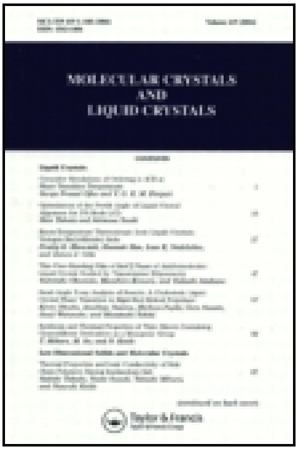

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STUDIES OF ANTIFERROELECTRIC MOLECULAR ORDERING IN A RE-ENTRANT NEMATIC MIXTURE

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Studies of Antiferroelectric Molecular Ordering in a Re-Entrant Nematic Mixture

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Molecular orientational ordering of the 25% mixture of 6OCB in 8OCB is studied by refractometry and quasi-static dielectric permittivity measurements. Temperature and pressure dependence of g-factors is investigated in various mesophases. The compatibility of the observed features with molecular models of re-entrance phenomenon is discussed.

Keywords: refractive indices; dielectric constants; liquid crystals; antiferroelectric

INTRODUCTION

Since the discovery of the re-entrant behaviour several molecular models describing it appeared in the literature. Probably the most clearly and extensively developed are those by Longa and de Jeu[1] (LdJ) and by Indekeu and Berker[2] (IB). In the LdJ model liquid crystal is described as a mixture of monomers and dimers. Both, attractive (dispersion and induction) and repulsive (steric) interactions between them are taken into account. Attractive forces are responsible for the formation of the smectic phase with the smectic layer thickness equal to the length of the dimer. With decreasing temperature or increasing density due to variation of the dimers concentration the packing of the dimers in the smectic layers may become unfavourable and repulsive forces may take over resulting in the re-entrance of the nematic phase. In accordance with experimental observations this model predicts that the re-entrant behaviour is observed for the ratio of the dimmer-to-monomer length equal 1.3-1.4. The smectic layer thickness equals to the length of the dimer and remains constant in the mesophase.

IB model is based on the alternative presentation of the mesophase: only electrostatic molecular interactions and steric hindrance of the molecular permeation along their axes (caused by atomistic structure) are taken into consideration. As the result interaction between the antiparallel dimers becomes almost zero and energetically favourable associations of at least three molecules become important. Spin-gas model of such trimers is built-up and diversity of re-entrance phenomena (including multiple re-entrance of nematic and smectic phases) is demonstrated. In this model the mechanism responsible for the re-entrance phenomena is specific arrangement of molecular trimers due to permeation and libration of the molecules. The smectic layers in this model are composed of interdigitated partial bilayers and the constancy of the smectic layer thickness is predicted by this model.

Although these models explained many features of the re-entrant mesophases (including variation of the smectogenic part of the liquid crystal potential parameters implied, for example, by the model[3]) they remain in the initial state. Numerous non-realistic approximations are used with the only aim to get the final picture. Before starting extensive development of these models the main question should be answered: what is the mechanism driving the re-entrant behaviour? To answer it further experimental investigations, comparison with the predictions of the theories are necessary.

In this work we study molecular ordering in a classic representative of the re-entrant mesogens: mixture 6OCB-8OCB (25 wt.%). We use refractometry and dielectric measurements for this (the order parameters are taken from Raman depolarization measurements) with the main aim to get deeper understanding of the mechanisms responsible for the re-entrance of the nematic phase in this mixture.

EXPERIMENTAL

The refractive indices of the mixture were measured by two methods: by Abbe refractometer IRF-454 (LOMO) and from the transmittance spectra measurements in the Fabri-Perot type cell containing the mixture. The first method is capable of studying only temperature dependence at ambient pressure (the prisms were treated by lecithin to provide measurements of both refractive indices), while Fabri-Perot cell was inserted in the high-pressure autoclave[4] and both temperature and pressure dependences were studied.

