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Temperature Dependence of Refractive Indices and Order Parameter of *p-n*-Butoxy- and *p-n*-Amyloxy Benzoic Acids

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The refractive indices in the nematic and isotropic phases have been determined for the p-*n*-butoxy- and p-*n*-amyloxybenzoic acids. The orientational order parameter in the nematic phase has been calculated for both the compounds using Vuks formula. The variation of order parameter with respect to reduced temperature for both these compounds show a considerable difference from the theoretical curve obtained using Maier–Saupe theory.

I INTRODUCTION

There have been detailed studies, both experimental and theoretical on the liquid crystals which do not form dimers.[1,2] However, the case of the liquid crystals which form dimers[3–7] is more complex because of the existence of a thermal equilibrium between dimers and monomers at all temperatures. In such cases, the number of monomers (and dimers) changes with temperature and this effect is superposed on the phase transitions.[8] Therefore, one should expect the temperature dependence of the order parameter to be different from the conventional behavior.[1] It was this expectation which motivated us to study *p-n*-alkoxybenzoic acids. The compounds of this series are known to form dimers[5] and have an additional interest in them because only the dimers exhibit liquid crystalline behaviour while the monomers are not expected to. In this paper we present the refractive index

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data for *p*-*n*-butoxybenzoic acid (BBA) and *p*-*n*-amyloxybenzoic acid (ABA) in the nematic phase. Orientational order parameter has been evaluated as a function of temperature for both the compounds.

II EXPERIMENTAL

Murthy and Shukla[9] have measured the refractive indices of several liquids such as water, chlorobenzene and α-bromonapthalene by the Wedge method and the results were found to be accurate to within 0.001. Using their method, we have measured the refractive indices of the two compounds BBA and ABA. A thin air Wedge with an angle of ~1.5° was formed between the faces of two highly polished plane parallel glass plates. The glass plates were rubbed in the direction parallel to the refracting edge in order that the sample gets aligned when in the nematic phase. The sample in powder form was then introduced at the top of the wedge. The wedge was then kept in a furnace with its front surface normal to the collimated incident beam from a He-Ne laser (λ = 6328 Å). The beam was made to pass very close to the apex of the wedge. The distance d_1 between the positions of the direct transmitted beam and the first reflected beam from both the plates was measured accurately on a screen placed at a distance of about 2.5 meters from the wedge. The sample was then melted and allowed to flow down to the apex

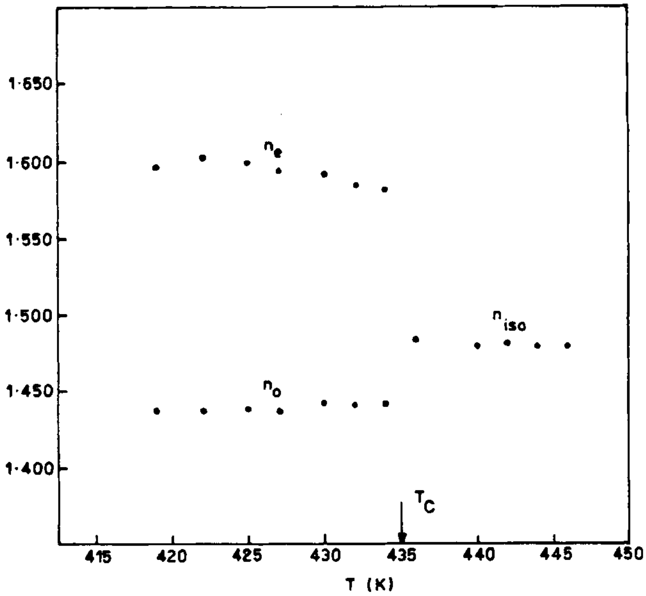

FIGURE 1 Variation of refractive indices with temperature for BBA.

