Phase transitions in a nematic binary mixture

A. Christine Rauch, Shila Garg,[a] and D. T. Jacobs
Physics Department, The College of Wooster, Wooster, Ohio 44691

(Received 6 August 2001; accepted 7 November 2001)

Our objective was to study mixtures of nematic liquid crystals with dissimilar dielectric anisotropies but similar phase properties. Using light scattering and microscopy, we have established the phase boundaries and transition widths of mixtures of 4′-*n*-pentyl-4-cyanobiphenyl and 4′-methoxybenzylidene-4-butylaniline. In addition to the isotropic-nematic transition, there is a second induced phase for certain concentrations, which we conclude is an induced smectic B phase. Recent theoretical works provide a model for nematic to induced smectic A transition by combining Flory–Huggins and Maier–Saupe–McMillan theories. From our phase transition data and the application of the above theoretical framework, we conclude that there is a possibility of strong interaction between the two mesogens that produces the smectic B phase. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1431589]

I. INTRODUCTION

The phase study of mixtures of liquid crystals has been a rich area for investigation by both theoreticians and experimentalists. Earlier papers have extended the Maier–Saupe theory for pure nematics to include binary mixtures and induced biaxial phases.[1–2] Recent theoretical work by Kyu, Chiu, and Kajiyama[3] provides a model for nematic—induced smectic A transition by combining Flory-Huggins and Maier–Saupe–McMillan (FH/MS) theories. The authors demonstrated that the coupling between phase separation and liquid crystal ordering can be done by a combination of the FH/MS theories, where the free energy of mixing for binary nematic mixtures was expressed as a free energy of mixing of isotropic liquids and the free energy of nematic ordering. Some of the phase diagrams generated by their model are applicable for mixtures of liquid crystals that individually do not exhibit a smectic phase. The phenomenon of inducing a smectic or a nematic phase is related to the forming of molecular complexes, but the exact process is not well understood.[4] Mixtures of nematic liquid crystals with strongly polar end groups (such as the cyano group) and other nonpolar molecules have been observed to exhibit an induced smectic phase even when the individual materials do not exhibit the phase.[5–9]

There are many ways of modifying the physical properties of liquid crystals; one obvious way is to substitute various chemical groups and, through synthesis, modify molecular sizes and hence the physical properties. The other method is to change the performance characteristics through the use of mixtures. The physical properties of binary mixtures of liquid crystals are of considerable interest since they are used in many applications. For example, a mixture at the right concentration of two substances, which individually have narrow nematic ranges, can display a nematic range substantially larger. Understanding the interactions between dissimilar materials can be of fundamental importance in being able to tune the physical property of materials. The usual assumption is that, in the absence of chemical reactions, the bulk physical properties add up as a weighted sum of the individual properties, but this may not always be the case. The scientific principles behind how dielectric anisotropies, viscosities, and the elastic and optical properties of the mixtures are related to the individual components are relevant in creating the right mixture, which can be regarded as a physically different material.

Our objective was to study a mixture of nematic liquid crystals with dissimilar dielectric anisotropies but similar phase properties, and we chose MBBA (4′-methoxybenzylidene-4-butylaniline) and 5CB (4′-*n*-pentyl-4-cyanobiphenyl) as suitable candidates for the study. Each of these materials has been the subject of a large number of investigations.[10] Their physical properties such as dielectric permittivities, elastic constants, and birefringence have been well-documented. Yet, there has been very little work reported on their mixtures except for the brief report by Park, Bak, and Labes.[11]

We have been able to establish the nature of the phase boundaries of two distinct phase transitions observed in this study. In addition to the isotropic-nematic transition, there is a second induced phase for certain concentrations of the mixtures, which we conclude is an induced smectic B phase. In addition, we report modulation of transmitted intensity by the temperature dependence of the refractive index anisotropy in the nematic phase. The present paper deals with the phase properties of the binary mixtures of 5CB and MBBA and our observations lead to the conclusion that there is a considerable cross interaction between the two materials.

