PRESSURE-VOLUME-TEMPERATURE RELATIONS IN THE LIQUID CRYSTAL
OF p-PENTOXYBENZILIDENE-p-n-BUTYLANILINE

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Pressure-volume-temperature relationships were determined using
the piston-cylinder methods for a liquid crystal, p-pentoxybenzilidene
-p-n-butylaniline. For the nematic state, the intermolecular potential
was found to be dependent on 3.6 powers of the density.

Many investigators have discussed on molecular interactions in isotropic liquid
states from the thermodynamic considerations of pressure(P)-volume(V)-temperature(T)
relationships.[1] In the case of liquid crystal-
line states, little has yet been known even about
such relationships. In the present study, the
molecular interactions in the nematic liquid
crystalline state of p-pentoxybenzilidene-p-n-
butylaniline (PBBA) are discussed from P-V-T
relationships.

Figure 1 shows the apparatus used for com-
pression measurements. The sample weighing about
3.5g[A] sealed in the cylinder[B] was compressed
by the piston[C] with the aid of the manual pres-
sure-generator[D]. The pressure was determined by
measuring the change in the electric resistance
of the manganin wire[E]. For calibration, the
liquid-solid phase transition point of benzene
(298.5K, 69.3MPa)[2] was adopted as a standard
one. The precision of pressure measurements was
within ±0.45% through the range from 0.1 to 100
MPa. The volume decrease of the sample was meas-
ured from the displacement of the piston using
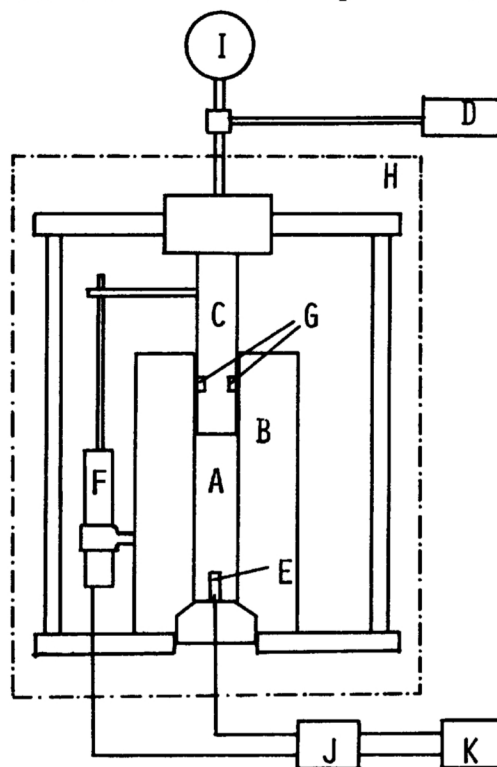a differential transformer[F]. The apparent

Figure 1. A schematic diagram of
the apparatus.

A:sample, B:cylinder, C:piston,
D:manual pressure-generator,
E:manganin wire, F:differential
transformer, G:Viton-gasket,
H:air bath, I:Bourdon's tube,
J:electric bridge, K:recorder.

volume change caused by the shrinkage of the Viton-gasket[G] was corrected using ethyleneglycol as a standard material for the compression measurements. The precision of the volume change measurements was within ±0.3%. The apparatus was thermostated (±0.02K) in an air bath[H]. The material, PBBA,

