

Chapter V

**DIELECTRIC STUDY IN NEMATIC AND INDUCED SMECTIC A
PHASES IN BINARY MIXTURES OF PENTYLOXY
CYNOBIPHENYL WITH THREE P-AZOXYBENZENES.**

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Introduction

The need for specific physical properties of liquid crystals for various practical applications, have led to the appearance of a large number investigations concerning mixtures of liquid crystals. Interesting results both from theoretical as well as application point of view have been obtained from these investigations. New types of phase diagrams, reflecting the presence under definite conditions of so-called “induced” phases, which are not observed in the starting individual components of the mixture, have been discovered.

One of the studies of binary mixtures that provides valuable source of information on molecular organization, intermolecular interactions and molecular dynamics is the dielectric study. In this chapter the static dielectric properties of the mixtures is presented whose phase diagrams and several other physical properties have been reported in Chapter III and IV.

Experimental

Cells made of ITO coated conducting glass plates in parallel plate capacitor geometry were used for dielectric measurements. The cell was calibrated with CCl_4 and the dielectric constant of para-xylene was determined. The measured values agreed within 2% of standard values. The cell temperature was maintained by a temperature controller with an accuracy of ± 0.5 °C. A magnetic field of 5kG was applied to align the samples. Components of the dielectric permittivities parallel and perpendicular to the director (ϵ_{\parallel} and ϵ_{\perp}) were determined respectively in homeotropic and homogeneous geometry by measuring the cell capacitance during cooling by an LCR bridge at 1 kHz. Details of the experimental set up and the relevant theory are discussed in Chapter II

Results and Discussions

Variations of dielectric permittivities with temperature for pure 5OCB and 5OAB compounds are shown in **Figure 5.1**. For 5OCB our measured values agree

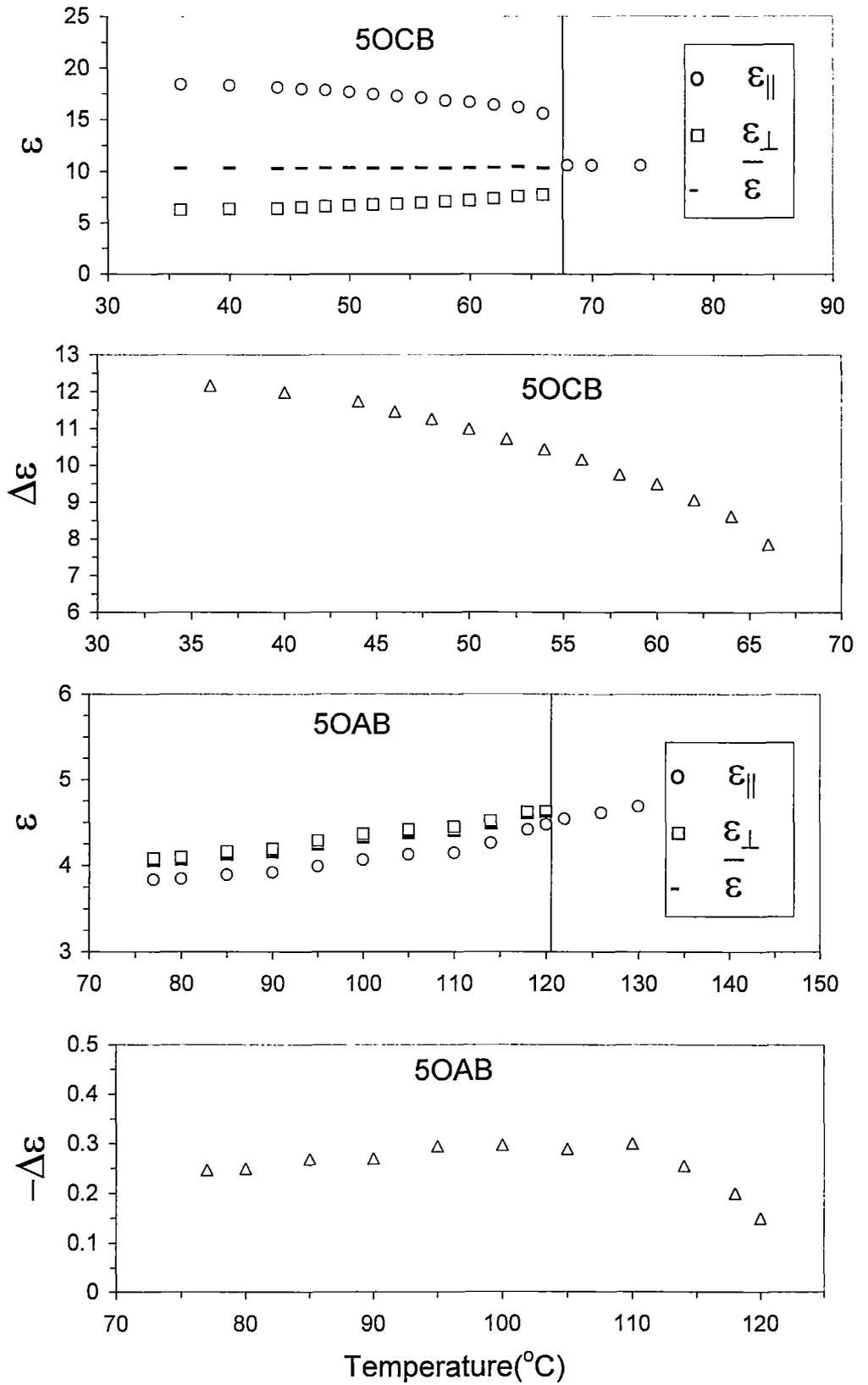


Figure 5.1. Variation of dielectric parameters with temperature of 5OCB and 5OAB.

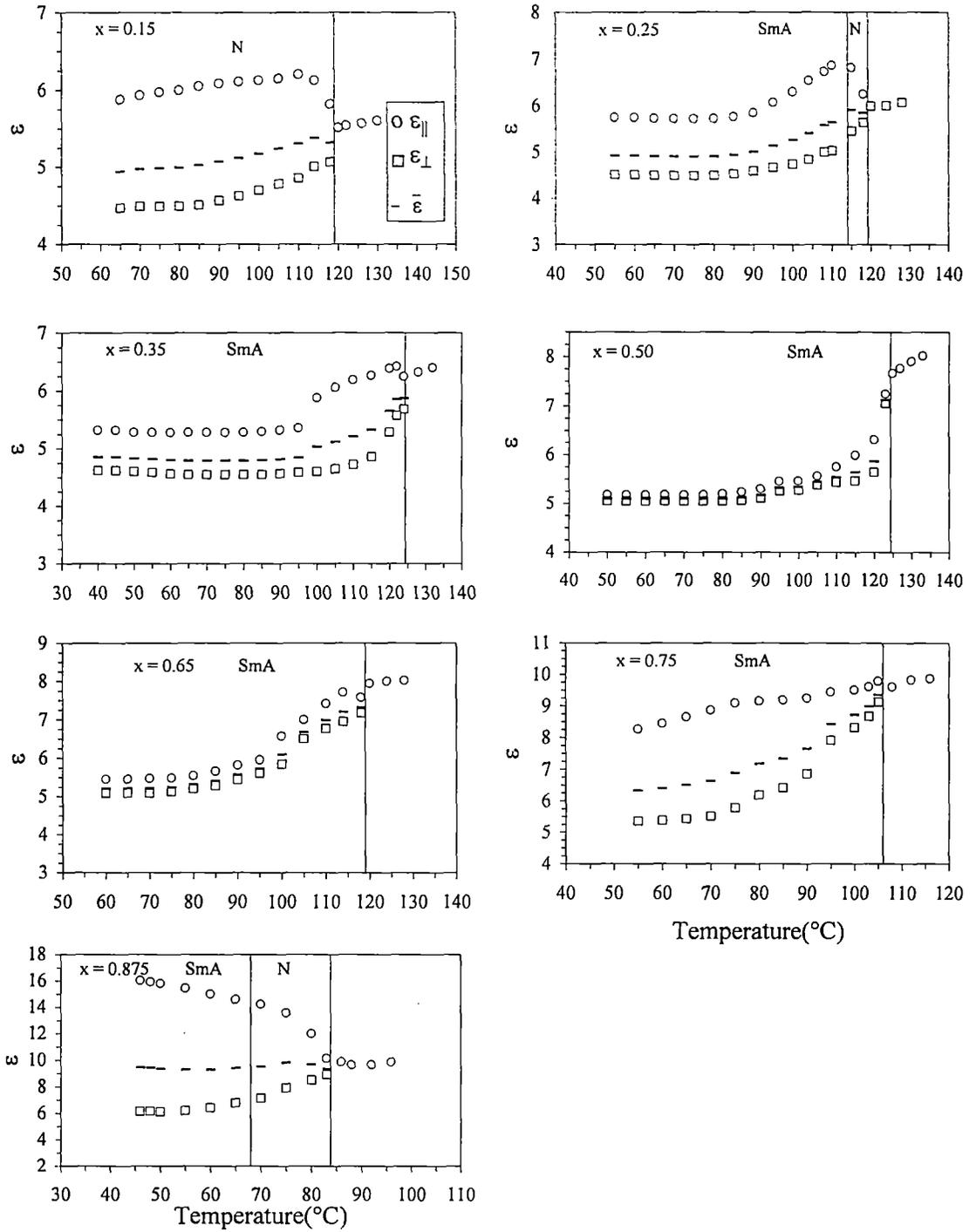


Figure 5.2. Variation of dielectric parameters with temperature of mixture A. x is the mole fraction of 5OCB.

well with the values reported previously [1], and it showed large positive dielectric anisotropy. Small negative dielectric anisotropy is observed in 5OAB as has been reported earlier [2,3]. The ϵ_{\parallel} and ϵ_{\perp} values are found to increase with temperature as observed by Nguyen *et al.* [4] in ϵ_{\perp} . However, decrease of ϵ_{\perp} values with temperature was also reported, ϵ_{\parallel} values remaining more or less constant [2,3]. Repetition of our measurements shows the same temperature dependence. Similar behaviour has also been observed in the mixtures studied. For 6OAB Konarski *et al.* [5] observed that ϵ values might differ due to different types of ordering in the sample as a result of sample thickness and nature and intensity of the ordering field; even the sample preparation history was found to have some effect.

