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CALCULATION OF LAYER THICKNESS IN SMECTIC A PHASE OF BINARY MIXTURES OF TERMINAL POLAR + TERMINAL NON POLAR MESOGENS.

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Abstract The variations of layer thickness with concentration in the smectic A phase of binary mixtures of a terminal polar (A) and a terminal non-polar (B) mesogens have been calculated and compared with their experimental values for eight different mixtures. The calculation is based on assumption regarding formation of AA and AB type dimers in the mixture. The agreements between calculated and experimental layer thickness for all the mixtures are very good.

INTRODUCTION:

Binary mixtures of nematogenic compounds, one having terminal polar group and other being terminal non polar, are of considerable interest as they show some peculiar behaviours, such as formation of enhanced or injected smectic phase. We have earlier extensively studied[1,2] two such systems (both containing n-pentyl cyanobiphenyl, 5CB, as the terminal polar nematogen), showing injected smectic phase, by small angle x-ray diffraction, density and refractive indices measurements. For these two mixtures birefringence (Δn), orientational order parameters, layer thickness, density and packing fraction all exhibit minimum at about 50 percent molar concentration of the terminal polar compound 5CB. The experimentally observed variations of layer thickness with mole fraction of 5CB in these mixtures have been successfully explained by assuming the formation of both homo-dimers and hetero-dimers in the mixtures [1,2]. In the present study we have applied the same theory to explain the variation of layer thickness with concentration for six mixtures for which relevent data have been reported by others [3-8]

We have also included the two systems studied by us [1,2].

RESULTS AND DISCUSSIONS

The names of the binary compounds of different mixtures are as follows :

Mixture 1 (reference 3):

A. Cyanohexyloxy biphenyl (6OCB).

B. Butyloxybenzilidene (4O.8).

Mixture 2 (reference 4):

A. nonyl cyanobiphenyl (9CB).

B. propyl phenyl heptylbenzoate (ME 37).

Mixture 3 (reference 5):

A. 4-cyanobiphenylidine-4'-n-octyloxyaniline(CBOOA).

B. Octyloxybenzilidene pentylaniline (8O.5).

Mixture 4 (reference 6):

A. Heptyloxy benzilidine cyano propene (HBOPC).

B. 3 nonyloxy phenyl dodecyl phenyl thiazodiazole(DPNOTD).

Mixture 5 (reference 7):

A. pentyl cyanobiphenyl (5CB).

B. 4,4'-di(n-heptyl)- azoxy benzene (7AB).

Mixture 6 (reference 8):

A. 4-cyanobiphenylidine-4'-n-octyloxyaniline(CBOOA).

B. 4,4'-di-n-heptyloxyazoxybenzene (HEPTOAB).

Mixture 7 (reference 1):

A. pentyl cyanobiphenyl (5CB):

B. pentyl phenyl hexyloxy benzoate(ME6O.5).

Mixture 8 (reference 2):

A. pentyl cyanobiphenyl (5CB).

B. pentyl phenyl pentyloxy benzoate(ME5O.5).

Data for mixtures 5 and 6 were taken as reported by Tsykalo[9] , as the original references were not available to us. It is well known that pure cyanobiphenyls having terminal polar group form association in the mesophase[10]. All the terminal polar compounds reported in this paper have their apparent molecular lengths, as determined from x-ray studies on mesophase, much larger than their molecular model lengths in the most extended configurations. Thus we can assume that all these molecules form associations in their pure state in the nematic phase. We have been able to explain the observed variation of the layer thickness with composition by assuming that the terminal polar molecules (molecule A) form dimers with itself as well as with the terminal non polar molecules(molecule B). Dabrowski et

al[11] have also mentioned the possibility of formation of such homo-complexes and hetero-complexes (dimers) in the mixtures showing induced smectic phase. The apparent molecular lengths of the terminal non polar molecules as determined from x-ray studies on the pure components are almost equal to their respective model molecular lengths. Therefore, we may assume that the terminal non-polar molecules exist as monomers only in the pure compounds. Hence in the mixture we have A,B,AA and AB type of molecules in the equilibrium. The mole fraction of different species can be calculated from the equilibrium constants K_A and K_{AB} of the "chemical reactions", $A + A \Longleftrightarrow AA$ and $A + B \Longleftrightarrow AB$ respectively.

The mean layer thickness (or apparent molecular length in nematic phase) d of the smectic phase may be written as[3]

$$d = x_A d_A + x_B d_B + x_{AA} d_{AA} + x_{AB} d_{AB} \tag{1}$$

where x_A , x_B , x_{AA} and x_{AB} are mole fractions of respective components in chemical equilibrium, d_A and d_B are taken to be equal to the lengths of the molecules A and B in their most extended configuration as obtained from a molecular model kit. d_{AB} is taken as the arithmetic mean of d_A and d_B , while d_{AA} has been adjusted so that in pure terminal polar compound, which has both A and AA molecules, the apparent molecular length equals ($= x_A\ d_A + x_{AA}\ d_{AA}$) the experimentally observed d value. The value of d calculated from equation (1) using different K_A and K_{AB} values of the mixtures are shown in Figures 1 and 2. In Table I we have given different K_A and K_{AB} values which produce the best fit curve to the experimental d values of different mixtures.

