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Temperature Variation of Transverse Correlation Length in the Smectic C and Nematic Phases of a Liquid Crystal from X-Ray and Neutron Diffraction Studies

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The transverse correlation length, ξ, in the nematic and smectic C phases of heptyloxyazoxybenzene (HAB) have been determined from neutron scattering and x-ray diffraction techniques. The experimental intensity values I(q) are fitted using least squares method to a Lorenztian function. The ξ values diverges near the smectic C to nematic transition indicating second order phase transition. The intermolecular distance throughout the mesomorphic range has also been determined.

Keywords: x-ray diffraction; neutron diffraction; correlation length; intermolecular distance

INTRODUCTION

Neutron and x-ray elastic scattering studies are the most direct techniques for studying structures of mesophases. The compound heptyloxyazoxybenzene (HAB), which has a smectic C and a nematic phase, has been extensively studied by different workers[1-7]. Initially A. de Vries had reported the presence of skewed cybotactic nematic phase in this compound[1]. From x-ray diffraction measurements, the orientational order parameters (OOP's) of HAB in the nematic phase were determined by Leadbetter et al[2] and the tilt angles in the smectic C and nematic phases by Chistyakov et al[3]. From x-ray critical scattering Terauchi et al has investigated the nature of the smectic C to

nematic phase transition[4]. In our earlier publication[7] we had reported the density, refractive indices (n_o, n_e), birefringence values and calculated OOP of this compound both in the smectic C and nematic phases from x-ray diffraction and optical studies. In this work, we have studied the transverse correlation length,ξ, throughout the mesomorphic range of this compound both from neutron and x-ray diffraction methods. Intermolecular distance as a function of temperature from x-ray diffraction measurements have also been reported. From the temperature variation of ξ, the nature of the smectic C - nematic phase transition in this compound has been examined.

EXPERIMENTAL

Transition temperatures of this compound were determined using a Mettler FP82 Thermosystem, and they agree with literature values. The measured transition temperature values are the following :

$$\text{Crystal} \underset{}{\overset{74^{\circ}C}{\rightleftharpoons}} \text{Smectic C} \overset{93^{\circ}C}{\rightleftharpoons} \text{Nematic} \overset{124^{\circ}C}{\rightleftharpoons} \text{Isotropic}$$

For neutron scattering experiment, the sample was kept inside a thin walled cylindrical container made of aluminium (size: 15mm length and 7mm diameter). The sample container is fitted with side wings of aluminium sheet which was wound by non-magnetic insulated heating coil. The sample was electrically heated, the temperature being controlled by a temperature controller (Indotherm 401) with a temperature uncertainty of $\pm$ 0.5°C. The neutron scattering experiment was done at Dhruva Reactor of Bhabha Atomic Research Centre, Bombay. The wavelength of the monochromatic incident neutrons was 1.08Å. The scattered neutrons were recorded by using the Profile Analysis Spectrometer (PAS) at TT-1015 at Dhuva[8], which can horizontally scan an angular range of 30° at a time. The resolution of the spectrometer ($\Delta d/d$) is ~ 1%. From the horizontal linear scan of the scattered neutrons recorded by the PAS we obtained diffuse equatorial maximum which is related to the transverse correlation length, ξ, perpendicular to the nematic director. On application of magnetic field the layers in the sample in the smectic C phase oriented normal to the field direction so that the director made an angle (tilt angle) with the magnetic field. Since in the experimental set-up used for neutron scattering, magnetic field could be applied only in the vertical direction, the transverse diffraction peaks shifted from the horizontal direction so that the recorded peak in PAS almost vanished. Hence the experiment was done with no magnetic field and satisfactory peaks in PAS

measurements were obtained.

X-ray diffraction photographs were taken in presence of magnetic field of about 6 Kilogauss, using nickel filtered Cu k_α radiation of wavelength λ = 1.5418 Å. The experimental set-up have been given in the earlier publication of Bhattacharya, Paul and Paul[9]. The x-ray diffraction photographs were scanned both linearly and circularly by an optical densitometer (VEB Carl Zeiss Jena Model 100). Measured optical densities were converted to x-ray intensities with the help of a calibration curve following the procedure of Klug and Alexander[10].

RESULTS AND DISCUSSION

From the angular distribution of neutron scattering from HAB in its mesomorphic phases, using monochromatic neutrons of wavelength 1.08Å, the transverse correlation length, ξ, at various temperatures have been calculated. We have assumed a Lorenztian functional form for the scattered intensity profile with linear background in the vicinity of the peak as

$$I(q) = I_b(q) + \frac{a}{b + (q - q_o)^2} \qquad (1)$$

with $I_b(q) = dq + e$, a background term, and q_o is the magnitude of the scattering vector (q) at the peak position. Here a, b, d, e and q_o are the fitting parameters, adjusted to obtain the best fit. A computer program using Lavenberg - Marquardt method[11] was written for this non-linear least squares fitting, initial values of the parameters being estimated graphically. Convergence was found to be good for all the experimental intensity profiles. The correlation length is defined as $\xi = 2\pi(b)^{-1/2}$. It has been found that the peak q_{max} in the measured distribution shifts to lower q values as the temperature increases. After background correction we have calculated the correlation lengths at various temperatures and it has been found that the ξ values diverges near the smectic C - nematic transition temperature as shown in Fig. 1.

