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Invited Article

E.S.R. and D.S.C. investigations of phase transitions in polymorphic 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines

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It is shown that the McMillan parameter $M = T_{S_AN}/T_{NI}$ (where T_{S_AN} and T_{NI} are respectively the temperatures of the smectic A to nematic (S_AN) and the nematic to isotropic (NI) phase transitions) is useful in analysing the crossover between second and first order behaviour of the S_AN transition in the *n*O.*m* homologous liquid crystal series (the 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines). Using a phase diagram of orientational ordering versus M for this series, as obtained in this work (from E.S.R. and D.S.C.), a symmetric tricritical point with mean field exponent $\beta_2 = 1$ is demonstrated. In a preliminary study of E.S.R. linewidth parameters B and C of nitroxide spin probes dissolved in members of the *n*O.*m* series exhibiting a first order S_AN transition, critical-type divergences are observed near this transition. In the case where M is closer to 0·959 (the value at the tricritical point), these divergences appear similar to those previously observed in related *n*O.*m* members with a second order S_AN transition; however, they are considerably enhanced for an M value closer to unity (i.e. more removed from the tricritical point). This indicates the importance of coupling between orientational and positional order parameters in the observed critical-type divergences.

1. Introduction

Ever since the synthesis reported by Kelker and Scheurle [1] of 4-methoxybenzylidene-4′-*n*-butylaniline (1O.4 usually referred as MBBA), the *n*O.*m* compounds have attracted a great deal of attention due to their ease in preparation and their rich but subtle polymorphism. The phase transitions and the critical behaviour in these compounds is unusually rich, and it has been a subject of considerable theoretical interest. Despite the work of many groups, there are still many unsolved problems which remain. One such problem is the order of the smectic A–nematic (S_AN) transition which forms the main focus of this article. Depending on the extent of the nematic phase, the order of the phase transition seems to vary from second order (for compounds having a large nematic phase extent) to first order. An early theoretical attempt to explain this behaviour is due to McMillan [2, 3], who extended the Maier–Saupe mean field theory [4] to incorporate the positional as well as the orientational ordering of the molecules in the smectic phase. However, experimentally observed [5–9] critical exponents do not agree with the mean field theoretical predictions. De Gennes [10], using a Landau expansion of the smectic free energy, emphasized the coupling between the smectic order parameter and the nematic or

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orientational order parameter S. When large fluctuations in S are permitted, this can cause the phase transition to be first order. A nematic phase of large extent, however, would result in S being saturated, thereby reducing the importance of the coupling term so the transition becomes second order. These theories thus imply the existence of a tricritical point at the crossover from second to first order behaviour. De Gennes and McMillan also suggested that the S_AN transition should be very similar to that of superfluid helium, and Alben [11] predicted a $^3He/^4He$-like tricritical point in binary liquid crystal mixtures. This is because the S_AN transition is characterized by a spatial dimensionality of three and an order parameter with two components (amplitude and phase).

However, the theoretical story is more complex, and Halperin *et al.* [12] have stressed the analogy between the smectic A phase hamiltonian and the superconductor hamiltonian, since the gauge invariance of the coupling of the nematic director ($\equiv$vector potential) and the smectic order ($\equiv$superconductor order parameter) parameters is similar. This analogy lead these authors to predict that the S_AN transition can never be truly second order, which of course rules out the possibility of a tricritical point. Though the de Gennes and McMillan theories have successfully provided a great deal of physical insight which has enabled the prediction and calculation of various physical properties near the S_AN transition, the critical exponents associated with the correlation length (ξ) are not correctly predicted. The critical exponents associated with $\xi_{\parallel}$ and $\xi_{\perp}$ are anisotropic [6]. Nelson and Toner [13] have more recently been able to show anisotropic exponents ν such that $\nu_{\perp} = \frac{2}{3}\nu_{\parallel}$ using the dislocation loop theory [14] for the smectic A melting.

Research efforts in our laboratory are focused on detecting the critical effects in static or equilibrium behaviour and in the dynamics, near the S_AN phase transitions, as revealed through magnetic resonance, differential scanning calorimetry (D.S.C.) and X-ray [15–17] scattering studies. In a recent investigation we were able to locate the tricritical point at the S_AN transition in mixtures of 4O.6/6O.4. The phase diagram as well as the critical exponent for the jump in the order parameter of a spin label verified the similarity of the S_AN transition to the superfluid transition in $^3He/^4He$ mixtures [15]. These studies were undertaken mainly to complement existing studies [5–9] on static aspects of the critical phenomenon near the NA transition. Furthermore, a systematic study of the *n*O.*m* series, through variation of the alkyl and alkoxy chain lengths while keeping the central core fixed, gives insight into the molecular aspects of the phase mesomorphism. Additionally, a great deal of fine-tuning of the nematic range can easily be accomplished through study of mixtures of the members of this series. Our preliminary studies of nematic order parameters near the S_AN transition [15] have been helpful in illustrating one very useful feature of such studies, viz. such mixtures can be used to examine the crossover phenomenon near the tricritical point.

The fluctuations in S are of great importance in driving the S_AN transition. Magnetic resonance line widths lend themselves directly to assessing the magnitude of such orientational fluctuations. Thus we have probed the dynamic aspects of the S_AN transition by measuring E.S.R. linewidth parameters (B, C). In an earlier paper [18] we have shown the connection between the correlation length and the B and C terms measured from the E.S.R. linewidths near the NI (nematic–isotropic) transition. The theory is suited for weakly ordered spin probes undergoing fast brownian motion. In the fast motional limit, time scale separation arguments may be applied to calculate the spin relaxation contribution of various cooperative motional modes of the liquid crystals to the B, C terms. We have demonstrated [19–21] that in 4O.6, the E.S.R. linewidth parameters (B, C) show critical divergences near the NI and the S_AN phase transitions in a manner consistent with the correlation length divergence near these phase transitions. In particular, the divergence in linewidths near the NI transition obeys the $\frac{1}{2}$ power law, characteristic of the Landau–de Gennes mean field theory, whereas near the second order S_AN transition a $\frac{1}{3}$ power law is observed that is consistent with dynamic scaling and the superfluid analogy.

The theoretical framework [18 (b), 19, 21] for the critical divergence of the spin probe linewidths near the S_AN transition is formulated using the dynamic scaling arguments proposed by Brochard and Jahnig-Brochard [22]. The relevant order parameter in the smectic A phase is a complex number (so that the dimensionality of the smectic order parameter Ψ is two), the modulus of which corresponds to the density of layers while the phase factor determines the position of the layers. Expanding the free energy near the S_AN transition in terms of this complex order parameter (including spatial gradients as well as coupling to the nematic director terms) followed by Fourier transformation, the wavevector (q) dependent free energy is obtained. Then by applying the equipartition theorem for each q mode, the amplitude of the fluctuation of the nematic and smectic order parameters for that particular mode is determined. Associated with these q modes are the dynamic relaxation times that depend upon the correlation lengths and also exhibit critical slowing down at the S_AN phase transition. The spin relaxation may then be looked upon as a *motional averaging* by q mode dynamics of the Fourier-analysed terms of the spin hamiltonian which are being modulated. Thus the anomalous contribution to the B, C term which appear to diverge near the S_AN transition is a consequence of the divergence of the correlation lengths as well as the critical slowing down of the dynamic relaxation times.

This paper presents a continuation of our studies of these matters. In §2 we review our previous study [15] of 4O.6/6O.4 mixtures, emphasizing particularly the D.S.C. method [16] to locate the tricritical point. We then demonstrate the very similar general behaviour for the entire homologous series with respect to the S_AN transition. Lastly, we present our preliminary results on the dynamics of spin labels near the weakly first order S_AN transition of 6O.4(23) and 7O.5(24). Our conclusions appear in §3.

2. Results and discussion

2.1. *Mixtures of 4O.6 and 6O.4*

To analyse the order of the S_AN transition we have employed a D.S.C. method recently developed by Navard and Cox [25]. These authors show that the ratio (N) of the D.S.C. 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 D.S.C. 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_AN 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_AN transition takes place, and it is limited to a rather narrow composition range (75–81 per cent of 4O.6).

