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N.M.R. investigations and the molecular field theory of nematic mixtures

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N.M.R. measurements have shown that the mixture E5 can be described by a single order parameter. Based on molecular field theory the nematic-isotropic transition and the temperature dependence of the order parameter in the nematic phase are considered for a binary mixture of nematogens. Guided by the results of the N.M.R. measurements the binary mixture is treated as an effective medium characterized by a single order parameter. Soft attractive forces are taken into account as well as the excluded volume. The coexistence of nematic and isotropic phases in the phase transition region is discussed in detail.

1. Introduction

Mixtures of nematic liquid crystals have been investigated extensively, in particular, in connection with their use in liquid crystal displays. The microscopic theory of nematic mixtures has been developed from different starting points. Humphries, James, and Luckhurst [1] extended the Maier-Saupe theory for pure nematogens to multicomponent nematogenic mixtures. Usually, an order parameter for each component of a mixture is introduced, and these order parameters are, in general, different from each other. However, our N.M.R. measurements have shown, that the order parameters of the components of the five component mixture E5 of cyanobiphenyls (see table 1) are equal to each other; in consequence the mixture as a whole can be described by a single order parameter S . It is the aim of this paper to use a simple model describing a mixture with a single order parameter to understand the experimental data. The mixture E5 consists of two and three components, which are very similar to each other, and we may consider this mixture as a binary one. Therefore, we formulate our model for a binary mixture to avoid unnecessarily complicated formulae.

We first (§1) present the N.M.R. measurements of the order parameters of the mixture E5 and discuss the experimental results which are the background of the theoretical considerations described in the following sections. In §3, we follow the theory of binary mixtures of nematic liquid crystals developed by Humphries, James, and Luckhurst [1] and further by Palffy-Muhoray, Dunmur, Miller, and Balzarini [2], but we introduce only one order parameter for the whole mixture treating it as an effective medium. Applying the results of Palffy-Muhoray *et al.* [2] to the mixture E5, we find two different order parameters which are clearly distinct from each other. In addition to the model considered in [2], we take into account the effect of the excluded volume of the rigid rod-like molecules, following Nakagawa and Akahane [3]. In §4 we present the results of the calculations. At the end of the paper, we discuss the use of a single order parameter to describe a binary mixture in the molecular field

Table 1. Composition of the mixture E5, nematic-isotropic transition temperatures and the molecular lengths of the components.

Substance	Concentration/%	$T_{NI}/^{\circ}\text{C}$	Molecular length/ \AA
$\text{C}_5\text{H}_{11}\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$	40	35	15.4
$\text{C}_7\text{H}_{15}\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$	25	42	17.5
$\text{C}_5\text{H}_{11}\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$	10	67.5	15.9
$\text{C}_7\text{H}_{15}\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$	10	75	18.0
$\text{C}_8\text{H}_{17}\text{OC}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$	10	80	19.5

approximation and we mention some physical mechanism which might explain microscopically why we see only one order parameter in our N.M.R. spectra.

We do not consider the problem of the steeper descent of the experimental curve for the order parameter near the phase transition in comparison with the curve predicted with the molecular field approximation. In this respect, we remain within the framework of Maier-Saupe theory and are not able to obtain complete agreement between theory and experiment; a discussion of this problem is found in [4].

2. Experimental results

We have used ^{13}C N.M.R. spectroscopy to measure the orientational order of the molecules in the nematic phase. The cross-polarization technique with proton decoupling assures a high sensitivity and a good resolution of the spectra in the nematic phase. The position of the sharp spectral lines is determined by the shielding tensors $\sigma_{\alpha\beta}$ (σ_{11} , σ_{22} , σ_{33}). The components vary between -100 ppm and $+100$ ppm for the aromatic carbons and only -20 to $+20$ ppm for the aliphatic carbons. We concentrate our attention therefore on the shifts of the lines of the central aromatic rings. The line shift of a carbon i in an axially symmetric phase is given by [5]

$$\nu_i^i - \nu_{\text{iso}}^i = -\nu_0[\sigma_{\zeta\zeta}^i S + \frac{1}{3}(\sigma_{\xi\xi}^i - \sigma_{\eta\eta}^i)D + \frac{4}{3}\sigma_{\zeta\eta}^i S_{\zeta\eta} + \frac{4}{3}\sigma_{\zeta\xi}^i S_{\zeta\xi} + \frac{4}{3}\sigma_{\eta\xi}^i S_{\eta\xi}]. \quad (1)$$

