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Phase Equilibria in Liquid Crystal Mixtures

Abstract: The thermodynamic relationships for mixtures of nonmesomorphic compounds are applied to liquid crystalline materials. Equations developed for ascending solid solutions have been applied to mixtures of liquid crystalline materials. Computer programs, written to calculate the theoretical curves for such mixtures, are found to agree with the experimental data obtained for 4-alkyl and 4-alkoxy 4′-cyanobiphenyls and a series of p,p′-dialkoxyazoxybenzenes. The heats and temperatures of the transitions of the pure components, necessary for the theoretical calculations, were determined by polarized light microscopy and by differential thermal analysis. Polarized light microscopy was also used to determine the transition temperatures of the mixtures.

Introduction

The calculation of solid-to-liquid crystal transition temperatures has been the subject of considerable work based on the Schröder-van Laar equations. However, there has been very little work on the liquid-crystal-to-isotropic transition based on any sound thermodynamic theory. In this paper the thermodynamics developed and presented by Reisman [1] are shown to be applicable to liquid crystals.

In the study of multicomponent systems, the variation of the equilibrium constant with temperature is a very important factor. Consider a mixture of any two compounds A and B in the molten state, which, depending upon their relative starting concentrations, will begin to precipitate either pure A or B on cooling to a particular temperature. At this temperature, the system becomes isobarically univariant, and it is necessary to define only one variable, the temperature, in order to completely define the system. If the component precipitating out of the melt is A, an equilibrium between solid and molten A is established,

$$A^{(S)} \overset{K_{NA}}{\rightleftarrows} A^{(L)}, \tag{1}$$

in which the superscripts S and L designate the solid and liquid phases respectively. A similar equilibrium will be established for the concentration and temperature at which B precipitates out of solution,

$$B^{(S)} \overset{K_{NB}}{\rightleftarrows} B^{(L)}, \tag{2}$$

and the equilibrium constant is related to the mole fraction by

$$K_{NA} = \frac{N_A^{(L)}}{N_A^{(S)}}, \tag{3}$$

and

$$K_{NB} = \frac{N_B^{(L)}}{N_B^{(S)}}. \tag{4}$$

Through the use of standard thermodynamic equations, the relation between the equilibrium constants and the temperatures can be shown to be

$$\ln K_{NA}^0 - \ln K_{NA}^0 = -\frac{\Delta H_A^0}{R}\left(\frac{1}{T} - \frac{1}{T_A^0}\right), \tag{5}$$

where K_{NA}^0 is the equilibrium constant for the process at the melting temperature T_A^0, and ΔH_A^0 is the change in enthalpy for the component A in going from the molten to the solid phase. A similar equation can be written for the component B. Substituting the values of K_{NA} from Eq. (3) in Eq. (5), we obtain

$$\ln \frac{N_A^{(L)}}{N_A^{(S)}} - \ln \frac{N_A^{0(L)}}{N_A^{0(S)}} = -\frac{\Delta H_A^0}{R}\left(\frac{1}{T} - \frac{1}{T_A^0}\right), \tag{6}$$

where $N_A^{0(S)}$ and $N_A^{0(L)}$ are the mole fractions of the component A present at the melting point of pure A and are obviously equal to one. Because the system is such that only pure solid A is in equilibrium with the molten mixture, $N_A^{(S)}$ is also equal to one, and Eq. (6) may be simplified to

$$\ln N_{\mathrm{A}}^{(\mathrm{L})} = -\frac{\Delta H_{\mathrm{A}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}^{0}}\right). \quad (7)$$

A similar consideration of component B gives

$$\ln N_{\mathrm{B}}^{(\mathrm{L})} = -\frac{\Delta H_{\mathrm{B}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right). \quad (8)$$

Equations (7) and (8) are the familiar van't Hoff freezing point equations. They are also known as the Schröder-van Laar equations [2, 3] and have been applied to the study of crystalline-to-liquid-crystalline transitions quite successfully by several authors [4–8]. The temperature-mole fraction relations generated by these equations are called simple eutectic systems, and are valid only if the solids are completely immiscible.

It appears that the transition from the crystalline solid can be calculated with the same reliability regardless of whether the compound is melting to an isotropic liquid or to some mesomorphic state. Examples of the application of these equations to binary mixtures of liquid crystals will be given in this paper.

The transition from a liquid crystalline phase to either another liquid crystal or to an isotropic liquid has been shown to be first order with a change in enthalpy that is readily measured by differential scanning calorimetry [9]. These transitions in binary mixtures should thus be amenable to calculation by means of the above equations. An examination of the experimental data for binary mixtures in cases in which the compounds have identical mesophases reveals that in general the transition temperatures of these mixtures can be adequately represented by a straight, or in some cases, slightly concave line joining the transition temperatures of the two pure components. This observation has been used by Hulme et al. [10] in order to determine empirically the transition temperatures for mixtures of nematic compounds. If an attempt is made to treat these liquid crystal transitions theoretically as if they were of the simple eutectic type, one encounters difficulties immediately. This is due to the fact that in all cases of compounds which exhibit identical mesophases, those mesophases are completely miscible, and one of the assumptions made during the development of the Schröder-van Laar equations was immiscibility of the lower temperature phase. This made $N_{\mathrm{A}}^{(\mathrm{S})}$ in Eq. (6) unity and permitted simplification of Eq. (7). If, on the other hand, the lower temperature phase precipitates as a completely miscible solution, such a simplification is not valid and Eq. (6) must be rewritten as