II. EXPERIMENT

The phase boundaries for mixtures of the nematics 5CB and MBBA were determined by microscopy and by transmitted light intensity measurements. The individual materials were chosen for the absence of a smectic phase and their

[a]Author to whom correspondence should be addressed. Electronic mail: sgarg@wooster.edu

TABLE I. Sample concentrations of 5CB and MBBA. The isotropic-nematic transition temperatures determined by the transmitted intensity experiment are shown.

Sample number	Mass 5CB (grams)	Mass MBBA (grams)	Percent 5CB	Isotropic-nematic transition (°C)
1	N/A	0	100	31.2
2	1.595	0.400	79.9	39.6
3	1.198	0.804	59.8	45.6
4	0.799	1.197	40.0	48.1
5	0.400	1.599	20.0	42.6
6	0	N/A	0	37.7
7	0.597	1.403	29.8	47.5
8	0.814	1.202	40.4	48.4
9	1.000	1.007	49.8	48.1
10	1.413	0.600	70.2	40.9
11	N/A	0	100	⋯

positive and negative dielectric anisotropies, respectively. 5CB was purchased from EM Industries and MBBA from Frinton Labs. Several mixtures were prepared with concentrations varying from 0% 5CB to 100% 5CB by mass (see Table I). Care was taken to store and handle MBBA in a dry-nitrogen environment to avoid water contamination. The transition temperatures of the pure MBBA were lower than expected from its reported literature value.[10] Despite this problem, the binary mixtures yielded interesting and repeatable observations. We constructed cells with dimensions of 2.5 cm by 2 cm from cleaned microscope slides and a 36 μm Dupont Mylar spacer. The glass surface was untreated and the cells were sealed with epoxy after being filled with the mixtures.

Initially, the experiment was conducted with a very simple setup using unpolarized laser light passing through the cell, which was housed in a thermostat, with the transmitted light intensity detected by a photodiode. Temperature of the cell was initially raised to 55°C and maintained there until the mixture went isotropic. At this point the heaters were tuned off and the mixture was allowed to cool, while the temperature of the cell and the photodiode voltage were recorded every 18 seconds until the mixture reached room temperature. Initially, all the light intensity is transmitted by the clear isotropic phase, but when the mixture goes through the Nematic-Isotropic (NI) transition, a large percentage of light is scattered by the droplets formation and subsequent phase changes that occur in the mixture. Due to this scattering, the intensity reaching the photodiode falls sharply. The temperature where there is such a sharp fall is recorded as a phase-transition temperature.

Figure 1(a) shows typical recorded data for a mixture of 70% 5CB and 30% MBBA. The isotopic-nematic transition is identified clearly. However, the data collected for 30% 5CB and 70% MBBA shows two sharp transitions [see Fig. 1(b)] with data in the middle region (nematic phase) showing an oscillatory behavior of the transmitted light intensity. These two sets of data were typical of the type of data for all the mixtures, i.e., some of the mixtures displayed one transition and others two, but all of them displayed oscillations in transmitted intensity in the nematic phase due to birefringence. Due to the fact that the transition temperatures were only roughly determined by this scanning method, a more precise experiment was developed.