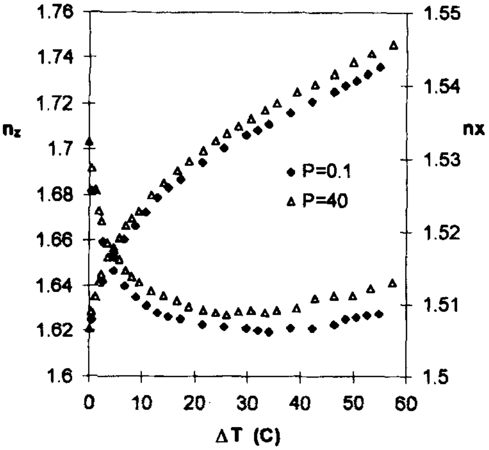

FIGURE 1 Temperature dependence of the refractive indices at two pressure values (shown in the legend) measured by refractometer (filed symbols) and in the Fabri-Perot cell (open symbols).

The inner walls of the cell were covered with the Cr film 15 nm thick to provide sufficient reflection of the light of both polarizations and with AL-3046 (JSR), 75 nm thick, to align the liquid crystal with the pre-tilt lower than 2 degrees. The transmittance spectra were recorded in the spectral interval 400-900 nm by the spectrometer MMS-1 (Zeiss) as a function of temperature at different pressures. The refractive indices of the liquid crystal were deduced from fitting the spectra of the empty cell and that one filled with the liquid crystal by the spectrum computed with taking into account multiple reflections at all interfaces and absorption in the metal layers. The results of the measurements at 589 nm are presented in Figure 1 together with those obtained with the Abbe refractometer. The accuracy of the measurements is ±0.001. Although lecithin is known to produce homeotropic alignment with considerable deviations from 90 degrees, the data obtained with both methods at similar conditions coincide within the experimental uncertainty.

Dielectric constants of the mixture at ambient pressure were measured by impedancemeter BM538 (Tesla) at 1 kHz. Liquid crystal was placed in a glass cell with the inner walls having ITO electrodes. Liquid crystal was either planar or homeotropically aligned by AL-3046, or AL-655 (both of JSR), respectively. The cells with the thickness in the range 3-6 μm were taken and the cell thickness was optically controlled (either birefringence or optical thickness of the cell was determined by transmittance spectrum measurements) during the dielectric data acquisition. The measurements were done with low electric field (<0.2V) and the results were verified by measuring parallel dielectric constant in the cells with planar alignment using measuring electric field sufficiently high (about 10V) to reorient the liquid crystal. The accuracy of the measurements is estimated to be ±5%, although the reproducibility was much better. The results are presented in Figure 2 and are in good agreement with the data available in the literature[5].

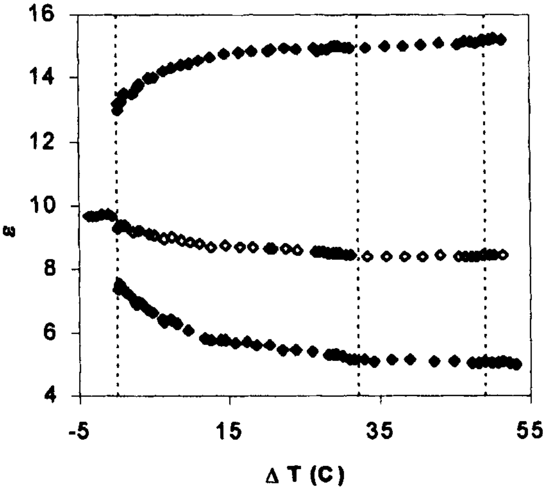

FIGURE 2 Dielectric constants of the mixture 8OCB-6OCB as a function of temperature at ambient pressure. Phase transition temperatures are shown by dashed lines. Average dielectric constant in mesophases is shown by open symbols.

RESULTS AND DISCUSSION

Refractive indices n_i and dielectric susceptibility ε_{ii} of the mesophase are related to the molecular parameters through:

$$n_i^2 - 1 = 4\pi N f_{ii} \langle \alpha_{ii} \rangle \qquad (1)$$

$$\varepsilon_{ii}^2 - 1 = 4\pi N f_{ii} \left[\langle \alpha_{ii} \rangle + \frac{F_{ii}}{kT} \langle \mu_i^{eff} \cdot \mu_i^{eff} \rangle \right] \qquad (2)$$

where N is the molecular number density; kT is Boltzman factor and absolute temperature; F - is the reaction field α and μ^{eff} are molecular polarizability and effective dipole moment.

