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POSSIBLE NON-EXISTENCE OF "BLUE PHASE IIB"

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ABSTRACT

Certain cholesterogenic mixtures have been claimed to exhibit three "blue" phases (BP), two of which are connected by a second-order transition. This effect has been seen only in mixtures. It is shown that there are two-phase regions over large temperature ranges, and that compositional segregation can cause the appearance of a second-order phase transition where in fact none exists.

The phase diagram of CB15-E9 mixtures is presented, along with evidence of chemical segregation. The boundary of the "BPIIb" region coincides with that of a two-phase region. It is predicted that pure systems or mixtures not showing broad two-phase regions will not show "BPIIb".

I. STATEMENT OF PROBLEM

For a long time it has been known that the "blue" phase (BP) occurs in two crystalline forms[1], called BPI and BPII in order of their temperatures of appearance when both are seen in the same sample. Recently Johnson, Flack and Crooker[2] (JFC) and Rao, Her, and Ho[3] (RHH) have claimed that certain mixtures of the chiral biphenyl CB15 with biphenyl nematic mixtures display three crystal forms, which Flack and Crooker call BPI, BPIIa, and BPIIb (this notation is used in this paper). There are first-order phase transitions between BPI and BPIIa, and between BPIIa and BPIIb, but a second-order transition between BPI and BPIIb. The existence of this second-order transition was used by Hornreich and Shtrikman[4] to place limits on the possible structures for BPI and BPIIb.

It is my claim that the purported second-order phase transitions are actually artifacts of the use of mixtures, and that "BPIIb" is actually BPI+isotropic.

II. MIXTURE EFFECTS

The second-order phase transition has never been observed in pure compounds. The mixture on which the most work has been done, CB15-E9, has at least four components (the other mixture has five) and shows two-phase regions extending over as much as a degree in temperature. It is well-known that when two phases of a mixture are in equilibrium, the compositions of the individual phases will differ. This composition shift is a function of temperature. Thus, on entering a two-phase region from one in which only one phase exists, the composition of the phase originally present will deviate from that of the whole sample. The curve of composition vs. temperature will be continuous, with a change in slope at the boundary of the two-phase region. Such a change in slope may be reflected in a change in the slope of the wavelength vs. temperature curve, thus mimicking a second-order transition. The rest of this paper will be devoted to an analysis of the CB15-E9 phase diagram and the effects of phase separation on the wavelength vs. temperature curves.

It will be shown below that the transition temperatures for CB15-E9 increase monotonically as a function of the E9 content. Thus, as one enters a two-phase region from below (lower temperatures), the phase in equilibrium in the one-phase region will become richer in E9 than the sample as a whole, causing a temperature-dependent increase in the reflection wavelength. This upturn is superimposed on the normal decrease in wavelength with temperature observed in most BP's.

III. VERIFICATION

The samples were made of CB15 and E9, both from BDH. A "master" mixture of 49.97% (all percentages are by weight) E9 in CB15 was made in large enough quantity so that the composition error induced by weighing error was <.1%. Then, a measured amount of E9 was added to a portion of the master mixture to form a "sub-master" mixture with 55.11% E9. All other samples were made from the master and sub-master mixtures. This procedure allowed the making of small quantities of a given mixture with no sacrifice in composition accuracy. The master and sub-master mixtures were stirred in the isotropic and cholesteric states and were kept isotropic in an oven for a day to reduce composition gradients. The other mixtures were stirred in the isotropic phase.

Each sample was made by placing a drop of the appropriate mixture between a clean, untreated glass slide and a clean coverslip. It was found that the use of alignment agents made it difficult to detect the boundaries of the two-phase regions, since layers of the BP would form at the surfaces, making it impossible to see if there were any isotropic liquid in the bulk. The sample was placed in a Mettler FP5/52 hotstage, and examined in transmission and reflection with a polarizing microscope. The sample was kept isotropic for an hour to remove any composition gradients. All phase boundaries were determined using a temperature scan rate of .01°/5min. This slow rate was necessary, for faster rates produced results differing from those obtained with the slow scan. Even at the slow rate, the temperature of a phase boundary on heating could be .1° higher than that seen on cooling. That hysteresis is observed even with a slow scan rate implies that equilibration can be very slow and that one must be careful in interpreting spectroscopic results obtained at faster rates, since such results may not be representative of a sample in equilibrium. The (BP+isotropic)-isotropic phase boundary was found using a slow scan in both directions. The temperature in equilibrium is taken to be the average of the up- and down-scan temperatures. The temperature was then dropped by .5° in a short time in order to produce a large number of small platelets, thus restricting the length scale over which diffusion would have to occur in order to produce chemical equilibrium. Without such precautions, each platelet would have a nematic-depleted zone around it which would take hours to dissipate. Such an effect is shown in Fig. 1.

