $\delta \hat{n}$ fluctuations, the x_{sol} dependence would be accounted for using similar terms in a free-energy expansion.

In this work, the effect of a non-mesogenic, low molecular weight, solvent (nhexane) on the continuous nematic to smectic-A (N-SmA) phase transition on octylcyanobiphenyl (8CB) and n-hexane (hex) binary mixtures (8CB+hex) as a function of n-hexane mole fraction, x_{hex} , was studied using high-resolution accalorimetry without continuous stirring. This was done so as not to mask demixing or phase separation effects. The introduction of n-hexane on 8CB causes a dramatic change in the N-SmA phase transition behavior. The heat capacity peak associated with the N-SmA transition, δC_p , shifts towards lower temperature non-monotonically and becomes progressively larger as the hexane concentration increases. The dispersive part of heat capacity C''_n associated with the N-SmA transition abruptly appears as a peak for $x_{hex} \ge 0.08$ but is zero for $x_{hex} \le 0.06$ indicating a crossover from continuous (second-order) behavior to first-order behavior for the N-SmA transition with a tricritical point at $x_{hex}^{TCP} \approx 0.07$. The integrated ac-enthalpy increases overall as a function of hexane molar fraction. A simple but consistently applied power-law analysis for δC_p with $x_{hex} \leq 0.06$ find a non-linear increase in the heat capacity effective critical exponent towards the tricritical value ($\alpha_{TCP} = 0.50$) as $x_{hex} \rightarrow x_{hex}^{TCP}$ is observed. A small hysteresis of the δC_p shape between heating and cooling is seen and is likely due to a microscopic

phase separation of the solvent, perhaps into intersticial region between smectic layers. The non-monotonic transition temperature shift and extended curvature of α_{eff} behavior with extended curvature as $x_{hex} \rightarrow x_{hex}^{TCP}$ as compared to the linear behavior seen in the previous study on continuously mixed 8CB+chex samples [12] may be due to the competing interactions of microphase separation and dilution effects. Both these effects have significant consequences on the higher temperature I-N phase transition as well and has been previously reported in chapter 3.

4.2 Results

4.2.1 The *N*-SmA Heat Capacity

The liquid crystal octylcyanobiphenyl, 8CB, has a molecular mass of $M_w = 291.44 \text{ g mol}^{-1}$ and a density of $\rho_{LC} = 0.996 \text{ g ml}^{-1}$ at 300 K. A single batch of 8CB, purchased from Frinton Lab, was degassed under vacuum for about two hours in the isotropic phase before use for pure and mixture samples. Spectroscopic grade n-hexane (molecular mass of 86.18 g mol⁻¹ and a density of 0.655 g ml⁻¹ at 298 K with a boiling point of 342 K) purchased from EM Science was used without further purification. The 8CB and n-hexane mixtures appear to be miscible up to an nhexane mole fraction of ≤ 0.12 . This was confirmed by polarizing micrographs of the samples and is consistent with the miscibility limit mentioned by Rieker [16]. Measurements were performed on seven samples as a function of n-hexane mole fraction x_{hex} ranging from 0 (pure 8CB) to 0.12.

Figure 4.1 illustrates the specific heat capacity variation over an extended temperature range for the $x_{hex} = 0.02$ sample. The dashed curve under the N-SmA heat capacity peak represents the *I-N* specific heat capacity wing C_p^{wing} , which is the hypothetical baseline behavior of C_p in the absence of the N-SmA transition. This wing is used to determine the excess specific heat associated with the N-SmA phase transition as

$$\delta C_p = C_p - C_p^{wing}. \tag{4.1}$$

The resulting δC_p data of the N-SmA transition on heating for 8CB+hex and pure 8CB samples over a ±1.5 K temperature range window about the δC_p peak is shown in Fig. 4.2 (upper panel). As the mole fraction of n-hexane increases,



Figure 4.1. Specific heat capacity for an 8CB+hex sample on heating with $x_{hex} = 0.02$. The dashed dotted line represents the C_p background, while the dashed curve acts as C_p^{wing} and represents the low temperature *I*-*N* C_p wing that would be expected in the absence of *N*-SmA transition.

the N-SmA heat capacity peak becomes larger than the pure N-SmA peak and with apparently larger wings on the high temperature side of the peak. Figure 4.2 (lower panel) shows the imaginary part of specific heat C''_p on heating as a function of temperature about T_{NA} . For the n-hexane mole fractions $x_{hex} \leq 0.06$, the C''_p is flat, indicating the second-order nature of the transition. For $x_{hex} \geq 0.08$, the C''_p reveals a peak indicating a first-order behavior of the transition. As the mole fraction of n-hexane increases beyond $x_{hex} \geq 0.08$, the C''_p peak becomes broader with a two-phase co-existence region growing from ~ 0.35 K at $x_{hex} = 0.08$ to ~ 0.85 K at $x_{hex} = 0.12$. The cross-over to the N+SmA coexistence region is continuous in contrast to an abrupt cross-over to the I+N phase coexistence region [25]. Unlike in the case of the *I-N* phase transition C_p peak, the N-SmA C_p peak lies approximately at the center of the coexistence region.

The N-SmA excess specific heat δC_p (upper panel) and imaginary part of specific heat C''_p (lower panel) on cooling are shown in Fig. 4.3. On cooling, the δC_p peaks exhibit larger C_p wings on both sides of T_{NA} but the low temperature wing appears progressively smeared in temperature. In addition, the δC_p on cooling exhibits sharp peaks up to $x_{hex} = 0.08$ then appears rounded for x > 0.08. The N-SmA C''_p behavior on cooling is similar to the heating scans in that $C''_p = 0$



Figure 4.2. Upper panel: The excess specific heat δC_p associated with the N-SmA transition on heating as a function of temperature about T_{NA} for pure and all 8CB+hex samples. See legend. Lower panel: The imaginary part of heat capacity on heating for all samples as a function of temperature about T_{NA} .

through T_{NA} for $x_{hex} \leq 0.06$, then reveals a peak for $x_{hex} \geq 0.08$. This indicates, as on heating, a cross-over from continuous to first-order transition behavior. However, the C''_p peaks for $x_{hex} \geq 0.08$ on cooling have markedly different shape than on heating. Here, as the temperature approaches T_{NA} from above, a sharp jump preceded by a relatively small wings occurs at ~ 0.1 K above T_{NA} for all 8CB+hex

samples. As the temperature cools further, a long C''_p tail is seen to a common trend at ~ 0.25 K for $x_{hex} = 0.08$ and ~ 0.4 K for $x_{hex} = 0.09$ and 0.12 below T_{NA} . The increase in the two-phase co-existence is similar to that seen on heating.



Figure 4.3. Upper panel: The excess specific heat δC_p associated with the N-SmA transition on cooling as a function of temperature about T_{NA} for pure and all 8CB+hex samples. The definition of the symbols are given on the inset. Lower panel: The imaginary part of heat capacity on cooling for all samples as a function of temperature about T_{NA} .

The N-SmA transition temperature T_{NA} is defined as the temperature of the δC_p peak maximum and the *I*-N transition temperature is taking at the lowest temperature of the isotropic phase prior to entering the *I*+N two-phase coexistence region [25]. Figure 4.4 (upper panel) shows the *I*-N and the N-SmA phase

transition temperatures as a function of x_{hex} . As x_{hex} increases, both transition temperatures decrease non-linearly with a bump at $x_{hex} \sim 0.07$. Figure 4.4(lower panel) shows the nematic temperature range $\Delta T_N = T_{IN} - T_{NA}$ as a function of x_{hex} revealing a similar non-linear trend with a similar bump at the same x_{hex} . The horizontal dashed, dashed dot, and dot lines represent nematic ranges for pure 9CB [26], 8CB+chex [12], and 8CB+10CB [8] at the tricritical point, respectively. The solid straight lines are the transition temperatures (Fig. 4.4-upper panel) and nematic range (Fig. 4.4-lower panel) for the 8CB+chex system [12]. It is observed that the ΔT_N values at the tricritical point are fairly same for 8CB+hex, 8CB+chex, and 8CB+10CB systems. However, it has different value for pure 9CB.

Since continuous transition behavior is observed for $x_{hex} = 0.06$ and first-order behavior at $x_{hex} = 0.08$, a tricritical point mole fraction is taken as $x_{hex}^{TCP} = 0.07$ with the corresponding nematic range at $\Delta T_N^{TCP} \simeq 4.63$ K. The vertical dashed line in both the panels of Fig. 4.4 indicates x_{hex}^{TCP} and a bold-bordered box in the lower-panel gives the location of the cross-over point whose width and height are the magnitude of uncertainties in x_{hex}^{TCP} and ΔT_N^{TCP} , respectively.

The effective N-SmA transition enthalpy (or ac-enthalpy) δH_{NA}^* was obtained by integrating δC_p in the range ± 3 K about T_{NA} . The dispersive enthalpy, $\delta H_{NA}''$ of the N-SmA transition, available only for $x_{hex} \geq 0.08$, and was obtained by integrating the N-SmA C_p'' peak. Since a fixed heating frequency was used, the non-zero $\delta H_{NA}''$ is only proportional to the transition latent heat. The resulting δH_{NA}^* and $\delta H_{NA}''$ for heating (\circ) and cooling (\bullet) scans as a function of x_{hex} for all 8CB+hex samples are shown in Fig. 4.5. The δH_{NA}^* values show an overall increase in value with increasing x_{hex} and are consistent on heating and cooling. A small apparent jump in δH_{NA}^* is seen at $\sim x_{hex}^{TCP}$. See Figure 4.5(upper panel). The $\delta H_{NA}''$ exhibits a sudden jump from 0 to ~ 0.28 J g⁻¹ at x_{hex}^{TCP} .

A summary of these results for 8CB+hex samples including pure 8CB is tabulated in Table 4.1. Included are the n-hexane molar fraction x_{hex} , the N-SmA transition temperatures T_{NA} , nematic range ΔT_N , integrated enthalpy change δH_{NA}^* , imaginary enthalpy $\delta H_{NA}^{"}$, McMillan ratio MR and height of excess heat capacity peaks h_M for all the 8CB+hex samples including pure 8CB.



Figure 4.4. Upper Panel: The *I-N* and *N*-SmA phase transition temperatures on heating (\circ) and cooling (\bullet) as a function of x_{hex} . Solid lines are guides to the eye. Lower panel: The nematic temperature range ΔT_N on heating (\circ) and cooling (\bullet) as a function of x_{hex} . The closed and open rectangular boxes represent the position of tricritical points for 8CB+chex [12] and 8CB+hex systems respectively and the width and height of the boxes represent the uncertainties on x_{hex}^{TCP} and ΔT_N^{TCP} respectively. The horizontal dashed, dashed dot, and dot lines are nematic ranges for pure 9CB[26], 8CB+chex, and 8CB+10CB [8] respectively at tricritical point. The solid straight lines are transition temperature (upper panel) and nematic range (lower panel) for 8CB+chex system [12].

4.2.2 Power-law Analysis of the *N*-SmA phase transition

Because the δC_p for the N-SmA transition in 8CB+hex remains continuous and sharp for $x_{hex} \leq x_{hex}^{TCP}$, a critical power-law analysis was attempted. The usual



Figure 4.5. Upper panel: The total integrated δC_p ac-enthalpy δH^*_{NA} on heating (\circ) and cooling (\bullet) as the function of x_{hex} . Lower panel: Integrated $C^{"}_p$ enthalpy $\delta H^{"}_{NA}$ on heating (\circ) and cooling (\bullet) as the function of x_{hex} . Solid lines are guides to the eye.

power-law form, in terms of reduced temperature, $|t| = |(T - T_c)|/T_c$, used to analyze the excess specific heat associated with the N-SmA transition is given by [11]

$$\delta C_p = A^{\pm} |t|^{-\alpha} (1 + D_1^{\pm} |t|^{\Delta_1}) + B_c, \qquad (4.2)$$

where B_c is the critical background, A^{\pm} are the amplitudes, and D_1^{\pm} are the correction-to-scaling amplitude with an exponent $\Delta_1 = 0.524$ [11], both above (+) and below (-) the transition. A full, non-linear, fitting of Eq.(4.2) to the δC_p data was attempted, but because the number of data close to the peak were relatively sparse, these fits did not properly converge and yielded unphysical set of fit parameters.

In order to shed some light onto the critical behavior, a simplified power-law analysis procedure was employed in order to estimate the variation of the critical exponent α as a function of x_{hex} . The procedure was consistently applied to all

Table 4.1. Summary of the calorimetric results for pure and all 8CB+hex samples on heating. Shown are hexane molar fraction x_{hex} , N-SmA transition temperature T_{NA} , nematic range $\Delta T_N = T_{IN} - T_{NA}$ (in Kelvin), integrated enthalpy change δH^*_{NA} , imaginary enthalpy δH^*_{NA} (in J/g), McMillan's Ratio MR, and heat capacity maximum $h_M \cong \delta C_p^{max}(N-A)$ in $(JK^{-1}g^{-1})$.

	r					
$\overline{x_{hex}}$	T_{NA}	ΔT_N	δH_{NA}^*	$\delta H_{NA}^{"}$	MR	h_M
0.00	306.09 ± 0.06	7.11 ± 0.11	0.59 ± 0.06	_	0.977	0.78
0.02	304.42 ± 0.09	5.53 ± 0.59	0.99 ± 0.10	—	0.982	1.00
0.03	304.09 ± 0.08	5.03 ± 0.41	1.04 ± 0.10	—	0.984	1.45
0.06	304.21 ± 0.14	5.27 ± 0.50	0.73 ± 0.07	—	0.983	0.78
0.08	303.60 ± 0.16	4.46 ± 0.63	1.17 ± 0.12	0.28 ± 0.03	0.986	2.07
0.09	301.93 ± 0.17	3.23 ± 0.96	1.64 ± 0.16	0.29 ± 0.03	0.989	2.94
0.12	301.09 ± 0.08	2.53 ± 1.41	1.55 ± 0.15	0.40 ± 0.04	0.989	1.96

samples including pure 8CB in order to compare the resulting fits. This procedure begins by approximating T_c for each continuous δC_p peak. This is done by plotting a $log(\delta C_p)$ vs log(|t|) and choosing T_c such that the high and low temperature wings appear linear and parallel to each other for low |t|. The rounded and non-power-law data points are then easily identified and removed from further analysis.

Figure 4.6 shows the resulting log-log plot of data above and below T_c for pure 8CB ($x_{hex} = 0$) and the highest concentration 8CB+hex sample that appears continuous as determined by C''_p ($x_{hex} = 0.06$). Now, a range of data up to $|t_{max}|$ was chosen in order to perform a simple linear fit, $log(\delta C_p) = log(A^{\pm}) - \alpha'_{eff}log|t|$. Here, $|t_{max}|$ varied smoothly from 8.9×10^{-4} for pure 8CB to 1.8×10^{-3} for the $x_{hex} = 0.06$ 8CB+hex sample. The resulting linear fits are also shown in Fig. 4.6 for data above and below T_c . The difference between $\alpha'_{eff}(T > T_c)$ and $\alpha'_{eff}(T < T_c)$ is taken as the uncertainty in α'_{eff} . The resulting α'_{eff} are not the true critical exponents because of this simplified analysis. However, an ad-hoc assumption is made that since the procedure is applied uniformly to all samples, the same error occurred and resulted in a multiplicative correction. Thus, comparing the pure 8CB result in this simplified analysis to the literature value of $\alpha_{eff} = 0.3$ [24], a corrected α_{eff} for the 8CB+hex samples is taken as an algebraic shift of +0.17, the difference of $\alpha'_{eff} - \alpha_{eff}$ for pure 8CB. This shift was then applied for all samples from $x_{hex} = 0$ to 0.06 and is taken as the approximate x_{hex} dependence of α_{eff} .

The resulting estimate of the N-SmA heat capacity effective critical exponent as a function of x_{hex} are shown in Fig. 4.7 along with the behavior observed in the


Figure 4.6. Upper panel: Excess specific heats associated to N-SmA phase transition as a function of reduced temperature for pure 8CB for $T < T_c$ (•) and for $T < T_c$ (•). Lower panel: Excess specific heats associated to N-SmA phase transition as a function of reduced temperature for hexane mole fraction $x_{hex} = 0.06$ for $T < T_c$ (•) and for $T < T_c$ (•). Slope of the straight line in each graph gives the effective critical exponent α_{eff} .

previous 8CB+chex study implying a more rigorous fitting procedure [12]. Here, a linear rapid rise in α_{eff} is seen as x_{hex} increases from 0 to 0.04 that reproduces very well the 8CB+chex trend then curves over for $x_{hex} > 0.04$ until intersecting the $\alpha_{eff} = 0.50$ TCP value. The upward arrow in Fig. 4.7 is the best estimate of x_{hex}^{TCP} for this 8CB+hex system.



Figure 4.7. The effective critical exponent as a function of hexane mole fraction. solid line represents the best estimate of α_{eff} as a function of x_{hex} . This line intersects the horizontal dashed line at the tricritical point, $x_{hex} \simeq 0.07$. The dashed-dot line is α_{eff} for 8CB+chex system from reference [12]. Vertical arrows indicate the location of the tricritical points for 8CB+chex (downward arrow) [12] and 8CB+hex(upward arrow).

4.3 Discussion and Conclusions

The continuous N-SmA liquid crystal phase transition of binary mixtures of 8CB and n-hexane has been studied using high-resolution ac-calorimetry as a function of n-hexane concentration, x_{hex} . Multiple heating and cooling cycles reproduce each other for $x_{hex} \leq 0.12$ along with no visual indication of phase separation support the view that the 8CB+hex binary system remained mixed (n-hexane miscible) for all samples studied here, without mechanical mixing. This is supported also by earlier x-ray studies of the smectic layer spacing in 8CB+hex that showed phase separation for $x_{hex} \gtrsim 0.1$ [16].

A recent calorimetric study of binary mixtures of 8CB with various, lowmolecular weight, solvents found dramatic changes to the character of the N-SmA phase transition [12]. In this work, the N-SmA transition approaches a tricritical point linearly. However, this study used cyclohexane, that has ring structure and employed continuous mixing during measurements as a function of cyclohexane mole-fraction, x_{chex} . The transition temperature T_{NA} decreases linearly as x_{chex} increases, the critical exponent α increases linearly from 0.31 (pure 8CB) to 0.50 at $x_{chex} = 0.046$, and the onset of the N-SmA latent heat occurs smoothly at TCP, $x_{chex}^{TCP} = 0.046$. These results were modelled using mean-field Landau-de Gennes theory incorporating the nematic free-energy, smectic free-energy, and a coupling between nematic and smectic order parameters. This model was extended to account for the solvent by adding a solvent mole-fraction coupling to ψ^2 and to $\psi^2 \delta S$ to the total solvent free-energy. Similar results were found in 8CB+biphenyl binary mixtures and a Landau-de Gennes model that accounted for change in the LC elastic constants with x_{sol} . However, a TCP was not found in 8CB+biphenyl system [17].

In this present study, several important differences emerge. As x_{hex} increases, T_{NA} decreases as well as the nematic range ΔT_N in a non-linear way. The character of N-SmA transition remains continuous up to $x_{hex} \simeq 0.07$ where it appears to jump suddenly to a first-order transition. The bump in T_{NA} and ΔT_N as well as the jump in $\delta H_{NA}^{"}$ all occur at x_{hex}^{TCP} . The critical behavior, estimated by the simple power-law analysis presented here, evolves with α_{eff} initially increases linearly as in the 8CB+chex system but then curves over to reach $\alpha_{eff} = 0.50$ at $x_{hex} \rightarrow x_{hex}^{TCP}$. Qualitatively, the correction-to-scaling terms D^{\pm} and the amplitude ratio A^{-}/A^{+} are changing their values towards the tricritical values as a function of x_{hex} . Here, the qualitative measurement of the amplitude ratio A^{-}/A^{+} was extracted examining the gap between two slope lines of the linear fit of log-log plot of δC_p vs |t| (Fig. 4.6) and the curvature of the curve at high |t| was observed to get qualitative measure of D^{\pm} .

The addition of n-hexane in 8CB may be thought of as a random dilution effect, decreasing both the transition temperature T_{NA} and the nematic range ΔT_{NA} accordingly. A key point to remember is that these experiments were done without continuous stirring and so should have revealed any effect of macroscopic phase separation, which was not observed. However, phase separation on much shorter micro- and/or nano-scale, such as intercalation of the solvent between the smectic layers, is certainly possible. These dilution and microphase separation effects, may lead to two competing interactions causing the non-linearity in the transition temperature T_{NA} , nematic range ΔT_N , effective critical exponent α_{eff} and jump in the imaginary enthalpy $\delta H''_{NA}$. The microphase separation promotes bulk-like behavior while the random dilution is a strong suppressor of any transition behavior and their superposition need not be linear. These effects also cause the change in coupling between the order parameters ψ and Q which consequently change the order of the N-SmA phase transition from continuous to first order with a critical point at $x_{hex}^{TCP} \simeq 0.07$.

We have undertaken a detailed calorimetric studies on the effect of non-mesogenic, low molecular weight solvent (hexane) on octylcyanobiphenyl (8CB) phase transitions with emphasis on the most extensively studied but controversial N-SmA phase transition. The dilution of 8CB due to the addition of n-hexane causes the change in the liquid crystal molecular interactions. Interesting and striking effects are observed in 8CB+hex system including the observation of nearly the same tricritical nematic range for 8CB+hex as that for 8CB+chex, and 8CB+10CB systems. But the nematic range for pure 9CB, which is very nearly at TCP, is quite different. This does not appear accidental and raises important questions as to the underlying physics. Continued research efforts are needed to understand the behavior of the such LC+solvent mixture systems as a model system for the intermolecular interactions responsible for mesogenic order. In particular, detailed scattering experiments such as x-ray or neutron as a function of solvent concentration and temperature through the N-SmA transition would be most desirable to explore the critical behavior of the smectic correlation length as susceptibility.

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Chapter

Isotropic to smectic-A phase transition in liquid crystal + acetone binary mixtures

5.1 Introduction

Recently, attention has been given to binary mixtures of liquid crystal and a compatible (*i.e.* miscible), low-molecular weight, solvent as a system in which the intermolecular potential responsible for the LC order can be screened or modified. The studies to date of LC+solvent systems have focused exclusively on the isotropic to nematic (*I-N*) [3, 4] and the nematic to smectic-A (*N*-SmA) [4, 5, 6, 7, 8] phase transitions as a function of solvent type and concentration. These studies differ from those systems that employ surfactant [9, 10, 11], to create a colloidal emulsion in that these LC+solvent binary mixtures are in equilibrium and miscible.

The direct first-order transition from the isotropic to the smectic-A (*I*-SmA) phase has attracted attention in experimental [12, 13, 14, 15, 16, 17, 18, 19, 20] and theoretical research [21, 22, 23, 24] as a prototypical symmetry breaking phase transition. High-resolution synchrotron x-ray diffraction study of the *I*-SmA phase transition in 10CB-aerosil showed that the transition remains first-order for all gel densities with systematic evolution of correlation length[17]. The study of phase transition behavior of 10CB in the presence of silica aerogels showed that the direct *I*-SmA transition occurs through the nucleation of smectic domains[16].

The effect of pressure on the I-SmA phase transition was examined and pointed out that the effect is to increase the transition temperature and to decrease the discontinuity of the transition[23]. The macroscopic dynamic behavior was studied in vicinity of the I-SmA transition and the dynamic equations were presented on the isotropic and smectic-A side of the phase transition incorporating the effect of an external electric field[24]. The existence of surface induced order was shown in the isotropic phase of 12CB, which has the direct I-SmA transition, confined to anapore membranes through specific-heat and x-ray scattering studies[12]. All the observations showed that the I-SmA transition is more first order than the very weak I-N transition indicating that the orientational order of SmA phase is higher than that in the nematic phase. Even though significant effort was applied for the study of the I-SmA transition behavior, many problems related to fundamentals of the transition are yet to be solved.

Modification of the smectic structure as well as the introduction of new smectic phases has traditionally been carried out in binary mixtures of two LCs, each exhibiting a different smectic structure. An early study on a binary LC mixture, dibenzoate and TBBA, reported the first SmA-SmA transition[25], which was modelled by an extension of the Meyer-Lubensky free-energy form [26]. Since this early work, a host of SmA-SmA type transitions have been explored in binary LC mixtures [27, 28, 29, 30, 31, 32, 33] though nearly all involve incommensurate smectic structures with very wide two-phase coexistence ranges. A rare example of a single LC system is the dimesogenic LC KI5 and KII5, but these highly asymmetric LCs also involve incommensurate smectic structures with long lived metastability [34, 35, 36]. Among these early studies only the Sm A_d - A_2 transition has been studied thoroughly.

Most recently, a new phenomenological model of a de Vries type smectic LC has been developed that also appears applicable to a smectic-smectic phase transition [37]. This theoretical work predicts the possibility of a sharp, true first-order transition between two smectic phases. In all these studies, the smectic phase was modified by the mixture of two smectic LCs typically having different smectic structures. Here, the difference in space packing drives the stability and structure, even for the single component dimesogenic LC [34, 35, 36]. A more attractive route to studying smectic ordering is directly modifying the intermolecular potential for an LC that only exhibits a single smectic phase.

In this work, we report a high-resolution ac-calorimetric study on the effects of a non-mesogenic, low-molecular weight, polar solvent (acetone) on the firstorder I-SmA phase transition in decyl-cyanobiphenyl (10CB) and acetone (ace) binary mixtures (10CB+ace) as a function of acetone concentration, x_{ace} . The addition of acetone to 10CB changes the phase behavior of the 10CB+ace system dramatically. Two distinct first-order phase transition features are observed in the mixture. The high-temperature transition feature shifts marginally to lower temperature while the low-temperature feature shifts markedly towards lower temperature with increasing x_{ace} . The ΔC_p peak evolves for both the transition features with significant effect on low-temperature phase transition feature. The two-phase coexistence region for the low-temperature feature increases as a function of x_{acc} while remains fairly constant for the high-temperature feature. The hysteresis in the ΔC_p shape on heating and cooling is observed and increases as x_{ace} increases only for the low-temperature feature. These results were reproducible upon multiple thermal cycles and not likely affected by macroscopic phase separation. An example of such phase separation behavior is seen in mixtures of 10CB with the non-polar solvent decane.

5.2 Results

The *I*-Sm*A* phase transition for pure 10CB occurred at $T_{IA} = 323.69 \ K$, in good agreement with the literature value[38, 18]. The excess real specific heat ΔC_p and the imaginary specific heat C''_p for pure 10CB and six 10CB+ace samples on heating are shown in Fig. 5.1 as a function of temperature about the lowest stable temperature of the isotropic phase $\Delta T_{IA} = T - T_{IA}$. The characteristic features of the *I*-Sm*A* transition in pure 10CB, a single, sharp, peak in ΔC_p and C''_p with small wings above and below T_{IA} , transform into two heat capacity features for the 10CB+ace samples. The high-temperature signature, labelled peak-1, appears as a small peak in ΔC_p and very small signature in C''_p . Peak-1 represents a very weak first-order transition into a phase labelled P_1 . The low-temperature peak, labelled peak-2, appears as a large peak in both ΔC_p and C''_p , that are similar in shape. This peak-2 clearly represents a much stronger first-order transition from the P_1 phase to a lower temperature phase labelled P_2 . The data shown in Fig. 5.1 are consistent after multiple heating and cooling cycles and so appear to be in equilibrium.



Figure 5.1. (a) Excess specific heat ΔC_p as a function of temperature about the lowest stable temperature of the isotropic phase T_{IA} for all 10CB+ace samples including the bulk 10CB showing two type of phase transition on the mixtures: high-temperature peak-1 and low-temperature peak-2. The definition of the symbols are given on the inset. (b) Imaginary part of the heat capacity C''_p as a function of temperature about T_{IA} . Data are shown on heating.

Peak-1 shows a small ΔC_p that grows slightly with a very small, slightly decreasing, C''_p feature as x_{ace} increases. Peak-2 begins as a large and sharp peak in

 ΔC_p with a similarly large and sharp peak in C''_p at the lowest x_{ace} sample. As x_{ace} increases, peak-2 shifts to lower temperature and broadens in both ΔC_p and C''_p . For both ΔC_p and C''_p peak-2 appears as a sharp jump on low-temperature side then a broad tail following the peak on the high-temperature side on the heating scan.