This D.S.C. technique was used in conjunction with an E.S.R. technique where a rigid spin label such as the cholestane nitroxide (CSL) was dissolved in the liquid

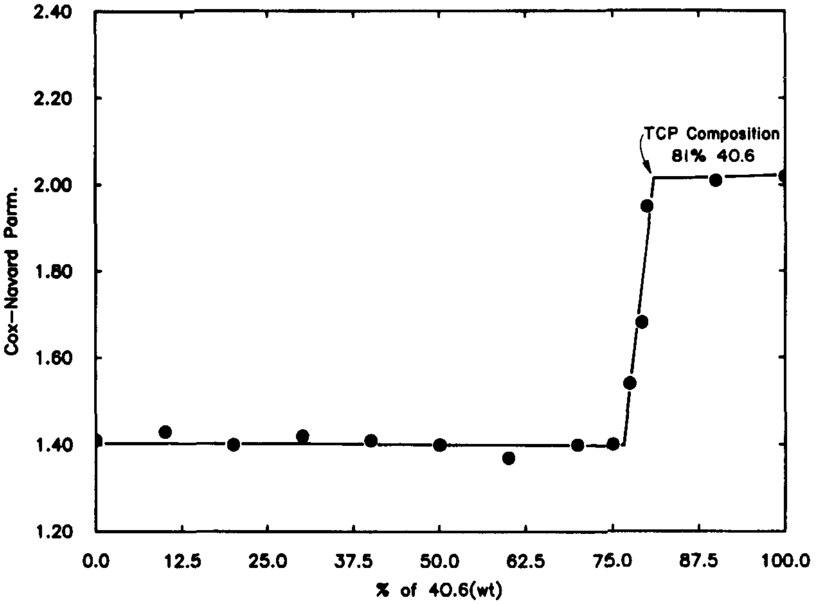


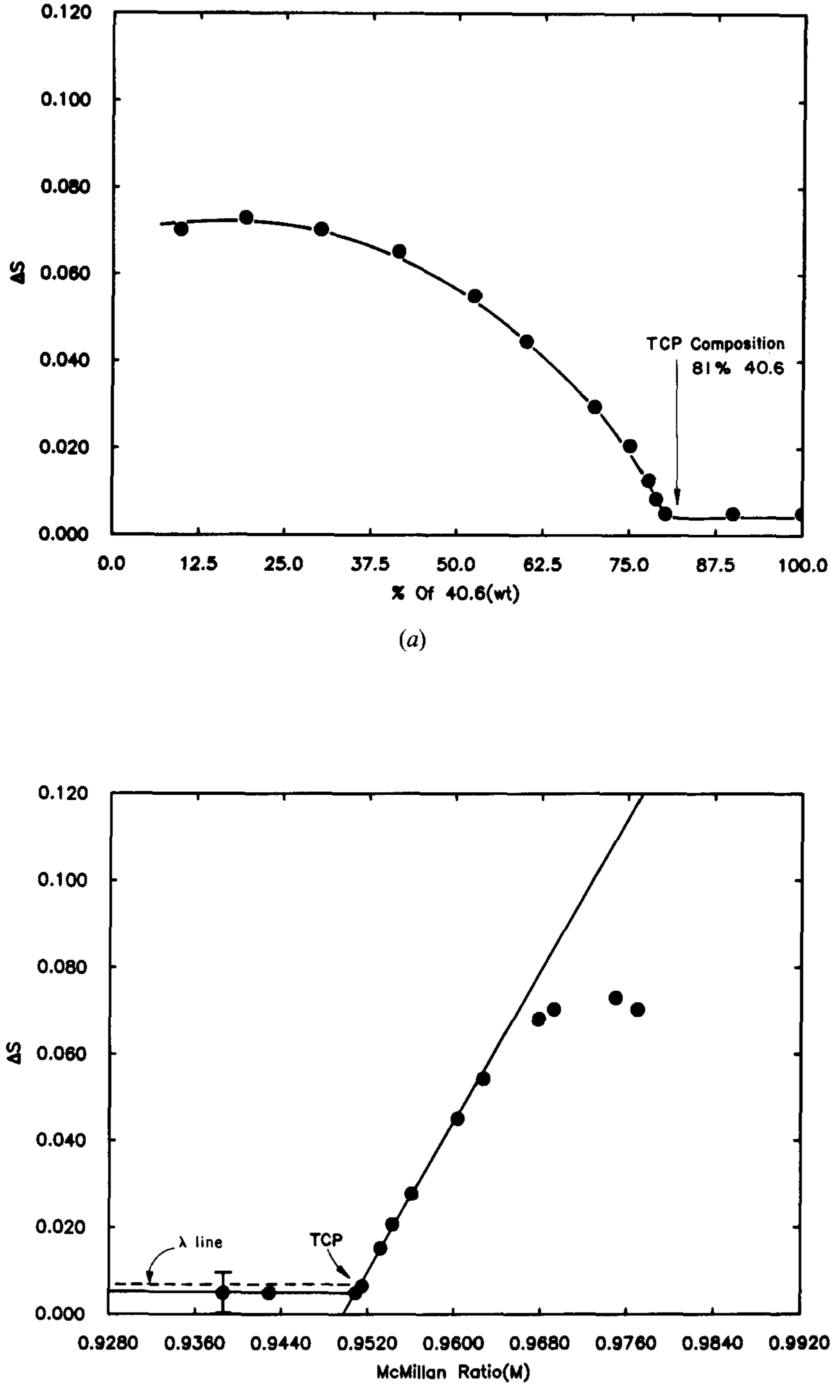
Figure 1. The Cox–Navard parameter, N from D.S.C. measurements versus percentage of 4O.6 in mixtures of 4O.6/6O.4. The tricritical composition is 81 per cent of 4O.6 as marked.

crystal, and the variation of its order parameter as a function of temperature through the S_AN transition was monitored. A discontinuous change in the order parameter at the S_AN phase transition (i.e. $\Delta S \neq 0$) indicates a first order phase transformation and vice versa. In figure 2 we show, for comparison, the jump in the nematic order parameter as a function of 4O.6 composition (figure 2(*a*)) and M (figure 2(*b*)) (both based on [15]). Clearly, the range over which ΔS decreases is rather broad. Nevertheless ΔS goes to zero at the same composition that N approaches 2. Thus, these two simple techniques provide relatively accurate and consistent ways to locate a tricritical point. Furthermore, the ΔS variation as a function T_{S_AN} was found to yield $\beta_2 \approx 1{\cdot}00 \pm 0{\cdot}05$ (*cf.* the solid line in figure (2)), a critical exponent which is defined as [15]

$$\Delta S \propto |T_{\mathrm{TCP}} - T_{S_AN}|^{\beta_2}. \qquad (1)$$

2.2. *Phase diagram and tricritical point for the nO.m homologous series*

We now examine the members of the *n*O.*m* homologous series that exhibit a weak first order, or else second order, transition. The object here is that through a variation of *n* and *m* one may cross over through a tricritical point in a S_AN transition. In the work of mixtures of 4O.6/6O.4 it was found that the mole fraction (of 4O.6) x could play the role of the *conjugate field* with which to study this crossover. More precisely, we could use $T_{S_AN}(x)$ as shown by equation (1) to describe the decrease of ΔS with x as the tricritical point is approached. However, for the *n*O.*m* homologous series, where T_{S_AN} becomes a function of *n* and *m*, we do *not* find that equation (1) applies to our data. This is indicative of the fact that we do not have the relevant independent field to perform our analysis of the density variables (e.g. ΔS) at the S_AN transition



(*a*)

(*b*)

Figure 2. ΔS, the difference in nematic order in the smectic and nematic phases in coexistence along the line of the first order transitions plotted as a function of (*a*) percentage of 4O.6 and (*b*) McMillan ratio, M for mixtures of 4O.6/6O.4. The tricritical point is marked and the λ line corresponding to the second order transition is also shown. (Data are from [15]).

for the homologous series. Instead, we recall from the study of mixtures [15] that the McMillan parameter, $M \equiv T_{S_AN}/T_{NI}$, was useful to *renormalize* the reduced temperature t so as to yield a universal curve for the dependence of S on temperature in the nematic phase. Furthermore, in the McMillan theory, the order of the S_AN transition is shown to be determined by M. The table shows a partial list of the members of the nO.m series along with their respective McMillan parameters, M. We find that the compounds having values of $M > 0{\cdot}959$ ($< 0{\cdot}959$) exhibit first (second) order S_AN transition with $M = 0{\cdot}959 \pm 0{\cdot}005$ at the tricritical point (TCP) (see later). This is in agreement with the value of $0{\cdot}951 \pm 0{\cdot}003$ (*cf.* figure 2 (*b*)) found in 4O.6/6O.4 mixtures. Of course, the value of M_{TCP} is expected to be different for different homologous series.

