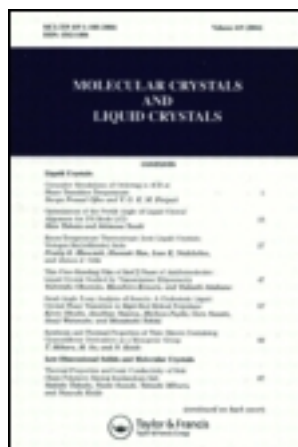


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# A Theoretical Model for the Phase Diagram of Mixtures of Nematic Liquid Crystals and Polymeric Solutes

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The Flory-Huggins lattice theory of regular solutions has been extended to describe mixtures of nematic liquid crystals with non-nematic polymeric solutes. The nematic phase is described in terms of a Maier-Saupe approximation. The phase diagrams obtained are in agreement with those reported in the literature. The theory has been applied to the specific case of a mixture of EBBA and PEO. The dependence of the order parameter on temperature at the phase separation is also predicted.

*Keywords: phase diagram, guest/host, polymer solutes*

## INTRODUCTION

Recently, interest has been growing in the study of mixtures of a liquid crystals with solutes which do not themselves form liquid crystal phases.<sup>1–4</sup> Typical solutes investigated are simple molecules like benzene, toluene etc (which are small compared to liquid crystal molecules) and polymers such as polystyrene (PS) and polyethylene oxide (PEO). These mixtures exhibit complex phase diagrams. When small molecules are added to a nematic liquid crystal it is found that on cooling from an isotropic phase, a two phase (isotropic plus nematic) region appears which reverts to a single nematic phase on cooling further.<sup>2,3</sup> For solutions of polymers second phase separation at still lower temperature can occur and the resulting phase diagram can be very complex.<sup>4</sup>

The study of phase diagrams of such mixtures, is often necessary when one attempts to investigate liquid crystal systems using spin probes since the spin probe acts as a guest species producing effects of the type mentioned above. Therefore, interpreting the experimental results requires a detailed understanding of the phase diagrams of the mixed systems.

Solutions of non-mesogens in nematic phases can be modelled in terms of a mixture of cylindrical molecules and spherical or polymeric molecules. These models are likely to be useful, not only for the thermotropic systems, but also for lyotropic nematic phases and for mixtures of Tobacco Mosaic virus and water.<sup>5,6</sup>

There have been several attempts to develop the theory of such models.<sup>7-13</sup> Those by Hida<sup>7</sup> and Humphries *et al.*<sup>8,9</sup> are the most relevant to the present context. Humphries *et al.* (hereafter referred to as HJL) extended the Maier-Saupe<sup>14</sup> theory (which has proved to be one of the most successful theories in interpreting a large number of experimental data) to mixtures. They treated the mixture as an ideal solution and therefore did not include the solute-solvent interaction term. Hida tried to correct this and used such a term for isotropic interaction between solute and solvent, but unfortunately he did not calculate the order parameter using Maier-Saupe theory. These inadequacies have been removed in the present paper by retaining both the solute-solvent interaction and Maier-Saupe theory. Further, since neither the work of both Hida or that of HJL includes the polymeric nature of the solute, we have used in our present work, the Flory-Huggins<sup>16</sup> treatment for the mixture of a nematic liquid crystal with a polymeric solute. This makes a quantitative comparison with the experimental results possible. The isotropic part of the interaction term between the solute and solvent ( $W$ ) has been included. Phase diagrams have been obtained for different values of  $W$  as well as for different values of  $M$ , the number of segments in the polymer species. In the limit where  $M = 1$  and  $W = 0$ , our results become identical to those of the HJL model.

## THE MODEL

The following arguments are similar to those of Humphries and Luckhurst<sup>9</sup> but include the polymeric nature of solute and the solute-solvent interaction term. The free energy in the nematic phase, of a mixture consisting of  $n_1^N$  cylindrical (nematic) molecules and  $n_2^N$  solute

molecules occupying  $M$  sites in a lattice is given by

$$F^N = n_1^N \mu_1^0 + n_2^N \mu_2^0 + kT[n_1^N \ln \phi^N + n_2^N \ln(1 - \phi^N)] \\ + \frac{1}{2} V_0 S^2 n_1^N \phi^N - n_1^N kT \ln Z^N + W \phi^N (1 - \phi^N) n^N \quad (1)$$

where

$$\phi^N = \frac{n_1^N}{n_1^N + M n_2^N} \quad (2)$$

[denoted by  $X$  (Molar Conc.) for  $M = 1$ ] is the volume fraction of the nematic liquid crystal

$n^N = n_1^N + M n_2^N$  is the total number of sites

$W$  is the interchange energy [if one starts with a lattice of pure solvent and solute and if an interior solvent molecule is substituted for an interior solute molecule, the total increase of energy is  $2W$ ].

