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A THEORY OF NEMATIC TO ISOTROPIC TRANSITION IN LIQUID CRYSTALS FORMING DIMERS

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ABSTRACT Using an extension of the Maier-Saupe theory it is shown that in the liquid crystals which form dimers, there is an abrupt change in the concentrations of dimers and monomers at the nematic to isotropic transition. Equations determining the temperature dependence of order parameter and the concentrations are derived. Applications of these results to some molecules are discussed.

There is a large number of liquid crystals which form dimers[1-5] (and, may be, higher polymers), but there has not been any systematic theory developed for their study. The motivation for the present work came from two observations:

(1) The formation of dimers is really an equilibrium process, i.e. a number of monomers are in thermal equilibrium with a number of dimers (we ignore, for simplicity, the formation of higher polymers or open dimers), which is formally represented by

$$B \rightleftharpoons 2A \tag{1}$$

where A and B denote a monomer and a dimer, respectively. So, really the problem one has to deal with is that of a mixture of two liquid crystals whose individual concentrations C_A and C_B vary with temperature.

(2) There is an indication that at the phase transition, there is an abrupt change in C_A and C_B[3,4].

The Maier-Saupe (M.S.) theory[6] for nematic to isotropic transition can be extended to describe the behaviour of such molecules resulting in a number of interesting consequences. Let N_A and N_B be the number of A and B molecules, then

$$N_A + 2N_B = N = \text{constant at all temperatures.} \tag{2}$$

where N denotes the total number of formula units of A. The concentrations C_A and C_B are given by

$$C_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{N - N_B} = 1 - \frac{N_B}{N - N_B} \tag{3}$$

and, $$C_B = 1 - C_A = \frac{N_B}{N - N_B} \tag{4}$$

If V_{AA}, V_{AB} and V_{BB} are the interaction strengths and S_A and S_B, the order parameters, then the effective potential on molecule A (in molecular-field approximation) is given by

$$\begin{aligned} V_A &= -V_{AA} S_A C_A P_2(\cos\theta_A) - V_{AB} S_B C_B P_2(\cos\theta_A) \\ &= -P_2(\cos\theta_A) . X_A \end{aligned} \tag{5}$$

where θ_A is the angle between the molecular long axis of A and the preferred direction. Similarly, for potential on B, one obtains

$$\begin{aligned} V_B &= -(C_A S_A V_{AB} + C_B S_B V_{BB}) . P_2(\cos\theta_B) \\ &= -P_2(\cos\theta_B) . X_B \end{aligned} \tag{6}$$

Now, the partition functions for the orientational part, associated with V_A and V_B, become

$$Z_{AO} = \int_0^\pi d\theta \cdot \sin\theta . \exp . \left\{ \frac{X_A}{kT} . P_2(\cos\theta) \right\} \tag{7}$$

and, $$Z_{BO} = \int_0^\pi d\theta \cdot \sin\theta . \exp . \left\{ \frac{X_B}{kT} . P_2(\cos\theta) \right\} \tag{8}$$

In order to compute the free energy, we have to include the vibrational contribution to the partition function, arising from the bond between two A molecules in a dimer. If the vibrational frequency is ν and the dissociation energy is D, then the partition function for the vibrational part is

$$Z_{vib} = \frac{\exp(-h\nu/kT + D/kT)}{1 - \exp(-h\nu/kT)} \tag{9}$$

The translational part of the partition functions for A and B are approximated by

$$Z_{Atr} = \left(\frac{M_A kT}{2\pi\hbar^2}\right)^{3/2} \tag{10}$$

and, $$Z_{Btr} = \left(\frac{M_A kT}{\pi\hbar^2}\right)^{3/2} \tag{11}$$

The total partition functions Z_A and Z_B are, then,

$$Z_A = Z_{A0} \cdot Z_{Atr} \tag{12}$$

and, $$Z_B = Z_{B0} \cdot Z_{vib} \cdot Z_{Btr} \tag{13}$$

Using the above partition functions one can calculate the total orientational energy, the total entropy and the Helmholtz free energy for the system. Of these, the free energy is given by

$$F = \frac{1}{2} N_A C_A V_{AA} S_A^2 + \frac{1}{2} N_B C_B V_{BB} S_B^2 + \frac{1}{2}(N_A C_B + N_B C_A) V_{AB} S_A S_B - kT \ln \frac{Z_A^{N_A}}{N_A!} - kT \ln \frac{Z_B^{N_B}}{N_B!} \tag{14}$$

