BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2429—2434 (1970)

Physical Chemistry of Binary Plastic Crystals. II. Dielectric Constant of the System, Carbon Tetrachloride and *t*-Butyl Chloride

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(Received March 19, 1970)

Careful measurements of the dielectric constant of a binary system of *t*-butyl chloride and carbon tetrachloride were made in the entire composition range and in three different phases, the liquid, the fcc solid, and the rhombohedral phases. The simple Debye theory applies to the liquid and the fcc solid, giving an effective dipole moment of *t*-butyl chloride of 2.11±0.01 D whereas in the rhombohedral phase, it was 2.00±0.03 D. Molecular polarization shows no discontinuity between the vapor, the liquid, and the fcc solid but there is a jump between the fcc and the rhombohedral solids. The molecular rotation in the plastic rhombohedral phase is more hindered by 450 cal/mol than in the liquid or the fcc phase. The 1 : 1 solid solution data were examined on the basis of the Onsager theory.

In the previous paper,[1] a dielectric and NMR study of *t*-butyl iodide dissolved in carbon tetrachloride in liquid and solid states was reported. It was then found that the solid solution formed a plastic crystal in which molecules not only reorient themselves but diffuse through the lattice with an

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[1] H. Chihara, M. Otsuru and S. Seki, This Bulletin, **39**, 2145 (1966).

activation energy of 6.8 kcal/mol. The solid solution was dealt with by the theory of regular solutions. The stable solid phase I immediately below the melting point was then believed to be of the fcc structure, but as Post reported later[2] it was rhombohedral phase. The fcc phase of carbon tetrachloride and its solid solution does exist, however, as a metastable phase as our reexamination of the phase relations has shown.[3] The question now arises if there is any difference in the state of molecular motion in the two plastic phases, fcc and rhombohedral. The difference between the liquid and the solid phases, if any, is also of great interest in view of elucidating the nature of plastic crystals.

t-Butyl chloride forms two plastic solid solutions with carbon tetrachloride, having different structures, fcc and rhombohedral. The fcc phase becomes metastable where the concentration of *t*-butyl chloride is low. This binary system has been investigated by the dielectric[4] and the NMR[5] methods but the studies emphasized the similarity of the motional behavior between the liquid and the plastic phases. The present paper describes a careful dielectric measurements on the binary system in an attempt to learn about the motion of solute molecules in different matrix structures of carbon tetrachloride.

Experimental

Materials. Commercial special grade carbon tetrachloride and *t*-butyl chloride were distilled after drying over calcium chloride; carbon tetrachloride bp 76.7—76.8°C, n_D^{20} 1.45986, *t*-butyl chloride, bp 50.5—50.8°C, n_D^{20} 1.38550, literature values are as follows: *t*-butyl chloride bp 50.5,[6] 51.0°C,[7] n_D^{20} 1.38470,[8] 1.38786.[7]

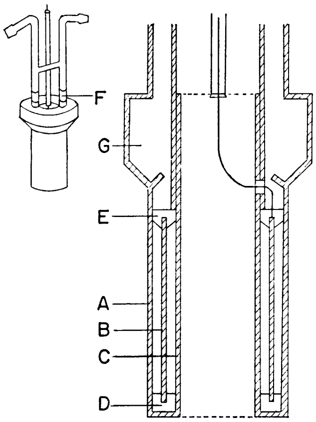

Fig. 1. The dielectric cell.

Equipments. The apparatus of the differential thermal analysis (DTA) is the same as the one reported earlier.[9]

The dielectric constant was measured by the heterodyne-beat method at the frequency of 1 MHz.

Two sample cells were used. One was the glass cell as described previously,[1] which often broke where the electrode leads were fused when the sample solution was remelted. A new cell, shown in Fig. 1 consists of three coaxial cylinders of nickel-plated copper A, B, and C that served as the electrodes: B is insulated from the cylinders A and C by the Teflon spacers D and F. To secure uniform temperature in the specimen, thermal conduction from the outside was reduced to a minimum by using thin-walled stainless steel pipes F through which the solution was charged or discharged. G is the space to allow for the thermal expansion of the specimen through the cutting of the spacer E. The new cell is sturdier than the previous one and also suffers smaller disturbances from environment. The air capacitance of either cell was about 18 pF. The cell was placed in a thick copper holder which was filled with toluene as the heat-exchange medium. The holder was cooled with Dry Ice in a Dewar vessel and the temperature of the cell, measured by a chromel-P-constantan thermocouple, was controlled manually with the heater wound around the holder.