TABLE I EQUILIBRIUM CONSTANTS K_A AND K_{AB} FOR MIXTURES

SAMPLE	COMPOUND A	COMPOUND B	K_A	K_{AB}	REFERENCE
MIXTURE 1	6OCB	4O.8	1000	800	Ref.3
MIXTURE 2	9CB	ME 37	1000	800	Ref.4
MIXTURE 3	CBOOA	8O.5	1000	800	Ref.5
MIXTURE 4	HBOPC	DPNOTD	1000	800	Ref.6
MIXTURE 5	5CB	7AB	1000	900	Ref.7
MIXTURE 6	CBOOA	HEPTOAB	1000	950	Ref.8
MIXTURE 7	5CB	ME 6O.5	1000	800	Ref.1
MIXTURE 8	5CB	ME 5O.5	1000	900	Ref.2

It is to be noted that the values of K_A and K_{AB} can be varied by about 10% without much change in the calculated values of d. However, it is seen from the Figures 1 and 2 that the agreement between the experimental and calculated d values is very good in each mixture reported in this paper, proving the validity of

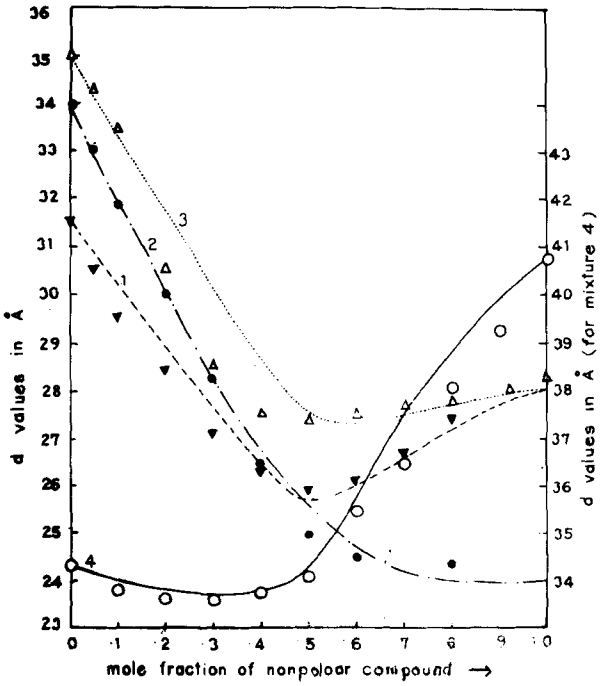

FIGURE 1 Variation of layer thickness with mole fraction of terminal non-polar compounds. Mixture 1 (4O8+6OCB) ; ▼ : experimental; dashed line : calculated. Mixture 2 (ME37+9CB) ; ● : experimental; dash-dot line : calculated. Mixture 3 (8O.5+CBOOA); Δ : experimental; dotted line : calculated. Mixture 4 (HBOPC+DONOTD); O : experimental; full line : calculated.

the assumptions made in our calculations. Furthermore, the K values obtained from the three different mixtures for 5CB are the same and similarly the K determined for CBOOA from two different mixtures have the same values (Table I). This shows the consistency of the model used by us.

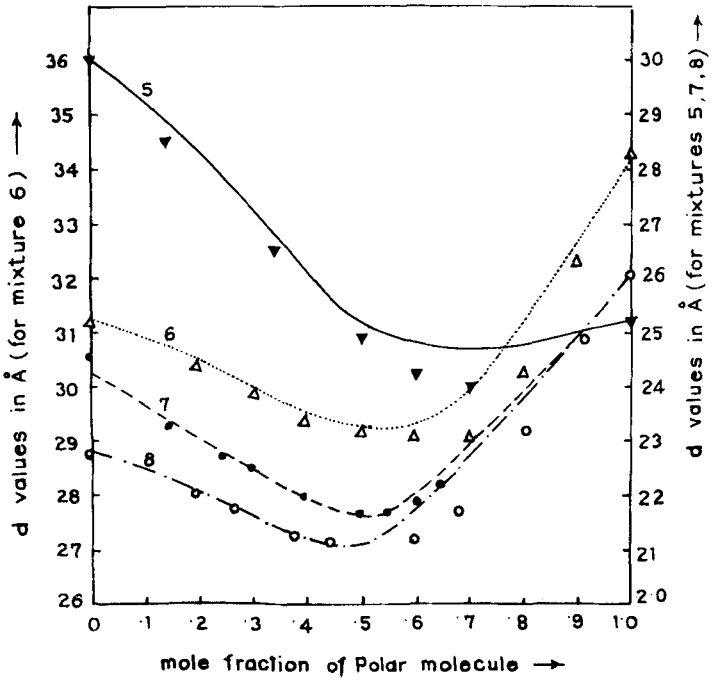

FIGURE 2 Variation of layer thickness with mole fraction of terminal polar compounds. Mixture 5 (7AB+5CB) ; ▼ : experimental; full line : calculated. Mixture 6 (HEPTOAB+CBOOA); Δ : experimental; dotted line : calculated. Mixture 7 (5CB+ME6O.5); ● : experimental; dashed line : calculated. Mixture 8 (5CB+ME5O.5); O : experimental; dash-dot line : calculated.

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