Cooling scans are generally consistent with heating in that they are reproducible after multiple cycles and exhibit two heat capacity peaks that evolve in a similar way as a function of x_{ace} . However, there are significant differences in the shape of ΔC_p and C''_p for peak-2, while the hysteresis of peak-1 shape is small. Figure 5.2 shows the ΔC_p and C''_p profile for the $x_{ace} = 0.14$ sample on heating and the following cooling scan. The vertical dash-dotted lines on both sides of each transition indicate the coexistence region between them. For peak-2, both the ΔC_p and C''_p peaks are within the coexistence region but asymmetric showing a jump on *entering* the coexistence region for both heating and cooling. For peak-2, the ΔC_p maximum occurs near the edge of the two-phase coexistence range where it first enters.

These stable and reproducible results for the 10CB+ace samples are in stark contrast to mixtures of 10CB with a less miscible solvent. A similar series of experiments were carried out on mixtures of 10CB and a non-polar solvent, decane. None of these measurements were reproducible and exhibited characteristics of progressive phase separation with multiple thermal cycles. Figure 5.3 shows a typical heat capacity profile for a 10CB+decane sample as a function of temperature for a decane mole fraction $x_{decane} = 0.10(5 \text{ wt.\%})$. As the sample is thermally cycled at the same scanning rate, peak-2 shifts towards higher temperature and ultimately merges with peak-1 just below the pure 10CB *I*-SmA transition. This indicates a phase separation effect due to the non-polar nature of decane that is not observed in the 10CB+ace system

The phase below peak-1 is initially labelled P_1 while the phase below peak-2 is initially labelled P_2 with the highest temperature phase being the usual isotropic. The I- P_1 phase transition temperature, T_1 , is defined as the lowest temperature of the isotropic phase prior to entering the $I+P_1$ two-phase coexistence region and the P_1 - P_2 phase transition temperature, T_2 , is taken as the lowest temperature of the P_1 -phase prior to entering the P_1+P_2 two-phase coexistence region. Figure 5.4



Figure 5.2. (a) Excess specific heat ΔC_p as a function of temperature about T_{IA} for $x_{ace} = 0.14$ on heating (\circ) and cooling (\bullet). The dotted curve under peak-1 is the baseline used for determining δH_1^* . (b) Imaginary part of the heat capacity as the function of temperature about T_{IA_w} for $x_{ace} = 0.14$. Vertical dashed lines show the coexistence regions for both the transition features.

(a) shows the $I-P_1$ and P_1-P_2 phase transition temperatures on heating and cooling as a function of x_{ace} . The dashed lines in the figure represent the lower bound of the coexistence region for each phase transition as determine by $C_p^{"}$ [39]. As x_{ace} increases, the $I-P_1$ transition temperature remains fairly constant with a small hysteresis between heating and cooling as well as a modest increase in the $I+P_1$ coexistence range for the higher x_{ace} as shown in Fig. 5.4 (b). Also, as x_{ace} increases the P_1-P_2 transition temperature decreases dramatically by ≈ 10 K at $x_{ace} = 0.36$ with an increasing hysteresis between heating and cooling $T_2^{heat} - T_2^{cool} = +0.44$ K



Figure 5.3. Excess specific heat ΔC_p as a function of temperature for 10CB+decane system at $x_{decane} = 0.10(5 \text{ wt.\%})$. First heating (\circ), first cooling (\bullet), second heating(Δ) and the second cooling(\blacktriangle) showing phase separation indicated by shifting of peaks towards higher temperature and becoming a single peak from two or more peaks.

at $x_{ace} = 0.05$ to $T_2^{heat} - T_2^{cool} = +2.41K$ at $x_{ace} = 0.36$. The $P_1 + P_2$ coexistence range also exhibits a large increase, reaching $T_{co-ex} = 6.95K$ as x_{ace} increases to $x_{ace} = 0.36$. See Fig. 5.4 (b).

In order to shed light onto the phase identification of P_1 and P_2 , cross-polarizing micrographs were taken at three different temperatures corresponding to the isotropic, P_1 and P_2 phases. These temperatures are shown by an "x" in Fig. 5.4 (a) and labelled a, b, and c respectively. Images were taken on a $x_{ace} = 0.18$ sample after heating from 310K at a rate of +0.2 K/min to the target temperature then waiting for about 5 minutes for equilibrium. As expected, the image at point a, (T = 324.2K) is uniformly dark indicating the isotropic phase. Textures were observed at point b (T = 321K) and c (T = 313K) and are shown in Fig. 5.5. Both the images are nearly identical revealing a typical smectic texture indicating that both the P_1 and P_2 are smectic phases.

The transition enthalpies, real and imaginary, can be used to reveal the energetics of the transition and can aid the phase identification of P_1 and P_2 . A complete integration of the entire ΔC_p peak over a wide temperature range from 310K to 325K for all 10CB+ace samples was performed. The peak-1 transition enthalpy was isolated by subtracting a minimally curved baseline below the ΔC_p



Figure 5.4. (a) Transition temperatures as a function of x_{ace} in 10CB+ace on heating(open symbol) and cooling (filled symbol). The points a, b and c indicate the set of points where polarizing micrograph images were taken. The texture at point a looks the typical isotropic texture and in b and c are shown in Figure 5.5. Doted lines are lower limit of transition temperature for P_1 and P_2 phases. (b) Coexistence regions $I + P_1$ (half-filled square) and $P_1 + P_2$ (half-filled circle) as a function of x_{ace} .

peak-1 then integrating to give δH_1^* . The enthalpy δH_1^* was then subtracted from the total $\delta H_T^* = \delta H_1^* + H_2^*$ to yield the ac-enthalpy change δH_2^* associated with the P_1 - P_2 phase transition. The integrated ΔC_p enthalpy δH^* and imaginary C_p'' enthalpy $\delta H''$ as a function of acetone mole fraction for pure 10CB and all 10CB+ace samples are shown in Fig. 5.6. Most of the real and imaginary enthalpy are contributed by peak-2. The ac-enthalpy δH_2^* for the P_1 - P_2 transition increases slightly, reaching a maximum value of $\delta H_2^* = 6.28 J/g$ at $x_{ace} = 0.10$ followed by a nearly linear decrease with increasing x_{ace} . Similarly, $\delta H_2''$ increases more dramatically,



Figure 5.5. Polarizing microscope micrographs taken in for the $x_{ace} = 0.18$ sample and at temperatures 321K (b) and 313K (c) respectively. The images b and c correspond to the points b and c respectively in Figure 5.4. The scale bar on bottom-right corners of each micrograph corresponds to 10 μ m.

reaching its maximum value at $x_{ace} \approx 0.22$ followed by a decrease with increasing x_{ace} . In contrast to the behavior of δH_T^* and δH_2^* , the ac-enthalpy for peak-1, δH_1^* remains essentially constant at $\delta H_1^* \simeq 0.8 J/g$ for all x_{ace} . However, the dispersive enthalpy $\delta H_1''$ begins at a constant value for the lower x_{ace} then decreases slowly as x_{ace} increases above $x_{ace} \simeq 0.15$. Clearly, most of the energetics are contributed by the P_1 - P_2 transition with values of δH^* and $\delta H''$ similar to those of pure 10CB. This observation as well as the micrograph, supports the identification of the P_2 phase being the pure 10CB smectic- A_d phase.

A summary of results for the 10CB+ace samples including pure 10CB on heating is tabulated in Table 5.1. Included are acetone molar fraction x_{ace} , the $I-P_1$ phase transition temperature T_1 , the P_1 - P_2 transition temperature T_2 (in Kelvin), integrated enthalpy change for the $I-P_1$ transition δH_1^* , integrated enthalpy change for the P_1-P_2 transition δH_2^* , total integrated enthalpy δH_T^* , imaginary enthalpy for the $I-P_1$ transition $\delta H_1''$, imaginary enthalpy for the P_1-P_2 transition $\delta H_2''$, and



Figure 5.6. (a) The integrated ΔC_p ac-enthalpy δH_1^* on heating for the *I*-*P*₁ transition (Δ) , the P_1 - P_2 transition (\bullet) and total enthalpy for both the transitions (\circ) as a function of x_{ace} . (b) Imaginary enthalpy associated with the *I*-*P*₁ transition (Δ) , the P_1 - P_2 transition (\bullet) and total for both the transitions (\circ) as a function of x_{ace} .

total imaginary enthalpy for both the transitions $\delta H_T''$ (in J/g).

5.3 Discussion and conclusions

The *I*-Sm*A* phase transition in LCs is a first-order phase transition and exhibits both orientational and partial translational order. The introduction of acetone to 10CB greatly affects the phase transition behavior. In the concentration range studied here, the binary mixture of 10CB+ace have reproducible ΔC_p features after multiple thermal cycles. Also, reproducible polarizing micrographs are seen

transit	ion δH_1^* , integra	tred entnarpy chai	inge ior une r1	1.5 of attraction of	1			
the I_{-}	P_1 transition δH	", imaginary enth	talpy for the P_1	$-P_2$ transition	$\delta H_2''$, and tota	l imaginary en	thalpy for both	1 the transitions
$\delta H_T''$ (j	in J/g).	4			I			
x_{ace}	T_1	T_2	δH_1^*	δH_2^*	δH_T^*	$\delta H_1''$	$\delta H_2^{"}$	$\delta H_T^{''}$
0.00	323.69 ± 0.14	323.69 ± 0.14		I	5.14 ± 0.51	1	I	1.82 ± 0.18
0.05	323.20 ± 0.14	321.19 ± 0.75	0.77 ± 0.08	5.19 ± 0.52	5.95 ± 0.60	0.77 ± 0.08	2.01 ± 0.20	2.78 ± 0.28
0.10	322.13 ± 0.10	319.79 ± 0.96	0.62 ± 0.06	6.28 ± 0.63	6.89 ± 0.69	0.97 ± 0.10	1.85 ± 0.19	2.82 ± 0.28
0.14	323.05 ± 0.07	319.27 ± 1.28	0.64 ± 0.06	5.52 ± 0.55	6.16 ± 0.62	0.92 ± 0.09	2.60 ± 0.26	3.53 ± 0.35
0.22	323.07 ± 0.18	317.57 ± 1.73	0.50 ± 0.05	4.75 ± 0.47	5.25 ± 0.53	0.36 ± 0.04	3.38 ± 0.34	3.74 ± 0.37
0.28	323.61 ± 0.25	317.55 ± 1.52	1.42 ± 0.14	4.30 ± 0.43	5.71 ± 0.57	0.46 ± 0.05	2.20 ± 0.22	2.66 ± 0.26
0.36	323.19 ± 0.25	316.33 ± 2.87	0.86 ± 0.09	1.85 ± 0.19	2.70 ± 0.27	0.20 ± 0.02	2.52 ± 0.25	2.72 ± 0.27

Table 5.1. Summary of the ac-calorimetric results for the 10CB+ace samples. Shown are acetone molar fraction x_{ace} , the *I*- P_1 phase transition temperature T_1 , the P_1 - P_2 transition temperature T_2 (in Kelvin), integrated enthalpy change for the I- P_1

after multiple thermal cycles as well as revealing uniform textures. These observations and results strongly indicate that for this range of x_{ace} , the acetone remains miscible and in equilibrium in mixtures with 10CB. This is likely due to the low x_{ace} range studied and the polar nature of both the acetone and 10CB. For similar concentrations of a non-polar solvent, decane, in mixtures with 10CB, clear evidence of phase-separation are observed as shown in Fig 5.3.

For the 10CB+ace samples, calorimetry revealed two, well defined features in both ΔC_p and $C_p^{"}$ that were reproducible after multiple thermal cycles and each exhibited different hysteresis as well as x_{ace} dependence. Both features have $C_p^{"} \neq 0$ and are inside their respective two-phase coexistence range. These characteristics of the two signatures indicate that both represent distinct first-order phase transitions. For the polarizing optical micrographs, a completely dark texture is observed for the highest temperature phase while a typical smectic texture is seen for both lower temperature phases. Also, the total enthalpy from both transition features for samples up to $x_{ace} = 0.28$ are very similar to the pure 10CB *I*-Sm A_d enthalpy. These observations identify the highest temperature phase as the isotropic phase and the lowest temperature phase as the smectic- A_d of pure 10CB.

Most of the total enthalpic contribution, real as well as imaginary, is from the P_1 -Sm A_d phase transition while the I- P_1 transition accounts for only ~ 10% of δH_T^* . Also, the concentration dependence of the I- P_1 enthalpy and transition temperature are different than that for the P_1 -Sm A_d dependence. Polarizing micrographs of P_1 phase clearly show a uniform smectic texture. Given the small energy associated with this transition, it is labelled a "weak smectic-A" (Sm A_w) phase. This Sm A_w phase exhibits smectic-A symmetry but is less ordered than the Sm A_d phase.

The observed phases may be explained in terms of the molecular interaction of acetone and the liquid crystal. In the isotropic phase, as usual, all the molecules are randomly oriented and thoroughly mixed. Due to the polar nature of both acetone and 10CB molecules, some screening of the 10CB dipole moment should be expected but at these concentrations the steric interactions are preserved. Thus, the acetone may interfere with the formation of cybotactic groups (typical in smectic- A_d) allowing a portion of the 10CB molecules to be present as individual molecules in the SmA phase. As the temperature lowers further, the LC interactions grow,



Figure 5.7. Cartoon representing a model showing molecular structure in isotropic, weak smectic-A and Smectic- A_d phase in 10CB+ace mixtures. Cylindrical rod with a black dot and a wiggly tail on it represents a 10CB molecule and small fan like structure represents an acetone molecule. Dotted ovals show dimer structure and a monomer with an acetone molecule anchored on a 10CB molecule.

eventually overcoming the partial dipole screening by the acetone allowing for the full formation of the $\text{Sm}A_d$ phase. The proposed weak smectic-A phase can be considered as a smectic-A layered structure comprised of a mixture of individual and cybotactic groups of 10CB. See Fig. 5.7 for the illustration of these phases.

The downward shift of the transition temperatures in 10CB+ace system is consistent with an impurity (dilution) effect [3]. The increasing co-existence region, and increasing hysteresis of the $\text{Sm}A_w$ - $\text{Sm}A_d$ transition ΔC_p shape on heating and cooling as a function of x_{ace} can be explained in terms of the interaction of acetone polar molecules with 10CB molecules. During a temperature scan, the heat capacity peak exhibits a jump when entering the coexistence region and leaves the region with a broad tail. As the coexistence region is approaching, nucleation process starts sharply and as coarsening processes, the screening by the acetone begins to slow the establishment of order, giving rise to a broad tail.

We have undertaken detailed calorimetric studies on the effect of non-mesogenic, low molecular weight polar solvent (acetone) on the first order I-SmA phase transition of decyl-cyanobiphenyl (10CB). Acetone dilutes the liquid crystal and changes the intermolecular potential among the molecules in the mixture. Dramatic change in phase behavior with a new transition feature from less orientationally order weak smectic-A to more orientationally ordered smectic- A_d including the isotropic to less-ordered weak smectic-A phase is observed due to the presence of acetone on 10CB. Both the transition features evolve in shape and size of ΔC_p as a function of x_{ace} . Downwards shifting of transition temperature for both the transitions with dramatic shifts on weak smectic-A to smectic- A_d transition temperature has been observed. These all reveal a new aspect of the effect of polar solvent interactions on the liquid crystal transitions. Continued experimental efforts are needed specifically, x-ray and/or neutron scattering studies probing the smectic structure as a function of solvent content and temperature would be particulary important and interesting.

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Chapter 0

Phase transitions in carbon nanotubes and liquid crystal composites

6.1 Introduction

Carbon nanotubes(CNTs) are highly anisometric rigid "string-like" particles with diameters on the order of nanometers and lengths ranging from micrometers to millimeters [1]. Since their discovery [1, 2, 3], extensive studies of their unique structure and properties as well as possible applications have been reported [4, 5, 6, 7]. Liquid crystals (LCs)[8, 9] are anisotropic fluids that exhibit numerous thermodynamically stable phases between an isotropic liquid and a three-dimensionally ordered solid. In their least ordered phase, the nematic, LCs show orientational order due to molecular self assembly and at the same time maintaining fluid flow properties. In the smectic phase, they show both orientational and partial translational order characterized by a 1-d density wave [8, 9]. Liquid crystalline substances have been extensively studied due to their applications and as important physical models of self-assembly [10].

When CNTs are dispersed in a liquid crystal, they can modify the physical properties and hence the phase behavior of the liquid crystal. In a well-dispersed CNT in a LC host, there is surface anchoring of the LCs on the CNT surfaces, presumably through the $\pi - \pi$ stacking of the hexagonal structure of both the biphenyl and graphene, that is strengthened by a binding energy originating from charge transfer between the LCs and CNT [11]. The dispersion of these rigid string-like nanoparticles can also locally pin the nematic director as well as the smectic layers given homogenous surface alignment. These physical interactions are responsible for the coupling between the orientational order parameter of the LC with that of the CNT and represent a unique physical assembly.

In recent years, the dispersion of carbon nanotubes in different liquids and liquid crystal media has attracted intense interest. Research has been focused on liquid crystalline phases of CNTs [12, 13, 14, 15, 16], dispersion and alignment of CNTs in thermotropic or lyotropic liquid crystals [17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27], and studies of LC+CNT composite system for improving electro-optical switching properties[28, 29, 30, 31, 32]. Recently, investigations on LC+CNT composites have shown that the orientational order can be transferred to the dispersed CNTs [17, 33]. It has also been observed that the aligned CNT can cause an increase of the orientational order in the LCs [34]. Such composites have been proposed as memory devices using their nanoelectromechanical properties [35].

Some research efforts have also been made on phase behavior and phase transitions of LC+CNT mixtures [36, 37, 38, 39, 40]. LC+CNT binary systems were investigated using optical microscopy and DSC, finding an enhancement of the isotropic to nematic (*I-N*) phase transition temperature revealing a "chimney" type phase diagram in LC+CNT mixtures over a narrow range of ~ 0.1-0.2 wt.%of CNT [36]. An *I-N* phase transition was observed in a LC+CNT suspension due to joule heating produced by a dc-electric field that rotates the CNT out of sample plane short-circuiting the electrodes and producing a current flow through the CNT [38]. A high-resolution ac-calorimetry and dielectric study of the *I-N* phase transition of 5CB+CNT showed the induction of local deformations of the nematic director and the formation of pseudo-nematic domains within the LC media [40]. Most of these studies were focused on the nematic ordering and the *I-N* phase transition behavior.

In this work, we study the phase transition behavior of the liquid crystal octylcyanobiphenyl, 8CB, doped with multiwall carbon naotubes (CNTs) as a function of concentration of CNT. The incorporation of CNTs in 8CB reveals a unique phase behavior. The *I-N* excess specific heat ΔC_p peak in 8CB+CNT samples is wider as compared to that in pure 8CB but the N-SmA excess specific heat δC_p peaks are sharp and the wings for all the 8CB+CNT samples and the bulk overlay each other. The *I*-N and the N-SmA phase transition temperatures shift slightly downwards as compared to that of pure 8CB but remains fairly constant as a function of CNT content up to 0.0060 weight fraction of CNTs. However, the order of the phase transition remains unchanged from bulk, the *I*-N is first-order and the N-SmA is continuous. The thermal transport properties of 8CB+CNT evolve in the ordered nematic and smectic-A phases as a function of temperature. New calorimetric features are observed in the nematic temperature range for intermediate CNT concentrations. The evolution of heat capacity peak, slight change in transition temperature and change in the thermal transport properties are likely due to the elastic coupling between LC director and the CNT.

6.2 Experimental

6.2.1 Materials and Sample Preparation

The liquid crystal, 4-cyano-4'-octylbiphenyl (8CB), used for this experiment was purchased from Frinton laboratory. Pure 8CB (2.3nm long and 0.5nm wide molecules with molecular mass $M_w = 291.44$ g mol⁻¹) has a weakly first-order isotropic to nematic phase transition at $T_{IN}^0 = 313.98$ K, the second-order nematic to smectic-A transition at $T_{NA}^0 = 306.97$ K, and strongly first-order crystal to SmA transition at $T_{CrA}^0 = 290$ K [41]. Multiwall carbon nanotubes (CNTs), synthesized by chemical vapor deposition technique, containing nanotubes $5 - 30 \ nm$ in diameter and $1 - 5 \ \mu m$ in length were obtained from Dr. Saion Sinha [42] and used without further processing. In general, the CNT are in the bundles due to the attractive Van der Waals interaction between individual nanotubes. There is also a possibility of physical entanglement among the tubes due to high aspect ratio and flexibility of nanotubes. When the CNT in the composite are in bundles they may have disordering effect in the host phase, possibly revealing strongly disturbed ordered domain in the vicinity of the CNT bundles and the natural LC domain between them. They can be disbundled by ultrasonication.

The 8CB was degassed under vacuum in its isotropic phase about two hours before use. The LC, proper amount of carbon nanotubes and relatively large amount of pure acetone were mixed in a vial. The mixture was then mechanically mixed in a touch-mixer for about an hour and ultrasonicated in an ultrasonic bath for about 10 hours in the isotropic phase of pure 8CB. After ultrasonication the dispersion was placed over the hot plate to evaporate the acetone slowly out of the mixture and then the mixture was degassed under vacuum at 318 K for about 2 hours. Different samples having ϕ_w ranging from 0.0005 to 0.0060 were prepared using the same procedure. Here, $\phi_w = m_{CNT}/(m_{LC} + m_{CNT})$ is the weight fraction of CNT, where m_{CNT} and m_{LC} are masses of CNT and LC respectively.

When the composite sample was ready it was introduced into an envelope type aluminum cell of dimensions ~ $12 \times 8 \times 0.5 \text{ mm}^3$. A 120 Ω strain gauge heater and 1 $M\Omega$ carbon-flake thermistor were attached on the opposite surfaces of the cell. The filled cell was then mounted in the high resolution calorimeter, the details of which can be found elsewhere [43, 44, 45].

6.2.2 Ac-Calorimetry

High resolution ac-calorimetric measurement were carried out on a home made calorimeter at WPI. In its ac mode, oscillating power $P_{ac} \exp(i\omega t)$ is applied to the cell containing a sample of finite thermal conductivity resulting in the temperature oscillations with an amplitude T_{ac} and a relative phase shift between temperature oscillation and input power, $\varphi = \Phi + \frac{\pi}{2}$ where Φ is the absolute phase shift. The amplitude of the temperature oscillation is given by [46],

$$T_{ac} = \frac{P_{ac}}{\omega C} \left(1 + (\omega \tau_e)^{-2} + \omega^2 \tau_{ii}^2 + \frac{2K_e}{3K_i} \right)^{-1/2}, \tag{6.1}$$

where, P_{ac} is the amplitude and ω is the angular frequency of the applied heating power, $C = C_s + C_c$ is the total heat capacity of the sample+cell which includes heater and thermistor. $\tau_e = C/K_e$ and $\tau_{ii}^2 = \tau_s^2 + \tau_c^2 = (C_s/K_s)^2 + (C_c/K_c)^2$ are external and internal relaxation times respectively. Here, K_s is the thermal conductance of the sample and K_e is the external thermal conductance to the bath. The relative phase shift between the applied power and resulting temperature oscillations is given by,

$$\tan \varphi = \frac{1}{\omega \tau_e} - \omega \tau_i = \frac{K_e}{\omega C} - \omega \left(\frac{C_s}{K_s} - \frac{C_h + C_\theta}{K_h + K\theta}\right),\tag{6.2}$$

where, $\tau_i = \tau_s + \tau_c$. The phase shift is related to both the heat capacity and the thermal conductance of the system. If frequency of the temperature oscillation is faster than the external equilibration time and slower than the sample internal equilibration time, *i.e.*

$$\omega \tau_i < 1 < \omega \tau_e. \tag{6.3}$$

Then, the Eq. 6.1 becomes

$$C \cong \frac{P_{ac}}{\omega T_{ac}}.\tag{6.4}$$

The region where the inequalities 6.3 are valid can be found experimentally plotting ωT_{ac} versus ω . The plateau observed in log-log scale of the curve is the region where the inequalities 6.3 are valid and gives the working frequency region for the calorimeter[47].

The specific heat at a heating frequency ω can be expressed as

$$C_p = \frac{C'_{filled} - C_{empty}}{m_s} = \frac{(P_{ac}/\omega T_{ac})\cos\varphi - C_{empty}}{m_s},\tag{6.5}$$

$$C_p'' = \frac{C_{filled}''}{m_s} = \frac{(P_{ac}/\omega T_{ac})\sin\varphi - (K_e/\omega)}{m_s},\tag{6.6}$$

where, C'_{filled} and C''_{filled} are the real and imaginary parts of the heat capacity, C_{empty} is the heat capacity of the empty cell, m_s is the mass of the sample (in the range of 15 to 30 mg). Equations (6.5) and (6.6) requires a small correction to account the non-negligible internal thermal resistance as compared to $R_e(=1/K_e)$ and this was applied to all samples [48]. The real part of heat capacity indicates storage (capacitance) of the thermal energy whereas the imaginary part indicates the loss (dispersion) of energy in the sample analogous to the real and imaginary parts of the complex permittivity. The imaginary part of the heat capacity exhibits its non-zero value only on the dispersive regions, such as a two-phase coexistence where the latent heat is released. But, it is zero at the temperatures corresponding to equilibrium, one-phase states[41].

The excess specific heat associated with a phase transition can be determined by subtracting an appropriate background C_p^{BG} from total specific heat over a wide temperature range. The excess specific heat is given by

$$\Delta C_p = C_p - C_P^{BG}.\tag{6.7}$$

For the N-SmA phase transition,

$$\delta C_p = C_p (N - SmA) - C_P^{BL}, \tag{6.8}$$

where, C_P^{BL} is the baseline or wing below N-SmA C_p phase transition peak.

The enthalpy change associated with a phase transition can be defined as

$$\delta H = \int \Delta C_p dT. \tag{6.9}$$

For a second-order or continuous phase transitions, the limits of integration are as wide as possible about ΔC_p peaks and the integration yields the total enthalpy change associated with the transition. But for the first-order transitions the situation is complicated due to the presence of the coexistence region and latent heat ΔH . In this case, the total enthalpy change is the sum of the pretransitional enthalpy and latent heat $\Delta H_{total} = \delta H + \Delta H$. An integration of the observed ΔC_p peak yields an effective enthalpy change δH^* which includes some of the latent heat contribution. The integration of the imaginary part of heat capacity given by Eq. 6.6 gives an imaginary enthalpy $\delta H''$ which is the dispersion of energy in the sample and is an indicator of the first-order character of the transition. In ac-calorimetric technique the uncertainty in determining the enthalpy is typically 10% due to the uncertainty in the baseline and background subtraction.

6.3 Phase transitions in 8CB+CNT

6.3.1 Overview

For pure 8CB, the *I-N* phase transition occurs at $T_{IN}^0 = 313.21$ K while the *N*-SmA transition occurs at $T_{NA}^0 = 306.09$ K, both are about 1 K lower than the highest values reported in the literature [49]. The *I-N* effective enthalpy $\delta H_{IN}^* = 5.13 \pm 0.51$ J/g, the *N*-SmA effective enthalpy $\delta H_{NA} = 0.59 \pm 0.06$ J/g and the *I-N* dispersive enthalpy $\delta H_{IN}^{"} = 0.60 \pm 0.06$ J/g in pure 8CB are within 10% of

the literature value [50]. These results are used for comparison to the composite results.

The resulting excess specific heat ΔC_p data for 8CB+CNT samples studied on heating as a function of temperature about T_{IN} are shown in Fig. 6.1(a). The T_{IN} is defined as the high temperature limit of the I+N coexistence range. The I-N and the N-SmA phase transitions are characterized by a distinct ΔC_p peak for all 8CB+CNT samples similar in character to those in pure 8CB. The ΔC_p wings are similar for all 8CB+CNT composite samples and pure 8CB below and above the transitions revealing that the bulk-like order fluctuations are present in the isotropic, nematic and smectic-A phases. In addition to the bulk-like 8CB transition signatures, a new ΔC_p feature is observed in the nematic range for intermediate values of ϕ_w from 0.0010 to 0.0020. This new feature presents as a small broad peak mid-way in the nematic phase.

The imaginary specific heat C''_p as a function of temperature about T_{IN} is shown in Fig. 6.1(b). The C''_p exhibits a sharp peak associated with the *I-N* phase transition and no peak corresponding to the *N*-Sm*A* phase transition. This is consistent with the *I-N* transition being weakly first-order and the *N*-Sm*A* being continuous or second-order phase transition for all ϕ_w . Surprisingly, the C''_p baseline does not remain zero and temperature independent for 8CB+CNT samples. Here, the C''_p baseline breaks to a linear temperature dependence in the nematic and smectic-*A* phases on cooling. See Figure 6.1(b). The negative slope of this linear behavior appears to be ϕ_w independent but the break temperature shifts towards the T_{IN} with increasing ϕ_w . This new observation will be discussed in detail in Section 6.3.3.

