

CHAPTER 13

THERMODYNAMICS OF LIQUID CRYSTALS AND THE RELATION TO MOLECULAR DYNAMICS: ESR STUDIES

J. H. FREED, A. NAYEEM and S. B. RANANAVARE

*Baker Laboratory of Chemistry
Cornell University
Ithaca
New York 14853
USA*

ABSTRACT. Molecular theories, derived from ESR studies of molecular dynamics, that provide a basis for understanding the stability of phases of thermotropic and lyotropic liquid crystals, are discussed.

1. Introduction

The statistical thermodynamics of liquid crystals is more complex than that for ordinary liquids, due to our incomplete understanding of the anisotropic interactions that stabilise these phases. In view of these difficulties, traditionally approximate methods are employed; these include molecular field theory away from the transition and/or Landau theory, near the phase transition. Molecular or microscopic theories such as Maier-Saupe [1] (for the N-I transition) and McMillan [2,3] (for the S_A -N transition), wherein the effect of fluctuations are neglected and the mean or average free energy of a single molecule is determined by spatial/orientational averaging of the intermolecular interactions, have proved to be very successful in illustrating molecular characteristics necessary for the existence of a given phase. On the other hand, the Landau theory of phase transitions provides a convenient formalism near the phase transition in which the symmetry and coupling of the various order parameters is incorporated in a straightforward manner [4,5]. The coupling of the various order parameters is the key feature of the liquid crystal phase transitions because of the relatively limited extent of the phase stability. The molecular field and the Landau theories are known to fail near second order transitions, since they do not take into account fluctuations correctly [6]. However, results of renormalisation group calculations indicate that near the tricritical point the Landau theory should be valid [7]. In section 2 we shall illustrate the interplay of these order parameter couplings and the principle of universality using ESR studies of the smectic A-nematic phase transition. Universality relations for nematic ordering in a homologous thermotropic series is considered in section 3. Similar matters are then addressed in section 4 for lyotropics consisting of lipid-cholesterol mixtures. Relevant issues of molecular dynamics then appear in section 5 for the thermotropics and section 6 for the lyotropics.

2. Smectic A-Nematic Tricritical Point and Crossover Behaviour

We have studied in detail the tricritical point corresponding to the crossover between first and second order behaviour in the nO_m homologous series for $4 < n < 8$ and $1 < m < 8$ [8,9]. We have

demonstrated the dominant role played by the alkyloxy chain length in governing the order of the S_A -N transition: for $n > 5$ (< 5) the transition is first (second) order and for $n = 5$, $m > 8$ (< 8 except for 5O.6) leads to a first (second) order transition [10]. Thus, for example 4O.6 (with $T_{NI} - T_{S_{AN}} = 23^\circ\text{C}$) has a second order transition, while 6O.4, which has the same length and the same $T_{NI} = 77.6^\circ\text{C}$, exhibits a weak first order transition (with $T_{NI} - T_{S_{AN}} = 8^\circ\text{C}$). Though surprising, we find this to be a quite general phenomenon for $nO.m$ and $mO.n$ mixtures subject to the above restrictions. We consider 4O.6 and 6O.4 mixtures (and some other members of the $nO.m$ homologous series). The mixtures of these compounds may be regarded as a minimum perturbation series, since $(n+m)$ is constant and the difference $(n-m) = 2$ is a minimum consistent with a crossover.

The order of the S_A -N transition may be determined by a recent DSC method developed by Navard et al. [11,12]. These authors show that the ratio (N) of the DSC peak heights H_2/H_1 for a given transition, performed with two different heating rates (r_2, r_1) is a function of the ratio r_2/r_1 ($\equiv R$) and the magnitude of N provides a simple way to discern the order of the phase transition. From a simple theory of DSC peak shapes for a first order transition it can be shown that in the limit of small heating rates, N varies as the square root of R , but for a second order transition N should be directly proportional to R . In our studies we typically used $R = 2$. An N value of 1.41 for 6O.4 was taken as an indicator of a (weakly) first order S_A -N phase transition. We present in figure 1 a plot of N versus composition of 4O.6 in mixtures of 4O.6/6O.4. The most dramatic changes in N occur just where the crossover between the first and second order S_A -N transition takes place, and it is limited to a rather narrow composition range (75-81% of 4O.6). The tricritical point in 4O.6/6O.4 mixtures is found by this technique to be at mole fraction of 4O.6: $x = 0.805 \pm 0.01$ for which the McMillan parameter $M(= T_{S_{AN}}/T_{NI}) = 0.955$.

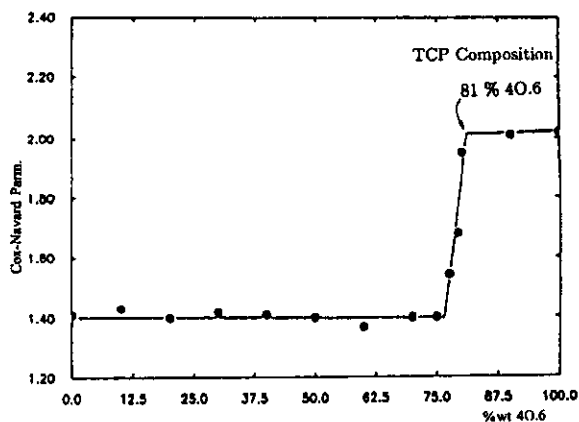


Figure 1. The Cox-Navard parameter N versus the percentage of 4O.6 in 4O.6/6O.4 mixtures. The tricritical composition is 81 per cent of 4O.6 as marked. (From [9]).

We have systematically studied the nematic order parameter, S , of the large and rigid spin probe CSL (5 α -cholestane) by ESR for an extensive range of 4O.6/6O.4 mixtures. It is well-known from many previous studies that CSL accurately reports on the overall or backbone molecular ordering within liquid-crystalline phases [13,14], and its low concentration (10^{-4} M) hardly perturbs the phase behaviour. We show in figure 2, the phase diagram for the 4O.6/6O.4 mixtures based upon the combined DSC and ESR studies. Both methods could be conveniently employed to determine

the phase transitions as a function of T and x , and to within the accuracy of the present measurements ($\pm 0.1^\circ\text{C}$ in T and $\pm 1\%$ in x) they are in good agreement. Indeed the tricritical point could be accurately determined from the ESR measurements (cf. figure 3a). We find the ESR method to be the more sensitive and no less convenient. This phase diagram (figure 2) looks remarkably similar to that obtained by McMillan [2] from his simple theoretical model [if % 60.4 is replaced by the parameter

$$\alpha^M = 2 \exp(-\pi r_0/d),$$

where d is the interlayer spacing and r_0 is the length of the rigid core of the liquid crystal molecule (cf. Chapter 14)], i.e., a greater fraction of 60.4 would, by increasing the d/r ratio, enhance the orientational-translational coupling term. The main disagreement with the McMillan model is the significantly larger value of $M(=T_{S_A N}/T_N)$ we obtain for the tricritical point. Similar trends and phase diagrams were also obtained for mixtures of 40.7/70.4 and of 40.8/80.4 [15].

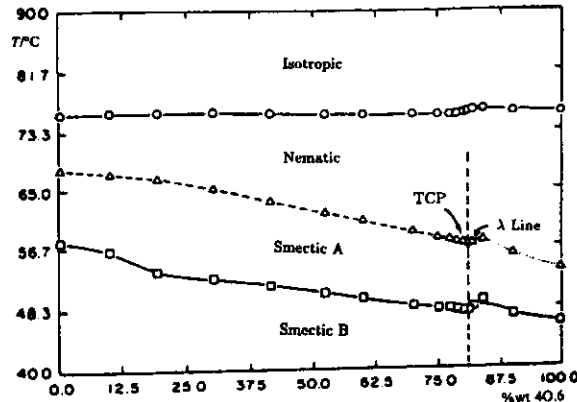


Figure 2. The phase diagram of 40.6/60.4 mixtures. (From [8]).