Density was measured by a pycnometer[10] in the liquid state.

The dielectric constants and the densities of liquids were in good agreement with the literature values.[11]

Results and Discussion

1) Differential Thermal Analysis (DTA).

Recent X-ray studies[2] of carbon tetrachloride showed that under certain conditions it exhibits monotropy immediately below the melting point; *i. e.*, the crystal formed upon solidification is of metastable cubic phase, which is transformed to a rhombohedral crystal on further cooling. Such phase relations were substantiated by our DTA work.[3] Figure 2 is a reproduction of the DTA result of pure carbon tetrachloride. The figure is self-explanatory but it is to be noted that the melting point of the cubic phase (peak G) is about 3.8°C lower than the melting point of the rhombohedral phase (peak E). Similar DTA curves were obtained, though the tem-

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2) R. Rudman and B. Post, *Science*, **154**, 1009 (1966).

3) K. Kotake, N. Nakamura and H. Chihara, This Bulletin, **40**, 1018 (1967).

4) W. P. Conner and C. P. Smyth, *J. Amer. Chem. Soc.*, **63**, 3424 (1941).

5) J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1704 (1953).

6) A. Turkewich and C. P. Smyth, *J. Amer. Chem. Soc.*, **62**, 2468 (1940).

7) J. Timmermans and Y. Dolcourt, *J. Chim. Phys.*, **31**, 85 (1934).

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9) H. Suga, H. Chihara and S. Seki, *Nippon Kagaku Zasshi*, **82**, 24 (1961).

10) M. R. Lipkin, J. A. Davison, W. T. Harvey and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

11) a) R. Guillien, *J. Phys. Radium*, **1**, 29 (1940). b) A. Mansingh and D. B. McLay, *Can. J. Phys.*, **45**, 3815 (1967). c) A. Audsley and F. R. Goss, *J. Chem. Soc.*, **1941**, 864.

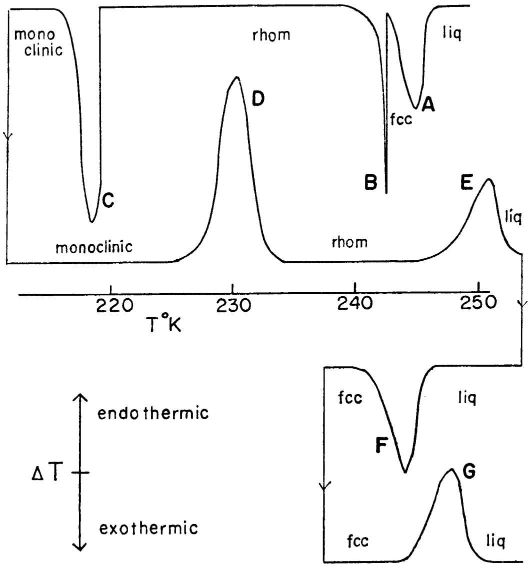

Fig. 2. DTA curves of carbon tetrachloride.

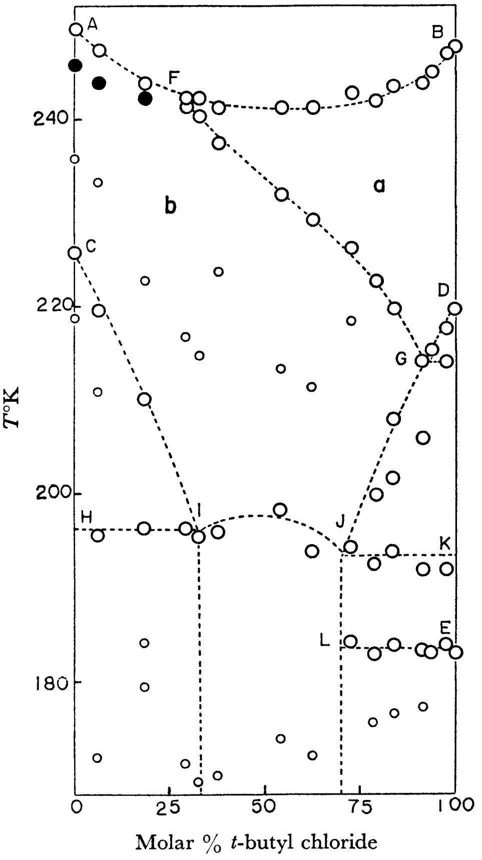

Fig. 3. The phase diagram of the system, CCl_4 - *t*-BuCl. Large and small circles represent the peaks on warming and on cooling, respectively. Closed circles represent the mp of metastable fcc phases. Dashed lines and capital letters refer to the work by Smyth *et al.*

