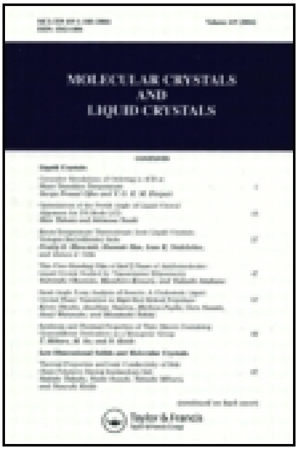

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A Mean Field Theory of Reentrant Phases in Some Binary Mixtures of Polar and Nonpolar Compounds

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A Mean Field Theory of Reentrant Phases in Some Binary Mixtures of Polar and Nonpolar Compounds

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In an earlier paper, the authors reported a mean field model for reproducing the double reentrant phase sequence of a pure compound with strong polar end groups. The present work is an extension of the earlier model to the case of a binary mixture consisting of a polar and a nonpolar component. The calculated phase diagram shows that the double reentrant polymorphism ceases to exist beyond a certain fraction of the nonpolar component. This aspect and other features of the phase diagram are in good qualitative agreement with experimental observations in some cases.

Keywords: meanfield, reentrant mixture, phase diagram

INTRODUCTION

In a previous work[1] we proposed a simple molecular mean field model that could furnish a consistent explanation of the double reentrant phenomenon in pure compounds of polar molecules. In essence the

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model assumes that, owing to the longitudinal dipoles at the ends, the molecules form dimers in antiparallel orientations which are in thermal equilibrium with the monomers. The more symmetric dimers with strong layering interaction (i.e., large value of McMillan's α parameter) form a bilayer high temperature smectic A phase with void space between them filled up with monomers. With the lowering of temperature, the dimerisation increases and beyond a critical association, for want of space filling monomers, the dimers begin to intercalate for better packing and the layer thickness as well as the strength of layering interaction decrease. This results to a situation where the nematic phase is free energetically favoured over the smectic phase. With further decrease of temperature a low temperature S_A phase reenters. This phase is virtually an all dimer phase with complete intercalation and the d/l ratio approaches unity.

The idea of intercalation in the above model entails a decrease in layer thickness with a lowering of temperature. The decrease in layer thickness with lowering of temperature is supported by experiments, e.g., Hardouin and Levelut[2] and Suresh et al.[3] This is not however a universal characteristic of the reentrant phenomenon. There are instances[4,5,6,7] where the layer thickness remains constant or in some cases, instead of decreasing, increases with lowering of temperature. A careful study of the experimental results points out that the increase or a constancy of layer thickness (with lowering temperature) is never followed by a second low temperature smectic phase with monolayer thickness. At present there exists not a single microscopic model which can explain both the above types of renetrant behaviours. The model by Longa and de Jeu[8] may be cited as an example which applies to the case where the lower smectic phase is a bilayer one. It can not explain the low temperature monolayer smectic phase. On the other hand our model[1] successfully reproduces the low temperature monolayer smectic phase but cannot explain the near constancy or an increase in layer thickness of the high temperature smectic phase. We feel that the increase in layer thickness may be due to a gradual decrease in overlap of monomers forming a dimer. This decrease means a lengthening of the core and consequently a decrease in McMillan α. This can bring about the reentrant nematic phase. Such a modification of our model would then apply to both types of situations mentioned above. As yet we have not been able to incorporate this mechanism into the self consistent scheme of our intercalation model. However the viability of the intercalation model is further tested in the present paper by reproducing a phase diagram of a binary system showing reentrant polymorphism.

To date, the following types of binary systems are known[9-13] to show reentrant polymorphism

i) Non polar-non polar
ii) Polar-non polar
iii) Polar-polar

(To be precise, polar and nonpolar compounds in this paper refer to terminally polar and terminally nonpolar compounds respectively) Out of these three the last two types are relevant to our model as it presupposes a dimer like association of molecules. In the present paper we have considered only a polar-nonpolar type of system for the sake of simplicity. A polar-polar system that can in principle be treated by the model requires a larger number of adjustable parameters as we have to deal with two different kinds of dimers.

