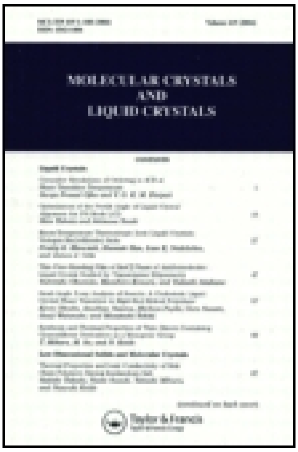

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A Relation Between the Order of Solutes Dissolved in Nematic Solvents I52, EBBA and in Binary Mixtures I52/EBBA at Different Mixing Molar Ratios

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Abstract The aim of this work has been to test the reliability of a simple relation connecting the order of probe molecules dissolved in binary nematic mixtures with that exhibited in each nematic component at the same reduced temperatures. In order to do this, a large amount of ^{1}H-LXNMR experiments at different temperatures has been performed, utilizing as solutes 1,4-difluorobenzene, 1,4-dichlorobenzene, 1,4-dibromobenzene and naphthalene in I52, EBBA and I52/EBBA mixtures at variable mixing percentages (50/50, 20/80 and 80/20 mol%). The results confirm that the orientations of the solutes in the mixtures can be predicted in a satisfactory way as a function of the mixing ratios, independently of the solutes and the temperatures. Finally, as a stimulation for future studies, a conjecture about the observed discrepancies is suggested.

Keywords Nematic Mixtures; Solutes Order Parameters; LXNMR .

INTRODUCTION

The orientation of a probe molecule dissolved in a binary mixture of nematic solvents, compared with that experienced (at the same reduced temperature) by the solute in the pure components, can give useful information about the mechanisms governing the orientation of molecules in liquid crystal mesophases. In particular, the detection of a correlation, based on the mixing molar ratios of the nematics and essentially independent of the nature of the solute and the temperature of the experiment, could validate the assumption, usually adopted by the *mean-field* theories, that the solvent is felt by the solute as a *continuum*. Moreover, such a relation could be seen as a proof that, when specific interactions are missing, additive orientational mechanisms account, at least at a first order level, for the orientation of the molecules.

Two LXNMR works about this argument are present in the literature. In the first paper [1], treating the orientation of *p*-xylene dissolved in ZLI1132, PCH-7, EBBA and in about equimolar mixtures PCH-7/EBBA and ZLI1132/EBBA, the behaviour of the solute order parameters is studied as a function of temperature and composition of the mixtures. Unlike what predicted by the authors on the basis of a solid theoretical derivation, the experimental results seem to indicate a significant deviation from the values expected by random mixing, so that opportune corrective factors, referred to as R_A and R_B, are introduced in the theoretical formulation.Interesting is the observation that there is an immediate correspondence between the $R_A/2$ and $R_B/2$ values and the weights obtained, at different temperatures, by Celebre et al. [2] for various rigid solutes in a 56.65/43.35 mol% ZLI1132/EBBA (it is worthwhile to recall that ZLI1132 is not a pure compound but a mixture of four different molecules [3]). These weights were determined making use of the simplest intuitive hypothesis that the mean-torque potential experienced by the solute in the mixture could be described by a linear combination of the potentials in the nematic components of the mixture: a subsequent normalization of the weights produced, at least at temperatures not Veryclose to the Nematic-Isotropic transition,the expectedvalues corresponding to the mixing molar ratio of themixture.similar behaviour is also showed by the re-normalized R_A and R_B factors of the paper [1] for *p*-xylene dissolved in ZLI1132/EBBA, so that the results of the two studies are in practice reconciled.

To check if the conclusions of the cited studies can be generalized to other mixtures, several ^{1}H-LXNMR experiments at different temperatures have been performed, utilizing the D_{2h} solutes 1,4-difluorobenzene, 1,4-dichlorobenzene, 1,4-dibromobenzene and naphthalene dissolved in I52, EBBA and in binary mixtures I52/EBBA at variable mixing percentage (50/50, 20/80 and 80/20 mol%). The choice of these nematic solvents is due to their value of dielectric anisotropy (slightly positive for I52, small and negative for EBBA): other studies are indeed in progress about the dependence of solute biaxiality on this property (for more information see ref. [3]).