$$C_5H_{11}O\text{-}\langle O \rangle\text{-}CH=N\text{-}\langle O \rangle\text{-}C_4H_9 \text{ ,}$$
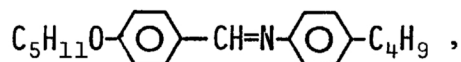
was obtained from Fuji Color, Co. Ltd. and was purified by vacuum distillation. The nematic state was found employing a differential scanning calorimetry in the temperature range from 325.65 to 342.65K.
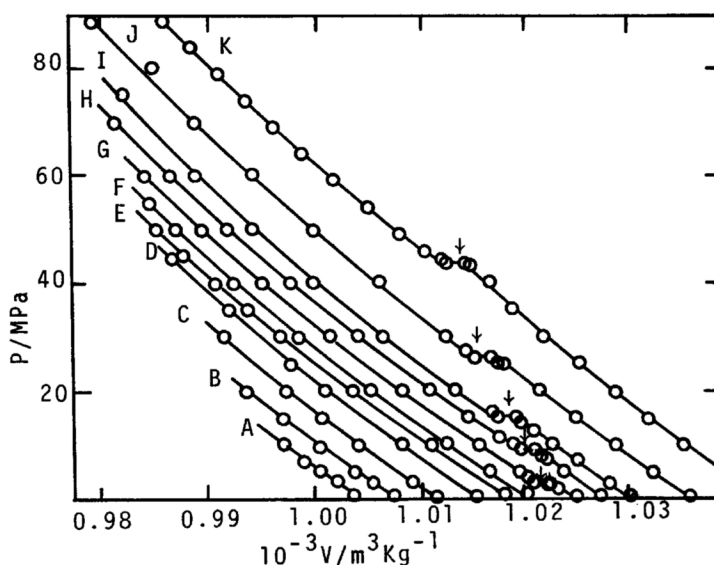

Figure 2. Pressure-volume isotherms.
A:330.45K, B:333.35K, C:335.85K, D:338.95K,
E:340.75K, F:342.55K, G:343.55K, H:345.55K,
I:347.35K, J:347.35K, K:356.45K, ↓:Isotropic
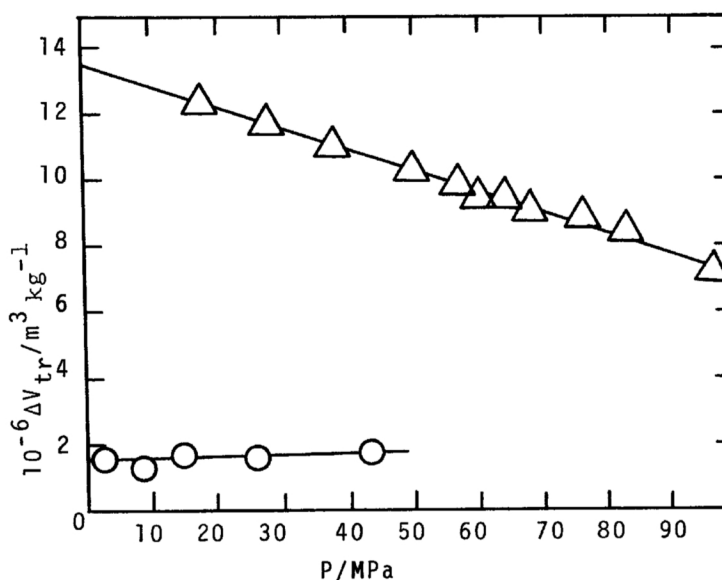liquid-nematic phase transition points.

It was observed that P-V isotherms had two plateaus which were corresponding to liquid-nematic (L-N) and nematic-solid (N-S) phase transitions. Figure 2 shows the isotherms near the L-N transition points. Figure 3 shows the relationships between the volume changes due to the phase transitions (ΔV_{tr}) and the phase transition pressures (P_{tr}) which can be estimated from the widths and the heights of the plateaus in the P-V isotherms. Figure 4 shows the relationships between the phase transition pressures P_{tr} and the phase transition temperatures (T_{tr}), for both phase transitions. Both P_{tr}-T_{tr} relationships were found to be

Figure 3. The volume changes due to phase transitions ΔV_{tr} plotted against the pressures.

△:Nematic-solid phase transitions,
○:Isotropic liquid-nematic phase transitions.

linear and their slopes(dP_{tr}/dT_{tr}) were calculated to be 3.125 and 3.594 MPa K^{-1} for

L-N and N-S, respectively. The transition entropy (ΔS_{tr}) was calculated using the

Clausius-Clapeyron equation 1,

$$\frac{dP_{tr}}{dT_{tr}} = \frac{\Delta S_{tr}}{\Delta V_{tr}} \quad \text{------(1).}$$