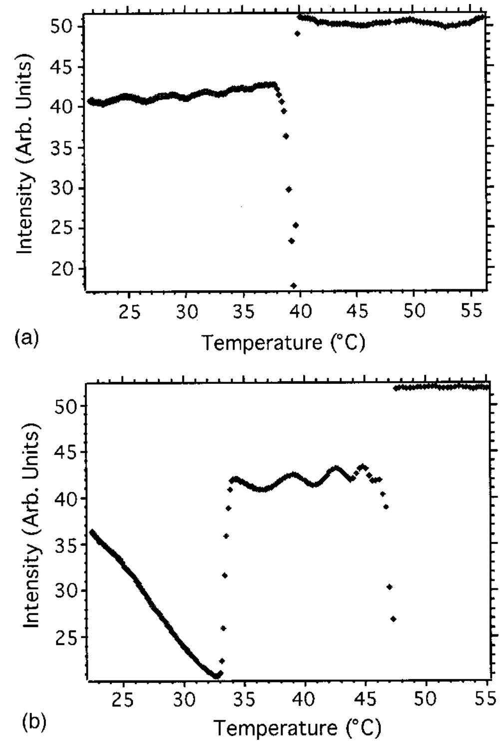

FIG. 1. (a) Transmitted intensity with respect to temperature, sample 10, 70% 5CB. The sharp drop in intensity corresponds to the isotropic to nematic phase transition. (b) Transmitted intensity vs temperature for sample 7, with 30% 5CB. The sharp drops in intensity correspond to phase transitions as described in the text.

We replaced the laser with a horizontally polarized laser and placed an analyzer in the transmitted beam, crossed in orientation to the laser's polarization. In addition, a beam splitter was used to direct a small portion of the incident light to another photodiode, and thus the incident light intensity was monitored. The temperature control algorithm was improved so that after initially heating the cell to a certain temperature, the temperature could be dropped by a certain amount and then held constant to within ± 0.01°C for a desired interval of time. By dropping the temperature in a stepwise fashion, it was concluded that the light intensity data corresponded to the average, stabilized temperature of the corresponding step. The program checked to make sure that the temperature stabilized before recording the photo voltage data.

With the modifications in place, the earlier experiments were repeated for a variety of mixtures. The diode monitoring the incident laser intensity indicated no systematic fluctuations throughout the experiment. The transmitted intensity data confirmed what was observed earlier. The mixtures between 20% 5CB and 60% 5CB consistently showed two transitions and an oscillatory behavior in the middle region (i.e., the nematic phase). The other mixtures displayed one transition only below which the transmitted intensity oscillated. Figures 2(a) and 2(b) show data for 50% 5CB and 100% 5CB, respectively. The initial photo voltage data in the

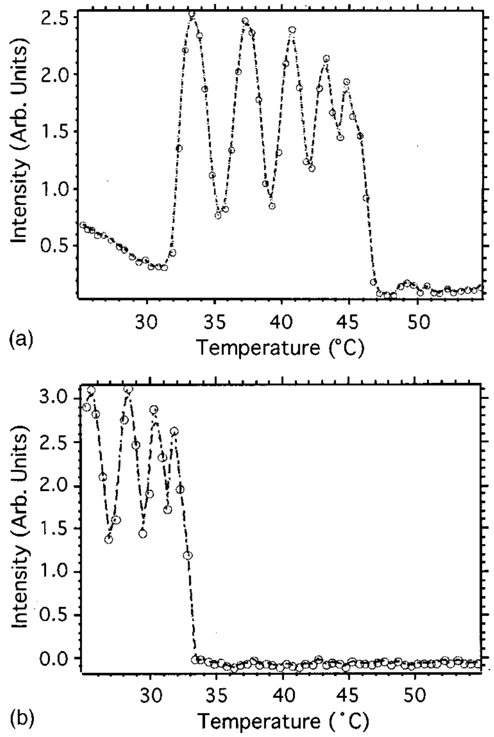

FIG. 2. (a) Transmitted intensity vs temperature for sample 9, with 50% 5CB when polarized laser light is used with an analyzer at 90° to the incident light polarization. The line is a guide to the eye. (b) Transmitted intensity vs temperature for sample 1, with 100% 5CB.