In this work are presented the results we have obtained, suggesting also a possible interpretation of the observed deviations from the predicted trends.

THEORY

The proton NMR spectra of rigid solutes dissolved in nematic phases are strongly affected by the partially averaged direct dipolar couplings $\tilde{D}_{ZZij}$ between the *i* and *j* protons, being *Z* the direction of the applied external static magnetic field. For nematics whose director alignes parallel to the magnetic field, the direct coupling can be written as [4]:

$$\tilde{D}_{ZZij} = \frac{2}{3} \sum_{\zeta,\xi} S_{\zeta\xi} D_{\zeta\xi ij} \qquad (1)$$

$\underline{\underline{D}}_{ij}$ is the dipolar coupling tensor expressed in the molecular frame and $S_{\zeta\xi}$ the generic element of the Saupe traceless ordering matrix [5] that, for a biaxial solute in an uniaxial environment (as a nematic), corresponds to

$$S_{\zeta\xi} = \frac{1}{2}\left\langle 3\cos\theta_\zeta \cos\theta_\xi - \delta_{\zeta\xi} \right\rangle = \frac{\int \left(3\cos\theta_\zeta \cos\theta_\xi - \delta_{\zeta\xi}\right) \cdot \exp\left[-\frac{U(\beta,\gamma)}{kT}\right] sin\beta d\beta d\gamma}{2\int \exp\left[-\frac{U(\beta,\gamma)}{kT}\right] sin\beta d\beta d\gamma} \qquad (2)$$

where θ_ζ is the angle between the director and the ζ molecular axis, $\delta_{\zeta\xi}$ the Kronecker delta function, (β,γ) the set of Euler angles defining the director orientation in the molecular frame and $U(\beta,\gamma)$ the mean torque potential describing the orientational interactions between the solute and the solvent. The debate about the nature and the form of $U(\beta,\gamma)$ is still open, as testified by the large number of works recently appeared in literature (see ref. 2 for a wide selection of papers in this field). In a "low profile" approach to the problem, a choice could be to express the mean-torque potential by a two-terms expansion in spherical harmonics series [3]

$$U(\beta,\gamma) = -B_0\,P_2(\cos\beta) - B_2\,sin^2\beta\cos 2\gamma \tag{3}$$

where $P_2(\cos\beta)$ is the second rank Legendre polynomial. The nature of the problem is encrypted in the B_k coefficients, but for our purposes it is possible to use the Equation (3) in a phenomenological way, namely without investigation about the nature of the coefficients. If we assume as valid the hypothesis of superposition of the effects (neglecting possible non-linear effects) and if we consider the solvent as a *continuum* (neglecting specific molecule-molecule interactions), for very dilute solutions it is possible to approximate the potential experienced by the solute in the mixture as a weighted mean of those in the single solvents [2]. In particular, for mixtures of I52 and EBBA, we have

$$U_{Mix}(\beta,\gamma) = w_{I52}\cdot U_{I52}(\beta,\gamma) + w_{EBBA}\cdot U_{EBBA}(\beta,\gamma) \tag{4}$$

where $w_{I52} = w_I/(w_I + w_E)$ and $w_{EBBA} = w_E/(w_I + w_E)$ are normalized weights that can be calculated making use of Equations (3) and (4) and solving the following algebraic system

$$\begin{cases} B0_{Mix}(\beta,\gamma) = w_I\cdot B0_{I52}(\beta,\gamma) + w_E\cdot B0_{EBBA}(\beta,\gamma) \\ B2_{Mix}(\beta,\gamma) = w_I\cdot B2_{I52}(\beta,\gamma) + w_E\cdot B2_{EBBA}(\beta,\gamma) \end{cases} \tag{5}$$

at each temperature. In an "ideal" behaviour of the mixtures, the coefficients w_{I52} and w_{EBBA} should be basically independent on the temperature and equal to the molar fractions of I52 and EBBA in the mixtures: in the following part of the paper we will test these hypotheses.