$$\frac{N_{\mathrm{A}}^{(\mathrm{I})}}{N_{\mathrm{A}}^{(\mathrm{LQ})}} = e^{-A}, \quad (9)$$

where $N_{\mathrm{A}}^{(\mathrm{I})}$ is the mole fraction of A in the isotropic liquid, $N_{\mathrm{A}}^{(\mathrm{LQ})}$ is the mole fraction of A in the liquid crystal, and

$$A = \frac{\Delta H_{\mathrm{A}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}^{0}}\right).$$

Similarly, for the B component

$$\frac{N_{\mathrm{B}}^{(\mathrm{I})}}{N_{\mathrm{B}}^{(\mathrm{LQ})}} = e^{-B}, \quad (10)$$

where

$$B = \frac{\Delta H_{\mathrm{B}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right).$$

The compounds in each phase are also related through the equations

$$N_{\mathrm{A}}^{(\mathrm{LQ})} = 1 - N_{\mathrm{B}}^{(\mathrm{LQ})}, \quad (11)$$

and

$$N_{\mathrm{A}}^{(\mathrm{I})} = 1 - N_{\mathrm{B}}^{(\mathrm{I})}. \quad (12)$$

By appropriate substitution of Eqs. (11) and (12) into Eqs. (9) and (10), the following expressions for the mole fraction as a function of temperature can be developed:

$$N_{\mathrm{A}}^{(\mathrm{I})} = \frac{e^{-A}\,(e^{-B} - 1)}{e^{-B} - e^{-A}}, \quad (13)$$

and

$$N_{\mathrm{B}}^{(\mathrm{I})} = \frac{e^{-B}\,(e^{-A} - 1)}{e^{-A} - e^{-B}}. \quad (14)$$

Expanding the values of A and B, we now obtain

$$N_{\mathrm{A}}^{(\mathrm{I})} = \frac{\exp\left[-\frac{\Delta H_{\mathrm{A}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}^{0}}\right)\right]\exp\left[-\frac{\Delta H_{\mathrm{B}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right) - 1\right]}{\exp\left[-\frac{\Delta H_{\mathrm{B}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right)\right] - \exp\left[-\frac{\Delta H_{\mathrm{A}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}^{0}}\right)\right]}, \quad (15)$$

and

$$N_{\mathrm{B}}^{(\mathrm{I})} = \frac{\exp\left[-\frac{\Delta H_{\mathrm{B}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right)\right]\exp\left[-\frac{\Delta H_{\mathrm{A}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right) - 1\right]}{\exp\left[-\frac{\Delta H_{\mathrm{A}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{A}}^{0}}\right)\right] - \exp\left[-\frac{\Delta H_{\mathrm{B}}^{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{B}}^{0}}\right)\right]}. \quad (16)$$

These values can now be substituted into Eqs. (9) and (10) to obtain values of $N_{\mathrm{A}}^{(\mathrm{LQ})}$ and $N_{\mathrm{B}}^{(\mathrm{LQ})}$ as follows:

$$N_A^{(LQ)} = \frac{\exp\left[-\frac{\Delta H_B^0}{R}\left(\frac{1}{T} - \frac{1}{T_B^0}\right)\right] - 1}{\exp\left[-\frac{\Delta H_B^0}{R}\left(\frac{1}{T} - \frac{1}{T_B^0}\right)\right] - \exp\left[-\frac{\Delta H_A^0}{R}\left(\frac{1}{T} - \frac{1}{T_A^0}\right)\right]}, \tag{17}$$

and

$$N_B^{(LQ)} = \frac{\exp\left[-\frac{\Delta H_A^0}{R}\left(\frac{1}{T} - \frac{1}{T_A^0}\right)\right] - 1}{\exp\left[-\frac{\Delta H_A^0}{R}\left(\frac{1}{T} - \frac{1}{T_A^0}\right)\right] - \exp\left[-\frac{\Delta H_B^0}{R}\left(\frac{1}{T} - \frac{1}{T_B^0}\right)\right]} \tag{18}$$

The crystal-liquidus line $N_A^{(LQ)}$ is not the same function of temperature as the liquidus line $N_A^{(l)}$, and a plot of the mole fraction vs temperature will show different values for $N_A^{(LQ)}$ and $N_A^{(LQ)}$. For typical organic compounds in which the transition is from a solid solution to an isotropic liquid, the heats of fusion are in the range of 10 000 cal/mol (41.86×10^3J/mol) and the melting temperatures are in the 300-400 K range. Such a plot [shown in Fig. 1 for two hypothetical compounds A and B, with values of $\Delta H_A^0 = 8000$ cal/mol (33.47×10^3 J/mol), $\Delta H_B = 10\,000$ cal/mol (41.86×10^3 J/mol), $T_A^0 = 350$ K, and $T_B^0 = 375$ K] verifies that the solidus and liquidus lines form a spindle. In this case, if one were to start with an equimolar mixture of these two compounds at 377.5 K, designated by point X in Fig. 1, and then cool the mixture to point Y (367 K), a solid would begin to precipitate. A mixture of solid and liquid would be obtained on further cooling until point Z (360 K), at which point a solid solution would exist. Thus a mixture of liquid and solid would coexist over a 7° temperature range in this example.