Temperature variations of the dielectric parameters - ϵ_{\parallel} , ϵ_{\perp} and $\bar{\epsilon}$ - of the mixture A for all seven compositions are shown in **Figure 5.2**. It is observed in Chapter III that when only 15% of the host 5OAB molecules are replaced by the guest 5OCB molecules, the resulting mixture (A_1) shows only nematic phase like the pure components but the thermal stability is enhanced. All the above dielectric parameters increase considerably from those of pure 5OAB and a cross over from negative to positive dielectric anisotropy takes place. This seems plausible since the minimum value of $\Delta\epsilon$ near T_{NI} is about 8 for 5OCB, whereas for 5OAB even the maximum $\Delta\epsilon$ value is only about -0.3 (**Figure 5.1**).

When one-fourth of the host molecules are substituted by 5OCB molecules the phase behaviour is drastically changed. The mixture (A_2) shows mainly induced SmA phase, nematic phase is observed within a very small temperature range ($\sim 5^{\circ}\text{C}$). In the nematic phase the above three dielectric parameters are found to be larger than those in mixture A_1 , as expected due to increased concentration of the guest molecules. However, in the low temperature region of the induced SmA phase, all the dielectric parameters are found to be less than the values found in the N phase. These values are even less than those obtained in the N phase of the mixture A_1 though concentration of 5OCB molecules has been increased. This is clearly shown in **Figure 5.3** in case of $\bar{\epsilon}$. The dielectric parameters decrease further, though slightly, in mixture A_3 also. From the equimolar mixture (A_4) the

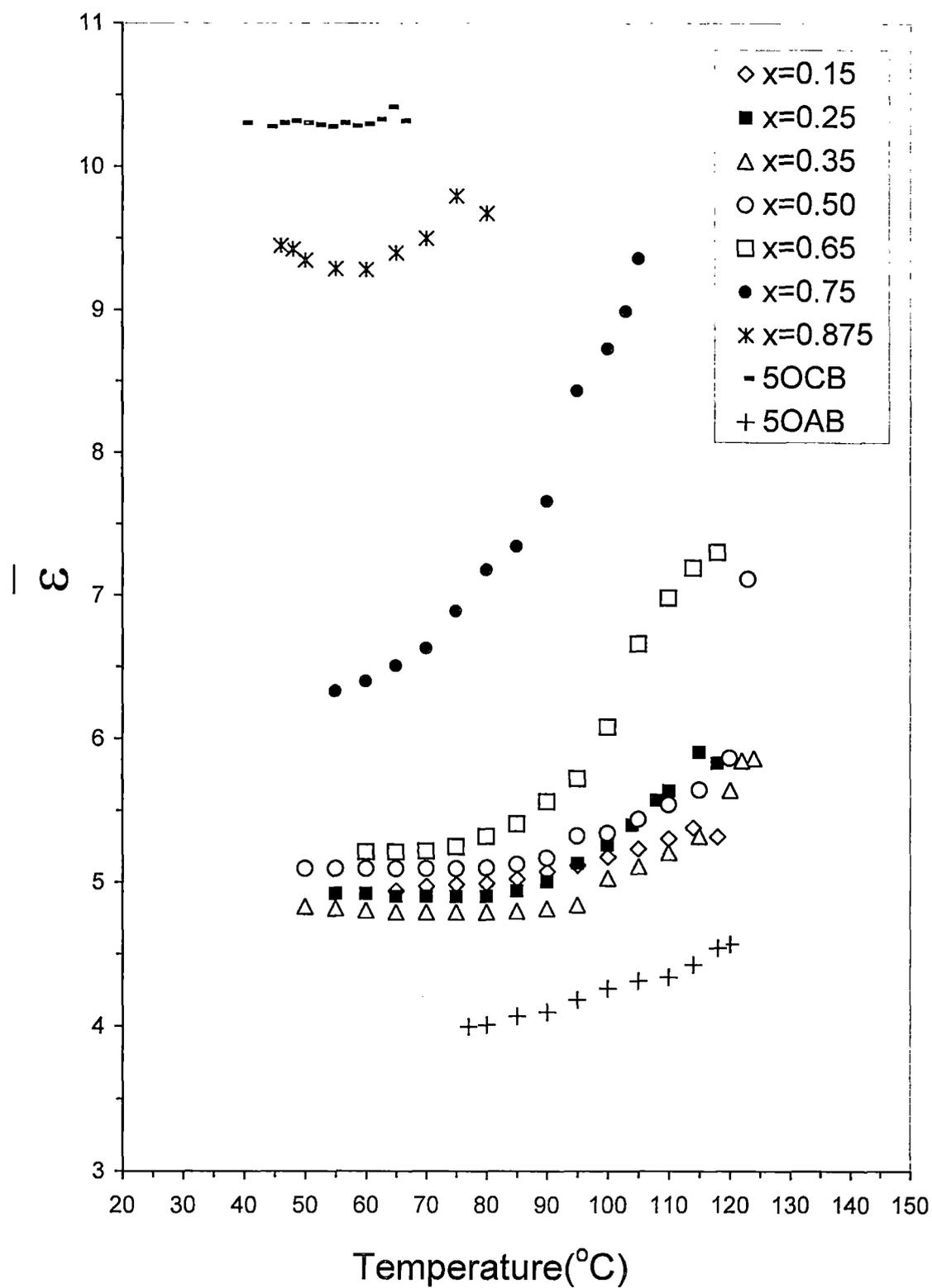


Figure 5.3. Variation of the average dielectric constant with temperature of mixture A. x is the mole fraction of 5OCB.

dielectric parameters start increasing and the increment is very fast with increased concentration of 5OCB. As noted earlier, the mixtures A₃ to A₆ exhibit only smectic phase. In the low temperature region of these mixtures the dielectric parameters increase very slowly with temperature, but near the T_{SI} transition (or T_{SN} in other mixtures), the increment is found to be quite fast.

According to Maier and Meier theory, described in Chapter II, in the low frequency field the dielectric permittivity depends on the molecular polarizability and dipole moments. Since $\bar{\alpha}$ and $\Delta\alpha$ are always positive and no discontinuous change is expected in their values at N-SmA transition, from equations 2.26 and 2.27 it is clear that less dielectric parameters in the SmA phase imply less effective dipole moment of the molecules. This, we presume, is a result of development of additional antiferroelectric ordering of the molecular dipoles in the stratified smectic structure. Some hetero-dimers may also form (discussed later). However, lowering of the ϵ values due to additional dipolar ordering at the onset of smectic phase is surpassed by the increased polarizability values when concentration of 5OCB molecules becomes 50% or more, as a result the dielectric parameters start increasing from the mixture A₄. On the other hand, this additional antiferroelectric type ordering in SmA phase gradually decreases (i.e. μ gradually increases) as the temperature is increased. Since the dielectric parameters depend on the squares of μ so they may increase with T as observed. In pure 7AB, a compound very similar to one of the hosts, decrease of ϵ_{\parallel} and anomalous increase of ϵ_{\perp} around N-SmA transition was observed and this was explained by introducing the idea of increased dipolar correlations between the molecules in the induced smectic phase [6].

In the mixture A₇, in addition to the induced SmA phase, nematic phase reappears with increased thermal stability than in mixture A₁. The observed features of dielectric constants are similar to those of pure 5OCB only with lower magnitudes. Moreover, no discontinuity in ϵ values is observed at T_{SN} transition, only there is a change in the slope (**Figure 5.2**). However, in mixture A₂ a discontinuous change was observed at T_{SN} transition.

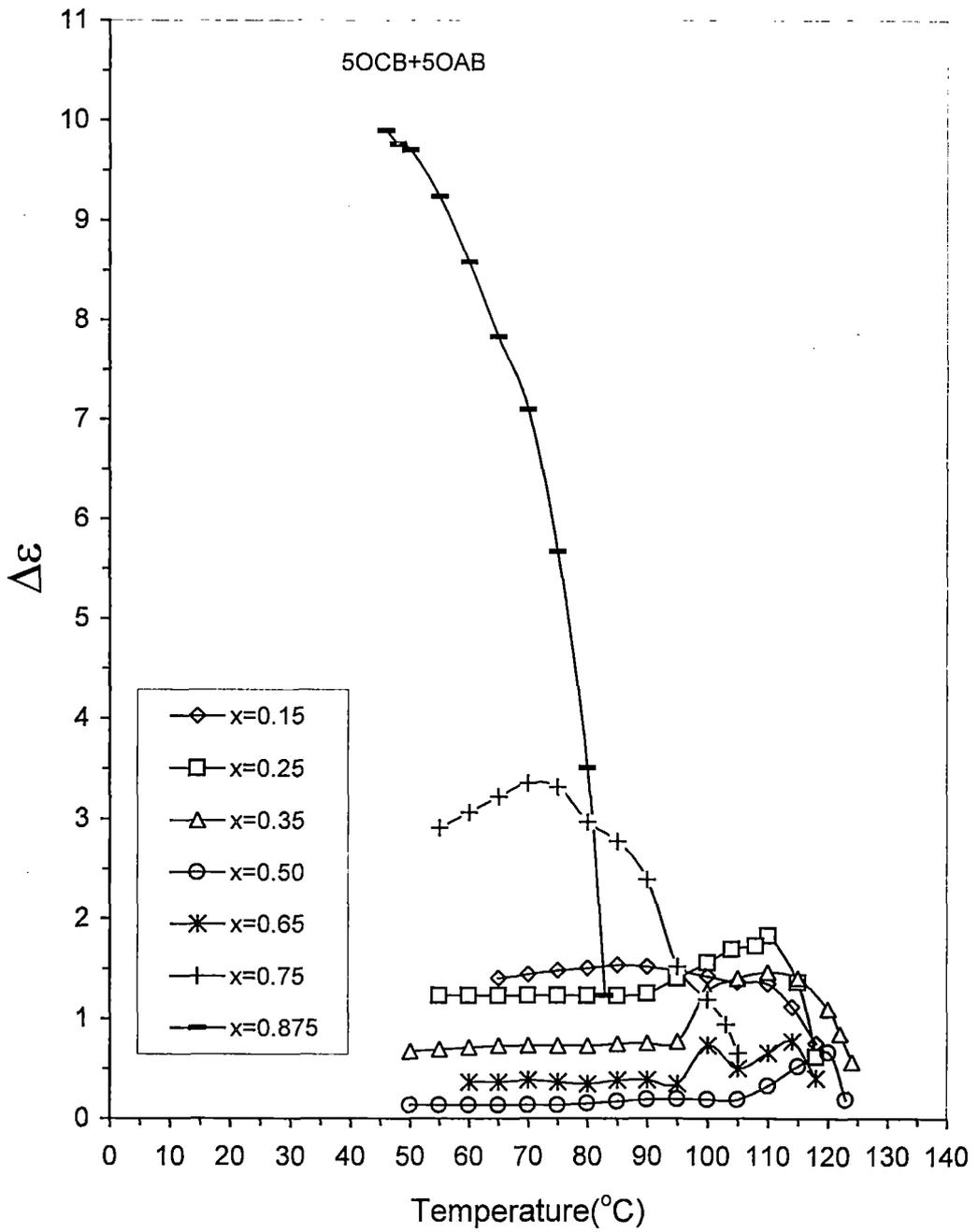


Figure 5.4. Variation of dielectric anisotropy with temperature of mixture A. x is the mole fraction of 5OCB. Lines are the guide to the eye only.