$V_0$  is parameter entering in Maier-Saupe theory and is related to the transition temperature  $T_{L0}$  of the pure nematic by

$$k T_{L0} = 0.2202 V_0 \quad (3)$$

$Z^N$  is the orientational partition function for the nematic component of the mixture

$$Z^N = \int_0^1 d\mu \exp \left[ \frac{V_0 \phi^N S P_2(\mu)}{kT} \right] \quad (4)$$

$S$  is the orientational order parameter for the nematic component

$$S = \frac{1}{Z^N} \int_0^1 d\mu P_2(\mu) \exp \left[ \frac{V_0 \phi^N S P_2(\mu)}{kT} \right] \quad (5)$$

The expression for the free energy in the isotropic phase can similarly be written with  $S = 0$ ;

$$F^I = n_1^I \mu_1^0 + n_2^I \mu_2^0 \\ + kT[n_1^I \ln \phi^I + n_2^I \ln(1 - \phi^I)] + W \phi^I (1 - \phi^I) n^I \quad (6)$$

The chemical potential terms  $\mu_1$  and  $\mu_2$  can be obtained from the free energy expressions

$$\begin{aligned}\mu_1^N &= \mu_1^0 + kT \ln \frac{\phi^N}{Z^N} + \frac{1}{2} V_0 (S\phi^N)^2 \\ &\quad + kT \left(1 - \frac{1}{M}\right) \left(1 - \phi^N\right) + W(1 - \phi^N)^2\end{aligned}\quad (7)$$

$$\begin{aligned}\mu_1^I &= \mu_1^0 + kT \ln \phi^I + kT \left(1 - \frac{1}{M}\right) \left(1 - \phi^I\right) \\ &\quad + W(1 - \phi^I)^2\end{aligned}\quad (8)$$

$$\begin{aligned}\mu_2^N &= \mu_2^0 + kT \ln (1 - \phi^N) + \frac{1}{2} M V_0 (S\phi^N)^2 \\ &\quad + (1 - M)kT\phi^N + WM(\phi^N)^2\end{aligned}\quad (9)$$

$$\begin{aligned}\mu_2^I &= \mu_2^0 + kT \ln (1 - \phi^I) + (1 - M)kT\phi^I \\ &\quad + WM(\phi^I)^2\end{aligned}\quad (10)$$

The phase boundaries in a mixture can be obtained by solving the equations

$$\mu_1^N = \mu_1^I \quad (11)$$

$$\mu_2^N = \mu_2^I \quad (12)$$

with the help of equation (5).

We have solved these equations for different values of  $W$  and  $M$ .

## METHOD OF CALCULATION

Here we briefly indicate the method of solving the equations. If we define a parameter  $R^2$  as

$$R^2 = \frac{3V_0 S\phi^N}{2kT} = \frac{3S\phi^N}{0.4404t} \quad \text{where } t = T/T_{L0} \quad (13)$$

then  $S$  and  $Z^N$  can be evaluated as a function of  $R^2$  as in the Maier-Saupe theory. For a fixed  $t$  and given  $R^2$ ,  $\varphi^N$  can be obtained from eq. (13).  $\varphi'$  is then varied until  $|\mu_2^N - \mu_2^I|$  is at an absolute minimum. The process is repeated for different  $R^2$  and hence for different  $\varphi^N$  until  $|\mu_1^N - \mu_1^I|$  is an absolute minimum. Thus we get  $\varphi^N$  and  $\varphi^I$  as functions of  $t$ . In this way the phase diagrams were obtained for different  $W/kT_{L0}$ 's as well as for different  $M$  values.

## RESULTS AND DISCUSSION

As mentioned earlier, if  $M = 1$  and  $W = 0$ ; the equations reduce to those of ref. 9 and hence we have not repeated those results here. Reference 9 has some printing errors and it may appear that the equations therein are different to those we have derived. However, the numerical results of ref. 9 are correct and agree with ours. We discuss the effect of  $M$  on the phase diagram below.

