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Optical microscopy, DSC and X-ray diffraction studies in binary mixtures of 4-pentyloxy-4'-cyanobiphenyl with three 4,4'-di(alkoxy)azoxybenzenes

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A large number of binary mixtures of 4-pentyloxy-4'-cyanobiphenyl (5OCB) and 4,4'-di(alkoxy)azoxybenzenes (*n*OAB) with *n*=5, 6 and 7 have been studied by optical microscopy, DSC and X-ray diffraction methods. Over a wide concentration range the smectic A (SmA) phase is induced and the nematic (N) phase of the parent compounds is absent. Instead of the tilted smectic C phase of 7OAB an orthogonal SmA phase is observed when only 12% of the host molecules are replaced by 5OCB molecules. Moreover, in some mixtures the thermal stability of the induced SmA phase is found to be more than 1.6 times the stability of the mesophases in the pure compounds. The N–isotropic or Sm–I transition temperatures slowly increases with increasing concentrations, reaching a maximum at $x_{5OCB}=0.50$ and then falling quite rapidly. In all the mixtures the enthalpy changes at the N–I transitions follow the simple additivity rule. In no mixture, except mixture C2, could the SmA–N transition be detected by DSC, although in all the mixtures the ratio T_{NA}/T_{NI} is found to be more than 0.95, which is in contradiction to McMillan's theory. Average intermolecular distances are found to have a minimum value near the equimolar concentration. From the concentration dependence of the smectic layer spacings it also appears that in all the mixtures the smectic A_d phase evolves from the smectic A₁ phase with increasing concentrations.

1. Introduction

The need for specific physical properties of liquid crystals for various practical applications has led to many investigations concerning mixtures of liquid crystals. Interesting results both from theoretical as well as application points of view have been obtained from these investigations. New types of phase diagrams have been discovered, reflecting the presence, under definite conditions, of the so-called induced phases that are not observed in the pure components. In many cases the smectic A (SmA) phase is induced when calamitic polar and non-polar nematics are mixed in appropriate proportions [1–9]. Maximum stability of the induced phase usually occurs for nearly equal concentrations of the two components [1, 2, 10]. Induction of smectic B and smectic E and columnar phases has also been reported [10–13].

Various models have been proposed to explain the induction of a higher order phase from lower order phases [14–21]. Strength of the polarity of the end

group, rigidity of the core structure and overall length of the molecules are found to have pronounced effects on the phase induction phenomena. For example, Raszewski [1] observed that the thermal stability of the induced phase increases when the mixtures (PCH+5AB), (5CB+MPAB) and (5CB+5AB) are considered successively (full names and molecular structures of the abbreviations are given in table 1).

To gain further insight, we have studied in detail three mixtures: mixture A (5OAB+5OCB), mixture B (6OAB+5OCB) and mixture C (7OAB+5OCB) where both of the mixture components are less polar than the previously studied systems such as (5CB+5AB), and the molecular length of one component increases systematically. Here we present details of the phase diagram as revealed by optical microscopy and DSC studies and the results of elastic X-ray scattering measurement on the mixtures. The dielectric response of the mixtures subject to a static field has been published recently [22]. Although the host *n*OAB molecules have a small but negative dielectric anisotropy, all the mixtures are found to have non-additive positive dielectric anisotropy. Temperature and concentration dependence of the

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Table 1. Molecular structures of the compounds studied and other related compounds.

nOAB	4,4'-di(alkoxy)azoxybenzenes
	$C_nH_{2n+1}-O-\text{C}_6\text{H}_4-N(O)=N-\text{C}_6\text{H}_4-O-C_nH_{2n+1}$
5OAB	5OAB $n=5$; 6OAB $n=6$; 7OAB $n=7$
5OCB	4-pentyloxy-4'-cyanobiphenyl
	$C_5H_{11}-O-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-CN$
5CB	4-pentyl-4'-cyanobiphenyl
	$C_5H_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-CN$
PCH	4- <i>n</i> -pentyl-4'-cyanophenylcyclohexane
	$C_5H_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-C\equiv N$
5AB	4,4'-di(pentyl)azobenzene
	$C_5H_{11}-\text{C}_6\text{H}_4-N=N-\text{C}_6\text{H}_4-C_5H_{11}$
MPAB	4- <i>n</i> -methyl-4'-propylazoxybenzene
	$CH_3-\text{C}_6\text{H}_4-N(O)=N-\text{C}_6\text{H}_4-C_3H_7$
CBOOA	4-cyanobenzylidene-4'- <i>n</i> -octyloxyaniline
	$C_8H_{17}-O-\text{C}_6\text{H}_4-N=C-\text{C}_6\text{H}_4-CN$

different dielectric parameters, including that of the effective dipole moments of the molecules (usually different from the molecular dipole moment [22–24]), have revealed interesting features of the molecular associations in the mixtures. Concentration and temperature dependence of the optical birefringence and density of the mixture systems will be reported elsewhere.

2. Experimental

Seven mixtures of different concentrations for the system (5OCB+5OAB), five mixtures of (5OCB+6OAB) and six of the system (5OCB+7OAB) were prepared. These are termed mixtures A, B and C, respectively. To obtain a homogeneous mixture, components were mixed thoroughly in the isotropic phase and kept in an oven for a few hours, the mixture being

shaken vigorously at regular intervals. Transition temperatures were obtained by observing textures under an optical microscope with crossed polarizers. Temperature was regulated with a Mettler FP 80/82 hot stage. Transition enthalpies were measured using a Mettler FP84 differential scanning calorimeter, using a scan rate of 5°C per minute. X-ray diffraction (XRD) photographs were recorded on a custom-built flat plate camera at different temperatures [25]. Samples were aligned by heating to the isotropic state and slowly cooling ($\sim 1^\circ\text{C min}^{-1}$) in the presence of a magnetic field of about 5 kG. Temperatures were measured and regulated with a precision temperature controller. Details of the experimental set-up and procedures adopted for X-ray measurements have been described before [25, 26].

3. Results and discussion

3.1. Texture and DSC studies

Composition, transition temperatures and transition enthalpies of the mixtures are summarized in table 2 and the phase diagrams are shown in figure 1. Observed transition temperatures and transition enthalpies of the pure components are also given in table 1, and are found to be in good agreement with previous reports [27]. Representative DSC curves are shown in figure 2. Concentration variations of transition enthalpies for smectic–isotropic (Sm–I) and nematic–isotropic (N–I) transitions are shown figure 3.

