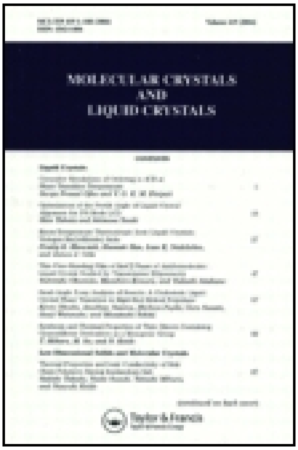

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ORDERING OF POLAR SOLUTES IN NEMATIC *MAGIC MIXTURES*: EVIDENCES OF DIPOLAR EFFECTS?

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The differences between experimental and calculated order parameters of polar solutes dissolved in zero electric field gradient nematic liquid crystal mixtures (magic mixtures) could be interpreted, in the context of a recently proposed model [1,2], as an evidence of small but detectable effects of solute polarity in the orientational mechanisms.

Keywords: polar solutes ordering; nematic magic mixtures; LXNMR

INTRODUCTION

The role played by molecular dipoles in inducing the ordering of solutes dissolved in nematic phases has been often investigated in the past but with controversial results. The mean-field models exclude in principle the dipolar interactions as responsible for ordering, due to the apolar nature of nematic phases [3]: the lowest-order non-vanishing multipole, effective in orientational mechanisms, is then considered the interaction of the solute electric quadrupole (*seq*) with the average electric field gradient (*aefg*) of the solvent. Nevertheless, a permanent dipole of the solute can induce a reaction field in the surrounding medium, so the polarity of the probe molecule could still affect the orientational order of the molecule [4]. Moreover, a usual approximation in the mean field approaches is to assume that all solutes (even if different in size, shape and electrostatic properties) experience roughly the same average environment: when this assumption is relaxed, also dipolar effects can emerge as cause of orientation [5]. On this basis, experimental results have been interpreted indicating the local (in particular, eccentric) dipoles as explanation of important orientating

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effects [6, 7]. More recently, further experimental studies suggest a little (or null) influence of axial dipoles [8], but the role of eccentric dipoles deserves more investigations. The last contribute to this subject, in our knowledge, is a very recent paper [9] where, in the zero ***aefg*** ("magic") nematic mixture 55 wt% ZLI1132+EBBA [10], the permanent dipoles (both axial and eccentric) seem to have a negligible effect on the ordering.

In the present paper we have revisited the data published by Chandrakumar and Burnell [11], regarding the ordering (obtained by proton NMR spectra recorded at different temperatures) of the polar molecules orthodichlorobenzene (ODCB), metadichlorobenzene (MDCB) and 1,3-bromochlorobenzene (BCB), dissolved in the ***magic mixtures*** 55 wt% ZLI1132+EBBA (henceforth called M1) and 70 wt% 5CB+EBBA [12] (henceforth called M2): in these nematic mixtures the ***seq-aefg*** interaction, commonly believed the most important long-range orientational mechanism [13], is expected to be negligible. The experimental data reported in [11] have been compared with the order parameters calculated by making use of a novel approach [1, 2]: one of the possible interpretations of the results lies on possible effects of molecular dipoles in influencing the order of the solutes.

THEORETICAL BACKGROUND

The ordering of apolar molecules dissolved in magic mixtures has been recently successfully described by making use of a strictly short-range anisotropic orientational potential $\boldsymbol{U}_{sr}$, where ***i)*** the solute is described as a hard rectangular box of suitable dimensions (taking into account molecular geometries and van der Waals radii); ***ii)*** the direct environment of the probe molecule is given at a molecular level and, finally, ***iii)*** the bulk of the anisotropic solvent is treated in an average way (the reader is referred to [1, 2] for a detailed description of the model). The orientating potential is thought as resulting from the balance of the tendency (σ_f) of each face of the box to align to its nearest solvent molecule (assumed axially symmetric) multiplied by the preference (Σ_f) of that single solvent molecule to align to the director of the mesophase. Under these conditions, the potential can be formulated in the following way:

$$U_{sr}/kT = -\frac{\varepsilon}{6}\sum_{f=1}^{6} F_f \cdot \sigma_f \cdot \Sigma_f \tag{1}$$