For a polar-nonpolar system under consideration the polar component either exhibits the I-N-S_A-K mesophases or the reentrant phase sequence but the nonpolar component has usually the I-N-K phase sequence, indicating that the layering interaction in it is rather small. In this context we propose that for such binary mixtures the polar component with a strong CN or NO_2 end group will form dimers being in chemical equilibrium with monomers of itself and the nonpolar component. The nonpolar component however does not form such bimolecular organization. We further assume that the monomers in both the components have similar geometrical structures. (This assumption might appear drastic. However in so far as we are presently interested in reproducing the basic features of reentrant phase sequence irrespective of any typical sample, the above assumption appears to do away with an additional parameter in the mean field). With this we next proceed to show that the binary mixture, with a lowering of temperature exhibits the reentrant phase sequence upto a certain concentration of the second component and the phase diagram in x (concentration)-T(temperature) plane is at least in good qualitative agreement with the experimental phase diagram.

MEAN FIELD FORMULATION

We envisage the binary mixture as a three component system: the polar molecules form dimers in equilibrium with monomers represented by $D \rightleftharpoons M + M$, while the nonpolar ones have only a monomeric state. The system thus constitutes of dimers in equilibrium with monomers of two types. The interaction between them is represented by an extension of McMillan potential as elaborated in the earlier work.[1] At a given concentration (x) of the nonpolar molecules and at a given temperature, the dimer association (hereafter denoted by 'a') is determined self consistently by the chemical equilibrium consideration. The dimers (being symmetrical molecules) have a larger layering interaction strength i.e., a larger McMillan's length parameter than the monomers. Hence, starting from the N-I transition temperature, as we go down in temperature the dimers stabilize in a bilayer smectic phase with a layer spacing equal to the length of dimers (hereafter to be referred as H.T.S_A phase or S_{Ad} phase).

It is worthwhile to recall the active role ascribed in our earlier work to the monomers for bringing about the bilayer smectic phase. The dimers when arranged in layers, leave out void space which per dimer is estimated to be the difference in volume between that of a dimer and a right cylinder of length and cross section equal respectively to the length of a dimer and cross section of its central core. At high temperature, there are plenty of monomers to fill in these void spaces. As the temperature goes down, more and more dimers are formed. Above a certain value of the association parameter (which can be determined from the geometry of dimers and monomers) there are not enough monomers to fill in the void spaces and consequently the dimers belonging to the neighbouring layers begin to intercalate. This causes a decrease in layer thickness. The core length of the dimers remaining unchanged we have a decrease in the value of McMillan's parameter α and hence a reentrant nematic phase results. In the above description of the model it is clear that the monomers, so to say, prop up the dimers in a bilayered arrangement. In other words the high temperature smectic phase is assumed to be an 'induced' smectic phase of monomers and dimers. This was incorporated in our model by taking a large layering interaction between the monomers and dimers. In the present case of a mixture we, however, have to deal with two kinds of monomers. The absence of H.T.S_A phase, in experimental observations, for higher concentration of nonpolar monomers suggests that we should ascribe different roles to these two types of monomers. We therefore assume that the polar monomers play the same active role as in our earlier work while the nonpolar monomers behave rather indifferently. This can be incorporated in our present work by taking a very weak layering interaction between the dimers and the nonpolar monomers. Therefore, even in the presence of a nonpolar component, the H.T.S_A phase is brought about by the dimer-dimer and the polar monomer-dimer interaction. As the temperature goes down the effective layering interaction decreases because of the continual decrease of layer thickness and eventually a reentrant nematic phase becomes free-energetically favoured over the smectic phase. With further lowering of temperature we approach a situation where the polar component is totally dimerized. At this stage the intercalation is complete and no further decrease in layer thickness is possible. At even lower temperature a second smectic phase reenters with completely intercalated dimers i.e., the layer thickness is equal to the monomer length (hereafter to be referred as L.T.S_A phase or S_{A1} phase). It should be mentioned that the nonpolar monomers present are randomly distributed in the layers filling in the intervening spaces in between the totally intercalated dimers. The nonpolar monomers can however give rise to an average layer thickness of low temperature smectic phase (L.T.S_A) different from the length of a polar monomer. In our model we have assumed, for the sake of simplicity, that the size of the two types of monomers are the same and hence any possible effect of non-polar monomer length on the layer thickness of the L.T.S_A phase has been ignored.

