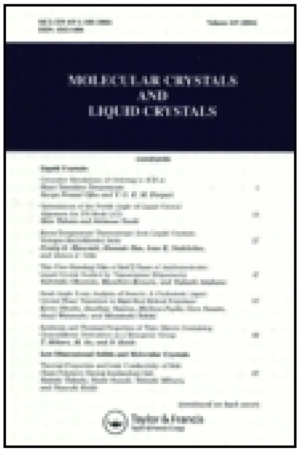

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Phase Diagram and Component Order Parameters in a Nematic Mixture: A Combined Deuterium and Proton NMR Study

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Deuterium and proton magnetic resonance results on mixtures of nematic perdeuterated para-azoxy-anisole (PAAd14) and potential nematic 4-4′ diacetoxy-2-2′ dimethyl azoxybenzene (Ac9Ac) are reported. The phase diagram is established and the order parameters of both components are determined. These data are compared with existing theories. The molecular mean field theory of Pallfy-Muhoray *et al.* is found to be adequate to describe the behaviour of the order parameters, implying that the nematic interaction parameters satisfy the geometric mean rule. The virtual clearing temperature and the molecular volume of Ac9Ac are estimated. It is also shown that the concept of pseudo-clearing temperature may be useful to predict the component order parameters in (dilute) solutions of Ac9Ac in terms of the order parameter of the pure solvent PAAd14. The same theory is found to be rather poor to describe quantitatively the phase diagram. The molecular field/lattice model of Brochard *et al.* predicts that in dilute solutions of Ac9Ac, the number of lattice sites occupied by one Ac9Ac molecule is much larger than its physical volume. Using a simple geometrical model to analyze the magnitude of the measured order parameters, we suggest that this number of sites should be identified with the average volume in which the orientational order of the solvent is perturbed by the presence of one solute molecule.

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1. INTRODUCTION

Liquid crystalline mixtures are of high technological and theoretical interest.[1] For applications, mixtures are usually more suitable than the pure components. On the theoretical side, the variety of physical situations associated with the nature of the components has inspired a large number of theories. These theories have been mainly based on lattice models, molecular field models or combination of these.[2-26] They generally predict the phase diagram and the order parameters of the components in terms of a few molecular parameters. In theories of binary mixtures, one component is usually a low molecular mass (lmm) nematic and the other component is either another lmm nematic or non nematic molecule (case a),[2-22] a flexible polymer (case b),[23-25] a semi-rigid polymer (case c),[26] a side-chain nematic polymer (case d),[22] a main-chain nematic polymer (case e). On the experimental side, considerable works on phase diagrams have been carried out. References about the various cases indicated are as follows: a,[1-20] b,[23,27,28] d,[29,30] e.[31] Binary mixtures of main-chain nematic polymers have also been studied.[32] Experimental work on order parameters is much more scarce and has mainly concerned the solute molecules alone,[33,34] the solvent molecules alone[13,18,27,28] and the mean order parameter of the mixture.[11]

We have recently reported independent measurements of the order parameters of both components in binary mixtures of a main-chain nematic polymer (DDA9) with perdeuterated para-azoxy-anisole (PAAd14).[35-37] The results obtained, in particular the finding that in dilute solutions of polymer, the order parameter of the polymer increases with chain length,[37] prompted us to study the intrinsic mesogenicity of the mesogenic unit (mesogen "9") of these polymers. It turns out that none of the possible candidate molecules which could be considered for this purpose, just differing by the nature of the end groups, are nematic by themselves. They just exhibit crystal to isotropic transition.[38] However, their close resemblance with usual mesogens suggests that they are potentially nematic, the nematic transition being hidden by crystallization. To overcome this problem, we studied mixtures of one of these molecules, namely 4-4′ diacetoxy-2-2′-dimethyl azoxy benzene (cf. Figure 2), hereafter called Ac9Ac[38] with PAAd14 (cf. Figure 1).

In this paper, we report proton and deuterium magnetic resonance (PMR and DMR) results concerning four Ac9Ac/PAAd14 mixtures. The phase diagram is established and the order parameters of both components are deduced. These data are analyzed in terms of two

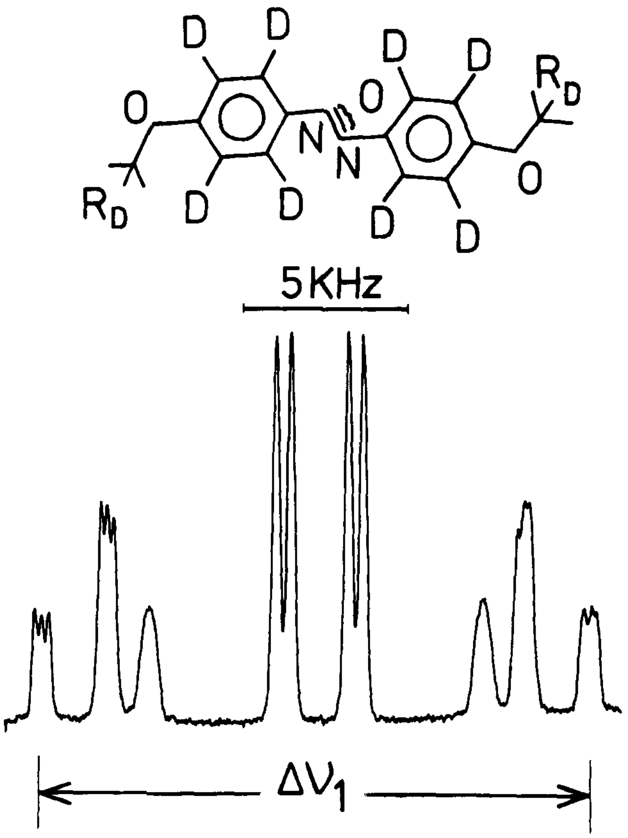

FIGURE 1 Typical DMR spectrum of PAAd14 in the nematic phase. Order parameters are deduced from quadrupolar splitting $\Delta\nu_1$ as explained in the text. See Ref. 39 for details.

theories: the theory of Pallfy-Muhoray *et al.*[11] and the theory of Brochard *et al.*[22] The main parameters of these models are deduced and the virtual clearing temperature and molecular volume of Ac9Ac are determined. These data are also used to test the validity and limitations of molecular theories to describe nematic mixtures. Finally, a simple picture of a (dilute) nematic mixture is proposed which incorporates some results of the analysis.

2. EXPERIMENTAL

The PAAd14/Ac9Ac mixtures were prepared in standard 5 mm diameter NMR tubes. The proper amounts of materials (total amount

~100 mg) were either simply mixed at room temperature in the powder form or dissolved in ethanol and dried to cast the solvent. The tubes were then degassed and sealed under primary vacuum. Both preparation methods turned out to be equivalent for our purpose. Four mixtures corresponding to Ac9Ac concentrations ϕ_M of 5, 10, 15 and 20% w/w, and a pure PAAd14 sample were prepared. The phase behaviour was observed visually in heated silicone oil. Nematic plus isotropic biphasic ranges were clearly observed in all mixtures. The NMR experiments were performed on a CXP90 Brücker spectrometer, at 90.1 MHz for PMR and 13.8 MHz for DMR. Some DMR experiments were also performed at 38.4 MHz on a WP250 spectrometer, giving essentially the same results. In order to obtain good reproductibility in the NMR experiments, the following procedure was followed. The DMR runs were performed first. The samples were first equilibrated at 152° C in the pure isotropic phase during ~1 hour. They were then cooled down rapidly at the lowest possible temperature in the pure nematic phase, and kept at this temperature for several hours (or even days for the 20% mixture) until a stable and well resolved DMR spectrum of PAAd14 was obtained. The samples were then heated by steps of 1 or 2° C, and the spectra were taken several times at a given temperature to insure that thermal and compositional equilibrium were reached, in particular in the biphase. The same thermal history and procedure were used in the PMR experiments.