In all the mixtures, both during heating and cooling (2°C min^{-1}), fan-shaped texture in the SmA phase and schlieren texture in nematic phase were observed. The N–I or Sm–I transitions were found, under the polarizing microscope, to be sharper than those involving crystal (Cr)–Sm, and Cr–N transitions because those transitions involve a supercooling effect. This is also reflected in the DSC curves for Cr–Sm transitions. Similar behaviour was observed in the phase diagram of the binary mixtures of 2CB and 10CB by Kabuno *et al.* [28]. The N–I or Sm–I transition temperatures in mixture A slowly increase with concentration, reach a maximum at $x_{5OCB}=0.50$ but then fall quite rapidly. Mixtures B and C show similar trends. In mixture A, the Cr–N or Cr–Sm transition temperatures slowly drop to a minimum at $x_{5OCB}=0.35$, increase up to the concentration $x_{5OCB}=0.65$, then decrease again. However, in mixture B, the Cr–Sm transition temperatures slowly decrease until concentration $x_{5OCB}=0.85$ is reached and then increase slightly. On the other hand, the mixture C shows a slow but regular decrease of the Cr–Sm transition temperatures. Thus a systematic variation of the Cr–Sm transition temperature is

Table 2. Transition temperature(°C) and transition enthalpies (kJ mol⁻¹) of the pure components and their mixtures. Values in parantheses denote supercooling temperatures.

Pure compounds		Transition temperatures	Transition enthalpies	
Component 1	5OCB	Cr 47.8 (31.7) N 67.4 I	ΔH_{NI} 0.12	
Component 2	nOAB			
n=5	5OAB	Cr 77.6 N 120.5 I	0.68	
n=6	6OAB	Cr 80.8 N 125.8 I	0.90	
n=7	7OAB	Cr 73 SmC 89.6 N 119.7 I	1.04	
			Transition Enthalpies	
Mixtures	Mole fraction x_{5OCB}	Transition temperatures	ΔH_{NI}	ΔH_{SI}
A (5OCB+5OAB)				
A1	0.15	Cr 70.9 (63.9) N 119 I	0.71	
A2	0.25	Cr 61.2 (55) SmA 114 N 119.2 I	0.55	
A3	0.35	Cr 46.2 SmA 124.3 I		3.07
A4	0.5	Cr 48.9 SmA 124.4 I		3.21
A5	0.65	Cr 58.1 SmA 119 I		1.42
A6	0.75	Cr 53.4 SmA 106 I		
A7	0.875	Cr 46 SmA 68 N 83.8 I	0.18	
B (5OCB+6OAB)				
B1	0.15	Cr 78.3(69.5) SmA 116 N 126.2 I	0.65	
B2	0.25	Cr 76.8 (54) SmA 125.2 I		2.78
B3	0.5	Cr 40.6 SmA 127 I		3.09
B4	0.75	Cr 36.2 SmA 106.8 I		0.23
B5	0.85	Cr 44 (24) SmA 89.2 I		0.18
C (5OCB+7OAB)				
C1	0.12	Cr 59 SmA 109 N 121.2 I	0.94	
C2 ^a	0.15	Cr 68.1(54.4) SmA 113.8 N 119.3 I	0.91	
C3	0.25	Cr 65.6 (41.1) SmA 121.2 I		3.34
C4	0.5	Cr 48.2 SmA 124.4 I		3.16
C5	0.75	Cr 44.7 SmA 109.4 I		0.10
C6	0.875	Cr 38 SmA 69.1 N 86.8 I	0.14	

^aFor mixture C2 only, the Sm–N transition enthalpy was determined as 0.56 kJ mol⁻¹.

observed with increasing chain length of the host molecules but no eutectic behaviour is seen. In general, the phase boundaries defined by N–I, Sm–N and Sm–Sm transitions are considered to be much more reliable than those involving Cr–Sm or Cr–Cr transitions, because the latter transitions involving the crystal phase are subject to substantial supercooling [28]. This is true in the present investigation also. However, a close study of the phase diagrams reveals the following interesting features:

(i) Only the N phase is observed in mixtures A with concentration $x_{5OCB} < 0.15$; all other mixtures exhibit either both N and SmA phases or only a SmA phase. In other words, whenever a small amount of 5OCB is introduced in the host 6OAB or 7OAB, induction of a SmA phase takes place. In the case of 5OAB, the mixing of 15% or more of 5OCB induces a SmA phase. Thus, over a wide concentration range, the N phase is completely

absent in all these mixtures. A binary mixture of two nematogens (6AB+6CB) is possibly the only example where such a complete absence of the N phase was reported earlier [3]. In contrast, in a mixture of (5AB+5CB) a nematic phase is found to be present at all concentrations [1].

(ii) Mesophase thermal stability of 5OCB is 35.7°C and in the hosts 5OAB, 6OAB or 7OAB the stability values are 42.9, 45.0 and 46.7°C. In some mixtures the stability increases substantially. For example, maximum thermal stability of the induced SmA phase is observed to be 86.4°C and is maximum in the equimolar mixture B3, as is usually observed in these types of mixtures [1, 2, 10]. However, in the mixtures A maximum stability of 78.1°C is observed at $x_{5OCB} = 0.35$. In the case of mixture C it occurs at $x_{5OCB} = 0.25$ and the value is 80.1°C. For the equimolar mixtures A4 and C4 the values are 75.5°C and 76.2°C respectively. The mixtures A exhibit only an