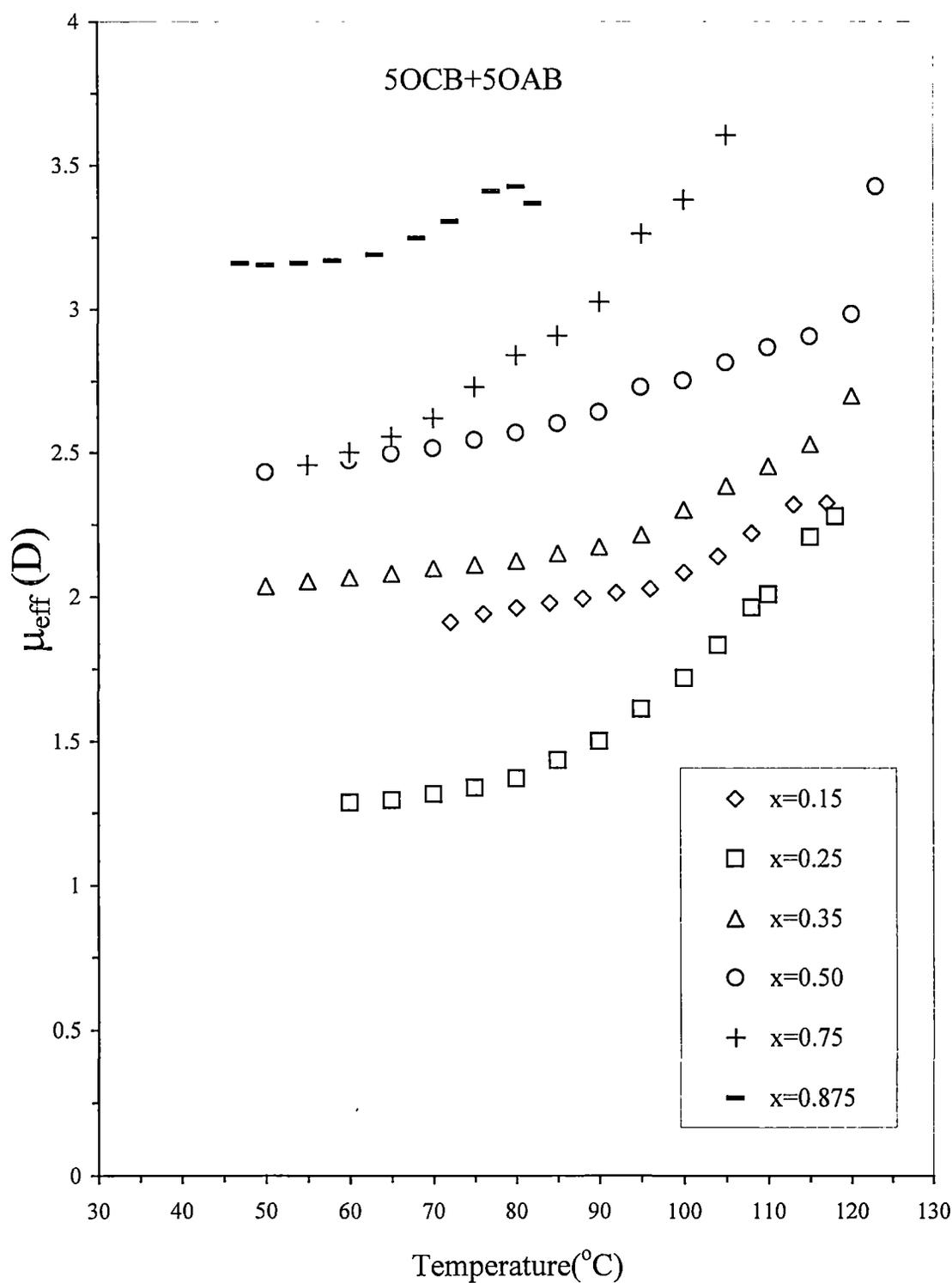


Figure 5.5. Temperature variation of effective molecular dipole moments of mixture A. x is the mole fraction of 5OCB.

The variation of dielectric anisotropy ($\Delta\epsilon$) with temperature is shown in **Figure 5.4** for all the A mixtures. In pure 5OCB, $\Delta\epsilon$ values are positive, quite high and decrease monotonically from about 12 to 8 and show a distinct first order transition at T_{NI} (**Figure 5.1**). On the other hand in 5OAB, $\Delta\epsilon$ values are comparatively very small but negative throughout. It increases from about 0.25 to 0.30, then remains constant over a considerable temperature range and finally decreases to about 0.15 rapidly near T_{NI} . All the mixtures, however, show positive dielectric anisotropy though the observed values in mixtures with low x_{5OCB} are very small and become comparable to pure 5OCB values at high 5OCB concentrations. In the mixture A_1 , it increases slowly with temperature from ~ 1.4 to ~ 1.5 and then decreases quite fast near T_{NI} , which is the observed trend in pure 5OAB. $\Delta\epsilon$ value decreases slightly as the concentration of 5OCB is increased to 25%, then a comparatively large decrement is observed at $x_{5OCB}=0.35$. Finally a minimum value in $\Delta\epsilon$ is observed in the equimolar mixture (A_4) and this minimum value (~ -0.14) is even less than what is observed in 5OAB. The minimum value of $\bar{\epsilon}$ was, however, observed in mixture A_3 as shown in **Figure 5.3**. From mixture A_5 , $\Delta\epsilon$ again increases with concentration initially very slowly and then very rapidly. The $\Delta\epsilon$ values of the mixtures A_2 to A_5 remain constant over a considerable range of temperature, then increase very rapidly to reach a maximum and finally decrease quite rapidly before going to isotropic phase. In the mixture A_7 , $\Delta\epsilon$ values become close to those of pure 5OCB (at low T it is about 10), decrease quite fast with temperature and no discontinuity is observed at T_{SN} or at T_{NI} as has been observed in pure 5OCB. Thus the behaviour of $\Delta\epsilon$ in the mixtures, like other dielectric parameters, is dominated by the dielectric behaviour of 5OCB when its concentration becomes 50% or more.

Since $\epsilon_{||}$ and $\bar{\epsilon}$ decrease slightly and ϵ_{\perp} slightly increases as the concentration of 5OCB starts increasing, the value of $\Delta\epsilon$ decreases with concentration. From the simple additivity rule ($\Delta\epsilon_{AB} = x_A \Delta\epsilon_A + x_B \Delta\epsilon_B$) [7] the expected value of $\Delta\epsilon$ at 80°C in A_1 is 0.966 and that in A_2 is 1.776 whereas the observed values are 1.509 and 1.235. (In case of 5OCB value of $\Delta\epsilon$ at 66°C was used in this calculation since its

T_{NI} value is 67.4°C). Therefore, simple additivity rule does not depict the real situation in these mixtures also as had been observed in other mixtures [8]. Moreover, the observed drop in $\Delta\epsilon$ in A_2 compared to A_1 is due to the increased dipolar correlation in the induced SmA phase. From equation 2.28 (Chapter II) it is clear that $\Delta\epsilon$ increases with $\Delta\alpha$ and it decreases with increasing value of the effective dipole moment (μ_{eff}) that, in the present case, happens with increasing temperature (Figure 5.5 below). $\Delta\alpha$ and S do not change appreciably with T in the low T region but they decrease rapidly in high T region as described in Chapter IV. Thus it may be inferred that μ_{eff} contributes more to $\Delta\epsilon$ in low T region while in high T region contribution of $\Delta\alpha$ is more. In nematogenic binary mixtures – like PAA + MBPAA [9] or ChP + NOBA [10] – even sign reversal of $\Delta\epsilon$ with temperature has been reported depending upon the relative contribution of $\Delta\alpha$ and μ_{eff} in $\Delta\epsilon$.