3. RESULTS

Figure 1 shows a typical DMR spectrum of PAAd14 in the nematic phase and Figure 2 shows the corresponding PMR spectrum of Ac9Ac. The $N + I$ biphase spectra exhibit an additional very sharp central line corresponding to the isotropic component. The following quantities were extracted from these spectra: (i) the temperatures T_N and T_I at which the first nematic drop appears and the last nematic drop disappears, respectively, on heating; (ii) the fractions f_{N_1} and f_{N_2} of PAAd14 and Ac9Ac molecules in the nematic component of the $\Delta\nu$ $N + I$ biphase and (iii) dipolar and quadrupolar splittings as defined in Figures 1 and 2.

The values of T_N and T_I were used to draw the coexistence curves of the phase diagram as shown in Figure 3. They are the same within experimental accuracy (better than 1° C) than those determined by visual observation of all samples simultaneously in heated silicone

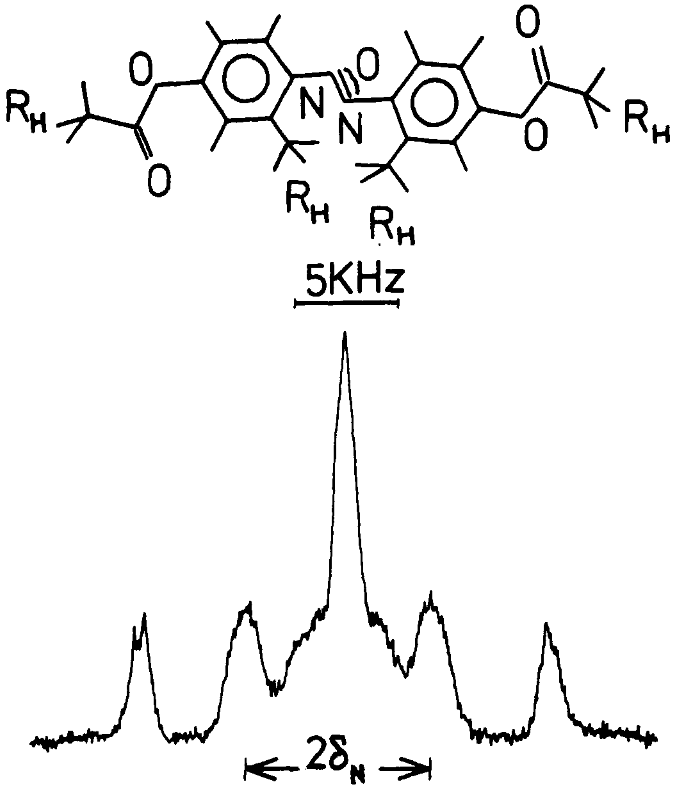

FIGURE 2 Typical PMR spectrum of Ac9Ac in the nematic phase. The external doublet and the sharp central line correspond to terminal methyl groups; the internal doublet and broad central line correspond to aromatic and attached methyl protons. Order parameters are deduced from dipolar splitting $2\delta_N$ as explained in the text. See Refs. 37, 38 and 40 for details.

oil. The nematic fractions extracted from DMR and PMR spectra were difficult to compare precisely because of uncertainty on absolute temperatures in both experiments, but their values are consistent with those deduced from the phase diagram.

The DMR splittings of PAAd14 (Figure 1) were analyzed in terms of structure, conformation and orientational order as in Ref. 39. Using the so-called ratio plots,[39] we have verified that addition of Ac9Ac to PAAd14 up to 20% w/w does not change measurably the average structure and conformation of the PAAd14 molecules. Consequently, the order parameter S_1 of PAAd14 in the mixtures was determined using the same correspondence between S_1 and the largest

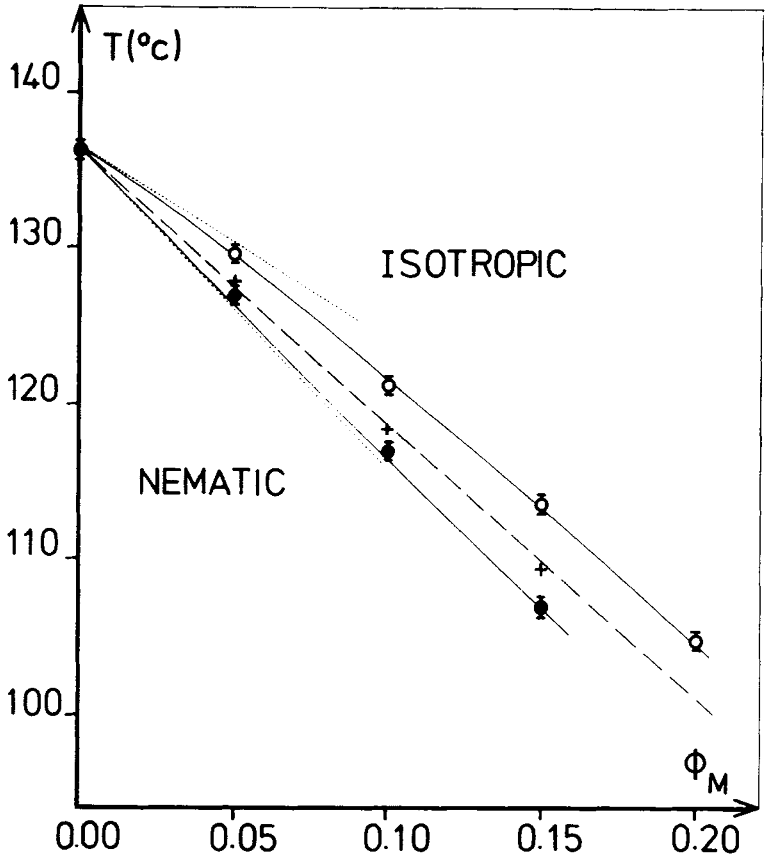

FIGURE 3 Phase diagram of PAAd14/Ac9Ac system. The dotted straight lines are the tangents, at $\phi_M = 0$, to the coexistence curves. The crosses are the pseudo-clearing points determined from the PAAd14 order parameter data as explained in the text and in Figure 4. The dashed straight line is Eq. 13 with $K = 0.43$ and $T_{NI_1} = 136°$ C.

quadrupolar splitting $\Delta\nu_1$ as in the pure sample.[39] The order parameter S_2 of Ac9Ac was determined by analogy with the work on nematic polymer DDA9-L.[36-38,40] Taking into account the differences between Ac9Ac and the polymer, essentially due to the presence of aliphatic spacers in the polymer, we could estimate the relation between S_2 and the main splitting $2\delta_N$ as defined in Figure 2. The result is:

$$2\delta_N/\text{KHz} \cong 23.6\, S_2 \qquad (1)$$

Figures 4 and 5 show the values of S_1 and S_2 respectively, in the four mixtures studied and in pure PAAd14. It is observed that in a given mixture, S_2 is always smaller than S_1 and that all curves have similar temperature dependences, with a monotonous decrease in the pure nematic phase, and a tendency to flatten off in the $N + I$ biphase. Note also that the 20% mixture is not stable in the pure nematic phase. These data—order parameters and phase diagram—are analyzed below in terms of recent theories.