EXPERIMENTS

For each selected molecule (1,4-difluorobenzene: DFB; 1,4-dichlorobenzene: DCB; 1,4-dibromobenzene: DBB and naphthalene: NFT) five 1 mol% solutions were prepared, dissolving the solute in the nematic solvents I52 (Merck Ltd., Darmstadt), EBBA (synthesized following standard procedures [6]) and in three different mixtures I52/EBBA (20/80, 50/50 and 80/20 mol%). The structures of the solvents molecules are reported in ref. [3]; the molecular reference system of the solutes has been chosen so that the molecule lies on the plane of symmetry σ_{xz}, the longer molecular axis being aligned along z . To each solution, 0.4 mol% 1,3,5-trichlorobenzene (TCB) has been added as internal orientational reference [7]: the triplet 1:2:1 originated by TCB, with splitting equal to $3D_{HH}$, has been useful to fine calibrate the $T_{red} = T/T_{NI}$, where T_{NI} is the Nematic-Isotropic transition temperature. The value of T_{NI} of the samples has been detected by an optical microscope, then the ^{1}H-NMR spectra have been recorded on a 7.04 T Bruker AC 300 spectrometer, equipped with a temperature control unit, at different, but common, reduced temperatures. The spectra were analysed by automated procedures [8] and the dipolar couplings have been used to obtain the experimental order parameters, assuming standard regular geometries of the solutes.

RESULTS AND DISCUSSION

The unknown weights of Equations (5) can be calculated at each temperature deriving the B_k values from the order parameters, showed in Figures 1 and 2, according to the Equations (2) and (3).

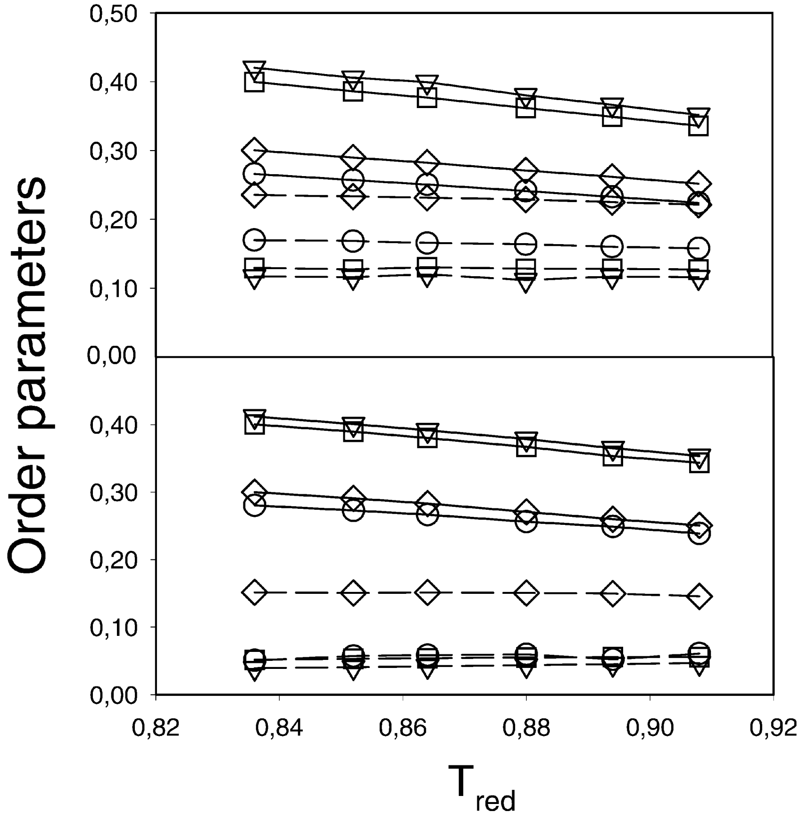

FIGURE 1 Variation of order parameters S_{zz} (solid lines) and S_{xx}-S_{yy} (dashed lines) *vs* reduced temperature for DFB(○), DCB(□), DBB(∇) and NFT(◊) in I52 (top) and in EBBA (bottom).