peratures of transitions were displaced for binary mixtures of CCl_4 and *t*-BuCl where the concentration of the latter was less than 25 mol%. For more concentrated solutions, the melting and freezing points coincide and the second exotherm (B in Fig. 2) is replaced by a stable transformation corresponding to the curve FG in Fig. 3. The phase diagram determined by the DTA method (Fig. 3) confirms the dielectric result.[4]

Because the structure of the plastic phase of *t*-butyl chloride is fcc,[12] the area a of Fig. 3 must correspond to the fcc phase, the area b similarly corresponding to the rhombohedral phase.

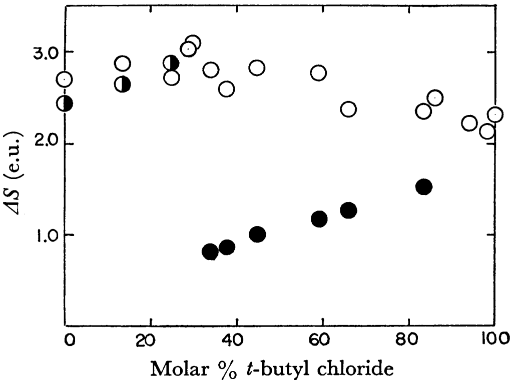

Fig. 4. Entropy of phase changes of CCl_4-*t*-BuCl. ● rhombohedral → fcc, ◑ rhombohedral → liquid, ○ fcc → liquid.

The entropy changes of the phase transitions were estimated from the area under the peak in the DTA curves and are shown in Fig. 4. To obtain the internal consistency, the experimental conditions including the volume of the specimen in the measuring tube were fixed for all compositions. The literature values of the entropy of fusion is 2.401 cal/deg·mol[13] for carbon tetrachloride and 2.00 cal/deg·mol[14] for *t*-butyl chloride. It is interesting to note that the entropy of fusion of the fcc phase, either stable or metastable, changes almost linearly with the composition, *i. e.*, the solid solution is very close to the ideal solution. Also, the entropy change from the rhombohedral to the stable fcc phase increases linearly as the solution becomes more concentrated in *t*-butyl chloride. Extrapolation of the line back to the zero concentration gives about 0.3 cal/deg·mol to the entropy of transition from the rhombohedral to the metastable fcc phase of

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[12] R. S. Schwartz, B. Post and I. Fankuchen, *J. Amer. Chem. Soc.*, **73**, 4490 (1951).

[13] J. F. Hicks, J. G. Hooley and C. C. Stephenson, *ibid.*, **56**, 31 (1944).

[14] A. Dworkin and M. Guillamin, *J. Chim. Phys.*, **63**, 53 (1966).

[15] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y. (1955).

pure carbon tetrachloride.

2) Dielectric Constants and Density. Uncertainty in the dielectric constant measurements was less than 0.1 pF, which arose from repeated assembly and disassembly. Samples were carefully frozen into plastic crystal phase to fill the space between the electrodes by slow cooling and annealing thereafter, and the dielectric constant values on warming and on cooling agreed well except in the region of the supercooled fcc phase, in contrast to the result of Smyth *et al.*,[4] who reported that the runs on two directions did not agree and that the dielectric constants were smaller on cooling. The values of the present work were reproducible to within 1%. The smoothed values for each temperature are listed in Tables 1—3. The values of the density are given in terms of the coefficients of the formula

$$\rho = a + bx + cx^2$$

where ρ is the density, x is mole% of *t*-butyl chloride and a, b and c are the coefficients.

TABLE 1. THE DIELECTRIC CONSTANT AND THE DENSITY IN LIQUID SOLUTIONS

The density is given in terms of a, b, and c in the formula $\rho = a + bx + cx^2$.

