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THE EFFECT OF INTRA AND INTER POTENTIAL FOR ISOTROPIC TO NEMATIC PHASE TRANSITION: A PRESSURE–VOLUME–TEMPERATURE MEASUREMENT STUDY

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ABSTRACT

A pressure–volume–temperature relation of 4-fluorophenyl *trans*-4′-heptylcyclohexanecarboxylate (7CCF) was studied. The volume of the phase transition point decreased with increasing temperature. The $-\mathrm{d}\ln T_c/\mathrm{d}\ln V_c$ value obtained was 2.98. This value, which includes information on the inverse power exponent of the potential function, was lower than those from 7CB or 7PCH, showing that the molecular softness effect of 7CCF arises from an intra-potential at phase transition larger than that of 7CB or 7PCH.

INTRODUCTION

The theory of nematics has been discussed by many authors [1–8]. However, the potentials postulated in these hypotheses differ. Previously, we have pointed out that these potentials should involve a molecular structural-dependent inner potential effect [11]. The character of this effect is not understood precisely. We have predicted also that the molecular structure in the rigid portion of nematogenic substances influences the transition equation. Tranfield and Collings [13] observed that in a pressure study of an alkoxyazoxyanisole homologous series the values of $V/T(\mathrm{d}T/\mathrm{d}V)$ at constant order decrease with increasing alkoxy carbon number. These results agree with our pressure–volume measurements near the transition points for the alkylcyanobiphenyl homologous series.

We have reported the effect of molecular rigidity on the transition equation (molecular rigidity in the rigid part of liquid crystal molecules containing a carboxyl group, cyclohexyl ring, or aniline group etc.). The cyclohexyl ring in the rigid part of nematogenic substances affects the way in which the volume of transition decreases more rapidly with increasing temperature under pressure. The carboxyl group which is a constituent of

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the rigid part of nematogenic substances will also play a role similar to the alkyl chain in the transition equation of nematic to isotropic phase transition. Previously, we have studied pressure–volume–temperature relations and transition properties for two alkylcyanophenylcyclohexane homologues [10,11]. In these studies, the cyclohexyl group plays a similar role in the transition equation to that of an alkyl chain. A softness effect will be expected on the carboxyl group in the rigid part of nematogenic substances. In this paper, we report $P-V-T$ relations and molecular rigidity effects of phase transition for 4-fluorophenyl *trans*-4′-heptylcyclohexanecarboxylate (7CCF).

EXPERIMENTAL

7CCF of electro-display grade (Chisso Co., Ltd) was used without further purification and its density was measured by a Lipkin–Devison type pyknometer. $P-V-T$ relations were measured with a piston-cylinder apparatus. Pressure variation was detected by a manganin pressure gauge mounted in the cylinder. The degree of compression of the sample was estimated by a differential transformer attached to one end of a piston. Both the analog output of the differential transformer and that of the manganin pressure gauge were fed to a microcomputer after appropriate amplification and digital conversion. The microcomputer also controlled an oil pressurizing pump to compress the sample at a predetermined sequence by monitoring these signals. The volume of the cylinder was about 10 cm^3. The error of measurement of pressures and volumes was within ±0.03 MPa and ±0.002%, respectively. The piston-cylinder apparatus was maintained in an air bath thermocontrolled to within ±0.01 K.

RESULTS AND DISCUSSION

Figure 1 shows a density vs. temperature curve for 7CCF near the transition point at atmospheric pressure. The clear point was found to be 306.35 K. The volume change which accompanied the phase transition was found to be 0.16%. This value was smaller than those from other nematogenic compounds (for example alkylcyanobiphenyl homologues (0.2%)). Figure 2 shows $P-V$ isotherms for 7CCF near the phase transition point from isotropic to nematic. A pressure plateau which occurs at phase transition was observed. Previously we showed that the molar volume which initiated the transition decreased with temperature and pressure [9,10]. In the case of 7CCF, as in other nematogenic compounds observed in our $P-V$ experiments, the volume at which the phase transition occurs decreased with increasing temperature. Figure 3 shows a log–log plot of the transition temperature vs. transition molar volume. The curve gave a linear relation

