Reentrant isotropic-nematic transition in lyotropic liquid crystals

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We consider a model based on the Maier and Saupe theory in order to explain the reentrant nematic-isotropic transition observed in lyotropic liquid crystals. By assuming a linear dependence of the micellar shape anisotropy with temperature, we show that it is possible to obtain a reentrant transition.

Experiments carried out on a three-component lyotropic mixture of potassium laurate, 1-decanol, and water have revealed the existence of a reentrant isotropicnematic transition.^{1,2} This transition is not predicted by the Maier and Saupe theory^{3,4} in the sense that in their theory the isotropic phase always occurs at temperatures higher than those of the nematic phase. This situation is what usually happens in genuine statistical models: the more symmetrical phase occurs at high temperatures. By genuine statistical model we mean, for example, that the interaction between the microscopic objects does not depend on temperature.

The reentrant transition is, thus, not caused by a simple entropy effect, which would make the high-temperature phase the disordered (isotropic) or more symmetrical phase. It has been suggested² that in the case of lyotropic mixtures this transition is driven by a temperaturedependent interaction caused by the thermal variation in the shape anisotropy of the microscopic objects (micelles). In this paper, therefore, we consider a model where we allow for the temperature dependence of the interactions in order to explain the reentrant transition. By assuming that the micellar shape anisotropy varies linearly with temperature, we show that it is possible to obtain a reentrant transition.

The model we consider here differs from that treated by Chen and Deutch.⁵ They explain the reentrant transition by the competition between short- and long-range interactions. In our model the transition is caused by the variation of the shape of the micelle with temperature. As one lowers the temperature, the microscopic object approaches the spherical shape giving no room for an orientational order.

Following Freiser,⁶ we assume that the orientational interaction W_{ii} between two micelles *i* and *j* is given by

$$W_{ij} = -\operatorname{Tr}(\Omega^i \Omega^j) \; ,$$

where Ω^i is the moment of quadrupole matrix of micelle *i* in the laboratory frame of reference. It is given by

$$\Omega^{i} = R^{+}(\phi_{i}, \theta_{i}, \psi_{i}) \Lambda R(\phi_{i}, \theta_{i}, \psi_{i}) ,$$

where ϕ_i , θ_i , and ψ_i are the Euler angles that define the orientation of micelle *i*, and $R(\phi_i, \theta_i, \psi_i)$ is the rotation matrix from the frame of reference attached to the micelle to the laboratory frame of reference; and R^+ is the transpose of R. Since we are not interested in a possible

biaxial nematic phase, we consider here only the case where the micelles have cylindrical symmetry. Moreover, we will treat only the case of discotic micelles for which

$$\mathbf{\Lambda} = \begin{bmatrix} -\frac{1}{2}\lambda & 0 & 0\\ 0 & -\frac{1}{2}\lambda & 0\\ 0 & 0 & \lambda \end{bmatrix},$$

where λ is proportional to a^2-c^2 , c being the thickness of the micelle and a its radius.

The molecular-field approximation may now be calculated by assuming that each micelle interacts with z nearest neighbors. By doing that we obtain the well-known result of Maier and Saupe.^{3,4,6} However, since we are interested in the qualitative aspects of the problem, we will not follow this approach at this point. Instead, we first simplify the model by restricting the allowed orientation of the micelles. Their orientations are restricted to be only parallel to the three Cartesian axes of the laboratory frame of reference. In this case the interaction $W_{ij} = -3\lambda^2/2$ if micelle *i* is parallel to *j*, and $W_{ij} = 3\lambda^2/4$ if *i* is orthogonal to *j*.

This simplified model is therefore equivalent to the three-state Potts model^{7,8} which within the mean-field approximation is known to possess a first-order transition as does the original model of Maier and Saupe. Doing a mean-field calculation we get the following free energy per micelle:

$$f = -\frac{3}{4}z\lambda^2 S^2 + \frac{k_B T}{3} [2(1-S)\ln(1-S) + (1+2S)\ln(1+2S) - 3\ln 3],$$

where S is the order parameter defined by

 $S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle$.