With these remarks we now proceed to write down the self consistent equations.

The mean field experienced by the monomers and the dimers of type 1 (polar component) and monomers of type 2 (non polar component) can be written as

$$\begin{aligned} V_M = &- \Bigg[(1-x)\Bigg\{(1-a)\, V_{mm}\left(\eta_m + \sigma_m\, \alpha_{mm} \cos\frac{2\pi Z}{d}\right) \\ &+ a\, V_{md}\left(\eta_d + \alpha_{md}\, \sigma_d \cos\frac{2\pi Z}{d}\right)\Bigg\} \\ &+ x\, V_{m2}\left(\eta_2 + \alpha_{m2}\, \sigma_2 \cos\frac{2\pi Z}{d}\right)\Bigg]\, P_2(\cos\theta_m) \end{aligned} \tag{1a}$$

$$\begin{aligned} V_D = &-\Bigg[(1-x)\Bigg\{a\, V_{dd}\left(\eta_d + \alpha_{dd}\, \sigma_d \cos\frac{2\pi Z}{d}\right) \\ &+ (1-a)\, V_{dm}\left(\eta_m + \alpha_{dm}\, \sigma_m \cos\frac{2\pi Z}{d}\right)\Bigg\} \\ &+ x\, V_{d2}\left(\eta_2 + \alpha_{d2}\, \sigma_2 \cos\frac{2\pi Z}{d}\right)\Bigg]\, P_2(\cos\theta_d) \end{aligned} \tag{1b}$$

$$V_2 = -\left[x\, V_{22}\left(\eta_2 + \alpha_{22}\,\sigma_2 \cos\frac{2\pi Z}{d}\right)\right.$$

$$+ (1 - x)(1 - a)\, V_{2m}\left(\eta_m + \alpha_{2m}\,\sigma_m \cos\frac{2\pi Z}{d}\right)$$

$$\left. + (1 - x)\, a\, V_{2d}\left(\eta_d + \alpha_{2d}\,\sigma_d \cos\frac{2\pi Z}{d}\right)\right] P_2(\cos\theta_2) \qquad (1c)$$

where x represents concentration of the second component. The suffixes M, D and 2 refer respectively to monomer and dimer of type '1' and monomer of type '2'. V_{mm}, V_{md}, V_{dd} etc. are the coupling constants for the interaction mean field with the first suffix representing the component molecule that experiences the mean field and the latter suffix indicating the mean field producing agent. Other notations are as in reference 1.

With a simple assumption that a dimer is of twice the volume of that of a monomer (ϑ) of either type we get

$$a = 1 - N_m/(1 - x)N \qquad (2)$$

with

$$2N_d + N_m = (1 - x)N$$

where N is the total number of molecules in the binary mixture and N_m, N_d are respectively the number of monomers and dimers of polar component.

We next introduce the partition functions of monomers of type '1', dimers and monomers of type '2' as Z_m, Z_d and Z_2 respectively. Apart from the layering cum orientational contribution, Z_d also contains a contribution from the vibrational degree of freedom. Assuming the translational, the vibrational and the orientational cum layering interaction to be independent of one another we get

$$Z_m = Z_{mo}Z_{mt},\ Z_d = Z_{do}Z_{dt}Z_{dv} \quad \text{and} \quad Z_2 = Z_{2o}Z_{2t}$$

where the subscripts 'o', t and v refer respectively to orientational cum layering, translation and vibration respectively. Z_{dv} is taken to be $\exp(\epsilon_s/KT)$ where $-\epsilon_s$ is the vibrational ground state energy. We further introduce the parameter

