THE NEMATIC-ISOTROPIC TRANSITION AT HIGH PRESSURES I : THE P-V-T EQUATION OF STATE

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THE NEMATIC-ISOTROPIC TRANSITION AT HIGH PRESSURES I : THE P-V-T EQUATION OF STATE

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Résumé. — Nous présentons les résultats de mesures thermodynamiques à haute pression sur trois nématiques et un cholestérique au voisinage de leur point de clarification. Nous étudions tout particulièrement la variation avec la température de la discontinuité de volume, de la compressibilité, et de la densité à la transition. Nous trouvons des corrélations significatives entre les variations de ces paramètres en fonction de la température et le degré de flexibilité des bouts de chaînes dans chaque molécule. Cette tendance est en bon accord avec les résultats de calculs théoriques pour des molécules semi-flexibles. On peut rendre compte de la variation de la densité à la transition en utilisant uniquement des forces répulsives.

Abstract. — We report the results of high pressure thermodynamic measurements on three nematics and one cholesteric in the vicinities of their clearing transitions. We focus in particular on the variation with temperature of the volume discontinuity, compressibility, and transition density. Significant correlations are found between the variations of these parameters with temperature and the degree of end chain flexibility present in each molecule. These trends are shown to be in agreement with the results of theoretical calculations for semiflexible molecules. The variation of the transition density can be accounted for by involving repulsive forces only.

A high pressure capability enables one to utilize both temperature and density as independent experimental variables. In this paper we will show how these probes can be used to quantitatively explore the nature of the intermolecular forces responsible for the nematic ordering and the effects of conformational changes on nematic stability. In a subsequent paper, referred to as II, the results of light scattering studies of the pretransitional behavior at high pressures will be presented.

The liquid crystals studied in these experiments were encapsulated in a brass bellows sealed by a ball and cone arrangement. A miniature slidewire potentiometer attached to one end of the bellows was used to detect expansion or contraction of the liquid. The apparatus consisting of bellows, approximately 4 cm^3 of enclosed liquid, potentiometer, and supporting metal framework was immersed in oil in the interior of a large high pressure bomb having electrical feedthroughs. The potential accuracy of the apparatus was assessed through a trial measure of the density of water over the same range of temperatures and pressures that the liquid crystals would be subjected to. It was found that the handbook values for the density of water were reproduced to within 0.2 % for density variations spanning a range of 10 %. Relative density changes would therefore be expected to be correct to within 2 %.

Altogether four liquid crystals were studied : N-(p-methoxybenzylidene)-p-butylaniline (MBBA), N-(p-cyanobenzylidene)-p-octyloxyaniline (CBOOA), 4,4′-bis (heptyloxy)-azoxybenzene (HAB), and cholesteryl nonanoate (CN). This last compound was included in order to see if a cholesteric would behave any differently from a nematic. Pressure-temperature phase diagrams for all four of these materials had already been obtained [1].

Figure 1 shows one of the isotherms measured for MBBA. By reference to the straight lines drawn as guides to the eye, it may be seen that there is a fundamental asymmetry between the nematic (high pressure) and isotropic (low pressure) sides of the transition. On the nematic side the compressibility is seen to vary over a wide range of densities, presumably

