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Physical Chemistry of Binary Plastic Crystals. I. The System of Carbon Tetrachloride and *t*-Butyl Iodide*

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The binary system, carbon tetrachloride-*t*-butyl iodide, was studied by the proton magnetic resonance, the dielectric measurements and the X-ray diffraction. The complete phase diagram, constructed by the differential thermal analysis, shows a solid solution region where carbon tetrachloride is more than 50 mole%. Detailed studies of the solid solution containing 6.6 mole% of *t*-butyl iodide reveals that the solution can be described by the theory of regular solutions; its molecular polarization above the transition temperature obeys the Debye formula giving the dipole moment of *t*-butyl iodide a value of 1.6 debye units. The high-resolution nuclear magnetic resonance experiments with the same phase shows that carbon tetrachloride molecules diffuse in the solid solution with an energy of activation of 6.8 kcal./mole. The transition temperature varies with the composition, and below it the rotational motion of the solute molecules is more hindered. Pure *t*-butyl iodide shows motional narrowing around −150°C in the NMR line shape, above which temperature a reorienting molecular model can account for the magnitude of second moment of the nuclear magnetic resonance absorption.

Plastic crystals[1] are a class of molecular crystals which show enhanced plasticity in a temperature region below the melting point. Except in the case of inert monatomic crystals, they undergo one or more phase transitions accompanied with a large increase in entropy, due primarily to the acquisition of the molecular rotational or orientational degrees of freedom.

Thus, carbon tetrachloride is one of typical plastic crystals, having a phase transition at −47.7°C (225.5°K) with the entropy of transition, 4.86 cal./deg. mole. In its plastic phase between −47.7° and −22.9°C (m. p.), the molecules in solid carbon tetrachloride are in the state of hindered rotation, its potential barrier being estimated to be 2.4 kcal./mole.[2] The crystal structure in this plastic phase is that of face-centered cubic.[3]

If a compound having a permanent dipole moment is dissolved in a matrix of carbon tetrachloride and if they form a plastic solid solution, there will be a possibility of obtaining some information about the crystal field in the matrix compound by dielectric measurements. In the present study, *t*-butyl iodide was chosen as such a solute in the hope that one might get at an anomalous dispersion in a convenient radio-frequency region. The result turned out not to be the case, but instead, the plastic phase was found to be close to an ideal liquid solution and to be described by the theory of regular solutions. Some results obtained by proton magnetic resonance techniques will also be reported.

Similar studies have been described for the systems, CCl_4–$C(CH_3)_4$[4] and CCl_4–$C(CH_3)_3Cl$[5-7].

Experimental

Meterials.—Commercial special grade carbon tetrachloride was distilled after drying over calcium chloride; m. p. −22.9°C. The *t*-butyl iodide prepared by the method of Stone and Schechter[8] was purified through fractional distillation under reduced pressure and further under vacuum over mercury to minimize decomposition: Semi-microanalysis gave C, 26.21%; H, 4.94%; I, 68.63% (calcd. C, 26.10; H, 4.93; I, 68.97%), a purity of some 99.5%; n_D^{20} 1.4920 (literature value 1.4890) and m. p. −37.0°C. NMR spectrum and gas chromatography detected no impurities. The X-ray powder diffraction spacings taken at −78°C are given in Table I.

Equipments.—The high-resolution NMR spectra were recorded on a Varian A-60 analytical spectrometer combined with an attachment for temperature variation.

The broad-line NMR spectra were obtained with a Robinson-type autodyne oscillator-detector operated at about 20 Mc./s. The temperature of the specimen was

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[1] See for example, *J. Phys. Chem. Solids,* **18**, No. 1 (1961).

[2] H. Chihara and T. Shinoda, This Bulletin, **37**, 125(1964).

[3] B. Post, *Acta Cryst.,* **12**, 349 (1959).

[4] E. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **69**, 2176 (1965).

[5] A. Turkevich and C. P. Smyth, *J. Am. Chem. Soc.*, **62**, 2468 (1940).

[6] W. P. Conner and C. P. Smyth, ibid., **63**, 3424 (1941).

[7] J. G. Powles and H. S. Gutowsky, *J. Chem. Phys.*, **24**, 1061 (1956).

[8] H. Stone and H. Schechter, *J. Org. Chem.*, **15**, 491 (1950).