4. ANALYSIS

4.1. Order parameters

The order parameters can be analyzed in terms of the theory of Pallfy-Muhoray *et al.*[11] This theory is a generalization to binary mixtures of the Maier-Saupe (MS) theory[42] of pure nematics. It predicts that, if the nematic interaction parameters u_{ij}^P $(i, j = 1,2)$ per unit number density of component j satisfy the mean geometric rule:[8]

$$u_{12}^P = u_{21}^P = (u_{11}^P u_{22}^P)^{1/2} \tag{2}$$

then, the order parameters S_1 and S_2 are given by:

$$S_1 = f'(\alpha) \tag{3}$$

$$S_2 = f'\left(\sqrt{\frac{u_{22}^P}{u_{11}^P}}\,\alpha\right) \tag{4}$$

where the function f' is:

$$f'(\alpha) = \frac{d}{d\alpha} f(\alpha) \tag{5a}$$

with

$$f(\alpha) = \ln \int_{-1}^{1} \exp[\alpha P_2(\cos\theta)]\, d(\cos\theta) \tag{5b}$$

The parameter α, temperature T and volume fraction ϕ of component 2

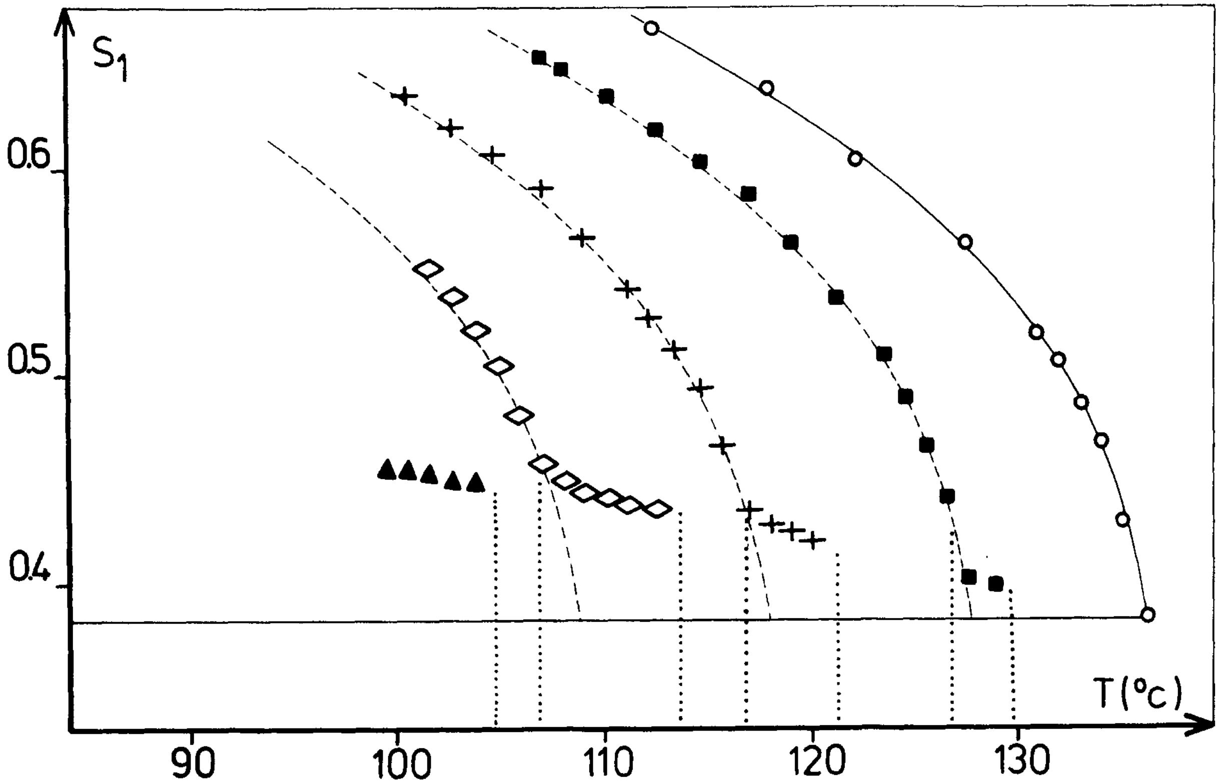

FIGURE 4 Order parameters of PAAd14 versus temperature in pure PAAd14 (○) and in four mixtures, (■): 5%, (+): 10%, (◇): 15%, (▲): 20% w/w. The dashed lines are obtained by translation of the full line (corresponding to pure PAAd14) along the temperature axis. Intersections of these lines with the horizontal $S_1 = 0.38$ determine the pseudo-clearing temperatures $T_p(\phi)$. The biphasic range is indicated for each mixture by vertical dotted lines.