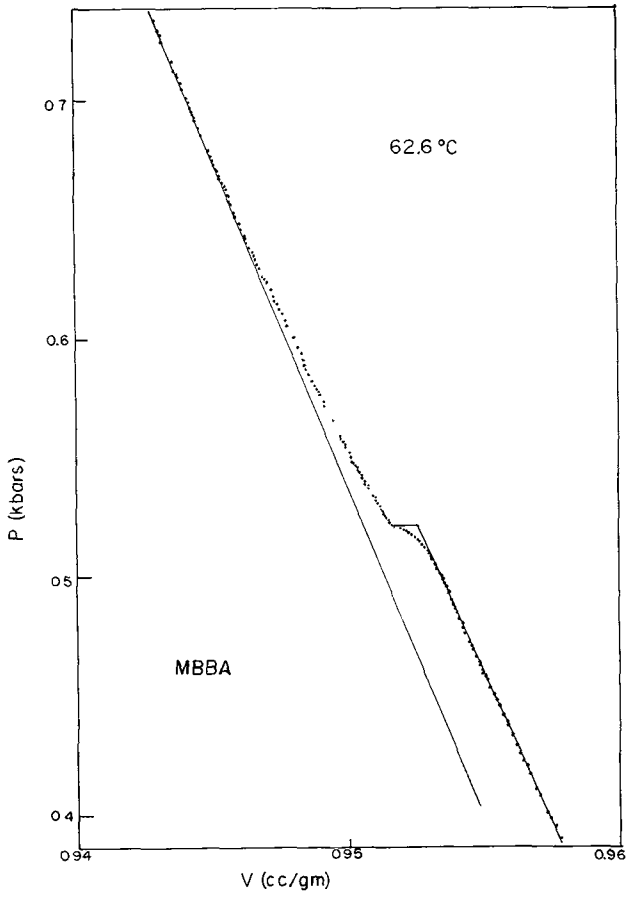

FIG. 1. — The 62.6 °C isotherm for MBBA.

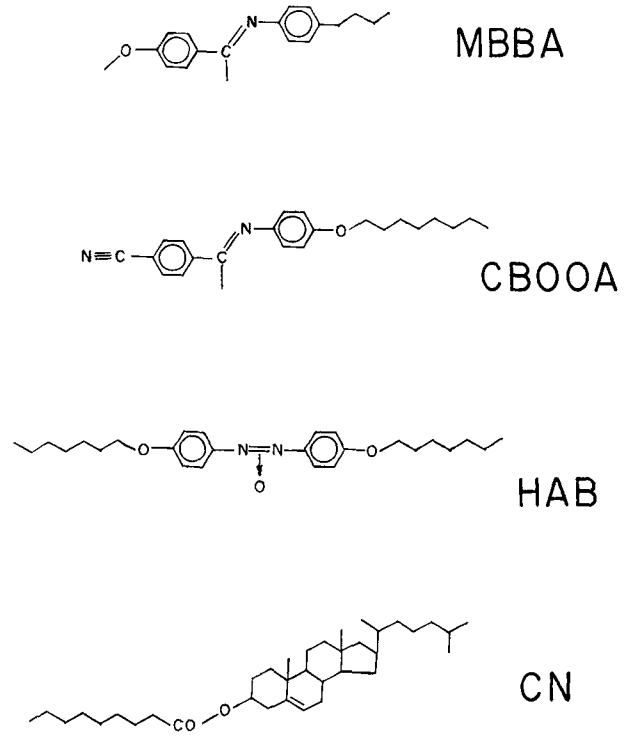

FIG. 2. — The molecular structure of the liquids investigated.

because the order parameter is also changing over this same range. On the isotropic side, however, there is if anything only a small range of densities over which the compressibility exhibits a pretransitional increase, although some of this rounding could be an impurity effect.

The volume change at the transition was taken to be the horizontal segment shown in the figure. Although this method of determing ΔV is somewhat arbitrary, it can at least be done consistently from one isotherm to the next. The relative temperature variation of the volume discontinuity can thus be well established, even though the absolute value of ΔV is somewhat uncertain.

All the isotherms we have obtained are qualitatively similar to that in figure 1 ; they vary only in the quantitative values of ΔV and the compressibility K_T which are found for the different molecules and temperatures. To a large extent these differences can be attributed to the effects of end chain flexibility. In figure 2 we show the three nematics in order of increasing flexibility and also the cholesteric CN which appears to be only slightly less flexible than HAB.