We show in figure 3a the orientational order parameters measured at the S_A -N phase transition for a range of x plotted as a function of $T_{S_A N}(x)$, (with $T_{S_A N}$ versus x given in figure 2). The plot in figure 3a to the right of the tricritical point [i.e., $x < 0.80$] shows the values of S_N and S_{S_A} in coexistence at $T_{S_A N}(x)$ corresponding to a first order transition, whereas the single line (within experimental uncertainty) to the left of the tricritical point is the lambda line associated with the second order transition. Figure 3c is the corresponding figure for the members in the $nO.m$ series [9] (but see later). These results may be compared with the equivalent results for $^3\text{He} - ^4\text{He}$ mixtures [7]. In particular, in the latter case the mole fraction (m.f.) of ^3He is plotted versus $T(\text{m.f.})$, the transition temperature. As Brisbin et al. have pointed out [16] $S_A - S_{S_A} = \Delta S$ is the non-ordering density for the S_A -N transition analogous to the mole fraction difference in the $^3\text{He} - ^4\text{He}$ case. In the latter case, it is known that "the two branches of the phase separation curve are linear near the [tricritical point] meeting there at a finite angle, and that the lambda line emerges precisely from this peak." [7]. This is exactly the character of the phase diagram in figure 3a for the S_A -N phase transition. It is, to our knowledge, the first such demonstration for a liquid-crystalline tricritical point. Note that in the present case the lambda line is horizontal (and is discussed later).

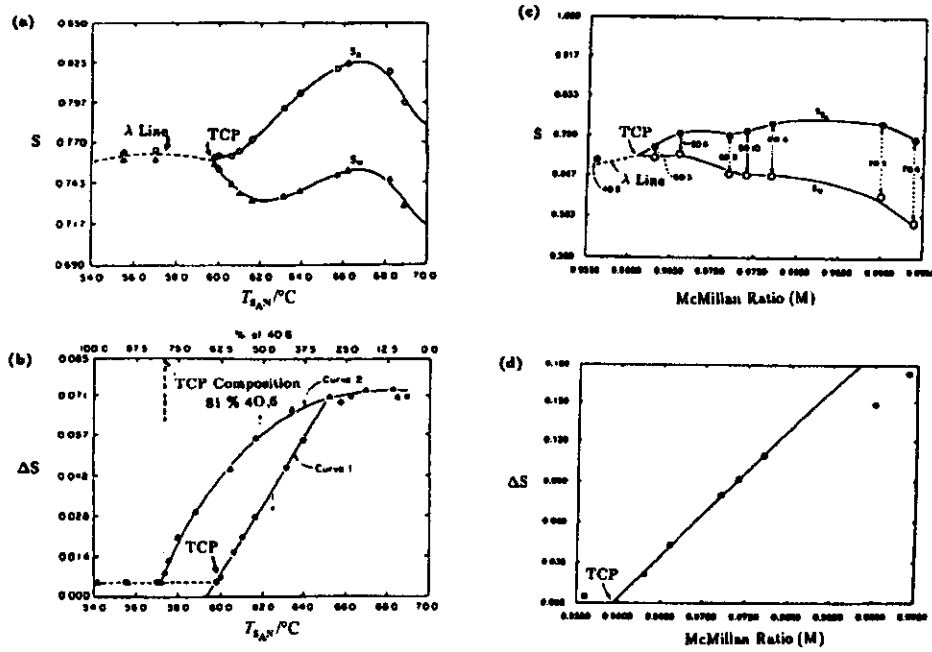


Figure 3. S_{S_A} and S_N are the extrapolated values of the nematic order parameter from the smectic and the nematic phase, respectively at the S_A -N phase transition (figures a,c). M is the McMillan parameter. Lines drawn in figures b and d correspond to the best fit value of β_2 the critical exponent for 40.6/60.4 and nO_m compounds respectively. (From [8,9]).

To continue with the analogy between the ^3He - ^4He superfluid transition and the S_A -N transition we note that for the former, Δ the chemical potential difference between ^3He and ^4He is the conjugate field g to the mole fraction, whereas for the latter we may take as the conjugate field g to ΔS one that couples to the orientational order of the molecular long axis. Brisbin et al. [16] and others have done this by varying the alkyloxy chain length in a different homologous series; we have kept the molecular length d constant but have continuously (but gently) varied the $d/r(x)$ ratio in the 40.6/60.4 mixtures. Thus x , regarded as a monotonic function of $r(x)$ (or $d/r(x)$), can play the role of the conjugate field; however see later for more general considerations of the conjugate field. Thus figure 2 is in the T - g plane allowing us to study critical-to-tricritical crossover of unrenormalised exponents. [In general, we need to correct observed critical exponents by the Fisher renormalisation procedure i.e., scale them by $1 - \alpha$ where α is the critical exponent associated with the specific heat singularity. This correction becomes especially significant when there is an appreciable curvature in the T - g space phase diagram. The nearly linear dependence of T_{S_A-N} versus x in figure 2 indicates a rather mild variation in the conjugate field. Thus, to a good approximation we may treat $T_{S_A-N}(x)$ as a simple measure of x , the conjugate field]. The recent studies of specific heat and smectic coherence length have shown the crossover of the respective exponents α , ν_{\parallel} and ν_{\perp} from the superfluid ($n = 2$, $d = 3$) value to the mean field tricritical value. In fact, the anisotropic scaling relationship

$$\alpha + 2\nu_{\perp} + \nu_{\parallel} = 2,$$

explained by Lubensky [17], and Nelson and Toner [20,21] was found for all of the systems investigated [18,19].

By means of ESR, we may readily study the tricritical exponent β_2 associated with the non-ordering density, defined by:

$$\Delta S \propto |T_{\text{TCP}} - T_{S_A-N}(x)|^{\beta_2} \quad (1)$$

plotted in figure 3b. The very good linear fit, yielding $\beta_2 = 1.00 \pm 0.05$, which is the well-known mean field prediction expected for the tricritical point, is obtained as shown. (β_2 is the critical exponent associated with the non-order parameter ΔS . Note, that it is possible to obtain β , the critical exponent associated with the smectic order parameter ψ from the temperature variation of $\Delta S \equiv (S_{S_A} - S_N^{\text{extrapolated}}) \propto |\psi|^2$ cf. Chapter 14). However, a more direct method is preferable such as X-ray scattering). This result is thus further confirmation of the existence of a S_A -N tricritical point and hence of the second order character of the S_A -N transition for $T_{S_A-N} < T_{\text{TCP}}$.

	4	5	6	7	8
4	40.4 M=0.916 2nd order	40.5 M=0.898 2nd order	40.6 M=0.936 2nd order	40.7 M=0.925 2nd order	40.8 M=0.956 2nd order
5	50.4 M=0.951 2nd order	50.5 M=0.930 2nd order	50.6 M=0.966 1st order	50.7 M=0.956 2nd order	50.8 M=0.979 1st order
6	60.4 M=0.976 1st order	60.5 M=0.972 1st order	60.6 M=0.990 1st order	60.7 M=0.990 1st order	60.8 M=0.997 1st order
7	70.4 M=0.994 1st order	70.5 M=0.990 1st order	70.6 M=1.00 No Nematic	70.7 M=0.997 1st order	70.8 M=1.000 No Nematic
8	80.4 No Nematic	80.5 No Nematic	80.6 No Nematic	80.7 No Nematic	80.8 No Nematic

The more general case [9], wherein several members of the $nO.m$ homologous series that exhibit a weak first order or else a second order S_A -N transition, was studied. The object here was to examine how, by the variation of n and m , we may pass through the tricritical point for the S_A -N transition. Unlike the mixtures of 40.6 and 60.4, where the N-I transition temperature is independent of the composition, the N-I and S_A -N temperatures vary quite dramatically as a function of n and m [22] for the members of the $nO.m$ homologous series. Thus, the choice of the

conjugate field for the non-ordering density is non-trivial. We reconsidered the use of $T_{s,N}$ as the conjugate field variable to ΔS . From the McMillan theory it is well-known that the order of the S_A -N transition is governed by the ratio M . In the table a partial list of the members of the $nO.m$ series along with M and the order of the S_A -N transition is shown. Our analysis [9] of the Landau-de Gennes theory led us to suggest M as the conjugate field variable for ΔS [i.e., $M(m,n) = T_{s,N}(x,m,n)/T_{NI}(m,n)$; thus $M = M(x,m,n)$]. Hence, we plot in figure 3c and 3d S_N , $S_{s,N}$ and ΔS as a function of M yielding:

$$\Delta S \propto |M_{TCP} - M|^{\beta_2} \quad (2)$$

The striking similarity of figures 3a and 3b as well as figures 3c and 3d provides a direct confirmation of the choice of M as a conjugate variable. Furthermore, the critical exponent β_2 is 0.94 ± 0.12 and $M_{TCP} = 0.959 \pm 0.005$. These values are comparable to the values of β_2 ($= 1.00 \pm 0.05$) and $M_{TCP} = 0.953 \pm 0.003$ for the mixtures of 4O.6/6O.4. Of course the M_{TCP} is dependent upon the interaction parameters that are characteristic of the molecular nature of a particular homologous series, but the critical exponent β_2 should indeed be universal for the complex two component order parameter ($n = 2$ and $D = 3$) (similar to the tricritical point in $^4\text{He}/^3\text{He}$ mixtures). Thus, the main conclusion from these order parameter studies is that near a first order or a tricritical S_A -N transition, molecular field theory should be valid.