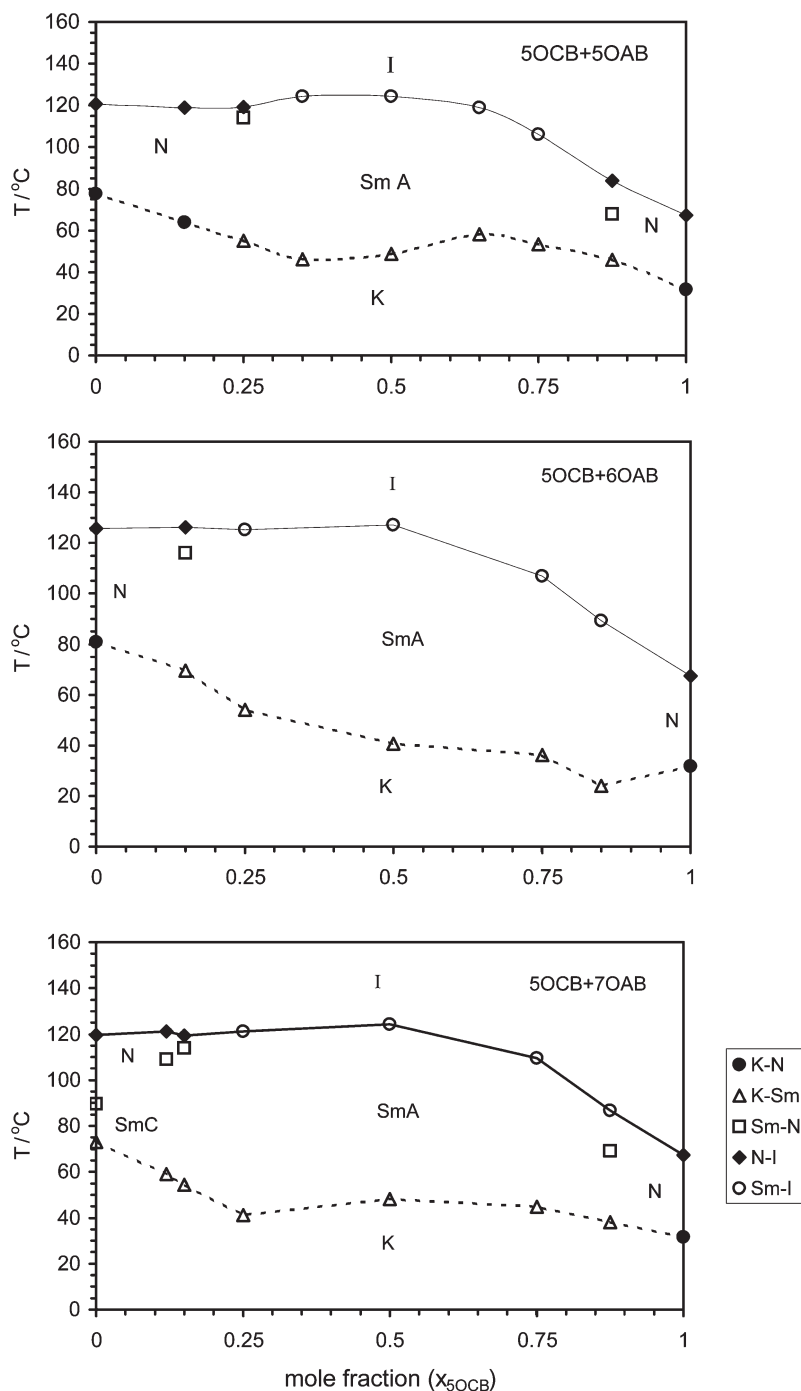


Figure 1. Phase diagrams of mixture A (5OCB+5OAB), B (5OCB+6OAB) and C (5OCB+7OAB).

induced SmA phase within the concentration range $x_{5OCB}=0.27$ to 0.75, where the nematic phase of the pure components is completely absent. This concentration range increases in B ($x_{5OCB}=0.25$ to 0.85), whereas in C the observed range is $x_{5OCB}=0.25$ to 0.75 as in A. From figure 1

it is clear that the area of the induced SmA phase increases when the chain length of the host molecules increases from five to six C atoms, then decreases when another C atom is attached to the chain. Of course, the decrement in the last case may also be the result of an odd-even effect as

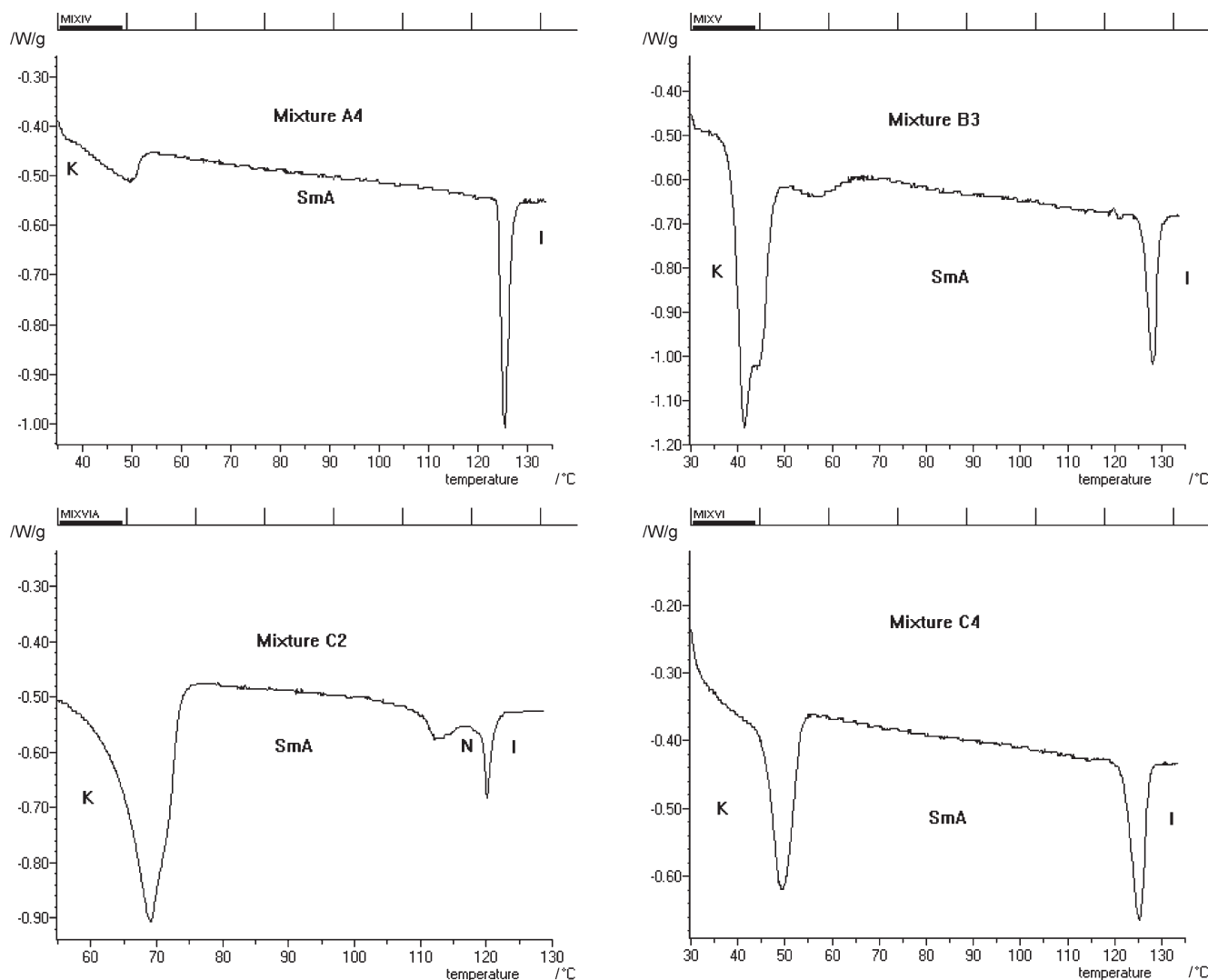


Figure 2. Representative DSC curves of the mixtures A4, B3, C2 and C4 during heating.

previously observed in many physical properties in members of the homologous series of isothiocyanatobenzenes [29].

