

Chapter - 5

STUDY OF DIELECTRIC ANISOTROPY OF AN ESTER/BIPHENYL MIXTURE EXHIBITING AN INDUCED SMECTIC PHASE

5.1 INTRODUCTION

In many binary systems consisting of nematic compounds smectic A_d phase induction is observed although the components do not possess smectic properties^[53,57-68,99,128-131]. The specific solute-solvent interactions are responsible for the formation of induced smectic phases.

In this paper I present the results of dielectric permittivity investigation of the binary mixtures of 4-n-pentyl 4'-cyanobiphenyl (5CB) and 4-n-pentyl phenyl 4-n' hexyloxy benzoate (ME6O.5) at different compositions along with their behaviour in pure states. The mixture shows smectic A_d phase in certain composition range. To understand the formation of the induced smectic phases and their influence on the adjacent nematic phase, study of the physical properties of this mixture had been undertaken by different workers in our laboratory. Small angle x-ray diffraction study, measurement of density and optical birefringence have been performed by Das and Paul^[128,131]. The ratio of bend and splay elastic constants had been determine by Adhikari and Paul^[132], magnetic susceptibility anisotropy by Pradhan and Paul^[133]. The dielectric method is a powerful tool for studying the properties of mesophases. Static field measurements give information about the dielectric anisotropy which strongly depend on dipole organisation and dipole-dipole interactions in this phase.

5.2 RELATIVE PERMITTIVITY OF MESOPHASES

We can study the response of the mesogenic substances to the application of electric field by its dielectric behaviour. The liquid crystal molecules may possess permanent dipole moments. In addition induced dipoles are created when an external field is applied. Because of geometrical anisotropy in the molecular structures liquid crystals show anisotropic dielectric behaviour. One can determine ϵ_{\parallel} and ϵ_{\perp} , parallel and perpendicular components of dielectric permittivity by applying electric field parallel and perpendicular to the director and measuring capacities of a parallel plate capacitor C_a , C_B and C_x in the air, benzene (as standard sample) and the liquid crystal respectively as the dielectric. The expression used for this is

$$\epsilon_x = 1 + \frac{(C_x - C_e)}{(C_B - C_e)} (\epsilon_B - 1) \quad 5.1$$

where ϵ_B and ϵ_x are the relative permittivity of benzene and mesogenic substance — that of air is taken as 1.

5.2.1 Description of experimental set-up and measurement technique

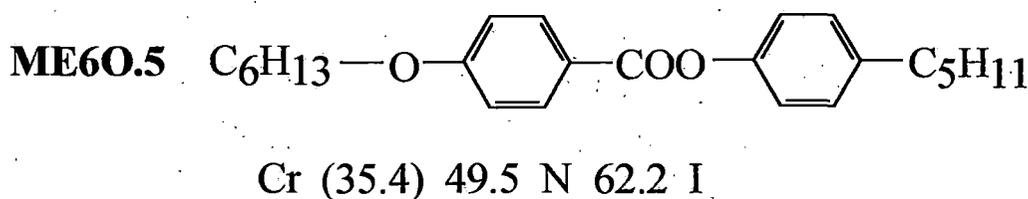
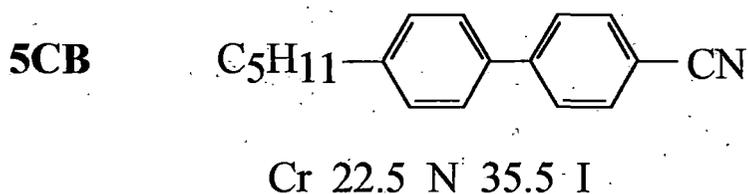
A brief description of experimental set-up has already been given in earlier paper^[134]. A cell was constructed by means of two plane tin oxide coated (thickness = 7000Å and conductivity = 10.5–11.1 Ω/\square) conducting glass plates separated by glass spacers of thickness ~ 150 μm . A small portion of the plate was previously chosen by marking it with glass cutter to keep effective area of the liquid under consideration constant. Two glass plates were sealed together in three sides by using high temperature adhesive and was baked in an oven for several hours. The conducting glass plates were given to us as gifts by Dr Murray Bennet, Solarix Thin Film Division, USA.