3. Universality in Nematic Ordering

In this section we present some of our efforts to interrelate various physical properties of liquid crystals. We have attempted to characterise the phase transitions in the spirit of the principle of corresponding states. That is, we have tried to define the reduced variables which eliminate the dependence upon physical quantities that merely serve to locate the phases in temperature, composition space.

We examine in figure 4a the respective behaviour of S_N versus T for 14 different 4O.6/6O.4 mixtures corresponding to x ranging from 0 to 1. An analogous plot for the members of the $nO.m$ compounds as indicated in the caption appears in figure 4c. We use the reduced temperature $t_N \equiv 1 - T/T_{NI}$ as in the dimensionless abscissa in these figures. In figures 4a and 4c there is a large spread of such curves attributable to the large range of $\Delta T_N(x) = (T_{NI} - T_{s,N}(x))$ versus x and the n,m (i.e., alkyl or alkyloxy chain length) respectively. However, when S_N is plotted in figures 4b and 4d versus t_N^U :

$$t_N^U = (T_{NI} - T)/\Delta T_N = t_N/(1 - M) \quad (3)$$

a single universal curve is obtained. We have observed this identical behaviour for 16 other cases of pure compounds and mixtures from the $nO.m$ homologous series as shown in figure 4d. Note that this universal curve is obtained not only for those mixtures exhibiting a second order transition, but it also applies to the cases of first order transitions after replacing $T_{s,N}$, the observed phase transition temperature by $T_{s,N}^*$ ($< T_{s,N}$). Recall (cf. Chapter 14) that this is the temperature at which the second order transition would have occurred if a first order transition had not. We obtained $T_{s,N}^*$ empirically as the single adjustable parameter (for each x) to have S_N versus t_N^U fall on the universal curve in figures 4b or 4d. These results for $(T_{s,N} - T_{s,N}^*)$ are consistent (within experimental uncertainties) with the simple Landau theory we now summarise.

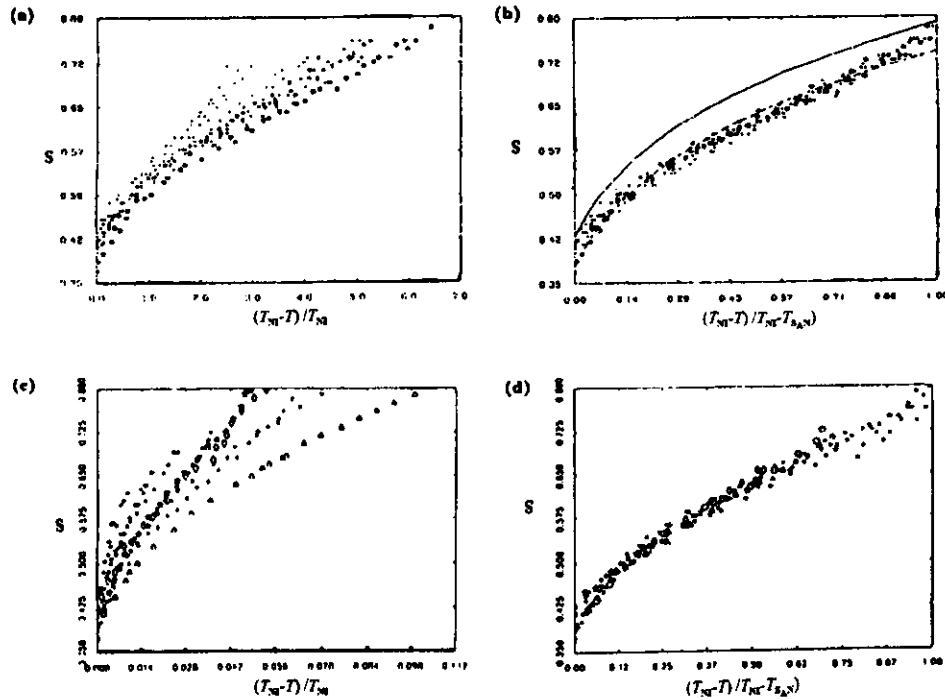


Figure 4. Figures a and c show a plot of S versus the conventional reduced temperature as labelled on the x axis, for 4O.6/6O.4 and various $nO.m$ compounds (4O.6, 4O.7, 4O.8, 5O.4, 5O.7, 7O.4, 7O.5, 6O.4, 5O.10, 6O.3, 6O.5, 5O.6) respectively. Figures b and d show the same data on the new reduced scale t_N^U as defined in the text. (From [8]).

In order to interpret the success of this scaled t_N^U we first note the following: (1) $S_{S_A N}$, the order parameter in the nematic phase at the second order $T_{S_A N}$ (or apparent $T_{S_A N}^*$ for first order cases) is equal to 0.760 ± 0.005 for all members of the homologous series; in fact, the constancy of $S_{S_A N}(x)$ with x appeared in figure 3a as a horizontal lambda line; (2) S_N , the value of S_N at the N-I transition, is nearly the same for all members of the homologous series. We now incorporate these observations into the simple Landau theory for the S_A -N transition. We first write the free energy in terms of nematic and smectic order parameters in the usual manner as [4] (see also the equivalent equations (47)-(51), Chapter 14):

$$F = \alpha(T, x) \psi_0^2 + \beta_0(T, x) \psi_0^4 + \gamma \psi_0^6 + \delta S^2 / [2\chi(T, x)] - C(T, x) \delta S \psi_0^2, \quad (4)$$

where δS is the change in S induced by the coupling to ψ_0^2 , and where we have explicitly denoted the expansion parameters in terms of their functional dependence on T and x for the 4O.6/6O.4 mixtures; (for other members of the $nO.m$ series we shall regard x in a more general sense reflecting the variation of n and m). In equation (1), $\alpha = \alpha_0 [T - T_{S_A N}^*(x)]$, (and is not to be confused with McMillan's α^M parameter). We optimise F with respect to δS leading to $\delta S = C \psi_0^2 \chi$ (cf. Chapter 14), which can be substituted back into equation (1). It then follows that a tricritical point

is predicted for $\chi(T_{s,N}(x)) = 2\beta_0/C^2$. For $\chi(T_{s,N}(x)) < 2\beta_0/C^2$ there is a second order transition at $T_{s,N} = T_{s,N}^*$, whereas for $\chi(T_{s,N}(x)) > 2\beta_0/C^2$ there is a first order transition at $T_{s,N} = T_{s,N}^* + \beta_0^2/16\alpha_0\gamma$.

Our observation that $S_{s,N} = 0.76$ at $T_{s,N}^*$ in all cases suggests that we may rewrite $\alpha(T, x) = \alpha(S) = \alpha_0[S - S_{s,N}]$ in equation (1), with α_0 a constant, i.e., the S_A -N transition is driven by the nematic order parameter in the sense that a precise value, $S_{s,N}$ must be achieved for the second order transition to the smectic phase to occur. Given that the N-I transition occurs at nearly the same T_{NI} for all 4O.6/6O.4 mixtures (cf. figure 2) with approximately the same value of S_{NI} , the use of t_N^U could just be a convenient scaling between the end-points of the nematic phase consistent with these other facts. In particular, if S_N versus T were linear, i.e.,

$$S_N = S_{NI} + b(x)(T_{NI} - T),$$

then these facts mean that

$$b(x) = (S_{s,N} - S_{NI})/[T_{NI} - T_{s,N}^*(x)]$$

with a universal curve

$$S_N = S_{NI} + (S_{s,N} - S_{NI})t_N^U.$$

Actually, except near T_{NI} , the curves in figures 4a and 4b are linear, but this deviation from linearity near T_{NI} could just induce the small scatter obtained near T_{NI} . The fact that other homologues of different chain length (yielding different values of T_{NI}) also obey the same universal curve suggests that T_{NI} is an adjustable reference temperature for which a common value of S_{NI} is obtained. Thus, to treat the general case we should replace T and x by $t = T/T_{NI}$ and M . Note, also that the $(\partial S/\partial T)_x$ is not a constant quantity, see figures 4a and 4b. But, in the scaled form i.e., dS/dt_N^U is independent of M , hence, it is independent of x , m , and n , but nevertheless it does depend on t_N^U (see figures 4b and 4d).

