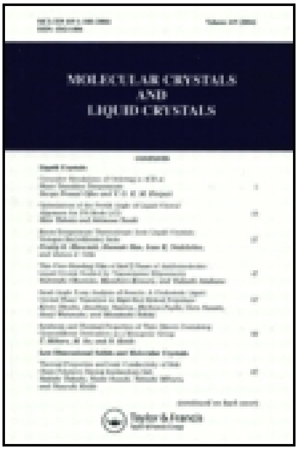

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Mean Field Model for Liquid Crystals Composed of Anisometric Micelles

M. C. Holmes [a] & N. Boden [b]

[a] School of Physics and Astronomy, Preston (Lancashire) Polytechnic, Preston PR1 2TQ, Great Britain

[b] Department of Physical Chemistry, University of Leeds, Leeds, LS2 9JT, Great Britain

Version of record first published: 17 Oct 2011.

To cite this article: M. C. Holmes & N. Boden (1985): A Mean Field Model for Liquid Crystals Composed of Anisometric Micelles, Molecular Crystals and Liquid Crystals, 124:1, 131-138

To link to this article: http://dx.doi.org/10.1080/00268948508079471

Mol. Cryst. Liq. Cryst., 1985, Vol. 124, pp. 131–138
0026-8941/85/1244–131/$15.00/0

Printed in the United States of America

A Mean Field Model for Liquid Crystals Composed of Anisometric Micelles†

M. C. HOLMES

School of Physics and Astronomy, Preston (Lancashire) Polytechnic,
Preston PR1 2TQ, Great Britain

and

N. BODEN

Department of Physical Chemistry, University of Leeds, Leeds LS2 9JT,
Great Britain

(*Received August 22, 1984*)

The lamellar-nematic transition in the caesium-perfluoro-octanoate-water system changes from second to first order at a tricritical point as the volume fraction of surfactant is increased [N. Boden, P. H. Jackson, K. McMullen and M. C. Holmes, Chem. Phys. Letters, **65** (1979) 476]. This observation is explained by applying McMillan's model of smectic ordering to a system of disc-shaped particles with both attractive and repulsive long range interactions. In the lamellar phase the lamellae are envisaged as consisting of layers of disc-shaped micelles which, at the lamellar-nematic transition, simply disperse to form an orientationally ordered micellar solution. Using this model the main features of the phase diagram are explained.

INTRODUCTION

Lyotropic nematic mesophases have been identified[1,2] in surfactant-water mixtures and shown[3,4] to consist of solutions of anisometric micelles which possess long range orientational order. Nematic phases of disc-shaped micelles, N_D, occur as the precursor to the lamellar L

---

†Paper presented at the 10th International Liquid Crystal Conference, York, 15th–21st July 1984.

phase, whilst those consisting of rod- or cylindrical-shaped micelles N_C act as the precursor to the hexagonal H phase.[5] There is a one-to-one correspondence in the symmetries of the phases involved in the lyotropic isotropic (I) $-$ N_D $-$ L transitions and the thermotropic I $-$ nematic(N) $-$ smectic $A(S_A)$ transitions exhibited by rod-shaped molecules. A similar correspondence in symmetries exists between the phases involved in the lyotropic I $-$ N_C $-$ H transitions and those in the thermotropic I $-$ N $-$ columnar transitions exhibited by disc-shaped molecules. These observations seem paradoxical when considered in terms of the intrinsic shapes of the particles which are seen to be opposite in the corresponding lyotropic and thermotropic sequences. However, we expect the symmetries of the ordered phases, not the particle shape, to dictate the phase transition behaviour. We might, therefore, anticipate that these lyotropic transitions can be understood in terms of McMillan's mean field theory which has been shown to account for the general features of the thermotropic S_A $-$ N[6] and columnar $-$ N[7] transitions. In this paper we shall explore whether McMillan's theory can be extended to predict the major features of the phase diagram (Figure 1) for the caesium perfluorooctanoate-water system which forms a N_D phase.[8] It should be noted, however, that this theory was developed for a single component system and as a consequence we cannot expect it to predict the biphasic regions in the phase diagram of a binary system. These biphasic regions would not be present in a phase diagram in which the composition variable is chemical potential rather than volume fraction.