The prepared cell was calibrated with benzene, p-xylene, carbon tetrachloride as standard liquid and measured dielectric permittivity value were within $\pm 0.14\%$ of literature values. Capacitance of the cell was measured by a digital LCR meter bridge (VASAVI ELECTRONICS, Model No. - VLCR7) at 10 kHz. Constant voltage across the capacitor was 0.35V r.m.s., low enough not to produce any electric field induced instability. The mesogenic sample was filled into the cell as isotropic liquid and slowly cooled to the desired temperature in a magnetic field of ~ 5 kG to get aligned sample. The cell was housed in a thermostated block and its temperature was controlled within $\pm 0.5^\circ\text{C}$. Then ϵ_{\parallel} and ϵ_{\perp} were measured with the same cell at varying temperatures keeping the electric field parallel and perpendicular to the director respectively. From the values of ϵ_{\parallel} and ϵ_{\perp} at a temperature, one can calculate the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ (for positive anisotropy) and mean relative dielectric permittivity

$$\bar{\epsilon} = \frac{1}{3} (\epsilon_{\parallel} + 2\epsilon_{\perp}). \quad 5.2$$

The principal dielectric permittivity ϵ_{\parallel} and ϵ_{\perp} were measured for 7CB at different temperatures as shown in Fig.-5.1 for the standardisation of the apparatus. These values agreed within 4% of the values given in references^[135-137].

Both the components 5CB and ME6O.5 were gifted by E. Merck, U.K. The transition temperatures ($^{\circ}\text{C}$) of the pure compounds are given below. Supercooling temperature is shown in parentheses.



Eight mixtures (1–8) with mole fractions of ME6O.5 equal to 0.2925, 0.3573, 0.4403, 0.5014, 0.5992, 0.6975, 0.7512 and 0.8155 were prepared by weighing the components and mixing thoroughly in their isotropic state. Phase transition of the components as well as their mixtures were studied by observing textures under crossed polarisers.

5.3 RESULTS AND DISCUSSIONS

Phase diagram of the mixtures is presented in Fig.-5.2. From x-ray diffraction study Das and Paul^[128] inferred that the smectic phase is an A_d phase. I observed that $\text{Sm}A_d$ phase is induced over a wide concentration range of ME6O.5 however mixtures with ME6O.5 concentration less than 0.36 and greater than 0.82 do not induced $\text{Sm}A_d$ phase. It is also noted that maximum thermal stability of $\text{Sm}A_d$ phase is around 0.65 concentration of ME6O.5. The principal dielectric permittivities for the pure compounds 5CB and ME6O.5 are presented in Fig.-5.3a

and 5.3b. Our values of ϵ_{\parallel} and ϵ_{\perp} for 5CB are consistent with other published results^[130,135,137]. The author is not aware of any published dielectric permittivity data for ME6O.5.

Though both the pure structure show positive dielectric anisotropy, their behaviours are different. Dielectric anisotropy ($\Delta\epsilon$) decreases with increasing temperature in 5CB while it is almost constant in ME6O.5. For the polar compound 5CB, $\Delta\epsilon$ is large over the entire temperature range due to the highly polar end group which lies along the director axis. Here $\bar{\epsilon}$ is less than ϵ_{iso} at T_{NI} . For the weakly-polar compound ME6O.5 $\Delta\epsilon$ is very small, ϵ_{iso} and $\bar{\epsilon}$ almost coincide at T_{NI} . These facts are in conformity with the observations of Madhusudana and Chandrasekhar^[138] that in N phase short range antiferroelectric order exists in systems having axial moments and no such ordering exists in non-polar system.

Variations of permittivity components with temperature for all the mixtures are shown in Fig. - 5.4 -5.4. The observed permittivity components of the mixtures in N phase are as expected from the simple rule of mixtures. However a significant jump in the parallel permittivity components at the smectic-nematic (Sm-N) transitions is observed in all cases. This is due to the increased antiparallel dipole-dipole correlation in the layered structure of SmA_d phase. The change of ϵ_{\perp} at the Sm-N transition is continuous at the lower and higher concentrations and is discontinuous in between. Similar effects have been observed^[130] in mixtures of 5CB and ME5O.5. But opposite behaviour was observed^[128,131] in case of order parameters. At lower and higher concentrations, change of order parameters at Sm - N transition is first order and it is second order in between.