The self-consistent equations to be solved can now be derived by minimising F with respect to S_A, S_B and N_B subject to the condition given in equation (2), i.e.

$$\frac{\partial F}{\partial S_A} = 0 \; ; \; \frac{\partial F}{\partial S_B} = 0 \text{ and } \frac{\partial F}{\partial N_B} = 0 \, . \tag{15}$$

The mean field equations, thus obtained for the order parameters S_A and S_B are

$$S_A = \frac{1}{Z_{A0}} \int_0^\pi d\theta \cdot \sin\theta \cdot P_2(\cos\theta) \exp \cdot \left\{ \frac{X_A}{kT} \cdot P_2(\cos\theta) \right\} \tag{16}$$

$$S_B = \frac{1}{Z_{B0}} \int_0^\pi d\theta \cdot \sin\theta \cdot P_2(\cos\theta) \exp \cdot \left\{ \frac{X_B}{kT} \cdot P_2(\cos\theta) \right\} \tag{17}$$

These two equations have been discussed by Humphries et al[7] in a different context. The equilibrium dimer concentration is given by

$$\frac{N_B}{N_A^2} = \frac{C_B(1+C_B)}{(1-C_B)^2 \cdot N} = \frac{Z_B}{Z_A^2} \cdot \exp\left[\frac{1}{2kT}\left(C_A^2 V_{AA} S_A^2 + C_B^2 V_{BB} S_B^2 + 2 C_A C_B V_{AB} S_A S_B\right)\right] \tag{18}$$

As a special case, we shall consider a system where the monomer is not a liquid crystal, and so not ordered, i.e. $S_A=0$. This situation is not a hypothetical one but of practical value because there exist molecules with only one benzene ring, but which form dimers, thus exhibiting liquid crystalline properties. For example, p-n-Alkoxybenzoic acids, having only one benzene ring, do show liquid crystalline properties, purely as a result of dimer formation. These molecules, therefore, can be suitably represented by putting $S_A = 0$ in above equations. Thus we get for free energy,

$$F = \frac{1}{2} N_B C_B V_{BB} S_B^2 - kT \ln \frac{Z_A^{N_A}}{N_A!} - kT \ln \frac{Z_B^{N_B}}{N_B!} \qquad (19)$$

with $Z_A = 2 Z_{Atr}$, and, for order parameter

$$S_B = \frac{\int_0^{\pi} d\theta . \sin\theta . P_2(\cos\theta) \exp\left[\frac{V_{BB} S_B C_B}{kT} . P_2(\cos\theta)\right]}{\int_0^{\pi} d\theta . \sin\theta . \exp\left[\frac{V_{BB} S_B C_B}{kT} . P_2(\cos\theta)\right]} \qquad (20)$$

The equation (18) determining C_B now becomes

$$\frac{N_B}{N_A^2} = \frac{C_B(1+C_B)}{(1-C_B)^2 . N} = \frac{Z_B}{Z_A^2} \exp . \left[\frac{V_{BB} S_B^2 C_B^2}{2kT}\right] \qquad (21)$$

Equation (20) is the usual self-consistency equation for the order parameter except for the important difference that C_B enters the right hand-side. Since C_B is also temperature dependent, as can be seen from equation (21), the temperature dependence of S_B, according to our theory will be different from that in the M.S. theory. The details of solving the equations (20) and (21) and thereby determining C_B and S_B as a function of temperature will be given elsewhere. Using these equations we have determined the temperature dependence of S_B and C_B for p-n-heptyloxybenzoic acid (PHBA). The input parameters were $D \simeq 10$ Kcal/mole[5], $\nu = 200$ cm^{-1} and the nematic to isotropic transition temperature was taken as 423.5 K. In Figure 1 the variation of order parameter of PHBA with temperature is shown. Dots indicate the experimental data of Deloche and Cabane[5], while the continuous curve is as obtained from M.S. theory. Our results are shown as a broken-line plot in this figure and compare well with experiment[5].