- (iii) Another interesting point is that instead of the SmC phase present in 7OAB, an orthogonal SmA phase is observed as soon as some 5OCB molecules are introduced, confirming the previous observation that in no case was an induced smectic phase with tilted director found [20].

In all the mixtures, the enthalpy values associated with the N–I transitions are found to decrease linearly with increasing mole fraction of 5OCB (figure 3) following a simple additivity rule [30]. However, the change in enthalpy at the SmA–I transition is non-linear in all the mixtures, with a maximum near the equimolar concentration. Dunmur and Walker [31], in a binary

mixture of 4-*n*-pentyloxybenzoate, also observed a large entropy change in the central part of the phase diagram where the stability of the induced smectic phase was maximum. The large transition enthalpy ($\sim 3 \text{ kJ mol}^{-1}$) associated with the SmA–I transition in mixtures A3, A4, B2, B3, C3 and C4, compared with the N–I transition ($< 1 \text{ kJ mol}^{-1}$), indicates strong intermolecular interaction. However, comparatively smaller SmA–I transition enthalpies have also been observed in some mixtures (A5, B4, B5 and C5). In mixture A6 the SmA–I transition could not be detected by DSC. It might be noted that in pure 7OAB the value of ΔH for the SmC–N transition is 1.59 kJ mol^{-1} ; in 11OAB where a SmC–I transition takes place, its value is $10.07 \text{ kJ mol}^{-1}$; and in 10CB its value is 2.83 kJ mol^{-1} at the SmA–I transition [27].

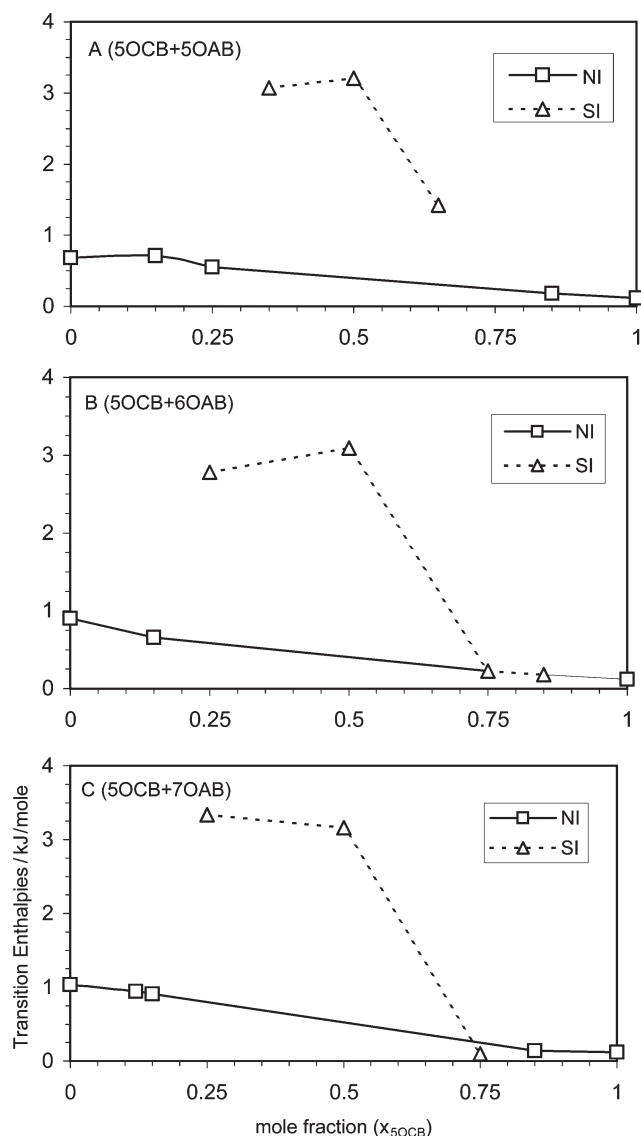


Figure 3. Transition enthalpies at N–I and SmA–I transitions for the mixtures A, B and C. Lines are a guide to the eye only. Uncertainties in measurement are within 1% of the measured values.

According to McMillan's theory [32–34] if the ratio T_{NA}/T_{NI} is greater than 0.87 then the SmA–N transition should be first order. Although in all the present mixtures this ratio is found to be more than 0.95, in no case could the SmA–N transitions be detected by DSC, except for the mixture C2 where the value of the transition enthalpy was found to be 0.56 kJ mol^{-1} .

3.2. X-ray studies

Representative XRD photographs in the N and SmA phases are shown in figure 4. The presence of the N and

induced SmA phases are confirmed from the photographs. The nature of the SmA phase sub-type is discussed below. In the X-ray photographs of mixtures C, the presence of the SmC phase is not observed.

Molecular parameters determined from the XRD photographs are the average intermolecular distance (D) in both smectic and nematic phases, the layer spacing (d) in the smectic phase and the apparent molecular length (l) in the nematic phase. The length of the molecule in the N phase may differ from its length in all-*trans* conformation because the molecules are on the average tilted with respect to the director; there may be molecular associations of a dimeric nature, especially if the molecules are strongly polar and the molecules may not be in the most extended conformation. Thus the correlation length along the director may be termed as apparent molecular length.

We obtained D values at different temperatures from the peak positions of the outer equatorial halos in the diffraction patterns, using a modified Bragg formula $D = 1.117\lambda/2 \sin \theta$ because of the cylindrical symmetry of the molecules [25, 35, 36]. The photographs were digitized by a scanner and the peak positions determined by fitting pixel colour values obtained from an equatorial scan. The apparent molecular length l and smectic layer spacing d were determined similarly from the inner meridional arc using the Bragg equation. As an illustrative set, colour values obtained from the equatorial scan of the X-ray photograph at 50°C of mixture A3 is presented in table 3 and the fitted curves for locating the peaks are shown in figure 5. Uncertainty in the D measurement is $\pm 0.05 \text{ \AA}$; those in l or d are $\pm 1.0 \text{ \AA}$.

