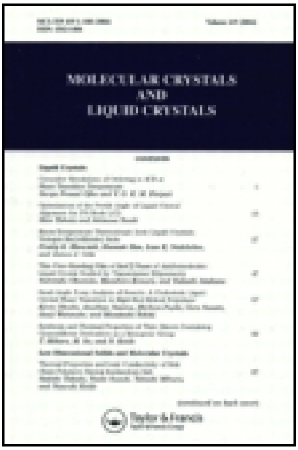

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Phase Diagrams of Binary Liquid Crystal Mixtures

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A series of four binary mixtures of smectic liquid crystalline compounds was prepared and their thermodynamic properties measured by differential thermal calorimetry. Calculations using ideal solution theory were carried out and were compared to the experimental phase diagrams. Plots of ideal ΔH and ΔS values for the mixtures were also prepared and were compared to experiment. It is concluded that large deviations from ideality are caused by a great variety of very subtle electronic and geometric forces present in the mixtures, and that no one of the explanations put forward to date is of itself adequate to describe the observed deviations from ideality.

The use of the van't Hoff equation to predict the transition temperatures of binary mixtures of liquid crystals has been shown to be valid for the solid-to-mesophase transition by several authors.[1-4] Its use has also been extended to the mesophase to isotropic transition.[5] These latter calculations predict the experimental temperatures quite well providing the components of the mixture have similar structures and thus form nearly ideal mixtures in the mesophase. For cases in which the ΔH values for the two components are small and are similar in magnitude, there is for all practical purposes a linear relationship between the transition temperatures of the two pure components, and the two-phase region is so small that the transition appears almost as sharp as if it were that of a pure single component.

There are, however, many other situations where these ideal calculations are not valid and one must use regular solution theory in order to calculate the experimental temperatures. Van Hecke has carried out such calculations for mixtures displaying both minimum and maximum deviations from ideality.[6]

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His equations allow the estimation of the regular solution parameters providing one knows the transition temperatures, the enthalpy changes in the pure components and the temperature of the minimum or maximum in the system. He has noted a relationship between the molar volume of the components and these parameters for the minimum forming systems. Other workers have noted irregularities from ideality and have attributed the deviations to specific molecular interactions in the mesophase. Dave, studying binary systems in which one of the components was not mesomorphic attributed specific group interactions in the molecules as the cause of the observed temperature enhancement.[7] A similar reasoning was used by Schroeder and Schroeder for a series of nitro-substituted anils.[8] Labes has suggested the formation of charge transfer complexes as the cause of mesomorphic enhancement,[9,10] while Griffin has cited cases of temperature enhancement in which one of the components is reported to form a bimolecular smectic layer ($d > 1$), while the other does not.[11] Incompatibility of the smectic phases due to this structure difference has been suggested as the reason for deviation from ideality.[12,13]

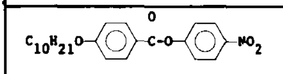
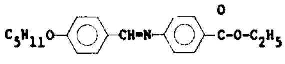
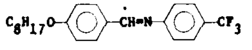
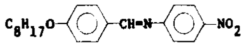
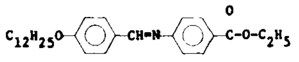
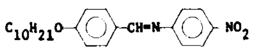
We have now experimentally tested some of these suggestions, particularly the last, by preparing and measuring the transition temperatures and enthalpy changes in binary mixtures in which the components have been shown by x-ray analysis to form either monomolecular or bimolecular layers. The phase diagrams of these mixtures were then calculated using ideal solution theory, and these ideal calculations were compared to the experimentally observed values. The results are discussed in terms of the structure of the smectic layers of the individual components as well as the energy requirements necessary to produce significant temperature variations.