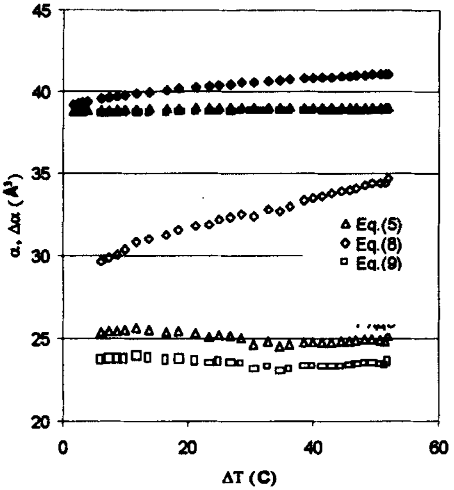

FIGURE 3 Average molecular polarizability $\alpha = 1/3(\langle\alpha_{zz}\rangle + 2\langle\alpha_{xx}\rangle)$ (filled signs) and molecular polarizability anisotropy $\Delta\alpha = (\langle\alpha_{zz}\rangle - \langle\alpha_{xx}\rangle)/\langle P_2 \rangle$ (open signs) obtained from the refractometric measurements (equation (1)) at ambient pressure for the mixture of 8OCB and 6OCB using different approximations for the local field anisotropy (numbers of the relevant equations[6]are shown in the legend). The order parameters are taken from Raman measurements[6], density values are from [12].

Given the order parameters $\langle P_2 \rangle$ and the local field anisotropy are known (in our case they were measured by Raman scattering[6]), one can determine using equation (1) molecular polarizabilities from the refractive indices measurements. One can see from the results of such calculations presented in Figure 3, that if the local field anisotropy is estimated correctly (see discussion[6] where much attention is paid to the validity of the results) not only the average molecular polarizability, but also polarizability anisotropy calculated from refractometry data do not vary with the temperature and the phase state confirming applicability of the molecular ($\langle P_2 \rangle$, α_i) and structural (f_{ii}) parameters obtained in this work and elsewhere[6] for analysis of the dielectric constants of the studied mixture.

Unlike the refractive indices, dielectric constants are not so easily interpreted in the terms of molecular polarizability and dipole moments. Although generalized Lorentz model can be used to treat the local field anisotropy, the cavity field factor may depend on the molecular orientation and this should be taken into account to perform averaging in equation (2). After Maier and Meier considerations[7] of the anisotropic dielectric, where anisotropy of the molecular shape (and hence molecular orientational correlations) was entirely neglected, several attempts of more rigorous treatment appeared. Basing on the same continuum theory of dielectrics, Derzhanski and Petrov[8] introduced anisotropic cavity for the mesogen molecule. Unfortunately, to avoid complications of averaging tensorial products they voluntarily replaced them by averaging permittivities. Therefore the applicability of their final expressions is not clear. Bordevijk[9] used an alternative Kirkwood approach, which enabled explicit account of molecular correlations, but restricted himself to the simplest (unrealistic) cases of zero polarizability anisotropy, or perfect orientational order. Therefore, to analyse dielectric permittivity data we use expressions proposed by Dunmur et al.[10]:

$$\frac{\left(\varepsilon_{\parallel} - n_{\parallel}^{2}\right)\left[\varepsilon_{\parallel} - \left(\varepsilon_{\parallel} - n_{\parallel}^{2}\right)\Omega_{\parallel}\right]}{\varepsilon_{\parallel}\left(n_{\parallel}^{2} - 1\right)^{2}} = \frac{g_{\parallel}\left(1 + 2\langle P_2 \rangle\right)\mu^{2}}{4\pi N\left(3\alpha + 2\Delta\alpha\langle P_2 \rangle\right)^{2} kT} \qquad (3)$$