The variation of D with temperature is similar in all the mixtures; this is shown only for mixture A in figure 6. D values are found to increase slowly with temperature; in mixture A it varies from 4.82 to 5.08 \AA , in mixture B from 4.81 to 5.09 \AA and in mixture C from 4.86 to 5.09 \AA . However, near the N–I or SmA–I transitions, the values are significantly larger. For example, in mixture B at concentration $x_{\text{SOCB}} = 0.75$, the D value is 5.15 \AA , and in mixture C at concentrations $x_{\text{SOCB}} = 0.15$ and 0.50 , the values are 5.18 and 5.12 \AA , respectively. Except for values near the transitions there is little difference between the D values of the three mixture systems; the average is 4.95 \AA . The reported value of D for 5OCB, the strongly polar component of the mixtures, varies from 4.7 to 4.95 \AA [37], and in 7OAB, one of the weakly polar components, it varies from 4.80 to 4.87 \AA [38]. Thus it may be inferred that the D values are greater in the mixtures than in the pure components. Also, in all the mixtures, as well in the pure components, D increases with T ,

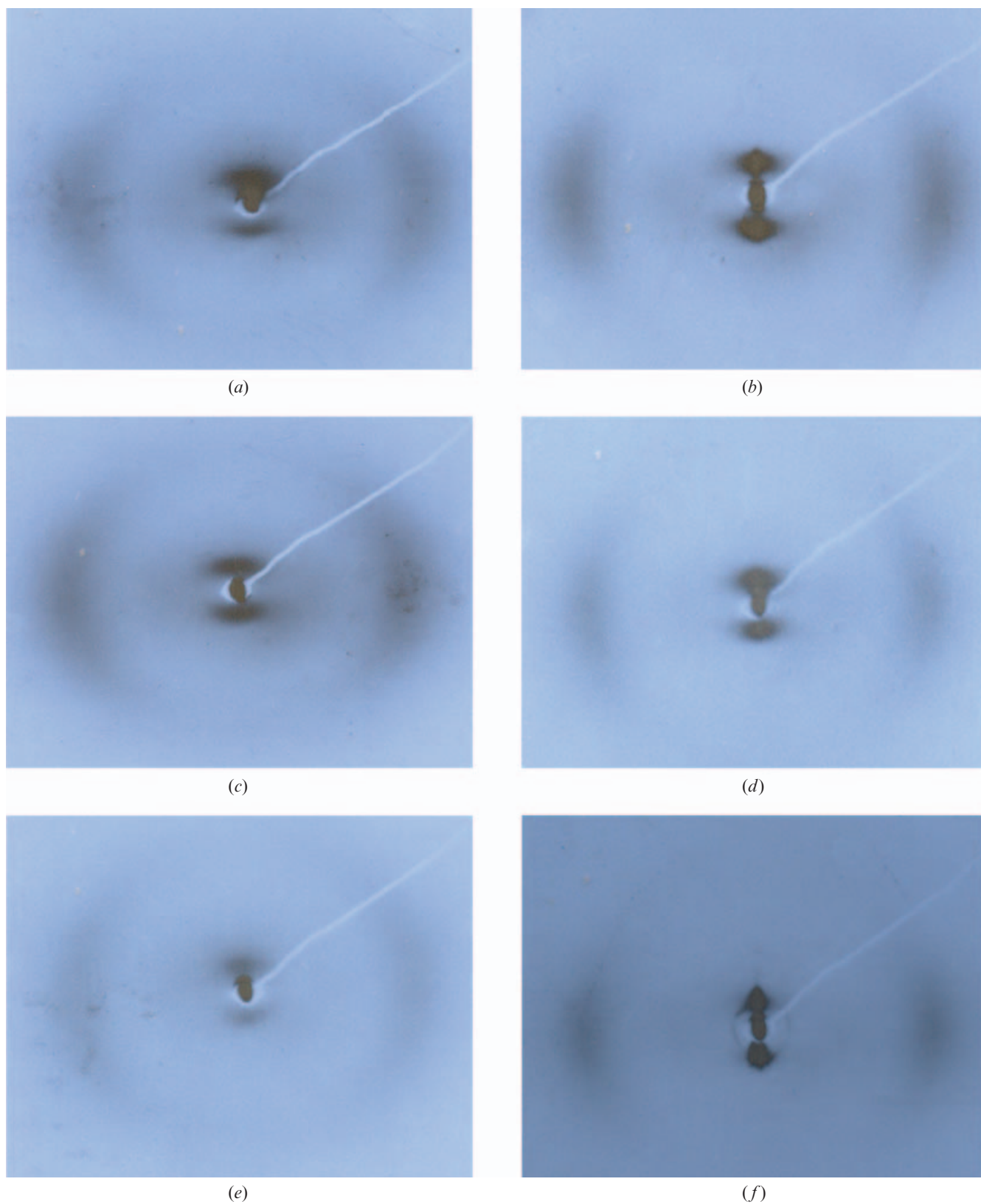


Figure 4. X-ray diffraction photographs of mixture (a) A1 at 110°C in N phase, (b) A4 at 90°C in SmA phase, (c) B1 at 120°C in N phase, (d) B3 at 70°C in SmA phase, (e) C6 at 85°C in N phase, and (f) C3 at 110°C in SmA phase.

Table 3. Colour values obtained from the equatorial scan of X-ray diffraction photograph of mixture A3 at 50°C. Scanning along constant pixel row value=113.

Right outer crescent		Left outer crescent	
Pixel column value	Colour value	Pixel column value	Colour value
774	94	510	90
775	94	511	90
776	92	512	89
777	89	513	82
778	92	514	85
779	86	515	87
780	85	516	81
781	83	517	82
782	82	518	79
783	82	519	74
784	75	520	76
785	75	521	75
786	80	522	77
787	77	523	74
788	74	524	75
789	79	525	74
790	77	526	78
791	75	527	76
792	77	528	80
793	83	529	83
794	81	530	79
795	81	531	78
796	84	532	87
797	85	533	83
798	85	534	86
799	88	535	92
800	93	536	92
801	90	537	93
802	95	538	98
803	98		

suggesting a decrease in the density of molecular packing with temperature. This observation is consistent with the observed decrease of density of all the mixtures with increasing temperature. At $T^*=0.9T_{NI,SI}$ the variation of D with concentration of 5OCB is shown in figure 7. The nature of the variation of D is same in all the three mixtures: initially it decreases with concentration of 5OCB, reaches a minimum and increases thereafter. The minimum occurs near the equimolar concentration for mixtures B and C, but for A it arises at higher concentration.