Figure 1 shows the phase diagram for  $W/kT_{L0} = -2$  and  $M = 1$ . This type of phase diagram has been observed for non-polymeric

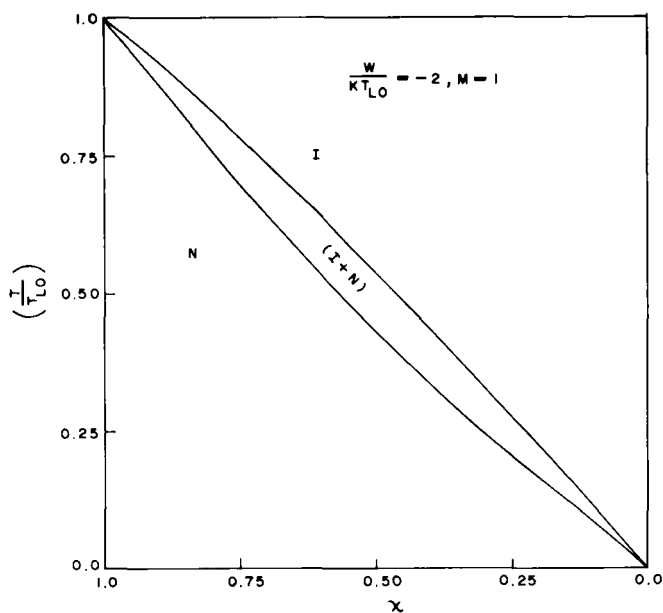


FIGURE 1 Calculated phase diagram for  $W/kT_{L0} = -2$  and  $M = 1$ . This type of phase diagram has been observed for non-polymeric solutes.

solutes. Hida has also obtained similar diagrams for  $\Delta > 1$ . It may be noted that our  $W$  and his  $\Delta$  are related by  $\Delta \approx -0.44 (W/kT_{L0})$ .

For  $(W/kT_{L0}) > -1.5$  we obtain a different type of phase diagram, with the second phase separation at lower temperature as observed for polymeric solutes. Figure 2 shows the results for  $(W/kT_{L0}) = 1$  and  $M = 1$ . Hida has reported this type of phase diagram for  $\Delta < 1.0$ . This type of phase diagram is also obtained by Humphries and Luckhurst<sup>9</sup> but for solute concentrations higher than those normally used experimentally. The increase of  $M$  causes the lowering of the solute concentration for second phase separation as will be seen below.

Next we shall discuss the effect of  $M$  on the phase diagram for a given  $W$ . Figure 3 shows the phase diagram for  $(W/kT_{L0}) = -1$  and  $M = 1$  and 2. Note that for a fixed volume fraction of solute, the  $T(\varphi, I)$  increases with  $M$  for all  $\varphi$  values. But the  $T(\varphi, N)$  shows both decrease and increase with increase in  $M$  depending on the solute concentration.

Figures 4 and 5 show the phase diagrams for  $(W/kT_{L0}) = 0$  and 1 respectively for two different  $M$  values. It can be seen that the temperature of the second phase separation decreases with  $M$ . We find

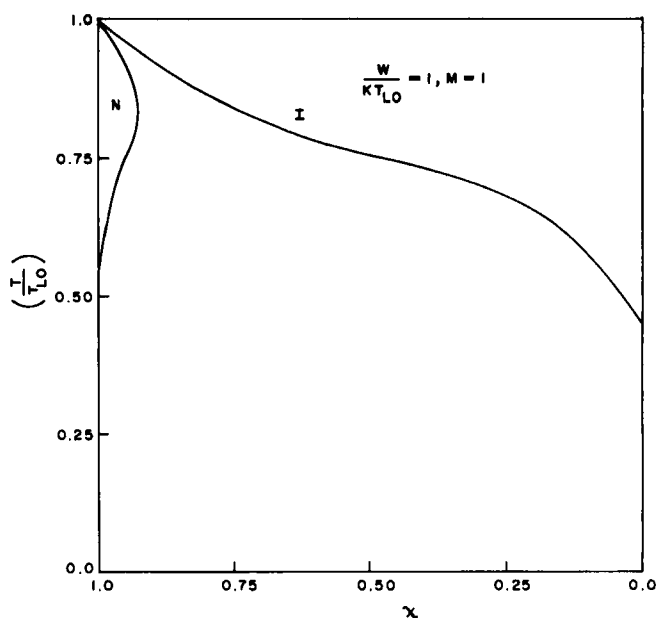


FIGURE 2 Calculated phase diagram for  $W/kT_{L0} = 1$  and  $M = 1$ .