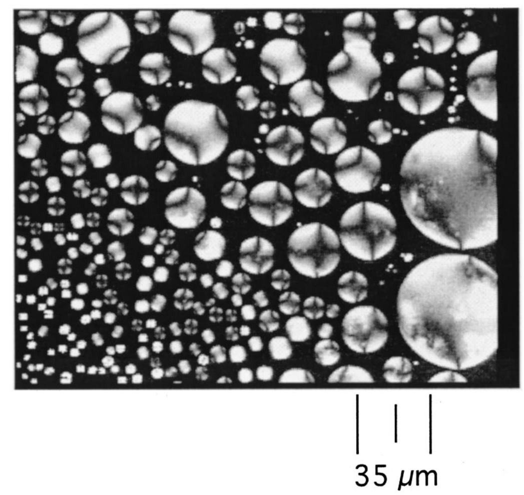

FIG. 3. Nematic droplets in 60% 5CB at the NI transition.

isotropic phase shows zero intensity since we now have a polarized incident beam and a crossed analyzer in the transmitted beam. As a result, the phase transitions now correspond to an increase in transmitted intensity. The temperatures where the phase transitions occurred are tabulated in Table I.

A separate experiment determining the phase-transition temperatures was conducted using visual observations through a Nikon Optiphot2-polarizing microscope. The experimental details are similar to those described in Ref. 12. Video images collected by a Javelin CCD camera mounted on the microscope were digitized using a Miromotion DC20 digitizer board on a Power Macintosh 6500. The same cells used in the previous experiment to measure transition temperatures were used in this part of the experiment. An INSTEC HS1-RTS1 temperature-controlled stage was used for this part of the experiment. Our microscope data was taken on cooling the mixtures from the isotropic phase at a rate of 0.025 °C/min and shows the phase transitions as well as the width of transitions for all of the compositions. Figure 3 shows the nematic droplet formation as observed through a microscope at the NI transition. A clear schlieren texture is visible as the isotropic material cools into the nematic phase and the droplets coalesce to form the bulk phase. The first appearance of droplets is indicated as the start of the isotropic-nematic mixed phase. The disappearance of the last of the isotropic phase indicates the onset of pure nematic phase. Similarly, the temperatures corresponding to the start of the dendritic growth and the disappearance of the nematic texture are monitored for the lower transition.

III. ANALYSIS AND DISCUSSION

A. The phase diagram

Figure 4(a) shows the phase-transition temperatures observed at each composition from the data collected in the light-scattering experiment. Two coexistence curves are evident. The first transition starting from the isotropic phase is clearly characterized as an isotropic-nematic transition based on our microscope observations. Figure 4(b) shows the two coexistence curves determined by the microscope data. The phase transition curves in Figs. 4(a) and 4(b) look very similar even if individual transition temperatures are not identical. This is to be expected, since the data are generated by two different techniques, namely light scattering and microscopy. The temperature control and hardware used to detect the transitions are clearly different and will introduce some variation in the transition points. The measurements on the mixture of 40% 5CB were repeated and can be seen from our data (in Figs. 4) to be fairly reproducible.

The curvature of the isotropic-nematic transition has been shown[13] to depend on a parameter, c, which is called the strength of interaction of the mesogens or the cross interaction parameter. The authors[13] use a combined Maier–Saupe and Flory–Huggins theory based on a mean-field model, which ignores chain rigidity, length, etc. of the individual mesogens, but considers only the interaction parameters of the mesogens.

The parameter c characterizes the relative strength of the cross interaction between dissimilar mesogens as compared to that in the same species. A small value of c indicates a weak interaction and that each nematic is more stable in its pure state than the mixed state; no smectic phase can be induced. For a $c>1$, cross interactions are more significant, the mixed phase is more stable, and there is a strong possibility of the appearance of an induced nematic or a smectic phase. In addition, the convex shape of the upper transition is the result of a strong mesogenic interaction.[13] For high nematic order parameter, a stable nematic phase can occur at higher temperatures than the individual nematics for middle