Temperature variation of the apparent molecular length l in the nematic phase, and that of the smectic layer spacing d for the A mixtures are shown in figure 8. Values of l and d at concentrations $x_{5OCB}=0.15$ to 0.35, show a substantial increase with temperature. In the remaining A mixtures, the variation is not very pronounced, except at $x_{5OCB}=0.65$ in the lower temperature region. In mixture B, at concentrations

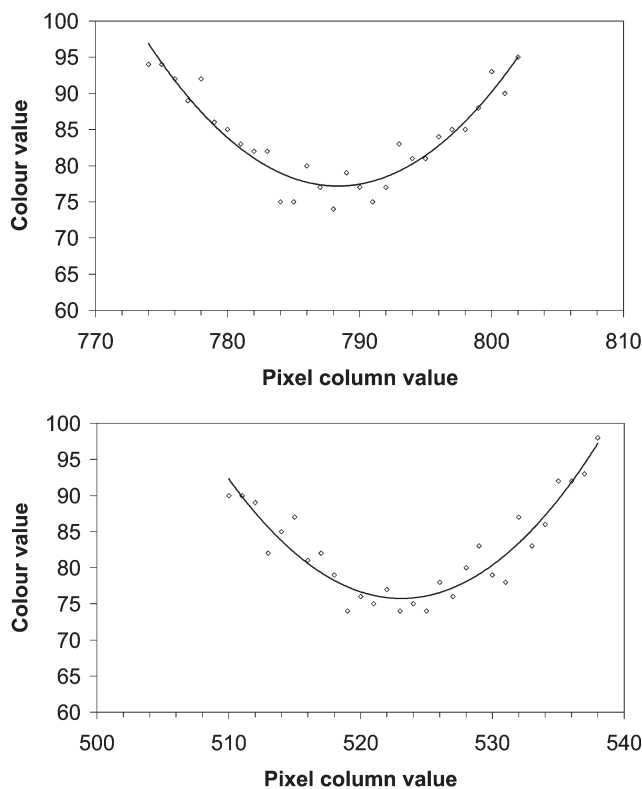


Figure 5. Fitted curves for locating the peaks to find the D values. Top: right outer crescent. Bottom: left outer crescent. Photograph: mixture A3 at 50°C.

$x_{5OCB}=0.15$ and 0.25, the d values show substantial increase with increasing temperature. However, at higher concentrations the increase is less significant. In mixture C, temperature variation of l or d is considerable only in mixtures having both N and SmA phases. As reported by Bhattacharjee *et al.* [37] the dependence of l with temperature, for the pure component 5OCB, is minor, varying from 24 to 25 Å. Its values in 5OAB and 6OAB at 80°C are 22.5 and 27 Å, respectively; in 7OAB it is 28.8 Å at 98°C in the nematic phase, as observed by Chistyakov and Chaikowsky [39] In the SmC phase of 7OAB, Leadbetter and Norris [40] observed the layer spacing as 24.0 ± 0.4 Å. However, they did not discuss the temperature variation of l or d . The values of l in mixtures A vary between 22.5 and 24.85 Å. The layer spacings d vary from 22.2 to 24.8 Å. These values are similar to those of the pure components. In mixtures B, at concentration $x_{5OCB}=0.15$, which has a narrow nematic phase, the l value is 27.8 Å, which is close to the value of the pure component 6OAB. The d values vary between 23.0 and 25.8 Å. In mixture C, at concentrations $x_{5OCB}=0.12, 0.15$ and 0.85, the l values show little variation with temperature. The average values are, respectively, 30.14, 28.5 and 26.9 Å, which

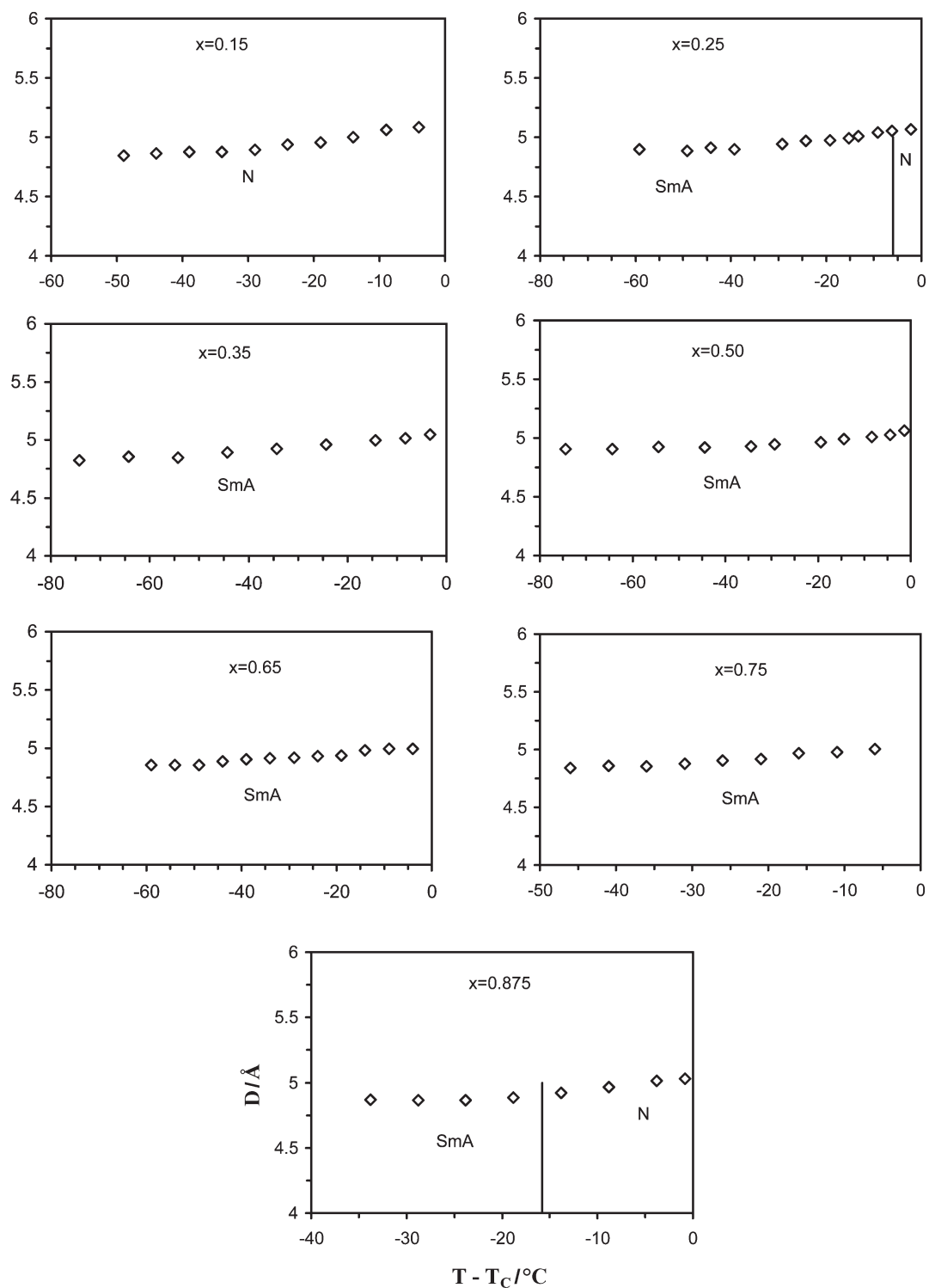


Figure 6. Temperature dependence of average intermolecular distance D of mixture A.

are greater than the pure component values. The d values vary from 25.0 to 29.0 Å, also greater than the pure compound values.