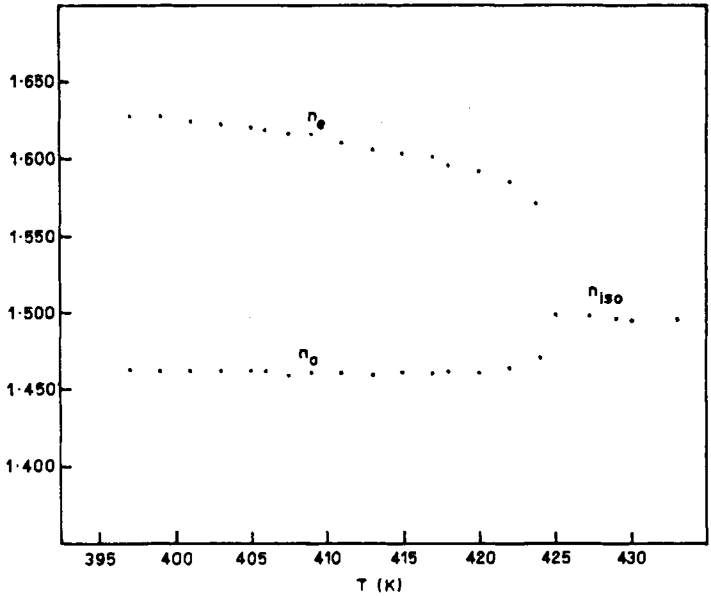

FIGURE 2 Variation of refractive indices with temperature for ABA.

of the wedge, and was then slow-cooled to room-temperature. In the nematic phase, the direct beam gets split into two refracted spots owing to the birefringence. The distance d_2^o and d_2^e of these two spots from the intial direct spots were measured as a function of temperature. The ordinary (n_o) and extraordinary (n_e) refractive indices were then calculated using the formula

$$n_{oe} = \left(1 + \frac{2d_2^{oe}}{d_1}\right) \tag{1}$$

Both the compounds are known to show only one liquid crystalline phase i.e. nematic. Whereas BBA is nematic from 419 K to 435 K, ABA shows nematic behaviour in the range 397 K to 425 K. The temperature variation of the measured ordinary (n_o) and extraordinary (n_e) refractive indices for BBA and ABA is shown in Figure 1 and Figure 2 respectively. The temperature of the sample was controlled to within one degree at all temperatures.

III CALCULATION OF ORDER PARAMETER

The orientational order parameter S is defined as

$$S = \tfrac{3}{2}\langle\cos^2\theta\rangle - \tfrac{1}{2} \tag{2}$$

where θ is the angle made by the long molecular axis with the preferred direction and the brackets denote an average over the molecules in a macroscopic volume. In literature, there are two methods available for evaluating S from refractive index data.[10] First method is based on Vuks formula[11] and the second is due to Neugebauer.[12] In the first method, the order parameter is given by[10]

$$S = \left(\frac{\bar{\alpha}}{\alpha_{\parallel} - \alpha_{\perp}}\right) \cdot \frac{n_e^2 - n_o^2}{\overline{n^2} - 1} \tag{3}$$

where $\overline{n^2} = \frac{1}{3}(n_e^2 + 2n_o^2)$. $\bar{\alpha}$ is the average molecular polarizability, and, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the principal molecular polarizabilities in directions parallel and perpendicular to the optic axis. The scaling factor $[\bar{\alpha}/(\alpha_{\parallel} - \alpha_{\perp})]$ in Eq. (3) can be determined in the following way.

$\mathrm{Log}[(n_e^2 - n_o^2)/(\overline{n^2} - 1)]$ is plotted vs $\log(1 - T/T_c)$. The straight line plot is extrapolated to $T = 0$, and the intercept at $T = 0$ leads to the scaling factor. These plots are shown in Figure 3 and Figure 4 for BBA and ABA, respectively. The values of scaling parameters as obtained were 1.758 for BBA and