Figure 5 shows the relationships
between the transition entropy
ΔS_{tr} thus obtained for both phase
transitions and the pressure.
The transition entropies under
the atmospheric pressure were cal-
culated to be 15.9 and 1.3 J K^{-1}
mol^{-1} for N-S and L-N phase tran-
sitions respectively, and their
magnitudes were slightly smaller
than those which had been deter-
mined using a differential scan-
ning calorimetry(18.1, 1.8 J K^{-1}
mol^{-1}). In the isotropic liquid
and nematic phase transition L-N,
a linear relationships was found
between log T_{tr} and log V_{tr}^i where
V_{tr}^i denoted the volume of the
liquid phase at the transition
points. Therefore, the melting
equation 2 of Hiwatari and Matsuda,[3)]

$$V_{tr}^i = V^* (\frac{C}{kT_{tr}})^{3/n} \quad \text{------ (2),}$$

where V^* and C denote a reduced
volume and an energy constant,
and n is the exponent of the
inverse powers of intermolecular
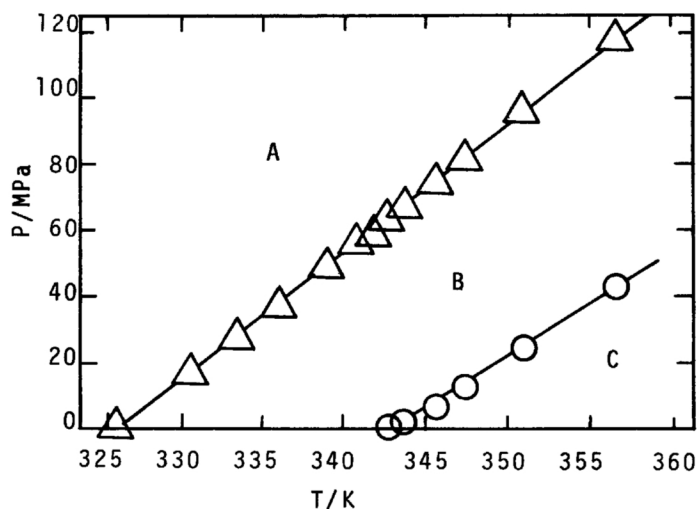distances,can be applied to the

Figure 4. The phase diagrams of the liquid
crystalline PBBA.

A:Solid phase, B:Nematic phase, C:Isotropic
liquid phase, △:Nematic-solid transition
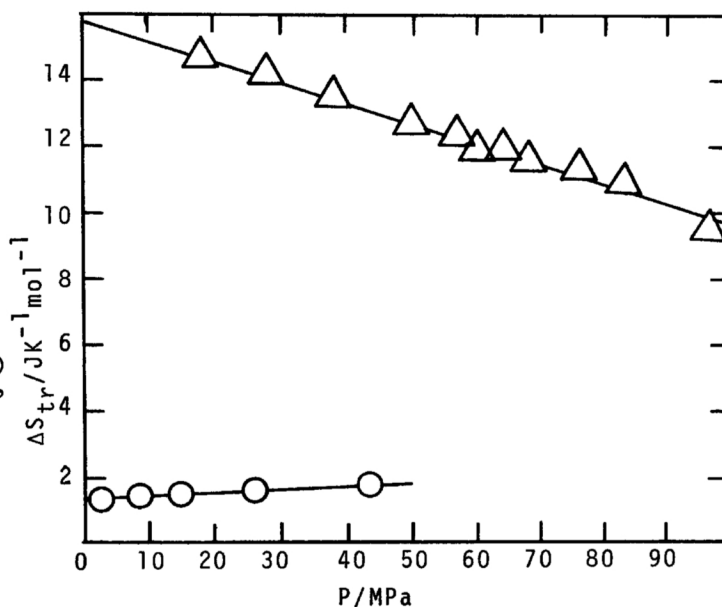points, ○:Isotropic liquid-nematic transi-
tion points.

Figure 5. The transition entropy ΔS_{tr} plotted
against the pressure.
△:Nematic-solid phase transitions,
○:Isotropic liquid-nematic phase transitions.

L-N transition. According to equation 2, n was found to be 10.8, therefore the repulsive potential energy Φ in the nematic state of PBBA is expressed by $\Phi \propto 1/r^{10.8}$ or $\Phi \propto \rho^{3.6}$. For the nematic state of p-azoxyanisole, Mccoll reported that the potential was proportional to $\rho^{3.7}$ [4].

References

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4) J. R. Mccoll; Physics Letters, 38A 55 (1972).