EXPERIMENTAL

Six pure liquid crystals synthesized *via* standard techniques and all having confirmatory spectral data were prepared[14] and were used in the preparation of the binary mixtures. The structures and the pertinent thermal data for the compounds are given in Table I. The enthalpy values were obtained by differential scanning calorimetry using the Dupont 990 DSC/DTA, and the mesophases were classified by polarized light microscopy and x-ray analysis. Table II lists x-ray data for these materials taken using a W. H. Warhus low-angle camera consisting of a vacuum chamber and flat film cassette. Nickel filtered copper Kα radiation impinged on the sample held in a 0.7 mm glass capillary. The mixtures were prepared by weighing the individual components into test tubes, heating the mixture until it was completely isotropic, maintaining this temperature until complete mixing (glass rod) was assured and then allowing crystallization to occur. Four sets of binary mixtures were

TABLE I

Thermal data for pure compounds

Structure		MW	Transition Temperatures (°K)	ΔH (cal/mole)	ΔS (e.u.)
	(A)	399.5	$C \xrightarrow{334.4} S_A$	10107	30.20
			$S_A \xrightarrow{352.4} I$	559	1.58
	(B)	339.4	$C \xrightarrow{348.0} S_A$	7399	21.20
			$S_A \xrightarrow{(337.8)} S_B$	695	2.06
			$S_A \xrightarrow{369.6} I$	1395	3.77
	(C)	377.4	$C_1 \xrightarrow{310.1} C_2$*	603*	1.94*
			$C_2 \xrightarrow{332.1} S_B$	5019	15.10
			$S_B \xrightarrow{355.4} I$	2415	6.80
	(D)	354.4	$C \xrightarrow{365.2} I$	10702	29.30
			$I \xrightarrow{(358.9)} N$	145	00.40
			$N \xrightarrow{(356.5)} S_A$	198	00.55
			$S_A \xrightarrow{(345.4)} C$	9923	28.70
	(E)	437.6	$C \xrightarrow{344.5} S_A$	10502	30.5
			$S_A \xrightarrow{372.0} I$	1606	4.3
	(F)	382.5	$C \xrightarrow{336.3} S_A$	9830	29.20
			$S_A \xrightarrow{368.3} I$	600	1.63

*This transition only appears after sample has been previously heated to the mesophase, and not on the first heating of a recrystallized sample.

prepared in this manner. The compositions of these mixtures is shown in Table III. The ideal solution calculations were made utilizing previously described programs,[5] with the temperatures and ΔH values as measured for the pure components.

DISCUSSION AND RESULTS

The experimentally determined phase diagrams along with the ideal calculations are shown in Figure 1 for the binary mixtures studied.

TABLE II

X-ray data for pure compounds

Compound	Temperature (°K)	Phase	Distances (from diffraction rings), (Å)	Molecular Length, ℓ (space filling models), (Å)
A	335.2	S_A	d_1 = 31.4[18]; 32[19] D = 5.4[1]	28.2; 27.4[18]
B	358.2	S_A	d_1 = 23.5 d_2 = 11.7 D = 5.2	26.1
C	344.2	S_B	d_1 = 26.1 d_2 = 13.0 D = 5.1	25.7
D	357.7	N	'd' = 29.0 'D' = 5.3	26.1
E	358.2	S_A	d_1 = 32.7 D = 5.2	35.1
F	349.2	S_A	d_1 = 35.4 D = 5.1	28.7

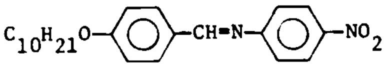
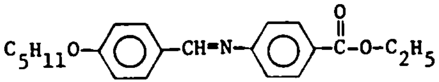
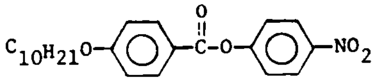
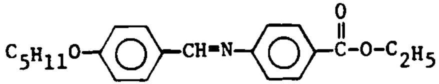
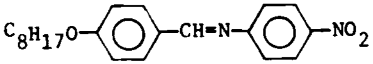
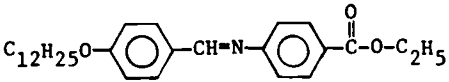
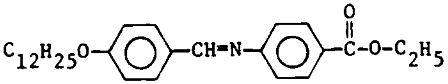
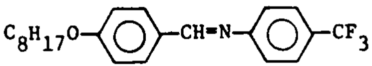
d_1 = smectic layer spacing (first order ring)

d_2 = smectic layer spacing (second order ring)