TABLE I. X-RAY DIFFRACTION SPACINGS OF SOLID t-BuI AT −78°C (in Å)

d	I	d	I	d	I
5.04	w	2.22	s	1.47	f
4.45	s	2.07	m	1.45	f
4.04	f	2.01	f	1.42	f
3.85	f	1.92	w	1.38	w
3.75	w	1.88	m	1.36	f
3.61	s	1.79	w	1.33	f
3.36	w	1.74	m	1.30	f
3.08	m	1.71	f	1.28	f
2.70	s	1.65	w	1.26	f
2.61	m	1.59	f	1.23	w
2.53	f	1.53	f		
2.24	w	1.51	f		

s: strong, m: moderately strong, w: weak, f: faint

determined with a Chromel-P-constantan thermocouple attached at the bottom of the specimen tube. The temperature drifted by about 2°C during a single sweep of magnetic field through resonance.

X-Ray powder diffraction photographs were taken by a camera of 35 mm. in diameter. The sample in a Li glass capillary (0.5 mm. in diameter) was chilled with a cold stream of nitrogen from its top. The temperature of the specimen was held constant to within a few degrees during exposure to nickel-filtered Cu$K\alpha$ radiation, ranging from 2.6 hr. for t-butyl iodide to 8—16 hr. for carbon tetrachloride or the mixtures.

The dielectric constant and loss were measured with the same equipments as have been described previously.⁹⁾ The sample container (see Fig. 1) consists of coaxial cylinders of Telex glass fitted inside with cylinders of platinum which serve as the measuring electrodes. The air capacitance of the cell is about 21 pF. This was inserted into a hole drilled through a heavy copper block to aid in slow change of the temperature. The specimens were frozen so as not to develop fissures or vapor snakes while freezing. The plastic nature of the crystal allowed its close fitting between the electrodes if maintained some degrees below the melting point. The dielectric constant of pure carbon tetrachloride agreed satisfactorily with the values obtained by Guillien¹⁰⁾ over the range of temperature examined. When the specimen was frozen quickly or was not annealed in the plastic phase, its dielectric constant appeared smaller.

The apparatus of the differential thermal analysis is the same as the one reported earlier.¹¹⁾

Results and Discussion

Pure *t*-Butyl Iodide.—The differential thermal analysis showed no solid-state transition between −196°C and the melting point, −37.0°C.

The temperature dependence of the dielectric constant ε' and the loss factor ε'' was measured between 1 kc./s. and 1 Mc/s. showing no discontinuity nor anomalous dispersion. Absolute values of ε' and ε'' were poorly reproducible because the crystal tended to fissure between the electrodes. ε'' increased toward the lower frequency: It gives linear plots against the reciprocal of the frequency, $1/f$, as shown in Fig. 2. The figure indicates that

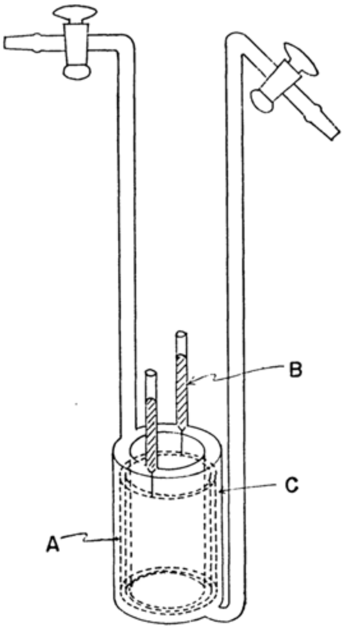

Fig. 1. The dielectric cell.
A's are the cylindrical platinum electrodes, B's are mercury terminals and C is the space for specimen.

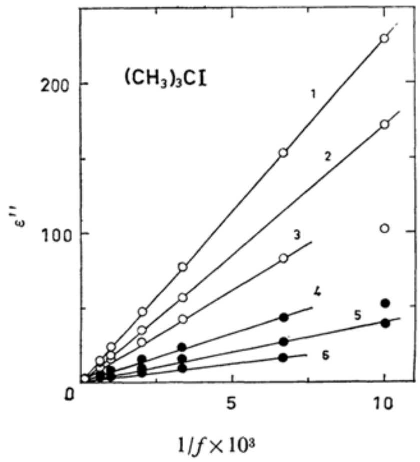

Fig. 2. The dielectric loss factor ε'' of t-BuI vs. the reciprocal of the frequency for two different coolings (open and closed circles);
1. −59°C, 2. −67°C, 3. −74°C, 4. −75°C, 5. −81°C, 6. −87°C.