We shall let $\alpha = \alpha_0(M)(t - t_{s,N}(M))$, so that along the lambda line of second order transitions $t = t_{s,N}(M)$ as observed. We must also have $\beta = \beta(t, M)$ such that $\beta_{TCP} = \beta(M_{TCP}, t) = 0$ to be consistent with the experimental results in figures 3a and 3c.

Motivated by this new type of temperature scaling, we have attempted a similar approach in the smectic A phase as shown in figures 5a and 5b. Clearly, there is very little difference between the results using the conventional form of the reduced temperature $t = (T_{s,N} - T)/T_{s,N}$ and our proposed scaling form $t = (T_{s,N} - T)/(T_{NI} - T_{s,N})$ i.e., scaling by the phase extent. However it may be noted that the extent of the smectic phase in 4O.6/6O.4 mixtures varies between 8-12°C. In the next section we consider this scaling form in systems based on phospholipids where the extent of the smectic A ($\equiv L_c$ phase) is quite extensive ($> 60^\circ\text{C}$).

4. Lipid-Cholesterol Mixtures

Somewhat similar features were also found in the lyotropic liquid-crystalline phase (L_c) formed by phospholipids with water [23]. These systems were studied both as a function of temperature and the mole fraction of an additional component, cholesterol, in pseudo-binary (i.e., ignoring the water) mixtures of POPC/cholesterol [24], DMPC/cholesterol and pseudo-ternary mixtures of DMPC/POPC/cholesterol [25]. The orientational order parameter for cholestane (and also 16PC,

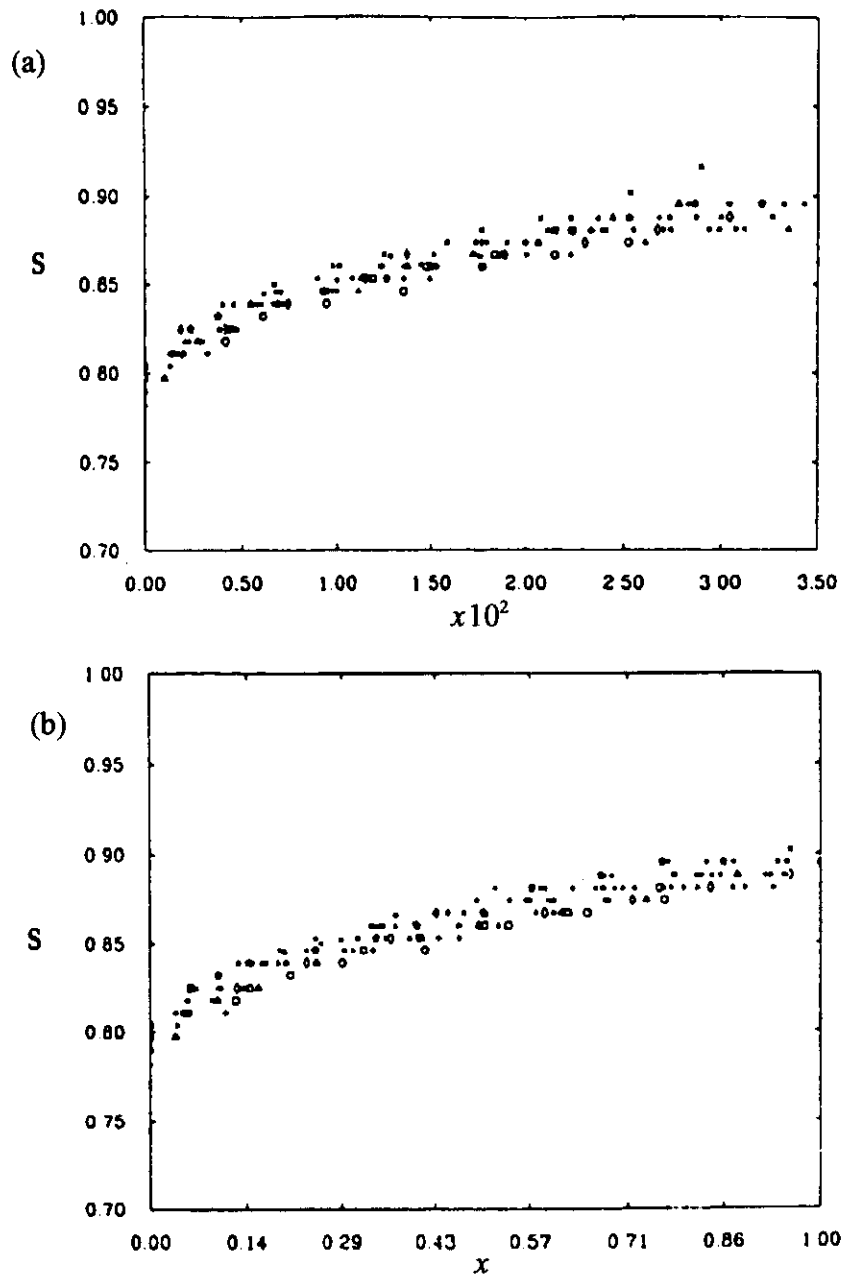


Figure 5. S in the S_A phase of 4O.6/6O.4 mixtures: (a) $x = (T_{SAN} - T) / T_{SAN}$; (b) $x = (T_{SAN} - T) / (T_{SAN} - T_{AB})$. (From [8]).

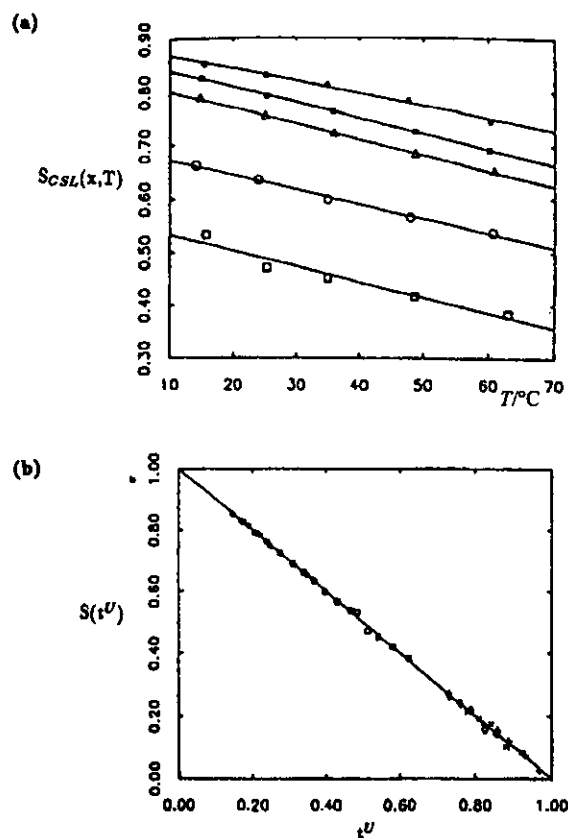


Figure 6. (a) S_{CSL} versus temperature for CSL in POPC/cholesterol mixtures; (b) S_{CSL} versus t^U for CSL in POPC. ([From 23]).

not shown) varies linearly with temperature, an example of which is shown in figure 6a for POPC/cholesterol. The various curves correspond to different concentrations of cholesterol. The remarkable feature of these is the virtual independence of the slope $(\partial S/\partial T)_x$ with respect to the composition of cholesterol for all x less than 0.3. From such a simple behaviour it was possible to show that the disorder parameter: $1 - S(t^U)$ is just the scaled t^U :

$$1 - S(t^U) = t^U \equiv \frac{[T - T_1^*(x)]}{[T_0(x) - T_1^*(x)]}; \quad (5)$$

this is illustrated in figure 6b. Here, the reference temperatures $T_0^*(x)$ and T_1^* are the extrapolated temperatures corresponding to $S=0$ and $S=1$ respectively at a given x . Since, the slope is independent of x , the difference $[T_0(x) - T_1^*(x)]$ must be constant for all x . This implies that the ordering effect of cholesterol can be thought of simply as equivalent to a shift of the temperature scale.