D = intermolecular spacing within layer; calculated from $2D \sin\Theta = 1.17\lambda$

TABLE III

Structure of components in the binary mixtures

1	 (F)	 (B)
2	 (A)	 (B)
3	 (D)	 (E)
4	 (E)	 (C)

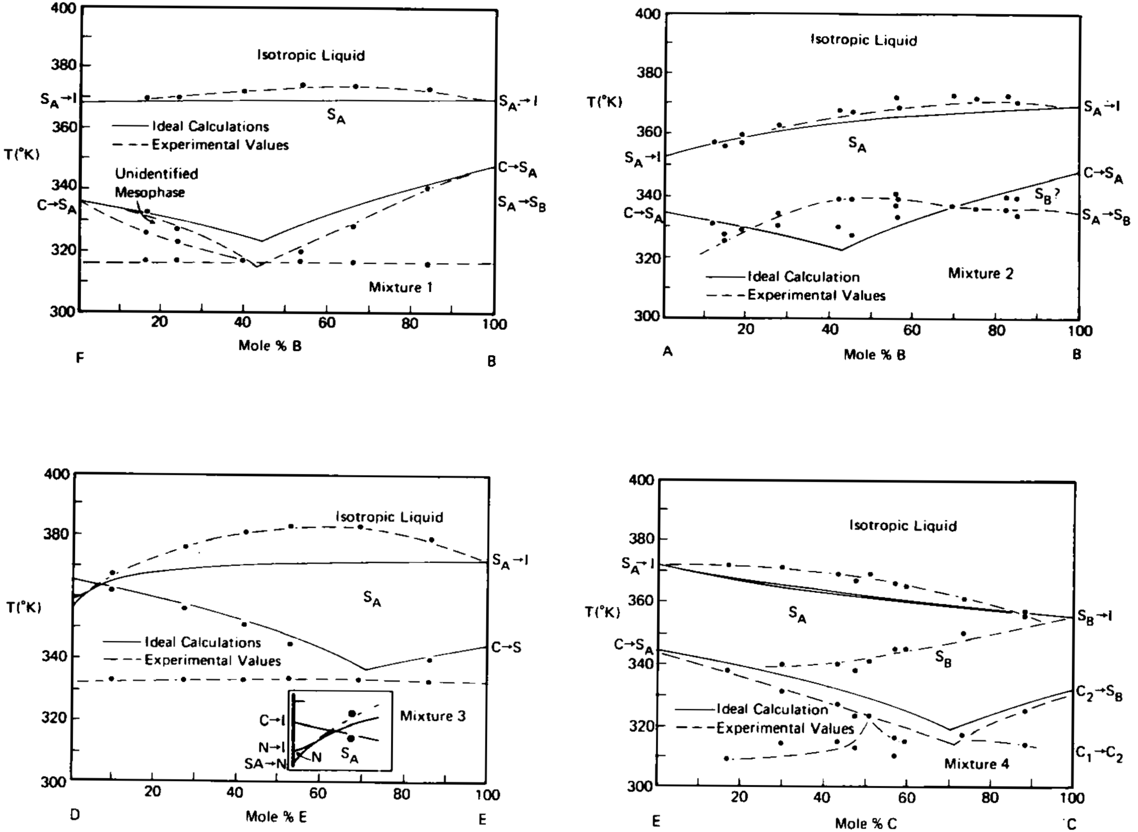


FIGURE 1 Calculated and experimental phase diagrams for the four mixtures. 1) F and B, 2) A and B, 3) D and E, 4) E and C.