We see from Figure 1 that the L $-$ N_D transition line changes from second-order (where coexisting phases have identical compositions) to first-order (where coexisting phases have different compositions) at a tricritical point, T_C^3, with increasing volume fraction of amphiphile ϕ_A. This behaviour, together with the triple point $T_3(LNI)$ is reminiscent of the phase behaviour (Figure 2) predicted by McMillan[6] for thermotropic S_A $-$ N $-$ I transitions. The interaction driving the N $-$ S_A transition arises from the mutual attraction of the aromatic cores of the lath-like mesogenic molecules; this will increase as the ratio of the lengths of the aromatic core and the molecule decreases, i.e. as the length of the alkyl end chains increases. In the McMillan theory the strength of this interaction is modelled by the parameter α and we see from Figure 2 that the S_A $-$ N transition changes from second order to first order at $\alpha = 0.70$, whilst for $\alpha > 0.98$ the S_A phase goes directly to the I phase. To establish a correlation between the phase behaviour depicted in Figures 1 and 2 it is necessary for ϕ_A and α to be directly, functionally dependent. To appreciate the

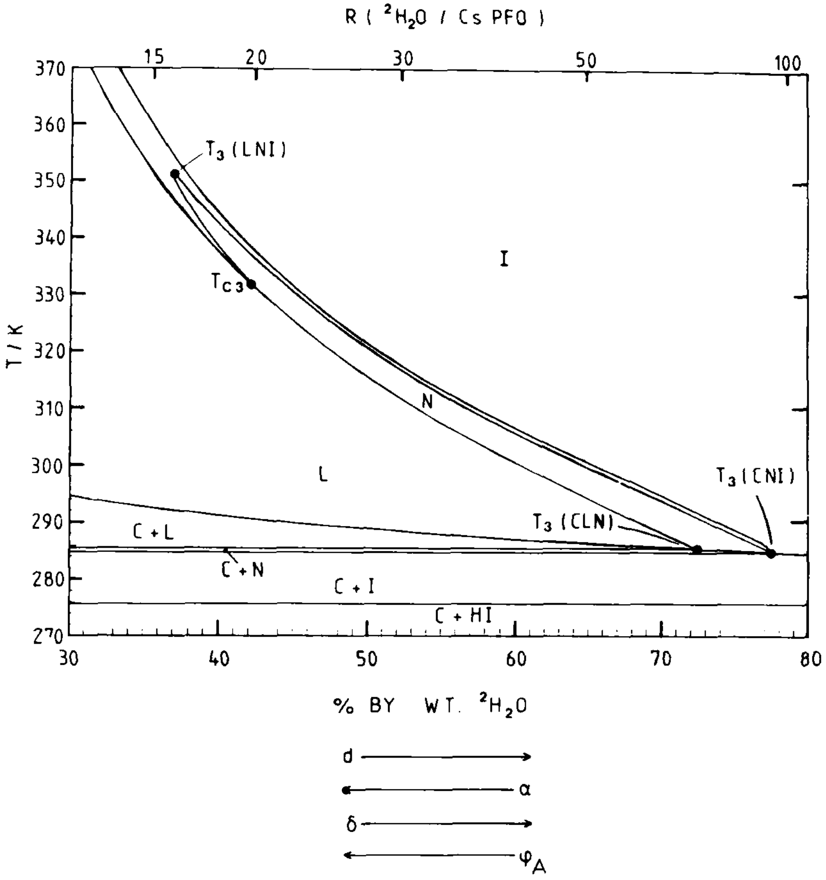

FIGURE 1 Portion of phase diagram of the caesium perfluoro-octanoate-water system showing the temperature and composition ranges of the nematic phase. [This is an updated version of the diagram previously published.][8]

significance of this relationship it is first necessary to describe the mechanism of the lyotropic $N_D - L$ transition in the caesium perfluoro-octanote-water system.