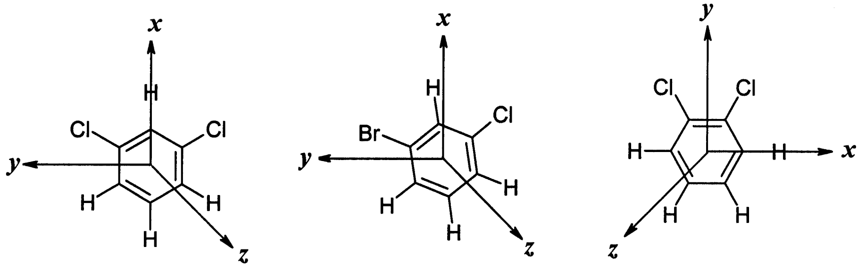
where F_f is the length of the f-th face; $\sigma_f = P_2(\cos\varphi_f)$ and $\Sigma_f = P_2(\cos\theta_f)$ are expressed, by means of second Legendre polynomials, as functions of the angle φ_f of the solvent molecule respect to the f-th face and of the orientation θ_f of the f-th solvent molecule respect to the mesophase director; ε is the amount of orientational energy for unit length (the minus sign in Eq. (1) is to favour the parallel alignment). As said above, this purely short-range model gave excellent results [1, 2] in reproducing the order parameters (represented by the $S_{\alpha\beta}$ elements of the traceless ordering Saupe matrix [14]) for apolar, symmetric molecules (where the crude description of the solute proved to be sufficient in keeping the essential features of the size and shape of the solute) dissolved in the M1 zero *aefg* nematic mixture. For polar, asymmetric molecules, as the solutes treated in this work, the model is expected to provide an incomplete description of the molecular ordering for two main reasons: 1) the size, the shape and the symmetry of the solute are badly reproduced by a simple hard parallelepiped; 2) although the selected nematic solvents are magic mixtures (where, as said above, the ***seq-aefg*** interaction should be negligible), possible dipolar orientational effects cannot in principle be excluded.

RESULTS AND DISCUSSION

In Figure 1 the studied molecules and their molecular frames, chosen so that the Saupe matrices are diagonal, are shown (the BCB, due to its low symmetry, is rotated of about 4° around the z axis).

The geometries adopted for MDCB and ODCB are taken from [15]; the BCB structure has been extrapolated from MDBC by substitution of a Cl atom with a Br atom (assumed C_{ring}-Br bond length = 1,89 Å); the usual vdW radii [16] have been chosen for the atoms forming the molecules. The resulting dimensions of the rectangular boxes representing the solutes are reported in Table 1.

The order parameters $S_{\alpha\beta}$, as resulting from the adoption of the anisotropic potential given in Eq. (1), have been evaluated by numerical



metadichlorobenzene (MDCB) **1,3-bromochlorobenzene (BCB)** **orthodichlorobenzene (ODCB)**

FIGURE 1 Structures and reference systems of solutes.

TABLE 1 Dimensions F of the Boxes Representing the Polar Solutes

F/Å	MDCB	BCB	ODCB
X	7.4	7.4	7.4
Y	8.9	9.1	7.8
Z	3.5	3.7	3.5

integration, by making use of the Metropolis-Monte Carlo scheme [17]. The calculations have been performed on a DIGITAL workstation Alpha-600 (O.S.: Digital Unix V. 4.0) and about 100 min of CPU for each point were required. In Figure 2, calculated (solid lines) and experimental data [11] are shown.

It is evident from the figure that the used approach reproduces the most of solutes orientation: this represents, in our opinion, a further proof of the dominant role of short-range interactions in dictating the solute ordering and a good confirmation of the soundness of our model. Anyway the discrepancies are significantly large when compared to what found for apolar molecules [1, 2]; so they can be used to investigate the presence of other (for instance, dipolar) effects. In principle we assume the discrepancies in the solutes biaxialities $\Delta S_{\mathrm{biax}} = (S_{yy} - S_{xx})^{\mathrm{calc}} - (S_{yy} - S_{xx})^{\mathrm{exp}}$ (henceforth called simply ΔS) as arising mainly from two factors: the inadequacy of the box (Ξ_{box}) to properly describe the asymmetric solutes and the presence in the probe molecules of eccentric dipoles (X_μ), not considered in the utilized anisotropic potential. Following these assumptions and looking at the Figure 2, we can write:

$$[\Delta S_{\mathrm{TOT}}]_{ODCB} = [\Delta S(\Xi_{\mathrm{box}})]_{ODCB} + [\Delta S(X_\mu)]_{ODCB} < 0 \tag{2a}$$

$$[\Delta S_{\mathrm{TOT}}]_{MDCB} = [\Delta S(\Xi_{\mathrm{box}})]_{MDCB} + [\Delta S(X_\mu)]_{MDCB} \sim 0 \tag{2b}$$

$$[\Delta S_{\mathrm{TOT}}]_{BCB} = [\Delta S(\Xi_{\mathrm{box}})]_{BCB} + [\Delta S(X_\mu)]_{BCB} > 0 \tag{2c}$$

Given the magnitude and molecular orientation of dipole moments in BCB and MDCB are in practice the same [18], it is reasonable to assume

$$[\Delta S(X_\mu)]_{BCB} \sim [\Delta S(X_\mu)]_{MDCB} \tag{2d}$$

Finally, from relation (2b), $[\Delta S(X_\mu)]_{MDCB} \sim -[\Delta S(\Xi_{\mathrm{box}})]_{MDCB}$.