(mole %)	Temperature (°C)				
	20.0	10.0	0.0	−11.4	−22.0
0.00	2.240	2.258	2.276	2.300	2.324
1.39	2.319	2.347	2.374	2.407	2.437
4.23	2.471	2.509	2.548	2.592	2.632
8.87	2.712	2.760	2.812	2.875	2.937
11.98	2.936	3.000	3.068	3.151	3.227
21.05	3.505	3.612	3.723	3.855	3.978
37.26	4.731	4.911	5.114	5.360	5.603
51.03	5.775	6.036	6.283	6.636	6.782
64.16	6.762	7.122	7.487	7.913	8.178
77.69	7.832	8.270	8.720	9.276	9.855
100.00	10.04	10.61	11.25	12.05	12.09
a	1.5935	1.6116	1.6316	1.6519	1.6740
$b \cdot 10^2$	−8.279	−8.336	−8.448	−8.636	−8.755
$c \cdot 10^6$	7.664	7.725	7.949	9.176	9.569

TABLE 2. THE DIELECTRIC CONSTANT IN THE S.C. PHASE

x (mole %)	Temperature (°C)				
	−30.0	−35.0	−40.0	−45.0	−50.0
21.05	4.28	4.31	—	—	—
37.26	—	6.39	6.50	—	—
51.03	—	8.06	8.25	8.38	—
64.16	—	9.68	10.06	10.37	10.64
77.69	11.28	11.68	12.00	12.27	12.49
100	15.85	16.11	16.34	16.53	16.68

TABLE 3. THE DIELECTRIC CONSTANT IN THE RHOMBOHEDRAL PHASE

x (mole%)	Temperature (°C)					
	−25.0	−30.0	−40.0	−50.0	−60.0	−70.0
0.00	2.40	2.41	2.43	—	—	—
1.39	—	2.51	2.52	—	—	—
4.23	—	2.71	2.72	—	—	—
8.78	—	3.04	3.07	3.09	—	—
11.98	—	3.37	3.42	3.46	—	—
21.05	—	—	4.13	4.16	—	—
37.26	—	—	6.14	6.29	6.38	—
51.03	—	—	7.54	7.72	7.87	7.99
64.16	—	—	—	9.69	9.97	10.20
77.69	—	—	—	10.82	11.03	11.23

3) Polarization at Infinite Dilution. The dielectric constant in both the cubic and the rhombohedral phases has negative temperature coefficients as is evident from Tables 2 and 3. The negative coefficient is commonly encountered in polar plastic crystals[1,15] and is generally interpreted as being due to the effect of thermal agitation opposing the orientation of molecules in the electric field. It is therefore interesting to see if the Debye theory for the liquid solution applies to the plastic solid solution. This is equivalent to seeing if the application of the Debye theory might lead to a reasonable value of the effective dipole moment of solute molecules in the solid state.

To obtain the specific polarization at infinite dilution, the Halverstadt-Kumler's method[16] was used. If linear relationships hold for the dielectric constant and the density,

$$\varepsilon_{12} = \varepsilon_1 + \alpha w_2$$

and

$$\rho_{12} = \rho_1 + \beta w_2 \tag{1}$$

the specific polarization is given by the equation

$$p_\infty = p_1\left\{1 + \frac{3\alpha}{(\varepsilon_1-1)(\varepsilon_1+2)} - \frac{\beta}{\rho_1}\right\} \tag{2}$$

where w_2 is the weight fraction of the solute, the suffix 1 referring to the solvent and the suffix 2 to the solute. The experimental results of Tables 1 to 3 were used to derive the values of α and β in the region of dilute solutions. In the absence of the density values of the solid solution, the ρ_1 values of pure carbon tetrachloride were taken from Ref. 17 and the β value was assumed to be equal to that in the liquid solution. This assumption would not lead to a serious error in p_∞ since a variation of 10% in the value of β changes the value of p_∞ by only 1%.*2 The values of moler polarization at

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16) R. J. W. Le Fevre, "Dipole Moments," Methuen & Co. Ltd., John Wiley & Sons, Inc., London-New York (1953).

17) P. F. Higgins, R. A. B. Ivor, L. A. K. Staveley and J. J. des C. Virden, *J. Chem. Soc.*, **1964**, 5762.

*2 The use of the liquid β value in the solid solution may be justified by considering that the solid solution can be described by the regular solution theory.[18]

18) I. Prigogine and V. Mathot, *J. Chem. Phys.*, **20**, 49 (1953); V. Mathot and A. Desmyter, *ibid.*, **21**, 782 (1953).

