Nematic-isotropic phase transition of binary liquid crystal mixtures

Deng-Ke Yang[a]; Y. Yin[a]; H. Liu[a]

[a] Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent, USA

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DENG-KE YANG*, Y. YIN and H. LIU

Chemical Physics Interdisciplinary Program and Liquid Crystal Institute, Kent State University, Kent,
OH 44242, USA

We experimentally studied the nematic–isotropic phase transition of (a) binary mixtures consisting of nematic and racemic liquid crystals and (b) binary mixtures consisting of positive and negative dielectric liquid crystals. We observed that the phase transition temperature is very sensitive to the chemical structures of the constituent components. We also used Maier–Saupe theory to calculate the transition temperature of binary mixtures. By fitting the experimental data, we obtained the interaction coupling constant between the constituent components.

1. Introduction

Multiple component liquid crystal (LC) mixtures are widely used in LC devices because of their enlarged LC phase regions [1–4]. One of the major applications of LCs is in flat panel displays which usually utilize nematic LCs. In this application, the nematic phase must exist in a wide temperature region. A nematic liquid crystal (NLC) transforms from the crystalline phase (or smectic phase) into the nematic phase at a melting point, and then transforms from the nematic phase to the isotropic phase at a clearing point. Low melting point temperature and high clearing point temperature are desired. The melting point temperature can be decreased by using a eutectic mixture [1, 5–7]. At the eutectic concentration, the melting point of the mixture is lower than those of the components because of the incompatibility of the crystalline structures of the components [4, 8]. The clearing point temperature of a mixture is, however, usually lower than the arithmetic mean of the clearing point temperatures of the components [4, 9, 10]. Hsu and Johnson studied nematic binary mixtures constructed from homologous series [9, 10]. Humphries and Luckhust used Maier–Saupe theory to study the nematic–isotropic (N–I) transition of the binary mixtures [4, 11]. The N–I transition of mixtures consisting of components with different molecular structures is more complicated and interesting [4, 12–14].

In this paper we report a study of the N–I phase transition of three binary systems. The first system was simple and consisted of two NLCs. The interaction between the two nematic molecules was found to be strong and the clearing temperature is slightly below the molar fraction-weighted arithmetic mean of the clearing temperatures of the components. The second system was a mixture of a NLC and a racemic LC, because chiral NLCs are usually constructed from nematic hosts and chiral dopants. The interaction between the nematic and chiral molecules is weak and the clearing point temperature of the mixture was decreased. The third system was a mixture of positive and negative dielectric NLCs, because mixing positive and negative dielectric LCs is a method to adjust dielectric anisotropy. The interaction between the positive and negative dielectric nematic molecules was weaker and the clearing point temperature was significantly decreased. We used Maier–Saupe theory to study the N–I transition and obtained good agreement with the experimental results.

2. Theory

We use the Maier–Saupe theory to study the N–I phase transition of binary mixtures [15]. We consider a binary mixture consisting of components A and B. The molar fraction of the B component is x. The single molecular potential for orientation for an A molecule is [11, 12, 16]

$$V_A = [-(1-x)u_{aa}S_A - xu_{ab}S_B](1/2)(3\cos^2\theta_A - 1) \quad (1)$$

and the single molecular potential for orientation for a B molecule is

$$V_B = [-(1-x)u_{ab}S_A - xu_{bb}S_B](1/2)(3\cos^2\theta_B - 1) \quad (2)$$

where u_{aa} is the interaction constant for an A molecule when surrounded by A molecules, u_{bb} is the interaction constant for a B molecule when surrounded by B