$$W = N\frac{Z_{dt}}{Z_{mt}^2}$$

Since it is not possible to write Z_{dt} and Z_{mt} explicitly, we assume their temperature dependence as that of a perfect gas and contributions from other parts are lumped together in 'WI' to define

$$W = N\frac{Z_d^e}{(Z_m^e)^2}\,T^{-3/2} = WI\,T^{-3/2} \tag{3}$$

With this we next write the free energy per unit volume (in units of monomer volume)

$$\begin{aligned}
F/N = {} & (1-x)\,[0.5(1-a)\{(1-x)(1-a)\,V_{mm}(\eta_m^2+\alpha_{mm}+\sigma_m^2) \\
& + (1-x)\,aV_{md}(\eta_m\eta_d+\alpha_{md}\,\sigma_m\sigma_d) + x\,V_{m2}\,(\eta_2\eta_m+\alpha_{m2}\,\sigma_m\,\sigma_2)\} \\
& + 0.25\,a\,\{(1-x)\,a\,V_{dd}\,(\eta_d^2+\alpha_{dd}\sigma_d^2) + (1-x)(1-a)\,V_{dm} \\
& (\eta_m\eta_d+\alpha_{dm}\,\sigma_m\sigma_d) + xV_{d2}\,(\eta_2\eta_d+\alpha_{d2}\sigma_2\sigma_d)\} \\
& + 0.5(1-a)\ln W - (1-a)\ln Z_{mo} \\
& - 0.5\,a\ln Z_{do} - 0.5\,a(\epsilon_s/KT) \\
& + (1-a)\ln(1-a) - (1-a) - 0.5a - 0.5\ln Z_{dt} + 0.5\ln N] \\
& + x[0.5\,xV_{22}(\eta_2^2+\alpha_{22}\sigma_2^2) \\
& + 0.5(1-a)(1-x)V_{2m}\,(\eta_m\eta_2+\alpha_{2m}\sigma_2\sigma_m) \\
& + 0.5(1-x)\,a\mathrm{V}_{2d}\,(\eta_d\eta_2+\alpha_{2d}\sigma_2\sigma_d) \\
& - \ln Z_{20} - \ln Z_{2t} + \ln(x\,N) - 1] \\
& + (1-x)[0.5\,a\ln(a/2) \\
& + (1-a)\ln(1-x) + 0.5a\ln(1-x)]
\end{aligned} \tag{4}$$

The two terms $(-0.5\ln Z_{dt} + 0.5\ln N)$ and $(-\ln Z_{2t} + \ln(xN) - 1)$ both being free from 'a' contribute equally in nematic, smectic and isotropic phases and are therefore dropped in our search for stability of the phases.

Minimizing the full free energy expression we get the following self-consistent equations,

$$\eta_j = \langle P_2(\cos\theta_j)\rangle \tag{5a}$$

$$\sigma_j = \langle \cos\frac{2\pi Z}{d} P_2(\cos\theta_j)\rangle \tag{5b}$$

With $j = m, d, 2$
and

$$a/(1-a)^2 = 2(1-x)\, WI\, T^{-3/2}\,(Z_{do}/Z_{mo}^2)$$
$$\exp[\{\epsilon_s + (1-x)X + xY\}/KT] \tag{6}$$

With

$$X = (V_{md} - 0.5\,V_{dm})\eta_m\eta_d + (V_{md}\alpha_{md} - 0.5\,V_{dm}\alpha_{dm})\sigma_m\sigma_d$$

$$Y = (V_{2d} - 0.5\,V_{d2})\eta_d\eta_2 + (V_{2d}\,\alpha_{2d} - 0.5\,V_{d2}\alpha_{d2})\sigma_d\sigma_2$$
$$- (V_{2m} - V_{m2})\eta_m\eta_2 - (V_{2m}\alpha_{2m} - V_{m2}\alpha_{m2})\sigma_m\sigma_2$$