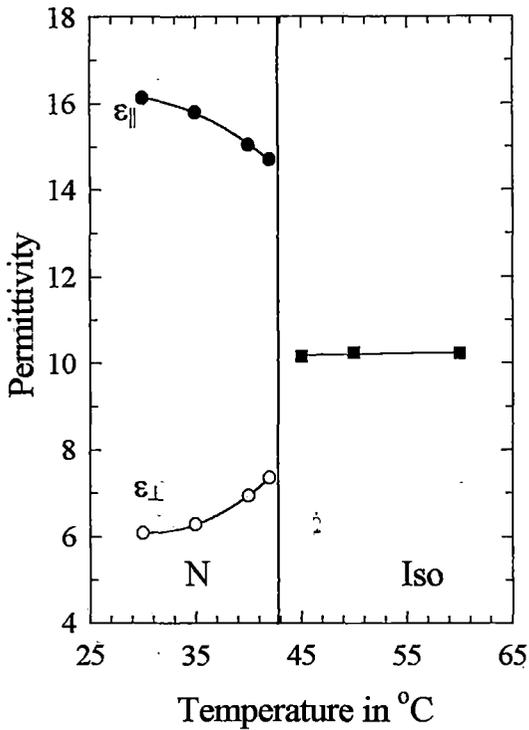


Fig. 5.1 Variation of permittivity with temperature of 7CB

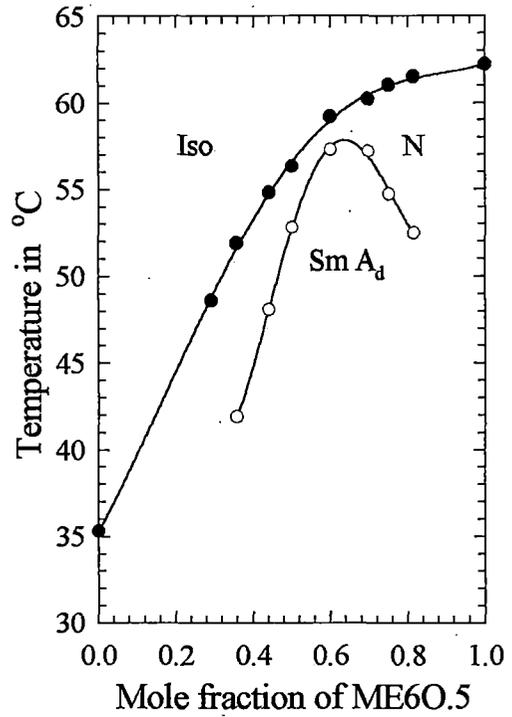
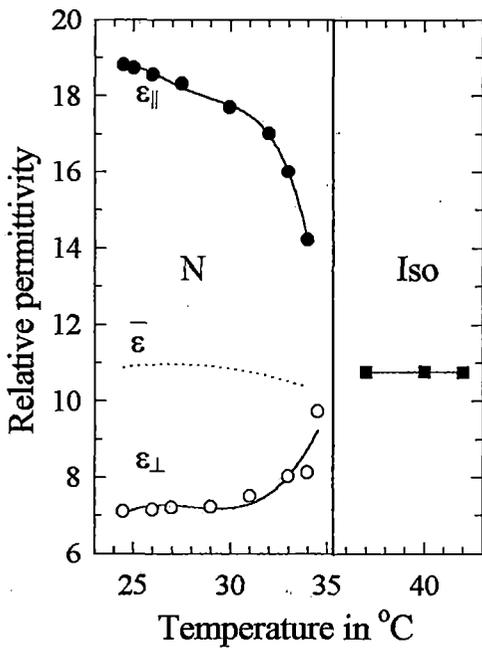
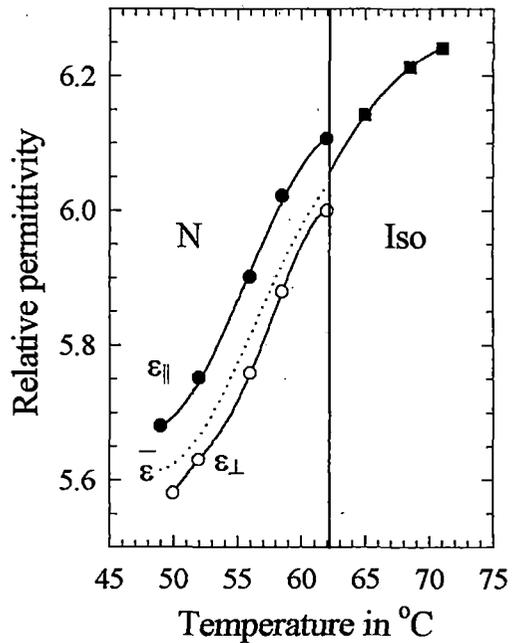