Numerous investigators [2] have discussed the role which flexible end chains play in altering the isotropic-nematic transition. Experimentally these effects are usually observed by studing an homologous series of molecules. In a high pressure experiment one can select one member of a series and study its isotropic-nematic transition under different conditions of density and temperature. This approach yields results

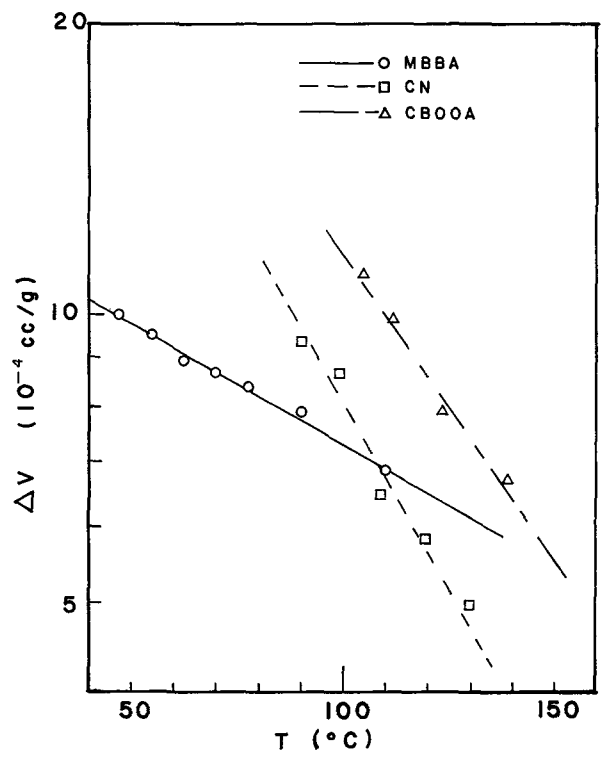

FIG. 3. — The volume discontinuity *vs.* temperature.

which are usually in closer contact with theoretical predictions and circumvents the vagaries which sometimes accompany the jump from one member of an homologous series to another.

An increase in end chain flexibility is expected to decrease the magnitude of the volume discontinuity [2]. The results shown in figure 3 are in accord with these expectations. As temperature is raised the increased flexibility in CN and CBOOA leads to a drop in ΔV which is much more dramatic than is found for the relatively inflexible MBBA. The ΔV for HAB was, unfortunately, too small to resolve. The presence of flexible end chains would also be expected to lead to an increase in the compressibility of the liquid. This trend is evident in figure 4 in which are displayed the compressibilities measured on the isotropic side of the transition. Similar results are found for the nematic side of the transition.

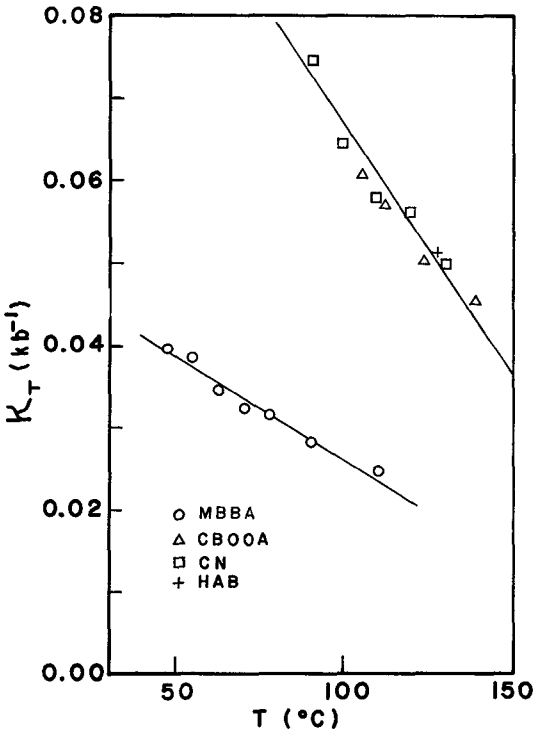

FIG. 4. — The isothermal compressibility of the isotropic phase *vs.* temperature.