Such considerations have lead us to consider M as an appropriate field value with which to study the crossover in a homologous series. It should not in any way be confused with the temperature variable, T, despite its definition. That is T_{S_AN} and T_{NI} are distinct values at the phase transition and are really functions of x for mixtures of n and m in the homologous series. Thus equation (1) is really not a critical exponent with respect to T, but with respect to $T_{S_AN} = T_{S_AN}(x, n, m)$, etc. Thus we shall write equation (1) as

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

For 4O.6/6O.4 mixtures, where $T_{NI}(x)$ is a constant independent of x [15], the proportionality of equation (2) reduces to that of equation (1). However, this is not so for the homologous series, because the T_{NI} values are observed to vary over a wide range [16]. In a similar spirit we shall use as our reduced temperatures: $t \equiv T/T_{NI}$, so that we scale with the T_{NI} characteristic of the particular n and m values.

In figure 3 (*b*) we show the jump in spin probe (C.S.L.) order parameter at the S_AN transition as a function of M, and in figure 3 (*a*) the limiting values of the nematic order parameter at the phase boundary are shown. The solid line in figure 3 (*b*) corresponds to $\beta_2 = 0{\cdot}94 \pm 0{\cdot}12$ in agreement with the mean field value of unity [26]. (The values of the D.S.C. parameter N for these compounds range between $1{\cdot}0$ and $1{\cdot}4$ except for 5O.6 ($N = 1{\cdot}5$) and 6O.3 ($N = 1{\cdot}54$) where these values exceed $\sqrt{2}$. This is consistent with our results in figure 1 for N in mixtures, in that only very near the tricritical point does N change from $\sqrt{2}$ to $2{\cdot}0$.) The straight line extrapolates to $M = 0{\cdot}959 \pm 0{\cdot}005$ where $\Delta S = 0$. Thus these results taken together with our previous results on the mixtures of 4O.6/6O.4 suggest that, for a weakly first order S_AN transition, the mean field theory is adequate in describing the transition. This was further corroborated by X-ray scattering studies [17] of 6O.4. We found that within experimental accuracy $\xi_\parallel/\xi_\perp$ remained constant as a function temperature near the S_AN transition. That is, the critical exponents $\nu_\parallel$ and $\nu_\perp$ are equal and are found to be close to the mean field theoretic value of $\frac{1}{2}$.

Our results also suggest that the mean field theory be applied with the following variables: the reduced temperature, $t = T/T_{NI}$, as introduced previously, and its conjugate field variable, M, which replaces x used for 4O.6/6O.4 mixtures. This is considered further in the Appendix.

2.3. *E.S.R. linewidths near the S_AN transition*

Guided by the results just described, we undertook a series of E.S.R. linewidth studies in compounds exhibiting a weakly first order S_AN transition. More particularly,

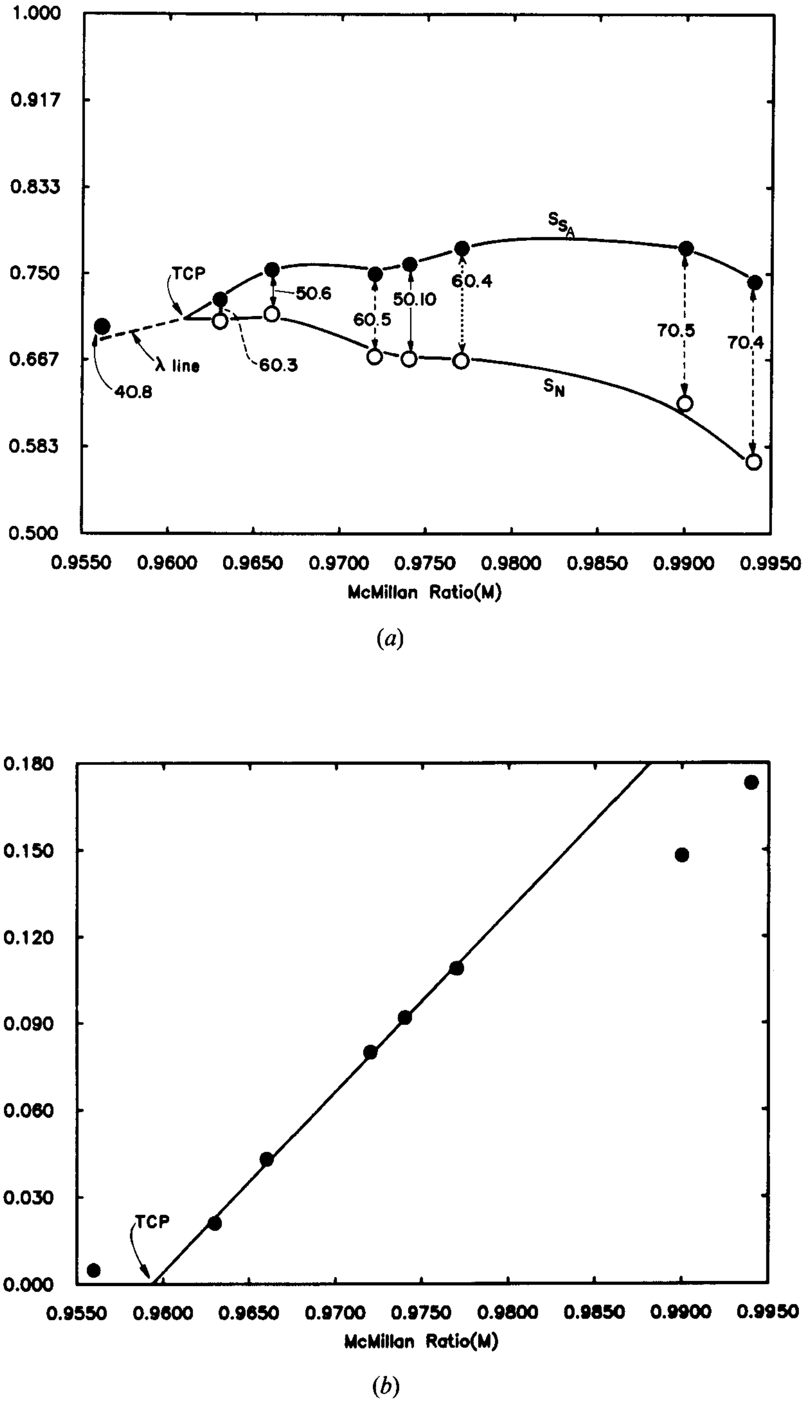
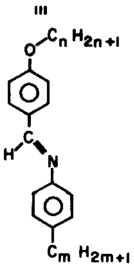


Figure 3. (*a*) The nematic order parameter S is plotted versus the value of McMillan ratio, $M(n, m) = T_{S_AN}/T_{NI}$ for nO.m homologues (as shown). The coexistence region and the λ line are shown. This figure has the appearance of a phase diagram with M acting as a crossover variable. (*b*) ΔS at the S_AN phase transition versus $M(n, m)$ for the nO.m homologues shown in (*a*). The straight line fit yields a $\beta_2 = 0{\cdot}94 \pm 0{\cdot}12$ and $M_{TCP} = 0{\cdot}959 \pm 0{\cdot}005$.

nO.m ≡

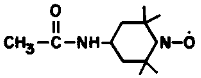


S_AN transition in the *n*O.*m* series: the McMillan ratio *M* and order of transition.