*Corresponding author. Email: dyang@lci.kent.edu

molecules, and u_{ab} is the interaction constant for an A molecule when surrounded by B molecules (or for a B molecule when surrounded by A molecules). θ_A is the angle between the molecular long axis of the A molecule and the liquid crystal director (the average direction of the molecular long axis). θ_B is the angle between the molecular long axis of the B molecule and the liquid crystal director. The orientational order parameter of A molecule is

$$S_A = \langle \frac{1}{2}(3\cos^2\theta_A - 1) \rangle =$$
$$\frac{1}{Z_A} \int_0^\pi \frac{1}{2}(3\cos^2\theta_A - 1)\exp(-V_A/k_B T)\sin\theta_A \, d\theta_A \quad (3)$$

and the orientational order parameter of a B molecule is

$$S_B = \langle \frac{1}{2}(3\cos^2\theta_B - 1) \rangle =$$
$$\frac{1}{Z_B} \int_0^\pi \frac{1}{2}(3\cos^2\theta_B - 1)\exp(-V_B/k_B T)\sin\theta_B \, d\theta_B \quad (4)$$

where $Z_A = \int_0^\pi \exp(-V_A/k_B T)\sin\theta_A \, d\theta_A$ is the partition function of A and $Z_B = \int_0^\pi \exp(-V_B/k_B T)\sin\theta_B \, d\theta_B$ is the partition function of B. The free energy per molecule associated with the orientational order of the system is

$$f = (1-x)\left(-k_B T \ln Z_A + \frac{1}{2}\langle V_A \rangle\right)$$
$$+ x\left(-k_B T \ln Z_B + \frac{1}{2}\langle V_B \rangle\right). \quad (5)$$

When the system is in the isotropic phase, there is no orientational order and the free energy associated with the nematic ordering is 0. In considering the phase behaviour of systems consisting of multiple components, phase separation may be of importance. Phase separation is determined by the molar fraction dependence of the mixing free energy, which is contributed by mixing entropy and mixing interaction energy. The contribution of the mixing entropy to the mixing free energy is always negative and favours mixing. The contribution of the mixing interaction energy may be positive and then favours phase separation. In the equilibrium state of a system involving more than one phase, the chemical potentials of each component in the phases is the same. In a nematic mixture, the mixing interaction energy depends on the intermolecular position and orientation. Because of partial phase separation, there is a two phase region between the nematic phase and isotropic phase [12].

In the determination of the phase diagram, at each temperature, the free energies (including both the position- and orientation-dependent parts) of the nematic and isotropic states are calculated as a function of the molar fraction. If the free energy–molar fraction curve of the nematic state is higher than that of the isotropic state at any molar fraction, the isotropic state is stable. If the free energy–molar fraction curve of the nematic state is lower than that of the isotropic state at any molar fraction, the nematic state is stable. If the two free energy–molar fraction curves cross each other, the nematic and isotropic states coexist. The molar fractions of the components in the two states can be determined by the molar fractions of two tangential points of a common tangential line to the two free energy–molar fraction curves [8]. Equivalently the molar fractions can be calculated from the equations obtained by setting equal chemical potentials of the components in the two states [12]. In the systems we experimentally studied, the N–I two phase region is smaller than 0.3 K. This indicates that the two tangential points of the free energy–molar fraction curves are close, and are also close to the crossing point (where the free energy of the nematic state becomes 0). In our calculation, the effect of phase separation is neglected as an approximation [11].

For the system consisting of pure A molecules, the N–I transition temperature T_A is related to the interaction constant u_{AA} by $T_A = 0.22019 u_{aa}/k_B$ [17]. For the system consisting of pure B molecules, the N–I transition temperature T_B is related to the interaction constant u_{BB} by $T_B = 0.22019 u_{bb}/k_B$.

We used the iteration method to solve equations (3) and (4), which gives the order parameters S_A and S_B as a function of temperature. We started with some initial values S_{Ao} and S_{Bo}, and used these values on the right hand side of equations (3) and (4) to calculate new order parameters. When the calculated order parameters became the same as the order parameters used in the calculation, the iteration was stopped. We then calculated the free energy by using equation (5). When the free energy was lower than that of the isotropic phase, the nematic phase was the stable phase. The algorithm was that for a given molar fraction, at each temperature, the order parameters were calculated and then the corresponding free energy, which was a minimum, was calculated. At high temperatures, the free energy of the nematic state with non-zero order parameters was higher than that of the isotropic phase; the isotropic phase with zero order parameter is the stable phase. The free energy of the nematic state decreased with decreasing temperature. At the I–N transition temperature T_C, the free energy of the nematic phase became 0.
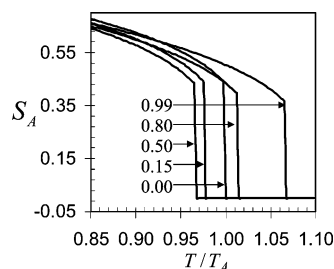
Figure 1. The theoretically calculated order parameter of component A as a function of temperature at various molar fractions of component B. The coupling constant u is 0.9.