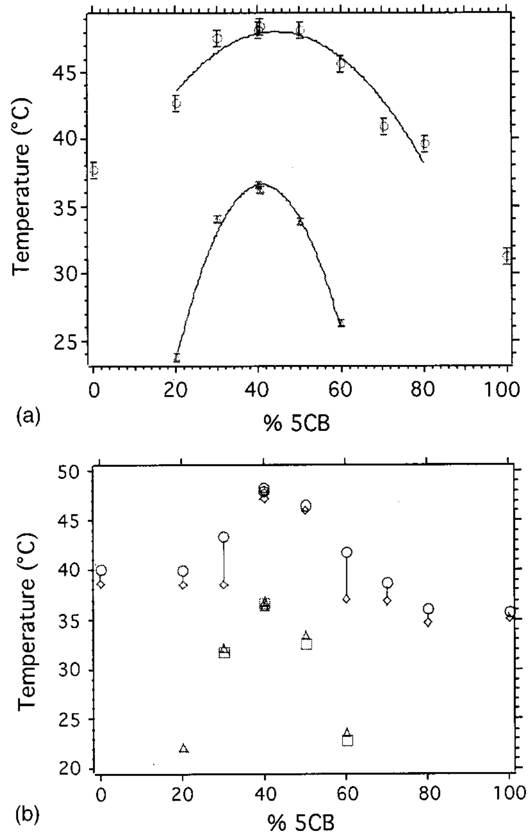

FIG. 4. (a) Phase transition data and the curve corresponding to fitting the points to a quadrataic function. The circles are the first transition observed, which is isotropic to nematic. The triangles, whose errors are smaller than the symbol size, are the second transition observed for some compositions. The equations and parameters used for the fits: $T_c(\text{upper})=(48.0\pm0.6)-(7.6\pm1.4)10^{-3}|(x-(0.44\pm0.2)|\hat{}2$, chi squared=5.8, $T_c(\text{lower})=(36.6\pm0.3)-(0.029\pm0.001)|(x=(0.41\pm0.3)|\hat{}2$, chi squared=0.37, where x is the mass fraction of 5CB. (b) Microscope data for phase transitions and coexistence regions. The appearance of nematic droplets (circles) signals the onset of the mixed regions and the disappearance of the isotropic (diamonds) the start of the pure nematic state. Similarly, the start of the dendritic growth (triangle) is the nematic-smectic B coexistence region and the disappearance of the nematic regions (square) the onset of pure smectic B. The vertical lines indicate the widths of transitions. Note that there are two sets of data points plotted for the 40% mixture to show repeatability.

compositions (50–50), as compared to compositions rich in either of the components.

Since the shape of the transition curve is very sensitive to this parameter c, we have tried to interpret our data using Chiu and Kyu's model.[13] They have generated a family of curves for both the isotropic-nematic and nematic-nematic phase transitions and the shape of our upper transition curve is consistent with the value of $c>1$ in comparison to their theoretically generated curves. The authors have also demonstrated the effect of molecular weight on the phase diagrams of nematic mixtures. The shape of our upper phase curve corresponds[13] to the ratio of the component molecular weights equal to one and a c of 1.2. For our mixtures, the ratio of molecular weights of 5CB and MBBA is approximately one (exact value is 0.93). The parameter c can be accurately calculated if the curve exhibits an azeotropic point by knowing the composition at the azeotropic point and the NI transition temperatures of the two components. In our phase diagram [Fig. 4(a)] the azeotrope for the upper curve is estimated by fitting a parabolic curve to the nematic-isotropic transition data. From our curve fit shown in Fig. 4(a), we can identify the azeotropic point as: $\phi_1^{\text{Az}}=(0.44\pm0.02)$ where ϕ_1^{Az} is the concentration of 5CB in the mixture at the point.

The constant c can be calculated from a phase diagram using the Eq. (33) in Ref. 13,

$$c=\frac{(1-\phi_1^{\text{Az}})T_{\text{NI},2}-\phi_1^{\text{Az}}T_{\text{NI},1}}{(1-2\phi_1^{\text{Az}})\sqrt{T_{\text{NI},1}T_{\text{NI},2}}}. \tag{1}$$

$T_{\text{NI},1}$ and $T_{\text{NI},2}$ are the NI transition temperatures of the two pure components, i.e., 5CB and MBBA. ϕ_1^{Az} refers to the volume concentration of the first component in the mixture at the azeotropic point. We take 5CB to be our first component and thus ϕ_1^{Az} is the volume fraction of 5CB at the azeotrope. However, the ratio of densities of 5CB and MBBA is about one (their specific gravities are 1.01 and 1.027, respectively from the manufacturer's specifications) and thus the volume fractions are the same to within 2% as the mass fractions used in the preparation of our cells.