A summary of transition temperatures, the nematic temperature ranges, and enthalpies for all samples on heating is given in Table 6.1. Included are CNT weight fraction ϕ_w , the *I-N* transition temperature T_{IN} , the *N*-SmA transition temperature T_{NA} , the nematic range ΔT_N (in Kelvin), integrated enthalpy change δH_{IN}^* , imaginary enthalpy $\delta H_{IN}^{"}$ (in J/g), height of the *N*-SmA δC_p peak, h_{NA} (in J/gK) and δH_{NA} , integrated enthalpy change for the *N*-SmA transition (in J/g). All data presented here were taken at a heating frequency of 31.25 mHz and at a scanning rate of 0.2 K h⁻¹ for -3 K $\leq T_{NA} \leq$ 3 K and 1 K h⁻¹ for other ranges of temperature. For all 8CB + CNT samples each heating scan was followed by



Figure 6.1. (a) Excess specific heat ΔC_p as a function of temperature about T_{IN} for all 8CB+CNT samples including pure 8CB. Symbols listed in the inset are for $100 \times \phi_w$ and for both the panels. (b) Imaginary specific heat C''_p as a function of temperature about T_{IN} .

a cooling scan and experienced the same thermal history. A detailed discussion of the I-N and the N-SmA phase transition in 8CB+CNT is presented in the following Section 6.3.2.

6.3.2 The *I*-*N* and *N*-Sm*A* phase transitions

The *I-N* and *N*-Sm*A* transitions are characterized by analyzing the heat capacity (real and imaginary) profile, phase diagram, and transition enthalpies. An expanded view of the *I-N* excess specific heat ΔC_p and imaginary specific heat C''_p

Table 6.1. Summary of the calorimetric results for the 8CB+CNT samples on heating. Shown are CNT wt. fraction ϕ_w , the *I*-*N* transition temperature T_{IN} , the *N*-SmA transition temperature T_{NA} , nematic range ΔT_N (in Kelvin), integrated enthalpy change δH_{IN}^* , imaginary enthalpy δH_{IN}^* (in J/g), height of the *N*-SmA δC_p peak, h_{NA} (in J/g K) and δH_{NA} , integrated enthalpy change for the *N*-SmA transition in (J/g).

0/811/	and OH_{NA} , me	egrated entitial	py change io.			m(0/8)	
ϕ_w	T_{IN}	T_{NA}	ΔT_N	δH_{IN}^*	$\delta H_{IN}^{''}$	h_{NA}	δH_{NA}
0.000	313.21 ± 0.17	306.09 ± 0.03	7.12 ± 0.25	5.1 ± 0.5	0.60 ± 0.06	0.9 ± 0.1	0.59 ± 0.06
0.0005	312.54 ± 0.26	305.24 ± 0.07	7.32 ± 0.38	5.5 ± 0.6	0.53 ± 0.05	1.1 ± 0.2	0.69 ± 0.07
0.001	311.72 ± 0.26	304.67 ± 0.02	7.10 ± 0.39	6.2 ± 0.6	0.53 ± 0.05	1.0 ± 0.1	0.61 ± 0.06
0.0015	312.56 ± 0.19	305.32 ± 0.01	7.24 ± 0.29	5.4 ± 0.5	0.56 ± 0.06	1.0 ± 0.2	0.80 ± 0.08
0.002	312.62 ± 0.17	305.53 ± 0.01	7.09 ± 0.26	5.8 ± 0.6	0.65 ± 0.07	1.4 ± 0.2	0.67 ± 0.07
0.0025	311.75 ± 0.20	304.71 ± 0.01	7.04 ± 0.30	5.5 ± 0.6	0.54 ± 0.05	1.2 ± 0.2	0.67 ± 0.07
0.003	310.73 ± 0.37	303.49 ± 0.03	7.24 ± 0.56	5.4 ± 0.5	0.56 ± 0.06	0.9 ± 0.1	0.73 ± 0.07
0.004	312.06 ± 0.14	305.16 ± 0.03	6.90 ± 0.21	5.5 ± 0.6	0.71 ± 0.07	1.3 ± 0.2	0.67 ± 0.07
0.005	312.29 ± 0.19	305.08 ± 0.01	7.21 ± 0.28	6.3 ± 0.6	0.62 ± 0.06	1.0 ± 0.2	0.63 ± 0.06
0.006	311.73 ± 0.28	304.50 ± 0.01	7.23 ± 0.41	5.6 ± 0.6	0.67 ± 0.07	0.9 ± 0.1	0.65 ± 0.07

on heating as a function of temperature about T_{IN} are shown in Fig. 6.2. Generally, the ΔC_p peaks for the *I-N* transition in 8CB+CNT are broader than that in pure 8CB by about a factor of 2.5 but do not exhibit any systematic trend with ϕ_w . Similar behavior is also observed for the C''_p peak for all ϕ_w samples.

The ΔC_p behavior is consistent between heating and cooling as well as being reproducible after multiple thermal cycles. The ΔC_p wings above and below all transitions match each other on heating and cooling. The I-N ΔC_p cooling and heating peaks are well within the coexistence region. See Figure 6.3. But, there is a small hysteresis of the ΔC_p in the two-phase I+N region between heating and cooling with the cooling ΔC_p peak being slightly higher in temperature and height. The consistency of ΔC_p data on heating and cooling shows that the sample does not phase-separate on the macroscopic level and the sample is in equilibrium. However, the microscopic (nanoscopic) phase separation and diffusion of CNT in LC media may still occur.

The *I-N* phase transition temperature T_{IN} is defined as the temperature of C''_p inflection point on the high temperature side of the C''_p peak [51]. Here, T_{IN} represents the lowest stable temperature of the isotropic phase. The *N*-Sm*A* phase transition temperature T_{NA} is taken as the *N*-Sm*A* δC_p peak temperature. Both the T_{IN} and T_{NA} slightly decrease in value as compared to those in pure 8CB, T^0_{IN} and T^0_{NA} but remain essentially ϕ_w independent for the 8CB+CNT composites as shown in Fig. 6.4(a). The phase transition temperature shifts are ΔT_{IN} =



Figure 6.2. (a) Excess specific heat ΔC_p associated with the *I-N* phase transition as a function of temperature about T_{IN} . The definition of the symbols are given on the inset. Symbols listed in the inset are for $100 \times \phi_w$ and for both the panels. (b) Imaginary specific heat C''_p as a function of temperature about T_{IN} .

 $T_{IN} - T_{IN}^0 \simeq -1.08$ K and $\Delta T_{NA} = T_{NA} - T_{NA}^0 \simeq -1.11$ K for all ϕ_w studied. Because of uncertainty in the homogeneity of the 8CB+CNT samples, small noise appeared in the transition temperatures can be related to perfect mixing of 8CB+CNT samples. The nematic range, $\Delta T_N = T_{IN} - T_{NA}$ remains constant for all the samples as shown in Fig. 6.4(b). The coexistence region, ΔT_{I+N} , is determined taking the difference of high temperature and low temperature limits of C_p'' peak and is shown in Fig. 6.4(c). For this batch of pure 8CB, $\Delta T_{I+N}^0 = 0.26$ K while for all 8CB+CNT samples ΔT_{I+N} is larger at 0.50 K and shows no systematic ϕ_w dependence.


Figure 6.3. The excess specific heat ΔC_p associated with *I-N* phase transition as a function of temperature about T_{IN} on heating (\circ) and cooling (\bullet) for (a) $\phi_w = 0.001$ (b) $\phi_w = 0.006$. Grey symbols represent data points in the *I+N* two-phase co-existence region.

The excess specific heat δC_p associated with N-SmA phase transition as a function of temperature about T_{NA} is shown in Fig. 6.5 for pure 8CB and all 8CB+CNT samples on heating. The δC_p exhibits a sharp and distinct N-SmA transition peak for all samples. The δC_p wings overlay each other for all samples on both the low and high temperature sides of the transition. This strongly indicates that the nematic and smectic fluctuations remain essentially bulk-like and constant for all samples. Given no strong change in the δC_p behavior as a function of ϕ_w , no power-law fits were attempted. The C''_p does not exhibit any peak associated with



Figure 6.4. (a) The *I-N* and *N-SmA* phase transition temperatures on heating (\circ) and on cooling (\bullet) as a function of ϕ_w (b) Nematic range on heating (\circ) and cooling(\bullet) as a function of ϕ_w . (c) The *I+N* co-existence region on heating (\circ) and cooling(\bullet) as a function of ϕ_w .



Figure 6.5. Excess specific heat δC_p associated with *N-SmA* phase transition as a function of temperature about T_{NA} . Symbols listed in the inset are for $100 \times \phi_w$.

N-Sm*A* phase transition for all 8CB+CNT samples and pure 8CB, which indicates that the *N*-Sm*A* phase transition remains second-order for all ϕ_w samples.

An integration was performed on ΔC_p over a wide temperature range of ~ 299 to 316 K for all 8CB and 8CB+CNT samples to yield δH_T^* while an integration of δC_p over ± 3 K about T_{NA} yields δH_{NA} . The *I*-*N* ac-enthalpy is then determined as $\delta H_{IN}^* = \delta H_T^* - \delta H_{NA}$. The *I*-*N* imaginary enthalpy $\delta H_{IN}^{"}$ is obtained by integrating the $C_p^{"}$ peak. Figure 6.6 shows the δH_{NA} , δH_{IN}^* , and $\delta H_{IN}^{"}$ on both heating and cooling as a function of ϕ_w . While the 8CB+CNT *I*-*N* enthalpies appear slightly increased as compared to the bulk 8CB, the increase is within the experimental uncertainties. The incorporation of CNT at these concentrations leaves the transitions essentially bulk-like.

6.3.3 Thermodynamic Anomaly

As mentioned in Sec. 6.3.1, in the nematic range a new heat capacity feature was observed for an intermediate range of ϕ_w (= 0.0010, 0.0015 and 0.0020). This feature was observed reproducibly after multiple thermal cycles. The excess specific



Figure 6.6. (a) The integrated δC_p N-SmA enthalpy δH_{NA} on heating (\circ) and cooling(\bullet) as a function of ϕ_w (b) The integrated ΔC_p I-N enthalpy δH_{IN}^* (left axis: heating- \circ , cooling- \bullet) and imaginary enthalpy $\delta H_{IN}''$ (right axis: heating- \Box , cooling- \blacksquare) as the function of ϕ_w . The lines are only the guidance for the eye.

heat δC_p^x associated with this feature was isolated by subtracting a bulk-like ΔC_p nematic behavior as the background. The δC_p^x as a function of temperature below T_{IN} is shown in Fig. 6.7 and appears to evolve in this narrow range of ϕ_w . The δC_p^x feature initially appears as a broad sharp single peak at $\phi_w = 0.0010$, which generally narrows and sharpens for the $\phi_w = 0.0020$ that shifts farther below T_{IN} . The intermediate sample ($\phi_w = 0.0015$) exhibits multiple features, some sharp and some broad, that may be related to the sample homogeneity. The enthalpic contribution of this new feature was obtained by integrating δC_p^x to give δH_x and have $\delta H_x(\phi_w = 0.0010) = 0.31$, $\delta H_x(\phi_w = 0.0015) = 0.19$, and $\delta H_x(\phi_w = 0.0020) = 0.18$ J/g. No hints of this new feature is apparent for samples



Figure 6.7. Excess specific heat δC_p^x associated with new feature in the nematic range as a function of temperature about T_{IN} . All data are heating results. Symbols listed in the inset are for $100 \times \phi_w$.

with $\phi_w < 0.0010$ or $\phi_w > 0.0020$.

As shown in Fig. 6.1(b), there appears a sharp break in the C''_p baseline that changes with changing ϕ_w . On cooling, the $C''_p = 0$ baseline breaks to a linear temperature dependence with a negative slope at a temperature T_i . An example of this behavior is shown in Fig. 6.8(a) as an expanded view of the C''_p baseline for the $\phi_w = 0.0010$ 8CB+CNT sample. A simple linear fit to the negative sloped C''_p baseline region was done for all 8CB+CNT samples revealing a ϕ_w independent slope of $\sim (-0.015 \pm 0.003)$ J/gK². However, the x-axis intercept T_i shifts with changing ϕ_w , first decreasing dramatically from ~ 311.5 K to ~ 307.5 K as ϕ_w increases from 0.0005 to 0.0015 then slowly increases back to ~ 311.5 K as ϕ_w increasing from 0.0015 to 0.0050. See Figure 6.8(b). From Eqs. (6.2) and (6.6), the change in the expected $C''_p = 0$ baseline indicates a change in the temperature dependence of the samples' internal thermal conductivity. This is not influenced by the external thermal conductivity as an empty cell scan does not exhibit this behavior nor a pure 8CB sample+cell.

Both the δC_p^x features and the $C_p^{''}$ baseline x-intercept T_i are temperature de-



Figure 6.8. (a) The imaginary specific heat C''_p for the sample having $\phi_w = 0.0010$ as a function of temperature. The slopped C''_p intersects $C''_p = 0$ line at T_i . (b) The T_i as a function of ϕ_w . The open symbols (\circ) represent the T_i for the CNT concentrations and crosses (\times) represent the heat capacity maxima temperatures for the new features. The solid line is only the guidance for the eye.

pendent and seem to be correlated to each other. This implies that the energy (order) fluctuations are coupled to the thermal transport properties of the composite. These new behaviors are not likely due to the structural change or redistribution of CNT in LC medium because the features are reproducible on cyclic thermal scans. But, they are likely to arise from some temperature dependent properties of the composites. The possible T-dependent mechanisms are the order correlation lengths, the surface anchoring energy of the LC on the CNT, and the elasticity of the composite. In order for the thermal transport properties to change, the correlation length should be comparable to the mean-distance between CNT. However at T_i , the nematic correlation is long-range while the smectic correlation length is not much bigger than the molecular length and so, this mechanism is not likely to cause the observed feature. Similarly, a temperature dependent surface anchoring energy is not likely to play any role given the inert nature of the graphene in CNT. The elastic constants K_{ii} change dramatically for 8CB in the nematic phase. As the nematic stiffens there is a stronger bulk coupling between the director and the CNT that would effect thermal transport properties of the composite. This coupling becomes significant at a temperature where one of the K_{ij} becomes comparable to the stiffness of the CNT aggregates (not individual CNT strands) leading to the C''_p baseline change. This elastic coupling would also modify nematic director energy fluctuations and may perhaps lead to the δC^x_p feature.

6.4 Phase transition on 5CB+CNT

The normalized $\bar{\varepsilon}$ for different concentrations of LC+CNTs are shown in Fig. 6.9 as a function of temperature shift $\Delta T_{IN} = T - T_{IN}$, where T_{IN} is the *I*-*N* transition temperature for each concentration. The transition temperature is taken as the temperature where $\bar{\varepsilon}$ shows the first discontinuity when entering the *I*+*N* twophase coexistence region from the isotropic phase. Due to their high aspect ratio, CNTs also exhibit dielectric anisotropy and the value of average dielectric constant of aggregated CNTs is much larger than that of LCs [52]. The addition of a very tiny amount of MWCNT sample causes a large increase in dielectric constant for the LC+CNTs composites. To compare the dielectric behaviors properly for all the concentrations, the dielectric constants are normalized to the highest temperature (315 K) point studied. Bulk 5CB exhibits the classic temperature dependence of the dielectric constant, showing the isotropic to nematic phase transition at $T_{IN} = 308.1$ K, seen in Fig. 6.9 and Fig. 6.11a.

The dielectric constant of an anisotropic material like an LC is orientation dependent. A nematic LC confined between parallel plate electrodes maintains a constant director, \hat{n} , due to plate boundary conditions. Planar orientation of the LC molecules, being perpendicular to the probing field, show the smallest di-



Figure 6.9. Normalized average dielectric constant $\bar{\varepsilon}$ for pure 5CB and 5CB+MWCNTs as a function of temperature shift, ΔT_{IN} . The legend shows the concentrations of dispersed MWCNTs in weight % in 5CB. The absolutes values of T_{IN} for all concentrations are shown in Fig. 6.11a.

electric constant, ε_{\perp} ; and homeotropically oriented (parallel to the probing field) LC molecules exhibit the highest dielectric constant, ε_{\parallel} , assuming the LC has a positive dielectric anisotropy, $\Delta \varepsilon = (\varepsilon_{\parallel} - \varepsilon_{\perp})$. The average dielectric constant in a completely random mixture of the orientations is given by $\varepsilon_{iso} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$. In the uniaxial nematic phase, the average dielectric constant in an unrubbed capacitive cell can be written as $\overline{\varepsilon} = (a\varepsilon_{\parallel} + b\varepsilon_{\perp})$, which is lower than the extrapolated value of ε_{iso} . It should be noted that $\Delta \varepsilon$ depends on temperature and is proportional to the scalar order parameter, S(T). Now, as the system reaches the complete disorder state, *i.e.*, isotropic liquid, the order parameter drops down to zero. This leads to the idea of having no temperature dependence of ε_{iso} . As seen in Fig. 6.9, above the *I-N* transition temperature the dielectric constant flattens out in the isotropic phase and shows no significant temperature dependence $(\partial \varepsilon_{iso}/\partial T \neq f(T))$, indicating that bulk 5CB reaches complete disorder state with S(T) = 0.

The *I-N* phase transition for pure 5CB has been found at $T_{IN} = 307.8$ K by using the ac-calorimetry technique. The excess heat capacity, ΔC_p , associated with the phase transition was determined by subtracting an appropriate background C_p^{BG} from total heat capacity over a wide temperature range; $\Delta C_p = C_p - C_P^{BG}$ [41, 53]. The resulting ΔC_p data for LC+CNTs samples studied are shown in Fig. 6.10 over a 10 K temperature range window about T_{IN} . The transition temperature T_{IN} is taken as the approximate inflection point of C° vs T curve on the isotropic side of the transition. The excess heat capacity ΔC_p peaks evolved in size and have a small downward shift of the transition temperature with increasing wt% of CNTs. The small transition temperatures shift in the presence of CNTs is likely due to the large density differences between the liquid crystal and CNTs [54]. The nature of the ΔC_p wings in Fig. 6.10 for the *I-N* transitions are similar for all samples with two extra features on each side of the transition for the highest concentration (0.3 wt%) studied. This is possibly due to the transition of *pseudo-nematic* phases of dispersed CNTs in the LC media.

Small wt% of CNTs dispersed and suspended in the LC media do not appear to be frozen in the system but rather diffuse in the nematic matrix due to thermal fluctuation. This situation can be visualized as annealed random variables evolving with time. The nano-dynamics of CNTs induce local deformation of LC nematic director. As the CNT concentration increases the larger local deformation occurs. The local molecular arrangements have a profound impact on the dielectric response in a particular system and the larger the $\Delta\varepsilon$ the smaller the electric field is needed to reorient the director. Here, the $\Delta\varepsilon$ of aggregated CNTs is much higher than that of LCs and so presumably $\Delta\varepsilon$ increases locally in the LC+CNTs system. This results in locally ordered domains more responsive to the fixed probing field, hence the dramatic evolution in the nematic phase with increasing CNTs concentrations, clearly seen in Fig. 6.9. Figure 6.11c shows the normalized $\bar{\varepsilon}$ at the lowest temperature (302 K) as a function of concentration of CNTs. Clearly



Figure 6.10. Excess specific heat ΔC_p for pure 5CB and 5CB+MWCNTs as a function of temperature shift, ΔT_{IN} . The legend shows the concentrations of dispersed MWCNTs in weight % in 5CB. The absolutes values of T_{IN} for all concentrations are shown in Fig. 6.11a.

there is a crossover region between 0.1 to 0.2 wt%. Above the crossover region the locally ordered domains tend to align along the field and below the crossover region, the system is not as responsive to the low probing field. This explains the downward curvatures in the nematic phase for the higher concentrations observed in Fig. 6.9. Due to the elastic coupling and presumably strong anchoring of LCs to the nanotube-surfaces, both species co-operatively create local shortrange orientation order [55, 34]. In addition, the CNTs themselves may form a lyotropic nematic phase when they are dispersed in a fluid [13]. The curvatures $(\partial \varepsilon_{iso}/\partial T = f(T))$ in the isotropic phase for LC+CNTs seen in Fig. 6.9 are evidence of local *pseudo-nematic* order formed by CNTs in an isotropic liquid. The larger the CNT concentration the more curvature in $\bar{\varepsilon}$ occurs above T_{IN} consistent with the formation of local order as a lyotropic *pseudo-nematic*. It has been observed that for $T \geq 315$ K, the $\bar{\varepsilon}$ becomes independent of temperature for all concentrations, indicating that the *pseudo-nematic* order eventually erases and the system reaches a complete isotropic state.

The total enthalpy change associated with a first-order phase transition is the sum of the pre-transitional enthalpy (area under the pre-transitional ΔC_p wings) and the latent heat. Due to partial phase conversion $(N \leftrightarrow I)$ during a T_{ac} cycle, typical ΔC_p values obtained in two phase coexistence region are artificially high and frequency dependent. An effective enthalpy change δH_{IN}^* which includes some of the latent heat contribution was obtained by integrating the observed ΔC_p peak over a wide temperature range of around 300 to 312 K for all 5CB+CNTs samples. The integration of the imaginary part of the heat capacity given by Eq. (6.6) yields the imaginary transition enthalpy $\delta H_{IN}^{"}$, which is the dispersion of energy in the sample and an indicator of the first-order character of the transition. As fixed frequency was used for this work, $\delta H_{IN}^{"}$ is only proportional to the transition latent heat. In an ac-calorimetric technique, the uncertainty in determining the enthalpy is typically 10% due to the base-line and background subtractions. The results of δH_{IN}^* and $\delta H_{IN}^{"}$ as a function of CNT concentrations for all 5CB+CNTs samples are shown in Fig. 6.11b. The effective enthalpy δH_{IN}^* and the imaginary-enthalpy, $\delta H_{IN}^{"}$ fluctuates slightly, but overall are essentially constant with increasing CNT concentration. This taken with the sharpness of ΔC_p shown in Fig. 6.10 indicate that the presence of the CNTs do not induce quenched disorder.

6.5 Conclusions

We have undertaken a detailed calorimetric and dielectric studies on the effect of anisometric, rod like carbon nanotubes in octylcyanobiphenyl (8CB) and pentylcyanobiphenyl (5CB) on the weakly first-order I-N and the continuous N-SmAphase transitions. Slight change in transition temperatures occur as CNT are added in LC but remains fairly constant for all composites. Both transitions evolve without showing any systematic trend with change in ϕ_w . The order of the transition remains the same being the I-N first-order and the N-SmA second-order. The addition of CNT causes small change in order fluctuations in nematic and smectic-A phases. The change in thermal transport properties is observed as a function of carbon nanotube concentration and temperature due to the interaction



Figure 6.11. a) The transition temperature, ΔT_{IN} , as a function of MWCNTs concentration and comparison between the two techniques used for the measurements, b) ac-enthalpy (right) and imaginary enthalpy (left) as a function of MWCNTs concentration, for details see text, c) The normalized dielectric constant, $\bar{\varepsilon}$, as a function of MWCNTs concentration at the starting temperature, 302 K (left) and absolute dielectric constant in the deep isotropic phase (315 K) as a function of MWCNTs concentration (right).

of CNTs with LC molecules. The slight transition temperature change is likely due to the density differences between the liquid crystal and CNTs and due to the coupling between CNTs and LC ordering. But slight change in enthalpies is observed in the samples due to the addition of CNT.

These effects of incorporating the CNT with LC are likely due to the elastic coupling between the CNT and LC, the change in the elastic properties of the composite and the thermal anisotropic properties of CNT.

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l Chapter

Phase transitions in ocylcyanobiphenyl-barium titanate nanoparticle dispersions

7.1 Introduction

Liquid crystal (LC) based colloidal suspensions of nano-materials are of immense technological and scientific interest in recent years because of the capacity of the LC media acting as a platform for nano-material self-assembly. Various nanomaterials of zero-, one-, and two- dimensions have been dispersed and studied in LC medium to enhance the physical properties of LCs, liquid crystalline phase behavior of nano-material themselves, and synthesis of nano-materials by using liquid crystals as 'template'[1]. Being an anisotropic media, LC provides a good support for self-assembly of nano-materials and act as a tunable solvent for nanomaterial dispersion. Therefore, the LC mediated self assembly can be efficiently used to organize different kinds of nanomaterials into soft and well defined functional structures [2]. It has been observed that the addition of nanomaterials to LC materials has improved many special characteristics in the form of faster electro-optical response and low threshold switching [3, 4], low driving voltage [5], non-volatile memory effect [6, 7], enhanced photoluminescence [8]. These improvements and enhancement in properties are mainly due to the surface modification of the aligned layers [9, 10] and structure modification of the LC host [11, 12, 13, 14]

due to the incorporation of nano-scale materials. The self organization of nanomaterials in two and three dimensional space offered by the LC medium seems to be an ideal vehicle to explore and control the organization of matters on the nanometers to micrometers scale which is a key to the further development of nano-technology.

Recently, the hybrid system containing liquid crystal and ferroelectric nanoparticles such as barium titanate (BaTiO₃) and tin-hypodiphosphate $(Sn_2P_2S_6)$ attracts great interest in experimental [15, 16, 17, 18, 19, 20] as well as theoretical research[21, 22, 23]. These composites are interesting because of the observation of new properties that are not observed in pure LC and due to the interaction of the nano-sized particles with the anisotropic LC host. The ferroelectric nanoparticle of smaller size (around 20 nm) can influence the physical properties of liquid crystal without forming defects and disturbing the LC director [15]. It has been shown that the addition causes to increase the isotropic to nematic phase transition temperature [16], increase in dielectric anisotropy [15, 24], higher birefringence and lower voltage and conductivity [25]. However, some issues about the physical properties enhancement have not been clearly established. For example, the study [15] of a multicomponent liquid crystal ZL4801 doped with ferroelectric nanoparticle $Sn_2P_2S_6$ showed that the *I-N* transition temperature T_{IN} remains essentially same as that of the pure LC but a more recent study [26] on the same LC (with and without surfactant added in it) showed slight decrease (~ 2.3%) in the T_{IN} . Similarly, it has been shown that the addition of ferroelectric nanoparticle $BaTiO_3$ in 5CB does not change the Freedricksz threshold but enhances the dielectric response [27] but a more recent study [18] showed the significant decrease in the Freedricksz threshold. A very recent work on a single component LC 80CB doped with $BaTiO_3$ showed the significant changes in the physical properties with decrease in the I-N phase transition temperature due to the presence of BaTiO₃ [19]. Most of these studies are focused on the multicomponent liquid crystals and only in the nematic regions.

In this work, we study the phase transition behavior of single component liquid crystal octyl-cyanobiphenyl (8CB), which has nematic and smectic-A phases, doped with ferroelectric nanoparticle barium titanate-BaTiO₃ (BT) as a function of concentration of BT, ϕ_m . The incorporation of BT in 8CB causes to display a unique phase behavior. Both the *I-N* and the *N*-SmA transitions evolve in character remaining the order of phase transition same being the *I-N* first-order and the *N*-SmA transition second-order. The *I-N* ΔC_p peaks shift towards the lower temperature as well as the peaks are getting broader as a function of ϕ_m . A broad tail is observed on the *I-N* ΔC_p peak on the isotropic side of the phase transition on heating only. The *N*-SmA specific heat δC_p wings overlay each other very nicely for all 8CB+BT samples with a slight mismatch with that of the bulk except for the SmA side of *N*-SmA transition on heating. Both the *I-N* and the *N*-SmA transition temperatures decrease as ϕ_m increases. The *I-N* and *N*-SmA ac-enthalpy increase first for low- ϕ_m with their constant value for high- ϕ_m .

7.2 Results

For pure 8CB, the *I-N* phase transition occurs at $T_{IN}^0 = 313.17$ K while the *N*-SmA transition occurs at $T_{NA}^0 = 306.08$ K, both are about 1 K lower than the highest values reported in the literature [11]. The *I-N* effective enthalpy $\delta H_{IN}^* = 4.50 \pm 0.45$ J/g, the *N*-SmA effective enthalpy $\delta H_{NA} = 0.64 \pm 0.06$ J/g and the *I-N* dispersive enthalpy $\delta H_{IN}'' = 0.45 \pm 0.05$ J/g in pure 8CB are within 10% of the literature value [28]. These results are used for comparison to the composite results.