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9) H. Chihara, S. Okawa and S. Seki, This Bulletin, **37**, 1373 (1964).

10) R. Guillien, *J. phys. radium,* **1**, 29 (1940).

11) H. Suga, H. Chihara and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **82,** 24 (1961).

the real part of the complex conductivity γ' obeys the formula

$$\gamma' = \varepsilon'' f/1.8 \times 10^{12},$$

suggesting also that the low-frequency loss is due to d. c. conductivity. By fitting the Arrhenius type of equation

$$\gamma' = \gamma'_0 \exp(-E/\boldsymbol{R}T),$$

the activation energy E was estimated to be 3.8 to 6.8 kcal./mole, varying from specimen to specimen, probably because it depends on the crystal packing between the electrodes, the size of crystallites, or the extent of dislocations. These values of E are rather small for the activation energy of diffusion through crystal lattice; the charge carriers may be small fragments of *t*-butyl iodide molecules produced by photochemical processes, moving through dislocations.

The proton magnetic resonance line shapes are reproduced in Fig. 3 at two representative temperatures. Figure 4 is a graph of the second moment plotted as a function of the temperature. It is 27.8 gauss² at −160°C and decreases to 2.4 gauss² at −100°C. Above the melting point, the observed resonance line was as narrow as the inhomogeneity of the magnet. To compare with these figures, theoretical values of the second moments were calculated by the method of Van Vleck.[12] The molecular parameters employed were H–H 1.79 Å, C–H 1.10 Å, and C–C 1.54 Å, the bond angles being assumed all tetrahedral. The contribution of the iodine spins was ignored. The dipolar interaction between three methyl groups was calculated as if the three protons of a methyl group collapsed into the center of the equilateral proton triangle. Table II is the result of such calculations.

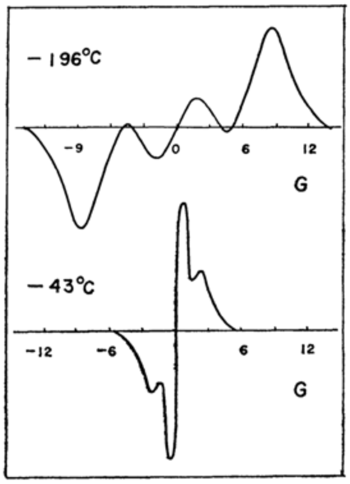

Fig. 3. The proton magnetic resonance (derivative) line shapes of *t*-BuI.

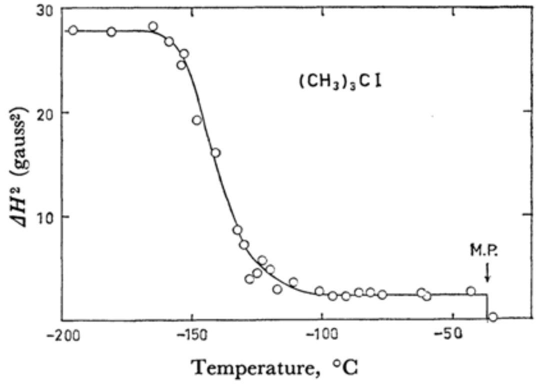

Fig. 4. Temperature dependence of the second moment of the proton magnetic resonance absorption of *t*-BuI.

TABLE II. THEORETICAL ESTIMATES OF THE SECOND MOMENTS OF SOLID *t*-BUTYL IODIDE IN GAUSS²

	Intra-methyl contribution (A)	Inter-methyl contribution in a molecule (B)	(A)+(B)
Rigid lattice	21.7	3.48	25.2
C_3-Rotation*	5.43	3.48	8.91
C_3'-Rotation*	0.64	0.87	1.51

* C_3-Rotation denotes the rotation of methyl groups around the C–C bonds.
C_3'-Rotation denotes the axial rotation of a whole molecule around the C–I axis.

The comparison between the observed and the theoretical values of the second moment shows that the lattice is rigid at the lowest temperature and undergoes a change through motional narrowing to a state in which are taking place not only the rotation*[1] of the methyl groups around the C–C axes but also the axial rotation of the entire molecule around the C–I axis. This does not contradict with non-existence of phase transition of this solid because a cooperative effect must be involved if a transition is to be seen by thermal measurements. The NMR experiments thus indicate that no bulk diffusion is occurring in solid *t*-butyl iodide.