In all the mixtures the value of the dielectric constant in the isotropic phase (ϵ_{iso}) is found to increase with temperature which, according to equation 2.30 (Chapter II), means that either α_{iso} or μ_{eff} or both increase with temperature. Though above T_{NI} normal expected behavior of ϵ_{iso} is to decrease with increasing T , values of ϵ_{iso} were also found to increase with temperature as observed in these mixtures. Such increasing effect has been observed in 7CB [11] (in which similar results for many other systems have been reported, also reference of similar unusual behaviour of several other physical properties have been given) in 8CB [12], in mixtures involving 5CB [13]. ϵ_{iso} is found to remain constant with T in mixtures involving 7CB [14]. Moreover, a significant discontinuity is observed between the values of ϵ_{iso} and $\bar{\epsilon}$ at T_{NI} or T_{SI} transition. The discontinuity is found to be maximum (about 8% change) at $x_{5\text{OCB}} = 0.5$. Such phenomena have been reported in many systems with high axial dipole moments [15-18] and no such behaviour is encountered in non-dipolar or weakly dipolar liquid crystal systems [6,19]. This again suggests [20,21] the presence of anti-parallel homo (or hetero) dimers in both smectic and nematic phases, in the isotropic phase monomer concentration increases at the expense of dimers. This has also been explained as a result of coupling of the

Table 5.1

Effective dipole moments, inclination angles and correlation factors for all the mixtures at some selected temperatures

5OCB+5OAB														
x=0.15					x=0.25					x=0.35				
T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}
108	2.22	44.9	1.06	0.45	110	2.01	44	1.61	0.66	110	2.46	48.2	0.90	0.48
100	2.09	46	0.97	0.29	100	1.72	49.5	1.43	0.51	100	2.30	49.5	0.80	0.41
92	2.01	46.4	0.93	0.19	90	1.50	56.1	1.27	0.42	90	2.18	54.3	0.66	0.37
88	1.99	46.9	0.92	0.17	80	1.37	57.4	1.20	0.36	80	2.13	54.6	0.63	0.35
80	1.96	48	0.89	0.15	70	1.32	58	1.16	0.34	70	2.10	54.8	0.62	0.34
x=0.50					x=0.75					x=0.875				
T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}
120	2.99	52.8	1.02	0.81	105	3.61	53.1	0.96	1.00	80	3.43	43.2	0.76	0.71
110	2.87	56.1	0.89	0.75	100	3.38	52.3	0.85	0.86	72	3.31	33.6	0.82	0.54
100	2.75	57.5	0.80	0.68	90	3.03	47.8	0.76	0.60	63	3.19	29.6	0.79	0.43
90	2.64	57.9	0.74	0.61	80	2.84	45	0.71	0.48	54	3.16	29.2	0.78	0.39
80	2.57	58.3	0.70	0.57	70	2.62	42.3	0.64	0.35	47	3.16	29.6	0.77	0.38
70	2.52	58.5	0.67	0.55	60	2.50	42.8	0.58	0.32					
5OCB+6OAB														
X=0.15					X=0.25					X=0.50				
T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}
110	3.00	51.5	1.54	1.39	120	3.00	48	1.21	1.15	120	3.32	53.9	1.18	1.02
98	2.75	52.2	1.32	1.11	110	2.77	50.1	0.98	0.96	110	3.12	54.6	1.04	0.88
90	2.63	52.9	1.21	0.95	100	2.61	50.8	0.88	0.81	100	2.91	55.2	0.92	0.76
82	2.54	52.6	1.16	0.86	90	2.49	51.9	0.78	0.74	90	2.78	55.8	0.83	0.67
74	2.47	53	1.09	0.80	80	2.40	52.8	0.71	0.67	80	2.67	56.5	0.76	0.61
					70	2.27	53.3	0.65	0.60	70	2.57	57.1	0.70	0.56
X=0.75					X=0.85									
T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}					
100	3.22	43.3	0.66	0.70	88	3.65	40.7	0.69	0.84					
90	3.00	45	0.56	0.61	80	3.61	36.3	0.68	0.88					
80	2.86	46.1	0.50	0.56	70	3.51	34.2	0.65	0.68					
70	2.76	46.6	0.46	0.52	60	3.34	32.5	0.60	0.58					
60	2.66	46.6	0.43	0.47	50	3.26	31.4	0.58	0.52					
50	2.59	46.9	0.41	0.45	40	3.18	30.8	0.55	0.48					
5OCB+7OAB														
X=0.12					X=0.15					X=0.25				
T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}
100	3.17	52.2	1.67	1.64	109	3.00	54.8	1.54	1.48	120	2.89	53.1	1.21	1.14
90	3.03	53.1	1.51	1.49	101	2.87	53.6	1.47	1.26	110	2.69	55.1	1.02	0.99
80	2.88	53.2	1.38	1.30	91	2.67	52.9	1.32	1.00	100	2.48	54.9	0.89	0.80
70	2.74	53.3	1.26	1.14	82	2.53	52.9	1.20	0.87	90	2.31	55.6	0.77	0.67
60	2.65	53.7	1.18	1.05	74	2.43	53	1.11	0.77	80	2.09	56.8	0.68	0.57
					66	2.32	53.5	1.02	0.68	70	2.08	57.1	0.63	0.50
										60	2.02	57.5	0.59	0.47
X=0.50					X=0.75					X=0.85				
T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}	T	$\mu(D)$	β	$g_{ }$	g_{\perp}
120	2.91	53.6	0.95	0.81	108	3.66	51.6	0.96	1.04	84	3.42	29.8	0.69	0.81
110	2.75	55.3	0.79	0.73	92	3.17	51	0.70	0.75	81	3.55	28	0.74	0.87
100	2.58	56.7	0.66	0.63	84	2.88	52.7	0.57	0.61	62	3.28	28.4	0.61	0.75
90	2.45	57.5	0.58	0.56	76	2.62	53.7	0.47	0.49	58	3.26	31	0.58	0.80
80	2.33	57.8	0.53	0.51	68	2.49	53.8	0.42	0.43	50	3.2	30.7	0.56	0.77
70	2.27	58.1	0.50	0.46	60	2.39	54.3	0.39	0.39	45	3.17	30.6	0.55	0.75
60	2.22	58.1	0.48	0.41	70	3.41	21.6	0.58	0.59	40	3.14	30.5	0.54	0.73

reducing residual short range nematic ordering with the intrinsic anti-parallel local ordering [11]. It was shown by Dabrowski *et al.* [22], by quasi elastic neutron scattering studies, that though in pure 5CB dimerization occurs causing steric hindrance to reorientation, in an equimolar binary mixture of (5CB + EPAB) the 5CB dimers are destroyed and complexation of 5CB and EPAB molecule takes place when the steric hindrance to reorientation of the dipoles is no longer present. Formation of this type of heterodimers after destruction of homodimers has also been reported elsewhere [23-25].

Using the observed ϵ_{\parallel} and ϵ_{\perp} data, the values of the molecular dipole moments in the mesomorphic phases of all the mixtures and their inclination angles (β) with the molecular long axes have also been calculated employing equations 2.26 and 2.27 (Chapter II). These calculated dipole moments within the mesophases are usually called effective dipole moments (μ_{eff}). Order parameter S, average molecular polarizability ($\bar{\alpha}$) and polarizability anisotropy ($\Delta\alpha$) values calculated from the measured refractive indices and densities, from Chapter IV, were used in the above calculation. Necessary Fortran program was developed. Calculated μ_{eff} and β values at some selected temperatures for all the mixtures are shown in **Table 5.1**. At this point we like to compare the calculated μ_{eff} values with the free molecular dipole moments (μ_{m}) of the pure components. It was shown for nCB series that μ_{m} did not vary appreciably for different homologues [26,27]. So the reported μ_{m} and μ_{eff} values – 4.9D and 4.67 D respectively – for 7OCB [28] have been taken as the values for 5OCB. Similarly the respective available values - 2.35D and 2.64D – of 6OAB [28] are taken as the values of μ_{m} and μ_{eff} for all the three nOAB compounds. In mixture A₁ the μ_{eff} value is found to increase from 1.91D at 72^oC to 2.33 D at 117^oC (**Figure 5.5**). This value should be around 2.94 D if calculated by simple additivity rule using the above μ_{eff} values of the components. The effective dipole moments of the molecules in the mesophase are, therefore, not only less than the molecular dipole moments of the pure compounds but also less than the values expected from additivity rule. Thus it may be inferred that anti-parallel 5OCB dimers are also present in the mixture but either their effective

moment is less than the value in pure 5OCB or μ_{eff} value of 5OAB molecules become less than the above quoted value or some hetero-dimers are formed with effective moment less than the μ_{eff} value of 5OAB molecules. In order to explain the gradual increase of μ_{eff} values with temperature, it may be assumed that the effective dipole moment of the 5OCB dimers and that of 5OAB molecules are minimum at low temperatures and they gradually increases with temperature or the number of hetero-dimers, if present, decreases with temperature. In the remaining mixtures similar temperature variation of μ_{eff} is observed. At the onset of the induced SmA phase the μ_{eff} value is indeed found to reduce from that in N phase confirming the development of additional anti-ferroelectric type of ordering as envisaged while discussing the concentration and temperature dependence of the dielectric parameters. In fact the requirement of reduced steric force to induce smectic phase is facilitated by the enhanced anti-ferroelectric type of ordering of the dipoles. When the concentration of 5OCB is increased further the value of μ_{eff} is also found to increase as expected.

In 1OAB, the molecular dipole was found to be inclined to the molecular axis at an angle (β) of 71° [28]. In the present mixtures (except A₇) the calculated β values are found to vary between 40 - 60° . Therefore, it might be inferred that the inclination angle of the effective dipole moments is reduced considerably from that of the host molecules due to the axial dipole moments of the guest 5OCB molecules. Moreover, as expected, the β values are found to decrease with increasing concentration of 5OCB.

In order to get a quantitative idea about the nature and extent of associations of the molecules in the mixtures, the value of the Kirkwood correlation factor (g) has also been calculated using Bordewijk theory of anisotropic dielectrics [29]. The correlation factor, as described in Chapter II, is defined as

$$g_\lambda = \frac{\left\langle \sum_{i \neq j} (\mu_\lambda)_i (\mu_\lambda)_j \right\rangle}{\left\langle \mu_\lambda^2 \right\rangle} \quad (1)$$

where correlation between the neighbouring dipole moments has only been taken into account, the subscript λ refers to axes \parallel and \perp to the molecular axes. The following expression was used for calculating g_λ :

$$\varepsilon_\lambda - \varepsilon_{\infty\lambda} = \frac{4\pi N \varepsilon_\lambda (\varepsilon_{\infty\lambda} + 2)^2}{9kT (2\varepsilon_\lambda + \varepsilon_{\infty\lambda})} \langle \mu_\lambda^2 \rangle f_\lambda(\varepsilon, \Omega_\lambda^\varepsilon) g_\lambda \quad (2)$$

where

$$f_\lambda(\varepsilon, \Omega_\lambda^\varepsilon) = \frac{2\varepsilon_\lambda + \varepsilon_{\infty\lambda}}{\varepsilon_\lambda - (\varepsilon_\lambda - \varepsilon_{\infty\lambda})\Omega_\lambda^\varepsilon} \quad (3)$$