When the temperature was decreased below T_C, the free energy of the nematic state was lower than that of the isotropic phase, and therefore the nematic phase became stable.

Figure 1 shows the calculated order parameter of component A as a function of temperature in a binary system where $T_B/T_A=1.068$. The coupling constant u defined by $u=u_{AB}/[(u_{AA}+u_{BB})/2]$ is 0.9. When the molar fraction of B is increased, the N–I transition temperature decreases first because the coupling constant is smaller than 1, and then increases because the N–I transition temperature of B is higher than that of A. The order parameters of A and B in the system with the molar fraction $x=0.15$ are shown in figure 2. The N–I transition of the two components occurs at the same temperature. The order parameter of A is slightly higher than that of B, because of the weak coupling between the two components and the low molar fraction of B.

3. Experiment and results

We experimentally studied binary mixtures of LCs whose chemical structures are shown in figure 3. 5CB, 8CB and MLC6247/6248 were obtained from Merck, ROCM1644 was from Roche Basel; they were used without further purification. Samples were sandwiched between two glass plates with a cell thickness of $10\,\mu m$. An Instec temperature controller with accuracy of
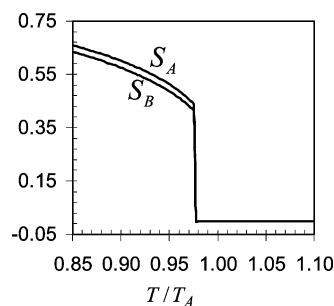

Figure 2. The theoretically calculated order parameters of A and B in the binary system as a function of temperature. The molar fraction of B is 0.15.
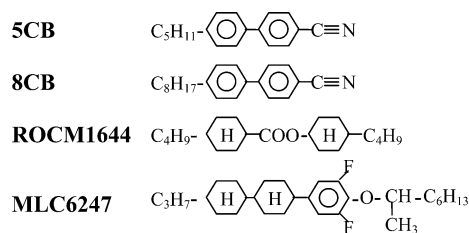

Figure 3. The chemical structures of the liquid crystals studied.

0.01 K was used to control the temperature. The LC samples were placed in the temperature controller and studied under a Nikon polarizing microscope.

Compounds 5CB and 8CB are NLCs with positive dielectric anisotropies around +10; their chemical structures are very similar. Their dielectric anisotropies are +11.0 and +8.5, respectively, and their N–I transition temperatures are 34.05 and 39.3°C, respectively. The transition temperatures of binary mixtures of these two components are shown in figure 4. The solid circles are the experimentally measured transition temperatures; the line is the theoretically calculated transition temperature. By fitting the experimental data, the coupling constant u is found to be 0.994; the fitting is fairly good. It has been reported that when the fraction of 8CB is around 0.31, the order parameters of the components are higher [18, 19]. It was proposed that the interaction between the molecules is stronger at that fraction. If this were true, we would expect the N–I transition temperature of the mixture with that molar fraction to be significantly higher; this was not observed in our experiment. The theoretically calculated transition temperature with one coupling constant agrees well with the experimental data for any fraction of 8CB in the region 0.0 to 1.0.