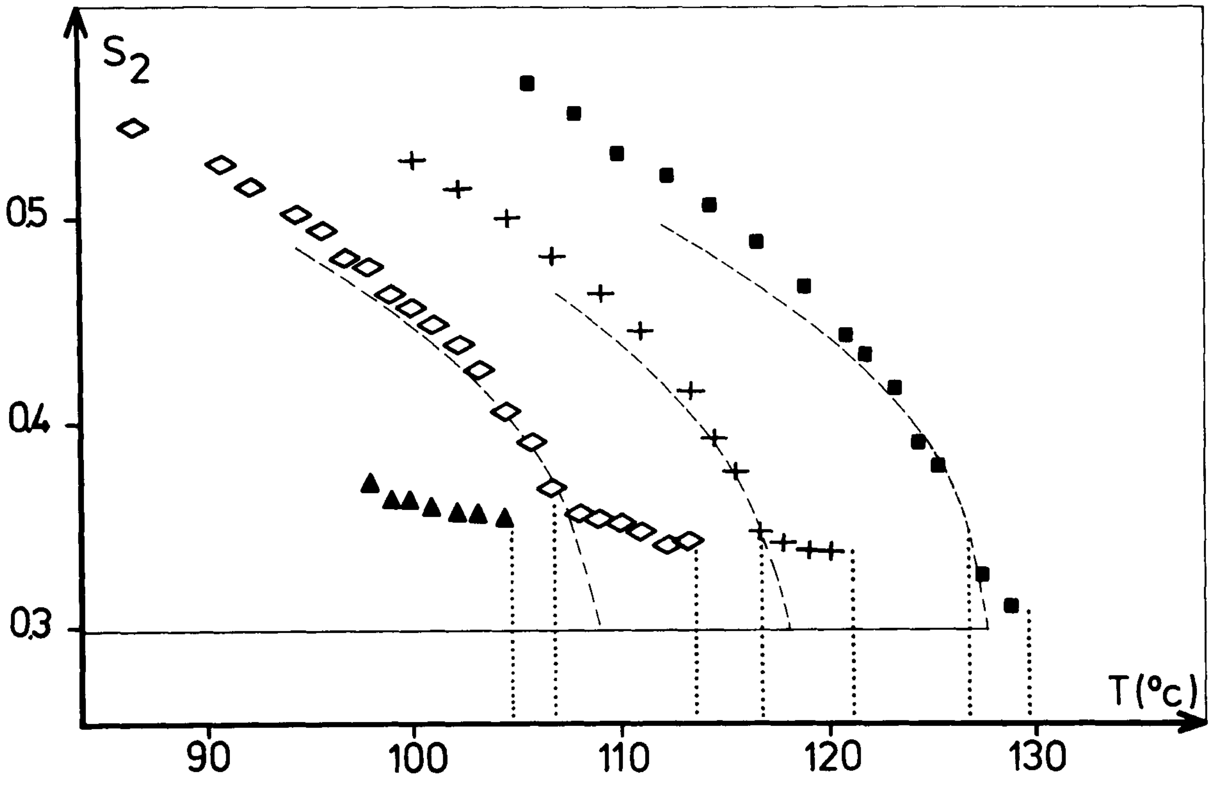

FIGURE 5 Order parameters of Ac9Ac in the four mixtures studied. Symbols are the same as in Figure 4. The dashed lines are the theoretical curves given by Eq. (15) with $K' = 0.79$ and S_1 given by the corresponding dashed curve of Figure 4.

in the nematic part of the mixture are related by the following equation:

$$\frac{T}{4.54} = (1 - \phi) T_{NI_1} \frac{f'(\alpha)}{\alpha} + \phi T_{NI_2} \frac{f'\left(\sqrt{\frac{u_{22}^P}{u_{11}^P}}\,\alpha\right)}{\sqrt{\frac{u_{22}^P}{u_{11}^P}}\,\alpha} \tag{6}$$

In this equation, the T_{NI_i} are the clearing temperatures of pure components i. They are related to the u_{ij}^P and to the molecular volumes v_i by the relation:

$$\frac{u_{22}^P}{u_{11}^P} = \frac{T_{NI_2} v_2}{T_{NI_1} v_1} \tag{7}$$

Equation (6) suggests the definition of an average clearing temperature $T_p(\phi)$ as follows:

$$T_p(\phi) = (1 - \phi) T_{NI_1} + \phi T_{NI_2} \tag{8}$$

Combining Eqs. (3) to (8), Eq. (6) can be rewritten:

$$\frac{T}{4.54\, T_p(\phi)} = \frac{f'(\alpha)}{\alpha} \left[(1 - \phi) \frac{T_{NI_1}}{T_p(\phi)} + \phi \frac{T_{NI_2}}{T_p(\phi)} \frac{S_2}{S_1} \sqrt{\frac{u_{11}^P}{u_{22}^P}} \right] \tag{9}$$

This equation shows that if S_1 and S_2 verify the following proportionality relation

$$S_2 \cong \sqrt{\frac{u_{22}^P}{u_{11}^P}}\, S_1 = \sqrt{\frac{T_{NI_2} v_2}{T_{NI_1} v_1}}\, S_1 \tag{10}$$

then Eq. (9) can be rewritten:

$$\frac{T}{4.54\, T_p(\phi)} = \frac{f'(\alpha)}{\alpha} \tag{11}$$

This equation is formally identical to that obtained in the MS theory of pure nematics having a clearing temperature $T_p(\phi)$. Consequently, if S_2 and S_1 are related by Eq. (10), S_1 is the same universal function of reduced temperature as that of pure component 1 provided that T_{NI_1} is replaced by $T_p(\phi)$. Equation (10) shows that the same temperature dependence holds for S_2. Figure 6 of Ref. 11 shows that Eq. (10) is verified for values of S_1 and S_2 such as $\max(S_1, S_2) \leqslant 0.5$.

It must be noted that for a given mixture of composition ϕ, $T_p(\phi)$ is not observable in practice since demixion into nematic plus isotropic biphase occurs before this temperature is reached. $T_p(\phi)$ is thus a pseudo-clearing temperature very similar to that introduced by Brochard[24] to describe the thermodynamic properties of dilute solutions of flexible polymers in nematic solvents.

This theory is now applied to analyze the order parameters data of Figures 4 and 5. In Figure 4, we have shifted the curve corresponding to pure PAAd14 along the temperature axis until the best superposition to the curves corresponding to the mixtures (in the pure nematic phase) is obtained. It is observed that for ϕ = 5, 10, 15%, this curve can very well represent the temperature dependence of S_1 in the mixtures, even for values of S_1 larger than 0.5. Extrapolation of this curve to $S_1 = S_{1NI_1} \cong 0.38$ as indicated in the figure allows the determination of the pseudo-clearing temperature T_p for each concentration ϕ. These values of $T_p(\phi)$ are reported on the phase diagram (Figure 3), and it is seen that the points indeed fall on a straight line as predicted by theory. Figure 6 shows the order parameter data replotted versus reduced temperature $T/T_p(\phi)$, including the biphasic points for which the corresponding values of T_p are deduced from the phase diagram. It is seen that S_1 and S_2 points indeed gather on the same respective curves, at least not too far from the pseudo-clearing point for S_2.

These results are now used to determine v_2 and T_{NI_2}. Introducing the mass fraction of component 2, ϕ_M, related to volume fraction ϕ by the relation, for $\phi << 1$,

$$\phi = \frac{M_1}{M_2}\frac{v_2}{v_1}\phi_M \tag{12}$$

Equation (8) can be written:

$$\frac{T_p(\phi) - T_{NI_1}}{T_{NI_1}} = -K\phi_M \tag{13}$$

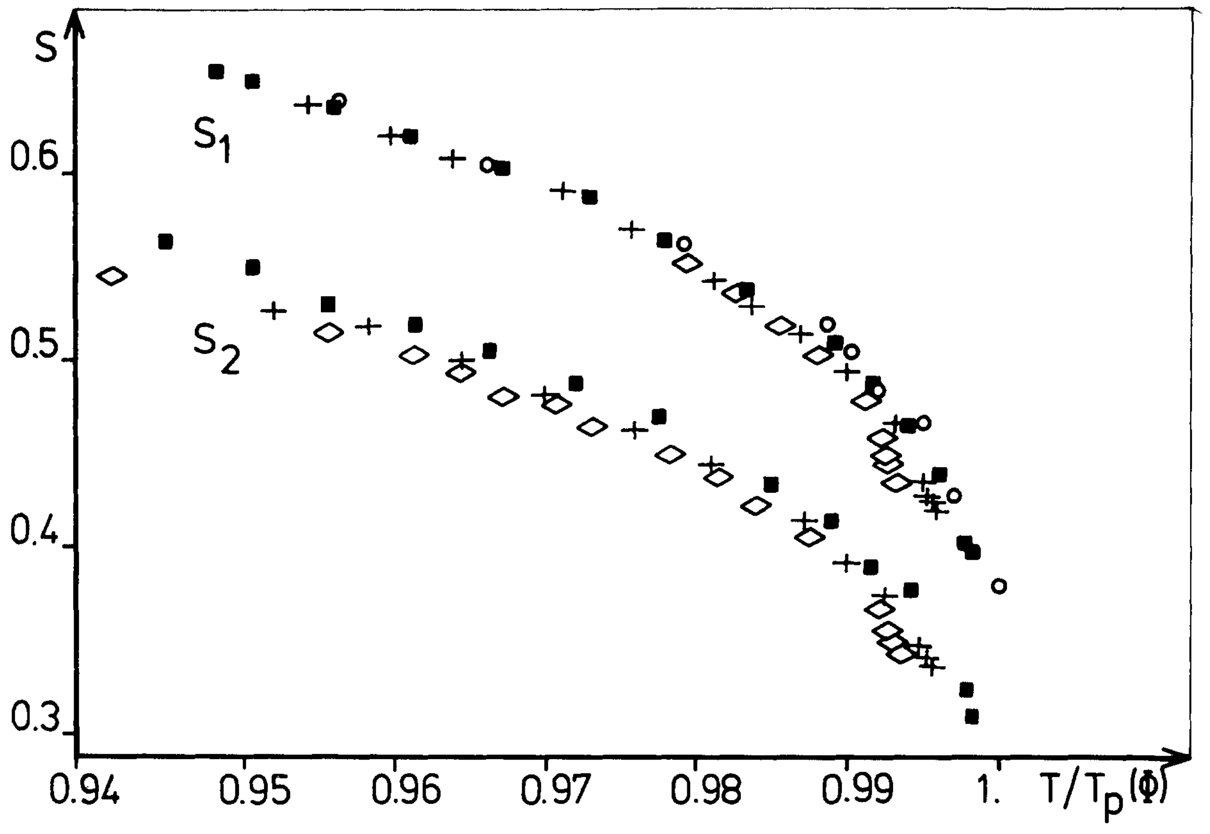

FIGURE 6 Order parameters of PAAd14 (S_1) and of Ac9Ac (S_2) versus reduced temperature $T/T_p(\phi)$. Symbols are the same as in Figure 4. Values of $T_p(\phi)$ are determined as shown in Figure 4 in the pure nematic phase, and from the phase diagram (Figure 3) in the biphase. Note that for PAAd14 (solvent), all points gather on the same universal curve, but for Ac9Ac (solute), this occurs only near the pseudo transition.

with

$$K = \frac{M_1}{M_2}\frac{v_2}{v_1}\left(1 - \frac{T_{NI_2}}{T_{NI_1}}\right) \tag{14}$$

The best fit of Eq. (13) to the data in Figure 3 yields $K \cong 0.430 \pm 0.05$.

A second relation between these parameters can be obtained using the S_2 data. Combining all the data of Figures 4 and 5, it is possible to represent S_2 versus S_1 as shown in Figure 7. According to theory[11], S_2 should be nearly proportional to S_1 (Eq. (10)) for $S_1 \leqslant 0.5$. The full line in Figure 7 is the best fit of a curve of the form:

$$S_2 = K'S_1 \tag{15}$$

to the points limited to $S_1 \leqslant 0.5$. It is seen that a good fit is obtained for $K' \cong 0.790 \pm 0.05$. The upward deviation from linearity for higher values of S_1 is also predicted by theory.[11] Combining Eqs. (10), (14), (15) and the values found for K and K', it is possible to

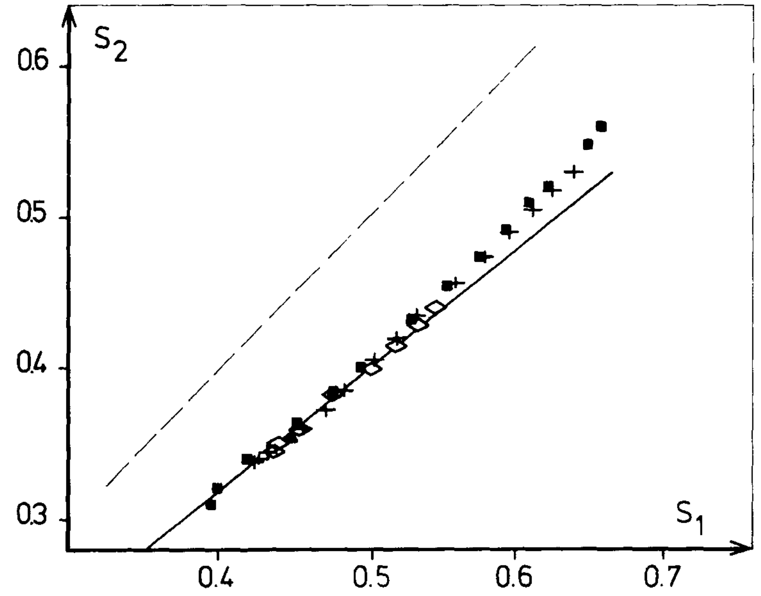

FIGURE 7 Ac9Ac order parameter S_2 versus PAAd14 order parameter S_1 in the four mixtures studied, including biphasic points. Symbols are the same as in Figures 4 to 6. The full straight line is Eq. (15) with $K' = 0.79$. The dashed straight line is $S_2 = S_1$.

deduce the virtual clearing temperature T_{NI_2} of Ac9Ac and the ratio of molecular volumes v_2/v_1. With $M_1 = 272$, $M_2 = 342$, $T_{NI_1} = 409\ K$, we obtain:

$$T_{NI_2} \cong 220 \pm 14\ K; \quad \frac{v_2}{v_1} \cong 1.16 \pm 0.08$$

The rather low value of T_{NI_2} is an indication of the poor mesogenic character of Ac9Ac, and consequently of the mesogenic unit of the corresponding main chain polymers, such as DDA9 polymers. This situation is probably related to the presence of the two methyl groups on the phenyl rings of the molecule. The value of v_2/v_1 is in complete agreement with what is expected from steric considerations. To be more specific, the mean massic volume of normal nematic PAA is 0.86 cm^3/g[39,42] corresponding to a molecular volume of $v_1 = 368$ Å^3. We can assume that the molecular volume of PAAd14 is the same. From this result, we deduce that the molecular volume of Ac9Ac is $v_2 \cong 427 \pm 33$Å^3. The ratio of densities of Ac9Ac and PAAd14 is estimated to $M_2v_1/M_1v_2 \cong 1.08 \pm 0.08$.

In conclusion to this section, it appears that the theory of Ref. 11 can be used to describe the order parameter data in the Ac9Ac/PAAd14 mixtures up to at least $\phi \cong 0.2$. This result implies that the basic assumption of the theory, namely the geometric mean rule, Equation (1), holds for this system. It has permitted to deduce the virtual clearing temperature of Ac9Ac and the ratio of molecular volumes of the components. It has the same limitations as the M–S theory concerning the quantitative predictions, essentially (i) the actual temperature dependence of the order parameter is not exactly that predicted and (ii) the value of the order parameters at the clearing point is too high compared to the measured ones. The comparatively good agreement between theory[11] and our experimental data comes from the fact that these two features were not explicitly used in the analysis.