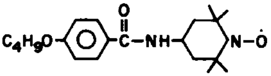
	m				
n	4	5	6	7	8
4	40·4 *M* = 0·916 II order	40·5 *M* = 0·898 II order	40·6 *M* = 0·936 II order	40·7 *M* = 0·925 II order	40·8 *M* = 0·956 II order
5	50·4 *M* = 0·951 II order	50·5 *M* = 0·930 II order	50·6 *M* = 0·966 I order	50·7 *M* = 0·956 II order	50·8 *M* = 0·979 I order
6	60·4 *M* = 0·976 I order	60·5 *M* = 0·972 I order	60·6 *M* = 0·990 I order	60·7 *M* = 0·990 I order	60·8 *M* = 0·997 I order
7	70·4 *M* = 0·994 I order	70·5 *M* = 0·990 I order	70·6 *M* = 1·0 No nem.	70·7 *M* = 0·997 I order	70·8 *M* = 1·00 No nem.
8	—	—	—	—	—

M is the McMillan ratio, T_{S_AN}/T_{NI}.

MOTA



P probe



our interest was to see if a critical divergence in E.S.R. linewidths could be observed near a weakly S_AN transition and, if so, whether it is similar to what is observed [19–21] at a second order S_AN transition. Careful quantitative studies of such phenomena are very time consuming, since they involve millikelvin temperature stability and control. Our present objectives were more of a preliminary nature: we wished to explore several liquid crystals and spin probes to observe general trends. Thus, in the present work we settled for $\pm 0{\cdot}1$ K temperature control, which is more convenient to obtain [15].

Our E.S.R. studies were conducted using spin probes shown in the table. Note that *P* probe is similar in structure to a liquid crystal molecule, and in *n*O.*m* compounds such as 4O.6 it exhibits [27] the ordering and dynamics similar to that expected for the liquid crystal molecules. MOTA, however, is smaller and more weakly ordered [20]; its location relative to the liquid crystal host molecules can vary with the phase, and this will influence its ordering and dynamics.

The liquid crystals we have used are 6O.4 ($M = 0{\cdot}976$) and 7O.5 ($M = 0{\cdot}990$). Thus, whereas both exhibit first order transitions (recall $M = 0{\cdot}959$ at the tricritical point), 6O.4 should be more nearly second order as judged from its M value. The phase diagrams of these compounds are well known and they were synthesized using standard procedures and purified by recrystallization from alcohol. The following is the phase sequence in these two compounds. The transition temperatures we observe compare well with prior work [28]; they are

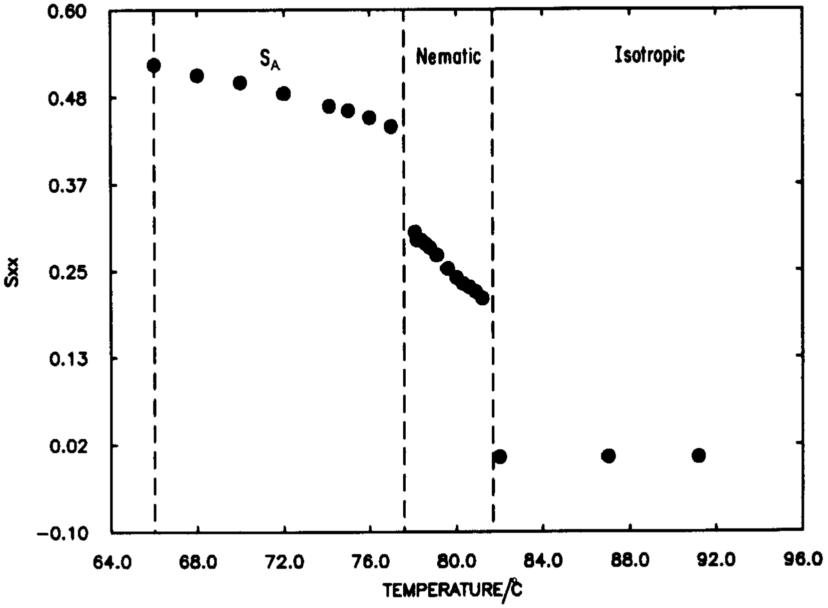
$$6\mathrm{O}.4\ \mathrm{I} \xrightarrow{77{\cdot}3^\circ} \mathrm{N} \xrightarrow{68{\cdot}9^\circ} \mathrm{S_A} \xrightarrow{59{\cdot}2^\circ} \mathrm{S_B} \xrightarrow{57{\cdot}6^\circ} \mathrm{S_G} \xrightarrow{\approx 30^\circ} \mathrm{K},$$

$$7\mathrm{O}.5\ \mathrm{I} \xrightarrow{83{\cdot}2^\circ} \mathrm{N} \xrightarrow{79{\cdot}6^\circ} \mathrm{S_A} \xrightarrow{68{\cdot}3^\circ} \mathrm{S_C} \xrightarrow{64{\cdot}0^\circ} \mathrm{S_B} \xrightarrow{56{\cdot}4^\circ} \mathrm{S_G} \xrightarrow{25{\cdot}2^\circ} \mathrm{K}.$$

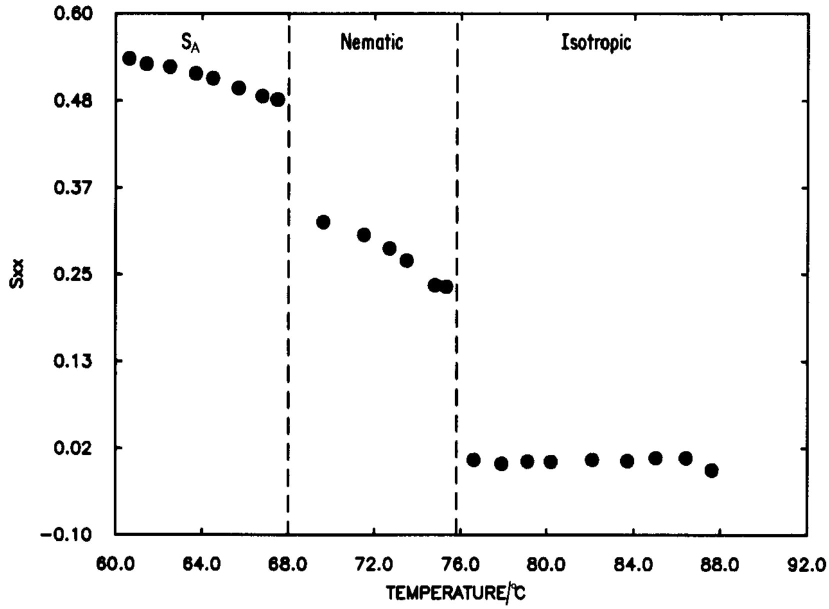
The NI, S_AN and S_BS_A phase transition temperatures were determined using D.S.C. while the BG transition occurs near room temperature and was detected from optical microscopy and also from X-ray scattering.

Spin probe doped samples were prepared using standard procedures [29]. First we note the salient features of the E.S.R. results. As is expected, we observe a discontinuity in the orientational order parameters of the spin labels at the NI, S_AN and smectic B–smectic A phase transitions. For the S_AN transition, we also expect a jump in the smectic order parameter (recall these are first order S_AN transitions). This information is, however, not obtainable from E.S.R. results. The intensity of the Bragg peaks in the small angle X-ray diffraction patterns provides a direct method to accomplish such a measurement of the smectic positional order parameter. We have recently completed, at the CHESS Synchrotron facility, a preliminary study to measure these order parameters, and this will be reported elsewhere.

The spin label (MOTA, *P* probe) (also see [27]) order parameters as a function of temperature are shown in figures 4 and 5. (For *P* probe the data collected were limited to isotropic, nematic and smectic A phases, since it proved very difficult to maintain the alignment of this probe with respect to the applied magnetic field in the low temperature phases.) In the smectic and nematic phases the *P* probe order parameter (*cf.* figure 5) variation bears a strong resemblance to the order parameter predictions of McMillan for the liquid-crystalline molecules. It is interesting to compare the ordering of these two probes in the smectic A phase. *P* probe ordering continues to increase with decrease in temperature as expected, whereas the order parameter of MOTA remains essentially constant. The same effect is clearly seen in 7O.5. In 7O.5, where the smectic C phase precedes the smectic B phase, similar trends continue. This



(*a*)



(*b*)

Figure 4. Order parameter S_{xx} for the *P* probe in (*a*) 7O.5 and (*b*) 6O.4 as a function of temperature. The phase boundaries are shown. Also see [27].

