PHYSICAL REVIEW A VOLUME 35, NUMBER 9 MAY 1, 1987

Temperature-concentration phase diagram for the blue phases of a highly chiral liquid crystal

J. D. Miller, P. R. Battle, and P. J. Collings
Department of Physics, Kenyon College, Gambier, Ohio 43022

D. K. Yang and P. P. Crooker
Department of Physics and Astronomy, University of Hawaii, Honolulu, Hawaii 96822

(Received 8 December 1986)

Polarizing microscopy, optical activity, reflection, and transmission measurements are used to determine the phase diagram for the blue phases of chiral 4″-(2-methylbutylphenyl)-4′-(2-methylbutyl)-4-biphenylcarboxylate (CE2) mixed with nonchiral 4-*n*-pentylbenzenethio-4′-*n*-heptyloxybenzoate ($\bar{7}$S5). These mixtures exhibit a chirality higher than previously investigated. The phase diagram shows two new features: (1) blue phase II becomes unstable at high concentrations of the chiral component, and (2) blue phase III possesses a wider temperature range than blue phase I for the most chiral mixtures.

Experimental and theoretical investigation of cholesteric liquid crystals has demonstrated that the transition from a chiral liquid crystal to the isotropic liquid phase is far more interesting than previously expected. For cholesteric liquid crystals of sufficiently short pitch, one or more blue phases exist in a narrow temperature range just below the transition to the isotropic liquid. The number of blue phases and the temperature range of each blue phase are dependent on the chirality of the liquid crystal. This dependence is revealed by temperature-concentration phase diagrams for both chiral-racemic mixtures,[1-3] mixtures of two chiral compounds of opposite handedness,[4] and mixtures of chiral and nonchiral compounds.[5] All these phase diagrams show an interesting similarity in the region where the blue phases become stable: As the chirality is increased, first blue phase I (BP I) appears, then blue phase II (BP II) becomes stable above BP I, and finally blue phase III (BP III) forms above BP I and BP II. Theoretical work has also predicted several phase diagrams, but none of these share this specific topology.[6,7]

Only one of these experimentally determined phase diagrams investigated a region of chirality significantly above the region where BP III appears.[1] In the region of extremely high chirality, the authors concluded that BP I becomes unstable quite abruptly, leaving only BP II and BP III over a wide range of chirality. Also of note is the fact that recent freeze-fracture experiments on another highly chiral liquid crystal seem to indicate that BP II is absent.[8] In this report we describe optical measurements on a mixture of a highly chiral liquid crystal and a nonchiral liquid crystal. The phase diagram for this system is determined completely, clearly showing that BP II disappears at high chirality.

The system consisted of the chiral liquid crystal 4″-(2-methylbutylphenyl)-4′-(2-methylbutyl)-4-biphenylcarboxylate (CE2) and the nonchiral liquid crystal 4-*n*-pentylbenzenethio-4′-*n*-heptyloxybenzoate ($\bar{7}$S5). The CE2 was obtained from BDH Chemicals; the $\bar{7}$S5 was provided by M. E. Neubert of the Liquid Crystal Institute, Kent State University.[9] Both compounds were used without further purification. Phase-transition temperatures were determined using two experimental arrangements. For concentrations of less than 50-wt. % CE2, a microscope with crossed polarizers was employed in order to observe the transitions in a thin sample (72 μm or less). The transitions were directly observable in reflected light for concentrations below 40 wt. %, due to the change in the wavelength of selective reflection at each transition. For concentrations between 40 and 50 wt. %, the selective reflection was too short for visual observation of the BP III-isotropic transition, so the intensity of transmitted light at 430 nm was monitored instead (the polarizers were slightly uncrossed). At the transition from BP III to the isotropic phase, the intensity changed from a decreasing function of temperature to a constant intensity with increasing temperature. For concentrations above 50-wt. % CE2, an experimental arrangement which measured both the optical activity and the transmitted intensity of light as it passed through a thick sample (1 cm) was utilized. For all but the BP III-isotropic liquid transition, the phase-transition temperature was determined by noting where an abrupt change in the optical activity or transmitted intensity occurred. The BP III to isotropic transition for the highly chiral concentrations was not nearly as evident, however, but revealed itself as a change in the temperature dependence of the transmitted light at 400 nm. In the BP III phase the transmitted intensity increased slowly with increasing temperature, whereas in the isotropic phase it increased quite rapidly just above the transition. This rapid increase was due to the large amount of scattering in our thick sample just above the transition.

The temperature control for the microscope experiments was achieved through the use of a Mettler FP5 hot stage; the temperature stability was better than 5 mK. A double oven arrangement supplied the temperature control for the measurements on the thicker samples, with the temperature of the inner oven controlled by an Instec mK1 card installed in an Apple IIe computer. The temperature homogeneity in the thick sample was less than 30

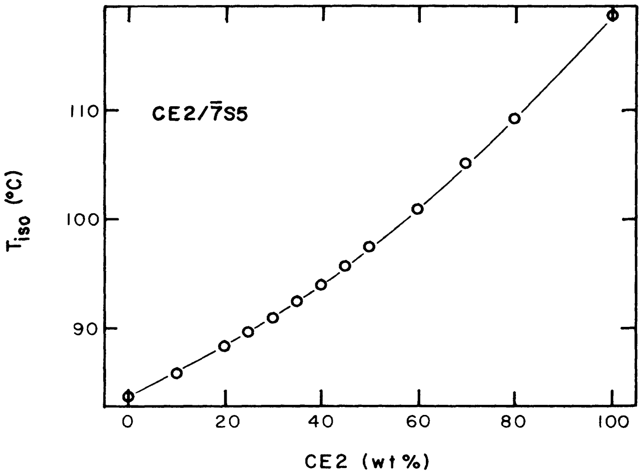

FIG. 1. Isotropic transition temperatures for the CE2/$\bar{7}$S5 system.