$$\frac{\left(\varepsilon_{\perp} - n_{\perp}^{2}\right)\left[\varepsilon_{\perp} - \left(\varepsilon_{\perp} - n_{\perp}^{2}\right)\Omega_{\perp}\right]}{\varepsilon_{\perp}\left(n_{\perp}^{2} - 1\right)^{2}} = \frac{g_{\perp}\left(1 - \langle P_2 \rangle\right)\mu^{2}}{4\pi N\left(3\alpha - \Delta\alpha\langle P_2 \rangle\right)^{2} kT} \qquad (4)$$

$$\Omega_{\parallel} = \frac{\varepsilon_{\parallel}}{\varepsilon_{\parallel} - \varepsilon_{\perp}} - \frac{\varepsilon_{\parallel}\varepsilon_{\perp}^{1/2}}{\left(\varepsilon_{\parallel} - \varepsilon_{\perp}\right)^{3/2}} \operatorname{arctg}\left(\frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\varepsilon_{\perp}}\right)^{1/2} \qquad (5)$$

$$\Omega_{\perp} = 2\frac{\varepsilon_{\parallel}\varepsilon_{\perp}^{1/2}}{\left(\varepsilon_{\parallel} - \varepsilon_{\perp}\right)^{3/2}} \operatorname{arctg}\left(\frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{\varepsilon_{\perp}}\right)^{1/2} - \frac{\varepsilon_{\perp}}{2\left(\varepsilon_{\parallel} - \varepsilon_{\perp}\right)} \qquad (6)$$

Their main advantage is that like those derived elsewhere[9] they account for the molecular correlations, but are applicable to the case of partial orientational disorder of anisotropic molecules. On the other hand, the effect of the local field anisotropy on the molecular polarizability contribution (the first term in (2)) is accounted in the same way, i.e. through equation

$$f_{ii} = 1 + L_{ii}\left(n_i^2 - 1\right) \qquad (7)$$

as for the treatment of the refractometric data.

Using equations (3)-(6) we derived from the dielectric permittivity data of Figure 2 correlation factors $g_{\parallel}$ and $g_{\perp}$ (molecular dipole moment was taken to be equal 5.2D, i.e. experimental value for 7OCB[11] determined by Kerr effect in dilute solutions), which are presented in Figure 4. Neglecting all drawbacks of the dielectric theories of anisotropic fluids, essential feature that is seen in Figure 4, is the absence of abrupt changes of the g-factors at the N-SmA and the SmA-N_r phase transitions.

Keeping in mind, that OCB molecules possess longitudinal dipole moment we shall consider only $g_{\parallel}$. The limit $g=0$ corresponds to completely correlated antiferroelectric molecular arrangement (which can be modelled by dimerized system with $\mu=0$) and $g=1$ corresponds to uncorrelated molecules, i.e. monomer system with $\mu=\mu_m$. Unfortunately, direct recalculation of g-factors into the dimers concentration is not possible, because relation between the dimer concentration and g-factor depends strongly on the model: either ferroelectric dimers are taken into account or not (in the IB model, for example, ferroelectric trimers play essential role). Even if to neglect ferroelectric associates the values of $g_{\parallel}$-factor presented in Figure 4 imply antiferroelectric dimers concentration higher than 0.5, i.e.much higher than predicts IB model[2]. On the other hand, in contrast to the estimates made from x-ray data[12] the fraction of monomers is much higher than few per cent. The last mentioned failure can be understood within LdJ model where it was shown that the layer thickness remains almost constant and equals to the length of the dimer in the whole smectic range and can not be used for estimating the position of the monomer-dimer equilibrium. In principle, LdJ model is compatible with the value of the observed g-factors.