For mixtures of pure 5CB and MBBA with NI transition temperatures (given in the literature) of 35.5 and 47°C, our calculated value of c from Eq. (1) comes out to be 2.2. But as can be seen from our measured transition temperatures of 31 and 37.5 °C [from Fig. 4(a)], our calculated c for the system can be as low as 1.8. Still, it is safe to conclude that $c>1$ from our data.

A second, lower transition is present in our data for certain concentrations. The nature of this phase is not obvious. The theoretical model[3] predicts the possibility of a nematic-nematic or a nematic-induced smectic transition. The second phase boundary can be described by an expression for a parabola and can be written as:

$$\phi-\phi_c=B\left(\frac{T-T_c}{T_c}\right)^{\gamma}, \tag{2}$$

where B is a constant.

In fact, both the transition curves are parabolic in shape which corresponds to $\gamma=0.5$, as can be seen in Fig. 4(a). According to the theoretical model developed in Ref. 3, a parabolic curve with $\gamma=0.5$ could describe either a nematic-nematic or a nematic-induced smectic A transition for the second phase boundary. Thus our parabolic fit does not allow us to distinguish between the two types of transitions, but it does allow us to rule out a nematic-crystalline transition. There have been numerous observations of an induced smectic in mixtures of strongly polar and nonpolar compounds, while the pure substances do not exhibit the phase.[5,8]

Our microscopic observations show the onset of the second phase transition through a dendritic growth (see Fig. 5). The morphology of the growth depends on the cooling rate. Recently, dendritic pattern formation has been observed at the nematic-smectic B interface of the CCHn family.[14] The final resulting phase of our mixtures that went through a second transition near room temperature was a mosaic phase a shown in Fig. 6. The texture of this phase rules out a smectic A phase. Preliminary x-ray data[15] of the 40–60 and

FIG. 5. (Color) Dendritic growth at the second transition (Nematic-Smectic B) in 30% 5CB.

the 50–50 mixtures of 5CB and MBBA confirm the absence of smectic A in the lower phase of our mixtures. On the other hand, the x-ray data does not exclude the possibility of a more ordered smectic B or a G phase. Either of these smectic phases can have a mosaic structure.[16] Our conclusion is that the second phase is an induced smectic B rather than G. We base it on the following: (i) The mosaic phase platelets observed by us are more oblong as for smectic B than rounded as they are in general for smectic G;[16] (ii) or ability to slide a coverslip across the material in the smectic phase (in smectic G phase, the coverslip will not slide but will eventually lift due to higher crystallinity);[17] and (iii) we prepared a homeotropically aligned cell with 30% 5CB and monitored the phase transitions under the microscope starting from the isotropic phase and ramping the temperature down as described earlier. The nucleation of the smectic B germs out of the homeotropically aligned nematic cell were circular in shape and these grew out into the mosaic phase. These observations are very similar to those described by Buka, Toth-Katona, and Kramer[18] during a nematic-smectic B transition in a homeotropic cell.

FIG. 6. (Color) Final mosaic phase in 40% 5CB and 60% MBBA.

B. Intensity oscillations

It is clear from Figs. 1 and 2 that there are regular oscillations in the second (nematic) phase region. These features were present in the pure nematics, as well as the mixtures in the nematic phase. We can model our system as a birefringent, uniaxial crystal, which when placed between two crossed polarizers has the transmitted light intensity given by:

$$\frac{I}{I_0}=\sin^2(2\pi)\sin^2\left[\frac{l(n_\parallel-n_\perp)}{\lambda}\pi\right], \tag{3}$$

where τ is the angle between the polarizer and the crystal axis, l is the thickness of the crystal, and $n_\parallel$ and $n_\perp$ are the two refractive indices parallel and perpendicular to the optic axis of the crystal.[19] Birefringence is defined as $\Delta n=(n_\parallel-n_\perp)$.