The resulting excess specific heat ΔC_p data for 8CB+BT samples studied on heating as a function of temperature $\Delta T_{IN} = T - T_{IN}$ are shown in Fig. 7.1(a). The isotropic to nematic phase transition temperature T_{IN} is taken as the point where $C''_p \neq 0$ on the isotropic side [29]. The *I*-N and the *N*-SmA phase transitions are characterized by a distinct ΔC_p peak for all 8CB+BT samples. The ΔC_p wings are similar for all 8CB+BT composite samples and pure 8CB below and above the two transitions revealing that the bulk-like order fluctuations are present in the isotropic and smectic-*A* phases. However, slight mismatch of the heat capacity wings on the nematic phase below T_{IN} close to the *I*-*N* transition is observed as ϕ_m changes.

The imaginary specific heat C''_p as a function of temperature about T_{IN} on heating is shown in Fig. 7.1(b). The C''_p exhibits a sharp peak associated with *I-N* phase transition and no peak corresponding to the *N*-SmA phase transition



Figure 7.1. (a) Excess specific heat ΔC_p on heating as a function of temperature about T_{IN} for all 8CB+CNT samples including pure 8CB. (b) Imaginary specific heat C''_p on heating as a function of temperature about T_{IN} . Same Symbols listed in the inset of (a) are used for both figures (a) and (b) and are for $100 \times \phi_m$.

revealing the *I-N* being a weakly first-order and the *N*-SmA transition being second-order phase transition for all ϕ_w consistent with that in pure 8CB.

The analysis of the *I-N* and *N*-Sm*A* transitions are carried out taking the closer view of the heat capacity (real and imaginary) profile, phase diagram, and transition enthalpies at each of the transition . An expanded view of the *I-N* excess specific heat ΔC_p and the imaginary specific heat C''_p on heating as a function of temperature about T_{IN} are shown in Fig. 7.2. The ΔC_p wings overlay nicely on the isotropic side for all ϕ_m samples but a larger than bulk ΔC_p is observed for $\phi_m = 0.008$ and 0.014 on the nematic side of the *I-N* transition. The ΔC_p peaks



Figure 7.2. (a) Excess specific heat ΔC_p associated with the *I-N* phase transition on heating as a function of temperature about T_{IN} for all 8CB+CNT samples including pure 8CB. (b) The *I-N* Imaginary specific heat C''_p on heating as a function of temperature about T_{IN} . Symbols listed in the inset are for $100 \times \phi_m$ and applied for both the figures (a) and (b).

progressively shift away from $\Delta T_{IN} = 0$ (T_{IN}) being ~ -0.2 K below T_{IN} for $\phi_m = 0.001$ to ~ -0.7 K below for $\phi_m = 0.014$. The ΔC_p peak also appear broader as a function of ϕ_m . The ΔC_p smoothly decreases from its maximum value as the temperature increases from a temperature corresponding to ΔC_p peak $(i.e. T_p)$ to T_{IN} . See Fig. 7.2 (a). Similarly, C''_p decreases smoothly as temperature increases from T_p to T_{IN} as shown in Fig. 7.2 (b). In other words, the ΔC_p and C''_p maxima at the *I-N* phase transition occur progressively closer to the low temperature limit of the I+N coexistence range.



Figure 7.3. (a) Excess specific heat ΔC_p on cooling as a function of temperature about T_{IN} . (b) Imaginary specific heat C''_p on cooling as a function of temperature about T_{IN} . The definition of the symbols are given on the inset. Symbols listed in the inset are for $100 \times \phi_m$.

The ΔC_p and imaginary specific heat C_p'' associated with the *I-N* phase transition on cooling are shown in Fig. 7.3. The ΔC_p behavior on cooling is consistent with heating in that they are reproducible after multiple thermal cycles and exhibit a distinct ΔC_p peak associated with the phase transition. However, The relative shift of ΔC_p peak from $\Delta T_{IN} = 0$ on heating is larger than that in cooling. Also, the ΔC_p rapidly decreases from its maximum value as the temperature decreases from T_{IN} to T_p in contrast to the ΔC_p heating behavior. The ΔC_p peak is widened as a function of ϕ_m but the rate of increasing the peak width is smaller on cooling as compared to that on heating. The ΔC_p wings for all 8CB+BT samples overlay



Figure 7.4. Excess specific heat δC_p associated with *N-SmA* phase transition (a) on heating (b) on cooling as a function of temperature about T_{NA} . Symbols listed in the inset are for $100 \times \phi_m$.

each other on the isotropic side of the transition but this behavior is different in the bulk sample on the nematic side of the transition indicating an enhanced nematic fluctuation caused by the addition of BT in 8CB. Similar behavior of shifting and broadening of the *I-N* transition C_p'' peaks are observed for all ϕ_m samples.

The excess specific heat δC_p associated with the N-SmA phase transition as a function of temperature about T_{NA} is shown in Fig. 7.4. The δC_p exhibits a sharp and distinct N-SmA transition peak for all samples. On heating, the δC_p wings overlay each other for all samples on smectic-A side of the transition but on the nematic side the pure 8CB show different wing behavior. See Fig. 7.4(a). On cooling, δC_p wings overlay each other on both sides of the transitions for all 8CB+BT samples with a small mismatch to the bulk specific heat wing behavior. Since the data on the coexistence region(peak area) are sparse no power-law fits were attempted for critical behavior analysis. However, a qualitative examination of the critical behavior was performed via a log-log plot of δC_p as a function of reduced temperature, $|t| = |(T - T_{NA})/T_{NA}|$ (figure not shown) and found essentially parallel trends of the 8CB+BT and pure 8CB above and below T_{NA} indicating no significant change in the critical exponents with the amplitude ratio remaining very close to 1.

The *I*-*N* phase transition temperature T_{IN} is defined as the temperature of inflection point on the high temperature side of the C''_p peak [29]. The *N*-Sm*A* phase transition temperature T_{NA} is taken as the *N*-Sm*A* δC_p peak temperature. The T_{IN} decreases monotonically until $\phi_m = 0.002$ followed by a non-linear decrease as ϕ_m further increases as shown in Fig. 7.5(a). This indicates two ϕ_m regime behavior, the low and high- ϕ_m regions are partitioned by the vertical dashed line in Fig. 7.5. The T_{IN} on cooling is systematically lower than that on heating. The heating peaks occur at T_p and are steadily lower than T_{IN} as indicated by dashed line in Fig. 7.5(a). The coexistence region, ΔT_{I+N} rapidly grows as ϕ_m increases in the high- ϕ_m region. See Fig. 7.5(b). The T_{NA} shows the similar behavior as that of T_{IN} , linear decrease in low- ϕ_m regime followed by a non-linear decrease for high- ϕ_m regime leaving a constant nematic range ΔT_N as a function of ϕ_m as shown in Fig. 7.5(c) and (d).

The total enthalpy δH_T^* was obtained by an integration of ΔC_p over a wide temperature range of ~ 300 to 318 K. The ac-enthalpy associated with N-SmA transition δH_{NA} is obtained by integrating δC_p over ± 3 K about T_{NA} . Then, the *I-N* ac-enthalpy is determined as $\delta H_{IN}^* = \delta H_T^* - \delta H_{NA}$. The δH_{IN}^* increases linearly for $\phi_m = 0$ to $\phi_m = 0.002$ and then remains fairly constant as a function of ϕ_m as shown in Fig. 7.6(a). Similar behavior is observed on δH_{NA} as a function of ϕ_m with linear increase in its value up to $\phi_m = 0.002$ followed by ϕ_m independent values for higher ϕ_m . See Fig. 7.6(c). However, the $\delta H_{IN}''$ increases very slightly up to $\phi_m = 0.002$ and then gradually decreases as a function of ϕ_m , again revealing two BT concentration regimes.

The differences in transition temperatures between heating and cooling scans,



Figure 7.5. (a) The *I-N* phase transition temperature as a function of ϕ_w . The dashed curve represents the *I-N* ΔC_p peak temperature on heating. (b) The *I+N* co-existence region as a function of ϕ_m . (c) The *N-SmA* phase transition temperatures as a function of ϕ_m . (d) The nematic range as a function of ϕ_m . All data shown are the average of heating and cooling. The solid and doted curves on (a)-(c) represent heating and cooling behavior respectively. The vertical dot line represents the boundary between low- ϕ_m and high- ϕ_m regime.



Figure 7.6. (a) The integrated $\Delta C_p I$ -N enthalpy δH_{IN}^* as the function of ϕ_w . (b) The imaginary enthalpy $\delta H_{IN}''$ as the function of ϕ_m . (c) The integrated $\delta C_p N$ -SmA enthalpy δH_{NA} as a function of ϕ_m . The lines are only the guidance for the eye. All data are averaged out from heating and cooling data. The vertical dot line represents the boundary between low- ϕ_m and high- ϕ_m regime.



Figure 7.7. The *I*-*N* (\circ) and *N*-Sm*A* (\bullet) phase transition temperature difference on heating and cooling as a function of ϕ_m . The vertical dot line represents the boundary between low- ϕ_m and high- ϕ_m regime.

 $T_c^H - T_c^C$, as a function of ϕ_m are shown in Fig. 7.7. This transition hysteresis is constant for the low ϕ_m regime followed by a gradual increase in the high ϕ_m regime for the *I-N* phase transition. This is consistent with the expected behavior of a first-order phase transition. However, the hysteresis for the *N*-SmA transition decreases smoothly in the low ϕ_m regime then becoming constant for all higher values of ϕ_m . While the uncertainties are large and encompass $T_c^H - T_c^C = 0$ for the *N*-SmA phase transition as a function of ϕ_m , they all remain systematically and unexpectedly negative.

7.3 Discussion and conclusions

The weakly first-order *I-N* and the continuous *N*-Sm*A* liquid crystal phase transitions of 8CB+BT composite system have been studied using high-resolution accalorimetry as a function of BT content, ϕ_m . Multiple heating and cooling cycles reproduce each other well for $\phi_m \leq 0.014$ while uniform textures are observed using polarizing microscopy images for all samples studied. Both results support the view that the BT nano-particles are well-dispersed in these composite samples.

The unusual shift of the ΔC_p maxima towards the low temperature limit of

the I+N coexistence range on heating is in contrast to the expected behavior on cooling, *i.e.* the ΔC_p maxima is near the high temperature limit of the I+Ncoexistence range. This is illustrated as a dashed line for the T_p behavior in Fig. 7.5(a). Clearly, the melting and ordering process of the I-N phase transition are driven by different dynamics. A possible scenario to explain this observed hysteresis emerges if there exists coupling of the ferroelectric nano-particles to the orientational order in the polar LC and that the LC mediates interactions through this coupling between BT particles. Given this view, entering the I+N coexistence range on heating would result in a sharp rise in ΔC_p followed by a stretched tail as the BT particles "unbind" from each other as the nematic phase disappears. See Fig. 7.2.

Conversely, on cooling into the I+N coexistence range there would be a sharp rise in ΔC_p due to nucleation of N domains followed on cooling by a tail as the BT particles begin to "bind" to one another. This tail on cooling would smoothly extend into the fully established N phase as shown in the tails of both ΔC_p and C''_p in Fig. 7.3. This physical picture, which essentially describes a Kosterlitz-Thouless (K-T) type transition [30], where the unbinding of vortices is equivalent to the unbinding of ferroelectric BT particle pairs, is supported by the observations at the N-SmA transition. Here, the N-Sm $A \delta C_p$ appears as sharp and distinct peaks with only slight mismatching of the wing behavior of the composite samples with that of the pure 8CB. Also, the T_{NA} shifts with shifting of T_{IN} in such a way that the nematic range ΔT_N remains unchanged.

These results clearly indicate that the BT particles are orientationally coupled to each other and the LC without significant positional coupling. This is not unexpected given the ferroelectric nature of the BT particles and that they are not likely positionally fixed *i.e.* form a gel and so would pin the SmA phase locally. This physical picture may also explain the apparent negative T_c hysteresis at the *N*-SmA phase transition. Here, the smectic domains are much smaller than the nematic domains and would "cut" coupling between BT particles so that heating into and out of the SmA phase would involve different dynamics. However, this is not a large effect and the data are not unambiguous.

The rapid and linear change in transition temperatures for the low- ϕ_m regime followed by a non-linear and gradual change for high- ϕ_m are likely due to different distribution of BT nano-particles in LC medium in two regimes. For low- ϕ_m regime, due to the small number of nano-particles, presumably floating of particles in LC medium rather produce disorder effect giving rise to rapid decrease in transition temperatures. However, for the high- ϕ_m , BT nano-particles interact each other via LC molecules producing somehow ordered effect revealing a gradual change in transition temperature as a function of BT content. The I+N coexistence region data also supports the existence of two ϕ_m regimes. The transition enthalpies are essentially constant but real parts (δH_{IN}^* and δH_{NA}) are slightly larger than that of the bulk due to the BT 'binding' having extra modes and the slight decrease in the imaginary I-N enthalpy reflects this binding of BT-BT and LC suppressing nematic dispersion.

We have undertaken a detailed calorimetric studies on the effect of ferroelectric nano-particles on octylcyanobiphenyl (8CB) on the weakly first-order I-N and the continuous N-SmA phase transitions. The addition of BT on 8CB causes the change in the liquid crystal molecular interactions which consequently gives rise the evolution of both the phase transitions. Interesting and striking effects are observed in 8CB+BT system including the unusual shift of I-N specific heat peaks on heating towards low temperature limit of I+N coexistence range. Isotropic ferroelectric nano-particle like BT, could be an important tool to change the physical properties of a LC media. Continued experimental efforts are needed specifically, probing the structural behavior of the composite as a function of BT content, BT size and temperature would be particulary important and interesting.

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Chapter 8

Concluding Remarks

In general, this work reveals dramatic effect produced by doping solvents on the I-N, N-SmA, and the I-SmA phase transition. It also shows the effect of nanomaterials like carbon nanotubes and ferroelectric Barium Titanate nano-particles on the I-N and N-SmA phase transitions.

In the 8CB+hex mixture, the introduction of n-hexane on 8CB causes the dramatic change in the phase transition behavior. The heat capacity peak associated with the *I-N* transition ΔC_p shifts towards lower temperature non-monotonically and becomes progressively smeared as the hexane concentration increases. There is significant hysteresis in the ΔC_p shape between heating and cooling, especially for higher hexane concentrations. On heating, the ΔCp peak exhibits a broad tail where the peak temperature is significantly below the nominal transition temperature. On cooling, the ΔC_p peak reveals a sharp jump reminiscent of the pure 8CB peak. The integrated ac-enthalpy remains fairly constant as a function of hexane molar fraction whereas the imaginary part of the enthalpy reveals a sharp increase at hexane mole fraction of around 0.07. The dilution of the liquid crystal causes the decrease in liquid crystal molecular interactions and change in viscoelastic properties, which consequently gives rise the evolution of the phase transitions. The results obtained in this work reveal new aspects of the effect of non-mesogenic disorder on the mesogenic ordering.

The heat capacity peak associated with the N-SmA transition, δC_p , shifts towards lower temperature non-monotonically and becomes progressively larger as the hexane concentration increases. The dispersive part of heat capacity C''_p associated with the N-SmA transition abruptly appears as a peak for $x_{hex} \geq 0.08$ but is zero for $x_{hex} \leq 0.06$ indicating a crossover from continuous (second-order) behavior to first-order behavior for the N-SmA transition with a tricritical point at $x_{hex}^{TCP} \approx 0.07$. The integrated ac-enthalpy increases overall as a function of hexane molar fraction. A simple but consistently applied power-law analysis for δC_p with $x_{hex} \leq 0.06$ find a non-linear increase in the heat capacity effective critical exponent towards the tricritical value ($\alpha_{TCP} = 0.50$) as $x_{hex} \rightarrow x_{hex}^{TCP}$ is observed. A small hysteresis of the δC_p shape between heating and cooling is seen and is likely due to a microscopic phase separation of the solvent, perhaps into intersticial region between smectic layers. The non-monotonic transition temperature shift and extended curvature of α_{eff} behavior with extended curvature as $x_{hex} \rightarrow x_{hex}^{TCP}$ may be due to the competing interactions of microphase separation and dilution effects.

Dramatic change in phase behavior with a new transition feature from less orientationally order weak smectic-A to more orientationally ordered smectic- A_d along with the isotropic to less-ordered weak smectic-A phase is observed due to the presence of acetone on 10CB. Both the transition features evolve in shape and size of ΔC_p as a function of x_{ace} . Downwards shifting of transition temperature for both the transitions with dramatic shifts on weak smectic-A to smectic- A_d transition temperature has been observed. These all reveal a new aspect of the effect of polar solvent interactions on the liquid crystal transitions.

Slight change in transition temperatures occur as CNTs are added in LC but remains fairly constant for all composites. Both transitions evolve without showing any systematic trend with change in ϕ_w . The order of the transition remains the same being the *I-N* first-order and the *N*-SmA second-order. The addition of CNT causes small change in order fluctuations in nematic and smectic-A phases. The change in thermal transport properties is observed as a function of ϕ_w and temperature due to the interaction of CNTs with LC molecules. The slight transition temperature change is likely due to the density differences between the liquid crystal and CNTs and due to the coupling between CNTs and LC ordering.

The addition of barium titanate (BT) on 8CB causes the change in the liquid crystal molecular interactions which consequently gives rise the evolution of both the phase transitions. Interesting and striking effects are observed in 8CB+BT
system including the observation of broad tail of the I-N specific heat on heating. Isotropic ferroelectric nanoparticle like BT, could be an important tool to change the physical properties of a LC media without using any expensive synthesizing technique.

8.1 Future Directions

Continued research efforts are needed to further understand the behavior of the systems we have studied.

- 1. Experimental efforts such as light scattering studies probing the nematic elastic constants as a function of solvent content and temperature would be particulary important and interesting for the LC+solvent mixtures.
- 2. Detailed scattering experiments such as x-ray or neutron as a function of solvent concentration and temperature through the N-SmA transition would be most desirable to explore the critical behavior of the smectic correlation length as susceptibility and probing the smectic structure for the LC+solvent systems.
- 3. Experimental efforts for studying the sample homogeneity in the liquid crystal and nanomaterials composite system would be interesting and are needed to understand the behavior of the LC+nanomaterial systems.

So far, I have studied the behavior of thermotropic liquid crystals only. I would like to study the behavior of various lyotropic liquid crystalline materials.



Appendix

A.1 Publications

- Krishna P. Sigdel and Germano Iannacchione; "Study of the isotropic to nematic and nematic to smectic-A phase transitions in liquid crystal and carbon nanotubes composites" Eur. Phys. J. E (2011), 34:34.
- Krishna P. Sigdel and Germano Iannacchione; "Calorimetric study of the nematic to smectic-A phase transition in octylcyanobiphenyl-hexane binary mixtures" Phys. Rev. E, 82, 051702 (2010).
- Krishna P. Sigdel and Germano Iannacchione; "Study of the isotropic to smectic-A phase transition in liquid crystal and acetone binary mixtures" J. Chem. Phys., 133, 174501 (2010).
- Krishna P. Sigdel and Germano Iannacchione; "Evolution of the isotropic to nematic phase transition in binary mixtures of octylcyanobiphenyl and n-hexane" J. Chem. Phys., 133, 044513 (2010).
- 5. Rajratan Basu, **Krishna P. Sigdel**, and Germano S. Iannacchione; "Study of the isotropic to nematic phase transition in carbon nanotubes dispersed liquid crystal composites" submitted to Liquid Crystal.
- Krishna P. Sigdel and Germano Iannacchione; "Calorimetric study of phase transitions in barium titanate- liquid crystal nano-colloidal dispersions" to be submitted.

Evolution of the isotropic to nematic phase transition in binary mixtures of octylcyanobiphenyl and n-hexane

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(Received 25 March 2010; accepted 25 June 2010; published online 30 July 2010)

High-resolution calorimetry has been performed to study the effect of dilution by a nonmesogenic, low-molecular weight solvent (linear n-hexane) on the isotropic-nematic (*I-N*) phase transition in the liquid crystal (LC) octylcyanobiphenyl (8CB) as a function of n-hexane concentration. Numerous temperature scans were performed without continuous mixing for pure 8CB and all mixture samples of n-hexane mole fraction ranging from x_{hex} =0.02 to 0.12. The *I-N* specific heat peak remains first-order for all samples and shifts toward lower temperature nonlinearly while the two-phase *I+N* coexistence width broadens linearly with increasing x_{hex} . Multiple heating and cooling scans are reproducible and indicate phase separation, if it occurs, must be on very short length scales and is reversible. These results may be a consequence of a competition between random dilution effects and the tendency to phase separate. It is shown that solvent dilution of a LC, if miscible and depending on solvent structure, can lead to a controlled altering of the intermolecular potentials and softening of the LC viscoelastic properties. © 2010 American Institute of Physics. [doi:10.1063/1.3466917]

I. INTRODUCTION

The effect of the disorder and impurities on condensed matter systems is an important and challenging problem to the fundamental understanding of phase ordering or selfassembly and continually attracts the attention of researchers. The disordered systems often display complex and rich phenomena, being the generalization of the pure (ideal) systems. Disorder can dramatically alter the physical properties of multicomponent, composite systems. In particular, the effect of disorder on phase transitions is important as the disorder typically couples to the order parameter, which can be usefully described as a random local field that is conjugate to the order parameter. This is usually realized in systems with random inclusions in a phase ordering media, e.g., a colloidal dispersion of solids in a complex fluid. Another form of disorder is presented by dilution effects, which imposes instead the random breaking or weakening of intermolecular bonds or interactions responsible for the phase ordering. Exploring a good physical system representing random dilution effects in a controlled manner offers a physical probe to unresolved problems in the understanding of mesophasic order.¹

Liquid crystals (LCs) are an attractive model system for studying mesophasic ordering and phase transitions. The phase behavior of LC is strongly influenced by disorder and impurities, and is easily handled allowing for unique control of the important physical parameters. Examples of induced random field-like disorder through random surface interactions are silica aerosil,^{2–5} aerogel,^{6,7} controlled porous glass,^{8–10} and other uniform cylindrical confinements.^{11,12} The LC phase behavior can also be altered by using external electric and magnetic fields.^{13,14} Also, by employing LC

+LC mixtures,^{15–18} new phases and phase diagrams have been explored. Finally, mixture systems comprised of water, surfactant, and a nematic liquid crystal have revealed unique arrangements of spherical micelles in a microemulsion upon full phase separation either by cooling into the nematic phase or the addition of an appropriate cosurfactant.^{19–21}

Recently, renewed attention has been drawn to miscible mixtures of liquid crystals and nonmesogenic, low-molecular weight solvents for furthering basic understanding of mesogenic order and tuning viscoelastic properties.^{22–26} An x-ray study of a binary mixture of a LC and n-hexane focusing on the nematic to smectic-*A* phase transition indicated from visual inspection that in 8CB/n-hexane mixtures (for n-hexane volume fraction of 0.1 and up) the solvent is not uniformly distributed throughout the host LC, and minimal, nonreproducible swelling is observed.²² The experimental studies on 8CB+cyclohexane ²⁶ system that enforced uniformity by continuous mixing revealed a linear decrease in isotropic to nematic transition temperatures, and constant latent heat during the transition with increasing solvent mole fraction.

The orientational order of the nematic phase can be described by a symmetric and traceless second rank tensor (Q_{ij}) and is established in three dimensions.¹ In general, the tensor (Q_{ij}) describes the uniaxial and biaxial nature of the orientational order. However, neglecting any biaxial ordering and aligning the axis of orientation with a principal axis of a local frame, nematic order can be approximated on short length by a scalar parameter *S* measuring the magnitude of orientational order about the orientational axis and on much longer length scales by a "headless" vector \hat{n} , the nematic director, which describes this axis. These approximations of the nematic order are related to (Q_{ii}) for uniaxial LCs by

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 $Q_{ij} = \frac{1}{2}S(3\hat{n}_i\hat{n}_j - \delta_{ij})$. The scalar order parameter *S* is typically used in a Landau–de Gennes free energy expansion to provide a mean-field model.¹

In this work, we study the effect of a nonmesogenic, low molecular weight solvent (n-hexane) concentration on the weakly first-order isotropic to nematic (I-N) phase transition on octylcyanobiphenyl (8CB) and n-hexane (hex) binary mixtures (8CB+hex) as a function of n-hexane concentrations. The introduction of n-hexane on 8CB causes the dramatic change in the phase transition behavior in 8CB+hex mixtures. The heat capacity peak associated with I-N transition ΔC_p shifts toward lower temperature nonmonotonically and becomes progressively smeared as the hexane concentration increases. There is significant hysteresis in the ΔC_p shape between heating and cooling, especially for higher hexane concentrations. On heating, the ΔC_p peak exhibits a broad tail where the peak temperature is significantly below the nominal transition temperature. On cooling the ΔC_p peak reveals a sharp jump reminiscent of the pure 8CB peak. The integrated ac-enthalpy remains fairly constant as a function of hexane molar fraction whereas the imaginary part of the enthalpy reveals a sharp increase at hexane mole fraction of around 0.07.

The presence of n-hexane in 8CB introduces two effects: impurity and viscoelastic softening. Both effects are in equilibrium but produce different results. The shift in transition temperature downward, general smearing of ΔC_p , and constancy of ∂H_{IN}^* are consistent with an impurity effect. The nonmonotonic transition temperature shift, narrowing of the nematic temperature range, hysteresis in the ΔC_p shape, and jump in $\partial H_{IN}''$ at $x_{hex} \approx 0.07$ appear to be indicative of changes in the effective viscoelastic properties of the composite. This later mechanism has a profound effect on the lower temperature nematic to smectic-A transition, which will be presented in a subsequent paper.

This paper is organized as follows. Following this introduction, Sec. II describes the preparation of sample, the calorimetric cell, and the ac-calorimetric procedures employed in this work. Section III describes the calorimetric results of the *I-N* phase transition in the 8CB+hex system. Section IV discusses these results from the point of view of swelling the LC (screening the LC intermolecular interaction), draws conclusions, and describes future directions.

II. EXPERIMENTAL PROCEDURE

The liquid crystal 8CB, purchased from Frinton Laboratory, has the chemical formula $C_8H_{17}-C_6H_5-C_6H_5-CN$, a molecular mass M_w =291.44 g/mol, and a density of ρ_{LC} =0.996 g/ml. Pure 8CB has a weakly first-order, isotropic to nematic phase transition at T_{IN}^0 =313.98 K, a second order nematic to smectic-A transition at T_{NA}^0 =306.97 K, and a strongly first-order crystal to SmA transition at T_{CrA}^0 =290 K.² The single batch of 8CB used for pure and mixture samples was degassed under vacuum for about 2 h in the isotropic phase before use. Spectroscopic grade (ultralow water content with a nominal 99.9% purity) n-hexane purchased from EM Science was used without further purification. The pure n-hexane has molecular formula C_6H_{14} , molecular mass of 86.18 g/mol, a density of 0.655 g/ml, and a boiling point of 342 K with no known mesogenic phases. The 8CB and n-hexane mixtures appear by visual inspection to be miscible up to an n-hexane mole fraction of 0.12. Measurements were performed on samples as a function of n-hexane mole fraction, $x_{\text{hex}} = n_{\text{hex}}/(n_{\text{hex}} + n_{\text{LC}})$, where n_{hex} and n_{LC} are the moles of hexane and liquid crystal used ranging from 0 (pure 8CB) to 0.12.

An aluminum "envelope" heat capacity cell, 15 mm in length, 8 mm in width, and ~ 0.5 mm thick, was prepared from a sheet of aluminum which was cleaned in progressive applications of water, ethanol, and acetone in an ultrasonic bath. The sheet was folded and sealed on three sides with super-glue (cyanoacrylate). Once the cell was thoroughly dried, the desired amount of liquid crystal followed by a relatively large amount of n-hexane was introduced to the cell. The mass of the sample and cell was monitored as the n-hexane was allowed to evaporate slowly until the desired mass of the n-hexane was achieved. At the point of the desired mass of the 8CB+hex mixture, the envelope flap was quickly folded and sealed with the super-glue. Careful massing of super-glue and sample during every stage of this process ensured that the proper amounts of materials were sealed within the cell. Extensive care was taken in handling the sample due to relatively rapid evaporative nature of n-hexane and total mass of the cell was periodically checked.