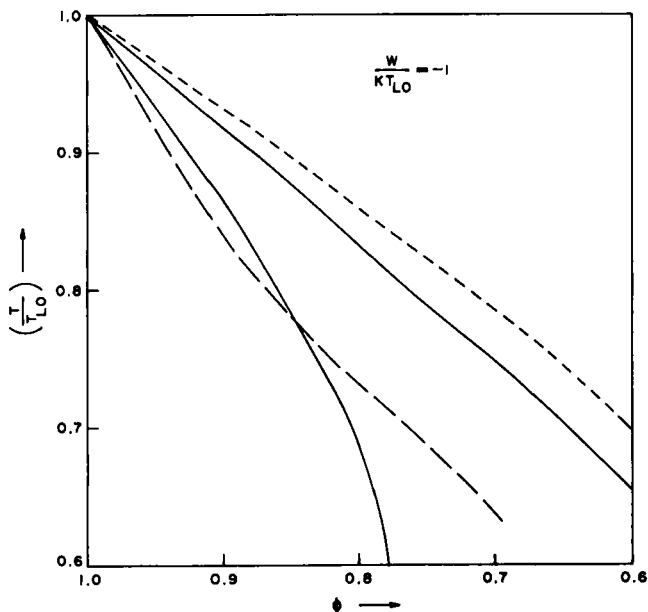


FIGURE 3 Calculated phase diagram for  $W/kT_{L0} = -1$ . The continuous curve is for  $M = 1$  and the broken curve is for  $M = 2$ .

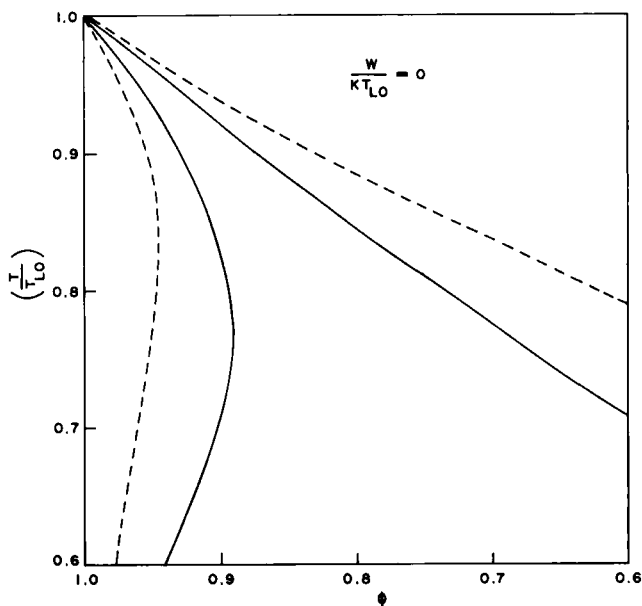


FIGURE 4 Calculated phase diagram for  $W/kT_{L0} = 0$ . The continuous curve is for  $M = 1$  and the broken curve is for  $M = 2$ .

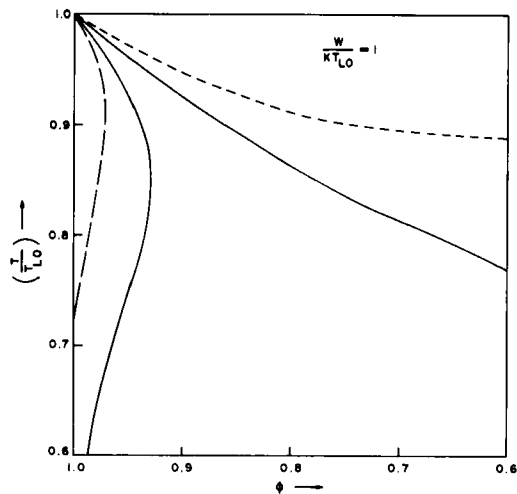


FIGURE 5 Calculated phase diagram for  $W/kT_{L0} = 1$ . The continuous curve is for  $M = 1$  and the broken curve is for  $M = 2$ .