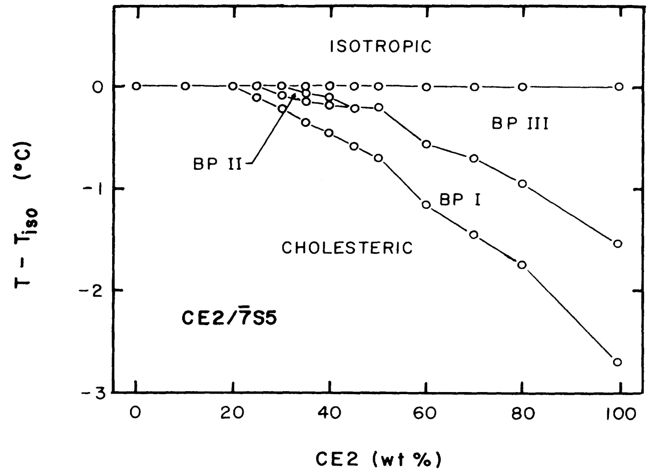

FIG. 2. Blue-phase transition temperatures relative to the isotropic transition temperature for the CE2/$\bar{7}$S5 system.

mK. Except for a constant shift of about 1 K between the data using the two different controllers, due ostensibly to a difference in absolute temperature calibration, the data show excellent consistency.

Figure 1 shows the isotropic temperature of the CE2/$\bar{7}$S5 system as a function of weight concentration of CE2. Figure 2 shows the phase diagram of the blue phases relative to the isotropic temperature. The most significant feature of the data is the disappearance of BP II between the concentrations of 40 and 45 wt. %. In fact, in the 40-wt. % sample the BP II phase was observable only with increasing temperature. With decreasing temperature, a slight supercooling of BP III caused a transition directly to BP I.

The lower-temperature blue phase which remained at concentrations above 45-wt. % CE2 was definitely BP I. The wavelength of the selective reflection of this phase corresponded to the selective reflection of BP I extrapolated from lower concentrations of CE2. This wavelength did not correspond to the selective reflection of BP II extrapolated from lower concentrations of CE2.

Because the wavelength of selective reflection was so short for most of the phase diagram, accurate measurements of it were not possible with our equipment. From extrapolation of measurements for low concentrations of CE2, we estimate the pitch to vary between 200 and 100 nm for the portion of the phase diagram where the blue phases are stable.

One must ask the question whether this unusual phase diagram is unique to this system or of general validity. The freeze-fracture experiments were performed using a chiral compound somewhat similar to CE2, and it seems that this compound also possesses only the BP I and BP III phases.[8] Likewise, additional measurements in one of our laboratories on chiral-racemic mixtures of compounds similar to CE2 also show evidence that BP II disappears at high chirality. The phase diagram in which BP I disappeared at high chirality[1] is now the only different example, so certainly more work with various highly chiral systems is needed at this time.

It should be pointed out that a phase diagram in which one of the blue phases appears and then disappears is not theoretically surprising. All calculations of the free energy for the various structures thought to represent the blue phases show that the free energies are extremely similar.[6,7] Which phase is stable at any one temperature and concentration changes if the theoretical parameters are even varied slightly. Changes in temperature or concentration could in principle change these parameters and cause the type of sequence of phases reported here.

These results are based on work supported by the National Science Foundation under Grant No. DMR-8416045 to Kenyon College and Grant No. DMR-8404519 to the University of Hawaii. This work was also supported in part by the Research Corporation under Grant No. C-1867 to Kenyon College.

---

[1] M. A. Marcus and J. W. Goodby, Mol. Cryst. Liq. Cryst. Lett. **72**, 297 (1982).

[2] K. Tanimoto, P. P. Crooker, and G. D. Koch, Phys. Rev. A **32**, 1893 (1985).

[3] P. J. Collings, Phys. Rev. A **33**, 2153 (1986).

[4] Th. Blumel, P. J. Collings, H. Onusseit, and H. Stegemeyer, Chem. Phys. Lett. **116**, 529 (1985).

[5] Th. Blumel and H. Stegemeyer, Phys. Lett. **104A**, 277 (1984).

[6] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **28**, 1114 (1983).

[7] H. Grebel, R. M. Hornreich, and S. Shtrikman, Phys. Rev. A **30**, 3264 (1984).

[8] J. A. N. Zasadzinski, S. Meiboom, M. J. Sammon, and D. W. Berreman, Phys. Rev. Lett. **57**, 364 (1986).

[9] See M. E. Neubert, R. E. Cline, M. J. Zawaski, P. J. Wildman, and A. Ekachai, Mol. Cryst. Liq. Cryst. **76**, 43 (1981).