4.2. Phase diagram

The same theory[11] can be used to analyze the phase diagram. It predicts, in particular, the existence of a nematic plus isotropic biphase. Calling ϕ_N and ϕ_I the volume fractions of component 2 in the nematic part of the biphase at the nematic-biphasic and biphasic-isotropic transitions, respectively, algebraic manipulation of Eqs. (23)

and (24) of Ref. 11 shows that for $\phi \rightarrow 0$, the ratio ϕ_N/ϕ_I is given by:

$$\left(\frac{\phi_N}{\phi_I}\right)_0 = \exp\left[-\frac{v_2}{v_1}\kappa_\infty\left(1 - \frac{T_{NI_2}}{T_{NI_1}}\right)\right] \tag{16}$$

with

$$\kappa_\infty = \frac{\Delta H_{NI_1}}{RT_{NI_1}} \tag{17}$$

where ΔH_{NI_1} is the clearing transition enthalpy of component 1. The second member of this equation can be calculated from the known thermodynamical data of PAA and the preceding results. The result strongly depends on the value of ΔH_{NI_1}. The values found in the literature are not very precise and scatter from ~573 to 757 J/mole.[41] With $T_{NI_1} = 409\ K$, we obtain values for κ_∞ ranging from ~0.169 to 0.223. With $T_{NI_2} = 220\ K$ and $v_2/v_1 = 1.16$, the predicted values of $(\phi_N/\phi_I)_0$ range between 0.913 and 0.887.

On the other hand, by extrapolating the coexistence curves to $\phi = 0$ in the phase diagram (Figure 3), we deduce the following equations for the tangents at the origin of these curves:

$$\phi_N^M \cong 2.04\,\frac{T_{NI_1} - T}{T_{NI_1}} \tag{18}$$

$$\phi_I^M \cong 3.72\,\frac{T_{NI_1} - T}{T_{NI_1}} \tag{19}$$

Combining Eqs. (12), (18) and (19), we deduce that the experimental value of $(\phi_N/\phi_I)_0$ is $\cong 0.548$, i.e. much smaller than the predicted one. The situation appears as if the value v_2/v_1 to be used in Eq. (16) was much larger than the ratio of molecular volumes. Taking v_2/v_1 as an adjustable parameter, agreement with experiment is obtained for v_2/v_1 ranging between ~5.8 and ~7.7. This result is not simply related to the limitations of the M–S theory to predict the correct value of κ_∞. This value is indeed $(\kappa_\infty)_{M-S} = 0.418$ for all pure nematics.[11] Using this value in Eq. (16), we obtain $v_2/v_1 \cong 3.1$, which is still too large.

This situation is not specific to the Ac9Ac/PAAd14 mixtures. In References 13 to 17, are reported a large number of data on phase diagrams of mixtures of nematics with a variety of non nematogen molecules. In all cases, analysis of these data in terms of Eq. (16) with $T_{NI_2} = 0$ yields values of v_2/v_1 (or equivalently of κ_∞) which are too large by at least a factor of 2. With $T_{NI_2} \neq 0$ which is the case in practice for non perfectly spherical solute molecules, the situation is worse.[46]

The reason for this is probably linked to the limitations of molecular theories to describe phase transitions. Brochard *et al.*[22] have developed a theory of nematic mixtures which combines the M–S theory of nematics[42] and the Flory-Huggins lattice model of mixtures.[43] The components 1 and 2 are assumed to occupy N_1 and N_2 lattice sites. The anisotropic interactions are characterized by nematic interaction parameters u_{ij}^B per unit volume fraction of component j. They are formally related to the corresponding parameters u_{ij}^P of Ref. 11 by the relation:

$$u_{ij}^P = u_{ij}^B v_i \tag{20}$$

This theory predicts that if $S_2 < S_1$ as it is the case here, for $\phi \to 0$ the volume fractions ϕ_N and ϕ_I are related by the following two equations:

$$\phi_N - \phi_I = N_2 \kappa_\infty \frac{T_{NI_1} - T}{T_{NI_1}} \tag{21}$$

$$\left(\frac{\phi_N}{\phi_I}\right)_0 = \exp\left\{-N_2\kappa_\infty\left[1 - \left(\frac{u_{12}^B}{u_{11}^B}\right)^2\right]\right\} \tag{22}$$

If the geometric mean rule is assumed, using Eqs. (2), (7) and (20), Eq. (22) can finally be written:

$$\left(\frac{\phi_N}{\phi_I}\right)_0 = \exp\left[-N_2\kappa_\infty\left(1 - \frac{T_{NI_2}}{T_{NI_1}}\right)\right] \tag{23}$$

This equation is formally identical to Eq. (16) with v_2/v_1 replaced by N_2. From the preceding analysis, Eq. (23) means that one Ac9Ac molecule occupies between 5.8 and 7.7 lattice sites. An independent determination of N_2 can be made using Eq. (21). Combining Eqs. (18) and (19), we obtain N_2 ranging between 7.5 and 9.9 sites. These values are in complete agreement with one another if one considers the experimental uncertainties. It can thus be concluded according to the theory of Brochard *et al.*,[22] that in the Ac9Ac/PAAd14 mixtures, one Ac9Ac molecule occupies between 6 to 10 lattice sites. In a picture where one lattice site is reasonably assumed to correspond to the volume occupied by one PAAd14 molecule (at least for dilute solutions), this result means that the presence of one Ac9Ac influences much more space than that its own volume.[47]

In the following, we propose a simple model in which we show that the number N_2 may be interpreted as corresponding to the average volume centered around one solute Ac9Ac molecule in which the orientational order of the nematic medium is perturbated by the presence of this molecule. This model is expected to be valid in all nematic mixtures where the solute is less mesogenic than the solvent.

5. A SIMPLE MODEL OF (DILUTE) NEMATIC SOLUTIONS

Although a dilute nematic mixture is a fluid, macroscopically homogeneous medium (in the absence of demixion), on a microscopic scale it can be considered as an heterogeneous medium in which (partially oriented) solvent molecules are embedded in a sea of (well oriented) solvent molecules. The order parameter of the solute is S_2 and the order parameter of the solvent very far from the solute is that of the pure solvent S_1^0. From this view-point, the solute molecule acts as a perturbation of the local orientational order. We reasonably expect that this perturbation is not limited to the physical volume of the solute, but extends in the medium over some distance, and consequently that the order parameter of the solvent varies more or less continuously from the value S_2 near the solute to S_1^0 very far from it (cf. Figure 8).

The simplest way to describe mathematically this situation is to assume a spherical model in which the perturbation is characterized by a correlation length ξ_0.[25,28,44] We have:

$$S(r) = S_2 \qquad 0 \leqq r \leqq b \quad (24a)$$

$$S(r) = S_1^0 + (S_2 - S_1^0)\frac{b}{r}\exp[-(r-b)/\xi_0] \qquad r \geqq b \quad (24b)$$

in which b is the radius of a sphere whose volume is the physical volume of the solute v_2:

$$\frac{4\pi}{3}b^3 = v_2 \quad (25)$$

At finite (but small) concentration, the medium can be considered as the juxtaposition of "spheres per solute molecule" whose radius R_e is given by:

$$\frac{4\pi}{3}R_e^3 = \frac{v_2}{\phi} \tag{26}$$

For $\xi_0 << R_e$, the local order parameter inside this sphere is given by Eqs. (24). At larger concentrations, when $R_e \sim \xi_0$, the order in one sphere is also perturbed by the presence of neighbouring spheres. In a first approximation, we can assume that the equations are the same but ξ_0 must be replaced by an effective correlation length $\xi > \xi_0$, which is an increasing function of ϕ (see Figure 8).