The measuring frequency ν_0 was 22.64 MHz. The derivation of this expression includes a separate averaging of internal motions and orientational fluctuations. For the central part of the molecule only hindered rotations of the benzene rings about the para axis are possible. This results in identical lines for the two ortho and meta carbon positions (see figure 1 (a)). It seems to us justified to assume a time independent molecular frame (ζ , η , ξ) and to perform the separate averaging.

The values of the shielding tensors are not well known for all carbons in different substituted aromatic rings and they cannot be calculated theoretically. We attempt therefore, to guess the location of the principal axis system of the ordering matrix. Then the off-diagonal elements in equation (1) are zero and there only two parameters are left: the orientational order S and the biaxiality of the orientational fluctuations D , which we are able to determine from measurement of the shifts of four spectral lines. For the biphenyls the para axis may be identified with the molecular long axis ζ . Small deviations from this direction influences the values of S and D but has no consequences for the question of different order parameters of the molecules in the mixtures. The components of the mixture E5 investigated are listed in table 1 together with the nematic-isotropic transition temperatures of the pure materials and their molecular lengths.

The most important requirement is an equivalent molecular sub-unit in all of the components and this is given by the benzonitrile ring in all five compounds. The

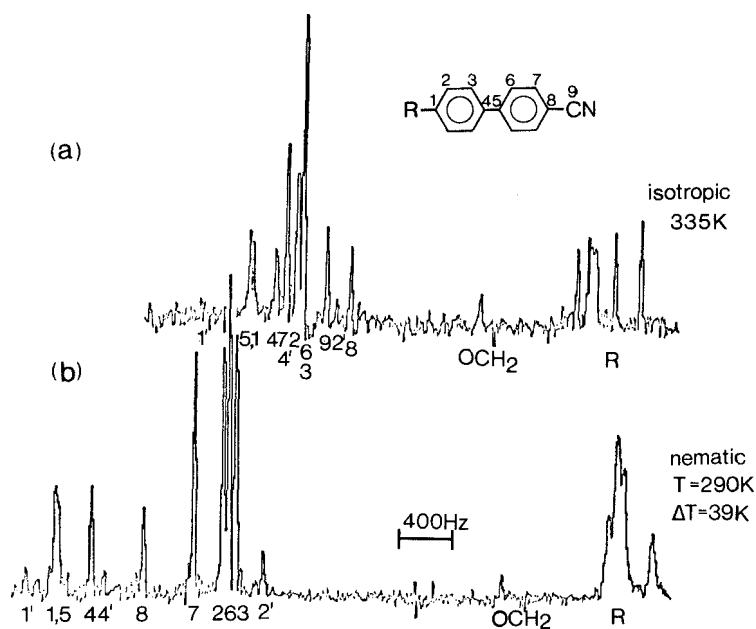


Figure 1. ^{13}C N.M.R. spectra of the mixture E5 in (a) the isotropic and (b) the nematic phase and the corresponding positions of the carbons.

corresponding shielding tensors for the six carbons in this ring (positions 5–8) are identical. The shielding tensors of the other ring (positions 1–4) are different for the substitution of an alkyl or alkoxy chain. This behaviour is reflected in the isotropic shift values σ_{iso} in figure 1 (a). The shift of the corresponding lines from the benzonitrile ring depends, according to equation (1), on the S and D values of that species and through (ζ, η, ξ) on the orientation of the molecular frame in the molecule. Inspection of figure 1 (b) shows that the lines from positions 5–8 are not broadened or split whereas the different shielding tensors of the alkoxybiphenyl produce clearly separate lines 1', 2', 4'.