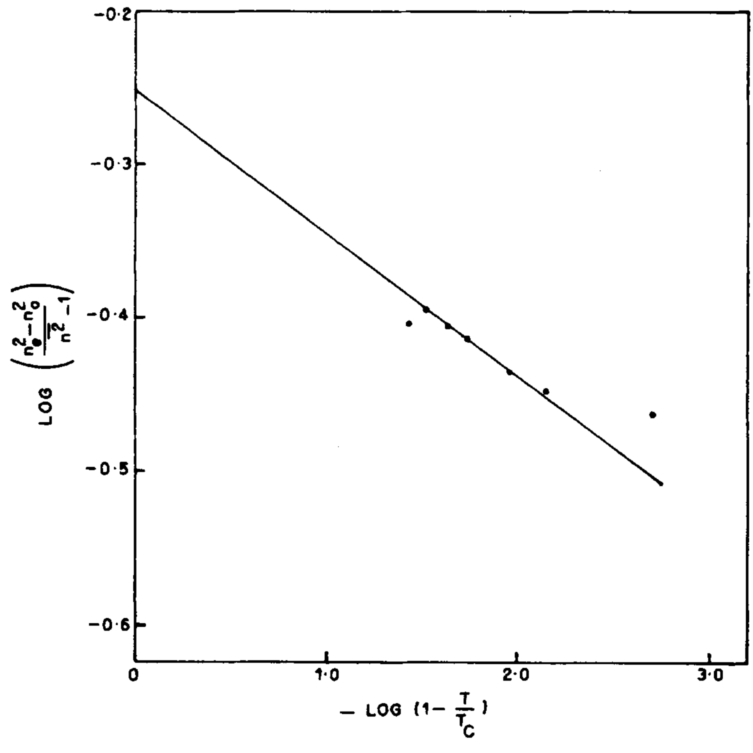

FIGURE 3 Determination of scaling factor for BBA.

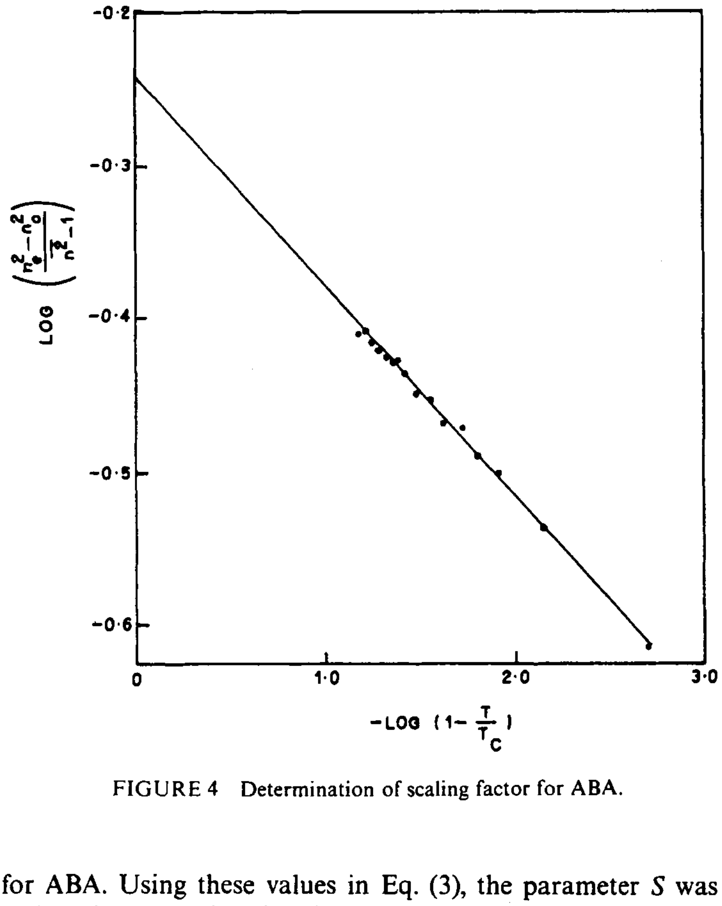

FIGURE 4 Determination of scaling factor for ABA.