The most important parameter measured in these experiments is the rate at which the transition density changes with temperature. Figure 5 displays all the isotherms measured for MBBA. On the scale of this figure the transition appears as a small wrinkle in the PVT surface of the fluid. The position of this wrinkle is seen to vary significantly with temperature. In figure 6 we show a full logarithmic plot of the transition densities for all four liquids, each scaled with respect to the value of its density ρ_0 at atmospheric pressure, *versus* the temperature, also scaled with respect to the atmospheric pressure value T_0. The straight lines show the initial slopes which are 0.61,

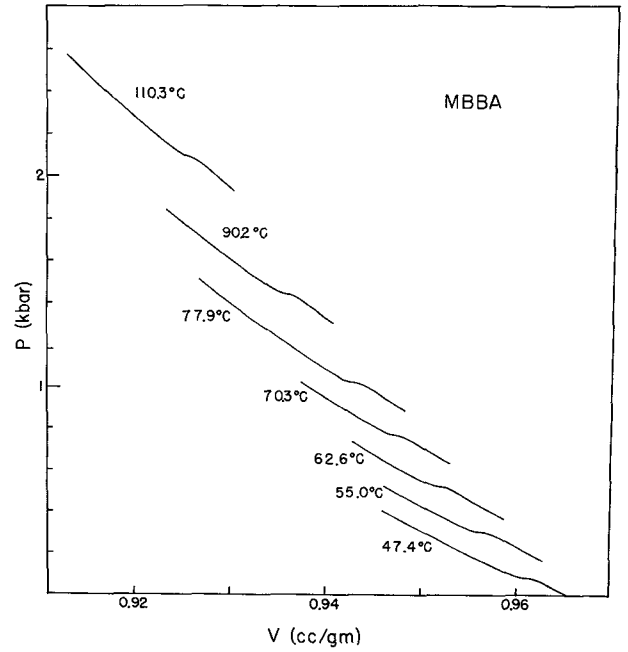

FIG. 5. — The P-V-T equation of state for MBBA near the clearing transition.

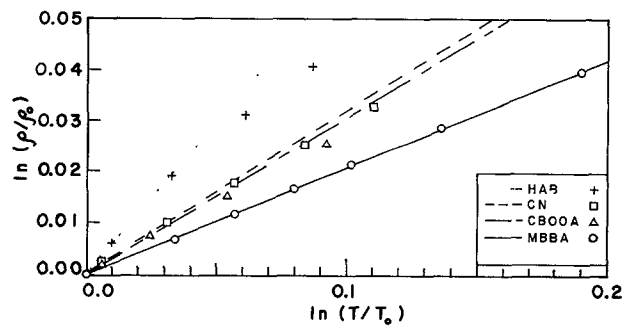

FIG. 6. — The transition density *vs.* temperature.

0.35, 0.31, and 0.21 for HAB, CN, CBOOA, and MBBA, respectively. Clearly the more flexible molecules start out with a more rapid change of density. It is not intuitively obvious that this should be the case, but again theoretical calculations anticipate such behavior. In figure 7 are plotted selected data from the work of Ågren and Martire [2] for a lattice model of impenetrable molecules with rigid central cores and flexible end segments. The parameter u is related to the energy required to bend a segment; its inverse is an effective temperature. In case (*a*) the molecule has one flexible segment on each end; in case (*b*) there are nine on each end. In both cases the rigid central core is ten segments long. Both the transition density and the volume discontinuity show the same trends found in our experimental data.

We believe that the slope of 0.21 found for MBBA in figure 6 represents approximately the limiting value to be expected when the complications of flexibility are removed. Indeed a similar value of 0.25 was found for