This model is now used to analyze the order parameter data of Figures 4 and 5. With $v_2 \cong 427$ Å^3, we obtain $b \cong 4.67$ Å. For $\phi_M = 0.05$, combination of Eqs. (12) and (26) yields $R_e \cong 12.7$ Å. With a self-diffusion coefficient D_t of PAAd14 molecules of $\sim 10^{-5}$ cm^2/s,[45] we find that the average time for one molecule to explore the volume of radius R_e is $\sim 4R_e^2/6D_t \sim 10^{-9}$ s, i.e. much shorter than the time scales of PMR and DMR. Consequently, for all concentrations experimentally considered in this work, the measured values of S_1 are the averages of $S(r)$ between b and R_e. We have:

$$S_1 = \frac{3}{R_e^3 - b^3}\int_b^{R_e} S(r)r^2dr \tag{27}$$

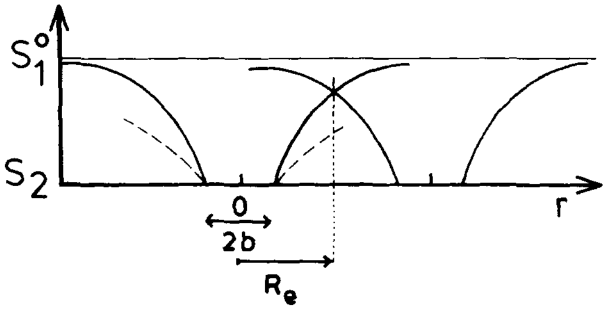

FIGURE 8 Simple spherical model of a dilute nematic mixture. The solute occupies a sphere of radius b and its order parameter is S_2. At infinite dilution, the order parameter of the solvent varies from S_2 at $r = b$ to S_1^0 at $r = \infty$ according to Eq. (24b). The dashed lines picture the influence of neighbouring solute molecules at finite dilution. See text for details.

Combining the data concerning S_2, S_1 and S_1^0 and inserting Eq. (24b) into Eq. (27) with ξ_0 replaced by ξ, it is possible to determine ξ for each temperature and concentration. The value of ξ_0 is obtained by extrapolating the values of ξ to $\phi = 0$. The results are shown in Figure 9 where we have represented ξ versus ϕ_M for several temperatures. It is seen that ξ decreases with ϕ, as expected, and tends to a value $\xi_0 \cong 5$ Å which is practically independent of temperature. Note also that for finite ϕ, ξ is found to diverge with increasing temperature just before entering the biphasic region.

The fact that ξ_0 is found to be independent of temperature strongly suggests that this distance is an intrinsic property of the Ac9Ac/nematic PAAd14 medium. In terms of the average orientational order of the medium, one can roughly consider that the order parameter is S_2 inside a sphere of radius $b + \xi_0$ and is S_1^0 outside this sphere. With the hypothesis that one PAAd14 molecule occupies one site, the sphere of radius $b + \xi_0$ corresponds to N_S sites given by:

$$N_S \cong \frac{4\pi}{3} \frac{(b + \xi_0)^3}{v_1}$$

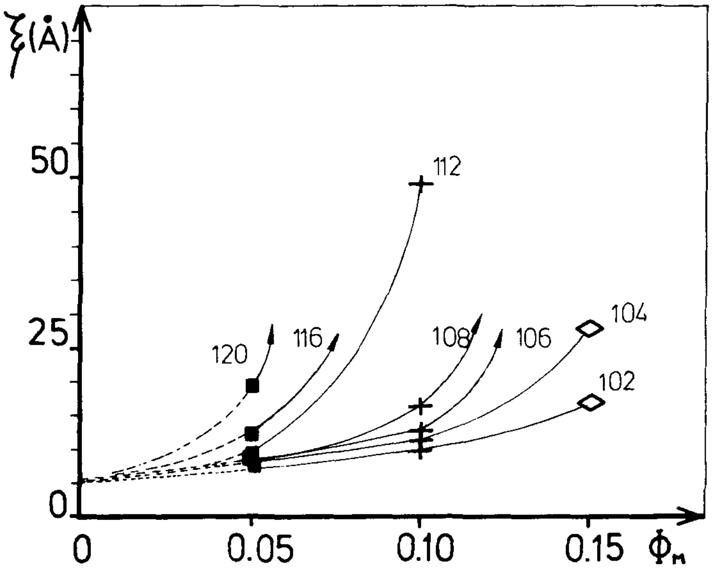

FIGURE 9 Correlation length ξ versus concentration for various temperatures in the nematic phase. Note that, for $\phi \rightarrow 0$, all curves converge towards $\xi_0 \cong 5$ Å, and that for a given concentration, ξ tends to diverge as the nematic-biphasic transition is approached.

With $b = 4.67$ Å, $\xi_0 \cong 5$ Å and $v_1 = 368$ Å^3, we obtain $N_S \cong 10.3$. This number is comparable to the value found for N_2 from the analysis of the phase diagram suggesting that these two numbers should be identified with one another. In short, N_2 corresponds to the average number of sites on which the orientation order is perturbed by the presence of one solute molecule. This analysis is supported by the fact that, near the demixion boundary, ξ is found to diverge. This means that the orientational order is strongly perturbed everywhere, whatever the (small, but finite) concentration, implying strong interaction between solute molecules which induces the phase separation.

6. SUMMARY AND CONCLUDING REMARKS

We have determined the phase diagram and the component order parameters of a binary system involving the low molecular mass nematogen PAA and the potential nematogen Ac9Ac, using combined proton and deuterium NMR methods. These data have been compared with recent theories. The molecular mean field theory of Pallfy-Muhoray *et al.*[11] appears to be adequate to describe the behaviour of the order parameters, implying that in this system, the mean geometric rule holds for the nematic interaction parameters. We have shown that the volume fraction average of the clearing temperatures of the two components may be considered as the pseudo-clearing temperature of the corresponding mixture. This concept appears to be useful to predict the component order parameters of this mixture in terms of the order parameters of the solvent, at least for dilute solutions, and not too far from the transition. The quantitative limitations of this theory are the same as those of the parent Maier-Saupe theory.[42] On the contrary, the theory of Ref. 11, and probably all types of molecular theories appear to be rather poor to predict quantitatively the phase diagram. In these theories, the situation appears as if the volume of one solute molecule was much larger than the actual molecular volume. The theory of Brochard *et al.*[22] provides a more general framework to describe phase diagrams by identifying this volume to a number of lattice sites. Based on a simple model, we have proposed that this volume, or number of lattice sites occupied by one solute molecule, may be identified with the mean volume in which the nematic order is perturbed by the presence of one solute molecule, in infinitely dilute solution. This model is expected to apply to all nematic mixtures in which the solutes are poor or non nematogen.

It is worth noting that the situation found in the biphasic range of the PAAd14/Ac9Ac system appears to be intermediate between the case of quasi-spherical solute molecules in which the solvent order parameter is found to be constant (and minimum),[13] and the case of flexible polymer solutes in which the solvent order parameter is found to strongly decrease.[27] The present results support the statement made by Brochard[24] that in nematic mixtures, lower coexistence curve and clearing temperature are of different thermodynamical origins.