If a biaxiality parameter D exists its value is very small ($D \approx 0.05$ [6, 7]). Together with comparably small values of $\sigma_{\zeta\zeta}$ and $\sigma_{\xi\xi} - \sigma_{\eta\eta}$ for the para positions 1, 4, 5, 8 the neglect of the D term gives only a very small change in S equal for all positions and species. Ignoring this negligible effect we find

$$\nu_z^i - \nu_{\text{iso}}^i = -\nu_0 \sigma_{\zeta\zeta}^i S \quad (2)$$

instead of equation (1). According to the resolution shown in figure 1 (b) and the values for $-\nu_0 \sigma_{\zeta\zeta}^i$ in the range of 1000 to 1800 Hz differences in S of 0.01 for the five species should produce a line splitting large enough to be observed but actually not seen in the experimental spectra. Within this limit the orientational order parameter, S , is the same for all five molecular species in the mixture. It is most unlikely that for all five components an imaginable variation of the ζ axis in the molecule connected with a change in $\sigma_{\zeta\zeta}^i$ is compensated by an opposite change in S .

The calculation of the orientational order parameter S was made using for σ_{11}^i the values -93.5 , -88 , -92.5 , -98.5 ppm for the positions 1, 4, 5 and 8, respectively, and assuming $\sigma_{11}^i = \sigma_{\zeta\zeta}^i$ (the ζ axis being parallel to the para-axis). The resulting S values are shown in figure 7 together with theoretical curves calculated using the model described in the following section [2].

3. Molecular field theory for binary nematic mixtures

When treating mixtures of nematic liquid crystals, usually, different order parameters are introduced for different components of the mixture. After some approximations the phase diagrams and order parameters can be calculated as functions of composition and temperature. Most frequently, the molecular field approximation is applied in molecular theories of nematic mixtures. In order to find a model for the equal order parameters determined for E5, we look at a mixture of liquid crystals from another point of view. We assume that the mixture can be considered as an effective medium described by a single order parameter. This point of view corresponds to the virtual crystal approximation for disordered solids, which is an approximation used in treating disorder, roughly speaking, on the same level as the molecular field approximation is in calculating thermodynamic quantities. In our approach, the molecules of the different components of the mixture should not differ from each other too much. All components should therefore be nematogens.

The following approach is based on the theory of Luckhurst *et al.* [1] and Palfy-Muhoray *et al.* [2]. As suggested by the experimental data presented in §2 we propose a simplified version of the theory [1, 2] and start with a free energy F_N for the nematic phase which is a function of only one effective order parameter S (the capital letters N, I as indices indicate the nematic and the isotropic phase, respectively)

$$F_N = \frac{S^2}{2} \sum_{l,m=1,2} N_{l,N} \varrho_{m,N} u_{lm} + \sum_{l=1,2} N_{l,N} \left[\gamma_l + \frac{1}{\beta} \ln \varrho_{l,N} - \frac{1}{\beta} \ln Z(\beta S(u_{l1} \varrho_{1,N} + u_{l2} \varrho_{2,N})) \right]. \quad (3)$$

where β is $1/kT$. The number densities are defined by

$$\varrho_{l,N} = \frac{N_{l,N}}{V_N}, \quad \varrho_{l,I} = \frac{N_{l,I}}{V_I}$$

where $N_{l,N}$ ($N_{l,I}$) is the number of the l th kind of molecules in the nematic (isotropic) phase, and V_N (V_I) are the corresponding volumes. For simplicity we assume

$$V_N = v_1 N_{1,N} + v_2 N_{2,N},$$

where v_1, v_2 are the molecular volumes of species 1 and 2, respectively. Furthermore, γ_1, γ_2 are the single particle energies in the isotropic phase and the function $Z(x)$ is defined by

$$Z(x) = \int_0^1 \exp[xP_2(\zeta)] d\zeta, \quad P_2(\zeta) = 3/2(\zeta^2 - 1).$$

Equation (3) follows from the corresponding equations of Palfy-Muhoray *et al.* [2] by setting $S_1 = S_2$ where S_1 and S_2 are the distinct order parameters of both components in this theory. We choose the simplified model $S_1 = S_2$ because it describes the experimental results of §2 better than the more general model where $S_1 \neq S_2$. Concerning the phase diagram it is almost irrelevant, whether $S_1 = S_2$ or $S_1 \neq S_2$. The following considerations apply to both models, only the results for the order parameters are actually different for the two models.