In the DMPC/cholesterol mixtures and the DMPC/POPC/cholesterol mixtures, S also varies

linearly, with the temperature T , but the slope is no longer independent of the composition x . Thus while we can still scale the temperature to fit the data to equation (4), the scaling constant $[T_0(x) - T_1^*(x)]^{-1}$ is no longer independent of x . There are important differences in this case as compared to thermotropic liquid crystals: (i) the observed phase extent is relatively large; the data cover a 65°C temperature range, and do not even approach the low or high temperature phase boundaries and so the values of S at the phase boundaries has not yet been studied; ii) in phospholipids the nematic phase does not exist, hence it might be considered as a case where the McMillan parameter $\alpha^M > 0.85$, thus the lower ordering of CSL in the lipids as compared to the smectic A phase of $nO.m$ compounds is not too surprising.

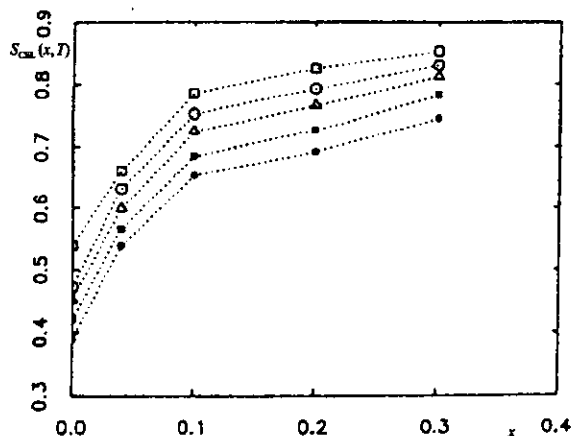


Figure 7. S_{CSL} versus the mole fraction of CSL in POPC. (From [23]).

Figure 7 is a plot of S for CSL versus the cholesterol mole fraction x . Here we see a strong non-linear dependence of S on x (for constant T). The order parameter S increases sharply up to 10 mole %, but it is not very sensitive to further addition of cholesterol. This is generally found in the lipid-cholesterol solutions. It is taken as evidence that they are non-ideal solutions, whereas in the thermotropic mixtures of 40.6 and 60.4, S varies linearly with x . We now consider a potentially very important application of S in such mixtures to understand their thermodynamics. Since the orientational order parameter $S_i(\{x\}, T)$ is an intensive thermodynamic property of the i th component of the solution, the variation of $S_i(\{x\}, T)$ as a function of x_i should be related to its activity in solution. [Here $\{x\}$ refers to the collective mole fractions of the various components]. We expect $S_i(\{x\}, T)$ will be linear with x_i if the solution is ideal; otherwise it would deviate from linear behaviour (analogous to the partial pressure in an ordinary isotropic non-ideal solution). We have pointed out that the orientational order parameter could offer a way to measure the activity coefficient in anisotropic solutions [23]. That is, when $S_i(\{x\}, T)$ varies non-linearly with x_i , the replacement of x_i by the activity of the i th component should relinearise the functional dependence, just as it does other intensive properties of the components of a solution (i.e., the partial pressure). Thus, we shall write;

$$S_i(x_i, T) - S_i(0, T) = b a_i(\{x\}, T) = b x_i \gamma_i(\{x\}, T), \quad (6)$$

where a_i is the activity of the i th component and γ_i is its associated activity coefficient. That is, in equation (6) we are neglecting any, presumably small, higher order terms in a_i .

Thermodynamics provides the following stability conditions for binary liquid mixtures. As long as the binary mixture is in stable equilibrium, the first derivative of the chemical potential of a component with respect to its mole fraction will be positive:

$$(\partial\mu_2 / \partial x_2)_{T,P} > 0. \quad (7)$$

Whereas the mixture will be unstable (phase separation) if

$$(\partial\mu_2 / \partial x_2)_{T,P} < 0. \quad (8)$$

Thus, at the phase boundary the derivative vanishes:

$$(\partial\mu_2 / \partial x_2)_{T,P} = 0. \quad (9)$$

Since the chemical potential of the i th component is

$$\mu_i = \mu_i^0(T) + RT \ln a_i \quad (10)$$

we readily find from equations (6) and (8) that

$$\partial \ln | \Delta S_2(x_2, T) | / \partial x_2 > 0, \quad (11)$$

where $\Delta S_2(x_2, T) = S_2(x_2, T) - S_2(0, T)$, if the binary mixture is stable. Whereas from equation (9) phase separation is predicted when

$$\partial \ln | \Delta S_2(x_2, T) | / \partial x_2 = 0. \quad (12)$$

It is obvious from equation (12) that the orientational order parameter will reach an extremum at the phase boundary.

It was found useful to fit the experimental results with the functional form

$$S_{\text{CSL}}(x, T) - S_{\text{CSL}}(0, T) = b x \exp[d(T)(1-x)^2] / [1 + c(T)x^q], \quad (13)$$

where x denotes the mole fraction of cholesterol in the mixtures. Although this equation is utilised in an empirical sense to interpolate between data points, it is rationalised later. Because the CSL spin probe is known to report on cholesterol due to its structural similarity, we may consider S_{CSL} and S_{chol} comparable [21,29]. Consequently, from equations (6) and (13) we obtain the activity of cholesterol as a function of x at constant temperature

$$a_{\text{chol}}(x, T) = x \gamma_{\text{chol}}(x, T) = x \exp[d(T)(1-x)^2] / \exp[d(T)][1 + c(T)x^q]. \quad (14)$$

This is similar to the behaviour of the activity of a component in a regular solution [30] except for the modification $1/(1 + cx^q)$. This modification was chosen to express the tendency toward saturation observed for the order parameter of the CSL spin probe at high cholesterol concentration. The coefficient $\exp(d)$ in the denominator is added to follow the Henry's law convention for the solute ($\gamma_{\text{chol}} \rightarrow 1$ as $x \rightarrow 0$). Once we have empirically obtained a good functional form of $\Delta S_{\text{chol}}(x, T)$ or $a_{\text{chol}}(x, T)$ as in equation (13) or (14), it is easy to locate the concentration of cholesterol x_i at which the limit of stability of the mixture is reached, and the phase separation starts to occur (cf. equation (12)). For DMPC/cholesterol mixtures, they are compared with reported results from various other experiments. The prediction of the phase

boundary turns out to agree very well with the results of Shimshick and McConnell [5] obtained by tempol-partitioning. Because the activities of the components in mixtures are related to each other by the Gibbs-Duhem equation

$$x d \ln \gamma_{\text{chol}} = -(1-x) d \ln \gamma_{\text{PC}}. \quad (15)$$

We can calculate the activity of the second component, once we know the activity of one component as a function of the composition in a binary mixture. By integrating the Gibbs-Duhem equation with equation (14) for a_{chol} in the DMPC/cholesterol mixture we find

$$\begin{aligned} a_{\text{DMPC}}(x_{\text{DMPC}}, T) &= \gamma_{\text{DMPC}}(x, T)(1-x), \\ &= (1-x)^{(1-c)/(1+c)}(1+cx^2)^{-1/(1+c)} \exp \left[dx^2 - \frac{2c^x}{1+c} \tan^{-1}(c^x x) \right], \end{aligned} \quad (16)$$

where x again denotes x_{chol} . By analogy to the partial pressure (i.e., $p_i - p_i^0 = a_i$, $p_i^0 - p_i^0 = (a_i - 1)p_i^0$), we would expect that the order parameter of DMPC will depend on x according to

$$S_{\text{DMPC}}(x, T) - S_{\text{DMPC}}(0, T) = b' [1 - a_{\text{DMPC}}(x, T)] = b' [1 - \gamma_{\text{DMPC}}(x, T)(1-x)]. \quad (17)$$

We show in figure 8 the variation of the order parameter of the DMPC molecule as a function of cholesterol mole fraction x as predicted by equations (16) and (17). It shows the maximum at x_1 which has been guaranteed by the Gibbs-Duhem equation. It is also compared with the outer maximum splitting of the ESR spectra of the 5-stearic acid spin probe in dispersion samples of DMPC/cholesterol (that is expected to report on the ordering of DMPC), which was found to reach its extremum at the phase boundary in the DMPC/cholesterol mixture [7]. Our prediction agrees rather well with the maximum splitting data. The discrepancy at low x could result from the fact that the maximum splitting is not in itself an accurate measure of the true thermodynamic order parameter.