The concentration dependence of the apparent molecular length l in the nematic phase and the layer spacing d of the smectic phase, of all the mixtures, is

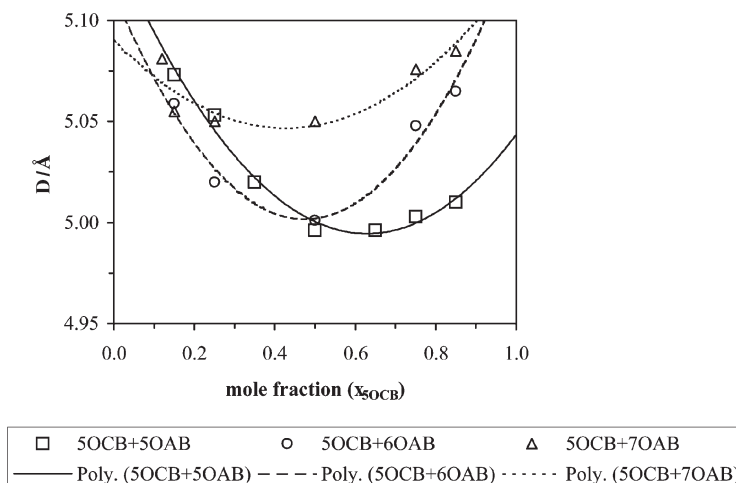


Figure 7. Variation of average intermolecular distance D with concentration of 5OCB (x_{5OCB}) at $T^*=0.9T_{NI,SmI}$. Curves fitted to the D values of the three mixtures are also shown.

shown in figure 9 at $T^*=0.9T_{NI,SmI}$. To gain further insight into the nature of molecular associations we have calculated d values considering two models. In the first model, it is assumed that the pure components exist as monomers and the layer spacing in the mixtures follows the simple additivity rule

$$d = x_A l_A + x_B l_B \quad (1)$$

where x and l are the concentration and monomer length of the subscripted components. Since $nOCB$ molecules are usually found to have dimeric association [37, 41–43], in the second model, d values were calculated by considering the system to consist of 5OCB dimers and monomers of $nOAB$, and using the modified formula

$$d = \frac{0.5x_A l_A + x_B l_B}{0.5x_A + x_B} \quad (2)$$

where l_A is the dimer length of 5OCB and l_B is the monomer length of $nOAB$.

The d values calculated using equations (1) and (2) are shown in figure 9 as dashed and dotted lines respectively. It is observed that the experimental values at lower concentrations almost agree with model 1 except for the mixtures A at concentrations $x_{5OCB}=0.35$ and 0.50 . At higher concentrations d varies according to model 2. In other words, in all the three binary systems at higher concentrations 5OCB molecules exist as dimers, whereas at lower concentrations they are mostly in monomeric form, as if the SmA_d phase is evolving from the SmA_1 phase. This also agrees with the nature of molecular associations in the induced smectic phase as revealed from dielectric studies [22].

In the binary system (7OAB+CBOOA) [44] and (7AB+5CB) [45], similar variation of d in the induced SmA phase was observed. This was explained by the displacement of the equilibrium mixture of monomers and dimers towards dimers with increasing concentration of the polar component [46]. Diele *et al.* [47] reported that even in a binary mixture of two nematogenic terminal non-polar compounds, which are expected to be in monomeric form, the layer spacing does not vary according to model 1. All these observations suggest that the strongly polar 5OCB molecules play the dominant role in phase induction and stability of these mixtures.

4. Conclusions

A large number of binary mixtures of 5OCB with 5OAB, 6OAB or 7OAB have been studied. Over a wide concentration range a smectic A phase is induced, and the nematic phase of the parent compounds is completely absent in as many as 11 mixtures out of the 18 studied. The tilted smectic C phase of 7OAB transforms to an orthogonal smectic A phase when only 12% of host molecules are replaced by 5OCB molecules. Moreover, in some mixtures the thermal stability of the induced SmA phase is found to be more than 1.6 times the stability of the mesophases in the pure compounds. The N–I or Sm–I transition temperatures in mixtures A slowly increase with concentration, reaching a maximum at $x_{5OCB}=0.50$, then falling quite rapidly. Mixtures B and C show similar behaviour. In all the mixtures the enthalpy values at the N–I transitions follow a simple additivity rule. However, the change in enthalpy at the SmA –I transition, in all the mixtures, is