Finally, it must be realized that (i) a large number of data could be collected in this study because of the combination of DMR and PMR which allowed independent observation of the solvent and solute molecules and (ii) the analysis could be pushed so far not only because of the existence of theories, but also of the existence of reasonably reliable methods to extract order parameters from the NMR spectra.

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References

1. H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980.
2. R. Alben, *J. Chem. Phys.*, **59**, 4299 (1973).
3. M. A. Cotter, *J. Chem. Phys.*, **66**, 1098 (1977).
4. M. A. Cotter and D. C. Wacker, *Phys. Rev. A*, **18**, 2669 (1978); *ibid*, **18**, 2676 (1978).
5. M. Warner and P. J. Flory, *J. Chem. Phys.*, **73**, 6327 (1980).
6. M. Warner, *Mol. Cryst. Liq. Cryst.*, **80**, 79 (1982).
7. C. Counsell and M. Warner, *Mol. Cryst. Liq. Cryst.*, **100**, 307 (1983).
8. R. L. Humphries, P. G. James and G. R. Luckhurst, *Faraday Soc. Symposium*, **5**, 107 (1971).
9. R. L. Humphries and G. R. Luckhurst, *Chem. Phys. Letters*, **23**, 567 (1973).
10. R. L. Humphries and G. R. Luckhurst, *Proc. Roy. Soc. London*, **A342**, 41 (1976).
11. P. Pallfy-Muhoray, D. A. Dunmur, W. H. Miller and D. A. Balzarini, in "*Liquid Crystals and Ordered Fluids*," vol. 4 (A. C. Griffin and J. F. Johnson, eds.), Plenum Press, N.Y., 1984, p. 615.
12. P. Pallfy-Muhoray, J. J. de Bruyn and D. A. Dunmur, *Mol. Cryst. Liq. Cryst.*, **127**, 301 (1985).

13. B. Kronberg, D. F. R. Gilson and D. Patterson, *J. Chem. Soc. Faraday II*, **72**, 1673 (1976).
14. B. Kronberg and D. Patterson, *ibid*, **72**, 1686 (1976).
15. D. E. Martire, G. A. Oweimreen, G. I. Ågren, S. G. Ryan and H. T. Peterson, *J. Chem. Phys.*, **64**, 1456 (1976).
16. G. Ishi and H. Yamada, *J. Physique* (colloques) **C3**, 374 (1979).
17. G. A. Oweimreen and M. Hasan, *Mol. Cryst. Liq. Cryst.*, **100**, 357 (1983).
18. J. R. McColl, *J. Chem. Phys.*, **62**, 1593 (1975).
19. W. R. Krigbaum, H. Hakemi, A. Ciferri and G. Conio, *Macromolecules*, **18**, 973 (1985).
20. M. Domon, thesis, University of Lille, France (1973).
21. J. Sivardière, *J. Physique*, **41**, 4416 (1980).
22. F. Brochard, J. Jouffroy and P. Levinson, *J. Physique*, **45**, 1125 (1984).
23. B. Kronberg, I. Bassignana and D. Petterson, *J. Phys. Chem.*, **82**, 1714 (1978).
24. F. Brochard-Wyart, *C.R. Acad. Sc. Paris*, t. 289 serie B, 229 (1979).
25. F. Brochard-Wyart, *C.R. Acad. Sc. Paris*, t. 290 serie B, 485 (1980).
26. A. ten Bosch, P. Maissa and P. Sixou, *J. Chem. Phys.*, **79**, 3462 (1983).
27. A. Dubault, C. Casagrande, M. Veyssié and B. Deloche, *Phys. Rev. Lett.*, **45**, 1645 (1980).
28. A. Dubault, thesis, University Pierre et Marie Curie, France (1981).
29. H. Finkelman, H. J. Kock and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **89**, 23 (1982).
30. C. Casagrande, M. Veyssié and H. Finkelman, *J. Physique* (*Lettres*) **43**, L671 (1982).
31. A. G. Griffin and S. J. Havens, *J. Polym. Sc.: Polym. Letters Ed.*, **18**, 259 (1980).
32. J. Watanabé and W. R. Krigbaum, *Macromolecules*, **17**, 2288 (1984).
33. D. F. Hillebrand and H. Wu, *J. Chem. Phys.*, **67**, 957 (1977).
34. Y. P. Lee and D. F. R. Gilson, *J. Chem. Phys.*, **70**, 2042 (1979).
35. F. Volino, A. M. Giroud, A. J. Dianoux, R. B. Blumstein and A. Blumstein, *Mol. Cryst. Liq. Cryst.*, **127**, 103 (1985).
36. F. Volino, *Proc. of the IUPAC International Single Topic Symposium on Non Crystalline Order in Polymers*, Napoli (Italy), 27–30 May 1985, p. 65.
37. F. Volino, M. M. Gauthier, A. M. Giroud-Godquin and R. B. Blumstein, *Macromolecules*, **18**(12), 2620 (1985).
38. R. B. Blumstein, M. D. Poliks, E. M. Stickles, A. Blumstein and F. Volino, *Mol. Cryst. Liq. Cryst.*, **129**, 375 (1985).
39. A. J. Dianoux, J. B. Ferreira, A. F. Martins, A. M. Giroud and F. Volino, *Mol. Cryst. Liq. Cryst.*, **116**, 319 (1985).
40. A. F. Martins, J. B. Ferreira, F. Volino, A. Blumstein and R. B. Blumstein, *Macromolecules*, **16**, 279 (1983).
41. "Source of Thermodynamical Data on Mesogens," *Mol. Cryst. Liq. Cryst.*, **115**, n° 1 to 4 (1984).
42. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959).
43. P. Flory, "*Principles of Polymer Chemistry*," Cornell Univ. Press, N.Y. (1971).
44. P. G. de Gennes, in "*The Physics of Liquid Crystals*," Clarendon Press, Oxford (1974).
45. F. Noack, *Mol. Cryst. Liq. Cryst.*, **113**, 247 (1984).
46. Other theories have led to similar conclusions. (i) Analysis of phase diagrams by Krigbaum *et al.*[19] of mixtures of PAA with non mesogenic molecules in terms of the theory of Warner and Flory[5] leads to values of κ_∞ which are too small by a factor of 6 to 7 compared to the experimental value. (ii) Hishi and Yamada[16] have extended the theory of Martire *et al.*[15] to non-spherical solutes. They predict that the ratio $(\phi_N/\phi_I)_0$ is given by: $(\phi_N/\phi_I)_0 = z_{20} \exp(-\ v_2/v_1\, \kappa_\infty)$, where z_{20} is a known function of u_{12}/u_{11}. For our case, with $u_{12}/u_{11} = 0.79$, we have $z_{20} \cong 1.30$. Taking v_2/v_1 as parameter, we find that v_2/v_1 must range between 3.87 and 5.11.

47. It is worth noting that the theory of Ref. 22 is more general than that of Ref. 11 since the geometric mean rule (Eq. (2)) is not assumed. In this case, for given values of the nematic interaction parameters u_{ij}, the plot S_2 versus S_1 is no more a single curve, but rather a whole set of isoconcentration and isothermal curves (cf. Figure 1 of Ref. 22). Thus, observation of a single curve in such plot proves that the mean geometric rule holds for this system.