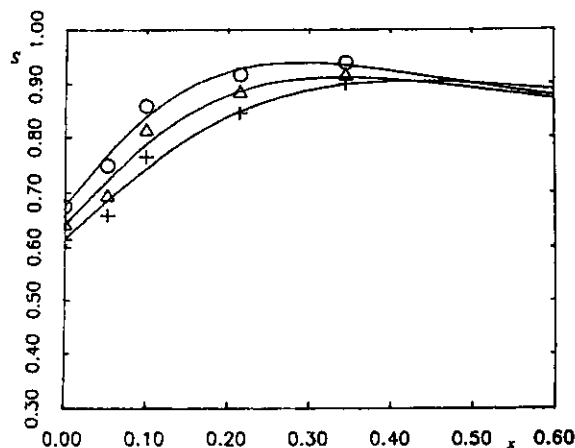


Figure 8. S_{DMPC} versus the mole fraction of CSL. The three lines correspond to three different temperatures 35°C (○), 45°C (△), 55°C (+). (From [24]).

The calculation of a_{DMPC} is an example of the use of the Gibbs-Duhem equation in a two

component system. It should be noted that the Gibbs-Duhem equation is applicable to any multicomponent system. In fact, for a multicomponent solution, knowledge of the activity of one component at all compositions $\{x\}$ allows us to obtain the activities of all the components [36].

Let us now consider the possibility of a critical point. At the critical point not only is equation (9) fulfilled, but also the conditions

$$\left(\partial^2 \mu_2 / \partial x_2^2\right)_{T,P} = 0, \quad \left(\partial^3 \mu_2 / \partial x_2^3\right)_{T,P} > 0 \quad (18)$$

would have to be satisfied simultaneously [37]. For a DMPC/cholesterol mixture it is found that there is no x_c in $0 < x < 1$, such that equations (9) and (18) are simultaneously satisfied. Consequently, we may conclude that a critical point does not exist in DMPC/cholesterol binary model membranes (at atmospheric pressure).

5. Dynamics: Thermotropics

Motivated by these results of studies on the $nO.m$ homologous series, we undertook a series of ESR linewidth studies in compounds exhibiting a weakly first order S_A -N transition. The interest was to see if a critical divergence in ESR linewidths would be observed near a weakly first order S_A -N transition, and, if so, whether it was similar to what is observed [32,33] at a second order S_A -N transition; i.e., what was the effect of the crossover on the critical divergence? Careful quantitative studies of such phenomena are very time consuming, since they involve millikelvin temperature stability and control. Instead in this study, we explored several liquid crystals and spin probes to observe general trends. Thus, it was sufficient to have just ± 0.1 K temperature control, which is much more convenient to obtain [8].

At the S_A -N transition in 7O.5 a rather strong divergence in B and C for both MOTA and P-probe was observed. The extent of the divergence is quite dramatic compared to the previous results near the second order S_A -N transition in 4O.6. Equally significant is that this is the first case for P-Probe (which is not expelled), showing a divergence on the nematic side of the S_A -N transition. However, in 6O.4 the B and C values associated with MOTA show a weaker critical divergence at the S_A -N transition than in 7O.5 and the exact situation for the P-probe B and C parameters is not clear because of lack of data very close to the transition. The general trends are quite similar to what is observed in the 4O.6 solvent [32] with its second order S_A -N transition. In this respect, it is useful to recall that the McMillan parameter $M = 0.936$ for 4O.6, 0.976 for 6O.4, and 0.990 for 7O.5. Thus, smectic driven fluctuations of the orientational order (i.e., the $C\delta S \psi_0^2$ term in equation (4)) are much more likely in 7O.5 than either 4O.6 or 6O.4. In the model proposed for the critical divergences in B and C (cf. Chapter 14) [33], we relied on the expulsion effect of the smaller spin probes to obtain a modulation of spin relaxation by the smectic-like fluctuations of the solvent near the S_A -N transition (cf. Chapter 14). The observation of significant divergences for the spin probe, but only in 7O.5 with its very short (3.7°C) nematic range, suggests that the direct coupling between orientational and positional order parameters can play a significant role when the former is not saturated. This matter is clearly worthy of further study utilising other homologues of the $nO.m$ series.

Let us recall the possible effect of the crossover from second to first order behaviour on the relevant equation for the spectral density. We use it in the simpler form (for $c \rightarrow 0$)

$$J(0) \approx M_g k_B T \tau_m / 32\pi \xi \propto \tau_m / \xi; \quad (19)$$

the divergence in $J(0)$ is determined by τ_m/ξ . According to dynamic scaling theory described in Chapter 14 for the second order transition, $\tau_m \propto (T - T_{S_A N})^{-1}$ and $\xi \propto (T - T_{S_A N})^{-1/2}$ yielding a $-3/2$ power law result for $J(0)$. For the first order transition mean field theory yields $\xi \propto (T - T_{S_A N})^{1/2}$, so the $J(0)$ would diverge as $(T - T_{S_A N})^{-1/2}$. The theory leading to this equation is based on the expulsion effect as noted previously. It was assumed that this effect would modulate the values of S and/or of τ_m , the rotational correlation time felt by the spin probe. It did not take into account the jump in S at the first order S_A -N transition, because it dealt with the second order S_A -N transition. The finite ΔS can either add to or replace the expulsion effect in modulating the electron spin relaxation of the probe. This seems a likely explanation for (i) the observed increase in the critical type divergence, and (ii) the critical type behaviour for P-Probe (which is not expelled by the transition) for a first order S_A -N transition.

6. Dynamics: Lyotropics

6.1. CORRELATION OF D_T^+ WITH S

We now consider whether the lateral diffusion coefficient D_T of CSL (measured by dynamic imaging of diffusion - ESR, cf. Chapter 12) may be related to the ordering S , which we have shown provides a direct measure of solution non-ideality. We show in figure 9a that at each value of temperature, $\ln D_T$ varies linearly with $S^2(x, T)$ for POPC/cholesterol mixed solvents. More precisely, we find empirically that [23,25]

$$D_T(S, T) = D_T^0 \exp\left\{-[\alpha(T) S^2(x, T) + \beta]/RT\right\}, \quad (20)$$

with $D_T^0 = 9.18 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, $\beta = 1303R \text{ K}$, and

$$\alpha(T) = a' + b'/T$$

with $a' = -3364R \text{ K}$ and $b' = 1.303 \times 10^6 R \text{ K}^2$ for this system. The validity of equation (20) is illustrated in figure 9b. The values of $\alpha(T)$ shown in figure 9c, were obtained from the variation of $\ln D_T$ with S for each T , as was the value of $D_T^0(T) = D_T^0 \exp(-\beta/RT)$. Figure 9b shows the universal linear curve obtained when $\ln[D_T(x, T)/D_T^0(T)]$ is plotted versus $\alpha(T) S^2(x, T)/RT$ for each value of x (i.e., constant x behaviour).

It has also been possible to fit our results on D_T for 16-PC to an equation of the form of equation (20) as illustrated in figure 9c. There is somewhat more (random) scatter due in part to the somewhat greater error in the measurements of D_T^{16-PC} versus D_T^{CSL} . Nevertheless, we find that these results are also well-fit by equation (20) with $D_T^0 = 1.06 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, $\beta = 2317R \text{ K}$ with $a' = -2.60 \times 10^4 R \text{ K}$ and $b' = 8.56 \times 10^6 R \text{ K}^2$. Note that for both probes $\alpha(T)$ decreases monotonically with temperature over the range studied. This smaller value of $\alpha(T)$ at the higher temperatures implies a weaker dependence for D_T^{CSL} and D_T^{16-PC} on S at the higher temperatures.