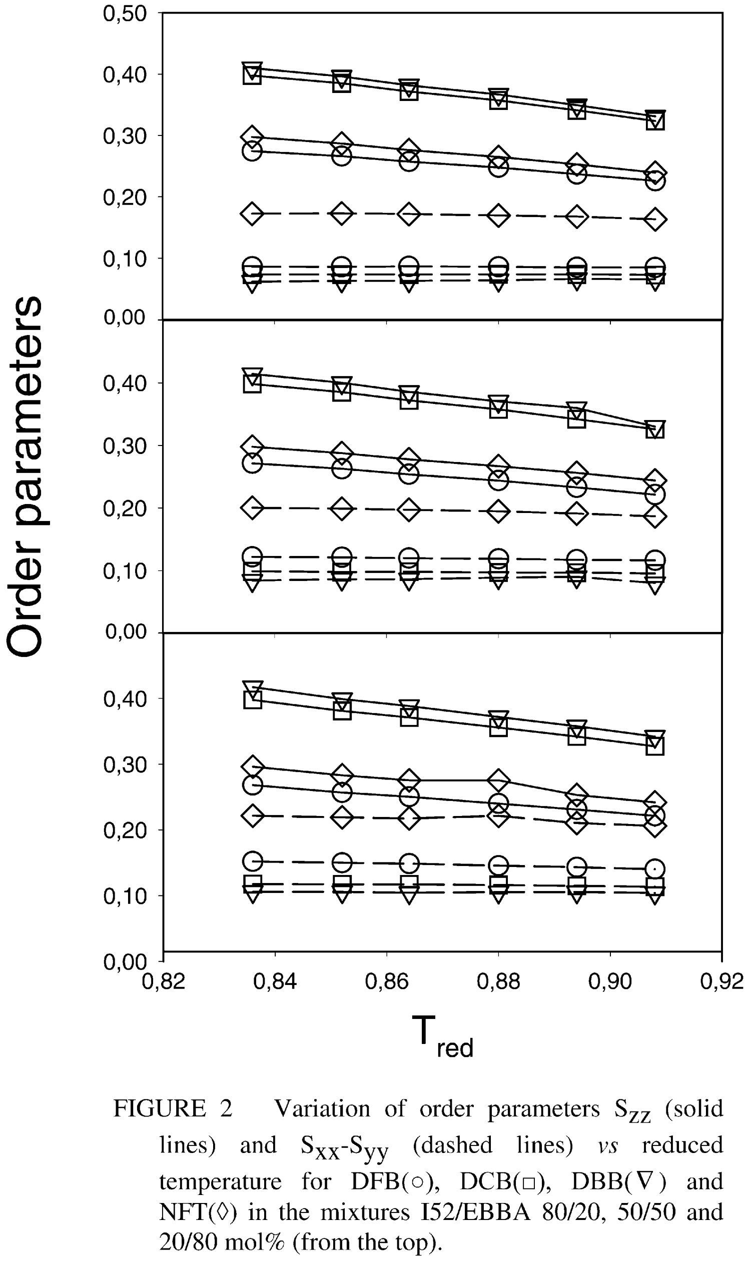

FIGURE 2 Variation of order parameters S_{ZZ} (solid lines) and S_{XX}-S_{YY} (dashed lines) *vs* reduced temperature for DFB(○), DCB(□), DBB(∇) and NFT(◊) in the mixtures I52/EBBA 80/20, 50/50 and 20/80 mol% (from the top).

In Figure 3 only the values of the weight w_{I52} *vs* T_{red} are showed (being w_{EBBA} =1- w_{I52}) for different solutes in the I52/EBBA mixtures. Looking at the figure, it is clear that w_{I52} is essentially independent of the nature of the solute and the temperature of the experiment: the values are distributed around their mean (dashed line) in a range of ±2σ (dotted lines), σ being the standard deviation of the data. This evidence confirms the results reported in the previously cited study of the same solutes in an about equimolar mixture of ZLI1132 and EBBA [2]. On the contrary, the agreement between the mean values of w_{I52} and the molar fractions of I52, although acceptable taking in account the simplicity of the model, is worse than in ref. [2]. A conjecture about this different observed behaviour, at least at a phenomenological level, could be based on the different values of T_{NI} of the two solvents in the mixtures: about the same for ZLI1132 (T_{NI} = 345 K) and EBBA (T_{NI} = 353 K), very different for I52 (T_{NI} = 378 K). A further proof of this supposition is given by the case of *p*-xylene in PCH-7/EBBA [1] (T_{NI} of PCH-7 = 331.5 K): unlike we already said in the Introduction Section about the *p*-xylene dissolved in ZLI1132/EBBA, the re-normalization of R_A and R_B factors gives values far enough from the molar fractions of the mixture components; so, a large ΔT_{NI} probably implies a considerable deviation from the ideal behaviour. Again, the largest discrepancy of the observed weight from the theoretical value is observed in the 50/50 mixture: this could suggest a relation with the excess temperature T_{EX} [9], defined as the difference between the observed T_{NI} of the mixture and the weighted mean of T_{NI}'s of the nematic solvents constituting the mixture.