The Phase Diagram of the System, Carbon Tetrachloride-*t*-Butyl Iodide.—The phase diagram of the binary system was constructed by means of a series of differential thermal analysis (DTA) runs at different compositions. The heating rate was about 0.7—1.0°C/min. The phase diagram as well as typical DTA curves are shown in Figs. 5A and 5B in which capital letters indicate points and lower-case letters indicate areas on the phase diagram. Where the concentration was near the eutectic point C, the endothermic anomalies in the DTA curves were poorly resolved and therefore their temperatures are not very precise. While

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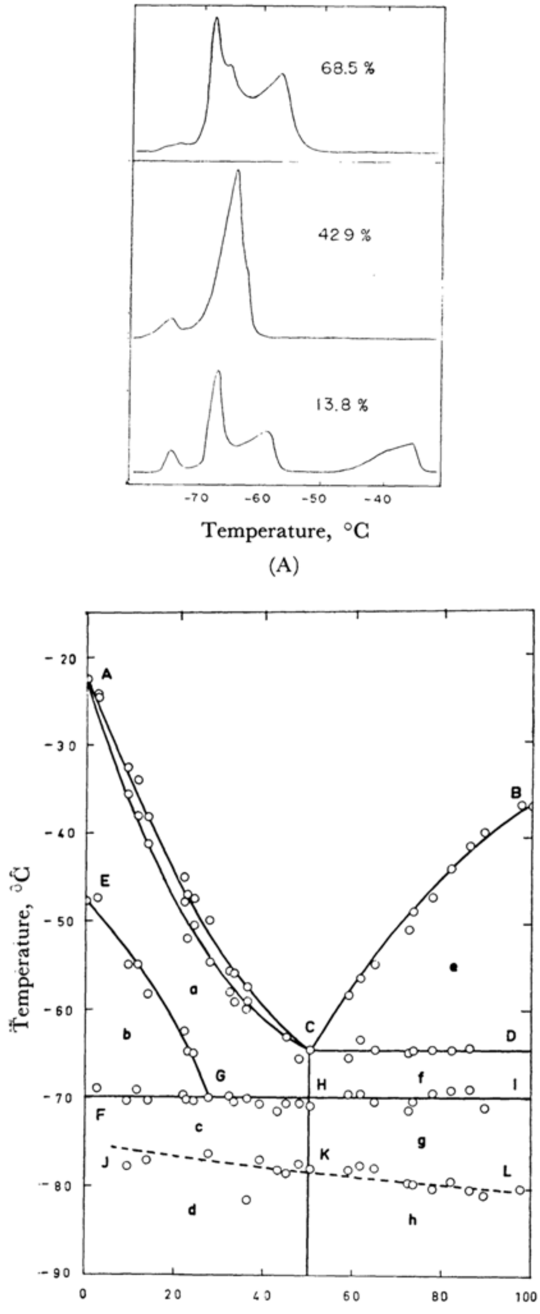
*1 No discrimination of the words, rotation or reorientation, is made in this paper.[2]

12) J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).



(A)

(B)

Fig. 5. Some typical DTA curves (A) and the phase diagram (B) of the system, CCl_4 - *t*-BuI.

the state of aggregation in each area will be discussed in later Sections, it suffices here to mention that within a limited range of the concentration (carbon tetrachloride richer than about 50 mole%), the system forms a solid solution, and also that a phase transition corresponding to that of pure carbon tetrachloride may be seen at a lower temperature. Therefore in such a concentration range, it is expected that the solute, *t*-butyl iodide, behaves as a built-in probe to study the molecular motions in the binary solid.

The areas on the phase diagram will now be briefly characterized. The area a corresponds to the solid solution. The point E is the transition temperature of pure carbon tetrachloride and the line EG shows its variation with the composition. In the area b, pure carbon tetrachloride coexists with the solid solution having varying composition. At the line FI, phase separation into pure components occurs. The origin of the thermal anomaly[*] corresponding to the line JL is not apparent but it does not appear in either of the pure components and its magnitude on the DTA curves is not perfectly reproducible. While the DTA curves in Fig. 5A may be taken as indicating that the anomaly is more prominent nearer the point J, there is no such definite tendency. Since complete phase separation occurs below −70°C, this anomaly must be associated with some effect of the interface or boundary of phases. The point C is a kind of eutectic point and the system is invariant here. The area, f, therefore, represents the solid solution of the composition C and pure *t*-butyl iodide.