The u_{lm} are the mean energies of the anisotropic interaction between the molecules of kind l and m . If we assume $u_{lm} = \bar{u}_{lm}$ where \bar{u}_{lm} obeys the geometric mean rule

$$\bar{u}_{12} = \bar{u}_{21} = (\bar{u}_{11} \bar{u}_{22})^{1/2}, \quad (4)$$

then the phase diagram showing the transition temperature versus the volume fraction is a straight line [8]. In a very recent paper, Kloczkowski and Luckhurst [9] showed that the transition temperature does exhibit a small negative deviation (< 1 per cent) from the linear behaviour. This deviation is too small to explain the majority of experimental data [3] which indicate that the coexistence curve (neglecting the width of the coexistence region) is convex from below. According to these experimental results we introduce a new parameter δ in our theory by

$$u_{12} = u_{21} = (u_{11}u_{22})^{1/2} + \delta. \quad (5)$$

The dependence of the coexistence curve on δ is shown schematically in figure 2. In a recent paper, Attard and Luckhurst [10] discussed the pretransitional behaviour in nematogenic mixtures. For mixtures of rods and rods, they obtain a diagram for the composition dependence of the divergence temperature of the field-induced second rank order parameter which exhibits the same dependence on the deviation δ from the geometric mean rule as the transition temperature shown in figure 2.

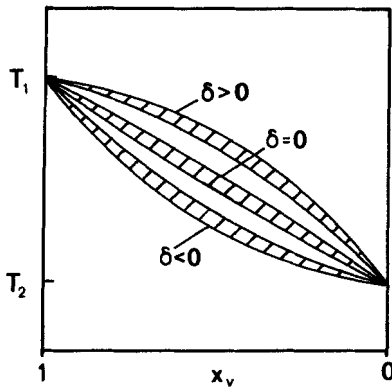


Figure 2. Phase diagram of a binary nematic mixture for different values of the excluded volume parameter δ . x_v is the volume fraction of component 1.

From [3] it is known that deviations from the rule (4) may be connected with the intermolecular repulsion forces due to the finite volume of the molecules. Starting with a generalized van der Waals approach [11] the interaction constants u_{lm} can be written approximately as [3]

$$u_{lm} = \bar{u}_{lm} + \frac{5\pi}{32} \Delta v_{lm}(\varrho) kT, \quad (6)$$

where Δv_{lm} represents the pair-excluded volume effect resulting from the hard-core intermolecular repulsions and the \bar{u}_{lm} are associated with the anisotropic attractive potential. Δv_{lm} is completely determined by the geometry of the constituents. Assuming equation (4) for \bar{u}_{lm} , in general, the geometric mean rule does not hold for the u_{lm} . In this sense, a non-vanishing δ may be interpreted as an effect of the finite volume of the molecules. Assuming the molecules to be hard spherocylinders Δv_{lm} is given by [3]

$$\Delta v_{lm} = \frac{1}{1 - \varrho D} \left[4r + \frac{4}{3} \frac{\varrho r^2}{1 - \varrho D} A \right] l_l l_m, \quad (7)$$

where $2r$ is the effective diameter of the molecules (roughly equal for both kinds), l_i is the length of the i th molecule, ρ , D , A are the averaged particle density, molecular volume and molecular surface area, respectively. Taking into account that the u_{ii} are related to the nematic-isotropic transition temperature T_i of the pure components via

$$u_{ii} = 4.54153v_i k T_i, \quad (8)$$

which is known from simple Maier-Saupe theory [12], we can calculate from (5)–(8) the value of δ if some effective molecular parameters are known.