High resolution ac-calorimetric measurements were carried out on a home built calorimeter at WPI. The sample cell consists of an aluminum envelope mentioned above whose dimensions closely match the size of the heater. A 120 Ω strain gauge heater and a 1 M Ω carbon-flake thermistor were attached to the opposite faces of the cell using GE varnish. The completed cell was then mounted into the calorimeter, the details of which can be found elsewhere.^{27–29} In the ac-mode, oscillating heating power $P_{ac} \exp(i\omega t)$ is applied to the cell resulting in temperature oscillations with amplitude T_{ac} and a relative phase shift between T_{ac} and input power, $\varphi = \Phi + \pi/2$, where Φ is the absolute phase shift between $T_{\rm ac}$ and the input power. The relative phase shift also provides crucial information regarding the order of the phase transition.²⁸ With the definition of the heat capacity amplitude, $C^* = P_{ac}/(\omega T_{ac})$, the specific heat at a heating frequency ω can be expressed,

$$C_p = \frac{C'_{\text{filled}} - C_{\text{empty}}}{m_s} = \frac{C^* \cos(\varphi) f(\omega) - C_{\text{empty}}}{m_s},$$
 (1)

$$C'' = C''_{\text{filled}} = C^* \sin(\varphi) g(\omega) - \frac{1}{\omega R_e},$$
(2)

where C'_{filled} and C''_{filled} are the real and imaginary parts of the filled cell heat capacity, C_{empty} is the heat capacity of the empty cell, m_s is the mass of the sample (in the range of 15–40 mg), and R_e is the external thermal resistance between the cell and the bath. The functions $f(\omega) \approx g(\omega) \approx 1$ are small correction factors due to the non-negligible internal resistance R_i of the sample compared to R_e .³⁰ Typically, in equilibrium and in a single-phase region without dynamics on the time scales of the induced temperature oscillation, C''=0 and



FIG. 1. (a) The specific heat on heating as a function of temperature for the x_{hex} =0.06 sample illustrating the overall background (dashed-dot) and low-temperature wing under the *N*-SmA peak (dashed) behavior used to determine ΔC_p and δH_{IN}^* . (b) Dispersive part of heat capacity on heating for the x_{hex} =0.06 sample illustrating $\delta H_{IN}''$ and the *I*-*N* transition temperature T_{IN} . See text for details.

the real part is the total heat capacity. A nonzero C'' indicates dispersive dynamics the most common example being the latent release at a first-order phase transition.³⁰

The excess specific heat associated with a phase transition can be determined by subtracting an appropriate background C_p^{BG} from the total specific heat over a wide temperature range; $\Delta C_p = C_p - C_p^{\text{BG}}$. Figure 1(a) illustrates this subtraction, the dashed-dot line represents the background.

The enthalpy change associated with a phase transition is defined as

$$\delta H = \int \Delta C_p dT, \tag{3}$$

where the integration is usually carried over as wide a temperature range as possible. For first-order phase transitions, the situation is complicated due to the presence of coexistence region as well as a latent heat ΔH . The total transition enthalpy change for weakly first-order phase transitions is the sum of the pretransitional enthalpy and latent heat associated with the transition and is given by $\Delta H_{tot} = \delta H + \Delta H$. Due to partial phase conversion $N \rightleftharpoons I$ during a T_{ac} cycle, typical ΔC_p values using ac-calorimetry obtained in twophase coexistence region are frequency dependent and remarkably high. The integration of observed ΔC_p yields an effective enthalpy δH_{IN}^* , which includes some but not all of the latent heat contributions. In addition, the enthalpic contribution of a nearby phase transition must be subtracted to further isolate the appropriate ΔC_p . This typically involves defining the ΔC_p wing contribution that underlays the lower temperature transition. The integration of the imaginary part of heat capacity given by Eq. (2) yields the imaginary transition enthalpy $\delta H''_{IN}$, which is the dispersion of energy in the sample and an indicator of the first-order character of the transition. Figures 1(a) and 1(b) illustrate the way how we calculate the effective ac-enthalpy change δH_{IN}^* and imaginary enthalpy $\delta H_{IN}''$, respectively. The shaded regions give δH_{IN}^* and $\delta H_{IN}''$. In ac-calorimetric technique the uncertainty in determining the enthalpy is typically 10% due to the base line and background subtractions.

To ensure the calorimetric cell was properly sealed, the sample-cell system was loaded into the calorimeter and a fast heating followed by a fast cooling temperature scans was performed. The ΔC_p base lines during the cooling and the heating were compared and if closely overlapping each other, then no loss of mass due to evaporation of the n-hexane occurred. If the cell was found to be properly sealed, then a slow detailed heating scan followed by an equivalent cooling scan was done. All 8CB+hex samples experienced the same thermal history with data taken at a heating frequency of 0.031 25 Hz and a final slow scanning rate of ± 0.4 K/h.

III. RESULTS

A. Overview

For pure 8CB, from the same batch used for all mixture samples, the *I*-*N* phase transition occurs at T_{IN}^0 =313.20 K while the *N*-SmA transition occurs at T_{NA}^0 =306.09 K, both are about 1 K lower than the highest values reported in the literature.³¹ In addition, the effective enthalpy δH_{IN}^* =4.67±0.47 J/g and the dispersive enthalpy δH_{IN}^* =0.59±0.06 J/g for the *I*-*N* transition in pure 8CB, which is within 10% of the literature value.⁶ These results indicate the relative purity of the LC and are used for comparison to the mixture results for internal consistency. A summary of transition temperatures, nematic temperature ranges, and enthalpies for all samples on heating is given in Table I.

The resulting excess specific heat data for 8CB+hex samples on heating are shown in Fig. 2(a) over a 3 K temperature range about T_{IN} . Here, ΔC_p are presented in J/K/g of the sample. The ΔC_p peaks of the *I-N* transition shift toward lower temperature as well as progressively smearing with increasing x_{hex} . Also, the *I-N* ΔC_p peak on heating exhibits a broad wing, or tail, on the isotropic side of the transition. Figure 2(b) shows the dispersive part of heat capacity C'' for pure 8CB and 8CB+hex samples on heating. The I-N transition C'' peaks are also smeared with progressively longer tail on the isotropic side as the hexane concentration increases. Interestingly, the temperature of the C'' peak does not coincide with the temperature of the ΔC_p peak on heating. Because of the mismatch between C'' and ΔC_p peaks in temperature and the long ΔC_p tail on the isotropic side, the temperature of the I-N transition on heating is taken as the approximate inflection point of C'' on the isotropic side.

On cooling the excess specific heats shown in Fig. 3(a) and imaginary heat capacities shown in Fig. 3(b) reveal consistent behavior. Using the jump in C'' on the high-side of the transition, T_{IN} shifts to lower temperature monotonically consistent with T_{IN} from heating scan. The ΔC_p peaks of the *I-N* transition are smeared for higher hexane mole fractions but with a broad tail on nematic side of the transition. This is

\mathcal{F}_{I+N} (in recent), creative at change \mathcal{F}_{IN} , and dispersive change \mathcal{F}_{IN} (in \mathcal{F}_{S}).						
<i>x</i> _{hex}	T_{IN} ΔT_N		δT_{I+N}	δH^*_{IN}	$\delta H''_{IN}$	
0.00	313.20 ± 0.07	7.11 ± 0.11	0.25 ± 0.21	4.67 ± 0.47	0.59 ± 0.06	
0.02	309.95 ± 0.39	5.53 ± 0.59	1.08 ± 1.17	3.99 ± 0.40	0.33 ± 0.03	
0.03	309.12 ± 0.27	5.03 ± 0.41	1.00 ± 0.81	4.19 ± 0.42	0.40 ± 0.04	
0.06	309.48 ± 0.33	5.27 ± 0.50	1.17 ± 0.99	3.36 ± 0.34	0.32 ± 0.03	
0.08	308.06 ± 0.42	4.46 ± 0.63	2.26 ± 1.26	3.79 ± 0.38	1.27 ± 0.13	
0.09	305.16 ± 0.64	3.23 ± 0.96	2.08 ± 1.92	4.11 ± 0.41	0.97 ± 0.10	
0.12	303.62 ± 0.94	2.53 ± 1.41	2.65 ± 2.82	4.09 ± 0.41	1.15 ± 0.12	

TABLE I. Summary of the calorimetric results for pure 8CB and the 8CB+hex samples on heating. Shown are n-hexane molar fraction x_{hex} , *I-N* transition temperature T_{IN} , nematic temperature range ΔT_N , *I+N* coexistence region δT_{I+N} (in Kelvin), effective ac-enthalpy change δH_{IN}^* , and dispersive enthalpy $\delta H_{IN}^{"}$ (in J/g).

contrast to that seen on heating. Significant hysteresis in ΔC_p shape is observed at *I-N* phase transitions on heating and cooling for higher hexane mole fractions. In particular, ΔC_p of the *I-N* transition on cooling appears more step-like with increasing x_{hex} . Heating and cooling ΔC_p results for various cycle for a given n-hexane concentration match each other well.

B. Phase diagram

The *I-N* and *N*-SmA phase transition temperatures as a function of n-hexane mole fraction are shown in Fig. 4(a) for heating and cooling scans. As previously described, the *I-N* phase transition temperature T_{IN} is defined as the high temperature limit of the *I+N* coexistence region from isotropic to nematic region, determined from *C*" for heating and cooling scans. See Fig. 1(b), which illustrates this procedure. The *N*-SmA phase transition temperature T_{NA} was determined in two ways: for lower x_{hex} samples it is simply the *N*-SmA ΔC_p peak temperature, whereas for higher concentrations,

where the *N*-SmA transition exhibits a peak in C'', T_{NA} is taken as high temperature limit of *N*-SmAC'' peak. The *I*-*N* transition temperatures for heating and cooling as function of x_{hex} are consistent with each other, but T_{IN} on cooling becomes progressively lower than on heating with increasing x_{hex} . The *I*-*N* ΔC_p peak temperature given by dashed line in Fig. 4(a) becomes significantly smaller on heating and reflects the unique smeared nature of the transition.

As the mole fraction of n-hexane increases the transition temperatures decrease nonlinearly with a plateau or bump at $x_{hex} \approx 0.07$ for both T_{IN} and T_{NA} . See Fig. 4(a). Figure 4(b) shows the nematic temperature range $\Delta T_N = T_{IN} - T_{NA}$ as a function of n-hexane mole fraction revealing an overall decrease in ΔT_N with a plateau similar to that seen in $T_{IN}(x_{hex})$ and $T_{NA}(x_{hex})$. The nematic range decreases from 7.11 K for pure 8CB to 2.53 K for the x_{hex} =0.12 sample. The behavior of ΔT_N simply indicates the greater suppression of orientational order (nematic phase) relative to smectic ordering due



FIG. 2. (a) The excess specific heat ΔC_p on heating as a function of temperature about T_{IN} for pure 8CB and all 8CB+hex samples. See legend. (b) The dispersive part of heat capacity on heating for all samples as a function of temperature about T_{IN} . Note the broad ΔC_p and C'' wing on the high-temperature side of the peaks.



FIG. 3. (a) The excess specific heat ΔC_p on cooling as a function of temperature about T_{IN} for pure 8CB and all 8CB+hex samples. See legend. (b) The dispersive part of heat on cooling for all samples as a function of temperature about T_{IN} . Note the sharp jump in ΔC_p and C'' on the high-temperature side of the peaks as well as progressive step-like character of ΔC_p with increasing x_{hex} .

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FIG. 4. (a) The *I*-*N* and *N*-SmA phase transition temperatures as a function of x_{hex} on heating (\bigcirc) and cooling (\bullet). Solid lines are guide to the eye and dashed line indicates the temperature of the ΔC_p peaks on heating. (b) The nematic temperature range ΔT_{IN} on heating (\bigcirc) and cooling (\bullet) as a function of x_{hex} . Dashed-dot lines indicate the transition temperature shifts in 8CB+cyclohexane. See Ref. 26. The vertical dotted corresponds to the point where $\delta H'_{IN}$ exhibits a jump in magnitude. (c) The *I*+*N* coexistence region on heating (\bigcirc) and cooling (\bullet) as a function of x_{hex} .

to the presence of the solvent. The I+N coexistence region on heating and cooling as a function of x_{hex} is shown in Fig. 4(c). The region increases linearly as x_{hex} increases.

C. The I-N phase transition enthalpy

The effective *I-N* transition enthalpy δH_{IN}^* was obtained by integrating ΔC_p from 299 to 317 K for pure 8CB and all 8CB+hex samples then subtracting the *N*-SmA transition enthalpy. See Fig. 1(a). The dispersive enthalpy of *I-N* transition was obtained by integrating C" just over the *I-N* C" peak and then scaling by mass of the sample m_s . See Fig. 1(b). In this work, fixed heating frequency was used, thus $\delta H_{IN}''$ is only proportional to the transition latent heat.

The resulting δH_{IN}^* and $\delta H_{IN}''$ for heating and cooling scans as the function of hexane mole fraction for all 8CB + hex samples are shown in Fig. 5. The δH_{IN}^* values are all approximately shifted from that seen in pure 8CB but otherwise independent of x_{hex} and are consistent on heating and cooling. See Fig. 5(a). The dispersive enthalpy of the *I-N* transition $\delta H_{IN}''$ exhibits a sudden jump from 0.32 to 1.27 J/g



FIG. 5. (a) The total integrated ΔC_p ac-enthalpy δH_{IN}^* and (b) integrated C'' enthalpy $\delta H_{IN}''$ of the *I*-N transition for heating (\bigcirc) and cooling (\bullet) as the function of x_{hex} . Solid lines are guide to the eye. The vertical dot line indicates the jump in $\delta H_{IN}''$. The thick solid line in (b) is the mean spacing between n-hexane molecules \bar{l} and the horizontal dashed line provides the point at which it crosses the vertical dotted line, $\bar{l}_{0.07}=23$ Å.

at $x_{\text{hex}} \approx 0.07$. This step increase in $\delta H''_{IN}$ at $x_{\text{hex}} \approx 0.07$ corresponds to the plateau region seen in Fig. 4 for the T_{IN} , T_{NA} , and ΔT_N as a function of x_{hex} .

IV. DISCUSSION AND CONCLUSIONS

The introduction of n-hexane to 8CB greatly affects the behavior of *I-N* phase transition. The main effect of solvent is to dilute the liquid crystal, resulting in two main changes: an impurity effect and viscoelastic softening of the mixture. The impurity mechanism introduces concentration fluctuations (random local transition temperatures) and a generic truncation of the order parameter correlation length. However, the presence of solvent can screen LC molecules from one another, a dilution effect, that softens the viscoelastic properties of the mixture with respect to that of pure LC. This viscoelastic softening can substantially change the role of order fluctuation in the phase transition leading to nonlinear shifts in T_c and hysteresis of the transition behavior.

Rieker²² studied the LCs/n-hexane systems on *N*-SmA phase transitions in LC/n-hexane systems and observed from visual inspection that for 8CB/n-hexane, the solvent was not uniformly distributed throughout the host LC and only a minimal, nonreproducible, swelling of the SmA layers was observed. However, these samples were of higher n-hexane concentration than ours, a reported volume fraction of 0.1. In the concentration range studied here, corresponding to a volume fraction from 0.015 to 0.06, visual inspection of sealed 8CB+hex samples over many months did not reveal any sign

of demixing/separation. Large scale phase separation is not likely to play a major role in the results reported here.

Broader peaks and significant tails of ΔC_p in isotropic side of the transition on heating for higher hexane mole fraction indicate that the melting of the samples takes place for large temperature range. But during the cooling scans crystallization starts sharply. Therefore, the melting and crystallization are driven by different dynamics which may be due to the coupling of viscoelastic properties with orientational order of the sample. Matching of heating and cooling ΔC_p results for various cycles for a given n-hexane sample indicates that the significant hysteresis observed during cooling and heating is not due to phase separation, rather due to the different dynamics in heating and cooling scans. Shifting ΔC_p toward lower temperature and diminishing I-N ΔC_p peak height indicate that the scalar order parameter S and correlation length ξ are greatly affected by n-hexane in the composites.

Nonlinear transition temperature dependence on n-hexane mole fraction in 8CB+hex mixtures is unique as compared to that seen in 8CB+cyclohexane.²⁶ The authors showed that for 8CB+cyclohexane systems I-N latent heat remains constant for all the cyclohexane concentrations. Similar behavior is observed in 8CB+hex system with a nearly constant ac-enthalpy for all n-hexane mole fractions studied. Details of the *I-N* heat capacity peaks were not published, so further comparison is not possible. The linear versus nonlinear transition temperature behavior in 8CB +cyclohexane and 8CB+hex systems can be accounted in the following two ways: the first is the linear structure of n-hexane as compared to cyclohexane ring structure and the second is the procedure of mixing the sample during the experiment. Our experiments do not involve any stirring of the sample during the experiment, whereas the study of 8CB+cyclohexane was done with continuous stirring of the samples during the experiments, which may wash out this behavior. Nonstirring effect may produce nanoscale phase separation which consequently can cause two driving forces to develop in two opposite directions. These forces probably cause the increment in transition temperature showing nonlinear behavior in the phase diagram. The dashed-dot lines in the phase diagram show the data from Ref. 26, which indicate the good agreement with our data in lower hexane concentration regime only but not for higher concentration regime.

A distinct jump in $\delta H_{IN}''$ at $x_{hex} \approx 0.07$ is observed that indicates the sudden change in dynamics of the *I-N* phase conversion. Since screening is presumably playing an important role, one measure of this effect is the mean distance between solvent molecules, \overline{l} . Assuming that the solvent molecules are uniformly distributed throughout the mixture, the value of \overline{l} may be estimated from the specific volume of the LC and that of the solvent. For 8CB and n-hexane, the specific volume (volume per particle) is v_{8CB} =486.14 Å³ and v_{hex} =218.17 Å³, respectively. We assume a linear variation as $v_{mix}=v_{8CB}$ at $x_{hex}=0$ to $v_{mix}=v_{hex}$ at $x_{hex}=1$ yielding a dependence of $v_{mix}(x_{hex})=-267.97(x_{hex})+486.14$ in units of Å³ for the volume per "average" molecule in the 8CB+hex mixtures. Considering uniformly distributed n-hexane molecules, each centered in a spherical unit cell, the volume per molecule can be calculated as $v_{\text{mix}} = x_{\text{hex}}(\pi \bar{l}^3)/6$, the volume of the unit cell times the number of n-hexane molecules gives the total sample volume divided by the total number of molecules. Equating these two definitions of v_{mix} gives

$$\overline{l} = [(6/\pi)(v_{\text{mix}}(x_{\text{hex}}))/(x_{\text{hex}})]^{1/3},$$
(4)

where the linear $v_{\text{mix}}(x_{\text{hex}})$ dependence is used. For \bar{l} smaller than the length scale for the LC interaction, approximately the LC molecular length, the screening effect on the LC interaction potential should be dominant. The $\delta H_{IN}''$ jump occurs around at hexane mole fraction of ~0.07 where the mean distance between the hexane molecules \bar{l} is found to be approximately equal to 8CB molecular length (≈ 23 Å). The functional dependence of $\bar{l}(x_{\text{hex}})$ is shown in the lower panel of Fig. 5.

We have undertaken a detailed ac-calorimetric study on the effect of nonmesogenic, low molecular weight solvent (n-hexane) on octylcyanobiphenyl (8CB) with an emphasis on the weakly first-order *I-N* phase transition. The dilution of the liquid crystal causes the decrease in liquid crystal molecular interactions and change in viscoelastic properties, which consequently gives rise to the evolution of the phase transitions. The results obtained in this work reveal new aspects of the effect of nonmesogenic disorder on the mesogenic ordering. Nonmesogenic solvents like n-hexane could be an important tool to probe and tune intermolecular potentials of liquid crystals. Continued experimental efforts are needed specifically, light scattering studies probing the nematic elastic constants as a function of solvent content and temperature would be particularly important and interesting.

ACKNOWLEDGMENTS

This work was supported by the Department of Physics at WPI.

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Study of the isotropic to smectic-A phase transition in liquid crystal and acetone binary mixtures

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(Received 22 August 2010; accepted 24 September 2010; published online 1 November 2010)

The first-order transition from the isotropic (I) to smectic-A (Sm A) phase in the liquid crystal 4-cyano-4'-decylbiphenyl (10CB) doped with the polar solvent acetone (ace) has been studied as a function of solvent concentration by high-resolution ac-calorimetry. Heating and cooling scans were performed for miscible 10CB+ace samples having acetone mole fractions from $x_{ace}=0.05$ (1 wt %) to 0.36 (10%) over a wide temperature range from 310 to 327 K. Two distinct first-order phase transition features are observed in the mixture whereas there is only one transition (I-Sm A) in the pure 10CB for that particular temperature range. Both calorimetric features reproduce on repeated heating and cooling scans and evolve with increasing x_{ace} with the high-temperature feature relatively stable in temperature but reduced in size while the low-temperature feature shifts dramatically to lower temperature and exhibits increased dispersion. The coexistence region increases for the low-temperature feature but remains fairly constant for the high-temperature feature as a function of x_{ace} . Polarizing optical microscopy supports the identification of a smectic phase below the high-temperature heat capacity signature indicating that the low-temperature feature represents an injected smectic-smectic phase transition. These effects may be the consequence of screening the intermolecular potential of the liquid crystals by the solvent that stabilizes a weak smectic phase intermediate of the isotropic and pure smectic-A. © 2010 American Institute of Physics. [doi:10.1063/1.3502112]

I. INTRODUCTION

Liquid crystals $(LCs)^{1,2}$ are anisotropic fluids that have numerous thermodynamically stable phases exhibiting molecular order in between an isotropic liquid and a threedimensionally ordered solid. Recently, attention has been given to binary mixtures of liquid crystal and a compatible (i.e., miscible), low-molecular weight, solvent as a system in which the intermolecular potential responsible for the LC order can be screened or modified. The studies to date of LC+solvent systems have focused exclusively on the isotropic to nematic (*I-N*) ^{3,4} and the nematic to smectic-*A* (*N*-Sm *A*) ^{4–8} phase transitions as a function of solvent type and concentration. These studies differ from those systems that employ surfactant^{9–11} to create a colloidal emulsion in that these LC+solvent binary mixtures are in equilibrium and miscible.

The direct first-order transition from the isotropic to the smectic-A (*I*-Sm A) phase has attracted attention in experimental^{12–20} and theoretical research^{21–24} as a prototypical symmetry breaking phase transition. High-resolution synchrotron x-ray diffraction study of the *I*-Sm A phase transition in 10CB-aerosil showed that the transition remains first-order for all gel densities with systematic evolution of correlation length.¹⁷ The study of phase transition behavior of 10CB in the presence of silica aerogels showed that the direct *I*-Sm A transition occurs through the nucleation of smectic domains.¹⁶ The effect of pressure on the *I*-Sm A

phase transition was examined and pointed out that the effect is to increase the transition temperature and to decrease the discontinuity of the transition.²³ The macroscopic dynamic behavior was studied in vicinity of the I-Sm A transition and the dynamic equations were presented on the isotropic and smectic-A side of the phase transition incorporating the effect of an external electric field.²⁴ The existence of surface induced order was shown in the isotropic phase of 12CB, which has the direct I-Sm A transition, confined to anapore membranes through specific heat and x-ray scattering studies.¹² All the observations showed that the *I*-Sm A transition is more first-order than the very weak I-N transition indicating that the orientational order of Sm A phase is higher than that in the nematic phase. Even though significant effort was applied for the study of the I-Sm A transition behavior, many problems related to fundamentals of the transition are yet to be solved.

Modification of the smectic structure as well as the introduction of new smectic phases has traditionally been carried out in binary mixtures of two LCs, each exhibiting a different smectic structure. An early study on a binary LC mixture, dibenzoate and TBBA, reported the first Sm A-Sm A transition,²⁵ which was modeled by an extension of the Meyer–Lubensky free-energy form.²⁶ Since this early work, a host of Sm A-Sm A type transitions have been explored in binary LC mixtures^{27–33} though nearly all involve incommensurate smectic structures with very wide twophase coexistence ranges. A rare example of a single LC system is the dimesogenic LC KI5 and KII5, but these highly asymmetric LCs also involve incommensurate smectic struc-

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tures with long lived metastability.^{34–36} Among these early studies only the Sm A_d - A_2 transition has been studied thoroughly.

Most recently, a new phenomenological model of a de Vries type smectic LC has been developed that also appears applicable to a smectic-smectic phase transition.³⁷ This theoretical work predicts the possibility of a sharp, true first-order transition between two smectic phases. In all these studies, the smectic phase was modified by the mixture of two smectic LCs typically having different smectic structures. Here, the difference in space packing drives the stability and structure, even for the single component dimesogenic LC.^{34–36} A more attractive route to studying smectic ordering is directly modifying the intermolecular potential for an LC that only exhibits a single smectic phase.

In this paper, we report a high-resolution ac-calorimetric study on the effects of a nonmesogenic, low-molecular weight, polar solvent (acetone) on the first-order I-Sm A phase transition in decyl-cyanobiphenyl (10CB) and acetone (ace) binary mixtures (10CB+ace) as a function of acetone concentration, x_{ace} . The addition of acetone to 10CB changes the phase behavior of the 10CB+ace system dramatically. Two distinct first-order phase transition features are observed in the mixture. The high-temperature transition feature shifts marginally to lower temperature while the low-temperature feature shifts markedly toward lower temperature with increasing x_{ace} . The ΔC_p peak evolves for both the transition features with significant effect on low-temperature phase transition feature. The two-phase coexistence region for the low-temperature feature increases as a function of x_{ace} while remains fairly constant for the high-temperature feature. The hysteresis in the ΔC_p shape on heating and cooling is observed and increases as x_{ace} increases only for the lowtemperature feature. These results were reproducible upon multiple thermal cycles and not likely affected by macroscopic phase separation. An example of such phase separation behavior is seen in mixtures of 10CB with the nonpolar solvent decane.

The remaining sections of this paper are organized as follows. Section II describes the preparation of sample and the cell as well as the experimental ac-calorimetric procedure which we employed to this work. Section III describes the result of our study of 10CB+ace system. Section IV provides the discussion of our result, which shows the dilution effect of the acetone on 10CB phase transitions and draws conclusions with future directions.

II. EXPERIMENTAL

The liquid crystal, 4-cyano-4'-decylbiphenyl (10CB), was purchased from Frinton Laboratory and degassed in the isotropic phase for about 2 h before use. Pure 10CB (2.45 nm long and 0.5 nm wide molecules³⁸ with molecular mass M_w =319.49 g mol⁻¹) has a direct first-order isotropic to smectic-*A* phase transition without being into a nematic phase and strongly first-order Sm *A* to crystal phase transition. HPLC grade, 99.9+% pure acetone (M_w =58.08 g mol⁻¹ and boiling point 330 K) from Aldrich was used without further treatment. A specified amount of 10CB

was transferred to a vial to which a relatively large amount of acetone was added and ultrasonicated to thoroughly mix. The acetone was then allowed to slowly evaporate until the desired mass of mixture was reached. At this point, the mixture was introduced into an envelope type aluminum cell of dimensions $\sim 15 \times 8 \times 0.5$ mm³ having a 120 Ω strain gauge heater and 1 $M\Omega$ carbon-flake thermistor preattached to opposite sides.³ The filled cell was then mounted in the calorimeter, the details of which can be found elsewhere.^{39–41}

High-resolution heat capacity measurements were carried out in a home-built calorimeter at WPI. In the ac-mode, oscillating power $P_{\rm ac} \exp(i\omega t)$ is applied to the cell containing a sample of finite thermal conductivity resulting in the temperature oscillations with an amplitude $T_{\rm ac}$ and a relative phase shift between temperature oscillation and input power, $\varphi=\Phi+(\pi/2)$, where Φ is the absolute phase shift. The amplitude of the temperature oscillation is given by

$$T_{\rm ac} = \frac{P_{\rm ac}}{\omega C} \left(1 + (\omega \tau_e)^{-2} + \omega^2 \tau_{ii}^2 + \frac{2R_i}{3R_e} \right)^{-1/2},\tag{1}$$

where $P_{\rm ac}$ is the amplitude and ω is the angular frequency of the applied heating power, $C = C_s + C_c$ is the total heat capacity of the sample+cell, which includes the heater and thermistor, $\tau_e = CR_e$, and $\tau_{ii}^2 = \tau_s^2 + \tau_c^2 = (C_s R_s)^2 + (C_c R_c)^2$ are external and internal relaxation times, respectively. Here, R_i is the internal thermal resistance that is approximately equal to the thermal resistance of the sample and R_e is the external thermal resistance to the bath. The internal time constant, τ_{ii} , is the rms time required for the whole assembly of sample and cell to reach equilibrium with the applied heat and the external time constant, τ_e , is the time required to reach equilibrium with the bath. The relative phase shift between the applied power and resulting temperature oscillations is given by

$$\tan(\varphi) = \frac{1}{\omega \tau_e} - \omega \tau_i,\tag{2}$$

where $\tau_i = \tau_s + \tau_c$. If the frequency of the temperature oscillation is faster than the external equilibration time and slower than the sample internal equilibration time, then

$$\omega \tau_i < 1 < \omega \tau_e. \tag{3}$$

Experimentally, a log-log plot of ωT_{ac} versus ω reveals a plateau and this frequency region is where the inequalities of Eq. (3) are valid.⁴² Given satisfying the conditions of Eq. (3), Eq. (1) becomes

$$C \cong \frac{P_{\rm ac}}{\omega T_{\rm ac}}.\tag{4}$$

Defining $C^* = P_{ac}/(\omega T_{ac})$, the specific heat at a heating frequency ω can be expressed as

$$C_p = \frac{C'_{\text{filled}} - C_{\text{empty}}}{m_s} = \frac{C^* \cos(\varphi) - C_{\text{empty}}}{m_s},$$
(5)

$$C_p'' = \frac{C_{\text{filled}}'}{m_s} = \frac{C^* \sin(\varphi) - (1/\omega R_e)}{m_s},\tag{6}$$

where C'_{filled} and C''_{filled} are the real and imaginary parts of the heat capacity, C_{empty} is the heat capacity of the empty cell, m_s is the mass of the sample (in the range of 15–30 mg). Equations (5) and (6) need a small correction to account the nonnegligible internal thermal resistance as compared to R_e and this was applied to all samples.⁴³ The real part of heat capacity indicates storage (capacitance) of the thermal energy whereas the imaginary part indicates the loss (dispersion) of energy in the sample. The temperatures corresponding to equilibrium, one-phase states, exhibit a flat imaginary heat capacity, i.e., $C''_p=0$,⁴⁴ and the dispersive regions, such as a two-phase coexistence where the latent heat is released, have nonzero C''_p .