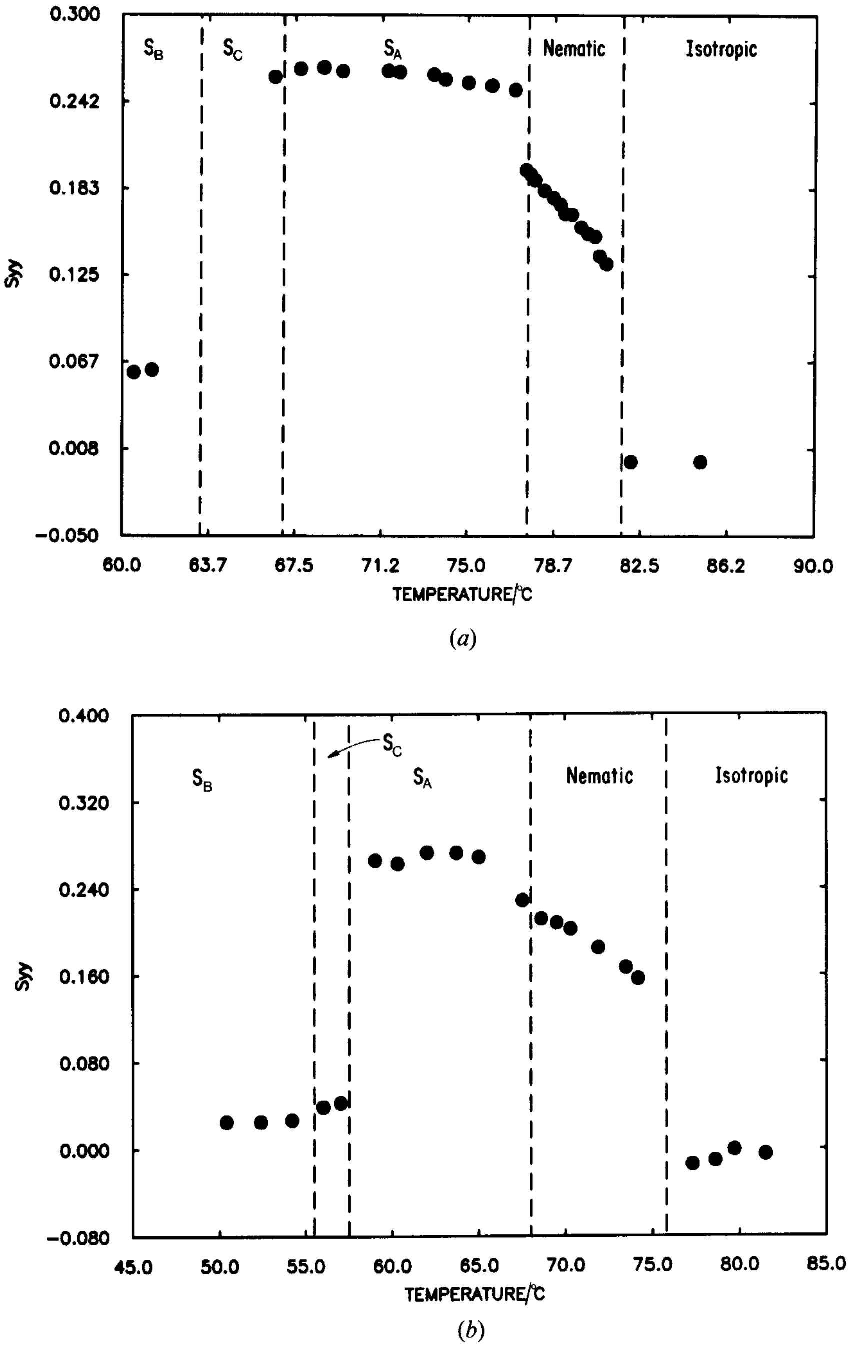
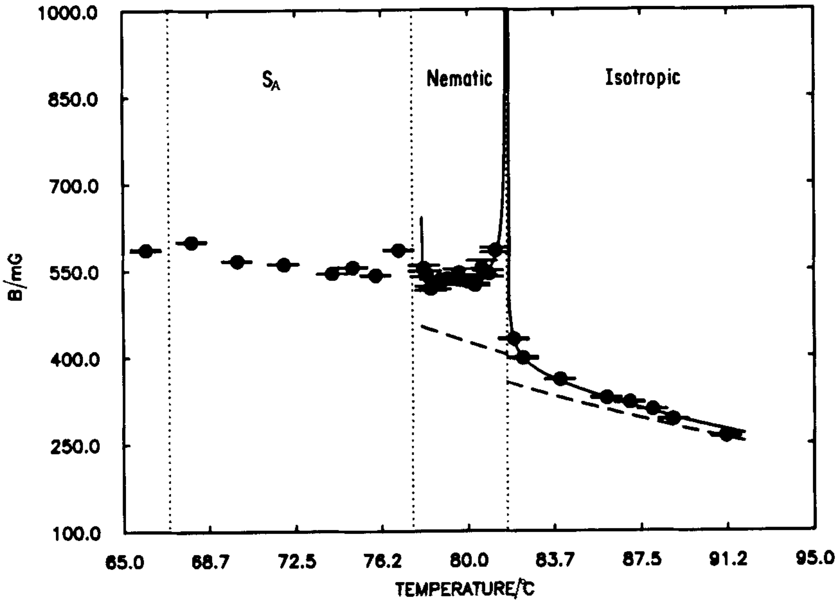
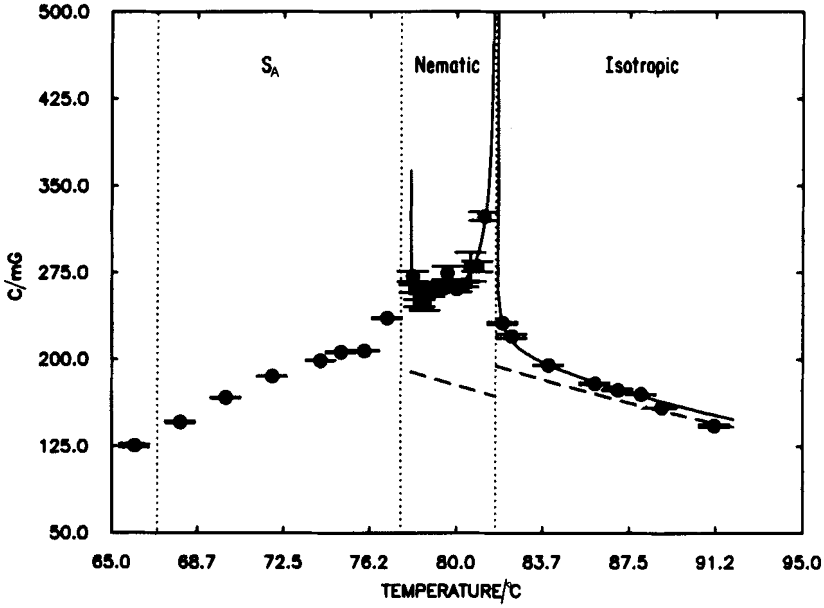