Fig. 5.2 Phase diagram of binary Mixtures (ME6O.5 + 5CB)

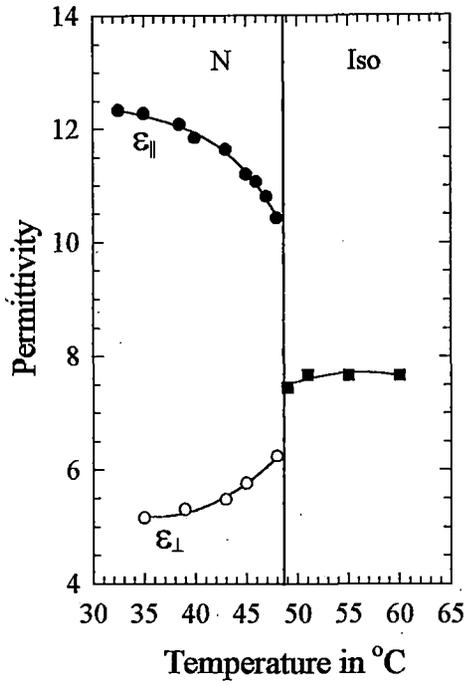


(a)

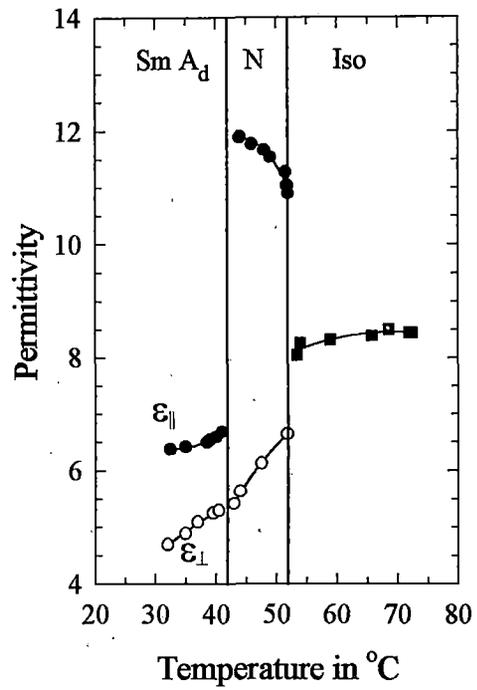


(b)

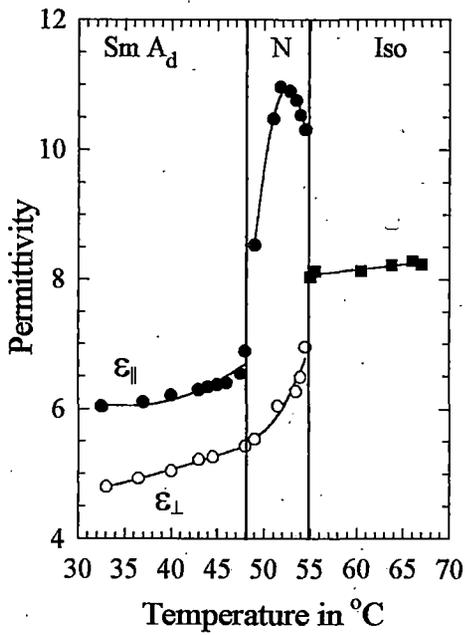
Fig 5.3 Variation of permittivity with temperature (a) 5CB, (b) ME6O.5



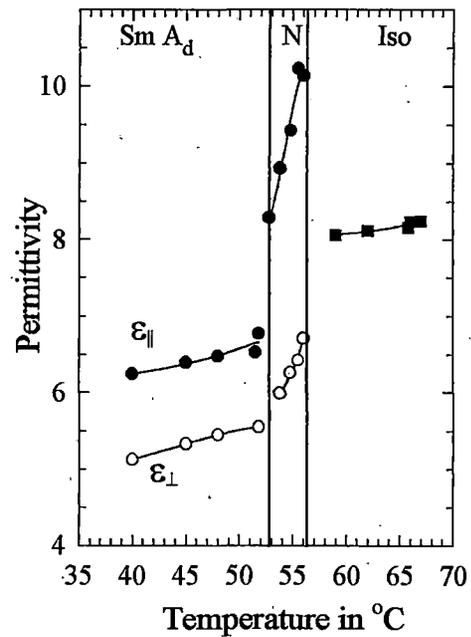
(a)