1.738 for ABA. Using these values in Eq. (3), the parameter S was calculated and is shown as dots in Figure 5 and Figure 6 for BBA and ABA, respectively. It may be mentioned that in order to get a more practical idea of the scatter in the values of S, we have plotted the values obtained from a number of experimental sets, both in Figure 5 and Figure 6. Also, it is important to note that since the nematic range of BBA extends only from 419 K to 435 K, and as mentioned earlier, the temperature was controlled only to within 1 K, it was not possible to obtain a large number of data points in Figure 3. However, we have repeated our experiment a number of times and the value of scaling factor as obtained from each such run did not differ appreciably.

In the Neugebauer method, the order parameter is given by[10]

$$S = \left(\frac{\bar{\alpha}}{\alpha_{\parallel} - \alpha_{\perp}}\right)\cdot f(B) \tag{4}$$

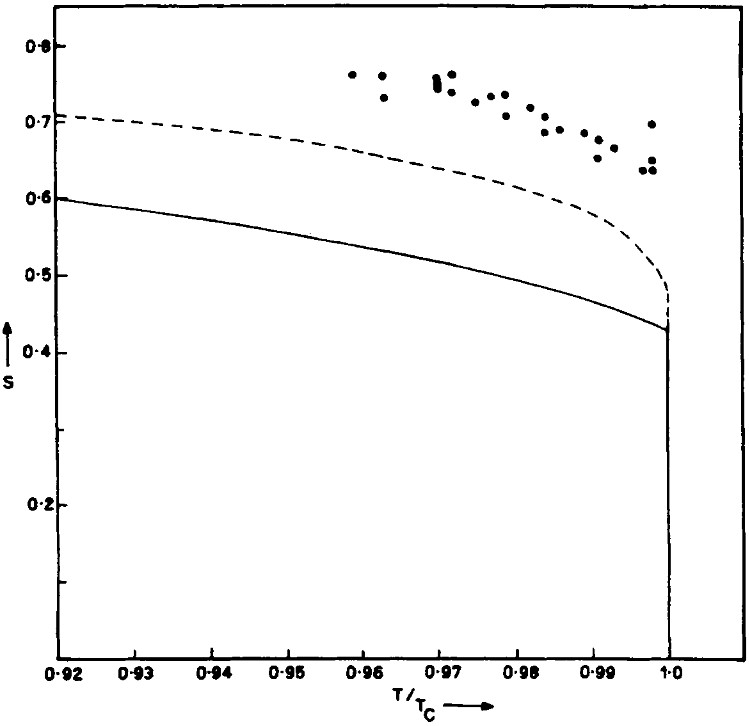

FIGURE 5 Order parameter versus reduced temperature for BBA, from experiment. Continuous curve is obtained from Maier-Saupe theory and broken curve is as obtained from reference (8).

where

$$f(B) = \frac{9}{4B}\left[\left(B^2 - \frac{10B}{3} + 1\right)^{1/2} + \frac{B}{3} - 1\right] \tag{5}$$

and,

$$B = \frac{\overline{n^2} - 1}{\overline{n^2} + 2}\left[\frac{n_e^2 + 2}{n_e^2 - 1} + 2\frac{n_o^2 + 2}{n_o^2 - 1}\right] \tag{6}$$

The scaling factor in this method can be determined by plotting log $f(B)$ vs log$(1 - T/T_c)$. The value of the scaling factor thus obtained was 2.185 and 2.100 for BBA and ABA respectively.

Although the values of scaling factors for each compound as obtained by using the Vuks method and the Neugebauer method differ considerably, it was found that the order-parameter values obtained by using Neugebauer