$\Omega_\lambda^\varepsilon$ is a factor which depends on the dielectric anisotropy of the system. The subscript ∞ signifies value at optical frequency. The value of $\varepsilon_{\infty\lambda}$ was taken as $1.05.n_\lambda^2$ to take into account the atomic polarization factor. The ensemble averages of the two components of the dipole moments were calculated following a procedure described by Bata and Buka [28]. Since the authors are not aware of any modifications of the above theory for calculating g_λ in mixtures, the weighted average of μ_λ of the components was used in place of μ_λ while calculating the ensemble averages. In addition, measured densities, \parallel and \perp components of the dielectric permittivities and the refractive indices, apparent molecular length in N phase or layer spacing in SmA phase determined from X-ray measurements and order parameters S determined from refractive indices data were used. Details of the calculation procedure has been described elsewhere [30]. For computations a software was developed by us. Calculated g_λ values at some selected temperatures are shown in **Table 5.1**. Here $g_\lambda = 1$ means no correlation, $g_\lambda = 2$ means perfect parallel correlation and $g_\lambda = 0$ means perfect anti-parallel correlation. In mixture A₁ the value of g_\parallel increases from 0.84 to 1.06 and g_\perp from 0.14 to 0.68. This means components of the effective dipole moment parallel to the molecular axes are arranged in slightly antiparallel manner at low temperature, as the temperature is increased these correlations gradually disappear. On the other hand, at low temperature the perpendicular components of the effective dipole moment are

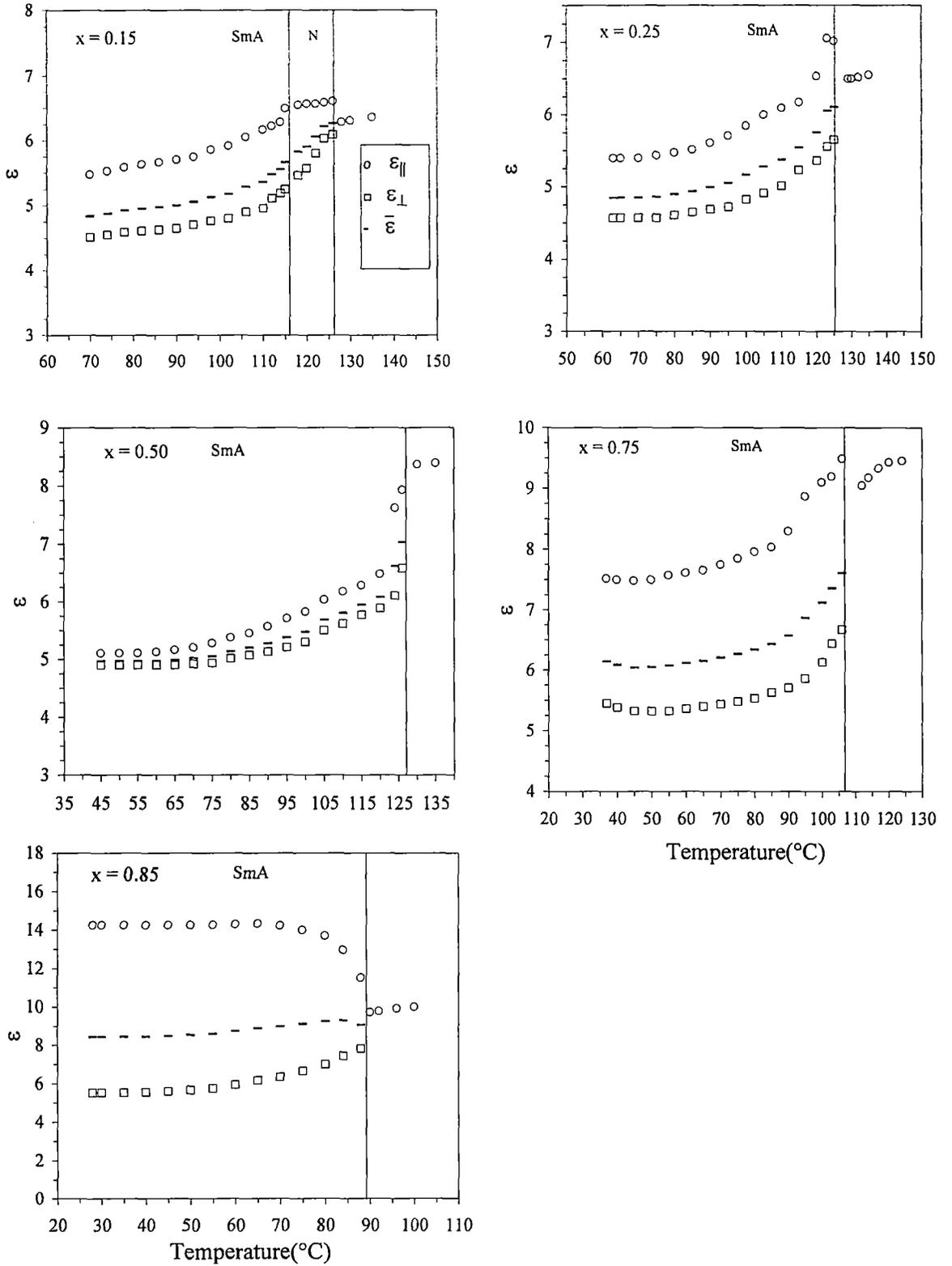


Figure 5.6. Temperature variation of dielectric parameters of mixture B. x is the mole fraction of 5OCB.

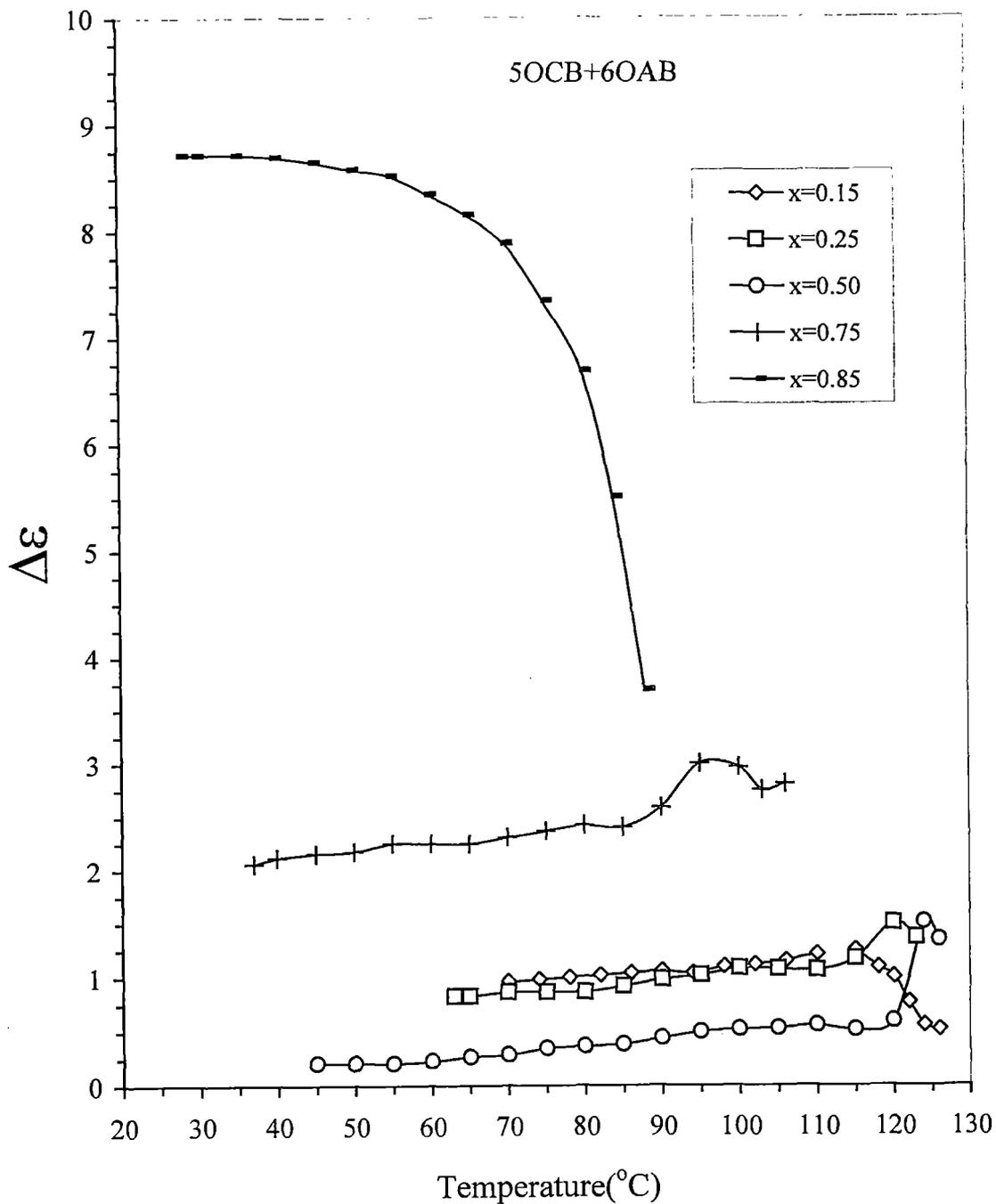


Figure 5.7. Temperature variation of dielectric anisotropy of mixture B. x is the mole fraction of 5OCB. Lines are guide to eye only.