(b)

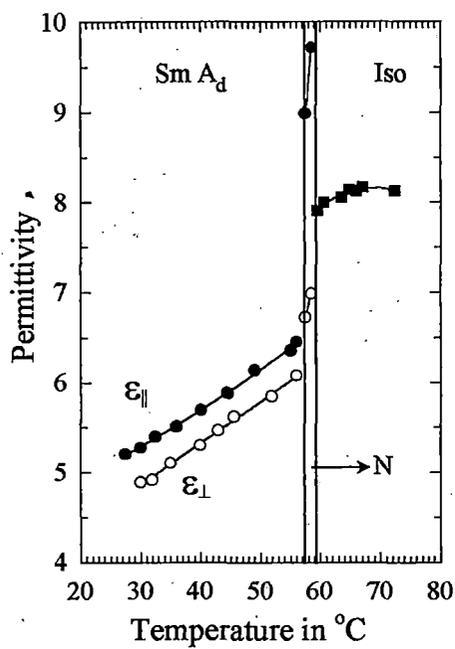


(c)

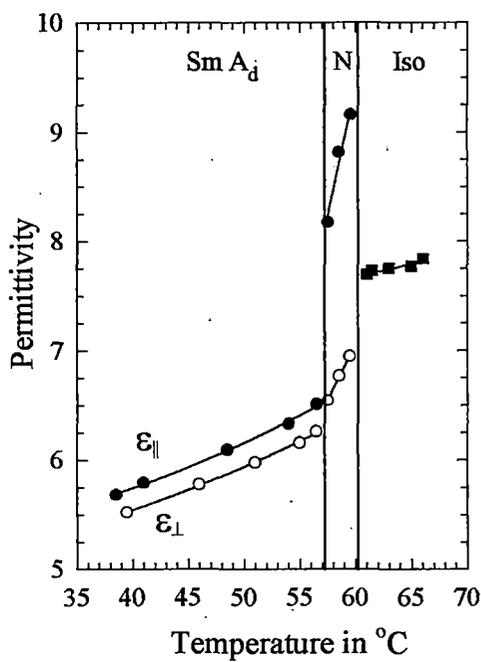


(d)

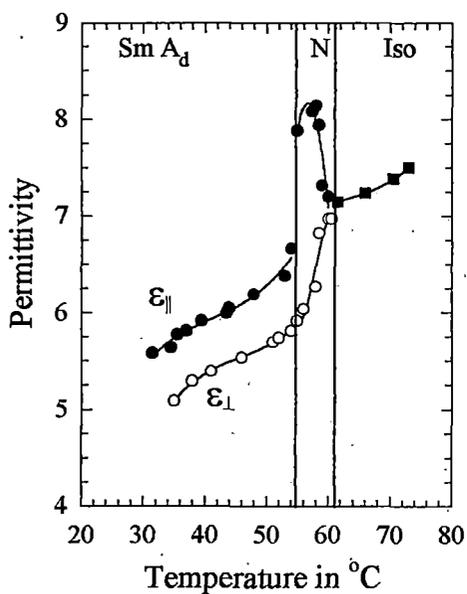
Fig. 5.4 Variation of permittivity with temperature (a) Mixture-1, (b) Mixture-2, (c) Mixture-3 and (d) Mixture-4



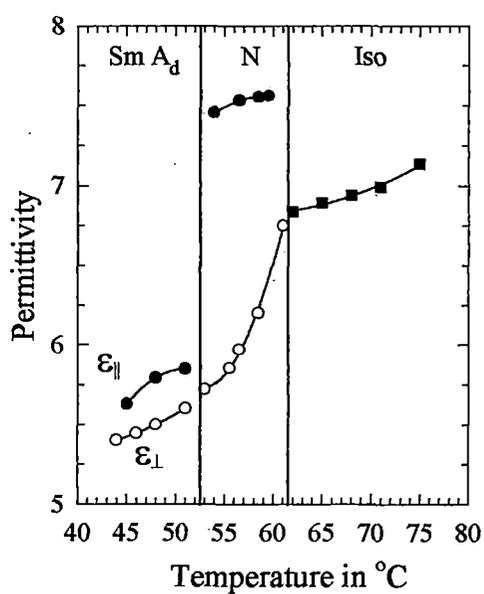
(a)