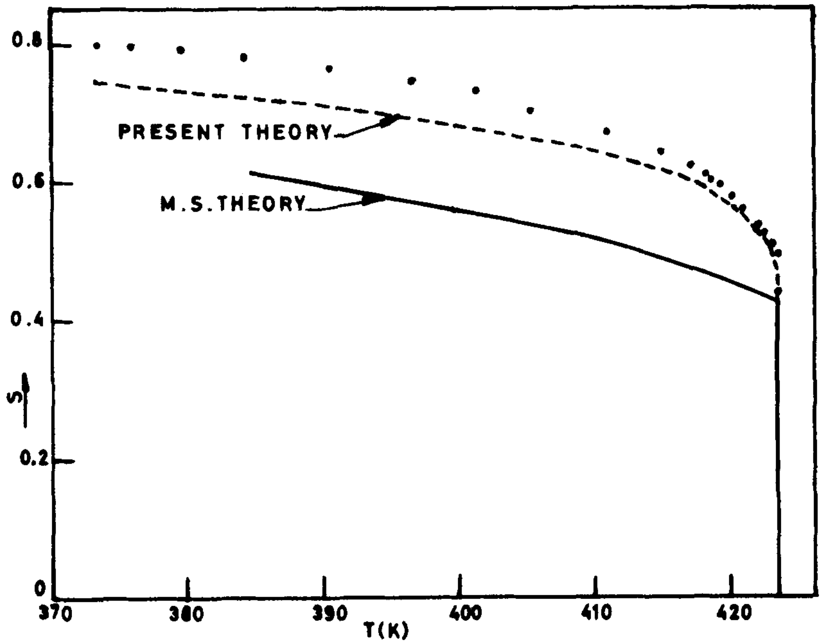

FIG._1 ORDER PARAMETER Vs TEMPERATURE

From their NMR studies, Deloche and Cabane[5] found that the relaxation time was directly proportional to order parameter. We have plotted S_B vs C_B as obtained from our theory in Figure 2. A near-straight line nature of this plot substantiates our theory.

Our calculations indicate that at the N → I transition of PHBA, there is a sudden decrease (~10%) in the concentration of dimers. The ideal thing to check this would be to do a Raman scattering experiment and to look for the vibrational mode of the hydrogen bond. The intensity of Stokes line should abruptly decrease at the N → I transition implying a reduction in dimer concentration. We have also estimated the transition entropy $\Delta S \sim 0.24$ R for PHBA.

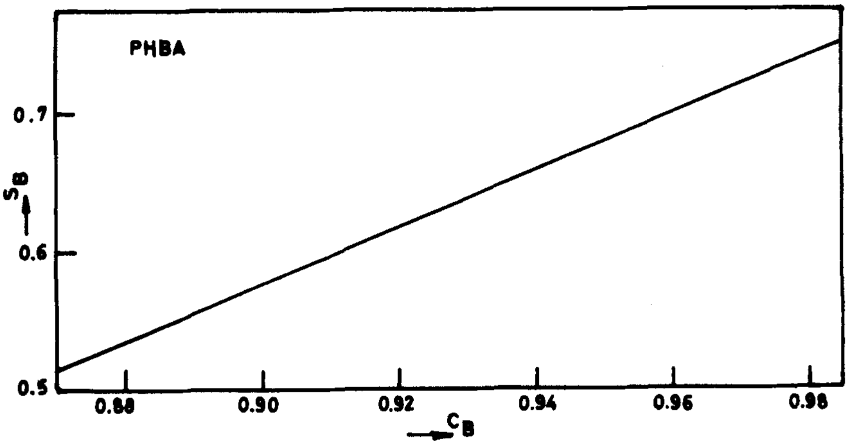

FIG. 2 S_B Vs C_B

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