At this point, two scenarios are possible:

a) $[\Delta S(X_\mu)]_{BCB} \sim 0$ (no dipolar orientational effects). This implies, from Eq. (2d), that $[\Delta S(X_\mu)]_{MDCB} \sim 0$, but, especially, also $|[\Delta S(\Xi_{\mathrm{box}})]_{MDCB}| \sim 0$ (Eq. (2b)): in this case the inadequacy of the box representing MDCB is (fortuitously?) null, but it is on the contrary considerable for BCB (from

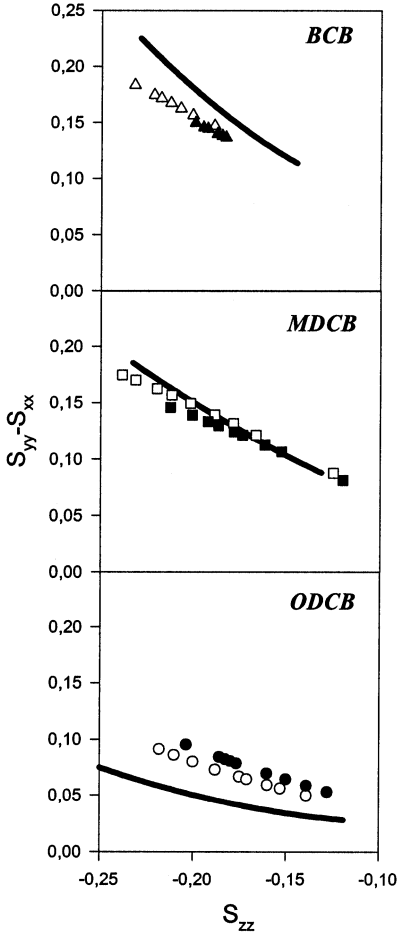


FIGURE 2 Calculated (solid lines) and experimental [11] order parameters for the solutes in M1 (55 wt% ZLI1132+EBBA, open symbols) and in M2 (70 wt% 5CB+EBBA, full symbols); from the top: BCB, MDCB and ODCB.

Eq. (2c), $[\Delta S(\Xi_{\text{box}})]_{BCB} = [\Delta S_{\text{TOT}}]_{BCB}$). Extrapolating the vanishing orientational effects of dipoles to ODCB molecule, we find a $[\Delta S(\Xi_{\text{box}})]_{ODCB}$ quite large in magnitude and of opposite sign respect to BCB. A plausible rationalization of these results is not trivial and out of the aim of this paper: more experiments should be planned and carried out to delineate satisfactory explanations;

b) $|[\Delta S(\Xi_{\text{box}})]_{MDCB}| \neq 0$ (inadequacy of the MDCB box contributes). In this case $[\Delta S(X_\mu)]_{MDCB} \neq 0$ (from Eq. (2b)) and also $[\Delta S(X_\mu)]_{BCB} \neq 0$

(from Eq. (2d)): dipolar effects seem then to be present as an effective orientational mechanism. Adopting this point of view, it is also possible to suggest an interpretation of the complete set of data reported in Figure 2. The dipolar effect (not accounted for by our potential) seems to increase the experimental order parameter corresponding to the direction of the dipole (x for MDCB and BCB, y for ODCB; see Fig. 1). This could explain the different sign of biaxiality discrepancies in BCB and ODCB: in the first case, the experimental value of S_{xx} is underestimated by the calculations (where, as said above, the dipolar effect is not taken into account), so the predicted $(S_{yy}-S_{xx})_{BCB}$ difference results too large (Fig. 2, top); in ODCB, on the contrary, it is the S_{yy} experimental value to be greater than the calculated one (being the dipole oriented along y), so the theoretical $(S_{yy}-S_{xx})_{ODCB}$ is smaller (Fig. 2, bottom). Only in the case of MDCB (Fig. 2, middle) the possible overvalue of orientational biaxiality is exactly compensated by the inadequacy of the box (that, *viceversa*, seems at this point to underestimate the biaxiality) and experimental data are by chance perfectly reproduced by the model.

A choice (or an exclusion) between the two alternatives is in principle impossible at this level, but a development of the model to better describe asymmetric solute-boxes is in progress: this improvement should allow to minimize the term $[\Delta S(\Xi_{box})]$, so getting a better insight about the real responsibility of dipolar effects in influencing the solute ordering.

CONCLUSIONS

The re-analysis of orientational data of three polar molecules in magic mixtures [11] has been carried out by a recently proposed strictly short-range model [1, 2]. Two plausible interpretations of the results have been given, one of these entailing an orientational effect of eccentric dipoles. This possibility cannot therefore be excluded; nevertheless, at this level it is better to avoid to draw firm conclusions. As a matter of fact, it is worthwhile to emphasize that in principle any consideration founded on comparisons between experimental and calculated data is a function of the used theoretical model and the adopted assumptions: in this sense, the calculated results are inevitably vitiated. Only from the convergence of several different cross tests the hypotheses (as the possible orientational action of molecular eccentric dipoles) gain solidity and reliability: in this sense, this study should be considered as a further contribution to the efforts to achieve a deeper understanding of the mechanisms governing the ordering in liquid crystalline mesophases.

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