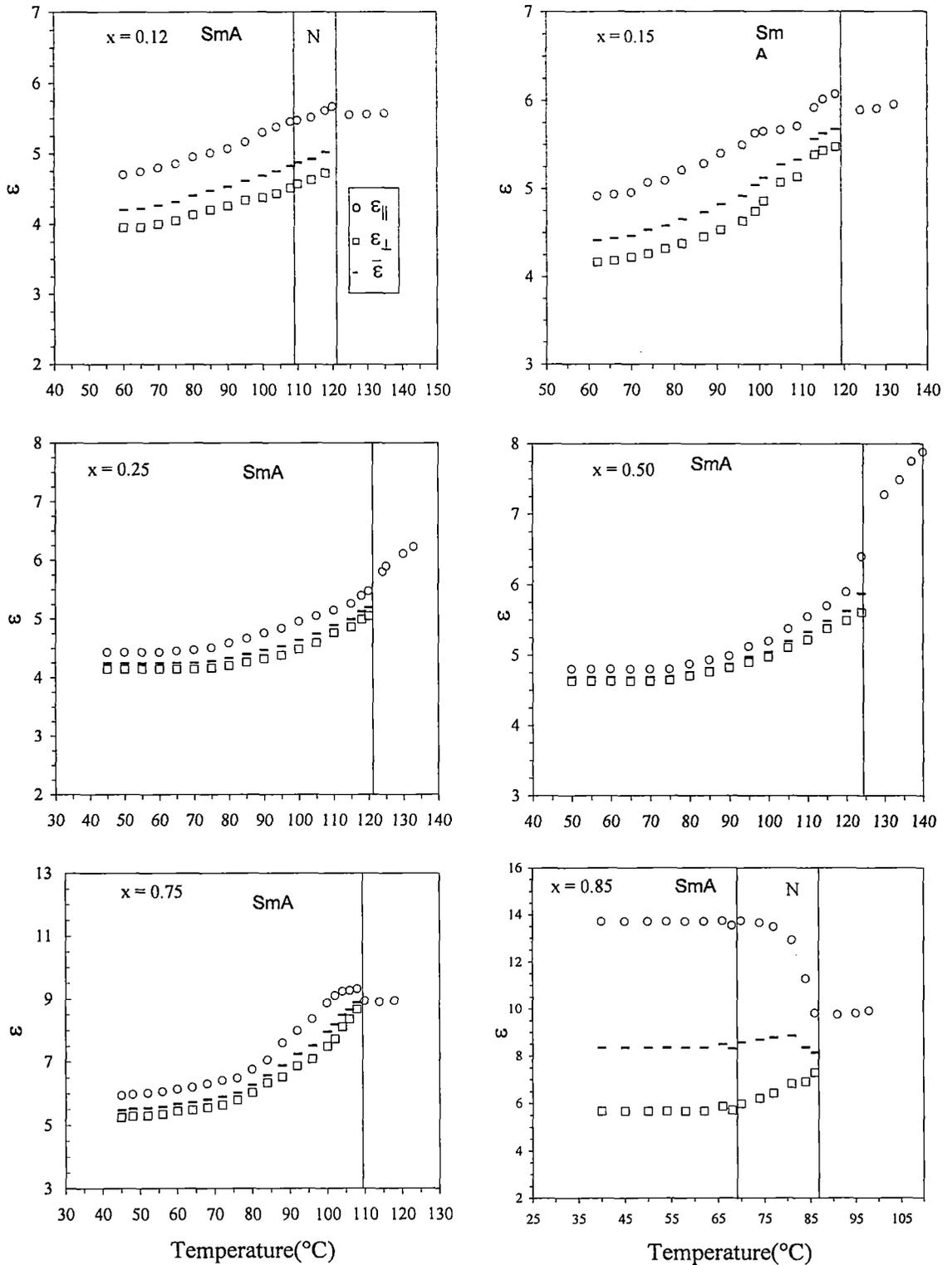


Figure 5.8. Variation of dielectric parameters with temperature of mixture C. x is the mole fraction of 5OCB.

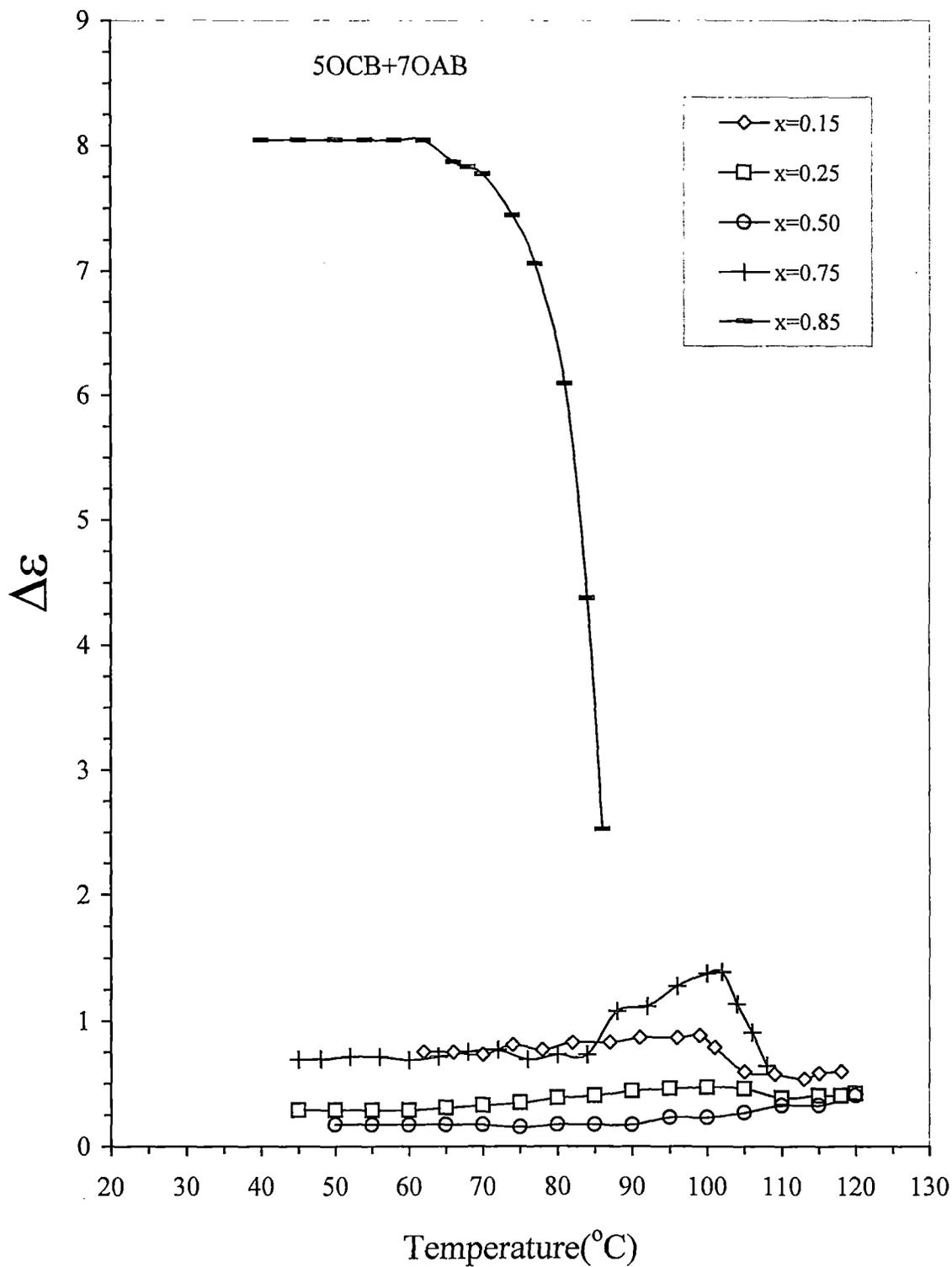


Figure 5.9. Variation of dielectric anisotropy with temperature of mixture C. x is the mole fraction of 5OCB. Lines are guide to eye only.

arranged in almost perfect anti-parallel fashion. The correlation gradually decreases with temperature but not completely destroyed even at high temperature. In mixtures with smectic phase similar type of correlation exists at low temperatures, only the extent of correlation is changed. For example in mixture A₄ the value of g_{\parallel} increases from 0.63 to 1.25 and g_{\perp} from 0.51 to 1.19. At higher temperatures, therefore, both the components show small but distinct parallel correlation. At $0.98T_{NI}$ the axial polar compounds 7CB showed [31] strong anti-parallel correlation of the parallel component of μ_{eff} ($g_{\parallel} = 0.30$) whereas two off-axis polar compounds PCPB and OCHB showed less ($g_{\parallel} = 0.57, 0.67$) correlation like the present mixtures [19]. Strong anti-parallel correlations in both the components of μ_{eff} have been observed in all members of isothiocyanatobenzenes [18].

Temperature dependence of the dielectric parameters - ϵ_{\parallel} , ϵ_{\perp} , $\bar{\epsilon}$ and $\Delta\epsilon$ - have been depicted in **Figures 5.6-5.7** for the mixtures B and in **Figures 5.8-5.9** for the mixtures C. From these figures it is evident that no significant change in the dependence of permittivity parameters on temperature takes place in these mixtures from that in mixture A. Similarly no significance departure is noticed on the dependence of the dielectric parameters on concentrations.

Variations of ϵ_{\parallel} , ϵ_{\perp} , $\bar{\epsilon}$, $\Delta\epsilon$ and ϵ_{iso} with concentrations are shown in **Figures 5.10-5.12** to see how these parameters behave in different mixture systems i.e. when the chain length of the host nOAB molecules is changed. All data in **Figures 5.10-5.12** are at $80^{\circ}C$ except the point corresponding to $x=0.875$ in the mixture A₇. This datum is at $73^{\circ}C$, $10^{\circ}C$ below T_{NI} of A₇. Values of ϵ_{\parallel} are found to decrease with chain length in all the mixtures up to $x_{5OCB} = 0.25$, however, in the mixtures B and C this is true in all compositions. ϵ_{\perp} values do not exhibit any such systematic variation with chain length. In all the mixtures ϵ_{\parallel} shows a decreasing trend at low concentrations but it increases very fast at concentrations above $x=0.5$. However, in all mixtures ϵ_{\perp} increases throughout, but slowly at low concentrations and very fast at high concentrations. The nature of variation of $\bar{\epsilon}$ with concentration is similar to that of ϵ_{\parallel} only it increases quite fast for $x_{5OCB} \geq 0.35$ in all the mixtures. Up to $x_{5OCB}=0.5$, values of $\bar{\epsilon}$ are found to be almost equal in A and B but considerably