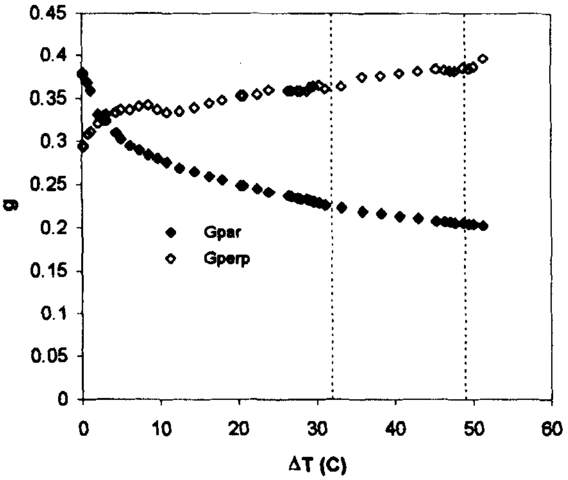

FIGURE 4 Molecular correlation factors derived from dielectric permittivity of the mixture 8OCB-6OCB using equations (3)-(6).

From Figure 4 one can see, that, as it is imposed by the LdJ model[1], concentration of dipoles increases with lowering the temperature and the number of dimers seems to be saturated in SmA phase. But, on the other hand, LdJ model is based on the hypothesis of fast variation of the dimers concentration in the SmA phase. This hypothesis is not supported by the experimental data of Figure 4: variation of g-factors in the nematic phase is more noticeable than in SmA phase. There are no also pre-transitional variations of $g_\parallel$ above the SmA-N_r transition which can destabilize smectic ordering. For the 25% mixture 6OCB - 8OCB the re-entrant smectic phase is not observed at least 30 degrees lower the N-SmA transition temperature. In terms of LdJ model this means that $t_3/t_1<0.9$. To provide this the dimers concentration x_d should vary at least 10% [1], while form Figure 4 one can conclude that in SmA phase it varies less than 5% (in the framework of LdJ model $g_\parallel = (1-x_d)$). In this sense IB model[2] seems to be much more appealing: it is not based on the concept of variation of the dimers concentration and predicts its slow increase for few per cents in the SmA phase. Unfortunately more detailed numerical comparison with these models is not possible. Both these theories use so many approximations, that one can tell only about qualitative comparison and in this sense IB theory better explains observed temperature dependence (or better to tell independence) of g-factors, while LdJ model is compatible with the observed concentrations of the antiparallel dimers.

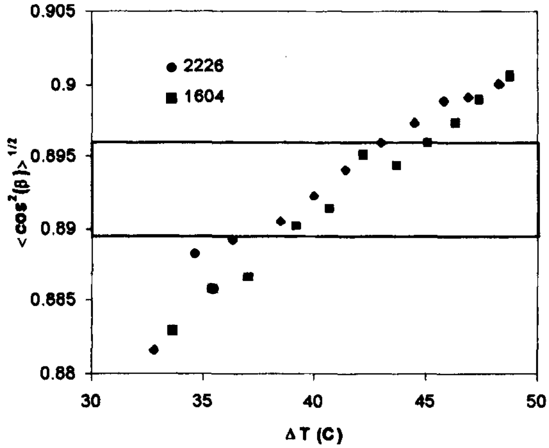

FIGURE 5 Temperature variation of $\langle \cos^2\beta \rangle^{1/2}$ calculated from the $\langle P_2 \rangle$ of two molecular fragments[6], cyano-group (2226) and benzene ring (1604) in the SmA phase. The grey area shows the range of the variation of the layer thickness[5].

Another theoretical prediction, which can be verified in this work is the smectic layer thickness dependence on the orientational order parameter. Experimental data on the layer thickness of the studied system available in the literature[5] evidence that it is practically constant within the temperature range of the SmA phase. IB and LdJ models also predict constancy of the layer thickness, but orientational disorder of the molecules is neglected in the models. On the other hand, keeping in mind variation of the order parameter $\langle P_2 \rangle$ one can expect some its variation, which is illustrated in Figure 5 (experimental points show $\langle \cos^2\beta \rangle^{1/2}$). It is seen, that given the molecular inclination governs the layer thickness, variations of the latter should be more considerable. Therefore one can expect that with the temperature decrease the alkyl tails of the molecules become more and more orientationally disordered in the SmA phase due to increase of the free volume accessible to them. This observation and conclusion are supported by the measurements of the orientational ordering of the alkyl probes in SmA and N_r phases[13]. This effect can play the leading role in the destabilization of the SmA phase and be responsible for the re-entrance phenomenon in the studied mixture.

Acknowledgements

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