We have also noted that equation (20) also applies to D_T^{CSL} in POPC/DMPC/cholesterol mixtures with $a' = -4363R$, $b' = 1.55 \times 10^6 R \text{ K}^2$, $\beta \approx 0$, $D_T^0 = 1.16 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Note, that in all these cases, the only dependence of D_T on x is through its dependence on $S(x, T)$, and we can regard $\alpha(T) S^2(x, T) + \beta$ as the temperature and composition dependent activation energy for translational diffusion (D_T^+). Thus the activation energy for translational diffusion is enhanced as the membrane ordering is increased by the addition of cholesterol, or by lowering the temperature.

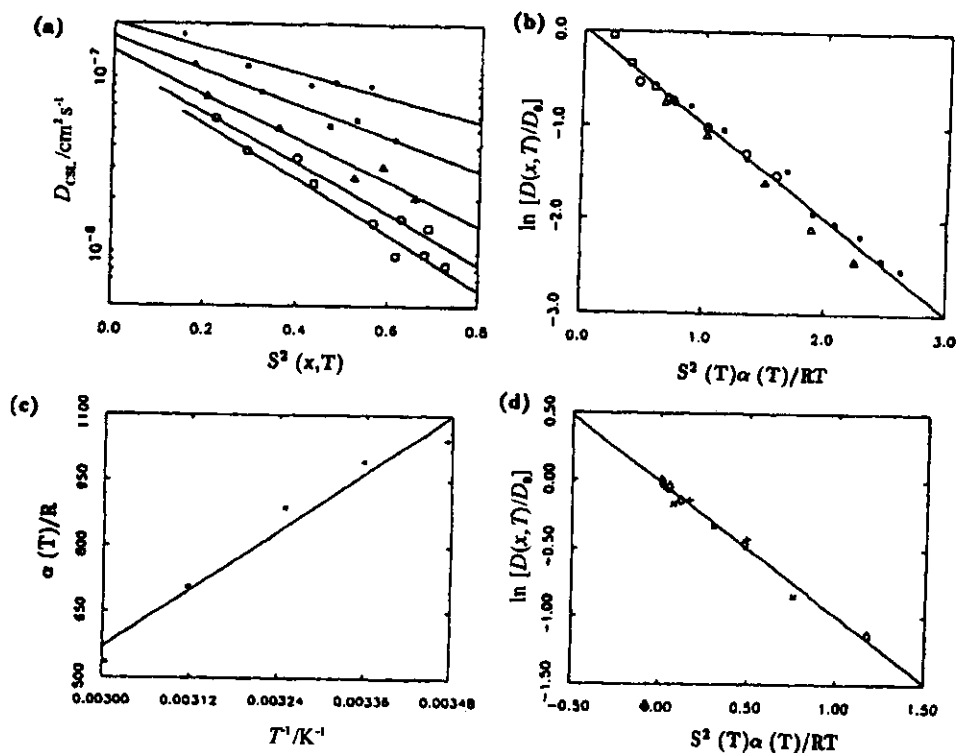


Figure 9. (a) $\ln(D)$ versus S^2 for CSL in POPC/cholesterol mixtures; (b) $\ln(D(x, T)/D_0(T))$ versus $\alpha(T)S^2$; (c) Temperature dependence of α ; (d) same as b but for 16 PC. (From [23]).

6.2. CORRELATION OF D_r^+ WITH S

We have found an empirical relation for CSL which is appropriate for all the PC/cholesterol mixtures studied (i.e., POPC, DMPC, and DMPC/POPC with cholesterol). It is

$$D_r^+ = D_r^{0+} \exp(-AS^2/RT), \quad (21)$$

where A is a constant for a given type of mixture. This equation implies that the activation energy of the rotational motion also depends on S^2 as is the case for translational motion. An interesting feature of equation (21) is that the constant A is independent of temperature, whereas in equation (20) α shows a considerable temperature dependence. D_r^{0+} is also temperature independent. The fits according to equation (21) are shown in figures 10a - 10c for the three mixtures. The best fitting A and D_r^{0+} are respectively: 16.5 kJ mol^{-1} and $1.78 \times 10^8 \text{ s}^{-1}$ for DMPC/cholesterol mixtures, 12.0 kJ mol^{-1} and $7.26 \times 10^7 \text{ s}^{-1}$ for the POPC/cholesterol mixtures, and 13.7 kJ mol^{-1} and $9.79 \times 10^7 \text{ s}^{-1}$ for the ternary mixtures. This, of course, suggests that the activation energy barrier for the rotational motion of a CSL molecule in the DMPC/cholesterol mixtures is slightly higher than in the POPC/cholesterol mixtures.

It is tempting to describe this correlation of D_r^+ and D_r^+ with S^2 in terms of a free volume

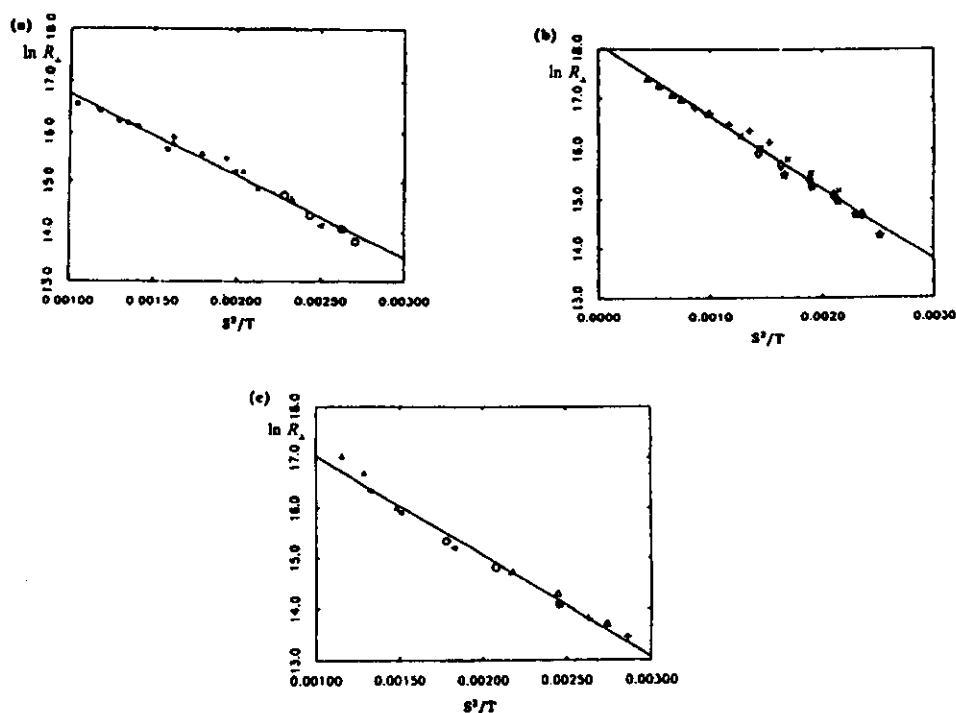


Figure 10. Plots of rotational diffusion coefficient D_R^\perp for CSL in (a) DMPC; (b) POPC; (c) DMPC/POPC mixtures. (From [25])

model [35] proposed by Diogo and Martins for nematic viscosities [36]. In their theoretical analysis an S^2 dependence of the activation energy was predicted. First, we briefly review the free volume diffusion model of Cohen and Turnbull [35]. Next, we consider how to incorporate the effects of ordering in a manner applicable either to translational diffusion or to rotational diffusion [25]. We obtain the results of Diogo and Martins slightly generalised and in a more compact fashion. The basic assumption of the free volume model is that each molecule of a system is confined to a cage by its immediate neighbours. The molecule is randomly rattling inside its cage until fluctuations in the density open up a hole within the cage large enough to permit a substantial displacement of the molecule. Thus, diffusion on a large scale occurs not as a result of an activation in the ordinary sense but rather as a result of a redistribution of the free volume within the liquid. Cohen and Turnbull assumed that the large scale diffusion coefficient can be written as

$$D = \int_{v^*}^{\infty} dv \bar{D}(v) p(v), \quad (22)$$

where $\bar{D}(v)$ (the small scale diffusion coefficient) is an apparent contribution to the overall diffusion arising from the diffusion in a cage with a free volume v , and $p(v)$ is the probability of occurrence of this free volume. [Note at this point that $\bar{D}(v)$ is not a diffusion coefficient in the absence of the cage; that is \bar{D}^0 . Since the space available for diffusion is limited, the