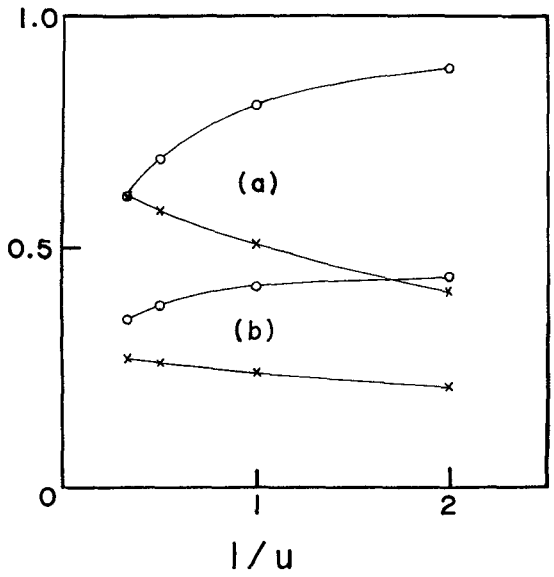

FIG. 7. — Volume discontinuity (×) and nematic transition density (O) *vs.* effective temperature u^{-1} for molecules with (*a*) long, (*b*) short flexible end chains. Data of Agren and Martire (reference [2].)

PAA which has no flexible segments at all [3]. The data for MBBA are replotted in figure 8 and compared to various theoretical predictions. The long-short dashed line has slope of 0.5 which is to be expected from the Maier-Saupe [4] model in which the anisotropic part of the intermolecular potential varies as r^{-6}. The dotted line having zero slope is the behavior which would follow from a hard rod model. A model incorporating both a steric repulsion and an attractive r^{-6} potential [3, 5] could be made to fit the data which

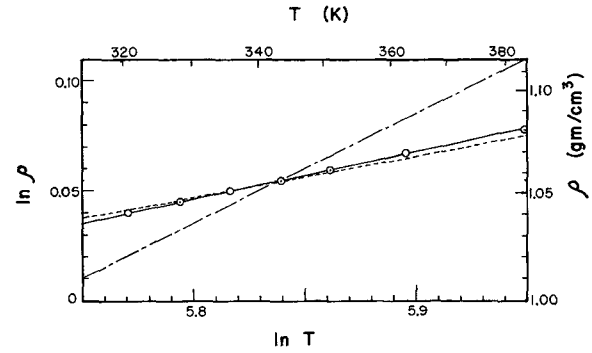

FIG. 8. — Transition density *vs.* temperature. Circles and —, data for MBBA ; . . . . hard rod model ; - ——, Maier-Saupe model ; - - - -, r^{-16} potential.

fall on the straight line between these two extremes. Such a treatment does not, however, put the attractive and repulsive forces on an equal footing. This point has been emphasized previously by Chandrasekhar and Madhusudana [6]. If we take, as is often done, an r^{-12} potential for the repulsive forces between atoms, then the anisotropic part of the potential existing between two quadrapolar shaped molecules built from these atoms will to first order vary as r^{-16}. In this case, the expected variation of the transition density would be as indicated by the dashed line in figure 8. These arguments lead us to conclude that the best experimental evidence indicates that the nematic ordering is almost entirely a result of the repulsive forces.

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References

[1] KEYES, P. H., WESTON, H. T., LIN, W. J., DANIELS, W. B., *J. Chem. Phys.* **63** (1975) 5006.

[2] WULF, A., DE ROCCO, A. G., *J. Chem. Phys.* **55** (1971) 12 ; DE JEU, W. H., VAN DER VEEN, J., GOOSSENS, W. J. A., *Solid State Commun.* **12** (1973) 405 ; MARČELJA, S., *J. Chem. Phys.* **60** (1974) 3599 ; AGREN, G. I., MARTIRE, D. E. **61** *ibid.* (1974) 3599 ; PINK, D. A., *ibid.* **63** (1975) 2533.

[3] MCCOLL, J. R., SHIH, C. S., *Phys. Rev. Lett.* **29** (1972) 85.

[4] MAIER, W., SAUPE, A., *Z. Naturforsch.* **14a** (1959) 882 and **15a** (1960) 287.

[5] DELOCHE, B., CABANE, B., JEROME, D., *Mol. Cryst. Liq. Cryst.* **15** (1971) 197.

[6] CHANDRASEKHAR, S., MADHUSUDANA, N. V., *Mol. Cryst. Liq. Cryst.* **24** (1973) 179.