Compound B is a common component in mixtures 1 and 2. It is mixed, in one case with compound A and in the other with compound F. Both of these latter components, as seen from Table II form bimolecular layers, while B forms the more usual monomolecular smectic layer. Figure 1 indicates that in both these instances the experimental values are only slightly enhanced compared to the ideal calculations. The small magnitude of the enhancement may be in large part due to the disparity in alkoxy chain lengths (5 vs. 10 carbons) of the components in these mixtures.[15] Also shown is the phase diagram obtained from the mixture of the Schiff's base ester E and the nitro Schiff's base D. In this case the calculations were made using the $S_A \rightarrow N$ enthalpy and temperature for compound D and the $S_A \rightarrow I$ values for compound E. The Schiff base ester forms monomolecular layers and while the nitro Schiff's base would be expected to be bimolecular by analogy with F, the x-ray analysis was carried out while it was nematic and thus no direct knowledge of the type of layer it would form in the smectic was available. Table II lists values for the diffuse inner ring 'd' and the very diffuse outer ring 'D' for this material. The system nevertheless was enhanced by as much as 10° from the ideal. In the case of mixture 4 both components form monomolecular smectic layers, and a deviation of at least 5° from ideality was observed.

Diagrams were also constructed in which the composition was plotted as a function of ΔH and ΔS of the mixtures (Figure 2). The ΔH values for each mixture were calculated as weighted molar averages based on the values determined for the pure components and the composition of the mixture. Also plotted on the same diagrams are the enthalpy and entropy changes that would be expected if the solutions were ideal, i.e., if the interactions between unlike molecules were exactly the same as the average interactions between like molecules. ΔH and ΔS values of end members were connected by linear extrapolation. Use was made of Walter's Law of Mixtures as the basis for our extrapolations.[16] The enhancement observed in the temperature composition curves indicates that in each of these mixtures there is some degree of 'excess' interaction between the components. For mixture 4 the situation is not so straightforward since extrapolation is not reasonable here, one component having only an S_A phase and the other component only an S_B phase. The amount of the enhancement in any of these systems bears no direct relationship to the fact that some of the mixtures are made up of components of different molecular layering and some of the same kind of smectic layering. In fact, the smallest deviation from ideality are for cases in which it has been established that the components have different types of smectic layers. Again, caution must be taken in interpretation of this lack of significant enhancement due to disparity in alkoxy chain lengths. It is clear then that although mixing of unimolecular and bimolecular smectic components may be one of the causes for temperature enhancement, it is certainly not the only one and in fact