The $N_D - L$ transition is second-order over most of the composition range of the nematic phase; this is a clear indication of a continuity in the structure of the amphiphile aggregates, an assertion confirmed by X-ray diffraction, nmr and electrical conductivity measurements.[9] Thus, we are led to infer that at the $N_D - L$ transition the nematogenic disc-shaped micelles simply condense on to the lamellar planes rather than aggregate into infinitely extending bimolecular lamellae. Intuitively, it seems natural to compare the role of

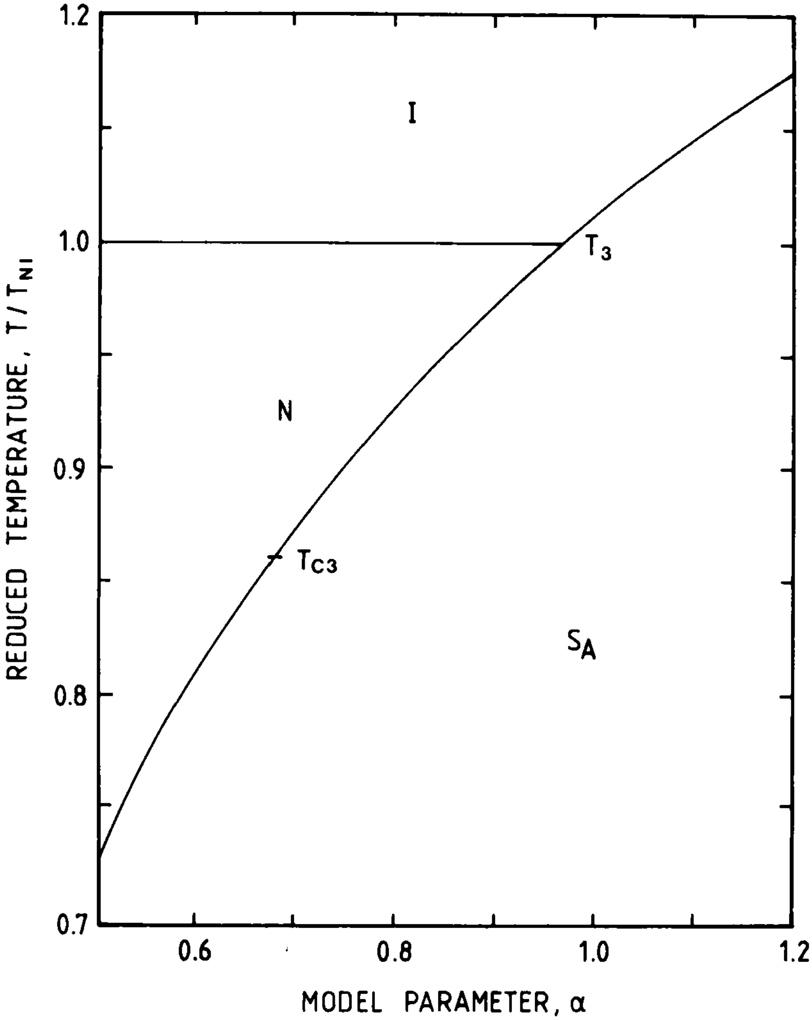

FIGURE 2 Phase behaviour predicted by McMillan model.[6] Transition temperatures correspond to T/T_{NI} where $T_{NI} = 0.2202\ u_0/k$.

the layers of water separating the lamellar planes to that of the alkyl end chains in the thermotropic S_A phase. But this cannot be correct because it would require the $L - N_D$ transition to change from second to first-order as ϕ_A (volume fraction of micelles) decreases, which is exactly the opposite of the observed behaviour. Clearly, the strength of the interaction driving the lyotropic $N_D - L$ transition increases as the separation of the micelles decreases; its origin must, therefore, be in the electric double layer repulsion between micelles in adjacent lamellae rather than in the mutual attraction of neighbouring micelles in the same layer. The electrostatic repulsive energy will be a minimum for a structure in which the micelles are arranged on a f.c.c. lattice and with their symmetry axes normal to the (111) planes: these planes are envisaged as constituting the amphiphilic layers of the L phase. The increasing inter-micellar repulsion with increasing ϕ_A accounts for the functional dependence of α upon ϕ_A as required by the phase diagram (Figure 1).