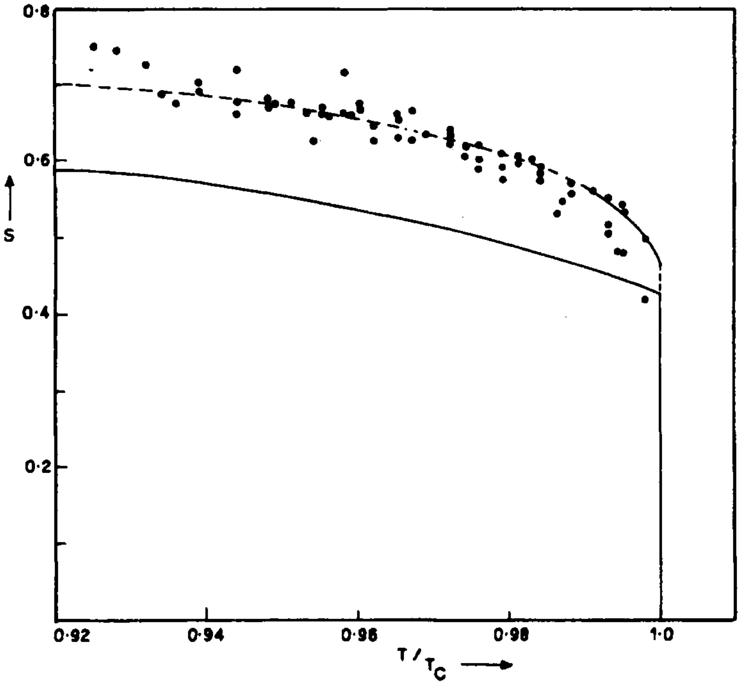

FIGURE 6 Order parameter versus reduced temperature for ABA, from experiment. Continuous curve is obtained from Maier–Saupe theory and broken curve is as obtained from reference (8).

method were only slightly higher (by ~0.005) than those obtained by using Vuks method. Hence, separate curves showing the results obtained by using the former method are not shown in Figure 5 and Figure 6.

IV CONCLUSIONS

From Figure 5 and Figure 6 we notice that the values of order parameter obtained for both the compounds are higher than the theoretically predicted values of Maier–Saupe theory, depicted as continuous curves. We attribute this to the dimer formation and to the existence of a dimer-monomer equilibrium. A theoretical model incorporating such a dimer-monomer equilibrium has recently been proposed by our group,[8] and it does yield higher values for the order parameter. This is also consistent with NMR results on *p*-*n*-heptyloxybenzoic acid,[7] which have been explained by our model.[8] The broken curves in both Figure 5 and Figure 6 depict the values calculated according to this model, using a value of 10 Kcal/mole for the dissociation energy of hydrogen bonds for the entire series of benzoic acids. One could further improve the agreement by adjusting the dissociation energy parameter, although this was not tried. However, we conclude that the hydrogen bond and the resulting dimer–monomer equilibrium plays an important role in these compounds.

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References

1. W. Maier and A. Saupe, *Z. Naturforschq.*, **14a**, 882 (1959); **15a**, 287 (1960).
2. R. L. Humphries, P. G. James, and G. R. Luckhurst, *Symposium of the Faraday Society*, **5**, 107 (1971).
3. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, New York, 1962.
4. I. Chistyakov, *Advances in Liquid Crystals*, Vol. 1 (edited by G. H. Brown), Academic Press, New York, 1975, p. 157.
5. E. F. Carr, *Pramana*, Suppl. No. 1 (edited by S. Chandrasekhar), 1975, p. 263.
6. C. Manohar, V. K. Kelkar, and J. V. Yakhmi, to appear in *Mol. Cryst. Liq. Cryst.*
7. B. Deloche and B. Cabane, *Mol. Cryst. Liq. Cryst.*, **19**, 25 (1972).
8. C. Manohar, V. K. Kelkar, and J. V. Yakhmi, *Mol. Cryst. Liq. Cryst. Lett.* **49**, 99 (1978).
9. M. V. R. K. Murthy and R. P. Shukla, to appear in *Optical Engg.* (1978).
10. R. G. Horn, *J. Phys.*, **39**, 105 (1978).
11. S. Chandrasekhar and N. V. Madhusudana, *J. Phys. Radium*, **30**, C4-24 (1969).
12. H. E. J. Neugebauer, *Can. J. Phys.*, **32**, 1 (1954).