Equating the potential energy of dimers in the field of monomers with the potential energy of monomers in the field of dimers

$$0.5(1-x)a[(1-x)(1-a)V_{dm}(\eta_m\eta_d + \alpha_{dm}\sigma_m\sigma_d)$$
$$+ x\,V_{d2}(\eta_2\eta_d + \alpha_{d2}\sigma_2\sigma_d)]$$
$$= (1-a)(1-x)^2\,V_{md}\,(\eta_d\eta_m + \alpha_{md}\sigma_m\sigma_d)$$
$$+ ax(1-x)V_{2d}\,(\eta_d\eta_2 + \alpha_{2d}\sigma_d\sigma_2)$$

In the absence of the second component and for the system in nematic phase we get

$$0.5V_{dm} = V_{md} \quad \text{and} \quad \alpha_{dm} = \alpha_{md} \tag{7a}$$

Next, considering the binary mixture ($x \neq 0$) in the nematic phase,

$$0.5V_{d2} = V_{2d} \tag{7b}$$

Using these identities in the smectic phase one has

$$\alpha_{d2} = \alpha_{2d} \tag{7c}$$

Further if one sets

$$V_{2m} = V_{m2} \quad \text{and} \quad \alpha_{2m} = \alpha_{m2} \tag{7d}$$

then equation (6) reads

$$a/(1 - a)^2 = 2(1 - x)WI\,T^{-3/2}\,(Z_{do}/Z_{mo}^2)\exp(\epsilon_s/KT) \tag{8}$$

Next, we define

$$(WI)_{N-I} = WI\,T_{N-I}^{-3/2}$$

As has been explained earlier[1] $(WI)_{N-I}$ is fixed from an assumed dimer volume fraction at *N-I* transition. The self consistent equation for dimer association is then given by

$$a/(1 - a)^2 = 2(1 - x)(WI)_{N-I}(T_{N-I}/T)^{3/2}(Z_{do}/Z_{mo}^2)\exp(\epsilon_s/KT) \tag{9}$$

Starting with *N-I* transition temperature and going downward in temperature, α_d is initially taken to be constant, equal to the input value α_{in}, until the monomer volume fraction reaches a value,

$$C_m = 1 - lm/l_d = 1 - 1/S \tag{10}$$

This is the concentration for which there are just enough monomers to fill up the void space mentioned earlier. As the concentration drops further the process of intercalation starts and the layer thickness begins to decrease. Assuming that the intercalation of dimers starts below the critical monomer concentration C_m the self consistent equations for α are given by

$$\alpha = \alpha_{in} \quad \text{for} \quad a \leqslant 1 - C_m$$

$$= 2\exp[a^2 s^2 \ln(\alpha_{in}/2)] \quad \text{for} \quad a > 1 - C_m \tag{11}$$

For a given x, the set of self consistent equations 5(a), 5(b), (9) and (11) are solved at different reduced temperatures and the stable phase is determined by comparing the full free energy in different phases. Calculations were then carried out at other concentrations (x) as well and the phase diagram is generated.

RESULTS

For numerical calculations we set (in conformity with the equations 7(a)-7(d))

$$V_{mm} = 2V_{md} = V_{dd} = 4.54\ K(T_{N-I})_1$$

$$V_{22} = 4.54\ K(T_{N-I})_2$$

$$V_{2m} = V_{m2} = \sqrt{V_{22}V_{mm}}$$

$$V_{d2} = 2V_{2d} = \sqrt{V_{22}\ V_{dd}}$$

In the above expressions $(T_{N-I})_1$ and $(T_{N-I})_2$ are the N-I transition temperatures of the polar and the nonpolar components respectively. In our calculations we however set $(T_{N-I})_1 = (T_{N-I})_2$ for simplicity.