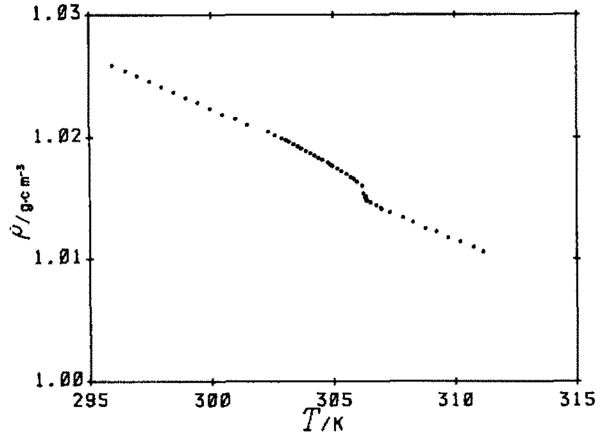


Fig. 1. Density as a function of temperature for 7CCF.

which had a slope (d ln T_c/d ln V_c) of −2.98. This relation predicts a simple formula $T_c \propto V_c^{-\gamma}$.

The theories of nematogenic phase give a transition equation which is a function of transition temperature and transition molar volume. Since the transition equation is a thermal energy-potential competitive relation, transition temperature reflects potential function. Transition temperature involves an intermolecular potential function with a function of intermolecular separation. The molar volume at transition point is dependent upon transi-

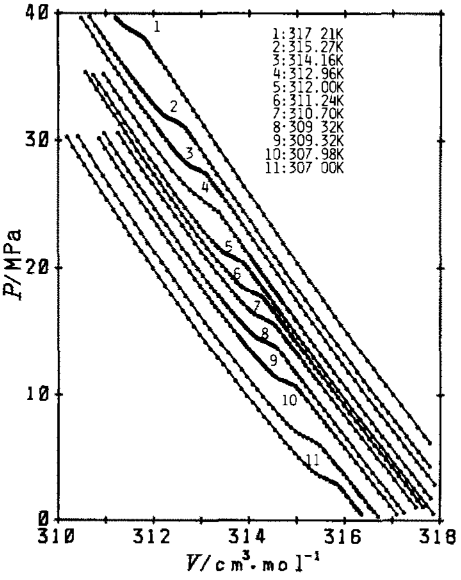


Fig. 2. Pressure–volume isotherms for 7CCF (11 typical isotherms of 22 runs).

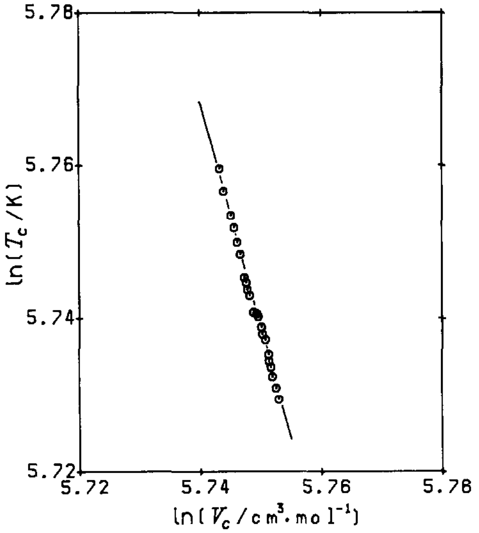


Fig. 3. Log–log plots of the molar volume at the transition points and transition temperature for 7CCF.

tion temperature and therefore there is a relation between volume and intermolecular potential. Table 1 shows the transition equation and intermolecular potential from some theories and calculated and experimental d ln T_c/d ln V_c values. The theory of Maier and Saupe gives a d ln T_c/d ln V_c value of −2 [3]. The theory of Pople and Karasz gives a d ln T_c/d ln V_c value of −4 [2]. These two theories give a constant d ln T_c/d ln V_c value regardless of molecular structure changes. To evaluate the molecular shape of the volume dependence of intermolecular potential, it is necessary to specify the effect of molecular length or molecular conformation. Previously, we have predicted that alkyl chains in the flexible parts of nematogenic molecules had an important role in the relation of phase transition volume and temperature, and that these relations did not coincide with the three main theories. For further clarification, characterization of the flexible chain