A few words must be added here about the possibility of the existence of a phase transition in solid *t*-butyl iodide. Baker and Smyth[13] reported the existence of a phase change at −75°C through their measurements of the dielectric constant. However, in the present study, no anomaly was observed at this temperature in the differential thermal analysis, the nuclear magnetic resonance, or the X-ray diffraction. Our measurements of

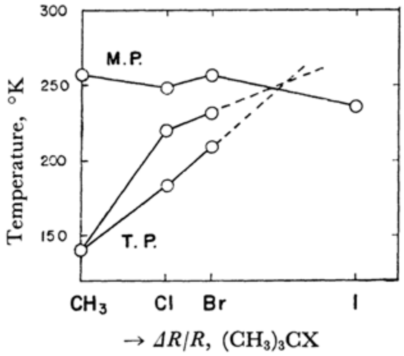


Fig. 6. Correlations between the temperatures of phase changes and the dissymmetry of molecules of $(CH_3)_3CX$.

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[*] The shape of the thermal anomaly is not a fixed one; it is sometimes a sharp peak and sometimes a broad maximum or a lambda-type anomaly. The temperatures at which these anomalies occur also show considerable scatter on either side of the line JL.

[13] W. O. Baker and C. P. Smyth, *J. Am. Chem. Soc.*, **61**, 2798 (1936).

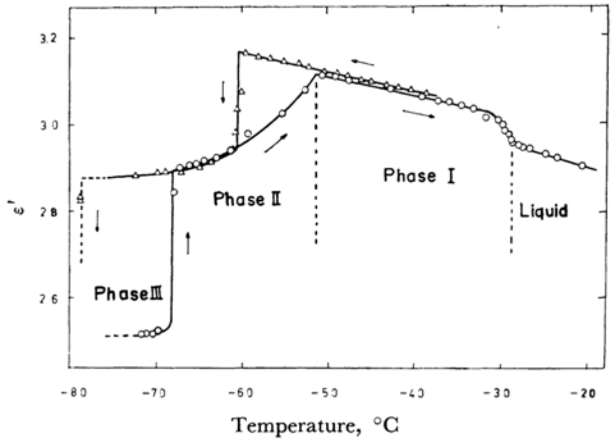

Fig. 7. Temperature dependence of the dielectric constant of a solid solution containing 6.6 mole % *t*-BuI at 15 kc./s.

the dielectric constant were not extended to a low enough temperature to show this because the contact of the specimen with the electrodes became poorer as we went down to lower temperatures. A comparison of the *t*-butyl compounds yields, however, an interesting diagram as shown in Fig. 6. Here, the melting point and the transition point are plotted as a function of the asymmetry parameter η of the molecules. The η is defined by

$$\eta = (R - R')/R = \Delta R/R$$

where R is the radius of the molecular sphere and R' is the distance from the central carbon atom to the periphery of the molecular sphere. Figure 6 suggests that *t*-butyl iodide would not have a transition in the solid state. A similar conclusion may be drawn from the type of analysis Miller and Smyth[14] developed for tetrahalomethanes.

A Solid Solution Containing 6.6—6.8 mole% of *t*-Butyl Iodide.—The solid solution containing 6.6—6.8 mole% of *t*-butyl iodide was chosen for detailed study because the peaks in the DTA curve are well resolved at such a concentration.

The precision of the equipments for the dielectric measurements did not permit us to work with a lower concentration of *t*-butyl iodide. The regions a, b, and c in the phase diagram (Fig. 5) will be referred to as the phases I, II, and III respectively.

Phase I.—The dielectric constant ε' at 15 kc./s. of the solid solution containing 6.6 mole% *t*-butyl iodide is shown in Fig. 7 through different phases. A good reproducibility of the ε' values indicates that close filling of the measuring cell with specimen has been attained. No dielectric dispersion and absorption were observed in the frequency range examined, therefore the results presented in Fig. 7 may be considered to represent the static dielectric constant.