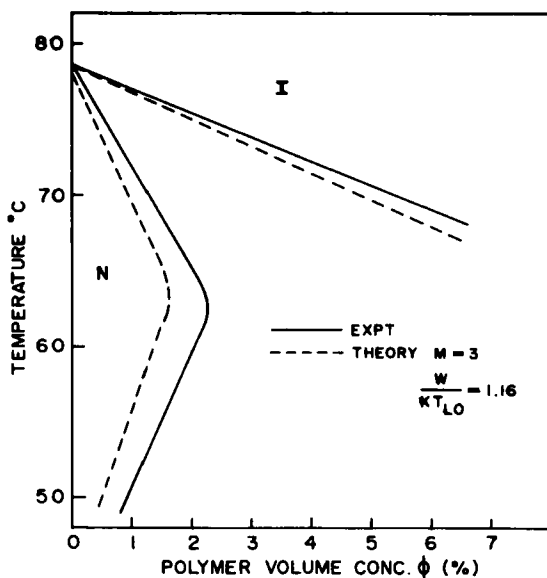


FIGURE 6 Calculated and observed phase diagram (ref. 4) for EBBA and PEO system. The broken curve is calculated with  $W/kT_{L0} = 1.16$  and  $M = 3$ . The experimental phase diagram is denoted by continuous curves.

that the equations do not have solutions for high values of  $M(>10)$  implying that the nematic phase can be destroyed by the addition of a very highly polymeric solute.

Kronenberg and Patterson<sup>13</sup> have also obtained similar phase diagrams for low solute concentrations. They have also indicated that experimental results in the case of MBBA with PEO and PS show such behaviour.

To test our results we have tried to obtain a fit for the experimental results on the EBBA/PEO system.<sup>4</sup> Figure 6 shows the calculated phase diagram with  $(W/kT_{Lo}) = 1.16$  and  $M = 3$  together with the results reported.<sup>4</sup> The value of  $M = 3$  is reasonable as it roughly corresponds to the ratio of molecular length of PEO 2100 to that of EBBA.

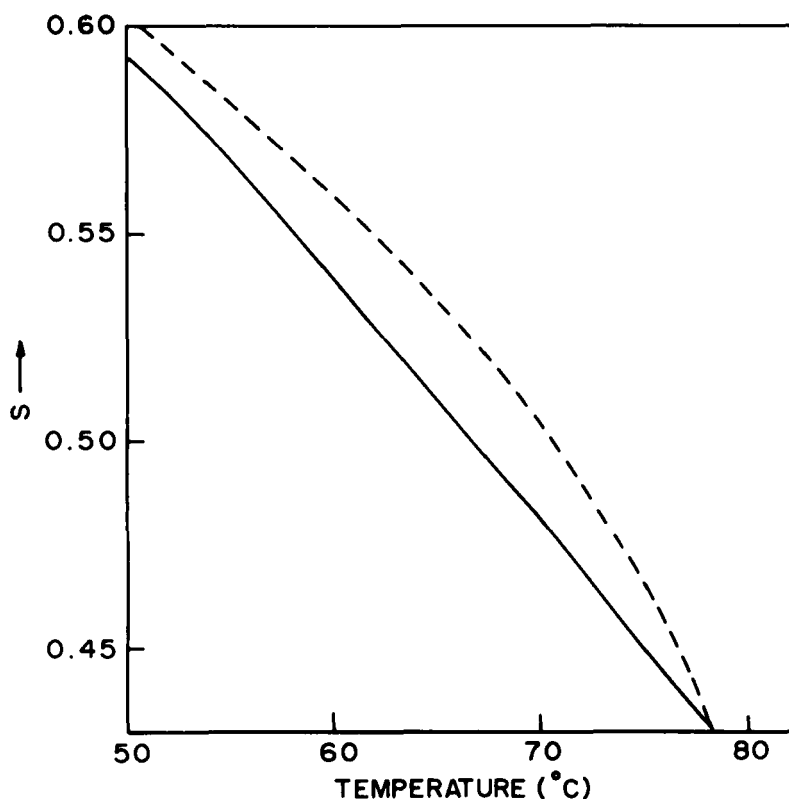


FIGURE 7 Calculated orientational order parameter as a function of temperature at the phase separation for (EBBA + PEO) system. The broken curve is that calculated for pure EBBA in Maier-Saupe approximation.

In Figure 7 we show the calculated order parameter as a function of temperature at the phase separation for the above system. It may be interesting to compare the results with the experiments.

The Maier-Saupe theory (apart from its relevance to experiments, as mentioned above) has the advantage that it has been extended by Mcmillan and others to smectic A phases.<sup>15</sup> It is expected that very soon, the interest in the mixtures of smectic liquid crystal and other types of solutes will also increase and the need for theories to describe them will arise.

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