From x-ray diffraction photographs the transverse correlation lengths in both nematic and smectic C phases of this compound have been determined from the linear scan of outer x-ray diffraction peaks along the equatorial direction. The x-ray intensity profile was first corrected for the use of a flat

plate camera following the inverse square law relation. The intensity profile was then corrected for broadening due to the width of the primary x-ray beam using a method of deconvolution based on substitution of successive foldings[12]. As in the case of the scattered neutron profile, the corrected x-ray intensity profile I(q) in the transverse q (wave vector) direction was also fitted to a Lorentzian form but with a quadratic background:

$$I(q) = \frac{a}{b + (q - q_o)^2} + cq^2 + dq + e \qquad (2)$$

where a, b, q_o, c, d and e are adjusted to obtain the best fit using the same

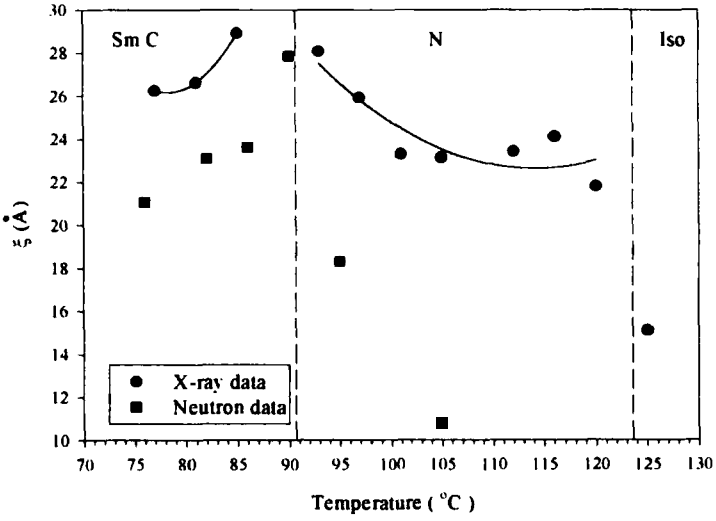

FIGURE 1 Variation of transverse correlation length ξ with temperature of HAB. Solid line is guide to the eye only.

procedure as in the neutron scattering data analysis. The temperature variation of ξ is shown in Fig. 1. It can be seen from this figure that ξ increases near the smectic C - nematic phase transition, as expected for a second order phase

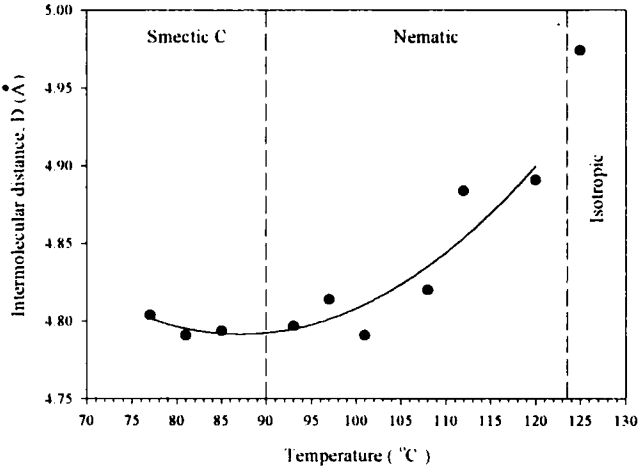

FIGURE 2 Variation of intermolecular distance, D, with temperature of HAB. Solid line is guide to the eye only.

transition. This has been supported by density and refractive index measurements[7]. The temperature uncertainty did not permit us to pursue this trend very close to the transition temperature. The same trend is seen in the ξ values obtained from neutron scattering data. However, the ξ values from x-ray diffraction are somewhat larger than those obtained from neutron scattering. We are unable to account for this difference, however, different methods of data analysis, specially for background correction, employed to calculate ξ from these two techniques may be responsible for this discrepancy. This rapid increase in transverse correlation length in the nematic phase above a smectic C to nematic phase transition has been predicted from theory[13,14] and also been observed experimentally[15] in a liquid crystalline mixture. The smectic correlation lengths are more than 5.4 times the intermolecular distance (D) and is less than 3 times D in the isotropic phase. This behaviour is as expected from previous studies[16].

Variation of the intermolecular distance, D, with temperature is shown in Fig. 2. The intermolecular distance is found to increase quite rapidly near the nematic - isotropic transition as is expected for a first order phase transition. The intermolecular distance changes from ~ 4.80 Å in the smectic phase to ~

4.95 Å in the isotropic phase. These values are typical for molecules having structure similar to HAB.

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