We will first discuss the behavior of the system in Phase I. The negative slope in Phase I region in Fig. 7 is the same as in liquid solution phase. This is analogous to the case of many plastic crystals[1] in which the molecular rotational (or reorientational) degrees of freedom are fully excited, opposing the effect of electric field that tends to orient the molecular dipoles in its direction and decreasing the molecular polarization. There is small but definite change in ε' in going from Phase I to the liquid over a narrow temperature region between the solidus and the liquidus lines of the phase diagram, in accordance with the change in the density upon melting. The rotational motion of the *t*-butyl iodide molecules in the carbon tetrachloride matrix is not perfectly free in Phase I but must see a finite potential energy barrier hindering general rotation.[2] The X-ray diffraction pattern of Phase I was essentially the same as that of the Phase I of solid carbon tetrachloride which is known to be a plastic phase. This means that, so far as the orientational degrees of freedom are concerned, Phase I may be approximately regarded as a liquid solu totion; it is, therefore, of interest to examine what extent it may be.

The interactions between the solute molecules being ignored, the molecular polarization P_{12} of a dilute solution of polar molecules (suffix 1) in a non-polar solvent (suffix 2) is given by

$$P_{12} = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{1}{d}(c_1 M_1 + c_2 M_2)$$

$$= \frac{4\pi N}{3}(c_1\alpha_1 + c_2\alpha_2) + \frac{4\pi N c_2}{9\boldsymbol{k}T} \cdot \mu^2$$

where c_1 and c_2 are mole fractions, M_1 and M_2 are the molecular weights, α_1 and α_2 are the optical polarizabilities, d is the density of the solution, and μ is the dipole moment of the solute molecule. Figure 8 shows a graph of the P_{12}

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[14] R. C. Miller and C. P. Smyth, ibid., **79**, 20 (1957).

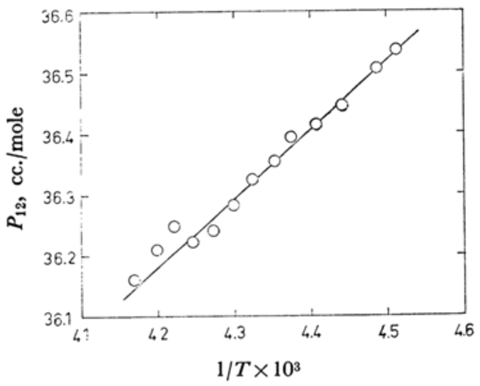

Fig. 8.

values plotted against the reciprocal of the temperature. In calculating P_{12} the density of the solution was assumed to be equal to that of pure carbon tetrachloride at corresponding temperature and evaluated from ε' values for pure carbon tetrachloride under the assumption of the temperature-independence of the molecular polarization of pure carbon tetrachloride. The plot is a good straight line, yielding a value of $\mu=1.6\times10^{-18}$ e.s.u. for the dipole moment of *t*-butyl iodide. There are no literature values to be compared with this dipole moment but the C–I bond moment has been estimated to be about 1.2×10^{-18} e.s.u. The difference is small and it is hard to decide if the difference is a real one.

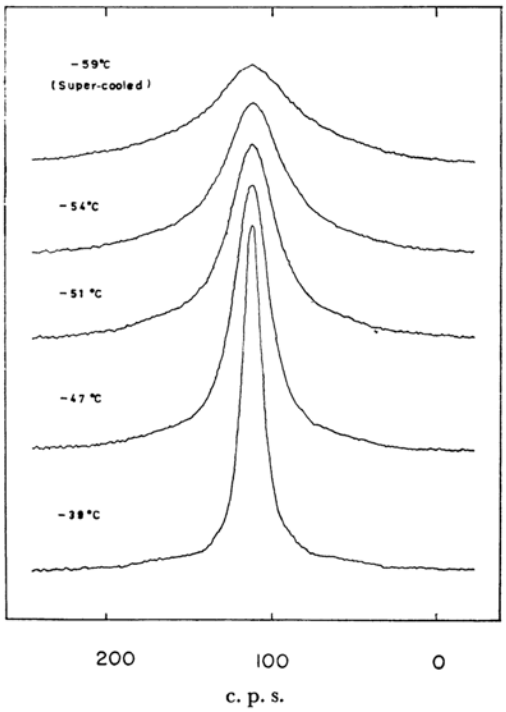

Fig. 9. High-resolution proton NMR of *t*-BuI in Phase I of the solid solution.