autocorrelation function of momentum (translational diffusion) or of angular momentum (rotational diffusion) decays much faster; thus $\tilde{D}(v)$ is larger than D^0 , $\tilde{D}(v) = g(v)\tilde{D}^0$, $g(v) > 1$ being a geometric factor]. Introducing two characteristic free volumes, a critical free volume v^* , large enough to permit a substantial displacement, and v^f , the average free volume per molecule, they expressed the diffusion coefficient by

$$\tilde{D} \approx \tilde{D}(v^*) \exp(-\lambda v^*/v^f), \quad (23)$$

where λ is a numerical constant. The average free volume is assumed to arise from the thermal expansion at constant pressure, which can be written approximately as

$$v^f = \alpha \bar{v} (T - T_0), \quad (24)$$

where α and \bar{v} are mean values of the thermal expansion coefficient and the molecular volume, respectively; and T_0 is the temperature at which the volume per molecule is reduced to the close-packing limit. Let δv denote the difference between v^* and v^f . Substituting equation (24) into equation (23) we obtain the result of Cohen and Turnbull [35]

$$\begin{aligned} D &= g(v^*) \tilde{D}^0(T) \exp\left(-\lambda v^*/[\alpha \bar{v} (T - T_0)]\right) \\ &= g(v^*) D^0(T) \exp\{-\beta/(T - T_0)\}, \end{aligned} \quad (25)$$

where $D^0(T) = \tilde{D}^0(T) \exp^{-\lambda}$ and $\beta = \lambda \delta v / \alpha \bar{v}$. This equation was developed for a simple liquid of hard spheres and has been successfully applied to explain the fluidity of a large number of glass-forming substances.

Diogo and Martins [36] have applied a similar approach to explain the temperature dependence of the viscosities of thermotropic nematics. Since the nematic viscosities can be associated with both the translational and rotational diffusivities of the nematogenic molecules, [37], Diogo and Martins had to consider both types of molecular mobility. We now use the result of Cohen and Turnbull and estimate the critical free volume v^* , and the small scale diffusion $D^0(T)$, in a manner somewhat related to that of Diogo and Martins, to calculate diffusion coefficients for rotational and translational motions of molecules in liquid-crystalline phases. Let us use diffusion in the isotropic phase of the liquid-crystalline material as the reference. We define the critical free volume for the isotropic phase, $v_i^* = v_i^f + \delta v$, where v_i^f is an average free volume per molecule, δv is an increase in the free volume sufficient for the displacement, and $D_i^0(T)$ is the small scale diffusion coefficient in the isotropic phase. [Here, D denotes either D_T or D_R .] If we assume that the critical free volume for rotation and translation is essentially the same, then both rotational and translational diffusion coefficients are given by equation (25) with $v^* \equiv v_i^*$ and $D^0(T) \equiv D_i^0(T)$

$$D_i(T) = g_i D_i^0(T) \exp\{-\beta_i/(T - T_0)\}, \quad (26)$$

where $\beta_i = \lambda \delta v / (\alpha_i \bar{v}_i)$.

We now consider the effects of the orientational order in the liquid-crystalline phase. This orientational order, due to the potential of mean torque experienced by each molecule, is usually taken to be that calculated by Maier and Saupe or Marčelja in the molecular field approximation [38]:

$$U(\theta) = -\rho(p, T) \epsilon S P_2(\cos \theta), \quad (27)$$

where θ is the angle between the long axis of the molecule and the director, S is the (nematic) order parameter, $\rho(p, T)$ is the number density, and ϵ is the interaction constant. The ordering of the long molecular axis produces a decrease in the average free volume at the disposal of a molecule. Therefore, if the molecule is to gain the critical free volume v_α^* , the cage has to expand considerably, first by an amount it was reduced by the nematic order Δv_α^* , and, additionally, by an amount δv , sufficient to reach the size of v_α^* , which is needed for the displacement. This can be written as $v_\alpha^* = v_1^* = v_1 + \delta v = (v_\alpha^f + \Delta v_\alpha^*) + \delta v$, with v_α^f and v_1 being average free volumes per molecule in the ordered and isotropic phases, respectively. In order to estimate Δv_α^* we proceed as follows. Let k be the isothermal compressibility of the ordered phase and V_α be the volume per particle in the ordered phase. Then, by definition

$$k = -V_\alpha^{-1} (\partial V / \partial p)_T. \quad (28)$$

If Δp_α denotes the associated fluctuation in the pressure leading to the increase in the size of the cage by Δv_α^* , then assuming that the temperature remains constant we can write

$$k \approx -V_\alpha^{-1} (\Delta v_\alpha^* / \Delta p_\alpha). \quad (29)$$

This should produce a change in the free energy per molecule: $\Delta G = V_\alpha \Delta p_\alpha$, provided the ordered phase is otherwise at equilibrium. On the one hand this change can be written in terms of equation (29)

$$\Delta G = V_\alpha \Delta p_\alpha = -k^{-1} \Delta v_\alpha^*. \quad (30)$$

On the other hand, since the temperature is constant, the change in the free energy can be associated with the change of the average energy of intermolecular anisotropic interactions, which in terms of the Maier-Saupe molecular field approximation can be written as

$$\Delta G = -\frac{1}{2} \rho(p, T) \epsilon S^2. \quad (31)$$

Thus, by comparing equations (30) and (31) we obtain

$$\Delta v_\alpha^* = [k \rho(p, T) \epsilon / 2] S^2. \quad (32)$$

The critical free volume v_α^* , is then

$$v_\alpha^* = [k \rho(p, T) \epsilon / 2] S^2 + v_\alpha^f + \delta v. \quad (33)$$

We note at this point that Diogo and Martins neglected $v_\alpha^f + \delta v$, i.e., they assumed $v_\alpha^* \sim S^2$.

Small scale translational or rotational diffusion can be considered to be an activation process: $D^i(T) \sim \exp(-E_i/RT)$, where $D = D_\tau$ or D_r . Since the ordering potential essentially influences only the rotational dynamics of the long molecular axis, cases of translational diffusion and of rotational diffusion about the long axis (characterised by D_τ^l) are insensitive to the presence of the potential. Therefore, both diffusion processes can be written as Arrhenius-like activation processes with activation energies close to that for the isotropic phase; $D_\alpha(T) = D_i(T) = D_0 \exp(-E_i/RT)$. However, for rotational diffusion of the long axis (characterised by D_r^l), a molecule has to pass over an additional barrier resulting from the ordering potential. In the Maier-Saupe molecular field approximation the height (the strength) of the nematic potential is

$E = \rho(p,T)eS$ (cf. equation (27)), so the net barrier should be

$$E_{D_i^*} = E_{D_i} + \rho(p,T)eS, \quad (34)$$

and the dependence of $D_i^*(T)$ upon temperature should be

$$D_i^*(T) = D_i^0 \exp\left\{-[E + \rho(p,T)eS]/RT\right\}.$$

Substituting these quantities $D^0(T)$ and v_α^* into equation (25), we obtain for translational diffusion and for rotational diffusion about the long axis

$$D(T,S) = g^D \exp\left(-\frac{E_D}{RT}\right) \exp\left(-\frac{\beta_{0r} + \theta S^2}{T - T_0}\right), \quad D = D_T \text{ or } D_R^1, \quad (35)$$

and for rotational diffusion about the short axis

$$D_R^2(T,S) = g^{D_i^*} \exp\left(-\frac{E_{D_i^*} + bS}{RT}\right) \exp\left(-\frac{\beta_{0r} + \theta S^2}{T - T_0}\right), \quad (36)$$

where $b = \rho(p,T)e$, $\beta_\alpha = \lambda\delta v/(\alpha_\alpha v_\alpha)$ and $\theta = \lambda k\rho(p,T)e/(2\alpha_\alpha v_\alpha)$. These equations display the S^2 dependence that we have observed experimentally as expressed in equations (20) and (21) respectively, where S is given by S_{CSL} . Further details, including the applicability of these results to mixtures, are given in [25]. A detailed study in a smectic A liquid crystal extends the theory to D_T^1 and D_R^1 and considers small and large diffusing molecules [39].

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