The minimization of f gives S as an implicit function of temperature, that is,

$$\frac{9}{4} \frac{z\lambda^2}{k_B T} S = \ln \left[\frac{1+2S}{1-S} \right]. \tag{1}$$

The first-order transition occurs at a temperature T given by

$$k_B T = \frac{9}{16 \ln 2} z \lambda^2 \, .$$

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At the transition, the order parameter jumps from S=0 (isotropic phase) to $S=\frac{1}{2}$ (nematic phase).

We now suppose that λ depends on temperature. We assume that only the thickness of the micelle varies with temperature and that it increases linearly with decreasing temperatures, that is,

$$c = c_0 [1 - \alpha(t - 1)]$$

with $\alpha > 0$, where $t = T/T_0$, and T_0 is the temperature at which the ordinary first-order transition takes place. The thickness of a disclike micelle is defined by the length of the paraffinic chains of the amphiphilic molecules⁹ and it is essentially an amphiphilic bilayer. The linear dependence with temperature of the thickness of bilayers in the case of lamellar lyotropic mixtures was determined by Luzzati *et al.*¹⁰ They concluded that the thickness of the amphiphilic bilayer increases linearly with decreasing temperatures.

Defining the parameter r by $r = a/c_0$, that is, the anisotropy of the micelle at the temperature of the ordinary nematic-isotropic transition, we see that λ is proportional to

$$\{r^2 - [1 - \alpha(t-1)]^2\}$$

Substituting this expression in Eq. (1) and recalling that $S = \frac{1}{2}$ at $T = T_0$, we obtain the following equation that relates the order parameter and temperature:

$$\frac{1}{t} \left[\frac{r^2 - [1 - \alpha(t - 1)]^2}{r^2 - 1} \right]^2 = \frac{1}{S4 \ln 2} \ln \left[\frac{1 + 2S}{1 - S} \right].$$
(2)

This equation is valid only for $\frac{1}{2} \le S < 1$; that is, for $t_R \le t \le 1$, where t_R is the reentrant transition temperature, the nontrivial solution of



FIG. 1. Order parameter S versus reduced temperature t for some values of α and r: (a) $\alpha = 5$, r = 6; (b) $\alpha = 3$, r = 4.23; (c) $\alpha = 2$, r = 3.3. In each case α and r were chosen so that $t_R = 0.615$.

$$t = \left[\frac{r^2 - [1 - \alpha(t-1)]^2}{r^2 - 1}\right]^2.$$

The trivial solution t = 1 gives the temperature of the ordinary transition.

Figure 1 shows the order parameter as a function of temperature, Eq. (2), for some values of r and α . This result is qualitatively the same result obtained from optical birefringence measurements carried out in a discotic nematic reentrant lyomesophase.²

The numerical values of α were chosen to be of the order of unity since α is the thermal expansion per degree of the amphiphilic molecule multiplied by the temperature of the ordinary nematic-isotropic transition. The values of r we have used are compatible with the shape anisotropy of discotic micelles observed experimentally.^{2,11}

- ¹L. J. Yu and A. Saupe, Phys. Rev. Lett. 45, 1000 (1980).
- ²Y. Galerne, A. M. Figueiredo Neto, and L. Liébert, Phys. Rev. A 31, 4047 (1985).
- ³Introduction to Liquid Crystals, edited by E. B. Priestley, P. J. Wojtowicz, and Ping Sheng (Plenum, New York, 1979).
- ⁴W. Maier and A. Saupe, Z. Naturforsch. 14a, 882 (1959); 15a, 287 (1960).
- ⁵Z.-Y. Chen and J. M. Deutch, J. Chem. Phys. 80, 2151 (1985).
- ⁶M. J. Freiser, Phys. Rev. Lett. 24, 1041 (1970).

- ⁷F. Y. Wu, Rev. Mod. Phys. 54, 235 (1982).
- ⁸R. B. Potts, Proc. Cambridge Philos. Soc. 48, 106 (1952).
- ⁹J. Charvolin, A. M. Levelut, and E. Samulski, J. Phys. (Paris) Lett. **40**, L587 (1979).
- ¹⁰V. Luzzati, H. Mustacchi, A. Skoulios, and F. Husson, Acta Cryst. 13, 660 (1960).
- ¹¹N. Boden and M. C. Holmes, Chem. Phys. Lett. 109, 76 (1984).