Another striking difference between Figures 1 and 2 is that for the caesium perfluoro-octanoate-water system the ratio of the transition temperatures T_{LN}/T_{NI} is constant at 0.98 over the composition range 42.5 to 70% by weight of ^2H_2O, whilst the original McMillan model predicts that the value for this ratio should decrease with α and is 0.70 at T_C^3. This unexpectedly large value of T_{LN}/T_{NI} at T_C^3 in the lyotropic system requires a relatively large scalar contribution to the micellar pair potential.[10] This could arise from either a small micelle eccentricity or a large intermicellar separation, or both of these factors.

In section 2 it will be shown that when an anisotropic repulsive term is included in the pair potential, McMillan's theory predicts the major features of the $L - N_D - I$ transitions shown in Figure 1.

In section 3 we shall consider the extent of the theory's validity in the light of experimental measurements, and consider its usefulness in the study of these systems.

THEORETICAL MODEL

We will assume firstly, that in the L phase the amphipilic lamellae consist of layers of disc-shaped micelles which, at the $L - N_D$ transition, simply disperse to form an orientationally ordered micellar solution. Secondly, the dimensions of the micelles are unchanged through the $L - N_D - I$ transitions.

Following McMillan, we start with the two-particle interaction potential

$$U(r_{12}, \cos\theta_{12}) = -\frac{u_0}{\pi^{3/2}}\left[\frac{1}{r_1^3}\exp\{-(r_{12}/r_1)^2\} - \frac{A}{r_2^3}\exp\{-(r_{12}/r_2)^2\}\right] \times [\delta + P_2(\cos\theta_{12})] \qquad (1)$$

where r_{12} is the intermicellar separation, θ_{12} is the relative orientation of the micelle symmetry axes and P_2 is the second Legendre polynomial. The parameters r_1 and r_2 determine the ranges of, respectively, the attractive and repulsive interactions; the Gaussian form of the repulsive interaction is chosen for convenience. u_0 is the strength of the anisotropic attractive part of the potential, this is scaled by the factor A in the repulsive part of the potential and δ is the relative weight of the scalar part which is assumed to be the same for both contributions. The self-consistent single particle potential is

$$U(\xi, \cos\theta) = -u_0\{\eta P_2(\cos\theta) + \alpha\sigma\cos\xi P_2(\cos\theta) + \delta\alpha\tau\cos\xi\} \quad (2)$$

where ξ equals $(2\pi z/d)$, d is the lamellar periodicity which is taken to be in the z direction, and θ is the angle between the micellar symmetry axis and the director. The order parameters are given by

$$\eta = \langle P_2(\cos\theta)\rangle \quad (3a)$$

$$\sigma = \langle\cos\xi P_2(\cos\theta)\rangle \quad (3b)$$

$$\tau = \langle\cos\xi\rangle \quad (3c)$$

Equation (2) is identical to McMillan's single particle potential except that here the dimensionless interaction strength is given by

$$\alpha = 2\{\exp - (\pi r_1/d)^2 - A \exp - (\pi r_2/d)^2\} \quad (4)$$

A value for u_0 was obtained from the value of T_{NI} (336.1 K) at the tricritical point composition (42.5% by weight ^2H_2O) using the Maier-Saupe[11] relation

$$u_0 = 4.542\ k\ T_{NI}. \quad (5)$$

Values of α and δ were then obtained from this value of u_0 and the tricritical point temperature T_C^3. The transition is found to be second-order for $\alpha < 0.17$ and $\delta > 2.4$; thus the variation of α and δ with ϕ_A must be as depicted in Figure 1. The inverse relationship between α and the lamellar periodicity d is the converse of that which pertains for thermotropic $S_A - N$ transitions; it implies that the composition dependence of α is dominated by the repulsive term. Since α is a positive quantity with $0 < A < 1$, it is easily shown that in order for α to increase as d decreases it is necessary that $r_2 > r_1$ and that both of these quantities be less than d/π.