If this were to be compared to the analogous liquid crystal-isotropic liquid system, it would mean there would be a temperature range over which the liquid crystal and the isotropic liquid would exist together. The result would be a diffuse transition extending over a temperature range. This is typically not seen in liquid crystals, the transitions of the mixtures being as sharp as those of the pure components. If, however, values for transitions typically encountered in liquid crystal transitions are substituted in Eqs. (15)–(18), the mole fractions obtained are such that differences between the liquidus-crystal and the liquidus line are indistinguishable. This is illustrated in Table 1 for the case of compounds A and B with values of $\Delta H_A^0 = 200$ cal/mol (0.836×10^3 J/mol), $\Delta H_B^0 = 250$ cal/mol (1.04×10^3 J/mol), $T_A^0 = 350$ K, and $T_B^0 = 375$ K. Thus one should expect the observed sharp transition for liquid crystal mixtures. A transition line joining the two pure components in this illustration would essentially be linear, corresponding to most experimental observations.

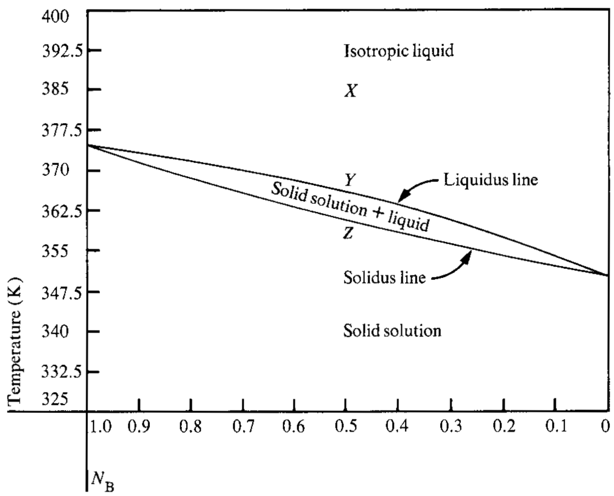


Figure 1 Typical solid solution melting curves for binary mixtures of organic compounds.

Table 1 Mole fractions of liquidus and liquidus-crystal lines in binary mixtures.

	$\Delta H_A^0 = 200$ cal/mol, $T_A^0 = 350$ K	$\Delta H_B^0 = 250$ cal/mol, $T_B^0 = 375$ K
T (K)	$N_A^{(l)}$	$N_A^{(LQ)}$
350	1.00	1.00
355	0.825	0.821
360	0.639	0.634
365	0.441	0.435
370	0.228	0.224
375	0.0	0.0

There are instances in the literature [8] in which the line is not straight but exhibits a slight concavity or convexity. Such deviations from linearity will appear in the theoretical calculations if there is a significant difference between the ΔH^0 values of the two pure components. A concave curve would be obtained for melting of the compounds A and B at the same temperatures but with values for $\Delta H_A^0 = 200$ cal/mol (0.836×10^3 J/mol), and $\Delta H_B^0 = 400$ cal/mol (1.673×10^3 J/mol). A convex curve would be obtained if the ΔH^0 values for the two compounds were interchanged.

For the most part, the temperatures of the liquid crystal transitions obtained in binary mixtures are quite close to those predicted by these equations. As we will see, however, there are some cases in which it is impossible to apply these directly, such as the case in which one of the end components has both a smectic and a nematic phase while the other has only a smectic phase. The experimen-

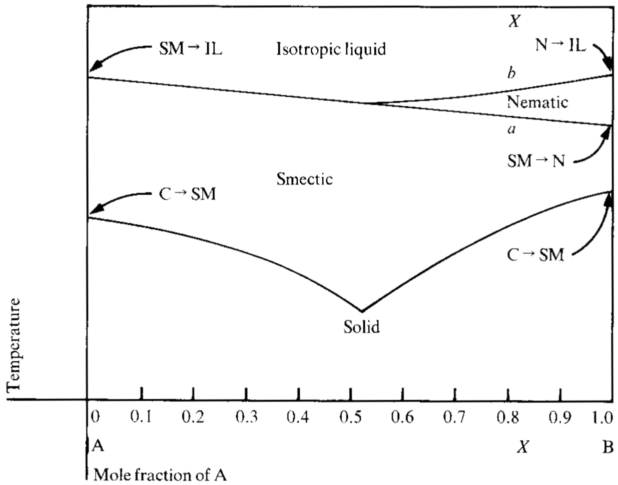


Figure 2 Typical phase diagram for dissimilar liquid crystals B (smectic + nematic)/A (smectic).

tal phase diagram is found to be similar to that shown in Fig. 2. In a particular mixture, represented by point X in Fig. 2, calculation of the nematic to isotropic transition cannot be carried out in the straightforward manner that is possible when both components have identical mesophases, for two reasons. First, compound A has no nematic to isotropic transition and so no values for $\Delta H^0_{A(N\rightarrow I)}$ or $T^0_{A(N\rightarrow I)}$ exist. Secondly, because compound A does not form a nematic mesophase, one does not know if the molecules of A have become nematic through the temperature range *a* to *b*. If they have become nematic, the enthalpy change from nematic to isotropic would have one value. If, however, the molecules are isotropic, the enthalpy change will have some other value. There is at present no way of carrying out this calculation. It should be noted here that if the molecules of A were not nematic through this temperature range, the phases would probably be immiscible and the equations used for the solid solution case would not be valid.