It is convenient to introduce dimensionless quantities as follows:

$$\left. \begin{aligned} \Delta &= \frac{\delta}{4.54v_1 k T_1}, & T &= \frac{1}{4.54T_1 \beta k}, \\ c &= a + \left(\sqrt{\left(\frac{v_1 T_1}{v_2 T_2}\right)} + \Delta \frac{v_1}{v_2} \right) (1 - a), \\ d &= \left(\sqrt{\left(\frac{v_2 T_2}{v_1 T_1}\right)} + \Delta \right) a + \frac{T_2}{T_1} (1 - a). \end{aligned} \right\} \quad (9)$$

The volume fractions a (b) of component 1 in the nematic (isotropic) phase are defined by

$$\begin{aligned} a &= v_1 \rho_{1,N}, & b &= v_1 \rho_{1,I}, \\ 1 - a &= v_2 \rho_{2,N}, & 1 - b &= v_2 \rho_{2,I}. \end{aligned}$$

To estimate the magnitude of Δ we give an example with $T_1/T_2 = 1.2$, $T = 1$, $N_{1,N} = N_{2,N}$, $\rho D = 0.35$, $l_1/2r = 4$ in table 2. According to table 2 Δ is approximately in the range -10^{-3} – 10^{-1} for reasonable values of the molecular parameters. Since these parameters are not well known and the temperature dependence of Δ is weak we will treat Δ merely as an arbitrary parameter.

Table 2. Δ as a function of the ratio $l_2/2r$ for the example described in the text.

Δ	-0.118	-0.048	-0.007	-0.003	-0.054	-0.199
$l_2/2r$	2.5	3	3.5	4	4.5	5

From equations (3) and (9) we find the total free energy of the system as

$$\begin{aligned} \bar{F} &= \frac{F_N + F_I}{4.54kT_1} = N_{1,N} \left[\frac{1}{2} c S^2 + T (\ln a - \ln Z \left(\frac{cS}{T} \right)) \right] \\ &\quad + N_{2,N} \left[\frac{1}{2} d S^2 + T (\ln(1 - a) - \ln Z \left(\frac{dS}{T} \right)) \right] \\ &\quad + T [(N_{1,0} - N_{1,N}) \ln b + (N_{2,0} - N_{2,N}) \ln(1 - b)], \quad (10) \end{aligned}$$

where $N_{1,0} = N_{1,N} + N_{1,I}$ and $N_{2,0} = N_{2,N} + N_{2,I}$. The order parameter S is the solution of the equation $\partial F / \partial S = 0$ and after some algebra we obtain

$$\left. \begin{aligned} S &= \frac{1}{c + (N_{2,0}/N_{1,0})d} \left[c \bar{S}(x) + \frac{N_{2,0}}{N_{1,0}} d \bar{S} \left(\frac{xd}{c} \right) \right], \\ T &= cS/x. \end{aligned} \right\} \quad (11)$$

Equation (11) is a parametric representation of the function $S(T)$. The function $\bar{S}(x)$ is defined by

$$\begin{aligned} \bar{S}(x) &= \frac{d}{dx} \ln(Z(x)), \\ &= \frac{1}{Z} \int_0^1 P_2(\zeta) \exp[xP_2(\zeta)] d\zeta. \end{aligned}$$

The number of molecules in both phases is determined by minimizing F with respect to $N_{1,N}$ and $N_{2,N}$. The phase transition occurs if the chemical potentials

$$\mu_{i,N} = \frac{\partial F_N}{\partial N_{i,N}}, \quad \mu_{i,I} = \frac{\partial F_I}{\partial N_{i,I}}, \tag{12}$$

are equal to each other in the nematic and isotropic phase. It is straightforward to write down equations (12) explicitly, but it is rather complicated to solve them. Therefore, we have minimized F numerically with standard routines taking into account the result in equation (11).