All data presented here were taken at a heating frequency of 0.196 rad/s and at a base scanning rate of 1 K h⁻¹. For all 10CB+ace samples, each heating scan was immediately followed by a cooling scan and each sample experienced the same thermal history.

The excess specific heat associated with a phase transition can be determined by subtracting an appropriate background C_p^{BG} from the total C_p over a wide temperature range. Then, the excess heat capacity is given by

$$\Delta C_p = C_p - C_P^{BG}.\tag{7}$$

The enthalpy change associated with a phase transition is defined as

$$\delta H = \int \Delta C_p dT. \tag{8}$$

For a second-order or continuous phase transition, the limits of integration are as wide as possible about the ΔC_p peak and gives the total enthalpy change (δH) associated with the transition. But, for a first-order phase transition, due to the presence of a coexistence region and a latent heat ΔH , the total enthalpy change is the sum of the integrated enthalpy and the latent heat, $\Delta H_{\text{total}} = \delta H + \Delta H$. A simple integration of the observed ΔC_p peak yields an effective enthalpy change δH^* for the first-order transition, which includes some of the latent heat contribution. The simple integration of the imaginary part of heat capacity given by Eq. (6) gives the imaginary transition enthalpy $\delta H''$, which is the dispersion of energy in the sample, a proxy of latent heat associated with the transition, and an indicator of the first-order character of the transition. In an ac-calorimetric technique the uncertainty in determining the enthalpy is typically 10% due to the uncertainty in the baseline and background subtractions.

III. RESULTS

The *I*-Sm *A* phase transition for pure 10CB occurred at T_{IA} =323.69 K, in good agreement with the literature value.^{18,45} The excess real specific heat ΔC_p and the imaginary specific heat C''_p for pure 10CB and six 10CB+ace samples on heating are shown in Fig. 1 as a function of temperature about the lowest stable temperature of the isotropic phase ΔT_{IA} =T- T_{IA} . The characteristic features of the



FIG. 1. (a) Excess specific heat ΔC_p as a function of temperature about the lowest stable temperature of the isotropic phase T_{IA} for all 10CB+ace samples including the bulk 10CB showing two type of phase transition on the mixtures: high-temperature peak-1 and low-temperature peak-2. The definition of the symbols is given on the inset. (b) Imaginary part of the heat capacity C''_p as a function of temperature about T_{IA} . Data are shown on heating.

I-Sm *A* transition in pure 10CB, a single, sharp, peak in ΔC_p and C''_p with small wings above and below T_{IA} , transform into two heat capacity features for the 10CB+ace samples. The high-temperature signature, labeled peak-1, appears as a small peak in ΔC_p and very small signature in C''_p . Peak-1 represents a very weak first-order transition into a phase labeled P_1 . The low-temperature peak, labeled peak-2, appears as a large peak in both ΔC_p and C''_p , which are similar in shape. This peak-2 clearly represents a much stronger first-order transition from the P_1 phase to a lower temperature phase labeled P_2 . The data shown in Fig. 1 are consistent after multiple heating and cooling cycles and so appear to be in equilibrium.

Peak-1 shows a small ΔC_p peak that grows slightly with a very small, slightly decreasing, C''_p feature as x_{ace} increases. Peak-2 begins as a large and sharp peak in ΔC_p with a similarly large and sharp peak in C''_p at the lowest x_{ace} sample. As x_{ace} increases, peak-2 shifts to lower temperature and broadens in both ΔC_p and C''_p . For both ΔC_p and C''_p peak-2 appears as a sharp jump on low-temperature side then a broad tail following the peak on the high-temperature side on the heating scan.

Cooling scans are generally consistent with heating in that they are reproducible after multiple cycles and exhibit two heat capacity peaks that evolve in a similar way as a function of x_{ace} . However, there are significant differences in the shape of ΔC_p and C''_p for peak-2, while the hysteresis of peak-1 shape is small. Figure 2 shows the ΔC_p and C''_p profile for the x_{ace} =0.14 sample on heating and the following cooling scan. The vertical dashed-dotted lines on both sides of



FIG. 2. (a) Excess specific heat ΔC_p as a function of temperature about T_{IA} for $x_{acc}=0.14$ on heating (\bigcirc) and cooling (\spadesuit) . The dotted curve under peak-1 is the baseline used for determining ∂H_1^* . (b) Imaginary part of the heat capacity as the function of temperature about T_{IA_w} for $x_{acc}=0.14$. Vertical dashed lines show the coexistence regions for both the transition features.

each transition indicate the coexistence region between them. For peak-2, both the ΔC_p and C''_p peaks are within the coexistence region but asymmetric showing a jump on *entering* the coexistence region for both heating and cooling. For peak-2, the ΔC_p maximum occurs near the edge of the twophase coexistence range where it first enters.

These stable and reproducible results for the 10CB +ace samples are in stark contrast with mixtures of 10CB with a less miscible solvent. A similar series of experiments were carried out on mixtures of 10CB and a nonpolar solvent, decane to highlight the effect of the polar nature of the diluting solvent. None of these measurements were reproducible and exhibited characteristics of progressive phase separation with multiple thermal cycles. Figure 3 shows a typical heat capacity profile for a 10CB+decane sample as a function of temperature for a decane mole fraction x_{decane} =0.10 (5 wt %). As the sample is thermally cycled at the same scanning rate, peak-2 shifts toward higher temperature and ultimately merges with peak-1 just below the pure 10CB I-Sm A transition. This indicates a phase separation effect due to the nonpolar nature of decane that is not observed in the 10CB+ace system.

The phase below peak-1 is initially labeled P_1 while the phase below peak-2 is initially labeled P_2 with the highest temperature phase being the usual isotropic. The $I-P_1$ phase transition temperature, T_1 , is defined as the lowest temperature of the isotropic phase prior to entering the $I+P_1$ twophase coexistence region and the P_1-P_2 phase transition temperature, T_2 , is taken as the lowest temperature of the P_1 phase prior to entering the P_1+P_2 two-phase coexistence region. Figure 4(a) shows the $I-P_1$ and P_1-P_2 phase transition



FIG. 3. Excess specific heat ΔC_p as a function of temperature for 10CB +decane system at x_{decane} =0.10 (5 wt %). First heating (\bigcirc), first cooling (\bigcirc), second heating (\triangle), and the second cooling (\blacktriangle) showing phase separation indicated by shifting of peaks toward higher temperature and becoming a single peak from two or more peaks.

temperatures on heating and cooling as a function of x_{ace} . The dashed lines in the figure represent the lower bound of the coexistence region for each phase transition as determine by $C_p^{n'}$ ⁴⁴ As x_{ace} increases, the *I*-*P*₁ transition temperature remains fairly constant with a small hysteresis between heating and cooling as well as a modest increase in the *I*+*P*₁ coexistence range for the higher x_{ace} as shown in Fig. 4(b). Also, as x_{ace} increases the *P*₁-*P*₂ transition temperature decreases dramatically by ≈ 10 K at $x_{ace}=0.36$ with an increasing hysteresis between heating and cooling $T_2^{heat}-T_2^{cool}$ =+0.44 K at $x_{ace}=0.05$ to $T_2^{heat}-T_2^{cool}=+2.41$ K at x_{ace} =0.36. The *P*₁+*P*₂ coexistence range also exhibits a large increase, reaching $T_{coex}=6.95$ K as x_{ace} increases to x_{ace} =0.36. See Fig. 4(b).



FIG. 4. (a) Transition temperatures as a function of x_{ace} in 10CB+ace on heating (open symbol) and cooling (filled symbol). The points *a*, *b*, and *c* indicate the set of points where polarizing micrograph images were taken. The texture at point *a* looks the typical isotropic texture and in *b* and *c* are shown in Fig. 5. Dotted lines are lower limit of transition temperature for P_1 and P_2 phases. (b) Coexistence regions $I+P_1$ (half-filled square) and $P_1 + P_2$ (half-filled circle) as a function of x_{ace} .





FIG. 5. Polarizing microscope micrographs taken in for the x_{acc} =0.18 sample and at temperatures 321 K (b) and 313 K (c), respectively. The images *b* and *c* correspond to the points *b* and *c*, respectively, in Fig. 4. The scale bar on the bottom-right corners of each micrograph corresponds to 10 μ m.

In order to shed light onto the phase identification of P_1 and P_2 , cross-polarizing micrographs were taken at three different temperatures corresponding to the isotropic, P_1 and P_2 phases. These temperatures are shown by an "x" in Fig. 4(a) and labeled *a*, *b*, and *c*, respectively. Images were taken on a x_{ace} =0.18 sample after heating from 310 K at a rate of +0.2 K/min to the target temperature then waiting for about 5 min for equilibrium. As expected, the image at point *a* (*T*=324.2 K) is uniformly dark indicating the isotropic phase. Textures were observed at points *b* (*T*=321 K) and *c* (*T*=313 K) and are shown in Fig. 5. Both the images are nearly identical revealing a typical smectic texture indicating that both the P_1 and P_2 are smectic phases.

The transition enthalpies, real and imaginary, can be used to reveal the energetics of the transition and can aid the phase identification of P_1 and P_2 . A complete integration of the entire ΔC_p peak over a wide temperature range from 310 to 325 K for all 10CB+ace samples was performed. The peak-1 transition enthalpy was isolated by subtracting a minimally curved baseline below the ΔC_p peak-1 then integrating to give δH_1^* . The enthalpy δH_1^* was then subtracted from the total $\delta H_T^* = \delta H_1^* + H_2^*$ to yield the ac-enthalpy change δH_2^* associated with the P_1 - P_2 phase transition. The integrated ΔC_p enthalpy δH^* and imaginary C''_p enthalpy $\delta H''$ as a function of acetone mole fraction for pure 10CB and all 10CB+ace samples are shown in Fig. 6. Most of the real and imaginary enthalpies are contributed by peak-2. The acenthalpy δH_2^* for the P_1 - P_2 transition increases slightly, reaching a maximum value of $\delta H_2^* = 6.28$ J/g at $x_{ace} = 0.10$ followed by a nearly linear decrease with increasing x_{ace} . Similarly, $\delta H_2''$ increases more dramatically, reaching its maximum value at $x_{ace} \approx 0.22$ followed by a decrease with

FIG. 6. (a) The integrated ΔC_p ac-enthalpy δH_1^* on heating for the *I*- P_1 transition (Δ) , the P_1 - P_2 transition (\bullet) , and total enthalpy for both the transitions (\bigcirc) as a function of x_{ace} . (b) Imaginary enthalpy associated with the *I*- P_1 transition (Δ) , the P_1 - P_2 transition (\bullet) , and total for both the transitions (\bigcirc) as a function of x_{ace} .

increasing x_{ace} . In contrast with the behavior of δH_T^* and δH_2^* , the ac-enthalpy for peak-1, δH_1^* remains essentially constant at $\delta H_1^* \simeq 0.8$ J/g for all x_{ace} . However, the dispersive enthalpy $\delta H_1''$ begins at a constant value for the lower x_{ace} then decreases slowly as x_{ace} increases above $x_{ace} \simeq 0.15$. Clearly, most of the energetics are contributed by the P_1 - P_2 transition with values of δH^* and $\delta H''$ similar to those of pure 10CB. This observation, as well as the micrograph, supports the identification of the P_2 phase being the pure 10CB smectic- A_d phase.

A summary of results for the 10CB+ace samples including pure 10CB on heating is tabulated in Table I. Included are acetone molar fraction x_{ace} , the *I*-*P*₁ phase transition temperature T_1 , the P_1 - P_2 transition temperature T_2 (in degrees kelvin), integrated enthalpy change for the *I*- P_1 transition δH_1^* , integrated enthalpy change for the P_1 - P_2 transition δH_2^* , total integrated enthalpy δH_T^* , imaginary enthalpy for the *I*- P_1 transition $\delta H_1''$, imaginary enthalpy for the P_1 - P_2 transition $\delta H_2''$, and total imaginary enthalpy for both the transitions $\delta H_T''$ (in J/g).

IV. DISCUSSION AND CONCLUSIONS

The *I*-Sm *A* phase transition in LCs is a first-order phase transition and exhibits both orientational and partial translational order. The introduction of acetone to 10CB greatly affects the phase transition behavior. In the concentration range studied here, the binary mixture of 10CB+ace have reproducible ΔC_p features after multiple thermal cycles. Also, reproducible polarizing micrographs are seen after multiple thermal cycles as well as revealing uniform textures. These observations and results strongly indicate that

TABLE I. Summary of the ac-calorimetric results for the 10CB + ace samples. Shown are acetone molar fraction x_{ace} , the I- P_1 phase transition temperature T_1 , the P_1 - P_2 transition temperature T_2 (in degrees kelvin), integrated enthalpy change for the I- P_1 transition δH_1^* , integrated enthalpy change for the P_1 - P_2 transition δH_2^* , total integrated enthalpy δH_T^* imaginary enthalpy for the I- P_1 transition δH_1^* , imaginary enthalpy for the P_1 - P_2 transition δH_2^* , total integrated enthalpy δH_T^* , imaginary enthalpy for the I- P_1 transition δH_1^* , imaginary enthalpy for the I- P_1 transition δH_1^* , imaginary enthalpy for the H_1 - H_2 transition δH_1^* , integrated enthalpy δH_2^* , and total imaginary enthalpy for both the transitions δH_1^* (in J/g).

x _{ace}	T_1	T_2	δH_1^*	δH_2^*	δH_T^*	$\delta H_1''$	$\delta H_2''$	$\delta H_T''$
0.00	323.69 ± 0.14	323.69 ± 0.14			5.14 ± 0.51			1.82 ± 0.18
0.05	323.20 ± 0.14	321.19 ± 0.75	0.77 ± 0.08	5.19 ± 0.52	5.95 ± 0.60	0.77 ± 0.08	2.01 ± 0.20	2.78 ± 0.28
0.10	322.13 ± 0.10	319.79 ± 0.96	0.62 ± 0.06	6.28 ± 0.63	6.89 ± 0.69	0.97 ± 0.10	1.85 ± 0.19	2.82 ± 0.28
0.14	323.05 ± 0.07	319.27 ± 1.28	0.64 ± 0.06	5.52 ± 0.55	6.16 ± 0.62	0.92 ± 0.09	2.60 ± 0.26	3.53 ± 0.35
0.22	323.07 ± 0.18	317.57 ± 1.73	0.50 ± 0.05	4.75 ± 0.47	5.25 ± 0.53	0.36 ± 0.04	3.38 ± 0.34	3.74 ± 0.37
0.28	323.61 ± 0.25	317.55 ± 1.52	1.42 ± 0.14	4.30 ± 0.43	5.71 ± 0.57	0.46 ± 0.05	2.20 ± 0.22	2.66 ± 0.26
0.36	323.19 ± 0.25	316.33 ± 2.87	0.86 ± 0.09	1.85 ± 0.19	2.70 ± 0.27	0.20 ± 0.02	2.52 ± 0.25	2.72 ± 0.27

for this range of x_{ace} , the acetone remains miscible and in equilibrium in mixtures with 10CB. This is likely due to the low x_{ace} range studied and the polar nature of both the acetone and 10CB. For similar concentrations of a nonpolar solvent, decane, in mixtures with 10CB, clear evidence of phase separation are observed as shown in Fig. 3.

For the 10CB+ace samples, calorimetry revealed two well defined features in both ΔC_p and C''_p that were reproducible after multiple thermal cycles and each exhibited different hysteresis as well as x_{ace} dependence. Both features have $C''_p \neq 0$ and are inside their respective two-phase coexistence range. These characteristics of the two signatures indicate that both represent distinct first-order phase transitions. For the polarizing optical micrographs, a completely dark texture is observed for the highest temperature phase while a typical smectic texture is seen for both lower temperature phases. Also, the total enthalpy from both transition features for samples up to x_{ace} =0.28 is very similar to the pure 10CB *I*-Sm A_d enthalpy. These observations identify the highest temperature phase as the isotropic phase and the lowest temperature phase as the smectic- A_d of pure 10CB.

Most of the total enthalpic contribution, real as well as imaginary, is from the P_1 -Sm A_d phase transition while the *I-P*₁ transition accounts for only ~10% of δH_T^* . Also, the concentration dependence of the $I-P_1$ enthalpy and transition temperature is different than that for the P_1 -Sm A_d dependence. Polarizing micrographs of P_1 phase clearly show a uniform smectic texture. Given the small energy associated with this transition, it is labeled a "weak smectic-A" (Sm A_w) phase. This $Sm A_w$ phase exhibits smectic-A symmetry but is less ordered than the $\operatorname{Sm} A_d$ phase. The scenario, possibly, would be because of some screening of the 10CB dipole moment due to the polar nature of both acetone and 10CB and the proposed weak smectic-A phase could be considered as a smectic-A layered structure comprised of a mixture of individual molecules and cybotactic groups (typical in smectic- A_d) of 10CB. However, structural studies such as scattering experiments are needed to get insight into the smectic layer structure of the system.

The downward shift of the transition temperatures in 10CB+ace system is consistent with an impurity (dilution) effect.³ The increasing coexistence region, and increasing hysteresis of the Sm A_w -Sm A_d transition ΔC_p shape on heating and cooling as a function of x_{ace} can be explained in terms of the interaction of acetone polar molecules with

10CB molecules. During a temperature scan, the heat capacity peak exhibits a jump when entering the coexistence region and leaves the region with a broad tail. As the coexistence region is approaching, nucleation process starts sharply and as coarsening processes, the screening by the acetone begins to slow the establishment of order, giving rise to a broad tail.

We have undertaken detailed calorimetric studies on the effect of nonmesogenic, low-molecular weight polar solvent (acetone) on the first-order I-Sm A phase transition of 10CB. Acetone dilutes the liquid crystal and changes the intermolecular potential among the molecules in the mixture. Dramatic change in phase behavior with a new transition feature from less orientationally order weak smectic-A to more orientationally ordered smectic- A_d including the isotropic to less ordered weak smectic-A phase is observed due to the presence of acetone on 10CB. Both the transition features evolve in shape and size of ΔC_p as a function of x_{ace} . Downward shifting of transition temperature for both the transitions with dramatic shifts on weak smectic-A to smectic- A_d transition temperature has been observed. These all reveal a new aspect of the effect of polar solvent interactions on the liquid crystal transitions. Continued experimental efforts specifically, x-ray and/or neutron scattering studies probing the smectic structure as a function of solvent content and temperature would be particularly important and interesting.

ACKNOWLEDGMENTS

This work was supported by the Department of Physics at WPI.

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Calorimetric study of the nematic to smectic-A phase transition in octylcyanobiphenyl-hexane binary mixtures

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(Received 27 July 2010; published 11 November 2010)

The continuous nematic to smectic-A (N-SmA) phase transition has been studied by high-resolution accalorimetry in binary mixtures of the liquid crystal octylcyanobiphenyl (8CB) and a nonmesogenic, lowmolecular weight, solvent n-hexane (hex) as a function of temperature and solvent concentration. Heating and cooling scans about the N-SmA transition temperature were repeatedly performed on pure and six 8CB+hex samples having hexane molar concentration ranging from x_{hex} =0.02 to 0.12. All 8CB+hex samples in this range of x_{hex} remain macroscopically miscible and exhibit an N-SmA heat capacity peak that shifts nonmonotonically to lower temperature and evolves in shape, with a reproducible hysteresis, as x_{hex} increases. The imaginary part of heat capacity remains zero up to $x_{hex}^{TCP} \approx 0.07$ above which the distinct peak is observed, corresponding to a jump in both the real and imaginary enthalpy, indicating the onset of first-order behavior. A simple power-law analysis reveals an effective exponent that increases smoothly from 0.30 to 0.50 with an amplitude ratio $A^-/A^+ \rightarrow 1$ as $x_{hex} \rightarrow x_{hex}^{TCP}$. This observed crossover of the N-SmA toward a tricritical point driven by solvent concentration is consistent with previous results and can be understood as a solvent softening of the liquid crystal and concument promoting of nematic fluctuations.

DOI: 10.1103/PhysRevE.82.051702

PACS number(s): 61.30.-v, 64.70.mj, 65.40.Ba

I. INTRODUCTION

Liquid crystals (LCs) are anisotropic fluids that exhibit a wide variety of phases and phase transitions where the nematic (*N*) and smectic-*A* (Sm*A*) are the best known [1,2]. The transition between the nematic and smectic-*A* (the *N*-Sm*A*) phases is interesting and important because it involves the breaking of a continuous symmetry as well as belonging to the same universality class as the superconducting transition in metals and the superfluid transition in ⁴He. The *N*-Sm*A* transition has been uses as a model phase transition for the study of confinement and disorder effects [3–5]. The phase transition behavior is also sensitive to an applied external electric or magnetic field [6,7] as well as with LC+LC mixtures [8–12]. Even though the *N*-Sm*A* transition has been extensively studied [13], there remains some unresolved issues regarding the fundamental nature of the transition.

Recently, attention has been drawn to the study of miscible mixtures of liquid crystals and nonmesogenic, lowmolecular weight, solvents as a way of exploring the fundamental nature of the LC interactions responsible for mesogenic order, critical behavior, and the tuning of viscoelastic properties [14–18]. X-ray diffraction experiments performed on the smectic-A and smectic-C phases of thermotropic liquid crystals doped with an organic solvent have shown that the smectic layer spacing increases with solvent content [18]. This research also demonstrated the formation of an organic lyotropic lamellar liquid crystal phase in which the solvent molecules largely intercalate between the smectic layers of the LC. It was also mentioned that from a visual inspection of octylcyanobiphenyl (8CB) and n-hexane (hex) mixtures that the solvent was not uniformly distributed throughout the host LC and minimal, nonreproducible, swelling of smectic layers occurred for solvent volume fractions ≥ 0.1 . It was then suggested that the amount of solvent that can be miscibly incorporated in an LC depends on the host LC, temperature, as well as the nature and amount of solvent; noting that the 8CB+hex mixture phase separates for a solvent to liquid crystal mole ratio ≥ 0.1 . Other studies of the effect of a biphenyl solvent on the splay and bend elastic constants and the rotational viscosity coefficient observed an anomalous behavior of the splay elastic constant K_{11} , the dielectric anisotropy $\Delta \varepsilon$, and the effective rotational viscosity coefficient γ_1^* near the N-SmA transition [19]. A theoretical study on the influence of nonmesogenic solvent on the N-SmA phase transition using Landau approach found a concentration induced tricritical point for the N-SmA transition and that the Frank elastic constants K_{11} , K_{22} , and K_{33} are modified as a function of solvent concentration near the *N*-SmA phase transition [16].

A recent calorimetric study of the *N*-SmA transition in mixtures of 8CB and cyclohexane (8CB+chex) was performed under continuous stirring conditions [14]. This study found a linear decrease of the transition temperatures T_{NA} and a linear increase of critical heat capacity exponent α with increasing mole fraction of cyclohexane x_{chex} . This behavior ends at a tricritical point (TCP) where the transition becomes first-order at x_{chex}^{TCP} =0.046, just below which α =0.5 and the nematic range $\Delta T_N = T_{IN} - T_{NA}$ =4.8 K. For x_{chex} > x_{chex}^{TCP} , the *N*-SmA latent heat smoothly increases nonlinearly from zero [14]. This work also presented a theoretical effort to understand the linear transition temperature shift along the same lines as Ref. [16].

To review the relevant concepts, the *N*-SmA phase transition is a nontrivial member of the 3D-XY universality class due to the anisotropy of its critical fluctuations parallel and perpendicular to the director [13,20,21]. The *N*-SmA critical behavior is strongly effected by the coupling between the smectic order parameter $\psi(\vec{r}) = \psi_0 \exp(i\vec{q_0} \cdot \vec{r})$ and the nematic

1539-3755/2010/82(5)/051702(8)

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order parameter $Q_{ii} = (1/2)S(3\hat{n}_i\hat{n}_j - \delta_{ij})$. Here, the ψ is the amplitude of the one-dimensional density wave, $\rho(\vec{r})$ = $Re[\rho_0 + \exp(i\vec{q_0}\cdot\vec{r})\psi(\vec{r})], q_0 = 2\pi/d$ is the wave vector corresponding to the layer spacing d, S is a scalar parameter measuring the magnitude of orientational order on short length scales, and \hat{n} is the nematic director describing spatial orientation of the orientational axis on longer length scales. The δS and $\delta \hat{n}$ couplings introduce two more terms in free energy expression as compared to the usual standard form. One term is of the form $\psi^2 S$, which is nematic-smectic order parameter coupling [1,22] and the other is smectic ordernematic director fluctuation coupling $\psi^2 \delta \hat{n}$ [23,24]. The former coupling reveals the effects of the elasticity of the nematic order prior to the onset of the smectic order and can drive the N-SmA transition from XY like to tricritical to weakly first order [25]. The coupling $\psi^2 \delta \hat{n}$ causes the anisotropic elastic deformations in the smectic. The strength of this coupling depends on the magnitude of the splay elastic constant K_{11} , which is directly proportional to S^2 . Since it is expected that a low-molecular weight solvent miscible in an LC would affect both δS and $\delta \hat{n}$ fluctuations, the x_{sol} dependence would be accounted for using similar terms in a freeenergy expansion.

In this work, the effect of a nonmesogenic, low molecular weight, solvent (n-hexane) on the continuous nematic to smectic-A (N-SmA) phase transition on octylcyanobiphenyl (8CB) and n-hexane (hex) binary mixtures (8CB+hex) as a function of n-hexane mole fraction, x_{hex} , was studied using high-resolution ac-calorimetry without continuous stirring. This was done so as not to mask demixing or phase separation effects. The introduction of n-hexane on 8CB causes a dramatic change in the N-SmA phase transition behavior. The heat capacity peak associated with the N-SmA transition, δC_p , shifts toward lower temperature nonmonotonically and becomes progressively larger as the hexane concentration increases. The dispersive part of heat capacity C''_p associated with N-SmA transition abruptly appears as a peak for x_{hex} \geq 0.08 but is zero for $x_{hex} \leq$ 0.06 indicating a crossover from continuous (second-order) behavior to first-order behavior for the N-SmA transition with a tricritical point at x_{hex}^{TCP} ≈ 0.07 . The integrated ac-enthalpy increases overall as a function of hexane molar fraction. A simple but consistently applied power-law analysis for δC_p with $x_{hex} \leq 0.06$ find a nonlinear increase in the heat capacity effective critical exponent toward the tricritical value ($\alpha_{TCP}=0.50$) as x_{hex} $\rightarrow x_{hex}^{TCP}$ is observed. A small hysteresis of the δC_p shape between heating and cooling is seen and is likely due to a microscopic phase separation of the solvent, perhaps into intersticial region between smectic layers. The nonmonotonic transition temperature shift and extended curvature of α_{eff} behavior with extended curvature as $x_{hex} \rightarrow x_{hex}^{TCP}$ as compared to the linear behavior seen in the previous study on continuously mixed 8CB+chex samples [14] may be due to the competing interactions of microphase separation and dilution effects. Both these effects have significant consequences on the higher temperature I-N phase transition as well and has been previously reported [26].