A second example for which the calculation cannot be carried out is that in which component A has a nematic phase while component B has both a smectic and a nematic phase. The smectic to nematic line cannot be calculated because compound A has no values for $\Delta H^0_{A(S\rightarrow N)}$ or $T^0_{A(S\rightarrow N)}$ to enter into the equations. As in the previous example, it is not clear whether A actually becomes smectic in the optically smectic temperature range. One should be able to calculate the nematic to isotropic transition in this case, since both components have this transition.

A third type of system which cannot as yet be handled is the case in which one component has only a smectic and the other only a nematic mesophase. Obviously here also, because the pure components do not have corresponding transitions, substitution in the necessary equations is impossible.

Experimental

• *Compounds*

The 4-alkyl-4′-cyanobiphenyls were prepared by following the method outlined by Gray [11], with 4-bromobiphenyl as a starting material. This was treated with the appropriate acid chloride in the presence of aluminum chloride. Reduction of the resultant p-substituted carbonyl compound gave 4-alkyl-4′-bromobiphenyl. Reaction of this bromo compound with cuprous cyanide resulted in the desired 4-alkyl-4′-cyanobiphenyl.

The 4-alkoxy-4′-cyanobiphenyls were also prepared by Gray's procedure [11]. The starting material for this synthesis was 4-nitro-4′-bromobiphenyl. This was reduced to the amino compound, diazotized and the diazonium salt converted to the corresponding hydroxy compound. The appropriate alkyl iodide gave the ether on reaction with 4-bromo- 4′-hydroxybiphenyl, and the bromine was subsequently replaced with a cyano group by reaction with cuprous cyanide.

Each of the compounds prepared by the above methods was either recrystallized or chromatographed until the transition temperatures corresponded to published values [12, 13]. To ensure purity, each was also subjected to combustion analysis and thin layer chromatography. The structure of each was also confirmed by 100 MHz NMR spectroscopy. The calorimetric data used in the calculations for each of these compounds were also those given in these references [12, 13].

• *Mixtures*

The mixtures used in this study were prepared by weighing each of the pure components to four places on an analytical balance into small glass vials. Each mixture was heated until it became isotropic and then was allowed to crystallize. This was repeated three times to ensure a homogeneous mixture.

• *Microscopy*

The transition temperatures and the type of mesophase present in each mixture were determined by polarized light microscopy using a Zeiss RA38 microscope equipped with a Mettler FP52 heating/cooling stage and an FP5 temperature controller. Each mixture, mounted on a microscope slide, was covered with a glass cover slip and examined microscopically from −20°C (253 K) until the complete extinction of the field indicated the presence of an isotropic liquid. In those cases in which the solid phase appeared to have more than one crystal form, crystallization was induced by three different methods: 1)

Table 2 Thermal data on a series of p-n-alkyl-p′-cyanobiphenyls compared to literature [11] results,

Compound	*Transition**	*Temperature* (°C)** *This work*	*Literature*	*Heat* (cal/mol)** *This work*	*Literature*	*Entropy* (cal/mol · K)	*Purity* (wt %)	(mol %)
p-n-pentyl-p′-cyanobiphenyl	Solid→Nematic	22.65	22.5	3754	4100	12.69	99.8	99.8
	Nematic→I.L.	34.73	35	99.72	—	0.324		
p-n-hexyl-p′-cyanobiphenyl	Solid→Nematic	14.25	13.5	4184	5800	14.55	95.0	94.8
	Nematic→I.L.	26.90	27	89.6	—	0.298		
p-n-heptyl-p′-cyanobiphenyl	Solid→Nematic	29.32	28.5	6427	6200	21.24	99.0	98.9
	Nematic→I.L.	42.05	42	219.8	—	0.697		
p-n-octyl-p′-cyanobiphenyl	Solid→Smectic A	19.48	21	6302	5300	21.52	99.9	99.9
	Smectic A→Nematic	32.60	32.5	72.9	—	0.238		
	Nematic→I.L.	39.54	40	294.4	—	0.941		
p-n-nonyl-p′-cyanobiphenyl	Solid I→Smectic A	40.91	40.5	8416	—	26.78	99.9	98.9
	Smectic A→Nematic	46.77	44.5	152.0	—	0.477		
	Nematic→I.L.	48.86	47.5	403.0	—	1.250		
	Solid II→Smectic A	29.10	—	6794	8000	22.47		
p-n-decyl-p′-cyanobiphenyl	Solid→Smectic A	41.26	—	7997	—	25.42	98.4	98.5
	Smectic A→I.L.	49.32	—	670.9	—	2.08		
p-n-undecyl-p′-cyanobiphenyl	Solid→Smectic A	50.92	—	10440	—	32.23	99.9+	99.9+
	Smectic A→I.L.	55.35	—	907.1	—	2.767		

*I.L.—Isotropic Liquid.
**Precisions are: temperature ±0.08°C, heat ±1.5%. On the basis of standard heat of fusion the fourth significant figure is justified.

recrystallization from a solvent; 2) slow cooling from the isotropic liquid (2°/min); 3) fast cooling from the isotropic liquid. These techniques allowed observation of the several polymorphs present in these cases. The liquid crystal transitions were confirmed by at least two observations of the temperature in a cooling mode and two in a heating mode. The rate of heating or cooling in each case was 2°/min.