We expect the following behaviour of the system. Above an upper temperature T_U the nematic phase vanishes and $N_{1,N} = N_{2,N} = 0$ minimizes F . Between a lower temperature T_L and T_U the two phases coexist and equation (12) can be solved with $0 < N_{1,N} < N_{1,0}$; $0 < N_{2,N} < N_{2,0}$. Below T_L the unique solution of equation (12) is $N_{1,N} = N_{1,0}$; $N_{2,N} = N_{2,0}$ and the mixture is purely nematic. This behaviour and some numerical examples are discussed in the next section.

4. Theoretical results

In this section we discuss the results of the effective medium theory of binary nematic mixtures with the help of some computations. Our model contains three essential parameters, namely T_1/T_2 , v_1/v_2 and the value of Δ . We choose those parameters either to be close to the NMR experiments on the mixture E5 (see

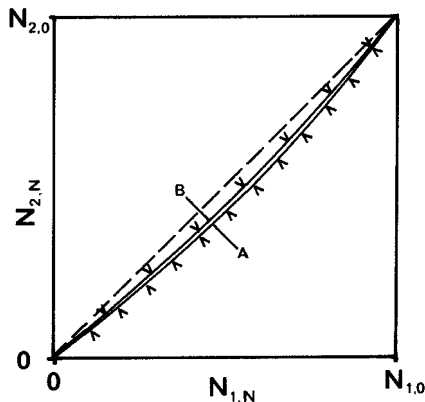


Figure 3. Particle number $N_{2,N}$ of component 2 in the nematic phase versus $N_{1,N}$ for two different values of Δ within the coexistence region (A, $\Delta = -0.15$; B, $\Delta = -0.05$). The arrows indicate the solution of equation (12) in temperature steps of 0.002 ; $T_1/T_2 = 1.5$, $v_1/v_2 = 1.5$, the volume fraction x_v of the mixture is 0.6 of component 1.

§2) or to compare the results with the corresponding calculations of Palffy-Muhoray *et al.* [2].

The typical behaviour, as described in the last section, may be illustrated in figure 3 by considering a mixture consisting of 50 mole per cent of component 1, with $T_1/T_2 = 1.5 = v_1/v_2$ as in [2] but with non-vanishing Δ . Because of the molecular volume ratio of 1.5 the corresponding volume fraction of component 1 in the total mixture $x_v = v_1 N_{1,0}/(v_1 N_{1,0} + v_2 N_{2,0})$ is 0.6. The two transition temperatures are $T_L = 0.8260$, $T_U = 0.8426$ ($\Delta = -0.05$) and $T_L = 0.7623$, $T_U = 0.7923$ ($\Delta = -0.15$) and the arrows indicate the solution for $N_{1,N}$ and $N_{2,N}$ in temperature steps of 0.002. These points differ only slightly from the straight line $N_{2,N} = N_{1,N} N_{2,0}/N_{1,0}$ for which the composition in both phases are equal ($a = b$). Since the arrows become closer for larger absolute values of Δ it is evident that the width $a - b$ of the coexistence region increases as illustrated in figure 4 for another set of parameters.

A more significant effect caused by a non-vanishing Δ occurs in the phase diagram. As expected from figure 2 the coexistence curves are convex from below if Δ is

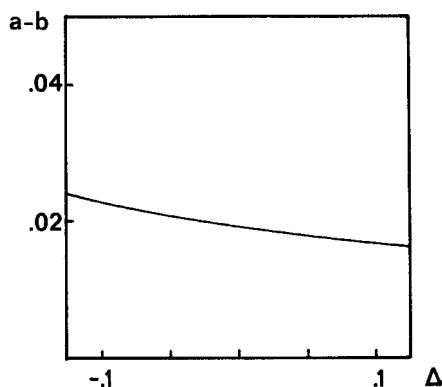


Figure 4. The composition difference ($a - b$) at the transition temperature T_L as a function of Δ : $T_1/T_2 = 1.2$, $v_1/v_2 = 1.1$, $x_v = 0.5$.