The large value for δ explains the unusually large value of 0.985 for T_{LN}/T_{NI} at T_C^3 and is also indicative of a weak anisotropic interaction potential. The latter is a consequence of both the continuous water medium separating the micelles and the small anisometry of the micelles.[12] The observed dependence of T_{NI} on ϕ_A (Figure 1) implies that u_0 increases with ϕ_A (equation 5) whilst the composition independence of the ratio T_{LN}/T_{NI} across the entire range of second order transitions implies that T_{LN} exhibits the same functional dependence on ϕ_A as T_{NI}, i.e. it is proportional to u_0. The value of T_{LN} is mainly determined by the third term in equation (2) which we see is proportional to $u_0\delta\alpha$ (the magnitude of the cross term is negligible for the values of α and δ involved here); thus, the product $\delta\alpha$ is essentially composition independent and this must be a consequence of the contrasting dependences of α and δ on ϕ_A.

3. How successful is the model?

Clearly the principal success of the model is in its ability to explain the phase diagram, Figure 1, in terms of disc shaped micelles interacting through a phenomenological potential which is physically reasonable; i.e. containing both attractive and repulsive components, and possessing a weak anisotropic term consistent with the small eccentricity of these micelles (~2 → 4). It therefore appears unnecessary to invoke micelle aggregation processes or micelle growth. However X-ray scattering experiments have shown that the mean aspect ratio of the micelles increases as the temperature is decreased[9] and within the N_D phase it increases as ϕ_a is decreased (an effect of both temperature and composition).[12] Changes in micelle size will have the effect of modifying the constants in the interaction potential, equation 2, so that although the main features of the phase diagram remain unaffected changes in, for example, order parameters, will take place over a correspondingly smaller temperature interval.

How valid is the assumption that the LN_D transition is a condensation of disc micelles onto translationally ordered planes? Experimental evidence is equivocal at present. In a recent paper[13] it was suggested that the equivalent transition in the decylammonium chloride/NH_4Cl/water system takes place by a series of micelle aggregations commencing in the N_D phase. Clearly further experiments are required to clarify this point. Since this is a mean field model, short range correlations have been ignored although they might be expected to be important. Indeed X-ray scattering in the N_D phase[9] shows rapid increases in both the orientational order parameter and the translational order as the temperature is decreased. This cannot be wholly explained by an increase in eccentricity (it only changes by ~8% across the N_D phase) changing the parameters of equation 2 and therefore is indicative of increasing short range correlations.

To summarise: the theory is successful in as much as it describes an idealised micellar system which exhibits mesophase behaviour. Comparison with experiment shows disagreements which originate from such micellar behaviour as micelle growth and perhaps even aggregation. To this extent the model allows 'liquid crystal' behaviour to be distinguished from purely 'micellar' behaviour.

Acknowledgments

We thank S. A. Corne and K. W. Jolley for providing the phase diagram shown in Figure 1 and R. W. Chantrell for guidance with computational procedures.

References

1. K. D. Lawson and T. J. Flaut, *J. Amer. Chem. Soc.*, **89**, 5490 (1967).
2. F. B. Rosevear, *J. Soc. Cosmet. Chem.*, **19**, 581 (1968).
3. J. Charvolin, A. M. Levelut and E. T. Samulski, *J. Physique Letters (Paris)*, **40**, L587 (1979).
4. Y. Hendrikx and J. Charvolin, *J. Physique*, **42**, 1427 (1981).
5. N. Boden, K. Radley and M. C. Holmes, *Mol. Phys.*, **42**, 493 (1981).
6. W. L. McMillan, *Phys. Rev.*A.*4* (1971) 1238; *ibid.*, **6**, 936 (1972).
7. G. E. Feldkamp, M. A. Handschy and N. A. Clark, *Physics Letters*, **85A**, 359 (1981).
8. N. Boden, P. H. Jackson, K. McMullen and M. C. Holmes, *Chem. Phys. Letters*, **65**, 476 (1979).
9. N. Boden, S. A. Corne, M. C. Holmes, P. H. Jackson, S. A. Jones and K. W. Jolley, *to be published.*
10. R. L. Humphries and G. R. Luckhurst, *Mol. Phys.*, **35**, 1201 (1978).
11. W. Maier and A. Saupe, *Z. Naturf.* A **14**, 882 (1959); *ibid.*, **15**, 287 (1960).
12. N. Boden and M. C. Holmes, *Chem. Phys. Letts.*, **109**, 76 (1984).
13. M. C. Holmes and J. Charvolin, *J. Phys. Chem.*, **88**, 810 (1984).