- *Theoretical calculations*

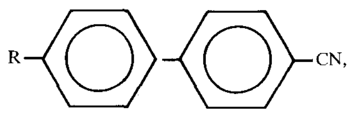
The theoretical curves were generated on a Tektronix 4013 terminal using an IBM 360/185 computer. The solid to mesophase transitions of the simple eutectic type were computed with a slightly modified version of an existing program [14]. The solid solution type systems were calculated by means of a program written for this research.

Results

Two broad classes of liquid crystalline compounds were used as mixtures for this work. The first were the 4-alkyl and 4-alkoxy-4′-cyanobiphenyls, and the second were p,p′-alkoxyazoxybenzenes. The synthesis of the cyanobiphenyls has been reported by Gray [11], and those syntheses plus several not reported previously were carried out in this laboratory. The calorimetry has also been reported by Gray; however, this work was recently repeated and extended to include the heats of the liquid crystal transitions [12, 13]. The values obtained from this latter work were used in the calculations. Mixtures of these compounds were prepared and the temperatures of the various transitions were measured microscopically, as described in the previous section.

The p,p′-dialkoxyazoxybenzenes were not prepared in this laboratory, and the values for the transition temperatures of the mixtures were taken from the literature [8], as were the values for the heats of the transitions [15]. Some of these values have also been determined by others, e.g., [16], and even though discrepancies were found, the differences were not large enough to affect these calculations substantially.

Table 2, taken from [12], gives the thermodynamic values used for the 4-alkyl-4′-cyanobiphenyls, and Table 3 from [13] gives those for the 4-alkoxy-4′-cyanobiphenyls. A series of ten mixtures of these two were prepared and the transition temperatures measured. The structure of 4-alkyl-4′-cyanobiphenyls is



and that of the 4-alkoxy-4′-cyanobiphenyls is

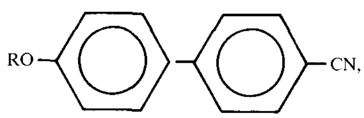


Table 3 Thermodynamic data on a series of p-n-alkoxy-p′-cyanobiphenyls.

Compound	*Transition*	*Temperature* (°C) *This work*	*Literature* [11]	*Heat* (cal/mol) *This work*	*Literature* [11]	*Entropy* (cal/mol · K)	*Purity* (wt%)	(mol%)
p-n-pentoxy-p′-cyanobiphenyl	Solid→Nematic	46.02	[48]*, 53	62.39	6900	19.54	99.17	98.68
	Nematic→Isotropic L.	66.61	67.5	71.7	—	0.211		
p-n-hexoxy-p′-cyanobiphenyl	Solid I→Nematic	55.57	58	7258	7100	22.07	99.96	99.96
	Solid II→Nematic	42.30	44	6976	—	22.10		
	Nematic→Isotropic L.	73.71	76.5	192	—	0.553		
p-n-heptoxy-p′-cyanobiphenyl	Solid I→Solid II	48.22	47.5	1631	—	5.08	99.99+	99.99+
	Solid II→Nematic	51.98	53.5	7510	6900	23.08		
	Nematic→Isotropic L.	72.48	75	144	—	0.416		
p-n-octoxy-p′-cyanobiphenyl	Solid→Smectic	53.00	54.5	7288	5900	22.30	99.94	99.92
	Smectic→Nematic	65.58	67	18.7	—	0.055		
	Nematic→Isotropic L.	79.03	80	235	—	0.668		
p-n-nonoxy-p′-cyanobiphenyl	Solid I→Solid II	53.32	—	1228	—	3.76	99.99+	99.99+
	Solid II→Smectic	61.29	—	9101	—	27.20		
	Smectic→Nematic	76.41	—	170	—	0.491		
	Nematic→Isotropic L.	78.45	—	292	—	0.831		

[ ]*—a low melting phase recorded by Gray et al., but not seen in this work.

Table 4 Binary mixtures prepared and studied.

Mixture no.	*Mixture*	*Mixture no.*	*Mixture*	*Mixture no.*	*Mixture*
1	C_8/C_7	5	C_8/C_{11}	9	C_{08}/C_{07}
2	C_8/C_6	6	C_{10}/C_{11}	10	C_{08}/C_{06}
3	C_8/C_5	7	C_7/C_9		
4	C_8/C_{10}	8	C_5/C_7		

Table 5 Calculated values for mole fractions of liquidus and liquidus-crystal curves: C_7/C_8 cyanobiphenyl mixture.