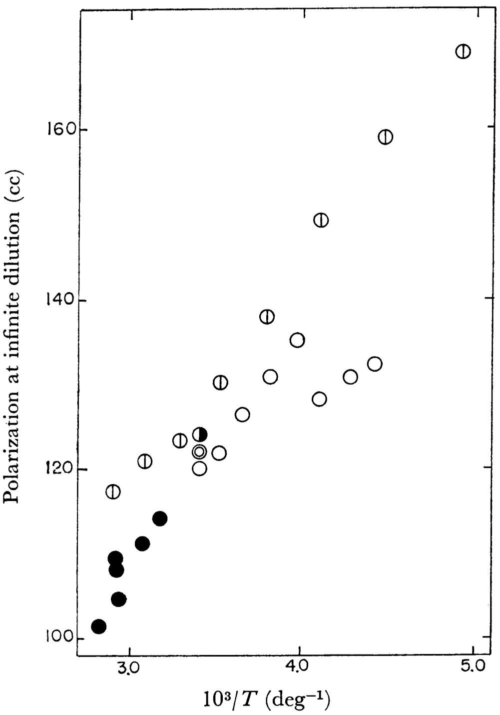

Fig. 5. Polarization at infinite dilution.
○; Present work, ●; in vapor,20) ⦶; in *n*-heptane,19) ◑; in benzene,21) ◎; in $CCl_4$11c)

infinite dilution thus derived are plotted against $1/T$ in Fig. 5, which also shows the results of other investigations.19–21) Our values for the liquid solution lie on a line extended from the values in the vapor phase, whereas there is a jump in the polarization between the liquid and solid (rhombohedral) phases and their slopes are also different.

Other conditions being equal, the difference in slope means a difference in the effective dipole moment between the liquid and the solid phases. By taking the electronic and atomic polarization to be 1.05 times the molar refraction, or 26.8 cc,22) the magnitude of the dipole moment is estimated as 2.00±0.03 D for the solid (rhombohedral) phase as compared with 2.11±0.01 D for the liquid phase. The smaller effective dipole moment in the solid should be an indication of the effect of a stronger intermolecular interaction, which also accounts for the jump of the polarization at the melting point. After Debye,23) we take

$$U = -\mu F\cos\theta' - V\cos\theta \qquad (3)$$

as potential energy of a solute molecule in the solid solution, where the first term represents the part due to the external field and the second term represents the potential energy hindering the molecular rotation. The angle θ is measured from the direction of the minimum hindering potential that is determined by the structure of the solid solution. The orientation polarization is given by

$$P^{o} = \frac{4}{3}\pi N\frac{\mu^2}{3kT}\left\{1-L^2(V/kT)\right\} \qquad (4)$$

where $L(y)$ is the Langevin function. Since there is a smooth continuity in the polarization between the vapor and the liquid, we assume that $L(y)=0$ in the liquid and the jump at the melting point is entirely due to non-zero $L(y)$ in the solid solution. Inserting the numerical values into Eq. (4), we obtain $V=0.9kT=450$ cal/mol. That $L(y)$ is put to zero in the liquid should not be taken to imply that there is no potential barrier in the liquid but it should be interpreted as meaning that the apparent potential barrier vanishes after averaging over all possible values of θ' and θ because of the symmetry of the barrier,24) its existence being expected from the structure of the liquid.25)

4) More Concentrated Solutions. We shall consider a more concentrated solution. If we take a 51.03% solution, the cubic and rhombohedral phases may be compared on similar grounds. To make a comparison with the case of dilute solutions meaningful, we deduce a quantity which corresponds to the orientation polarization in the Debye theory by applying the Onsager formula26) in the form

$$\frac{4\pi N\mu^2}{9kT} = \frac{1}{3}v_{12}\frac{100}{x}\left\{\frac{(\varepsilon-1)(2\varepsilon+1)}{3\varepsilon} - \frac{(2\varepsilon+1)(n_1^2-1)}{2\varepsilon+n_1^2}\,\frac{v_1}{v_{12}}\,\frac{100-x}{100} - \frac{2(\varepsilon+1)(n_2^2-1)}{2\varepsilon+n_2^2}\,\frac{v_2}{v_{12}}\,\frac{x}{100}\right\}\Big/ \left\{\frac{2\varepsilon+1}{2\varepsilon+n_2^2}\cdot\frac{n_2^2+2}{3}\right\}^2. \qquad (5)$$

Here ε is the dielectric constant of the solution, n is the refractive index, and v is the molar volume. Rough estimate of the molar volume of solid solution may be made on the basis of the theory of Pople and karasz,27) which relates the volume change to the entropy of fusion for the plastic crystals. Though

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19) C. P. Smyth and R. W. Dornte, *J. Amer. Chem. Soc.*, **53**, 545 (1931).