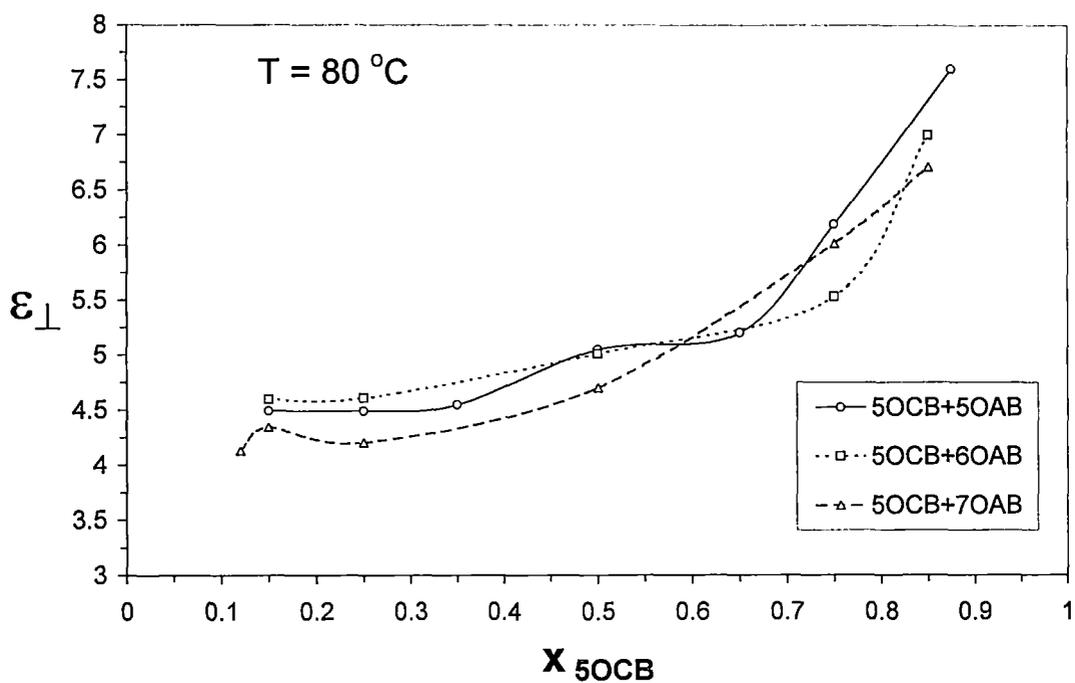
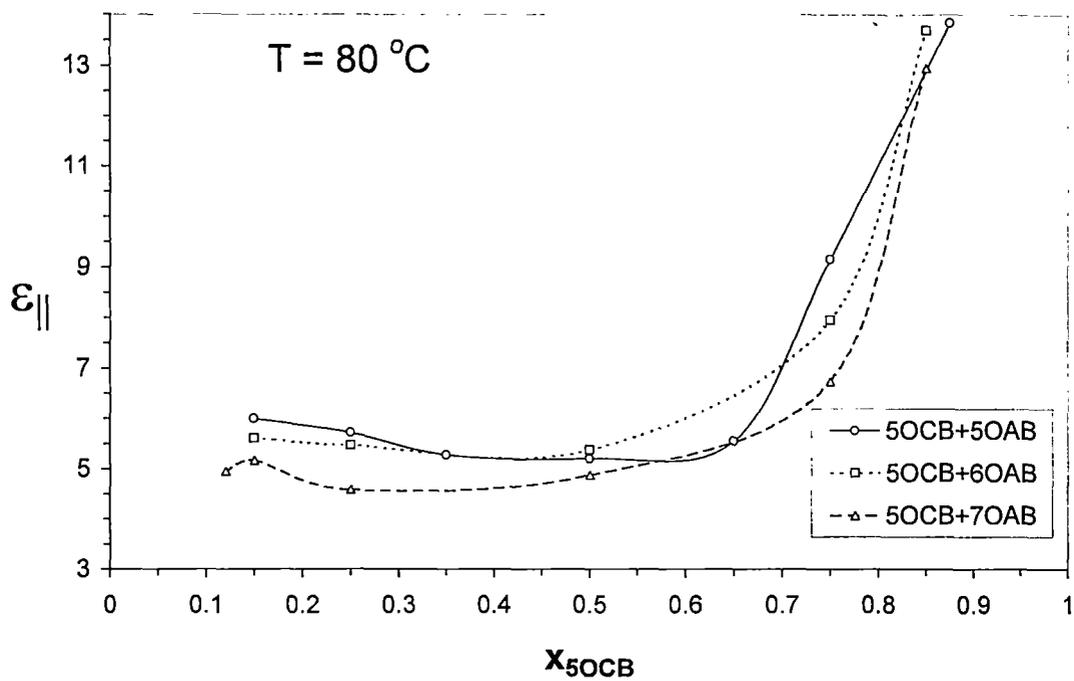


Figure 5.10. Concentration variation of dielectric permittivities $\epsilon_{||}$ and ϵ_{\perp} for all the mixtures. Lines are guide to the eye only.

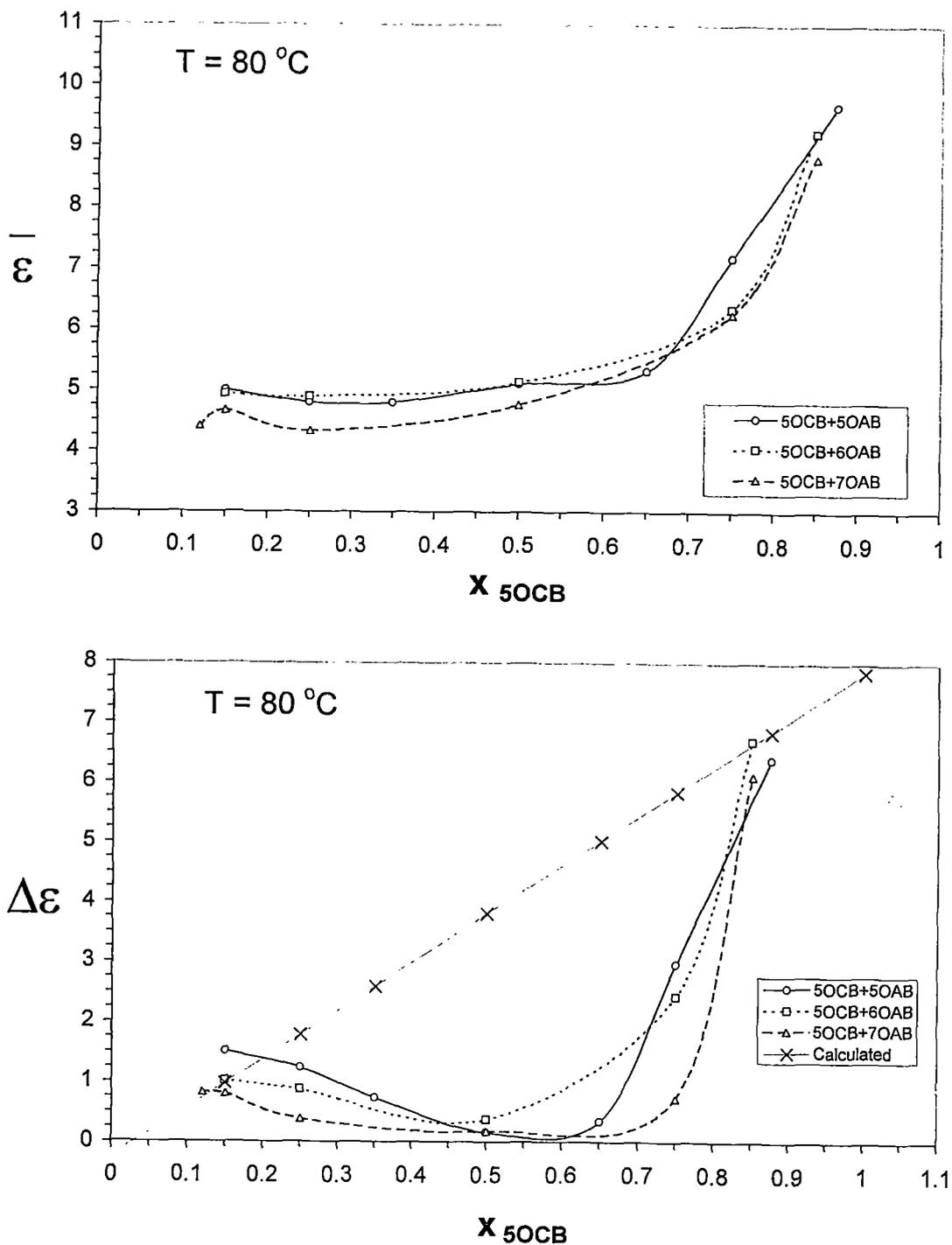


Figure 5.11. Concentration variation of $\bar{\epsilon}$ and $\Delta\epsilon$ for all mixtures. Anisotropy Value calculated from additivity rule for A are shown. Lines are guide to the eye only.