This paper is organized as follows; following this introduction, Sec. II describes the preparation of sample, the calorimetric cell, and the ac-calorimetric procedures employed in this work. Section III describes the calorimetric results and critical behavior of the *N*-SmA phase transition in the 8CB +hex system. Section IV discusses these results and draws conclusions.

II. EXPERIMENTAL PROCEDURES

The liquid crystal octylcyanobiphenyl, 8CB, has a molecular mass of M_w =291.44 g mol⁻¹ and a density of ρ_{LC} =0.996 g ml⁻¹ at 300 K. A single batch of 8CB, purchased from Frinton Laboratory, was degassed under vacuum for about two hours in the isotropic phase before use for pure and mixture samples. Spectroscopic grade n-hexane (molecular mass of 86.18 g mol⁻¹ and a density of 0.655 g ml⁻¹ at 298 K with a boiling point of 342 K) purchased from EM Science was used without further purification. The 8CB and n-hexane mixtures appear to be miscible up to an n-hexane mole fraction of ≤ 0.12 . This was confirmed by polarizing micrographs of the samples and is consistent with the miscibility limit mentioned by Rieker [18]. Measurements were performed on seven samples as a function of n-hexane mole fraction x_{hex} ranging from 0 (pure 8CB) to 0.12.

High resolution ac-calorimetric measurements were carried out using a homemade calorimeter. The calorimetric sample cell consists of an aluminum envelope 15×8 $\times 0.5$ mm³ in size. To prepare the cell, a sheet of aluminum was cleaned using successive application of water, ethanol, and acetone in an ultrasonic bath and then was folded and sealed on three sides with superglue (cyanoacrylate). Once the cell was thoroughly dried, the desired amount of liquid crystal followed by a relatively large amount of n-hexane was introduced to the cell. The mass of the sample and cell was monitored as the n-hexane was allowed to evaporate slowly until the desired mass of the n-hexane was achieved. At the point of the desired mass of the 8CB+hex mixture, the envelope flap was quickly folded and sealed with the superglue. After sealing the filled cell, a 120 Ω strain gauge and 1 M Ω carbon-flake thermistor were attached to opposite surfaces of the cell using GE varnish. The cell was then mounted into the calorimeter, the details of theory and operation can be found elsewhere [27-29]. Briefly, in the acmode, oscillating heating power $P_{ac}e^{i\omega t}$ is applied to the cell resulting in temperature oscillations with an amplitude T_{ac} and a relative phase shift, $\varphi = \Phi + \pi/2$, where Φ is the absolute phase shift between T_{ac} and the input power. Defining the heat capacity amplitude as $C^* = P_{ac}/(\omega T_{ac})$, the specific heat at a heating frequency ω can be expressed as

$$C_p = \frac{C'_{filled} - C_{empty}}{m_s} = \frac{C^* \cos(\varphi) - C_{empty}}{m_s}, \qquad (1)$$

$$C_{p}'' = \frac{C_{filled}''}{m_{s}} = \frac{C^{*}\sin(\varphi) - 1/(\omega R_{e})}{m_{s}},$$
 (2)

where C'_{filled} and C''_{filled} are the real and imaginary parts of the heat capacity of the filled cell, C_{empty} is the heat capacity of the empty cell, m_s is the mass of the sample (in the range of 15 to 40 mg), and R_e is the external thermal resistance between the cell and the bath (closely the same for all



FIG. 1. (Color online) Specific heat capacity for an 8CB+hex sample on heating with x_{hex} =0.02. The dashed dotted line represents the C_p background, while the dashed curve acts as C_p^{wing} and represents the low-temperature *I-N* C_p wing that would be expected in the absence of *N*-SmA transition.

samples and typically $R_e \sim 200$ K W⁻¹). Equation (1) and (2) require a small correction to account for the nonnegligible internal thermal resistance as compared to R_{e} , which was applied to all results [30]. The real part of the heat capacity can be thought of as the normal heat capacity indicating storage (capacitance) of the thermal energy whereas the imaginary part indicates the loss (dispersion) of energy, analogous to the real and imaginary parts of the complex permittivity. Temperatures corresponding to a one-phase region of the sample+cell, where any relaxation modes (typically structural in nature) relax much faster than ω , will exhibit a zero imaginary part of heat capacity, i.e., $C''_p=0$ [31]. Dispersive temperature regions have nonzero C''_p , such as the two-phase coexistence region of a first-order phase transition where the evolving latent heat interferes with the imposed constant sinusoidal heat distorting the resulting temperature response. Generally, the evolution of the latent heat occurs over a wide range of time scales related to the size of the converting domains. In this case, another heat source (or sink, as the temperature oscillates) appears that interferes with the pure sinusoidal input heat resulting in a peak in the imaginary part of heat capacity, the width of which in temperature is the two-phase coexistence region.

Figure 1 illustrates the specific heat capacity variation over an extended temperature range for the x_{hex} =0.02 sample. The dashed curve under the *N*-SmA heat capacity peak represents the *I-N* specific heat capacity wing C_p^{wing} , which is the hypothetical baseline behavior of C_p in the absence of the *N*-SmA transition. This wing is used to determine the excess specific heat associated with the *N*-SmA phase transition as

$$\delta C_p = C_p - C_p^{wing}.$$
 (3)

The enthalpy change associated with a phase transition is defined as

$$\delta H = \int \delta C_p dT. \tag{4}$$

For a second-order or continuous phase transition, the integration covers the entire δC_p peak over a wide temperature



FIG. 2. (Color online) Upper panel: the excess specific heat δC_p associated with the *N*-SmA transition on heating as a function of temperature about T_{NA} for pure and all 8CB+hex samples. See legend. Lower panel: the imaginary part of heat capacity on heating for all samples as a function of temperature about T_{NA} .

range as possible and gives the total enthalpy change δH associated with the transition. But, for a first-order transition the situation is complicated due to the presence of a coexistence region and a latent heat ΔH . Due to partial phase conversion during a T_{ac} cycle, typical δC_p values obtained in the two-phase coexistence region are artificially high and frequency dependent, due to the dynamics of the phase conversion. The pretransitional enthalpy δH is typically obtained by integrating the linearly truncated δC_p peak between hightemperature and low-temperature limits [31]. A simple integration of the observed δC_p peak yields an effective enthalpy change δH^* , which includes some of the latent heat contribution. Here, $\delta H < \delta H^* < \delta H + \Delta H$. The total enthalpy change for a weakly first-order phase transition is the sum of the integrated pretransitional enthalpy and the latent heat, $\Delta H_{total} = \delta H + \Delta H$, where ΔH_{total} can be obtained from nonadiabatic scanning calorimetry [31]. The integration of the imaginary part of heat capacity given by Eq. (2) yields the imaginary transition enthalpy $\delta H''$ and is a measure of dispersive component of the complex enthalpy. The quantity $\delta H''$ can be used as an accurate indicator of first-order behavior. Since the fixed heating frequency ω is used in this work, the $\delta H''$ is only approximately proportional to the latent heat. Since the two-phase conversion rate may be different for different samples, the proportionality between the $\delta H''$ and the latent heat changes as the sample changes and requires a detailed frequency scan for each sample to establish. In an ac-calorimetric technique the uncertainty in determining the enthalpy is typically 10% mainly due to the uncertainty in the baseline and background subtraction.



FIG. 3. (Color online) Upper panel: the excess specific heat δC_p associated with the *N*-SmA transition on cooling as a function of temperature about T_{NA} for pure and all 8CB+hex samples. The definition of the symbols are given on the inset. Lower panel: the imaginary part of heat capacity on cooling for all samples as a function of temperature about T_{NA} .

III. RESULTS

A. N-SmA phase transition heat capacity

The resulting δC_p data of the N-SmA transition on heating for 8CB+hex and pure 8CB samples over a ±1.5 K temperature range window about the δC_p peak is shown in Fig. 2 (upper panel). As the mole fraction of n-hexane increases, the N-SmA heat capacity peak becomes larger than the pure N-SmA peak and with apparently larger wings on the high temperature side of the peak. Figure 2 (lower panel) shows the imaginary part of specific heat C''_p on heating as a function of temperature about T_{NA} . For the n-hexane mole fractions $x_{hex} \leq 0.06$, the C''_p is flat, indicating the second-order nature of the transition. For $x_{hex} \ge 0.08$, the C''_p reveals a peak indicating a first-order behavior of the transition. As the mole fraction of n-hexane increases beyond $x_{hex} \ge 0.08$, the C''_n peak become broader with a two-phase coexistence region growing from ~0.35 K at x_{hex} =0.08 to ~0.85 K at x_{hex} =0.12. The crossover to the N+SmA coexistence region is continuous in contrast to an abrupt crossover to the I+Nphase coexistence region [26]. Unlike in the case of I-N phase transition C_p peak, the N-SmA C_p peak lies approximately at the center of the coexistence region.

The *N*-SmA excess specific heat δC_p (upper panel) and imaginary part of heat capacity C''_p (lower panel) on cooling are shown in Fig. 3. On cooling, the δC_p peaks exhibit larger C_p wings on both sides of T_{NA} but the low-temperature wing appears progressively smeared in temperature. In addition, the δC_p on cooling exhibits sharp peaks up to x_{hex} =0.08 then appears rounded for x > 0.08. The *N*-SmA C''_p behavior on





FIG. 4. (Color online) Upper Panel: the *I-N* and *N*-SmA phase transition temperatures on heating (\bigcirc) and cooling (\bigcirc) as a function of x_{hex} . Solid lines are guides to the eye. Lower panel: the nematic temperature range ΔT_N on heating (\bigcirc) and cooling (\bigcirc) as a function of x_{hex} . The closed and open rectangular boxes represent the position of tricritical points for 8CB+chex [14] and 8CB+hex systems, respectively, and the width and height of the boxes represent the uncertainties on x_{hex}^{TCP} and ΔT_N^{TCP} , respectively. The horizontal dashed, dashed dot, and dot lines are the nematic ranges for pure 9CB [32], 8CB+chex, and 8CB+10CB [10], respectively, at tricritical point. The solid straight lines are transition temperature (upper panel) and nematic range (lower panel) for 8CB+chex system [14].

cooling is similar to the heating scans in that $C''_p = 0$ through T_{NA} for $x_{hex} \le 0.06$, then reveals a peak for $x_{hex} \ge 0.08$. This indicates, as on heating, a crossover from continuous to first-order transition behavior. However, the C''_p peaks for $x_{hex} \ge 0.08$ on cooling have markedly different shape than on heating. Here, as the temperature approaches T_{NA} from above, a sharp jump preceded by a relatively small wings occurs at ~0.1 K above T_{NA} for all 8CB+hex samples. As the temperature cools further, a long C''_p tail is seen to a common trend at ~-0.25 K for $x_{hex}=0.08$ and ~-0.4 K for $x_{hex}=0.09$ and 0.12 below T_{NA} . The increase in the two-phase coexistence is similar to that seen on heating.

The *N*-SmA transition temperature T_{NA} is defined as the temperature of the δC_p peak maximum and the *I*-*N* transition temperature is taking at the lowest temperature of the isotropic phase prior to entering the *I*+*N* two-phase coexistence region [26]. Figure 4 (upper panel) shows the *I*-*N* and *N*-SmA phase transition temperatures as a function of x_{hex} . As x_{hex} increases, both transition temperatures decrease non-linearly with a bump at $x_{hex} \sim 0.07$. Figure 4 (lower panel) shows the nematic temperature range $\Delta T_N = T_{IN} - T_{NA}$ as a function of x_{hex} revealing a similar nonlinear trend with a similar bump at the same x_{hex} . The horizontal dashed, dashed



FIG. 5. (Color online) Upper panel: the total integrated δC_p ac-enthalpy δH^*_{NA} on heating (\bigcirc) and cooling (\bigcirc) as the function of x_{hex} . Lower panel: integrated C''_p enthalpy $\delta H''_{NA}$ on heating (\bigcirc) and cooling (\bigcirc) as the function of x_{hex} . Solid lines are guides to the eye.

dot, and dot lines represent nematic ranges for pure 9CB [32], 8CB+chex [14], and 8CB+10CB [10] at the tricritical point, respectively. The solid straight lines are the transition temperatures (Fig. 4, upper panel) and nematic range (Fig. 4, lower panel) for the 8CB+chex system [14]. It is observed that the ΔT_N values at the tricritical point are fairly same for 8CB+hex, 8CB+chex, and 8CB+10CB systems. However, it has different value for pure 9CB.

Since continuous transition behavior is observed for $x_{hex} = 0.06$ and first-order behavior at $x_{hex} = 0.08$, a tricritical point mole fraction is taken as $x_{hex}^{TCP} = 0.07$ with the corresponding nematic range at $\Delta T_N^{TCP} \approx 4.63$ K. The vertical dashed line in both the panels of Fig. 4 indicates x_{hex}^{TCP} and a bold-bordered box in the lower panel gives the location of the crossover point whose width and height are the magnitude of uncertainties in x_{hex}^{TCP} and ΔT_N^{TCP} , respectively.

The effective *N*-SmA transition enthalpy (or ac-enthalpy) δH_{NA}^* was obtained by integrating δC_p in the range ± 3 K about T_{NA} . The dispersive enthalpy, $\delta H_{NA}''$ of the *N*-SmA transition, available only for $x_{hex} \ge 0.08$, and was obtained by integrating the *N*-SmA C_p'' peak. Since a fixed heating frequency was used, the nonzero $\delta H_{NA}''$ is only proportional to the transition latent heat. The resulting δH_{NA}^* and $\delta H_{NA}''$ for heating (\bigcirc) and cooling (\bullet) scans as a function of x_{hex} for all 8CB+hex samples are shown in Fig. 5. The δH_{NA}^* values show an overall increase in value with increasing x_{hex} and are consistent on heating and cooling. A small apparent jump in δH_{NA}^* is seen at $\sim x_{hex}^{TCP}$. See Fig. 5 (upper panel). The $\delta H_{NA}''$ exhibits a sudden jump from 0 to ~ 0.28 J g⁻¹ at x_{hex}^{TCP} .

A summary of these results for 8CB+hex samples including pure 8CB is tabulated in Table I. Included are the n-hexane molar fraction x_{hex} , the N-SmA transition temperatures T_{NA} , nematic range ΔT_N , integrated enthalpy change δH^*_{NA} , imaginary enthalpy $\delta H''_{NA}$, McMillan ratio *MR* and height of excess heat capacity peaks h_M for all the 8CB +hex samples including pure 8CB.

B. Power-law analysis of N-SmA phase transition

Because the δC_p for the *N*-SmA transition in 8CB+hex remains continuous and sharp for $x_{hex} \leq x_{hex}^{TCP}$, a critical power-law analysis was attempted. The usual power-law form, in terms of reduced temperature, $|t| = |(T - T_c)|/T_c$, used to analyze the excess specific heat associated with the *N*-SmA transition is given by [13]

$$\delta C_p = A^{\pm} |t|^{-\alpha} (1 + D_1^{\pm} |t|^{\Delta_1}) + B_c, \qquad (5)$$

where B_c is the critical background, A^{\pm} are the amplitudes, and D_1^{\pm} are the correction-to-scaling amplitude with an exponent $\Delta_1=0.524$ [13], both above (+) and below (-) the transition. A full, nonlinear, fitting of Eq. (5) to the δC_p data was attempted, but because the number of data close to the peak were relatively sparse, these fits did not properly converge and yielded unphysical set of fit parameters.

In order to shed some light onto the critical behavior, a simplified power-law analysis procedure was employed in order to estimate the variation of the critical exponent α as a function of x_{hex} . The procedure was consistently applied to all samples including pure 8CB in order to compare the re-

TABLE I. Summary of the calorimetric results for pure and all 8CB+hex samples on heating. Shown are hexane molar fraction x_{hex} , N-SmA transition temperature T_{NA} , nematic range $\Delta T_N = T_{IN} - T_{NA}$ (in Kelvin), integrated enthalpy change δH_{NA}^* , imaginary enthalpy $\delta H_{NA}''$ (in J g⁻¹), McMillan's Ratio $MR = T_{NA}/T_{IN}$, and the heat capacity maximum $h_M \cong \delta C_P^{max}(N-SmA)$ in (J K⁻¹ g⁻¹).

x _{hex}	T_{NA}	ΔT_N	$\delta H^*_{N\!A}$	$\delta H_{NA}''$	MR	h_M
0.00	306.09 ± 0.06	7.11 ± 0.11	0.59 ± 0.06		0.977	0.78
0.02	304.42 ± 0.09	5.53 ± 0.59	0.99 ± 0.10		0.982	1.00
0.03	304.09 ± 0.08	5.03 ± 0.41	1.04 ± 0.10		0.984	1.45
0.06	304.21 ± 0.14	5.27 ± 0.50	0.73 ± 0.07		0.983	0.78
0.08	303.60 ± 0.16	4.46 ± 0.63	1.17 ± 0.12	0.28 ± 0.03	0.986	2.07
0.09	301.93 ± 0.17	3.23 ± 0.96	1.64 ± 0.16	0.34 ± 0.03	0.989	2.94
0.12	301.09 ± 0.08	2.53 ± 1.41	1.55 ± 0.15	0.40 ± 0.04	0.989	1.96



FIG. 6. (Color online) Upper panel: excess specific heats associated to *N*-SmA phase transition as a function of reduced temperature for pure 8CB for $T < T_c$ (\bullet) and for $T > T_c$ (\bigcirc). Lower panel: excess specific heats associated to *N*-SmA phase transition as a function of reduced temperature for hexane mole fraction $x_{hex} = 0.06$ for $T < T_c$ (\bullet) and for $T > T_c$ (\circ). Slope of the straight line in each graph gives the effective critical exponent α_{eff} .

sulting fits. This procedure begins by approximating T_c for each continuous δC_p peak. This is done by plotting a $\log(\delta C_p)$ vs $\log(|t|)$ and choosing T_c such that the high and low-temperature wings appear linear and parallel to each other for low |t|. The rounded and non-power-law data points are then easily identified and removed from further analysis.

Figure 6 shows the resulting log-log plot of data above and below T_c for pure 8CB ($x_{hex}=0$) and the highest concentration 8CB+hex sample that appears continuous as determined by $C_p''(x_{hex}=0.06)$. Now, a range of data up to $|t_{max}|$ was chosen in order to perform a simple linear fit, $\log(\delta C_p) = \log(A^{\pm}) - \alpha'_{eff} \log|t|$. Here, $|t_{max}|$ varied smoothly from 8.9×10^{-4} for pure 8CB to 1.8×10^{-3} for the x_{hex} =0.06 8CB+hex sample. The resulting linear fits are also shown in Fig. 6 for data above and below T_c . The difference between $\alpha'_{eff}(T > T_c)$ and $\alpha'_{eff}(T < T_c)$ is taken as the uncertainty in α'_{eff} and the average its value. The resulting α'_{eff} are not the true critical exponents because of this simplified analysis. However, an *ad-hoc* assumption is made that since the procedure is applied uniformly to all samples, the same error occurred and resulted in a multiplicative correction. Thus, comparing the pure 8CB result in this simplified analysis to the literature value of $\alpha_{eff}=0.3$ [25], a corrected α_{eff} for the 8CB+hex samples is taken as an algebraic shift of +0.17, the difference of $\alpha'_{eff} - \alpha_{eff}$ for pure 8CB. This shift was then applied for all samples from $x_{hex}=0$ to 0.06 and is taken as the approximate x_{hex} dependence of α_{eff} .

The resulting estimate of the *N*-SmA heat capacity effective critical exponent as a function of x_{hex} are shown in Fig.



FIG. 7. (Color online) The effective critical exponent as a function of hexane mole fraction. Solid line represents the best estimate of α_{eff} as a function of x_{hex} . This line intersects the horizontal dashed line at the tricritical point, $x_{hex} \approx 0.07$. The dashed-dot line is α_{eff} for 8CB+chex system from reference [14]. The vertical arrows indicate the location of the tricritical points for 8CB+chex (downward arrow) [14] and 8CB+hex (upward arrow).

7 along with the behavior observed in the previous 8CB + chex study implying a more rigorous fitting procedure [14]. Here, a linear rapid rise in α_{eff} is seen as x_{hex} increases from 0 to 0.04 that reproduces very well the 8CB+chex trend then curves over for $x_{hex} > 0.04$ until intersecting the $\alpha_{eff} = 0.50$ TCP value. The upward arrow in Fig. 7 is the best estimate of x_{hex}^{TCP} for this 8CB+hex system.

IV. DISCUSSION AND CONCLUSIONS

The continuous *N*-SmA liquid crystal phase transition of binary mixtures of 8CB and n-hexane has been studied using high-resolution ac-calorimetry as a function of n-hexane concentration, x_{hex} . Multiple heating and cooling cycles reproduce each other for $x_{hex} \le 0.12$ along with no visual indication of phase separation support the view that the 8CB +hex binary system remained mixed (n-hexane miscible) for all samples studied here, without mechanical mixing. This is supported also by earlier x-ray studies of the smectic layer spacing in 8CB+hex that showed phase separation for $x_{hex} \ge 0.1$ [18].

A recent calorimetric study of binary mixtures of 8CB with various, low-molecular weight, solvents found dramatic changes to the character of the *N*-SmA phase transition [14]. In this work, the N-SmA transition approaches a tricritical point linearly. However, this study used cyclohexane, that has ring structure and employed continuous mixing during measurements as a function of cyclohexane mole fraction, x_{chex} . The transition temperature T_{NA} decreases linearly as x_{chex} increases, the critical exponent α increases linearly from 0.31 (pure 8CB) to 0.50 at x_{chex} =0.046, and the onset of a N-SmA latent heat occurs smoothly at TCP, x_{chev}^{TCP} =0.046. These results were modeled using mean-field Landau-de Gennes theory incorporating the nematic free energy, smectic free energy, and a coupling between nematic and smectic order parameters. This model was extended to account for the solvent by adding a solvent mole-fraction coupling to ψ^2 and to $\psi^2 \delta S$ to the total solvent free energy. Similar results were found in 8CB+biphenyl binary mixtures

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and a Landau–de Gennes model that accounted for change in the LC elastic constants with x_{sol} . However, a TCP was not found in 8CB+biphenyl system [19].

In this present study, several important differences emerge. As x_{hex} increases, T_{NA} decreases as well as the nematic range ΔT_N in a nonlinear way. The character of *N*-SmA transition remains continuous up to $x_{hex} \approx 0.07$ where it appears to jump suddenly to a first-order transition. The bump in T_{NA} and ΔT_N as well as the jump in $\delta H_{NA}''$ all occur at x_{hex}^{TCP} . The critical behavior, estimated by the simple power-law analysis presented here, evolves with α_{eff} initially increases linearly as in the 8CB+chex system but then curves over to reach $\alpha_{eff}=0.50$ at $x_{hex} \rightarrow x_{hex}^{TCP}$. Qualitatively, the correctionto-scaling terms D^{\pm} and the amplitude ratio A^{-}/A^{+} are changing their values toward the tricritical values as a function of x_{hex} . Here, the qualitative measurement of the amplitude ratio A^{-}/A^{+} was extracted examining the gap between two slope lines of the linear fit of log-log plot of δC_p vs |t|(Fig. 6) and the curvature of the curve at high |t| was observed to get qualitative measure of D^{\pm} .

The addition of n-hexane in 8CB may be thought of as a random dilution effect, decreasing both the transition temperature T_{NA} and nematic range ΔT_{NA} accordingly. A key point to remember is that these experiments were done without continuous stirring and so should have revealed any effect of macroscopic phase separation, which was not observed. However, phase separation on much shorter microand/or nanoscale, such as intercolation of the solvent between the smectic layers, is certainly possible. These dilution and microphase separation effects, may lead to two competing interactions causing the nonlinearity in the transition temperature T_{NA} , nematic range ΔT_N , effective critical exponent α_{eff} and jump in the imaginary enthalpy $\delta H''_{NA}$. The microphase separation promotes bulklike behavior while the random dilution is a strong suppressor of any transition behavior and their superposition need not be linear. These effects also cause the change in coupling between the order parameters ψ and Q which consequently change the order of the *N*-SmA phase transition from continuous to first order with a critical point at $x_{hex}^{TCP} \approx 0.07$. We have undertaken a detailed calorimetric studies on the

effect of nonmesogenic, low-molecular weight solvent(hexane) on octylcyanobiphenyl(8CB) phase transitions with emphasis on the most extensively studied but controversial N-SmA phase transition. The dilution of 8CB due to the addition of n-hexane causes the change in the liquid crystal molecular interactions. Interesting and striking effects are observed in 8CB+hex system including the observation of nearly the same tricritical nematic range for 8CB+hex as that for 8CB+chex, and 8CB+10CB systems. But the nematic range for pure 9CB, which is very nearly at TCP, is quite different. This does not appear accidental and raises important questions as to the underlying physics. Continued research efforts are needed to understand the behavior of the such LC+solvent mixture systems as a model system for the intermolecular interactions responsible for mesogenic order. In particular, detailed scattering experiments such as x-ray or neutron as a function of solvent concentration and temperature through the N-SmA transition would be most desirable to explore the critical behavior of the smectic correlation length as susceptibility.

ACKNOWLEDGMENT

This work was supported by the Department of Physics at WPI.

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Eur. Phys. J. E (2011) **34**: 34

DOI: 10.1140/epje/i2011-11034-7

Effect of carbon nanotubes on the isotropic to nematic and the nematic to smectic-A phase transitions in liquid crystal and carbon nanotubes composites

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Regular Article

Effect of carbon nanotubes on the isotropic to nematic and the nematic to smectic-A phase transitions in liquid crystal and carbon nanotubes composites

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Received 16 December 2010 and Received in final form 30 January 2011 Published online: 8 April 2011 – © EDP Sciences / Società Italiana di Fisica / Springer-Verlag 2011

Abstract. A high-resolution ac-calorimetric study on the weakly first-order isotropic to nematic (I-N) and the continuous nematic to smectic-A (N-SmA) phase transitions of the liquid crystal octyl-cyanobiphenyl (8CB) doped with well-dispersed multiwall carbon nanotubes (CNTs) as a function of CNT concentrations is reported. Thermal scans were performed for all samples having CNT weight fraction from $\phi_w = 0.0005$ to 0.0060 over a wide temperature range well above and below the two transitions in pure 8CB. Both the I-N and the N-SmA transitions evolve in character and have their transition temperatures qualitatively offset by ~ 1.10 K lower as compared to that in pure 8CB for all 8CB+CNTs samples. The enthalpy change associated with each phase transition is essentially the same as that of pure 8CB and remains unchanged with increasing ϕ_w . However, there is an evidence that the thermal transport properties of the composites differ from the pure LC upon cooling below a ϕ_w -dependent temperature within the nematic phase. In addition, a new C_p feature is resolved for intermediate ϕ_w samples that appears to be correlated to this onset temperature.

1 Introduction

Carbon nanotubes (CNTs) are highly anisometric rigid "string-like" particles with diameters on the order of nanometers and lengths ranging from micrometers to millimeters [1]. Since their discovery [1–3], extensive studies of their unique structure and properties as well as possible applications have been reported [4–7]. Liquid crystals (LCs) [8,9] are anisotropic fluids that exhibit numerous thermodynamically stable phases between an isotropic liquid and a three-dimensionally ordered solid. In their least ordered phase, the nematic (N), LCs show orientational order due to molecular self-assembly and at the same time maintaining fluid flow properties. In the smectic-A (SmA) phase, they show both orientational and partial translational order characterized by a 1-d density wave [8,9]. Liquid crystalline substances have been extensively studied due to their applications and as important physical models of self-assembly [10].

When CNTs are dispersed in a liquid crystal, they can modify the physical properties and hence the phase behavior of the liquid crystal. The dispersion of these rigid string-like nanoparticles can locally pin the nematic director as well as the smectic layers given homogenous surface alignment. These physical interactions are responsible for the coupling between the orientational order parameter of the LC with that of the CNT and represent a unique physical assembly.

In recent years, the dispersion of carbon nanotubes in different liquids and liquid crystal media has attracted intense interest. Research has been focused on liquid crystalline phases of CNTs [11–15], dispersion and alignment of CNTs in thermotropic or lyotropic liquid crystals [16– 26], and studies of LC+CNT composite system for improving electro-optical switching properties [27–31]. Recently, investigations on LC+CNT composites have shown that the orientational order can be transferred to the dispersed CNTs [16,32]. It has also been observed that the aligned CNT can cause an increase of the orientational order in the LCs [33]. Such composites have been proposed as memory devices using their nanoelectromechanical properties [34].