Having seen that the system may be regarded as a liquid solution with regard to molecular orientation, an attempt was made to study the proton magnetic resonance in the hope that we might see the effect of self-diffusion in Phase I.15) Figure 9 shows the temperature dependence of the high-resolution NMR line shape for the sample containing 6.8 mole% *t*-butyl iodide. The experiment started from −59.5°C (with the supercooled Phase I) upwards. The line-width is so narrow as to indicate that the reorientational motion of *t*-butyl iodide molecules is fully excited; its variation with the temperature must then be due to diffusion of molecules in the solid solution. If one assumes, as is done frequently, that the line-width is determined by the spin-spin interaction time T_2, the half-peak width is inversely proportional to T_2. The time T_2 is now related to the diffusion coefficient D through Torry's equation16)

$$T_2 = \frac{1}{c}\cdot b^4 D$$

By virtue of the relations17)

$$\begin{aligned} D &= b^2\nu_D\cdot\exp(-\Delta G_d/\boldsymbol{R}T) \\ &= D_0\exp(-\Delta H_d/\boldsymbol{R}T) \end{aligned}$$

we have

$$cT_2/b^4 = D_0\exp(-\Delta H_d/\boldsymbol{R}T)$$

where ΔG_d is the Gibbs energy of activation, ν_D is the Debye cut-off frequency of the solid, c is a material constant independent of the temperature, b is the lattice parameter of the face-centered cubic lattice to which the equation is applicable. Because of the narrow temperature range studied, the b may be taken as a constant. The linear dependence of log T_2 on $1/T$ in Fig. 10 gives a value of 6.8 kcal./mole for ΔH_d of diffusion.

The origin of the residual line-width (Fig. 9)

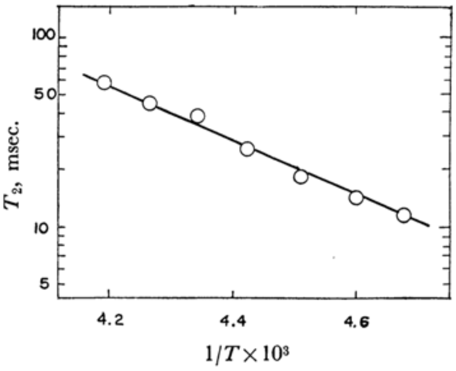

Fig. 10.

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15) See for example, H. Suga and S. Seki, This Bulletin, **35**, 1905 (1962).

6) Quoted by H. A. Resing, *J. Chem. Phys.*, **37**, 2175 (1962).

157) C. Zener, *J. Appl. Phys.*, **22**, 372 (1951).

must now be investigated more closely. The state of distribution of *t*-butyl iodide in the carbon tetrachloride matrix is not at once obvious: The solute molecules possibly form small aggregates by dipole-dipole forces in order to relax the local distortion of the matrix lattice and thus to minimize the total strain energy. Because no bulk seggregation was observed in Phase I, there must be an equilibrium set of concentrations for single solute molecules, pairs of molecules, etc. Judging from the case of vacancy pairs in inert gas solid,(18) the concentration of the pairs and the higher multiples of molecules will be less than a few tenth of one per cent. Therefore, it will be safe to assume that most of the solute is distributed uniformly throughout the solid solution. A uniform distribution means that an average *t*-butyl iodide molecule is separated from other nearest *t*-butyl iodide molecules by about 300 Å and that each *t*-butyl iodide molecule sees only carbon tetrachloride molecules at its neighbors. The proton-chlorine interactions thus contribute predominantly to the residual line-width; the second moment contributed by this type of interaction is greater than that by the intermolecular proton-proton interaction by a factor of 10^2, by a rough computation. Another order-of-magnitude estimate can be made with regard to the line-width itself. The maximum local magnetic field which a proton sees is about 80 c. p. s. due to chlorine nuclei, whereas the field due to other protons amounts only to 20 c.p.s., assuming that the nuclei are bound rigidly at the f. c. c. lattice points. The observed line-width ranges between 15 and 60 c. p. s.

These arguments suggest that what is being observed is the narrowing of proton resonance caused by the diffusion of the carbon tetrachloride molecules. Therefore, the observed heat of activation, 6.8 kcal./mole, is that for diffusion of carbon tetrachloride relative to *t*-butyl iodide molecules. Here the *t*-butyl iodide molecules behave like a built-in probe to study the motion of the non-magnetic or weakly magnetic molecules (carbon tetrachloride).