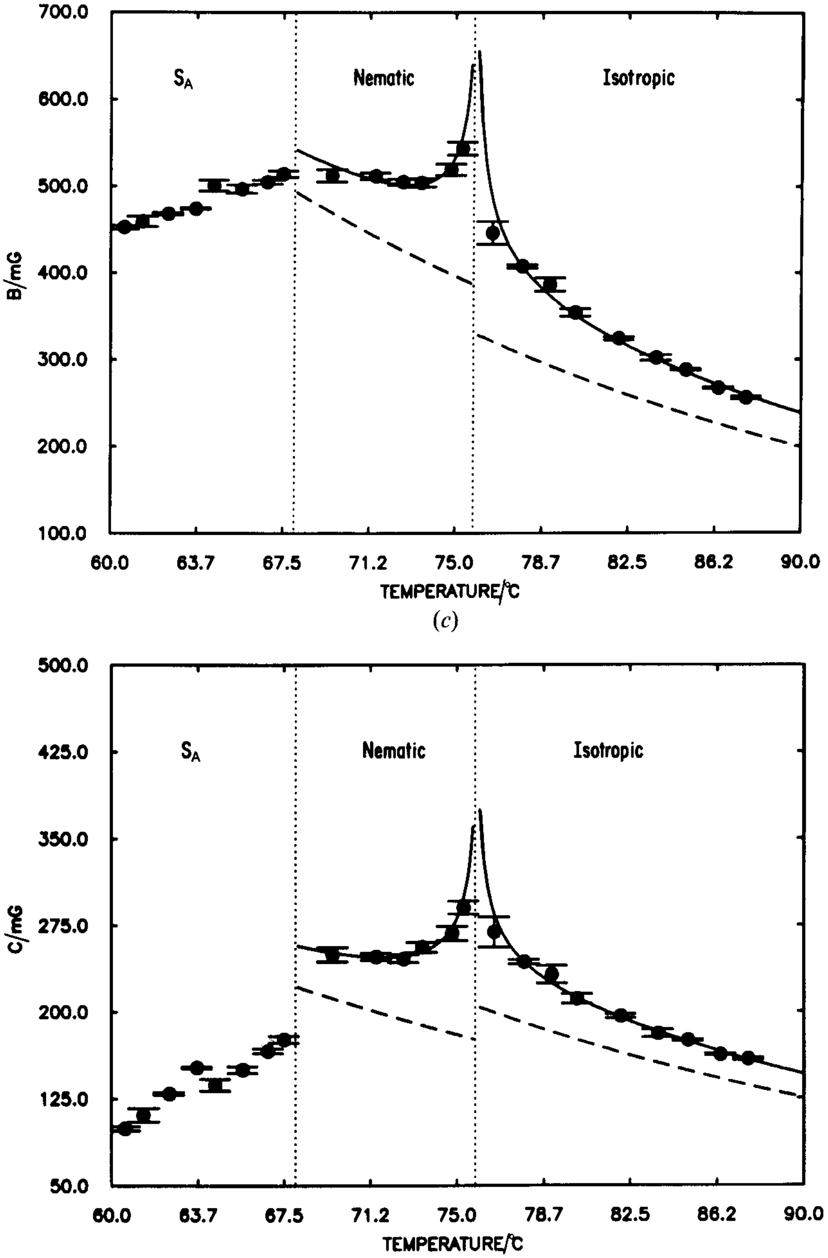
Figure 5. Order parameter S_{yy} for MOTA in (*a*) 7O.5 and (*b*) 6O.4. The phase boundaries are shown.


1000.0
850.0
700.0
550.0
400.0
250.0
100.0
B/mG
65.0
68.7
72.5
76.2
80.0
83.7
87.5
91.2
95.0
TEMPERATURE/°C
S_A
Nematic
Isotropic

(*a*)


500.0
425.0
350.0
275.0
200.0
125.0
50.0
C/mG
65.0
68.7
72.5
76.2
80.0
83.7
87.5
91.2
95.0
TEMPERATURE/°C
S_A
Nematic
Isotropic

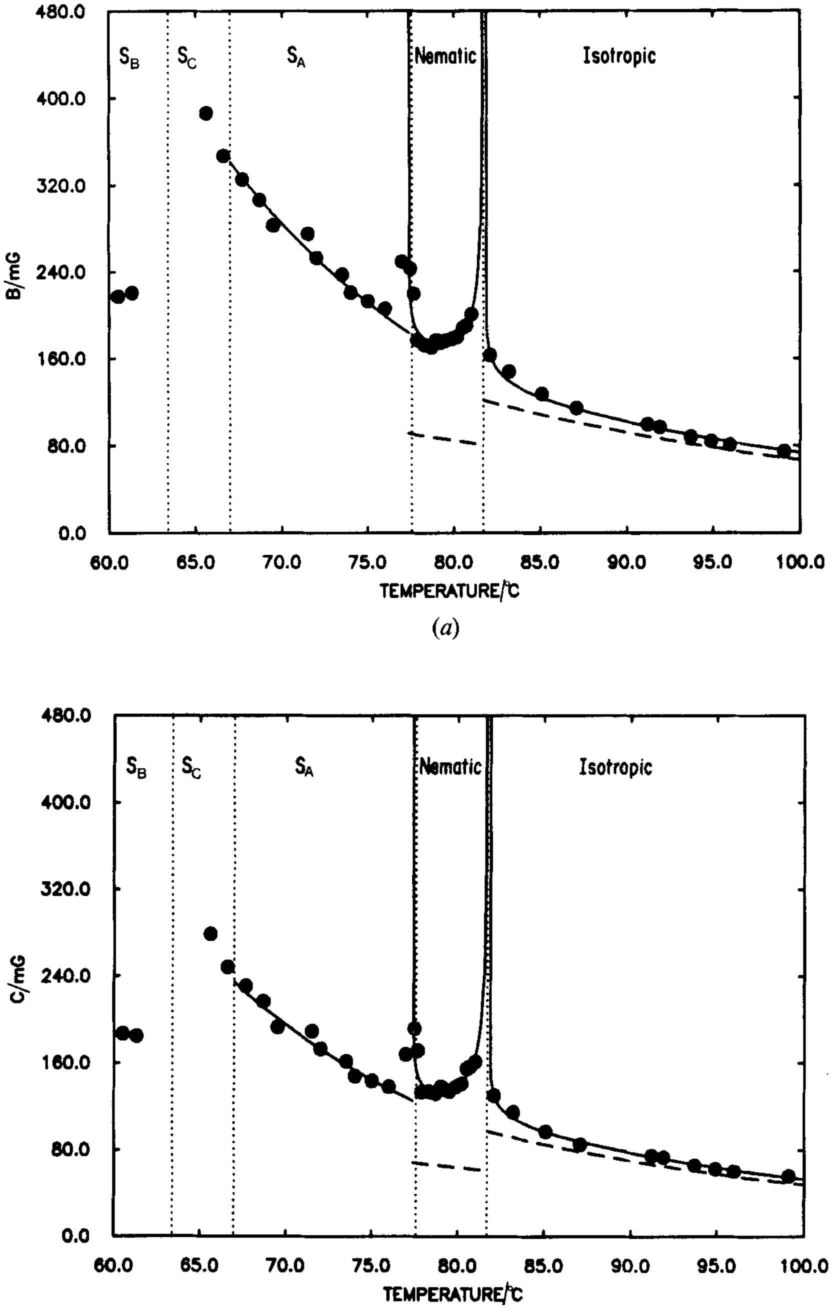
(*b*)



(*c*)

(*d*)

Figure 6. Linewidth parameters *B* and *C* for the *P* probe in the *n*O.*m* homologues versus temperature: (*a*) and (*b*) give *B* and *C* respectively for 7O.5 solvent, whereas (*c*) and (*d*) give *B* and *C* respectively for 6O.4 solvent. The solid lines are suggestive extrapolations; the dotted lines are estimates of the background (i.e. non-critical) contributions to the linewidths.


S$_B$
S$_C$
S$_A$
Nematic
Isotropic
B/mG
C/mG
480.0
400.0
320.0
240.0
160.0
80.0
0.0
60.0
65.0
70.0
75.0
80.0
85.0
90.0
95.0
100.0
TEMPERATURE/°C

(a)

(b)