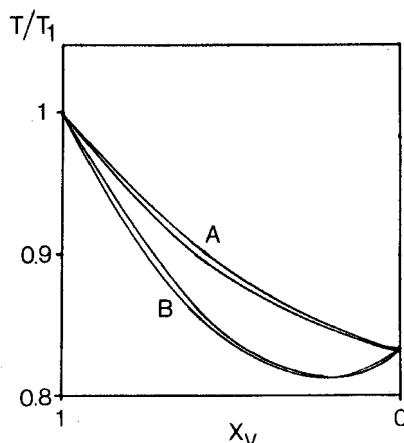


Figure 5. Calculated phase diagram for (A) $\Delta = -0.05$ and (B) $\Delta = -0.15$; $T_1/T_2 = 1.2$, $v_1/v_2 = 1.1$. The lower (upper) curve of each diagram is the volume fraction a (b) of the nematic (isotropic) phases.

negative (see figure 5). This behaviour agrees with the majority of experiments and coincides with the predictions of the simpler theories when the coexistence region is neglected [3, 4]. Assuming that a non-vanishing Δ results from the finite volume of the molecules (that is the presence of repulsive forces) Δ should be negative [3] (see table 2). Thus the theory gives a consistent description of the nematic–isotropic transition of a binary mixture. However it is more convenient to consider Δ as an arbitrary parameter because little information about the anisotropic molecular forces is available.

Together with the phase diagram, the theory predicts the temperature dependence of the effective order parameter, S . Since the order parameter S at the transition varies only slightly with composition and the value of Δ (see figure 6) their influence on the temperature dependence of the order parameter $S(T)$ is only weak. Accordingly the function $S(T)$ is similar to that of the original Maier-Saupe theory with its known disadvantages of a molecular field treatment. If we had assumed $S_1 \neq S_2$ we should have found the results obtained by Palfy-Muhoray *et al.* [2]; the influence of Δ on the order parameters is very small.

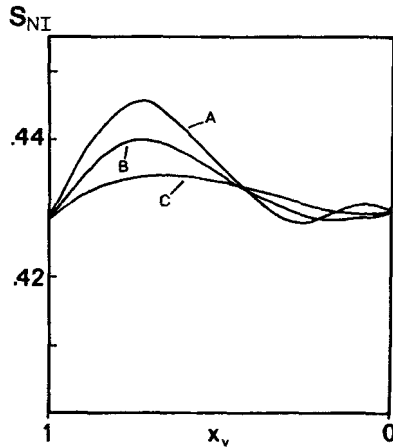


Figure 6. Order parameter at the transition $S_{NI} = S(T_L)$ as a function of the volume fraction of component 1 for (A) $\Delta = -0.15$, (B) $\Delta = -0.10$, (C) $\Delta = -0.05$; $T_1/T_2 = 1.2$, $v_1/v_2 = 1.1$.

We are now going to compare the results of our effective medium model with the calculations of Palfy–Muhoray *et al.* [2] which take into account the different order parameters for the components applying both models to a realistic example (see figure 7). The differences of the effective order parameter S and the component order parameters S_1 and S_2 are much larger than the errors of our N.M.R. experiment. From this we were persuaded to use only one order parameter for both components and for this reason our simplified model fits the experimental data better than the more general model with its different order parameters.

The quantitative agreement with experiment is rather poor; this may be explained by the failure of such simple molecular field theories which only take into account $P_2(\cos(\theta))$ terms as in pure nematogenic systems. Nevertheless our approach describes some features of experimental relevance in a simple manner.