TABLE 1

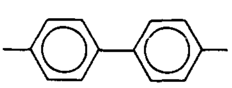
Calculated and observed value of −d ln T_c/d ln V_c [c]

	7CCF [a]	7CB [b]	7OAB [c]	7PCH [d]
Experimental	2.98	5.15	2.07	3.32
Maier et al.	2	2	2	2
Pople et al.	4	4	4	4

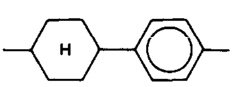
[a] Present study.
[b] Shirakawa et al. [9].
[c] Johnson and Collings [14].
[d] Shirakawa et al., in preparation.

of a flexible functional group in a nematogenic substance was studied. Mesogenic compounds are made up of two portions, a rigid core and a flexible chain. The 7CCF molecule has a carboxylic functional group and a cyclohexyl group in the rigid core. The carboxylic group is more flexible than the benzene ring. Therefore the rigid core group in 7CCF is more flexible than that of 7CB in alkylcyanobiphenyl homologues. In the case of alkylcyanophenylcyclohexane (RPCH) there is also a flexible entity in the rigid core group so that d ln T_c/d ln V_c is smaller than that of RCB homologues. Comparing these three d ln T_c/d ln V_c values with those of RCB, RPCH and RCCF at a constant alkyl chain number ($R = 7$), values are in the order 7CB, 7PCH, and 7CCF. The order of stiffness of rigid parts of these three compounds will be determined by the number of flexible bonds within them. The value of d ln T_c/d ln V_c decreases with increasing number of flexible functional groups. This may be an effect of stiffening of the flexible bonds from nematic to isotropic transition. In the case of alkylcyanobiphenyl homologues, the value d ln T_c/d ln V_c also decreased with increasing alkyl chain length. These results may be interpreted by a variation of the bond angle or/and bond length of the molecules. The molecular bond angles and bond length change with pressure. Therefore molecular interactions of these molecules do not increase with volume changes on pressure. The molecular interaction reaches thermal energy and phase transition occurs. As pressure is raised from atmospheric, the volume decreases. With rising pressure, the intramolecular and intermolecular potentials rise along the potential function curves. When the potential is larger than the thermal energy, isotropic to nematic phase transition occurs. The separation change due to inter- and intra-molecular strain with pressure may depend on the forms of potential functions. If the nematic to isotropic phase transition is dependent only upon the intensity of the intermolecular potential, the change in intermolecular separation in the total volume change is very important to the phase transition. The intramolecular potential has a buffering effect in phase transition under pressure i.e. the volume changes owing to intramolecular potential cushion elevation of intermolecular potential. Because of the cushion effect, the slope of the apparent intermolecular potential curve is lower than that of the intrinsic intermolecular potential curve. The phase transition of nematic liquid crystals takes place as follows. When the temperature reaches a potential barrier, the liquid crystal-forming molecule rotates in an axial plane. The rotation of the molecule prevents the potential barrier involving two potentials, intermolecular and intramolecular potential. The intramolecular potential is caused by molecular stiffness

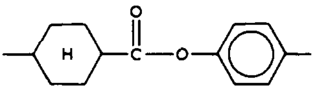
7CB



7PCH



7CCF



which resists deformation of the molecular form. The stiffness may originate from stretching or bending of molecular bonds. The buffering effect on potential rise in the isotropic to nematic phase transition may be caused by a volume change with bond angle or bond length change in molecules.

We conclude that carboxyl functional groups between the two rings of 7CCF play a role in softening potential and the origin of this buffering effect may be due to bond angle change and bond length change of the carboxyl group.

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