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INFLUENCE OF MOLECULAR ORDERING ON THE PRESSURE BEHAVIOUR OF THE NEMATIC-ISOTROPIC TRANSITION

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Abstract The effect of pressure on the nematic-isotropic transition in mixtures of 6OCB and 8OCB has been studied by DTA. The plot of dT/dp at 1 bar versus molefraction (x) of 6OCB shows an anomalous decrease in the range $0.1 < x < 0.28$. Experiments conducted under different thermal conditions of the sample seem to indicate that this anomalous behaviour is essentially due to the influence of molecular ordering which develops continuously and not due to any kinetic effects.

In an earlier paper(1) we had shown that for mixtures of 4'-n-hexyloxy-4-cyanobiphenyl (6OCB) and 4'-n-octyloxy-4-cyanobiphenyl (8OCB), the dT/dp versus molefraction of 6OCB (x) curve exhibits an anomalous decrease in the molefraction range of $0.1 < x < 0.28$. Considering the fact that the smectic A phase exists (at 1 bar) only until

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*AvH fellow, on leave of absence from the Raman Institute, Bangalore - 560 080, India x = 0.28, it was postulated that this anomaly could be the effect of molecular ordering although this could concievably also be due to kinetic effects. We have carried out some additional experiments under different thermal conditions of the sample, to ascertain the origin of this effect. The results indicate that not kinetic effects but ordering are the influencing factor for this anomalous pressure behaviour.

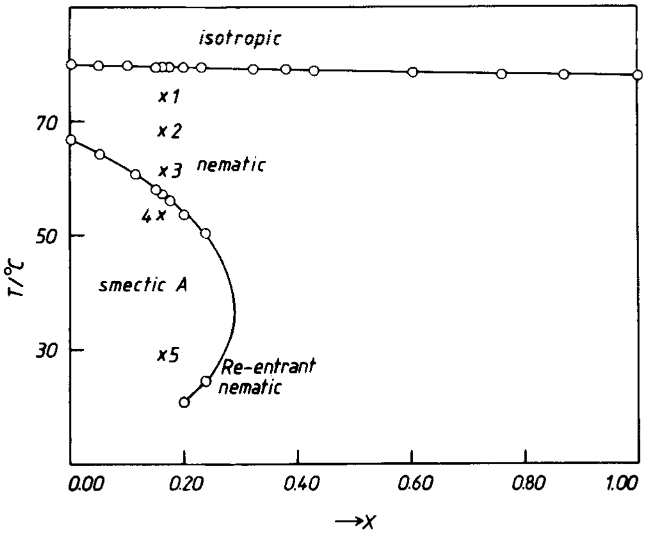

Figure 1: Transition temperatures T at 1 bar in mixtures of 6OCB and 8OCB versus the molefraction x of 6OCB (the starting temperatures of the DTA runs are indicated by x1, x2 etc; see text)

All experiments were carried out using DTA (2) as the probe to detect the nematic-isotropic transition at high pressure. Figure 1 shows the plot of the temperature (T) versus molefraction (x) curve evaluated at 1 bar while Figure 2 gives the dT/dp at 1 bar versus x curve for the nematic-isotropic (N-I) transition. It is clearly seen that although T_{N-I} at 1 bar for the mixtures is a continuously developing function of concentration, dT/dp at 1 bar is not. The dT/dp versus x curve exhibits an anomalous decrease in the range $0.1 < x < 0.28$, the minimum value occuring at $x = 0.162$. This value of x was chosen for carrying out our experiments described in the following.

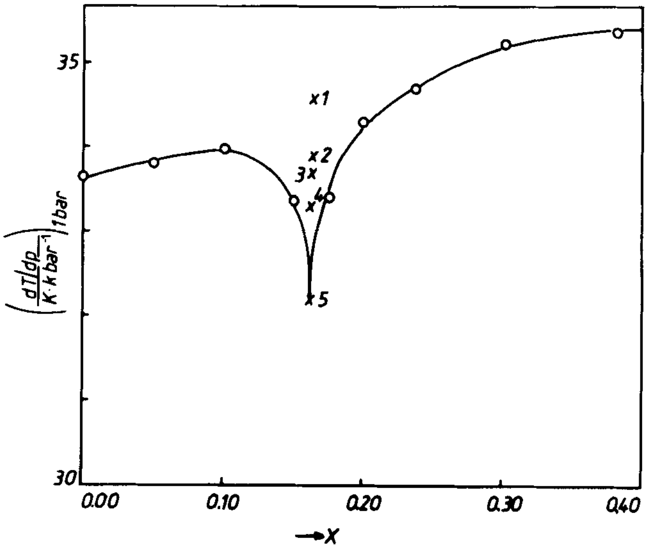

Figure 2: $(dT/dp)_{1bar}$ values for the N-I transition in 6OCB/8OCB mixtures versus molefraction x of 6OCB as obtained from DTA (o = data from reference 1; for explanation of x, see text)

In all, the mixture with $x = 0.162$ was studied under 5 different experimental conditions. The aim of the experiment was to evaluate the p-T boundaries of the N-I transition under different thermal conditions of the sample and then to evaluate, by a computer fit to the set of data points, the dT/dp at 1 bar for each experiment. The parameter that was different in each set of experiment was the temperature to which the sample was cooled with respect to the N-I transition temperature. Within a set of experiments, the substance was always cooled, at any pressure, to a common temperature ($T_R = T_{N-I} - T$) with respect to the N-I phase transition at that pressure and then, it was reheated at about (1 to 2) K/minute and the N-I transition temperature determined accurately. The T_R values in the case of the 5 different sets of experiments were about 5, 13, 19, 27 and 51 K. (Points marked as x1, x2, ..., in Figure 1 indicate the temperatures to which the samples were cooled (at 1 bar) in these sets of experiments). In addition, experiments were also conducted by stabilizing the temperature for about 1.5 to 2 hours at T_R before re-heating the sample into the isotropic phase. However, the transition temperature at any pressure was exactly the <u>same</u> irrespective of whether the temperature of the sample was stabilized or not. The dT/dp values for these 5 sets of experiments, evaluated from a least square fit of each set of data points, are shown in Figure 2. It is seen that the dT/dp values are strongly dependent on the T_R values to which the sample is cooled before re-heating. In fact, lower the T_R value, lower is the dT/dp. Experiments were also conducted for x higher than 0.28 by varying T_R. However, identical transition temperatures and hence dT/dp values were obtained regardless of the T_R value to which the sample was cooled. Therefore, on the basis of these results (especially from the absence of any stabilizing effect of tempering as well as from the fact that the runs starting from 1, 2 or 3 gave different dT/dp values) we tentatively conclude that the anomalous pressure behaviour of the N-I transition is not due to kinetic effects but due to equilibrium properties e.g. to the influence of molecular ordering which develops continuously as a function of temperature.

It may be recalled that Achard et al.(3) have recently shown that the smectic ordering influences the enthalpy change of the N-I transition. Since it is generally accepted that the Clausius-Clapeyron equation should be obeyed for the N-I transition, an anomaly seen in dT/dp might manifest itself in the volume and enthalpy changes at the transition. Detailed thermodynamic experiments are in progress to verify this point.

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