The next system studied consisted of 5CB and (MLC6247+MLC6248). MLC6247 is a chiral NLC and MLC6248 is the enatiomer of MLC6247. Equal amounts of MLC6247 and MLC6248 form the racemic mixture. The N–I transition temperature of the racemic mixture is 78.5°C. The reason for studying this system is
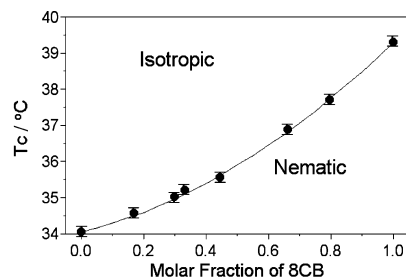

Figure 4. The N–I transition temperatures of binary systems consisting of 5CB and 8CB. See text for explanation.
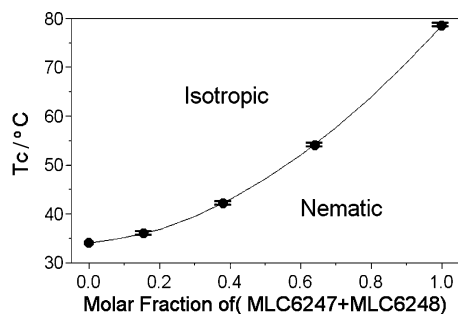
Figure 5. The N–I transition temperatures of binary systems consisting of 5CB and a racemic mixture of MLC6247/MLC6248. See text for explanation.

that chiral nematic (cholesteric) LCs are usually constructed by mixing a nematic host and a chiral dopant. It is important to know the interaction between nematic and chiral molecules. The racemic mixture is then mixed with 5CB. The phase transition temperature of the system as a function of the molar fraction of the racemic mixture is shown in figure 5. The solid circles are the experimentally measured transition temperature; the line is the theoretically calculated transition temperature. By fitting the experimental data, we obtain a coupling constant of $u=0.942$. It is worth noting that we could not fit the data if the weight percentage was used; however, the fitting is good when the molar fraction is used. The coupling constant is smaller than that between 5CB and 8CB.

The last system studied consisted of 5CB and ROCM1644. ROCM1644 is a NLC with a negative dielectric anisotropy of -0.9 and its N–I transition temperature is 46.4°C. The reason for studying this system is that mixing LCs with positive and negative dielectric anisotropies is a common method used to adjust dielectric anisotropy. It is important to know the interaction between positive and negative dielectric LCs. The phase transition temperature of the system as a function of the molar fraction of ROCM1644, as shown in figure 6. The solid circles are the experimentally measured transition temperatures; the line is the theoretically calculated transition temperature. By fitting the experimental transition temperature data, the obtained coupling constant is $u=0.905$. This weak coupling is probably due to the opposing dielectric anisotropies. When a 5CB molecule is parallel to a ROCM1644 molecule, their permanent dipole moments are perpendicular to each other; this orientation is not energetically favoured.

4. Conclusion

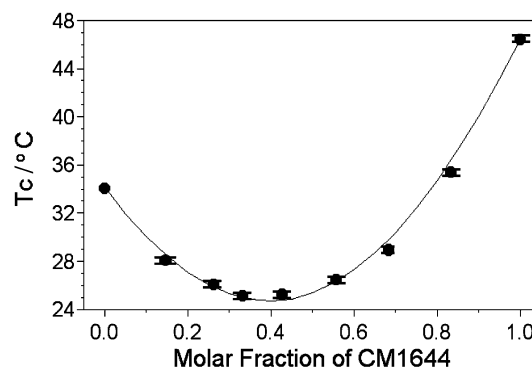We experimentally measured the N–I phase transition temperature as a function of the molar fraction of

Figure 6. The N–I transition temperatures of binary systems consisting of 5CB and ROCM1644. See text for explanation.

binary NLC mixtures. We also used the Maier–Saupe theory to calculate the phase transition temperature of the binary mixtures. Good agreement between the experimentally measured and theoretically calculated phase transition temperatures was achieved by using the interaction coupling constant as the only fitting parameter. The results show that the coupling between nematic and chiral molecules was weaker than that between two nematic molecules, and the coupling between positive and negative dielectric liquid crystal molecules was the weakest.

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