The large platelet was grown at a slow rate, after which the temperature was quickly decreased to encourage the formation of small platelets, which grew everywhere except near the large one. Clearly, the large platelet depleted its surroundings of E9, thus depressing the local transition temperature in its vicinity, and discouraging the growth of new platelets in the area. The (BP+iso)-BP and BP-BP phase boundaries were found by the same procedure as was used for the (BP+iso)-iso line.

BPII was identified either as the phase which transformed discontinuously to another BP on cooling, or as the phase in which it was possible to grow square platelets reflecting at their longest Bragg wavelength[5]. BPI was identified as the one to which another BP transformed on cooling, the only BP present in mixtures with a cholesteric Bragg wavelength greater than 540nm, or as the one which showed square platelets not displaying their longest Bragg wavelength. The various alternate identification methods were always consistent with each other when comparison was possible. The phase I identify as BPII appeared in the same parts of the phase diagram as JFC's BPIIa. The reflection wavelength for BPII in the (BPII+iso) region agreed with that of JFC's BPIIa. Likewise, there is agreement between the wavelengths for BPI (mine and JFC's), and between (BPI+iso) and BPIIb.

The phase diagram for the region of interest is shown in Fig. 2.

The existence of the peritectic shown in dotted lines is conclusively inferred from the other features actually measured. The reflection wavelengths actually did show breaks at the boundaries of two-phase regions, just as predicted. In particular, the spectral signature of the BPI-BPIIb transition occurred at the

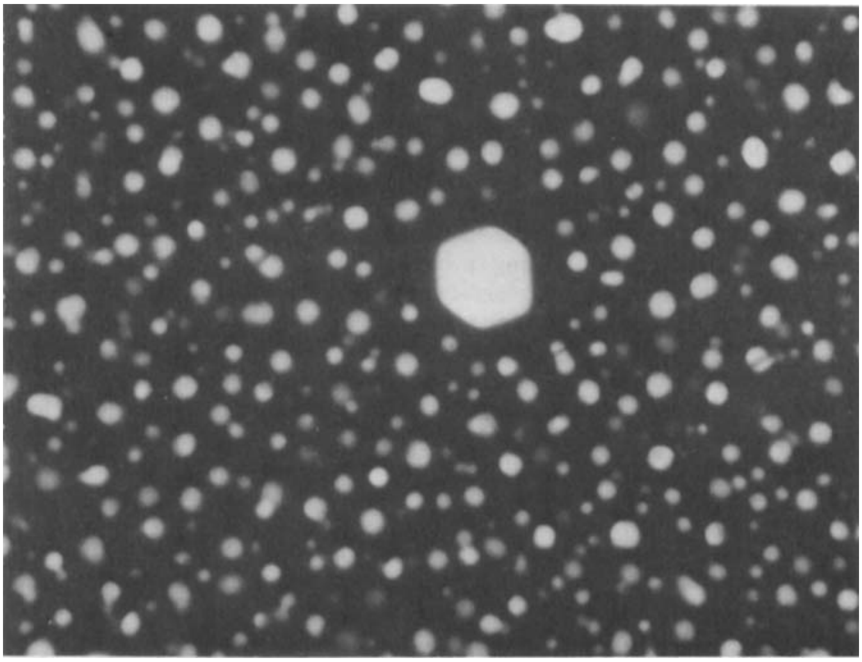


Fig. 1. Composition drift effect in (BPII+iso) region in 52.57% E9 in CB15 at 38.19°. Note clear zone around large platelet.

same temperature as the transition between BPI and (BPI+iso). Note that the BPII-only region is very narrow. In most samples it was so narrow that it could easily escape notice in a wide-range temperature scan. Thus, the wide regions labeled BPIIa in JFC's data and λ_{II} in RHH are actually (BPII+iso).