Temp (K)	*Mole fraction* (liquidus)	*Mole fraction* (liquidus-crystal)
312.5	1.00	1.00
313.0	0.772	0.771
313.5	0.548	0.547
314.0	0.350	0.349
314.5	0.173	0.173
315.1	0.0	0.0

where R stands for a straight chain hydrocarbon group in each case, and we use the shorthand C_x or C_{0x} for the alkyl and alkoxy derivatives respectively, where x represents the number of carbon atoms in the chain.

Table 4 lists the binary mixtures prepared and studied. Mixtures 1, 2, 3, 7, 9, and 10 are all systems in which one of the members of the binary mixture has both a smectic and a nematic mesophase while the other member has only a nematic. In the case of mixtures 1, 2, and 3, it is the C_8 that has two mesophases and the C_7, C_6 and C_5 each of which is only nematic.

Figure 3 is the binary phase diagram of the C_7/C_8 system showing both the theoretically calculated curves and the experimental points. The nematic to isotropic line was calculated by using the two values of $\triangle H^0$ determined for the N→I transition of each compound and shown in Table 2. Table 5 gives representative values calculated for $N^{(I)}$ and $N^{(LQ)}$ in this system. It is seen that these values are so close that they are experimentally indistinguishable and the observed sharp transition is that which one would expect. The experimental points in this case lie very close to the calculated line. The curve depicting the temperature at which the mixtures become completely liquid crystalline was calculated by considering the system as a simple eutectic, using the Schröder-van Laar equations. It can be seen that there is no correspondence between this theoretical curve and the experimental points that are observed. There is also no evidence of a constant eutectic temperature for all the range of mixtures. This is not too surprising a result when the similarity in size, shape and chemical constitution of the two molecules is considered. One should quite readily fit into the crystal lattice of the other and the formation of some degree of solid solution would be expected. This result has been noticed previously by Demus et al. [8] for adjacent compounds in a homologous series. The transition line for the smectic to nematic transition shows only the experimentally observed temperatures, there being no way to reliably extrapolate such a line until it cuts the C_7 axis in order to obtain a virtual smectic to nematic transition, and indeed there is no evidence that such a transition exists.

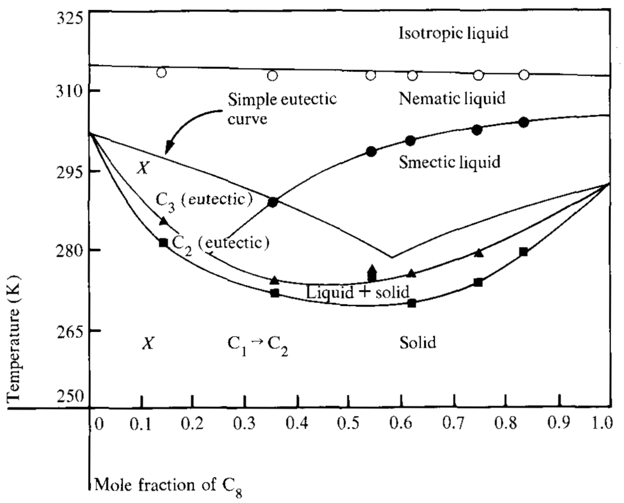


Figure 3 Binary phase diagram for C_7/C_8 mixture of cyanobiphenyls.

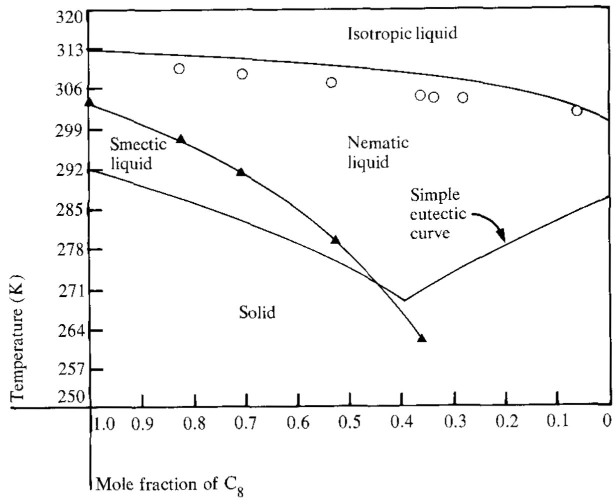


Figure 4 Binary phase diagram for C_8/C_6 mixture of cyanobiphenyls.

The phase diagram for mixture 2, the C_8C_6, is shown in Fig. 4. In this case none of the mixtures could be induced to crystallize due to severe supercooling and consequently no experimental verification of the calculated values for the transition to the liquid crystal could be obtained. The curve shown for this transition is that calculated by assuming a simple eutectic-type mixture. The calculated values for the nematic to isotropic transition in this case deviate considerably from the experimental values, and the curve has a definite convex shape while the experimental values are either a straight line or have a slightly concave curve. From a theoretical standpoint, the shape of the curves is readily understood because there is a large difference in transition heat between the C_8 and the C_6. It is possible that the difference in transition heats of the C_7 and C_8 compounds when compared with the C_6 arises from a difference in their crystal structures, which manifests itself in their nematic phases so that these pairs do not, in fact, form completely miscible mixtures. It is known that the C_8 smectic structure is unusual in that intercollated double layers are formed in which the paraffinic tails are intermeshed. The diagram for mixture 3, the C_8/C_5 combination, is the same as for mixture 2.