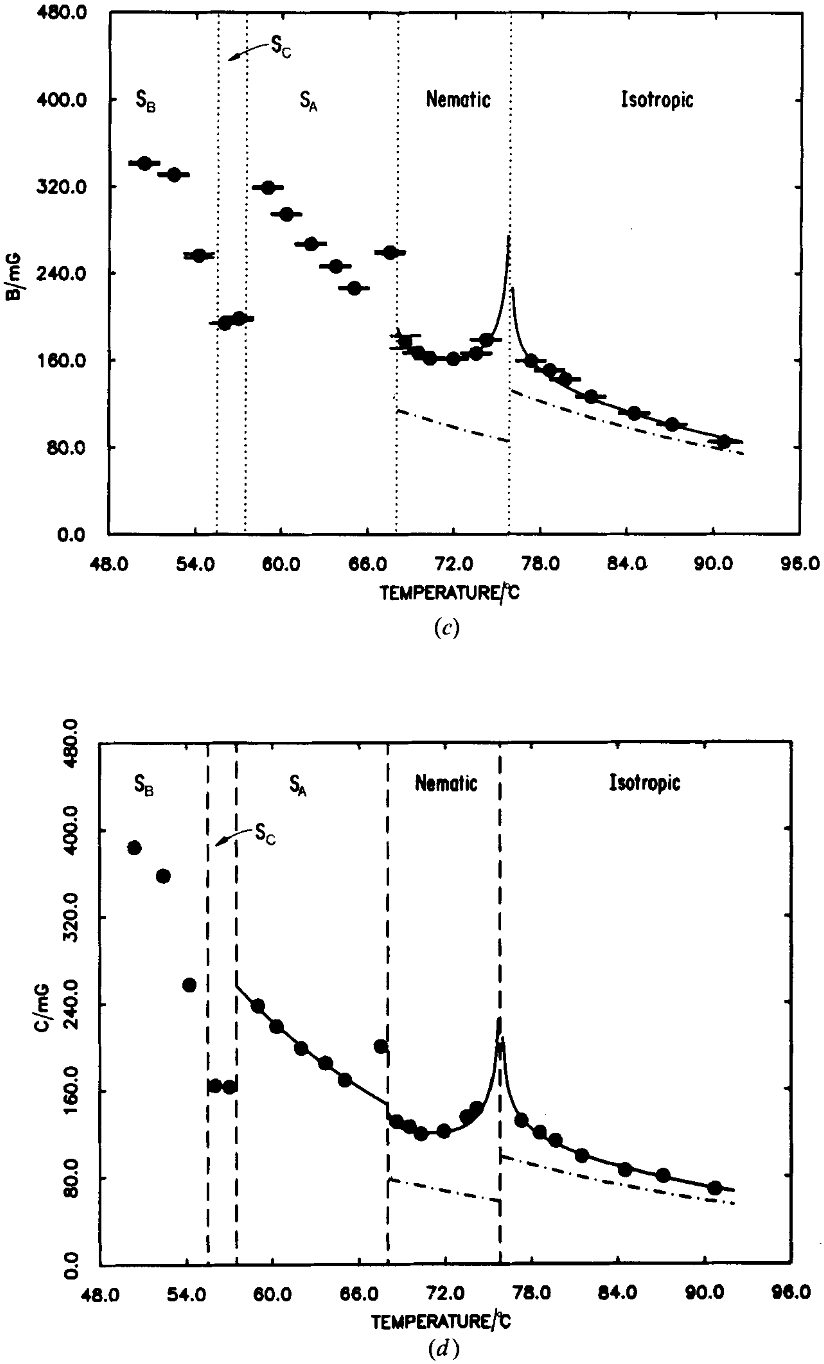


Figure 7. Linewidth parameters B and C for MOTA in the nO.m homologues. (*a*), (*b*), (*c*) and (*d*) are otherwise identical to figure 6.

effect can be rationalized in terms of rapid exchange of the smaller MOTA spin probe between the aromatic core region and the lower density hydrocarbon chain region of the smectic layers; whereas for the *P* probe, which is structurally similar to the liquid crystal, no such tendency is observed. Upon entering the smectic B phase, MOTA is completely expelled into the interlayer region, which is reflected in the reduction of its order parameter to zero.

Figures 6 and 7 depict the *B*, *C* parameter variation for *P* probe and MOTA in the various mesomorphic phases. The solid line drawn through the points in the isotropic and nematic phases include extrapolations to emphasize the critical enhancement of these parameters. The underlying lines reflect our initial estimation of the *background* linewidths, i.e. the contribution of rotational diffusional averaging of the magnetic parameters to the linewidths. A strong divergence in the spin label linewidth parameters on either side of the NI transition for both 6O.4 and 7O.5 supports our previous studies at the NI transition where a $\frac{1}{2}$ power law divergence in the *B* and *C* parameters was observed.

At the S_AN transition in 7O.5 a rather strong divergence in *B*, *C* for both MOTA and the *P* probe is observed. The extent of the divergence is quite dramatic compared to our previous studies near a second order S_AN transition in 4O.6. Equally significant is that this is the first time we have results for the *P* probe (which is not expelled), showing a divergence on the nematic side of the S_AN transition.

However, in 6O.4 the *B*, *C* values associated with MOTA show a weaker critical divergence at the S_AN transition, and the exact situation for *P* probe *B* and *C* parameters is not clear due to lack of accurate data very close to the transition. The general trends are quite similar to what is observed in 4O.6 [20] with its second order S_AN transition. In this respect, it is useful to recall that the McMillan parameter *M* is 0·936 for 4O.6, 0·976 for 6O.4 and 0·990 for 7O.5. Thus, smectic driven fluctuations of the orientational order are much more likely in 7O.5 than either 4O.6 or 6O.4. In the model that we have previously proposed for the critical divergences in *B* and *C* [19], we relied on the expulsion effect of the smaller spin probes to predict a modulation of spin relaxation by the smectic-like fluctuations of the solvent near the S_AN transition. The observation of significant divergences for the *P* probe, but only in 7O.5 with a 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 using other homologues of the *n*O.*m* series.

We do not present estimates of the critical exponents from the data of figures 5–7, since the limited temperature control will render such results inaccurate. The theoretical analysis leading to the solid lines shown in figures 5–7 are therefore meant to be suggestive rather than quantitatively accurate. Clearly, our present results show that it would be interesting to perform careful millikelvin temperature control on these systems. One question that could be addressed is whether there is a crossover from the critical exponent predicted ($\frac{1}{3}$) and found ($\approx \frac{1}{3}$) for a second order S_AN transition for the *B* and *C* parameters to the mean field prediction ($\frac{1}{2}$) for the first order S_AN transition.

Our previous analysis [19] for the calculation of the spectral density $J(0)$ can be easily extended to show the power law of the divergent contribution to the *B* and *C* parameters in the regime where the transition is first order. (In [24], x the exponent associated with the denominator of the relation between relaxation rate Γ_q and $q\xi$, was set equal to 1 in order to obtain an analytical result. For the superfluid case, however, the exponent value is $\frac{3}{4}$. But, in the present mean field case, x is indeed equal to 1, a rigorous requirement of the dynamic correlation function in the mean field limit [30].) One may use the final result for $J(0)$, the zero frequency spectral density that leads to a $\frac{1}{3}$ power critical exponent for a second order S_AN transition (in agreement with experiment):

$$J(0)^{\text{Critical}} \approx \frac{MkT\tau_m}{16\pi\xi} \propto \frac{\tau_m}{\xi}, \tag{3}$$

where M is a coefficient from the Landau expansion of the smectic free energy and τ_m is a characteristic relaxation time of the pretransitional smectic clusters. The divergence in $J(0)$ is determined by τ_m/ξ. According to the dynamic scaling theory [22 (a)] τ_m is expected to vary as $(T - T_{S_AN})^{-1}$ [31]. (These authors found considerable deviation from this expected behaviour near a second order S_AN transition for $t < 10^{-4}$.) For the second order S_AN transition, we expect ξ to vary as $(T - T_{S_AN})^{-2/3}$, yielding the $-\frac{1}{3}$ power result for $J(0)$; for the first order S_AN transition, mean field theory yields a $(T - T_{S_AN})^{-1/2}$ dependence for the ξ, so $J(0)$ would diverge as $(T - T_{S_AN})^{-1/2}$.

The theory leading to equation (3) 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_R, the rotational correlation time felt by the probe. It did not explicitly take into account jumps in S (i.e. ΔS), because it dealt with the second order S_AN transition. For the first order S_AN 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 critical-type divergence, and (ii) critical-type behaviour for the P probe (which is not expelled by the transition) for a first order S_AN transition.

3. Conclusions

(1) We find that M is a unifying parameter for considering a crossover from weakly first order S_AN transitions to second order transitions in the nO.m series. The plot of ΔS versus M yields a tricritical value for M as 0·959 ± 0·005 and a $\beta_2 = 0{\cdot}94 \pm 0{\cdot}12$. The latter value clearly suggests a mean field type of critical behaviour in the region of a weakly first order S_AN transition. Both M_{TCP} and β_2 are in agreement with the previous result from mixtures on 4O.6/6O.4.