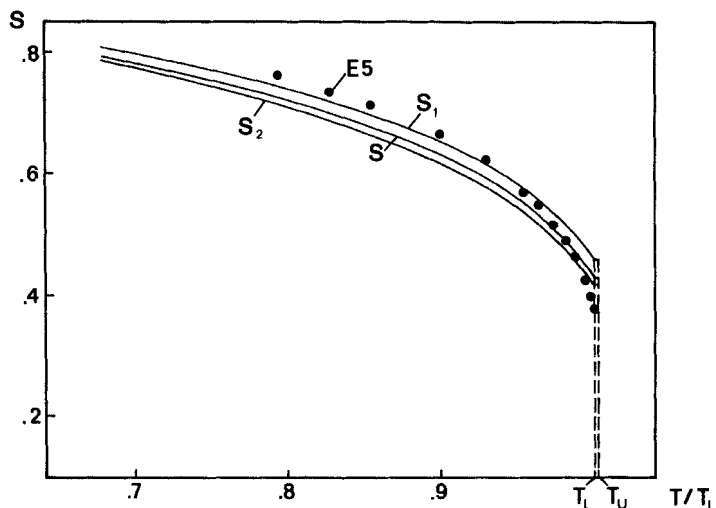


Figure 7. Order parameters S_1 , S_2 calculated from the Palffy-Muhoray *et al.* [2], order parameter S of the effective medium theory and the measured order parameter (\bullet) of the mixture E5 versus temperature. The parameters are calculated from the known data of the mixture E5; $T_1/T_2 = 1.2$, $v_1/v_2 = 1.05$, $x_v = 0.3$.

5. Discussion

Usually, a separate order parameter is introduced for each nematogen in a nematic mixture [1–4, 13]. Applying the molecular field approximation, the free energy has to be minimized with respect to the several order parameters, and, in general, as many equations result as there are components in the mixture, e.g. two equations for a binary mixture [2]. These two equations have unique solutions as given in [2], if the geometric mean rule (4) does not hold. In that case, the approach by Palffy-Muhoray *et al.* [2] yields different order parameters for the different components of the mixture, as long as $v_1 T_1/v_2 T_2 \neq 1$. On the other hand, supposing the validity of geometric mean rule (cf. equation (4)), the two equations become linearly dependent, and there is no unique solution of them. Different order parameters are solutions of the resulting equation as well as one single order parameter.

In our approach, we have treated the binary nematic mixture as an effective medium describing it by only one order parameter. Therefore, we only have one equation to determine this order parameter. This equation has always the unique solution of equation (11). The question, whether we have to characterize a binary mixture by one or two order parameters is decided *a priori* in the framework of the molecular field order parameter choosing the model at the very beginning.

Our results do not contradict the numerical results of Hashim *et al.* [14] who obtained two clearly different order parameters for the two nematogenes in a binary mixture. In [14] there was assumed, that the concentration of the component 1 is very low, and any molecule of kind 1 is surrounded only by molecules of kind 2. To that case the assumption of an effective medium does not apply, of course. The experimental findings of Bates *et al.* [15] for a binary mixture of 4-*n*-pentyl-4'-cyanobiphenyl and 4-*n*-pentyl-phenylthio-4'-octyloxybenzoate were interpreted in the framework of the theory by Palffy-Muhoray *et al.* [2] where $S_1 \neq S_2$. An interesting deuterium N.Q.R. and proton N.M.R. study on the phase diagram and the component order

parameters in a nematic mixture was made by Esnault *et al.* [16]. The results were interpreted in terms of the theory [2]. The component order parameters S_1 and S_2 fulfil the relation $S_2 = 0.79S_1$. Unfortunately, S_1 and S_2 were determined by different methods, and it is not clear from the paper [16] how reliable the absolute values of S_1 and S_2 actually are. While the experiments [15, 16] indicate $S_1 \neq S_2$, our experimental results for the mixture E5 are described much better by one effective order parameter than by different order parameters for the different components of the mixture (see figure 7).

From the study of the smectic A phase it is known [17] that cyanobiphenyls tend to dimerisation. The association of monomers to dimers and the decay of dimers into monomers is a dynamic process. That might be as rapid that we see some effective molecule by NMR, and then of course we expect only one order parameter for the whole mixture E5. However, we are at present not able to give an actual physical argument in favour of such a conjecture.

The problem of the steeper descent of the experimental curve in comparison with that calculated in our approach (see figure 7) has not yet been considered. It might be solved in the sense of Humphries, James and Luckhurst [4], however, then an additional arbitrary parameter necessarily enters the theory.

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