CONCLUSIONS

The results of this work seem to confirm that the order of solutes in nematic binary mixtures is dominated by the mixing ratio of the mixture solvents, regardless of the solutes and the temperatures; anyway the agreement with the values predicted by a simple linear model of superposition of effects can be more or less good according

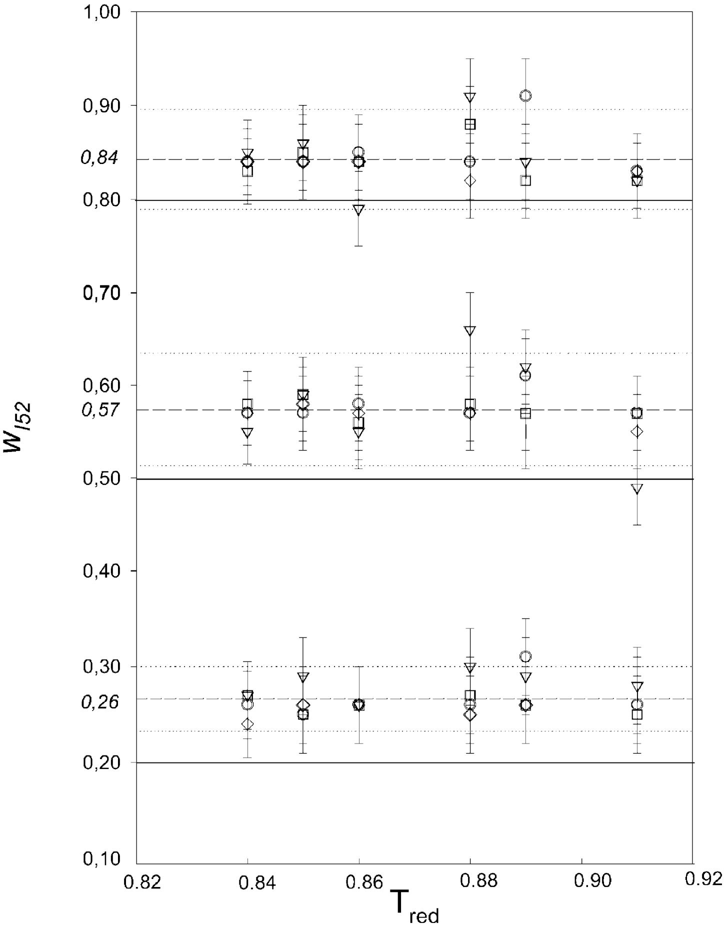

FIGURE 3 Distribution of w_{I52} *vs* reduced temperature for DFB(○), DCB(□), DBB(∇) and NFT(◊) in the mixtures I52/EBBA 80/20, 50/50 and 20/80 mol% (from the top). The dashed lines represent the means of experimental values, the solid lines the correct values of molar fraction of I52 in the mixtures, the dotted control lines lie at twice the standard deviation from the mean. The error bars result from a 1% estimated error on the experimental order parameters.

to the solvents constituting the mixture: we have planned to study other binary nematic mixture to ascertain the generalizability of our results and to test the guess that largest discrepancies are observed when the solvents in the mixtures have very different values of T_{NI}. Works are at present in progress to formulate a model taking in account T_{EX} and ΔT_{NI} to reproduce the deviations from the ideal behaviour.

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