We shall see below that wide two-phase regions make for a large composition-drift effect, causing a flattening of the wavelength-temperature curves.

An interesting consequence of the slowness of chemical diffusion is that the BPII-only region can disappear if the scan is too rapid. Starting with a sample containing BPII and a small amount of isotropic, I could lower the temperature and watch BPII turn into BPI, while the isotropic regions remained intact. After ten minutes at the new temperature, the BPI would transform back to BPII and the isotropic regions shrink. The II→I transition on cooling would start at the insides of platelets, and work its way out, sometimes stopping short

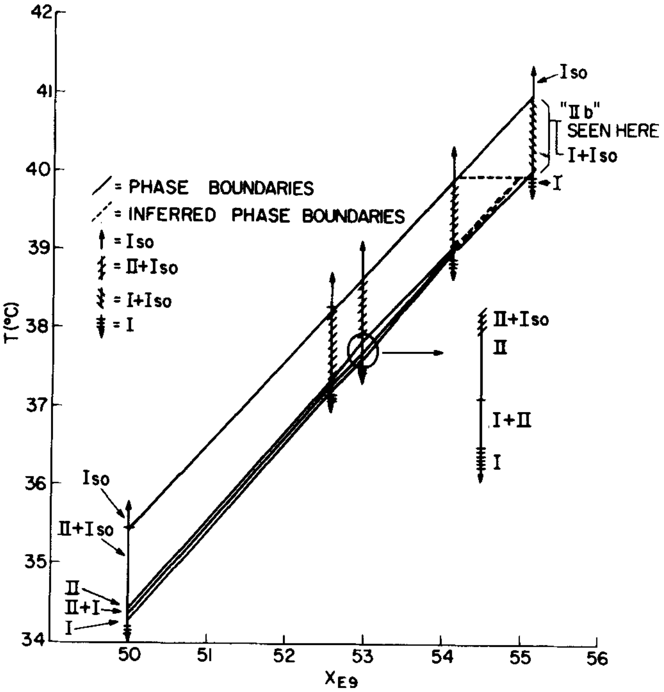


Fig. 2. Temperature-composition phase diagram for E9 in CB15.

of

the isotropic regions bounding the platelet. This behavior can be interpreted in terms of composition shifts within the platelet. In equilibrium in the (BPII+iso) region, the platelet is richer in nematogen than the sample as a whole. On slow cooling, the platelet loses nematogen to the isotropic liquid, and its composition follows the (BPII+iso)-BPII line on Fig. 2. However, if one cools quickly, the nematogen does not have time to diffuse out of the platelet. Since the platelet is now more nematogen-rich than it would be in equilibrium, its BPII-I transition temperature is higher than the equilibrium value. This effect is analagous to a shift towards the right in Fig. 2. Thus, the platelet may transform into BPI. If at this point the temperature is held constant, nematogen will diffuse out of the platelet, lowering its transition temperature, thus forcing a return to BPII if the final temperature is within the BPII-containing region. This "premature" BPII-I transition shows up first in the centers of platelets because diffusion takes longer from the center than the edge. Also, if the platelet was grown quickly, it will be more nematogen-rich in its center (grown at higher temperature) than its edge - an effect analagous to "coring" in metallurgy. These effects clearly show the role of chemical diffusion in allowing equilibration.

Consider a sample whose nematic content is large enough for there to be no BPII. As one enters the two-phase region, the sample splits into isotropic and BPI components. If one plots the composition of the BPI vs. the temperature, the points must lie on the (BPI+iso)-BPI boundary. Therefore, the temperature derivative of the "BPIIb" wavelength must be equal to the total temperature derivative of the wavelength on the (BPI+iso)-BPI line. If this line is defined by $x=X(T)$, and the sample's nematogen fraction is x_s, then:

$$\frac{d\lambda_{IIb}(x_s,T)}{dT}=\frac{d\lambda_I(X(T),T)}{dT} \tag{1}$$

This formula gives results which are consistent with the data for the experiments of JFC and RHH.