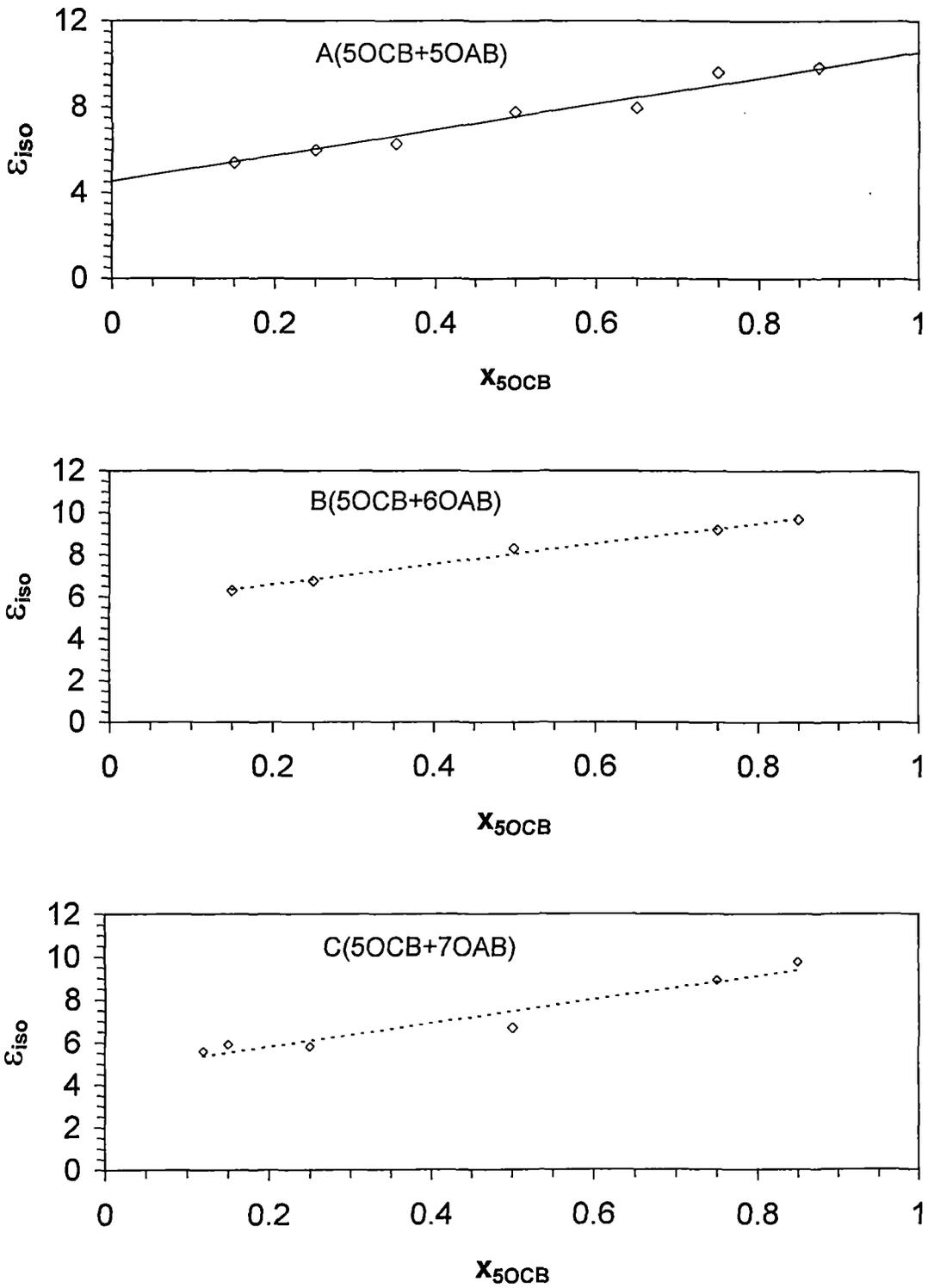


Figure 5.12. Concentration variation of ϵ_{iso} at $1.02 \times (T_{NI} \text{ or } T_{SI})$. In mixture A solid lines are values calculated from additivity rule. Other lines are guide to the eye only

less in C. On further increase of concentrations, $\bar{\epsilon}$ decreases with chain length except at $x_{5OCB} = 0.65$ in A. From **Figure 5.11** the dielectric anisotropy is found to decrease with chain length up to $x_{5OCB} = 0.5$ beyond which this trend is observed only in mixtures B and C. In all the mixtures $\Delta\epsilon$ also decreases with concentration, becomes minimum at $x_{5OCB} = 0.5$ and then increases very fast like $\epsilon_{||}$ and $\bar{\epsilon}$. But observed $\Delta\epsilon$ values are positive in all the mixtures at all concentrations. This suggests that the dielectric properties of all the mixtures are mainly governed by the dielectric behaviour of the guest 5OCB molecules. It may be mentioned here that mixtures B and C show maximum thermal stability at $x_{5OCB} = 0.5$ where a minimum in $\Delta\epsilon$ is observed. Maximum stability of mixture A occurs, however, at around $x_{5OCB} = 0.35$.

In **Figure 5.11**, the values of $\Delta\epsilon$, calculated from simple additivity rule only for the A mixtures, are also shown for comparison. We could not calculate $\Delta\epsilon$ for mixtures B and C since relevant data were not available. Moreover, in the above calculation $\Delta\epsilon$ value of 5OCB at 66°C was used since its T_{NI} value is 67.4°C as stated earlier. It is observed from the graph that negative mixing effect takes place in all the A mixtures except in A_1 . The negative mixing effect increases with concentrations up to $x_{5OCB} = 0.5$ and beyond that it decreases. This has been explained before in terms of the development of additional anti-ferroelectric type order at the induction of SmA phase. When concentration of 5OCB exceeds 50%, this negative effect of additional anti-ferroelectric order is surpassed by the increased molecular polarizability. Mixtures B and C behave in a similar manner. However, positive mixing effect had also been reported before [10,25].

Concentration variations of dielectric constants in the isotropic phase (ϵ_{iso}) at $1.02T_{NI}$ (or $1.02T_{SI}$) are shown in **Figure 5.12**. In all the mixtures ϵ_{iso} is found to increase linearly with concentrations, no systematic variation is, however, observed with chain length. It increases from 5.40 to 9.85 ($x_{5OCB} = .15$ to $.875$) in A, from 6.29 to 9.70 ($x_{5OCB} = .15$ to $.85$) in B and from 5.90 to 9.77 ($x_{5OCB} = .15$ to $.85$) in C. For the mixture A the ϵ_{iso} values expected from the additivity rule are also shown in **Figure 5.12** and the observed values are found to agree nicely with the calculated

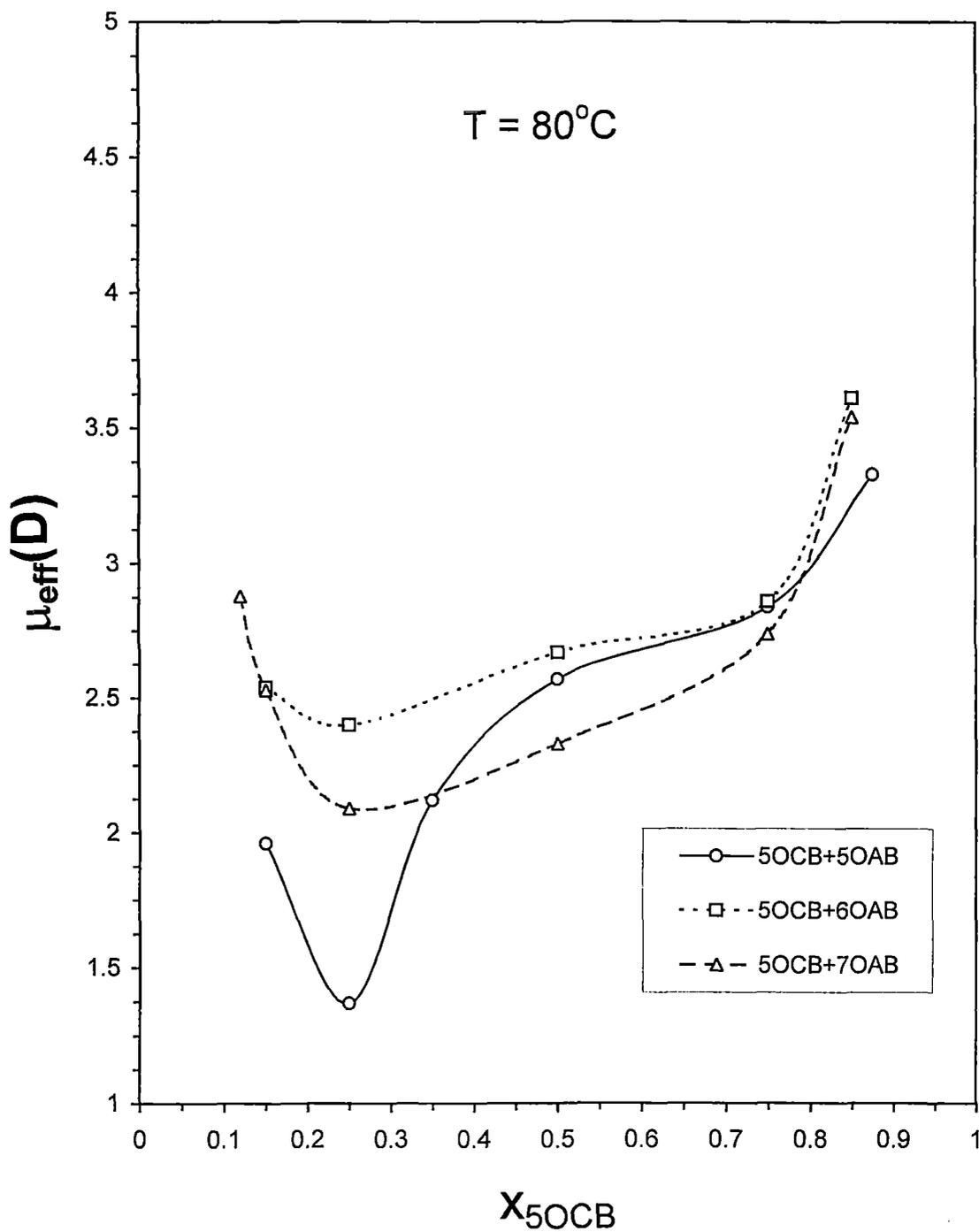


Figure 5.13. Concentration variation of effective dipole moments for all the mixtures. Lines are guide to eye only.

values. Since ϵ_{iso} values for 6OAB and 7OAB were not available it was not possible to show the calculated values for mixtures B and C. Agreement of the calculated and observed values means that the nature of molecular associations in the isotropic phase of the mixtures is similar to that of the pure components. Increase of ϵ_{iso} with concentrations may be due to increase of either the effective polarizability or the effective dipole moment of the molecules in the mixtures or the both with concentration. As mentioned before, this may happen due to increase of monomer concentration at the expense of dimmers.

The nature of temperature and concentration variations of μ_{eff} in mixtures B and C is also similar to that in mixture A. For example, it is seen from **Table 5.1** that the μ_{eff} values increase smoothly with temperature in mixtures B₁ and C₁ as is observed in the mixture A₁. Similarly at the onset of SmA phase μ_{eff} values decrease from those in the nematic phase. This effect is substantially more in A than in B and C. Then with increasing concentration of the guest molecules μ_{eff} values increase as before. The minimum value of μ_{eff} in C lies in between those of B and A and in all the mixtures it occurs at $x_{5\text{OCB}}=0.25$. All these features are clearly depicted in **Figure 5. 13**. Calculated g_{\parallel} and g_{\perp} values in the mixtures B and C also show similar trend as observed in mixture A. These observations suggest that the nature of molecular associations in mixtures B and C is similar to what has been described in case of A. Thus it may be inferred, in general, that anti-parallel 5OCB dimers are present in all the mixtures and additional anti-ferroelectric type of ordering is developed at the induction of SmA phase.

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