Some research efforts have also been made on phase behavior and phase transitions of LC+CNT composites [35– 39]. LC+CNT composites were investigated using optical microscopy and DSC, finding an enhancement of the isotropic to nematic (I-N) phase transition temperature revealing a "chimney"-type phase diagram over a narrow range of CNT weight fraction ~ 0.001–0.002 [35]. An I-N phase transition was observed in a LC+CNT composite due to Joule heating produced by a dc-electric field that rotates the CNT out of sample plane short-circuiting

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the electrodes and producing a current flow through the CNT [37]. A high-resolution ac-calorimetry and dielectric study of the I-N phase transition of 5CB+CNT showed the induction of local deformations of the nematic director and the formation of pseudo-nematic domains within the LC media [39]. Most of these studies were focused on the nematic ordering and the I-N phase transition behavior in LC+CNT composites.

In this work, we study the phase transition behavior of the liquid crystal octyl-cyanobiphenyl, 8CB, doped with multiwall carbon naotubes (CNTs) as a function of concentration of CNT. The incorporation of CNTs in 8CB reveals a unique phase behavior. The I-N excess specific heat ΔC_p peaks in 8CB+CNT samples are wider as compared to the peak in pure 8CB. The nematic to smectic-A $(N-\mathrm{Sm}A)$ excess specific heat δC_p peaks are sharp and their wings for all 8CB+CNT samples and that for the bulk 8CB overlay each other. The I-N and the N-SmAphase transition temperatures shift slightly downwards as compared to that of pure 8CB but remains fairly constant as a function of CNT content up to 0.0060 weight fraction of CNTs. However, the order of the phase transition remains unchanged from bulk, the I-N is first-order and the N-SmA is continuous. The thermal transport properties of 8CB+CNT evolve in the ordered nematic and smectic-A phases as a function of temperature. New calorimetric features are observed in the nematic temperature range for intermediate CNT concentrations. The evolution of heat capacity peak, slight change in transition temperature and change in the thermal transport properties are likely due to the elastic coupling between LC director and the CNT.

Our present work is organized as follows; following this introduction, sect. 2 describes the preparation of the sample, the calorimetric cell, and the ac-calorimetric procedure employed in this work. Section 3 describes the calorimetric results of the I-N and the N-SmA phase transition in the 8CB+CNT system and provides the discussion of the results. Section 4 concludes our work and presents future directions.

2 Experimental procedure

2.1 Materials and sample preparation

The liquid crystal, 4-cyano-4'-octylbiphenyl (8CB), used for this experiment was purchased from Frinton laboratory. Pure 8CB (2.3 nm long and 0.5 nm wide molecules with molecular mass $M_w = 291.44 \,\mathrm{g}\,\mathrm{mol}^{-1}$) has a weakly first-order isotropic to nematic phase transition at $T_{\mathrm{IN}}^0 =$ 313.98 K, the second-order nematic to smectic-A transition at $T_{\mathrm{NA}}^0 = 306.97 \,\mathrm{K}$, and strongly first-order crystal to SmA transition at $T_{\mathrm{CrA}}^0 \cong 290 \,\mathrm{K}$ [40]. Multiwall carbon nanotubes (CNTs), synthesized by chemical vapor deposition technique, containing nanotubes 5–30 nm in diameter and 1–5 μ m in length were obtained from Dr. Saion Sinha and used without further processing [41]. In general, the CNTs are in the bundles due to the attractive van der Waals interaction between individual nanotubes. There is also a possibility of physical entanglement among the tubes due to high aspect ratio and flexibility of nanotubes. When the CNTs in the composite are in bundles they may have a disordering effect in the host phase, possibly revealing strongly disturbed ordered domain in the vicinity of the CNT bundles and the natural LC domain between them. They can be disbundled by ultrasonication.

The 8CB was degassed under vacuum in its isotropic phase about two hours before use. The LC, proper amount of carbon nanotubes and relatively large amount of pure acetone were mixed in a vial. The mixture was then mechanically mixed in a touch-mixer for about an hour and ultrasonicated in an ultrasonic bath for about 10 hours in the isotropic phase of pure 8CB. After ultrasonication the dispersion was placed over the hot plate to evaporate the acetone slowly out of the mixture and then the mixture was degassed under vacuum at 318K for about 2 hours. Different samples having ϕ_w ranging from 0.0005 to 0.0060 were prepared using the same procedure. Here, $\phi_w = m_{\rm CNT}/(m_{\rm LC} + m_{\rm CNT})$ is the weight fraction of CNT, where $m_{\rm CNT}$ and $m_{\rm LC}$ are masses of CNT and LC, respectively. The prepared composites appear to be homogeneous up to $\phi_w = 0.0060$, as verified by the visual inspection and by homogeneous texture observed under the crossed-polarizing microscope. Beyond this concentration stable mixtures were not achieved.

When the composite sample was ready it was introduced into an envelope-type aluminum cell of dimensions $\sim 12 \times 8 \times 0.5 \text{ mm}^3$. A 120 Ω strain gauge heater and 1 M Ω carbon-flake thermistor were attached on the opposite surfaces of the cell. The filled cell was then mounted in the high-resolution calorimeter, the details of which can be found elsewhere [42–44].

2.2 Ac-calorimetry

High resolution ac-calorimetric measurement were carried out on a home-made calorimeter at WPI. In its ac mode, oscillating power $P_{\rm ac} \exp(i\omega t)$ is applied to the cell containing a sample of finite thermal conductivity resulting in temperature oscillations with an amplitude $T_{\rm ac}$ and a relative phase shift between temperature oscillation and input power, $\varphi = \Phi + (\pi/2)$, where Φ is the absolute phase shift. The amplitude of the temperature oscillation is given by [45]

$$T_{\rm ac} = \frac{P_{\rm ac}}{\omega C} \left(1 + (\omega \tau_{\rm e})^{-2} + \omega^2 \tau_{ii}^2 + \frac{2K_{\rm e}}{3K_{\rm i}} \right)^{-1/2}, \qquad (1)$$

where $P_{\rm ac}$ is the amplitude and ω is the angular frequency of the applied heating power, $C = C_{\rm s} + C_{\rm c}$ is the total heat capacity of the sample+cell which includes heater and thermistor. $\tau_{\rm e} = C/K_{\rm e}$ and $\tau_{ii}^2 = \tau_{\rm s}^2 + \tau_c^2 =$ $(C_{\rm s}/K_{\rm s})^2 + (C_{\rm c}/K_{\rm c})^2$ are external and internal relaxation times, respectively. Here, $K_{\rm s}$ is the thermal conductance of the sample and $K_{\rm e}$ is the external thermal conductance to the bath. The relative phase shift between the applied power and the resulting temperature oscillations is given by

$$\tan \varphi = \frac{1}{\omega \tau_{\rm e}} - \omega \tau_{\rm i} = \frac{K_{\rm e}}{\omega C} - \omega \left(\frac{C_{\rm s}}{K_{\rm s}} - \frac{C_{\rm c}}{K_{\rm c}}\right), \quad (2)$$

where $\tau_{\rm i} = \tau_{\rm s} + \tau_{\rm c}$. The phase shift is related to both the heat capacity and the thermal conductance of the system. If the frequency of the temperature oscillation is faster than the external equilibration time and slower than the sample internal equilibration time, *i.e.*

$$\omega \tau_{\rm i} \ll 1 \ll \omega \tau_{\rm e},\tag{3}$$

then, eq. (1) becomes

$$C \cong \frac{P_{\rm ac}}{\omega T_{\rm ac}} \,. \tag{4}$$

The region where the inequalities (3) are valid can be found experimentally plotting $\omega T_{\rm ac}$ versus ω . The plateau observed in log-log scale of the curve is the region where the inequalities (3) are valid and gives the working frequency region for the calorimeter [46].

The real and imaginary specific heat at a heating frequency ω can be expressed as

$$C_p = \frac{C'_{\text{filled}} - C_{\text{empty}}}{m_c} = \frac{(P_{\text{ac}}/\omega T_{\text{ac}})\cos\varphi - C_{\text{empty}}}{m_c}, \quad (5)$$

$$C'' = \frac{C''_{\text{filled}}}{m_{\text{s}}} = \frac{(P_{\text{ac}}/\omega T_{\text{ac}})\sin\varphi - (K_{\text{e}}/\omega)}{m_{\text{s}}},\qquad(6)$$

where C'_{filled} and C''_{filled} are the real and imaginary parts of the heat capacity, C_{empty} is the heat capacity of the empty cell, m_{s} is the mass of the sample (in the range of 15 to 30 mg). Equations (5) and (6) require a small correction to account for the non-negligible internal thermal resistance as compared to $R_{\text{e}}(=1/K_{\text{e}})$ and this was applied to all samples [47]. The real part of the heat capacity indicates storage (capacitance) of the thermal energy whereas the imaginary part indicates the loss (dispersion) of energy in the sample analogous to the real and imaginary parts of the complex permittivity. The imaginary part of the heat capacity exhibits its non-zero value only on the dispersive regions, such as a two-phase coexistence where the latent heat is released. But, it is zero at the temperatures corresponding to equilibrium, one-phase states [40].

The excess specific heat associated with a phase transition can be determined by subtracting an appropriate background C_p^{BG} from total specific heat over a wide temperature range. The excess specific heat is given by

$$\Delta C_p = C_p - C_p^{\mathrm{BG}}.$$
 (7)

For the N-SmA phase transition

$$\delta C_p = C_p (N - \mathrm{Sm}A) - C_p^{\mathrm{BL}},\tag{8}$$

where C_p^{BL} is the baseline or wing below the *N*-SmA C_p phase transition peak.

The enthalpy change associated with a phase transition can be defined as

$$\delta H = \int \Delta C_p \mathrm{d}T. \tag{9}$$

For a second-order or continuous phase transitions, the limits of integration are as wide as possible about ΔC_p peaks and the integration yields the total enthalpy change δH associated with the transition. But for the first-order transitions the situation is complicated due to the presence of the coexistence region and latent heat ΔH . In this case, the total enthalpy change is the sum of the pretransitional enthalpy and latent heat $\Delta H_{\text{total}} = \delta H + \Delta H$. An integration of the observed ΔC_p peak yields an effective enthalpy change δH^* which includes some of the latent heat contribution. The integration of the imaginary part of the heat capacity given by eq. (6) gives an imaginary enthalpy $\delta H''$ which is the dispersion of energy in the sample and is an indicator of the first-order character of the transition. In ac-calorimetric technique the absolute value uncertainty in determining the enthalpy is typically 10%, due to the uncertainty in the baseline and background subtraction.

3 Results and discussion

3.1 Overview

For pure 8CB, the *I-N* phase transition occurs at $T_{\rm IN}^0 =$ 313.21 K while the *N*-SmA transition occurs at $T_{\rm NA}^0 =$ 306.09 K, both are about 1 K lower than the highest values reported in the literature [48]. The *I-N* effective enthalpy $\delta H_{\rm IN}^* = 5.13 \pm 0.51 \, {\rm J/g}$, the *N*-SmA effective enthalpy $\delta H_{\rm NA}^* = 0.59 \pm 0.06 \, {\rm J/g}$ and the *I-N* dispersive enthalpy $\delta H_{\rm IN}^* = 0.60 \pm 0.06 \, {\rm J/g}$ in pure 8CB are within 10% of the literature value [49]. These results are used for comparison to the composite results.

The resulting excess specific heat ΔC_p data for 8CB+CNT samples studied on heating as a function of temperature about $T_{\rm IN}$ are shown in fig. 1(a). The $T_{\rm IN}$ is defined as the high-temperature limit of the I + N coexistence range. The I-N and the N-SmA phase transitions are characterized by a distinct ΔC_p peak for all 8CB+CNT samples similar in character to those in pure 8CB. The ΔC_p wings are similar for all 8CB+CNT composite samples and pure 8CB below and above the transitions revealing that the bulk-like order fluctuations are present in the isotropic, nematic and smectic-A phases. In addition to the bulk-like 8CB transition signatures, a new ΔC_p feature is observed in the nematic range for intermediate values of ϕ_w from 0.0010 to 0.0020. This new feature presents as a small broad peak mid-way in the nematic phase.

The imaginary specific heat C''_p as a function of temperature about $T_{\rm IN}$ is shown in fig. 1(b). The C''_p exhibits a sharp peak associated with the *I-N* phase transition and no peak corresponding to the *N*-SmA phase transition. This is consistent with the *I-N* transition being weakly first-order and the *N*-SmA being continuous or secondorder phase transition for all ϕ_w . Surprisingly, the C''_p baseline does not remain zero and temperature independent for 8CB+CNT samples. Here, the C''_p baseline breaks to a linear temperature dependence in the nematic and



Fig. 1. (a) Excess specific heat ΔC_p as a function of temperature about $T_{\rm IN}$ for all 8CB+CNT samples including pure 8CB. Symbols listed in the inset are for $100 \times \phi_w$ and for both the panels. (b) Imaginary specific heat C''_p as a function of temperature about $T_{\rm IN}$.

smectic-A phases on cooling. See fig. 1(b). The negative slope of this linear behavior appears to be ϕ_w -independent but the break temperature shifts towards the $T_{\rm IN}$ with increasing ϕ_w . This new observation will be discussed in detail in sect. 3.3.

A summary of transition temperatures, the nematic temperature ranges, and enthalpies for all samples on heating is given in table 1. All data presented here were taken at a heating frequency of 31.25 mHz and at a scanning rate of 0.2 K h^{-1} for $-3 \text{ K} \leq T_{\text{NA}} \leq 3 \text{ K}$ and 1 K h^{-1} for other ranges of temperature. For all 8CB + CNT samples each heating scan was followed by a cooling scan and experienced the same thermal history. A detailed discussion of the *I-N* and the *N*-SmA phase transition in 8CB+CNT is presented in the following sect. 3.2.

3.2 The I-N and N-SmA phase transitions

The I-N and N-SmA transitions are characterized by analyzing the heat capacity (real and imaginary) profile,

phase diagram, and transition enthalpies. An expanded view of the *I-N* excess specific heat ΔC_p and imaginary specific heat C_p'' on heating as a function of temperature about $T_{\rm IN}$ are shown in fig. 2. Generally, the ΔC_p peaks for the *I-N* transition in 8CB+CNT are broader than that in pure 8CB by about a factor of 2.5 (comparing the average FWHM of the composite samples to that of pure 8CB) but do not exhibit any systematic trend with ϕ_w . Similar behavior is also observed for the C_p'' peak for all ϕ_w samples.

The ΔC_p behavior is consistent between heating and cooling as well as being reproducible after multiple thermal cycles. The ΔC_p wings above and below all transitions match each other on heating and cooling. The I-N ΔC_p cooling and heating peaks are well within the coexistence region. See fig. 3. But, there is a small hysteresis of the ΔC_p in the two-phase I + N region between heating and cooling with the cooling ΔC_p peak being slightly higher in temperature and height. The consistency of ΔC_p data on heating and cooling shows that the sample does not phase-separate on the macroscopic level and the sample is in equilibrium. However, the microscopic (nanoscopic) phase separation and diffusion of CNT in LC media may still occur.

The *I-N* phase transition temperature $T_{\rm IN}$ is defined as the temperature of $C_p^{\prime\prime}$ inflection point on the high-temperature side of the $C_p^{\prime\prime}$ peak [50]. Here, $T_{\rm IN}$ represents the lowest stable temperature of the isotropic phase. The N-SmA phase transition temperature $T_{\rm NA}$ is taken as the N-SmA δC_p peak temperature. Both $T_{\rm IN}$ and $T_{\rm NA}$ slightly decrease in value as compared to those in pure 8CB, $T_{\rm IN}^0$ and $T_{\rm NA}^0$ but remain essentially ϕ_w -independent for the $8\mathrm{CB}\mathrm{+}\mathrm{CNT}$ composites as shown in fig. 4(a). The phase transition temperature shifts are $\Delta T_{\rm IN} = T_{\rm IN} - T_{\rm IN}$ $T_{\rm IN}^0\simeq -1.08\,{\rm K}$ and $\varDelta T_{\rm NA}=T_{\rm NA}-T_{\rm NA}^0\simeq -1.11\,{\rm K}$ for all ϕ_w studied. Because of the uncertainty in the homogeneity of the 8CB+CNT samples, the small noise appeared in the transition temperatures can be related to perfect mixing of 8CB+CNT samples. The nematic range, $\varDelta T_{\rm N} = T_{\rm IN} - T_{\rm NA}$ remains constant for all the samples as shown in fig. 4(b). The coexistence region, ΔT_{I+N} , is determined taking the difference of high-temperature and low-temperature limits of C_p'' peak and is shown in fig. 4(c). For this batch of pure 8CB, $\varDelta T^0_{\rm I+N} = 0.26\,{\rm K}$ while for all 8CB+CNT samples ΔT_{I+N} is larger at 0.50 K and shows no systematic ϕ_w dependence.

The excess specific heat δC_p associated with N-SmA phase transition as a function of temperature about $T_{\rm NA}$ is shown in fig. 5 for pure 8CB and all 8CB+CNT samples on heating. The δC_p exhibits a sharp and distinct N-SmA transition peak for all samples. The δC_p wings overlay each other for all samples on both the low- and high-temperature sides of the transition. This strongly indicates that the nematic and smectic fluctuations remain essentially bulk-like and constant for all samples. Given no strong change in the δC_p behavior as a function of ϕ_w , no power law fits were attempted. The C''_p does not exhibit any peak associated with N-SmA phase transition for all 8CB+CNT samples and pure 8CB, which indicates that

Table 1. Summary of the calorimetric results for the 8CB+CNT samples on heating. Shown are CNT weight fraction ϕ_w , the *I*-*N* transition temperature $T_{\rm IN}$, the *N*-SmA transition temperature $T_{\rm NA}$, nematic range $\Delta T_{\rm N}$ (in kelvins), integrated enthalpy change $\delta H_{\rm IN}^*$, imaginary enthalpy $\delta H_{\rm IN}^{\prime\prime}$ (in J/g), height of the *N*-SmA δC_p peak, $h_{\rm NA}$ (in J/g K) and integrated enthalpy change for *N*-SmA transition $\delta H_{\rm NA}$ (in J/g).

ϕ_w	$T_{\rm IN}$	$T_{\rm NA}$	$\Delta T_{\rm N}$	$\delta H_{ m IN}^*$	$\delta H_{ m IN}^{\prime\prime}$	$h_{\rm NA}$	$\delta H_{\rm NA}$
0.0000	313.21 ± 0.17	306.09 ± 0.03	7.12 ± 0.25	5.1 ± 0.5	0.60 ± 0.06	0.9 ± 0.1	0.59 ± 0.06
0.0005	312.54 ± 0.26	305.24 ± 0.07	7.32 ± 0.38	5.5 ± 0.6	0.53 ± 0.05	1.1 ± 0.2	0.69 ± 0.07
0.0010	311.72 ± 0.26	304.67 ± 0.02	7.10 ± 0.39	6.2 ± 0.6	0.53 ± 0.05	1.0 ± 0.1	0.61 ± 0.06
0.0015	312.56 ± 0.19	305.32 ± 0.01	7.24 ± 0.29	5.4 ± 0.5	0.56 ± 0.06	1.0 ± 0.2	0.80 ± 0.08
0.0020	312.62 ± 0.17	305.53 ± 0.01	7.09 ± 0.26	5.8 ± 0.6	0.65 ± 0.07	1.4 ± 0.2	0.67 ± 0.07
0.0025	311.75 ± 0.20	304.71 ± 0.01	7.04 ± 0.30	5.5 ± 0.6	0.54 ± 0.05	1.2 ± 0.2	0.67 ± 0.07
0.0030	310.73 ± 0.37	303.49 ± 0.03	7.24 ± 0.56	5.4 ± 0.5	0.56 ± 0.06	0.9 ± 0.1	0.73 ± 0.07
0.0040	312.06 ± 0.14	305.16 ± 0.03	6.90 ± 0.21	5.5 ± 0.6	0.71 ± 0.07	1.3 ± 0.2	0.67 ± 0.07
0.0050	312.29 ± 0.19	305.08 ± 0.01	7.21 ± 0.28	6.3 ± 0.6	0.62 ± 0.06	1.0 ± 0.2	0.63 ± 0.06
0.0060	311.73 ± 0.28	304.50 ± 0.01	7.23 ± 0.41	5.6 ± 0.6	0.67 ± 0.07	0.9 ± 0.1	0.65 ± 0.07





Fig. 2. (a) Excess specific heat ΔC_p associated with the *I-N* phase transition as a function of temperature about $T_{\rm IN}$. The definition of the symbols are given in the inset. Symbols listed in the inset are for $100 \times \phi_w$ and for both the panels. (b) Imaginary specific heat C_p'' as a function of temperature about $T_{\rm IN}$.

Fig. 3. The excess specific heat ΔC_p associated with the *I-N* phase transition as a function of temperature about $T_{\rm IN}$ on heating (\circ) and cooling (\bullet) for (a) $\phi_w = 0.0010$, (b) $\phi_w = 0.0060$. Grey symbols represent data points in the I + N two-phase coexistence region.



Fig. 4. (a) The *I*-*N* and the *N*-Sm*A* phase transition temperatures on heating (\circ) and on cooling (\bullet) as a function of ϕ_w . (b) Nematic range on heating (\circ) and cooling (\bullet) as a function of ϕ_w . (c) The *I* + *N* coexistence region on heating (\circ) and cooling (\bullet) as a function of ϕ_w .

the N-SmA phase transition remains second-order for all ϕ_w samples.

An integration was performed on ΔC_p over a wide temperature range of ~ 299 to 316 K for all 8CB and 8CB+CNT samples to yield $\delta H_{\rm T}^*$, while an integration of δC_p over ± 3 K about $T_{\rm NA}$ yields $\delta H_{\rm NA}$. The *I-N* ac-enthalpy is then determined as $\delta H_{\rm IN}^* = \delta H_{\rm T}^* - \delta H_{\rm NA}$. The *I-N* imaginary enthalpy $\delta H_{\rm IN}''$ is obtained by inte-



Fig. 5. Excess specific heat δC_p associated with the *N*-Sm*A* phase transition as a function of temperature about T_{NA} . Symbols listed in the inset are for $100 \times \phi_w$.

grating the C_p'' peak. Figure 6 shows the $\delta H_{\rm NA}$, $\delta H_{\rm IN}^*$, and $\delta H_{\rm IN}''$ on both heating and cooling as a function of ϕ_w . While the 8CB+CNT *I-N* enthalpies appear slightly increased as compared to the bulk 8CB, the increase is within the experimental uncertainties. The incorporation of CNT at these concentrations leaves the transitions essentially bulk-like.

3.3 Thermodynamic anomaly

As mentioned in sect. 3.1, in the nematic range a new heat capacity feature was observed for an intermediate range of ϕ_w (= 0.0010, 0.0015 and 0.0020). This feature was observed reproducibly after multiple thermal cycles. The excess specific heat δC_p^x associated with this feature was isolated by subtracting a bulk-like ΔC_p nematic behavior as the background. The δC_p^x as a function of tempera-ture below $T_{\rm IN}$ is shown in fig. 7 and appears to evolve in this narrow range of ϕ_w . The δC_p^x feature initially appears as a broad sharp single peak at $\phi_w = 0.0010$, which generally narrows and sharpens for the $\phi_w = 0.0020$ that shifts farther below $T_{\rm IN}$. The intermediate sample $(\phi_w = 0.0015)$ exhibits multiple features, some sharp and some broad, that may be related to the sample homogeneity. The enthalpic contribution of this new feature was obtained by integrating δC_p^x to give δH_x and have $\delta H_x(\phi_w = 0.0010) = 0.31, \ \delta H_x(\phi_w = 0.0015) = 0.19,$ and $\delta H_x(\phi_w = 0.0020) = 0.18 \,\text{J/g}$. No hints of this new feature are apparent for samples with $\phi_w < 0.0010$ or $\phi_w > 0.0020.$

As shown in fig. 1(b), there appears a sharp break in the C''_p baseline that changes with changing ϕ_w . On cooling, the $C''_p = 0$ baseline breaks to a linear temperature dependence with a negative slope at a temperature T_i . An example of this behavior is shown in



Fig. 6. (a) The integrated δC_p *N*-Sm*A* enthalpy $\delta H_{\rm NA}$ on heating (\circ) and cooling (\bullet) as a function of ϕ_w . (b) The integrated ΔC_p *I*-*N* enthalpy $\delta H_{\rm IN}^*$ (left axis: heating \circ , cooling \bullet) and imaginary enthalpy $\delta H_{\rm IN}^*$ (right axis: heating \Box , cooling \blacksquare) as the function of ϕ_w . The lines are only a guide to the eye.

fig. 8(a) as an expanded view of the C_p'' baseline for the $\phi_w = 0.0010 \ 8\text{CB+CNT}$ sample. A simple linear fit to the negative-sloped C_p'' baseline region was done for all 8CB+CNT samples revealing a ϕ_w -independent slope of $\sim (-0.015 \pm 0.003) \ \text{J/g} \ \text{K}^2$. However, the x-axis intercept T_i shifts with changing ϕ_w , first decreasing dramatically from $\sim 311.5 \ \text{K}$ to $\sim 307.5 \ \text{K}$ as ϕ_w increases from 0.0005 to 0.0015 then slowly increases back to $\sim 311.5 \ \text{K}$ as ϕ_w increasing from 0.0015 to 0.0050. See fig. 8(b). From eqs. (2) and (6), the change in the expected $C_p'' = 0$ baseline indicates a change in the temperature dependence of the samples' internal thermal conductivity. This is not influenced by the external thermal conductivity as an empty cell scan does not exhibit this behavior nor a pure 8CB sample+cell.

Both the δC_p^x features and the C_p'' baseline x-intercept T_i are temperature dependent and seem to be correlated to each other. This implies that the energy (order) fluctuations are coupled to the thermal transport properties of the composite. These new behaviors are not likely due to the structural change or redistribution of CNT in the LC medium because the features are reproducible on cyclic thermal scans. But, they are likely to arise from some temperature-dependent properties of the composites. The possible T-dependent mechanisms are the order correla-



Fig. 7. The excess specific heat δC_p^x associated with new feature in the nematic range as a function of temperature about $T_{\rm IN}$. All data are heating results. Symbols listed in the inset are for $100 \times \phi_w$.

tion lengths, the surface anchoring energy of the LC on the CNT, and the elasticity of the composite. In order for the thermal transport properties to change, the correlation length should be comparable to the mean distance between CNT. However at T_i , the nematic correlation is long range while the smectic correlation length is not much bigger than the molecular length and so, this mechanism is not likely to cause the observed feature. Similarly, a temperature-dependent surface anchoring energy is not likely to play any role given the inert nature of the graphene in CNT. The elastic constants K_{ii} change dramatically for 8CB in the nematic phase. As the nematic stiffens there is a stronger bulk coupling between the director and the CNT that would affect thermal transport properties of the composite. This coupling becomes significant at a temperature where one of the K_{ij} becomes comparable to the stiffness of the CNT aggregates (not individual CNT strands) leading to the C''_p baseline change. This elastic coupling would also modify nematic director energy fluctuations and may perhaps lead to the δC_p^x feature.

4 Conclusion

We have undertaken a detailed calorimetric studies on the effect of anisometric, string-like particles, carbon nanotubes on a weakly first-order I-N and the continuous N-SmA phase transitions of octylcyanobiphenyl (8CB) and CNT nano-composite. A slight change in transition temperatures occurs as CNT are added in 8CB but they remain fairly constant for all ϕ_w samples. Both transitions evolve without showing any systematic trend with change in ϕ_w . The order of the transition remains the same being the I-N first-order and the N-SmA second-order.



Fig. 8. (a) The imaginary specific heat C''_p for the sample having $\phi_w = 0.0010$ as a function of temperature. The slopped C''_p intersects the $C''_p = 0$ line at T_i . (b) T_i as a function of ϕ_w . The open symbols (\circ) represent T_i for the CNT concentrations and crosses (\times) represent the heat capacity maxima temperatures for the new feature. The solid line is only a guide to the eye.

The temperature-dependent but ϕ_w -independent change in thermal transport properties is observed due to the interaction of CNT with LC molecules. A slight change in enthalpies is also observed in the samples due to the addition of CNT. These effects of incorporating the CNT with LC are likely due to the elastic coupling between the CNT and LC, the change in the elastic properties of the composite and the thermal anisotropic properties of CNT. Continued experimental efforts probing the homogeneity of the sample, frequency-dependent dynamics, and elastic behavior of the homogenous sample as a function of CNT content and temperature would be particulary important and interesting.

We would like to thank Department of Physics at WPI for support.

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