Once again, as in the C_7/C_8 mixture, there is no way in which to calculate the smectic to nematic transition, and the lines shown are the experimental values. An interesting observation when comparing this transition for the above three mixtures is that the slope of the transition line increases as the difference in molecular length of the two components of each mixture increases. No theoretical explanation is offered for this observation.

Mixture 7, the C_7/C_9, is of the same type as the above examples; that is, the C_9 has both a smectic and a nematic phase while the C_7 has only a nematic. The experimental values for the nematic to isotropic transition in this case are closer to the calculated value than in the two previous examples, and the relationship is much more nearly linear.

Lack of materials prevented the preparation of more than three mixtures in this series and thus, although solid to mesophase temperatures were obtained which seemed quite close to the theoretical simple eutectic curve, more examples would be required to confirm this.

Mixtures 9 and 10, the C_{08} in combination with C_{07} and with C_{06}, are once again of the type in which one component, the C_{08}, has a smectic and a nematic mesophase while the other has only a nematic. The nematic to isotropic line for both these mixtures adheres quite well to the theoretical calculations. The solid to mesophase transition in the C_{08}/C_{07} mixture, as would be expected for adjacent members of a series, shows considerable evidence of solid solution formation. The C_{08}/C_{06} system, on the other hand, appears to follow the theoretical curve as calculated for a simple eutectic system. Once again, as in the alkyl substituted series, the smectic to nematic line has a steeper slope in the C_{06}/C_{08} series than in the C_{07}/C_{08}.

The system C_8/C_{10} in Fig. 5 is one in which one component, the C_8, has both a smectic and a nematic phase while the other, the C_{10}, has only a smectic. In this case the crystal to mesophase transition follows the values calculated as a simple eutectic mixture quite well, indicating very little formation of solid solution. In the case of the transition to isotropic liquid, however, the situation becomes more complex. Here the transition for some of the mixtures, up to about 30 mole percent of C_8, is from the smectic. The remainder, as the mole percent of C_8 is increased, is from the nematic, and it is not clear in this

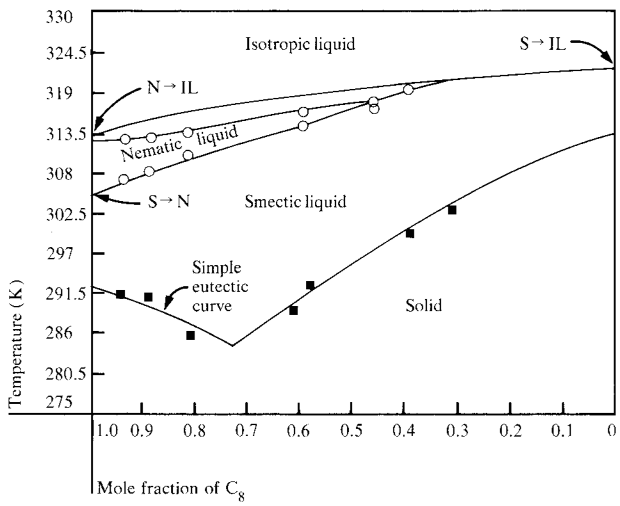


Figure 5 Binary phase diagram for C_8/C_{10} mixture of cyanobiphenyls.

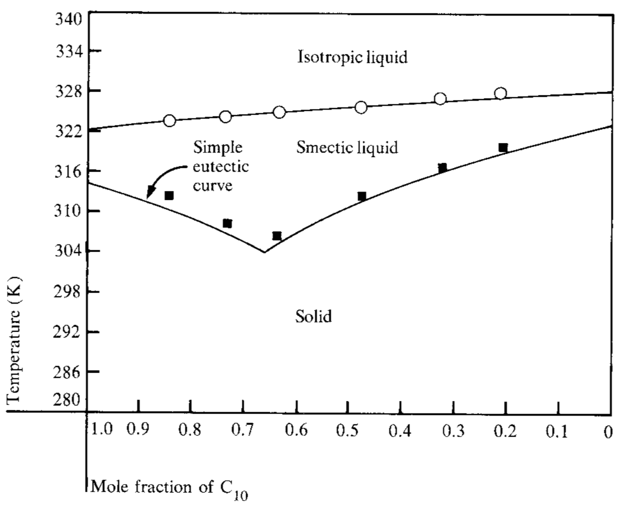


Figure 6 Binary phase diagram for C_{10}/C_{11} mixture of cyanobiphenyls.

case which value for ΔH^0 should be used in theoretical calculations, or if in fact there is justification for use of any of the values obtained from the pure components. The figure uses the heat of transition for the smectic to isotropic liquid for the C_{10} and for the nematic to isotropic liquid for the C_8, and the fit to the experimental values is rather poor.

The same situation remains for the C_8/C_{11} system; that is, one of the components has both smectic and nematic while the other has only smectic, and once again the liquid crystal to isotropic liquid experimental points do not agree with a calculated value.