IV. PREDICTIONS

Given the phase diagram explained above (Fig. 2), some predictions can be made about the wavelength-temperature curves that would be observed under true equilibrium conditions[6]. If the nematic fraction is smaller than 54.15% (vertical line at far left of Fig. 2) then the phase sequence is

I-(I+II)-II-(II+iso) (low temperature on the left)

and the wavelength-temperature curve should look like Fig. 3a. In data taken with a fast scan, the "BPIIb" could persist to higher temperatures than shown, and the small BPII-only region could vanish, thus reproducing the RHH result for 45% E9. (RHH's fractions don't agree with mine, possibly because they use volume fractions whereas weight percentages are used here). There are two composition regions surrounding the peritectic (~54.95%), one just to its left in which the phase sequence is

I-(I+II)-II-(II+iso)-(I+iso)

and another just to its right whose sequence is

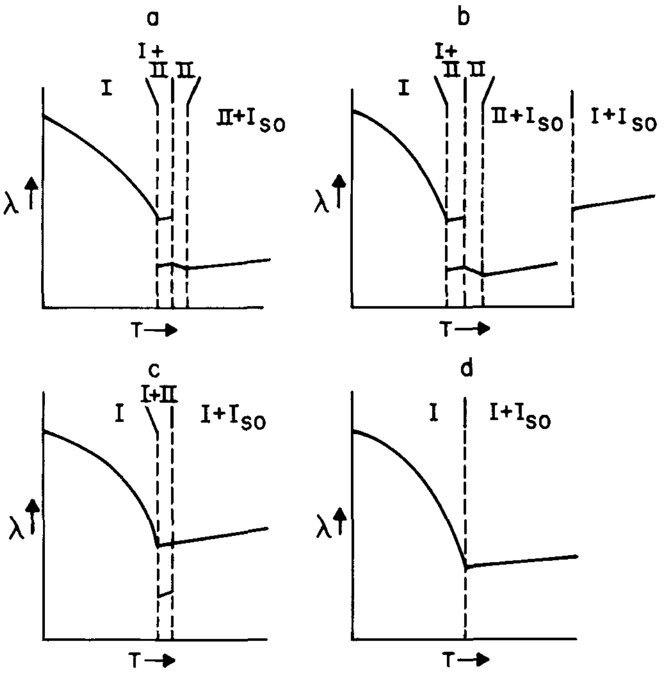
I-(I+II)-(I+iso).

The curves corresponding to these two regions are shown in Figs. 3b and 3c. The JFC data for $\lambda_c=540$nm might correspond with either of these possibilities. Finally, for large nematic concentrations (>55.05%, vertical line on far right of Fig. 2), the sequence is

I-(I+iso)

and the curve takes on the simple form shown in Fig. 3d.

This behavior is seen by JFC and RHH for nematic-rich compositions. Another prediction is that "BPIIb" will never appear in pure compounds or in



Figs. 3a-d. Qualitative λ-T curves predicted for CB15-E9 system at various compositions.

mixtures showing little phase separation, such as chiral-racemic mixtures in which the transition temperature of the racemate is equal to that of the pure chiral compound. Investigations of a system with these properties have revealed no "BPIIb" phase[7].

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REFERENCES

[1] H. Stegemeyer, K. Bergmann, Ber. Bunsenges Phys. Chem. **82**, 1309 (1978)
[2a] J. H. Flack, P. P. Crooker, Phys. Lett. **82A**, 247 (1981)
[2b] D. L. Johnson, J. H. Flack, P. P. Crooker, Phys. Rev. Lett. **45**, 641 (1981)
[3] B. B. Rao, J. Her, J. T. Ho, to be published in Phys. Rev. A (Rapid Communications)
[4] R. M. Hornreich, S. Shtrikman, Phys. Lett. **82A**, 345 (1981)
[5] M. Marcus, submitted to Phys. Rev. A
[6] The RHH and JFC data show the coexistence of BPIIa and BPIIb over wider temperature ranges than appear in the phase diagram (Fig. 2). This behavior may be due to non-equilibrium effects, which would also cause the non-observation of the BPII-only region. Such a region would show up as a bend in the λ-T curve over a temperature range of up to .15°.
[7] M. Marcus, J. Goodby, submitted to Mol. Cryst. Liq. Cryst. Lett.