The temperature dependence of the birefringence of a nematic liquid crystal can be described as being proportional to the order parameter of the nematic with a proportionality constant α. Huff *et al.*[20] develop a relationship for the order parameters of a nematic as a function of temperature based on Landau–de Gennes theory. Equation (3) can now be rewritten in terms of the order parameter's temperature dependence,

$$\frac{I}{I_0}=C\sin^2\left[A\left(1+\frac{1}{3}\sqrt{1+\frac{T_c-T}{B}}\right)\right]+D, \tag{4}$$

where $C=\sin^2(2\tau)$ is the amplitude of the oscillation,

$$A=\frac{\pi l}{2\lambda}\alpha\left(\frac{3}{4}S_c\right),\quad B=T_c-T^*,$$

D is the instrumental offset, T^* is the second-order phase-transition temperature and S_c the transition value of the order parameter.[19]

Since this project used mixtures of various percentages of 5CB and MBBA, we simply found the "best fit" to our data by varying the two parameters (T_c-T^*) and S_c. We fixed the oscillation amplitude C and the offset D in Eq. (4) by inspection of our data and performed an unweighted fit to one set of oscillations in the mixture with 60% 5CB with a transition temperature, T_c of 43.6 °C. The data and the fit are shown in Fig. 7 and the agreement of the function with our data is very good.

IV. CONCLUSIONS

By employing light-scattering and optical microscopy techniques, we observed definite phase transitions in mixtures of 5CB and MBBA. The upper transition is an isotropic to nematic and occurs at a higher temperature than a second transition that occurs for some compositions over the temperature range studied. The nematic phase is easy to identify because of the schlieren texture. There is a definite width to the NI transition corresponding to the first appearance of the nematic droplets and the final disappearance of the isotropic phase.

The second phase transition is consistent with the nematic-smectic B transition. The onset of smectic B phase with dendrites has been well-studied in other liquid crystal

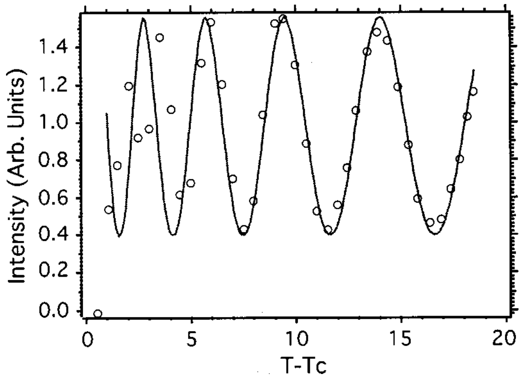

FIG. 7. Theoretical fit for the intensity oscillations using Eq. (7) in the text. The data points are from 60% 5CB run with NI transition temperature $T_c = 43.6\,°C$. The best fit parameters are: A=16.8 and B=10.3. C and D are kept fixed at 0.00116 and 0.0004.

systems. Even though the models proposed in Ref. 3 takes into account only the smectic A order parameter (not any of the higher smectic phases) and predict the appearance of an induced smectic A phase, they help to understand our data and interpret the interactions of the two nematic mesogens.

According to Kyu, Chiu, and Kajiyama,[3] for a value of the parameter $c=1.2$ and a nematic mixture with ratio of molecular weights of one, the shapes of the NI transition curve and the pure nematic to the coexisting nematic transition curve look very similar in shape and curvature to our two transition curves displayed in Fig. 4(a). We have determined the coexistence regions of our nematic-smectic B and the isotropic-nematic regions based on microscope observations and in general these shapes are in agreement with the above mentioned transition curves generated in Ref. 3. The width of the NI transition indicates the coexistence regions in Fig. 4(b), when the lower phase is a single nematic phase and thus, the curve defines a phase-transition curve with the highest point an azeotrope rather than a critical point. In Fig. 4(b), the region close to the azeotropic point of the NI transition reveals the narrowest width at the isotropic-nematic transition, as expected.