The mixture C_{10}/C_{11} is one in which each component has only a smectic phase, and the calculated phase diagram, as shown in Fig. 6, agrees very well with the experimental points both for the smectic to isotropic liquid and for the solid to smectic phase. The former was calculated as a solid solution type of system in which the molecules of the one component are completely interchangeable with the other in the smectic phase. The latter was calculated by assuming a simple eutectic system. The good agreement with experiment in this case is surprising when the similarity of the two molecules is considered.

The final type of system considered for mixtures of the cyanobiphenyl type of liquid crystal is the C_7/C_5 mixture, in which both components contain only a nematic mesophase. The nematic to isotropic liquid curve agrees fairly well with the experimental points, and although a theoretical solid to nematic curve could be calculated, no experimental points were available to test the validity of this curve because severe supercooling allowed none of the mixtures to solidify.

The p,p′-alkoxyazoxybenzenes used in this work are all examples of mixtures in which the only liquid crystal transition is from the nematic to the isotropic liquid. The application of the Schröder-van Laar equations to the solid to mesophase transition have been exhaustively analyzed in the paper by Demus et al. [8] and will not be discussed here. The nematic to isotropic transition which was not treated by Demus in any theoretical manner will on the other hand be analyzed by using the solid solution theory approach.

Table 6 gives the thermal data used for the calculation of the theoretical curves for these compounds. The experimental points were taken from the paper by Demus. In order to designate the components of the mixtures, the same shorthand method will be used as for the cyanobiphenyls, i.e., C_x where x represents the number of carbon atoms in the alkyl chains. The calculated and experimental values for mixture C_1/C_2 are shown in Fig. 7. The discrepancy between the calculated and the experimental values in this case cannot be explained as being simply due to a difference in ΔH^0 values of the two components. It is probably due instead to the unique characteristics known to be associated with the first member of a homologous series, since the same discrepancies are obtained when the C_1/C_3 and C_1/C_4 mixtures are examined. Other members of the series show remarkably good coincidence of calculated and experimental points. Figure 7 also shows the C_3/C_4 and C_4/C_5 mixtures. In each of these last two cases it is obvious that the solid solution treatment describes the nematic to isotropic transition very well, and that the molecules form completely miscible nematic mixtures in which the molecules of each component can interchange directly into each other's lattice.

Conclusions

1. The Schröder-van Laar equations adequately describe a great many of the solid to mesophase transformations in liquid crystal mixtures. Exceptions are usually due either to polymorphism in the solid or to the formation of some degree of solid solution [4–8].
2. The mesophase to isotropic transitions in liquid crystal mixtures can be well described theoretically by assuming a complete miscibility of the liquid crystal phases. This applies only to cases in which the components of the mixtures have identical mesophases. In other cases in which one component does not have the corresponding phase present in the other component, there does not seem to be an adequate theoretical description.
3. The small enthalpy changes found in liquid crystal transitions cause the spindle structure normally formed by the solid solution treatment of mixtures of organic compounds to be so narrow as to appear as a single line. Thus the transitions in liquid crystal mixtures are always sharp. This work has settled the ongoing controversy concerning the existence of a spindle in the binary phase diagrams of liquid crystals.

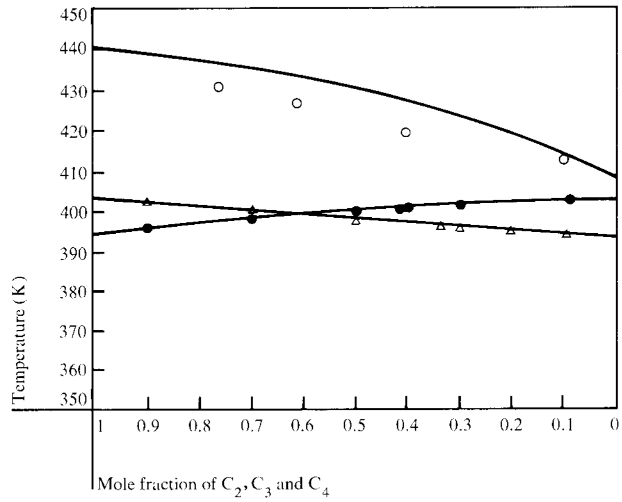
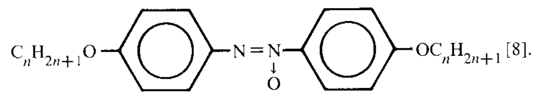


Figure 7 Binary phase diagrams for C_1/C_2 (○), C_3/C_4 (●), and C_4/C_5 (△) mixtures of dialkoxyazoxybenzenes.

Table 6 Thermal data on a series of p-p′-dialkoxyazoxybenzenes with the structure



n	$T_{(C\rightarrow N)}$ (K)	$\Delta H_{(C\rightarrow N)}$ (cal/mol)	$T_{(N\rightarrow I)}$ (K)	$\Delta H_{(N\rightarrow I)}$ (cal/mol) [16]
1	391.2	7067.0	408.3	137
2	409.6	6421.9	440.5	327
3	388.5	6429.1	396.6	161
4	375.0	5004.6	409.7	247
5	348.5	3487.0	396.2	173
6	354.3	9892.2	402.1	250

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