The range of S ($= l_d/lm$) and α_{in} (assumed value of the initial 'α' at T_{N-I} for a given initial concentration of dimers ($a = 0.2$ at T_{N-I}) that would given rise to a reentrant polymorphism was established in our earlier work.[1] We have chosen one set of values of S and α_{in} in that range and another outside the range for our present calculation. The latter was specifically chosen to show that a polar compound which does not have reentrant behaviour may show a reentrant polymorphism when mixed with a nonpolar compound. The relevant input parameters for the two cases are

Case I

$$S = 1.5$$

$$\alpha_{dd} = \alpha_{dm} = \alpha_{md} = 0.90(=\alpha_{in})$$

$$\alpha_{d2} = \alpha_{2d} = 0.5\alpha_{in}$$

$$\epsilon_s/KT_{N-I} = 10.0$$

Case II

$$S = 1.3$$

$$\alpha_{dd} = \alpha_{dm} = \alpha_{md} = 0.67 (= \alpha_{in})$$

$$\alpha_{d2} = \alpha_{2d} = 0.5\alpha_{in}$$

$$\epsilon_s/KT_{N-I} = 8.0$$

In each of the above cases, self consistent calculation was done for various values of concentration x. For each x the transition temperatures were found. The resulting phase diagrams are shown in Figure 1 [case I] and Figure 2 [case II] respectively.

Figure 1 shows, for the pure polar compound ($x = 0$), the phase sequence I-N-S_{Ad}-N_r-S_{A1}. As the concentration x of the nonpolar compound is increased the temperature range of existence of the H.T.S_A phase shrinks and eventually there is no reentrant behaviour beyond $x = 0.43$. The low temperature smectic phase is always there, but it is not shown beyond $T_{N-I}/T = 2.0$. Calculations were done upto $T_{N-I}/T = 2.0$ as a crystalline phase is likely to stabilize at such

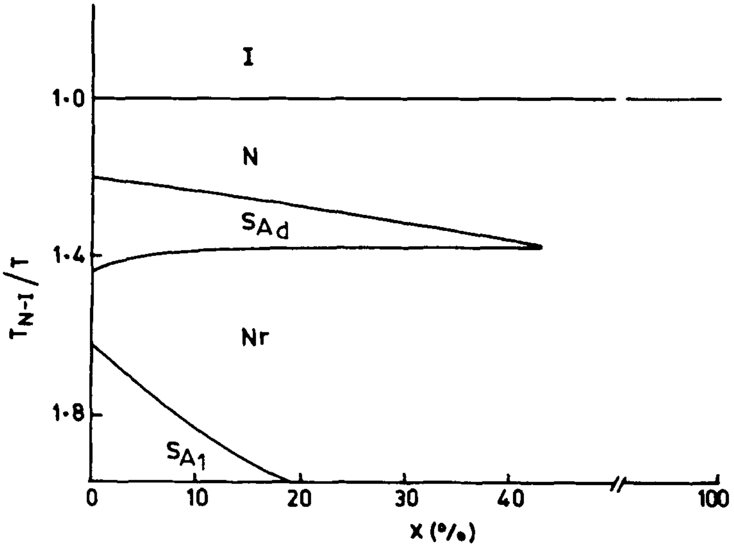

FIGURE 1 Calculated phase diagram for a binary system of a polar and a non polar components with $S = 1.5$, $\alpha_{in} = 0.90$, $\epsilon_s/KT_{N-I} = 10.0$.