20) R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1941).

21) A. Partz, *Z. Phys. Chem.*, **B7**, 327 (1930).

22) "Kagaku Binran," ed. by the Chemical Society of Japan, Maruzen, Tokyo (1966).

23) P. Debye, *Phys. Z.*, **36**, 100 (1935).

24) H. Fröhlich, "Theory of Dielectrics," Oxford University Press, London (1958), p. 51.

25) R. W. Gruebel and G. T. Clayton, *J. Chem. Phys.*, **46**, 693 (1967); A. H. Narten, M. D. Danford and H. A. Levy, *ibid.*, **46**, 4875 (1967).

26) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

27) J. A. Pople and F. E. Karasz, *J. Phys. Chem. Solids*, **18**, 28 (1961).

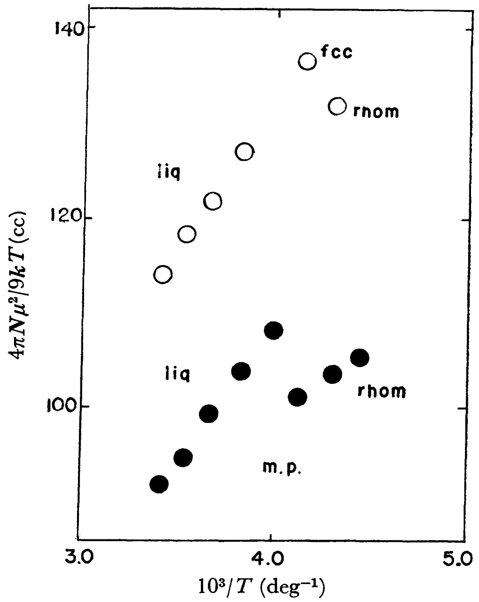

Fig. 6. Orientation polarization extrapolated to infinite dilution.

○ 51% mixture, derived by use of Eq. (5).

● dilute mixtures, derived by Halverstadt-Kumler method.

this theory was constructed for the pure substances, the extention to mixtures is possible on the assumption of perfectly random mixing in either phases. Precise application of this theory is not possible for rhombohedral phase of carbon tetrachloride, presumably due to the lower symmetry of the potential. Table 4 shows the parallelism of ΔS and $\Delta V/V_s$ among the fcc phases. V_s is estimated to be 92 cc, which is consistent with the density value, 1.349 g/cc, obtained from the equation $\rho=a+bx+cx^2$, where a is 1.760 g/cc for the fcc phase of carbon tetrachloride from the X-ray analysis[5] and b and c are mean values in liquid phase. The same value of molar volume is used for the rhombohedral phase of the mixture, though the actual value must be certainly less than it. The results are shown in Fig. 6, compared with the value of the orientation polarization obtained in the preceding section. An inspection of the figure immediately reveals that:

Table 4. The relation of the entropy changes ΔS from DTA and the relative volume changes $\Delta V/V_s$ on fusion

V and V_s are molar volumes of liquid and solid phases at the melting point, respectively, and the former are obtained by extrapolation of density *vs.* temperature curves for each concentration.

	CCl_4 fcc	*t*-BuCl fcc	51% mixture fcc
ΔS	2.7	2.0	2.9
$\Delta V/V_s$	0.050	0.046	0.051*
V	91.8	103.4	96.3
V_s	87.4	98.9	92*

* estimated values

1) the orientation polarization P^0 derived from Onsager's equation are systematically larger than P^0 at the infinite dilution, but the slopes are almost equal in the liquid phases.

2) P^0 for the fcc and liquid phases lie on a straight line, whereas P^0 for the rhombohedral phase falls short of the line.

These facts indicate that Onsager's treatment of dipole-dipole interaction is not adequate, mainly in the account of the short range interaction. However the defect of the theory is displayed in the liquid as well as in the solid phase in a similar fashion. The molecules are not as free in the rhombohedral phase as in the liquid or the cubic phases. The different behavior in the two solid phases is probably due to the different symmetry of the hindering potential of molecular rotation and is related to the factor $\overline{Z\cos\gamma}$ in the Kirkwood formula[28] which probably vanishes in the liquid and cubic phases.

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[28] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).