(b)



(c)



(d)

FIGURE 5 Variation of permittivity with temperature (a) Mixture-5, (b) Mixture-6, (c) Mixture-7 and (d) Mixture-8

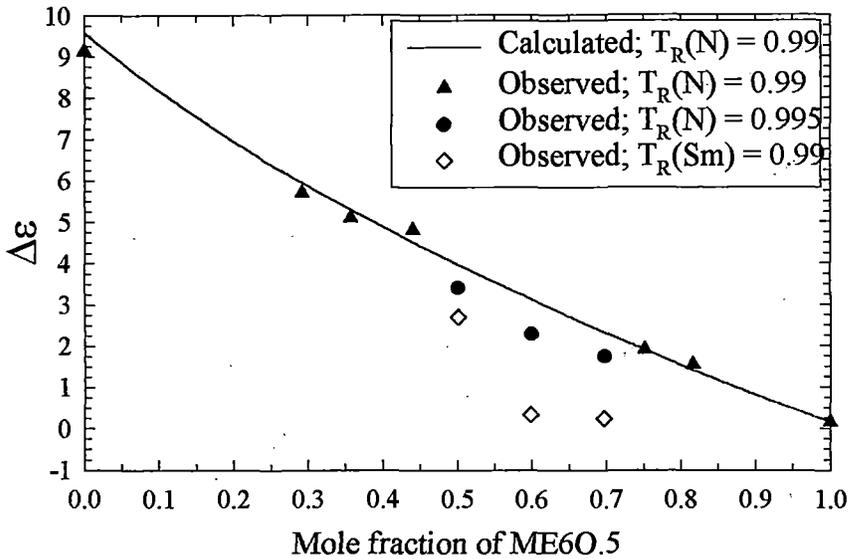


Fig. 5.6 Variation of permittivity anisotropy with mole fraction of ME6O.5

I have plotted $\Delta\epsilon$ as a function of concentration of ME6O.5 corresponding to a reduced temperature $T_R = (T/T_{NI}) = 0.99$ in Fig.-5.6. Since $T_R = 0.99$ for Mixtures-4, 5 and 6 is in the Sm A_d phase we have also shown data for $T_R = 0.995$ for those mixtures in N phase. I have also calculated the anisotropy $\Delta\epsilon$ for the mixtures using the additive rule^[130]

$$\Delta\epsilon_{12} = y_1(\Delta\epsilon_1) \left(\frac{S_{\text{expt}}}{S_{\text{cal}}} \right)_1 + y_2(\Delta\epsilon_2) \left(\frac{S_{\text{expt}}}{S_{\text{cal}}} \right)_2$$

where $\Delta\epsilon_{12}$ is the dielectric anisotropy of the mixture, y_1, y_2 are the volume-fractions of the components, S_1 and S_2 are the order parameters of the pure components at the same reduced temperature. However in the induced smectic region there are additional contributions to $\Delta\epsilon$ which are not considered in the theoretical calculations. As evident from Fig.-5.6 the calculated result for the dielectric anisotropy is in fair agreement with the experiment in the nematic phase.

It is also observed that $\Delta\varepsilon$ shows a minimum around $x = 0.65$. Similar results have been reported earlier^[130]. Variation of packing fractions, layer spacings and orientational order parameter $\langle P_2 \rangle$ from x-ray study and susceptibility measurements with molar concentration also show a minimum like this^[115,128,134,139]. At this composition, it is noted earlier, that stability of the SmA_d phase is maximum. In study of other binary mixtures having induced SmA_d phase, layer spacings show maxima rather than a minima^[68] at the composition of maximum stability which has been described in chapter 3.

I thus find that the degree of stabilisation of $Sm A_d$ phase plays a major role in determining the physical properties of the binary mixtures. The minimum values are observed probably for those concentration for which monomer concentration is large, maximum occurs when dimer concentration exceeds that of monomer.