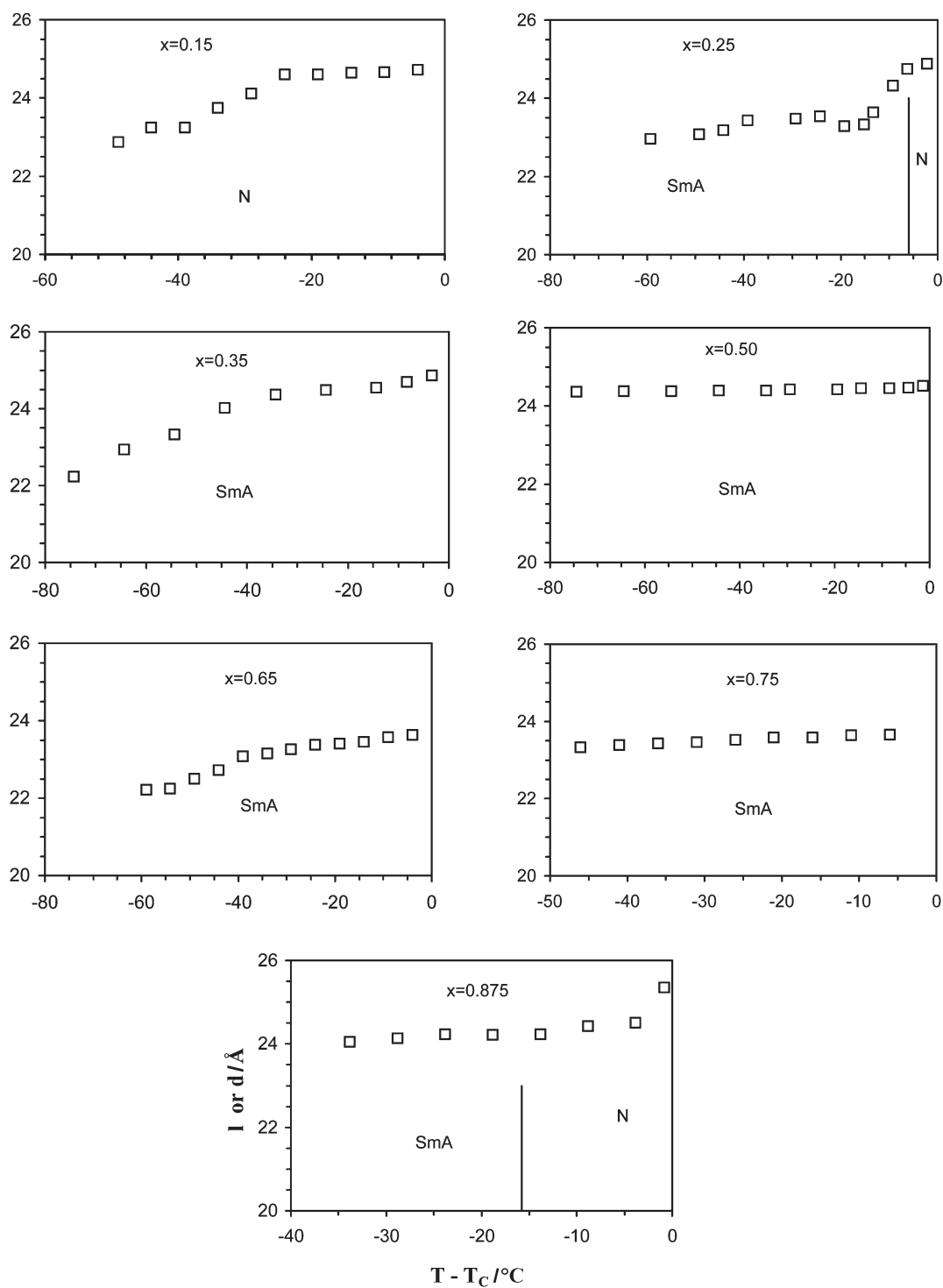


Figure 8. Temperature variation of apparent molecular length l and the smectic layer spacing d of mixture A.

non-linear. In no mixture (except for mixture C2) could the SmA–N transition be detected by DSC, although in all the mixtures the ratio of T_{NA}/T_{NI} is found to be more than 0.95. This is in contradiction to McMillan's theory

[32–34] which predicts that the SmA–N transition should be of first order if the ratio is greater than 0.87.

X-ray diffraction studies indicate that the average intermolecular distance is nearly the same in all the

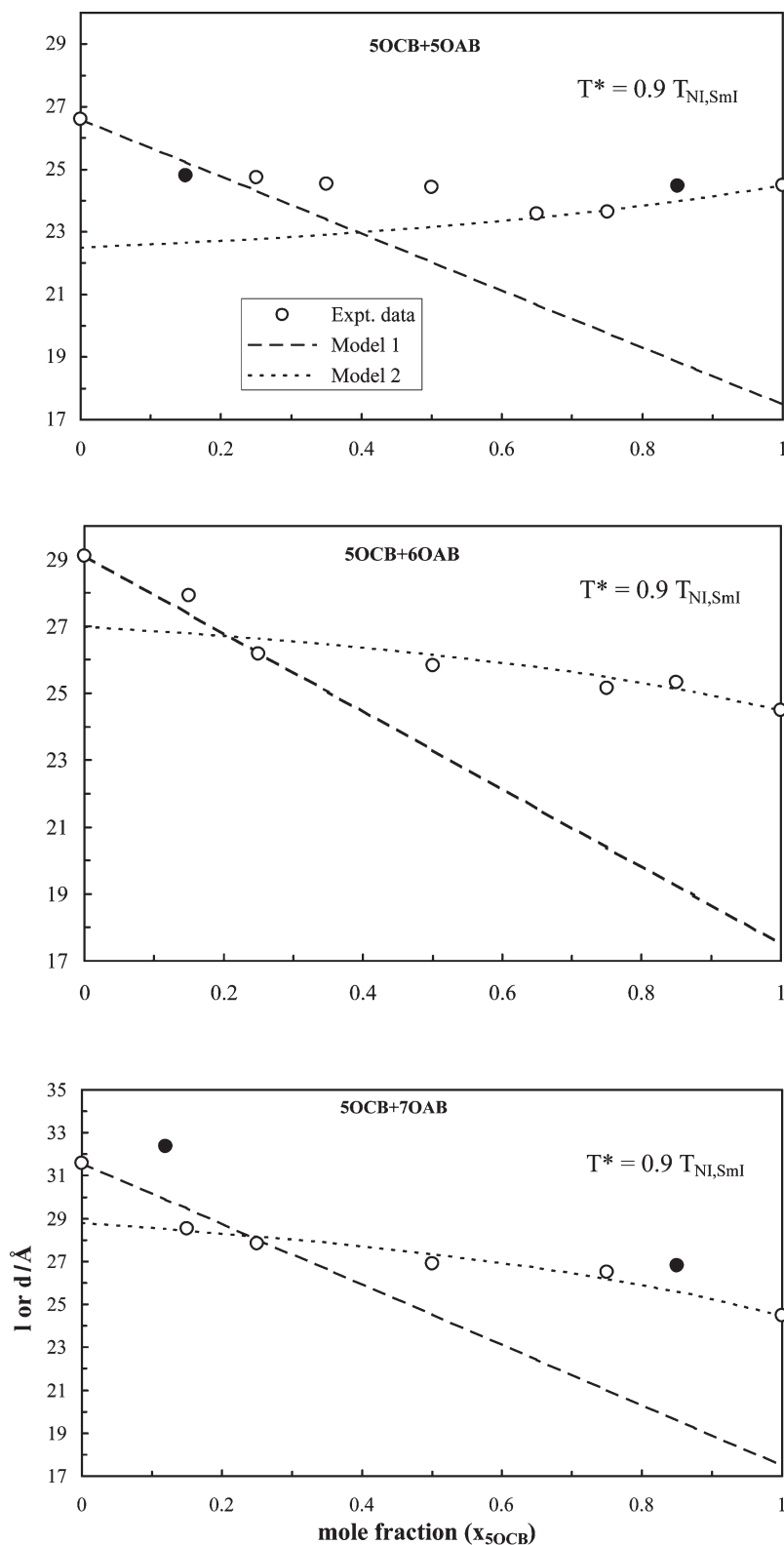


Figure 9. Concentration dependence of layer spacing d (open circle) and apparent molecular length l (filled circle). The dashed and the dotted lines represent d values calculated according to models 1 and 2, respectively.

mixtures, and is greater than that in the pure components. Also, it increases with temperature, suggesting a decrease in packing density. On the other hand, D values are found to decrease with increasing concentration of 5OCB, reaching a minimum near the equimolar concentration and then increasing. The apparent molecular lengths in the N phase, and the smectic layer spacings, show an increasing trend with temperature, indicating a decrease in molecular packing. From the concentration dependence of the smectic layer spacings it appears that in all the mixtures the phase structure becomes smectic A_d type from smectic A_1 type as the concentration increases.

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