It has been shown for a one-to-one molar mixture of these two liquid crystals that their dielectric permittivities do not algebraically add up, indicating at least a weak charge interaction between the two species.[11] This observation is consistent with our conclusion of strong cross interaction of the species based on the estimate of the parameter c. This strong interaction between 5CB and MBBA can also be qualitatively observed by the high viscosity of the mixtures with compositions around one-to-one molar ratio (48% 5CB by weight). It is easy to visualize this point by arguing that each 5CB molecule has a partner MBBA with which to associate. Due to the manner in which charges are distributed around the two mesogens with polar ends and nonpolar groups, it is not readily understandable how the two molecules in fact associate with each other and as a result how the charges interact. This interaction clearly affects the overall electrical and other physical properties of the mixtures. We are currently investigating such interactions between the species.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Peter Palffy-Muhoray and Dr. Mary Neubert of the Liquid Crystal Institute, Dr. Anisimov of University of Maryland and Dr. Peter Collings of Swarthmore College for very helpful discussions. The authors would also like to thank Dr. Satyendra Kumar for x-ray measurements on some of these mixtures. The author, S.G. was supported by NSF Grant No. DMR 9704579, while the author, D.T.J. was partially supported by NASA Grant No. NAG 8-1433.

[1] P. Palffy-Muhoray, J. J. de Bruyn, and D. A. Dunmur, Mol. Cryst. Liq. Cryst. **127**, 301 (1985).
[2] P. Palffy-Muhoray, D. A. Dunmur, W. H. Miller, and D. A. Balzarini, *Liquid Crystals and Ordered Fluids*, edited by A. C. Griffith and J. F. Johnson (Plenum, New York, 1984), Vol. 4, p. 615.
[3] T. Kyu, H-W. Chiu, and T. Kajiyama, Phys. Rev. E **55**, 7105 (1997).
[4] G. Derfel, Mol. Cryst. Liq. Cryst. **82**, 277 (1982).
[5] P. Diehl, H. R. Wasser, G. A. Nagana Gowda, N. Suryaprakash, and C. L. Khetrapal, Chem. Phys. Lett. **159**, 318 (1989).
[6] J. C. Hwang, H. Kikuchi, and T. Kajiyama, Polymer **33**, 1822 (1992).
[7] C. S. Oh, Mol. Cryst. Liq. Cryst. **42**, 1 (1977).
[8] A. Hauser, S. Ernest, A. Hamann, and G. Pelzl, Cryst. Res. Technol. **29**, 443 (1994).
[9] A. Buka, L. Bata, and K. Pinter, Mol. Cryst. Liq. Cryst. **108**, 211 (1984).
[10] W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach, London, 1980).
[11] J. W. Park, C. S. Bak, and M. M. Labes, J. Am. Chem. Soc. **97**, 4398 (1975).
[12] S. Garg, E. Bramley, and U. D. Kini, Mol. Cryst. Liq. Cryst. **325**, 209 (1998).
[13] H-W. Chiu and T. Kyu, J. Chem. Phys. **103**, 7471 (1995).
[14] T. Toth-Katona, T. Borzsonyi, and A. Buka, Mol. Cryst. Liq. Cryst. **339**, 175 (2000).
[15] Satyendra Kumar (private communication).
[16] G. W. Gray and J. W. G. Goodby, *Smectic Liquid Crystals: Textures and Structures* (Leonard Hill, London, 1984).
[17] Mary Neubert (private communication).
[18] A. Buka, T. Toth-Katona, and L. Kramer, Phys. Rev. E **51**, 571 (1995).
[19] F. Donald Bloss, *An Introduction to the Methods of Optical Crystallography* (Saunders College Publishing, 1961).
[20] B. Huff, J. J. Krich, and P. J. Collings, Phys. Rev. E **61**, 5372 (2000).