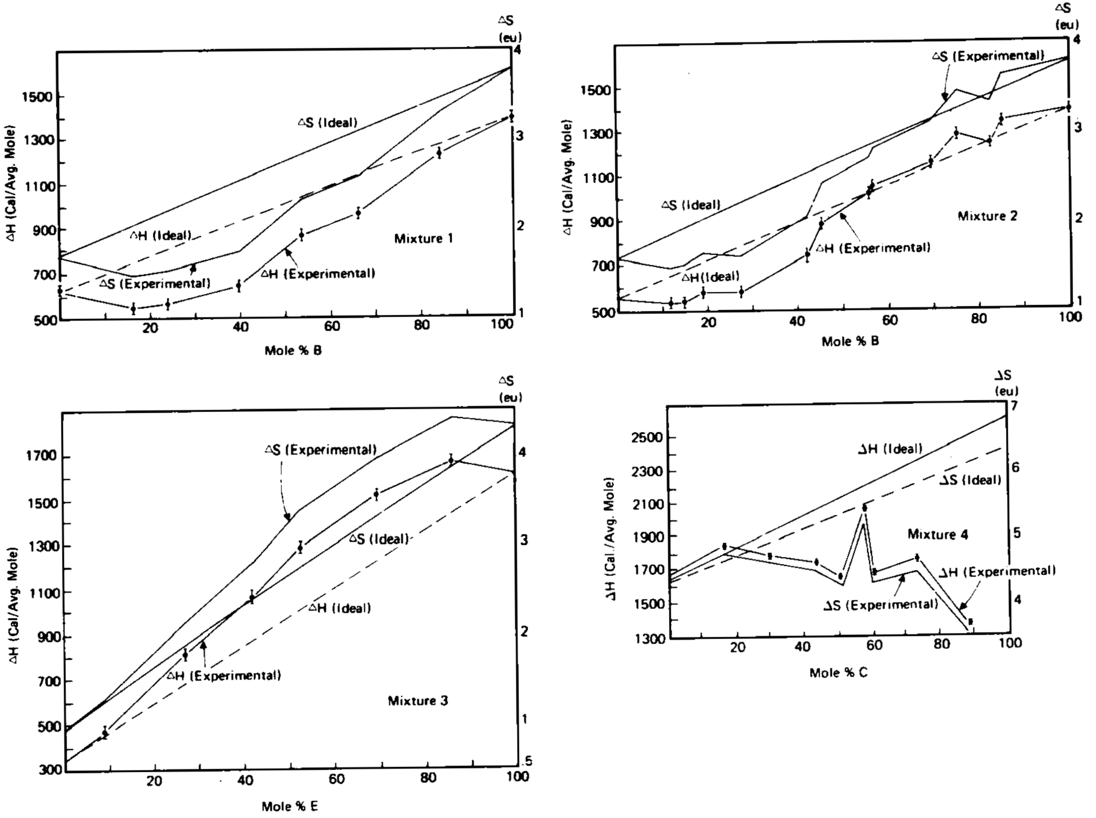


FIGURE 2 Experimental and ideal values for ΔS and ΔH as a function of composition. 1) F and B, 2) A and B, 3) D and E, 4) E and C.

it may be one of the less important. Perusal of the components used in this set of experiments does not reveal any obvious electronic interaction, other than the polar/nonpolar character of the component molecules[12] which can explain the observed results, and one can only conclude that indeed very subtle molecular interactions are required to produce large deviations from ideality in these systems. Billard has previously noted that the existence of a strong terminal dipole for one component is not always correlated with nonideality in mesophase-isotropic temperatures[17] and Labes[11b] has mentioned the difficulty in finding a single suitable molecular model for this enhancement. This is supported by the ΔH and ΔS plots where it can be seen that relatively small deviations from ideality in the enthalpic terms (<300 cal/mole) can lead to large deviations from ideality in the $S_A \rightarrow I$ temperatures. In mixture 1 (Figure 2) the deviation in ΔH is negative (excess repulsive forces), yet in mixture 3 (Figure 2) the deviation in ΔH is positive (excess attractive forces) and in mixture 2 (Figure 2) both positive *and* negative deviations are found. The net effect on $S_A \rightarrow I$ temperatures in all cases, however, was that it was enhanced (raised above the weighted mean value). With intermolecular interactions as small as 300 cal/mole causing profound changes in phase behavior it is not surprising that a variety of explanations have been put forward (some electronic; some geometric) to explain the enhancement at the molecular level. Many, if not all, of these factors may contribute to enhancement, but since interactions of only 300 cal/mole or so can cause dramatic effects, there may be no one, simple cause; instead there may be a variety of interactions which contribute concurrently to the enhancement, but which are each themselves of very weak strength. It is clear from our data that one cannot necessarily take enhanced $S_A \rightarrow I$ temperatures as an indication of strong intermolecular attraction between dissimilar component molecules. Since $T_{S_A \rightarrow I} = \Delta H/\Delta S$, each factor, ΔH and ΔS, must be considered separately as each can separately cause $T_{S_A \rightarrow I}$ to rise.

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