(2) We observe divergent-type behaviour in the B and C linewidth parameters of nitroxide spin-labels dissolved in members of the nO.m series exhibiting a weak first order S_AN transition. There is a clear indication that such divergences become more pronounced as M increases toward unity. We predict that the observed $\frac{1}{3}$ power law divergence in the B and C parameters for the second order S_AN transitions should crossover to a mean field $\frac{1}{2}$ power law for a weakly first order S_AN transition.

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Appendix

Landau–de Gennes theory within a homologous series

We shall first review the Landau–de Gennes theory for the S_AN transition and then adapt it to show that $M = T_{S_AN}/T_{NI}$, the McMillan parameter, is a relevant crossover variable for this transition. Here, for the nO.m homologous series, we consider $M = M(n, m)$, i.e. a function of n and m.

In a smectic A phase, molecules of a liquid crystal are arranged in a one dimensional periodic structure. For a monolayer smectic A phase, the molecular length gives the period of the one dimensional mass density wave, which can be written as

$$\varrho(z) = \varrho_0\left(1 + 2^{-1/2}|\Psi|\cos\left(\frac{2\pi z}{d}\right)\right), \tag{A 1}$$

where ϱ_0 is the average density of the liquid crystal and d its periodicity; $|\Psi|$ is the strength of the modulation and is identified as the amplitude of the complex smectic A order parameter. In the Landau theory the free energy density is expanded as a power series in Ψ about its value in the nematic phase where $|\Psi| = 0$;

$$F_{S_A} = \alpha|\Psi|^2 + \beta_0|\Psi|^4 + \gamma|\Psi|^6 + \dots, \tag{A 2a}$$

with α usually written as $a_0(T_{S_AN} - T)$ with a_0 positive, and the sign of β_0 governs the order of the transition, i.e. if β_0 is negative(positive) a first (second) order transition results; for $\beta_0 = 0{\cdot}0$ a tricritical phase transition is observed. The sixth order term is added to ensure the stability of such an expansion. In this model, a crossover to the tricritical point from a second order phase transition (i.e. $\beta_0 < 0$) is accomplished by finding a mechanism that changes β_0 to its tricritical value of 0. In general, such an effect can be achieved by coupling the order parameter to other density variables. In the case of the S_AN transition, the coupling of the nematic order parameter to the smectic A order parameter is introduced. Upon entering the smectic A phase, an enhancement in S is generally observed, so a coupling term of the type $-C|\Psi|^2\delta S$ to lowest order in $|\Psi|^2$ and δS is included; this term reduces the smectic A free energy. However, the enhancement of the nematic order in the smectic phase occurs at the expense of an increase in the nematic free energy; hence we add a term $\delta S^2/2\chi$ to account for this effect. We also note that in Landau or mean field theory [32], χ diverges near the NI phase transition with a power law:

$$\chi \approx \frac{\chi_0 T^\dagger_{NI}}{(T^\dagger_{NI} - T)} \tag{A 2b}$$

and $T^\dagger_{NI}$ is the apparent second order transition temperature, which is slightly higher ($\sim 0{\cdot}6°$–$1{\cdot}0°$) than the first order transition actually observed at T_{NI} [33, 34]. This term in δS^2 permits larger deviations in S (from its equilibrium value S_0) near the NI transition than deeper into the nematic phase. Minimizing the total free energy with respect to δS, and collecting terms, we obtain

$$F_{S_A} = F_0 + \alpha|\Psi|^2 + \beta|\Psi|^4 + \gamma|\Psi|^6 + \dots, \tag{A 3}$$

where

$$\beta = \beta_0 - \tfrac{1}{2}C^2\chi, \tag{A 4}$$

and

$$\delta S = \chi C|\Psi|^2. \tag{A 5}$$

It is clear from the form of β in equation (A 4) that it can become negative, thereby leading to a first order S_AN transition, when either χ is large or the coupling coefficient C is large.

In our previous work on 4O.6/6O.4 we let $\alpha = \alpha(T, x)$, $\beta_0 = \beta_0(T, x)$, etc. Thus, for example $\alpha = a_0(x)(T - T^*_{S_AN})$ (where the asterisk implies T_{S_AN} for second order

S_AN transitions or the temperature at which the second order transition would have occurred if it had not been for the first order transition). The results in the present paper suggest that we consider $t = T/T_{NI}$ and M in place of T and x. Furthermore, S in the nematic phase obeys a nearly universal curve for the nO.m series as well as for the mixtures [15] when plotted against $(1 - t)/(1 - M)$, i.e. $S = S(t, M)$. Thus we shall let $\alpha = a_0(M)(t - t_{S_AN}(M))$, so that along the λ line of second order transitions $t = t_{S_AN}(M)$ as observed. We must also have $\beta = \beta(t, M)$ such that $\beta_{TCP} = \beta(M_{TCP}, t) = 0$ to be consistent with our experimental results in figure 3.

We now wish to outline a simple analysis yielding a rather simple expression for the dependence of ΔS upon M. It reduces to a linear dependence of ΔS with M near the tricritical point as required for a relevant crossover variable. In order to calculate ΔS, we must know the value of $|\Psi|^2$ according to equation (A 5), along the line of the first order S_AN transitions. In the usual fashion, it is obtained by minimizing the modified form of the free energy (equation (A 3)) with respect to $|\Psi|$, subject to the constraint that $F_{S_A} = F_0$ corresponding to equilibrium between the two phases. We obtain for the S_A phase [32]

$$|\Psi|^2 = -\frac{\beta}{2\gamma}, \tag{A 6a}$$

and

$$4\alpha\gamma = \beta. \tag{A 6b}$$

The discontinuity in the nematic order parameter at the S_AN transition is from equations (A 4) to (A 6),

$$\Delta S = \frac{\chi_{NA}C^3}{4\gamma}(\chi_{S_AN} - \chi_{TCP}), \tag{A 7}$$

where we have set $\beta_0 = \frac{1}{2}C^2\chi_{TCP}$, since this renders $\beta = 0$ at the tricritical point. The use of equation (A 2a) enables us to write $\chi_{S_AN} \approx \chi_0/(1 - M^\dagger)$ and $\chi_{TCP} \approx \chi_0/(1 - M^\dagger_{TCP})$ so that equation (A 7) becomes

$$\Delta S = \frac{C^3\chi_0^2}{4\gamma}\left(\frac{(M^\dagger - M^\dagger_{TCP})}{(1 - M^\dagger)^2(1 - M^\dagger_{TCP})}\right). \tag{A 8}$$

When $\Delta M \equiv |M^\dagger - M^\dagger_{TCP}| < 1 - M^\dagger_{TCP}$, then an expansion of equation (A 8) leads to the form

$$\Delta S \approx \left(\frac{C^3\chi_0^2}{4\gamma}\right)\frac{\Delta M^\dagger}{(1 - M^\dagger_{TCP})^3}\left[1 + \frac{2\Delta M^\dagger}{1 - M^\dagger_{TCP}} + \dots\right]. \tag{A 9}$$

Thus, for $\Delta M^\dagger$ sufficiently less than $\frac{1}{2}(1 - M^\dagger_{TCP})$ a linear dependence of ΔS_{S_AN} on $\Delta M^\dagger$ with zero intercept should be observed. We imply in equation (A 9) that the term in the parenthesis containing χ_0, C and γ is not significantly dependent on M near the tricritical point within the homologous series, clearly a simplification.

In the case of 4O.6/6O.4 mixtures (*cf.* figure 2(*b*)) we observe the linear relation over a 3·5 K range from the tricritical point corresponding to $\Delta M^\dagger = 1{\cdot}3 \times 10^{-2}$, whereas $\frac{1}{2}(1 - M^\dagger_{TCP}) = 2{\cdot}6 \times 10^{-2}$, which does satisfy $\Delta M^\dagger < \frac{1}{2}(1 - M^\dagger_{TCP})$. For pure compounds (*cf.* figure 3(*b*)), $\Delta M^\dagger = 2{\cdot}1 \times 10^{-2}$ and $\frac{1}{2}(1 - M^\dagger_{TCP}) \approx 2{\cdot}3 \times 10^{-2}$, so we might expect some deviation from linearity in this case. It is interesting to note that computations by Kventsel *et al.* [35], based upon a modified McMillan theory, exhibit predictions similar to those of equation (A 8).

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