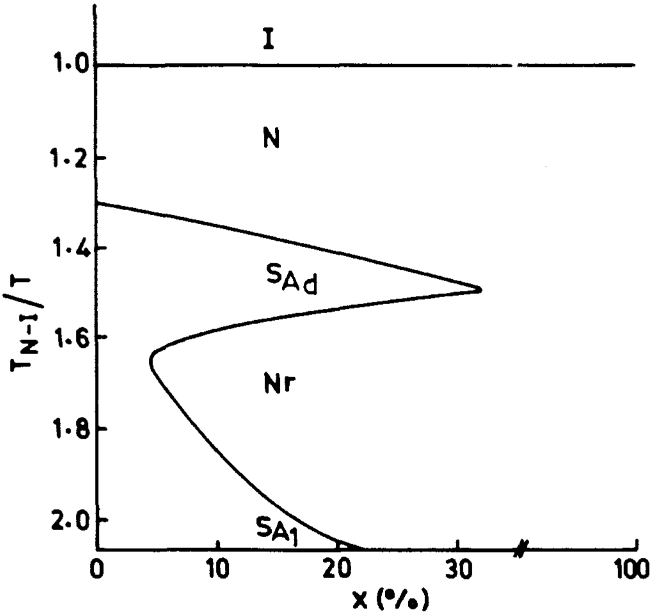

FIGURE 2 Calculated phase diagram for a binary system of a polar and a non polar components with $S = 1.3$, $\alpha_{m} = 0.67$, $\epsilon_s/KT_{N-I} = 8.0$.

a low temperature. The phase diagram thus reproduced is in good qualitative agreement with the experimental phase diagrams of the binary mixture of polar octyloxy-4′-benzoyloxy-4-cyanostilbene and nonpolar PAA.[10] In this experiment by Hardouin et al. it is seen that the reentrant behaviour persists upto about a PAA concentration of 0.1. The temperature range of H.T.S_A phase also shrinks (as in our calculation) with increasing percentage of PAA in the mixture. The sharp decrease of T_{N-I} with increasing concentration of PAA is not reproduced in our result as we took, for the sake of simplicity, the *N-I* transition temperatures of the two components to be the same. It however has to be pointed out that our model can not reproduce the appearance of an induced monolayer smectic phase observed in some experimental phase diagrams. In the phase diagram of a terminally polar and a terminally nonpolar component of Engelen et al.[4] the reentrant polymorphism which is present in the pure polar components (CBOOA or 8CBP) gradually disappears with the addition of terminally nonpolar components. This part is similar to our calculated phase diagram. However, their result shows an induced monolayer smectic phase over a wide range of concentration which is not captured at this stage of our theory.

The phase diagram of Figure 2 is similar except for the fact that a pure polar compound here does not have a reentrant behaviour. However, with increasing 'x' a reentrant polymorphism comes into existence and gradually disappears at about $x = 0.33$. We have not come across any experimental observation which shows this interesting aspect in a binary mixture of a polar and a nonpolar compound. This is however not uncommon in binary mixtures of polar compounds. As an example we can cite the case of the mixture of 60CB and 80CB studied by Guillon et al.[6] or the binary mixture of nitrocompounds studied in reference 13, 14. However in the latter case we do not distinguish between S_A and S_C phase. This agreement of the present model, proposed explicitly for polar-nonpolar mixture, with polar-polar binary mixture results in some cases is not altogether fortuitious. In the polar-polar case, if one of the polar components in pure form does not have a smectic phase (only I-N-K phase sequence) then the 'α' parameter for this component even when dimerized is very low. In this respect these molecules can be looked upon on the same footing as the second component monomers in our model calculation. This is why the phase diagrams of such binary systems e.g., the mixture of CBOOA and HBBA[11] along with the results in references 6, 13 and 14 have the same qualitative features as the ones we have presented in this paper.

We may also remark that an extension of the above model to polar-polar mixtures where the second component also forms a bilayer H.T.S_A phase is in principle possible. How far such an extension could be successful in reproducing experimental results is not however clear as the phase diagrams of two polar constitutents can be very complicated particularly if the disposition of the bridging groups (relative to the strongly polar end group) are different for the two constituents.[15] Efforts are also being made to incorporate a different type of association of monomers for forming dimers. These 'head to head' dimers are of twice the length of monomers. A gradual conversion, with lowering of temperature, of dimers of length 2 lm-r_o (l_m-monomer length, r_o-monomer or dimer core length) to those of length 2 l_m can lower the layering interaction as explained in the text. This can bring about a reentrant nematic phase even with an increase in the layer thickness of the high temperature smectic phase.

In conclusion we would like to thank the referee for bringing to our notice the paper of Indeku and Berker[16] which is the only work among the recent microscopic theories[16-20] of reentrant polymorphism to present a phase diagram of a mixture based on their frustrated spin-gas model of liquid crystals.

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