There are no other experimental or theoretical values available for comparison with this value of ΔH_d, but it seems to be a reasonable value in view of the low value of the rotational potential barrier height, 2.4 kcal./mole.(2) In the case of metals, Nachtrieb(19) demonstrated a proportionality relation between ΔH_d and the heat of fusion ΔH_f with an empirical constant of proportion:

$$\Delta H_d = 16.5\ \Delta H_f$$

This relation gives ΔH_d a value of 9.9 kcal./mole for carbon tetrachloride. The reason for the observed value to be smaller is not immediately apparent; the small observed value may show failure of the Nachtrieb's relation in the case of molecular crystals or it may be an indication of local distortion of the carbon tetrachloride host lattice in the vicinity of the solute molecules.

The direct determinations of the relaxation times T_1 and T_2 at this and still lower concentrations of *t*-butyl iodide, and also similar investigations using other *t*-butyl halides will be helpful in a more quantitative understanding of the molecular motion. Studies along these lines are being undertaken.

Phases II and III.—The Phase II of the binary solid is an inhomogeneous phase because pure carbond tetrachloride (of the low-temperature modification) keeps segregating upon cooling below the transition temperature. This is seen by the X-ray diffraction pattern which is a super-impose of the low-temperature pattern of carbon tetrachloride and the pattern of the solid solution.

The dielectric constant ε' is still large in Phase II, although its temperature coefficient is positive in contrast to the case of Phase I, showing that the molecular reorientation tends to be restricted progressively upon cooling. The reason for this is two-fold: One is the effect of smaller kinetic energy at lower temperatures and the other is the increase in the solute concentration in the solid solution part. In conformity with such view, there is a Maxwell-Wagner type of absorption in ε'' at −68°C at low frequency side of Fig. 11. An anomalous absorption extends towards higher frequencies, showing a possibility of finding a maximum in ε'' between 10^8 and 10^9 c. p. s. The reorientational motion of *t*-butyl iodide in Phase II is apparently more heavily restricted than in Phase I but is easier than in pure *t*-butyl iodide in which the dispersion is considered to occur around 5×10^4 c.p.s.

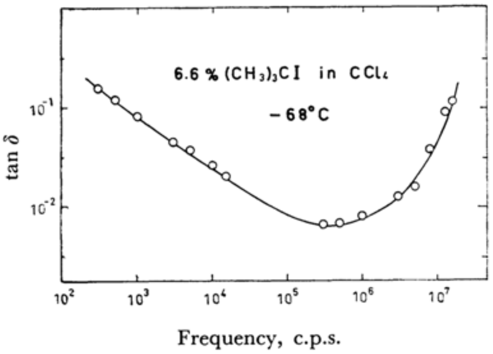

Fig. 11.

In Phase III the two components are completely separated (by X-ray diffraction). The dielectric constant changes discontinuously at the eutectic point (−70°C). The value of ε' (2.5) in this

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18) K. Iwamura, *Busseiron Kenkyu,* [2] **9,** 311 (1961); see also O. G. Peterson, D. N. Batchelder and R. O. Simmons, *Phil. Mag.,* **12,** 1193 (1965).

19) N. H. Nachtrieb and G. S. Handler, *Acta Met.,* **2,** 797 (1954). N. H. Nachtrieb, J. A. Weil, E. Catalano and A. W. Lawson, *J. Chem. Phys.,* **20,** 1189 (1952).

phase is comparable to the high frequency limit (2.6) for pure *t*-butyl iodide and the low temperature limit (2.4) for pure carbon tetrachloride.

Comparison of the Systems CCl_4 - *t*-BuX where X is CH_3, Cl or I.—The published phase diagrams for the systems carbon tetrachloride - $C(CH_3)_4$⁴⁾ and carbon tetrachloride - *t*-butyl chloride⁷⁾ differ in many respects from the diagram given in Fig. 5 of the present paper. Only portion that may be compared is where the transition point of carbon tetrachloride varies with the concentration of the second component. This portion is depicted in Fig. 12. The solid line in the figure gives what one would expect if it is assumed that the plastic solid phase (Phase I) forms a regular solution; i. e. the equation of the solid line in the figure is given by

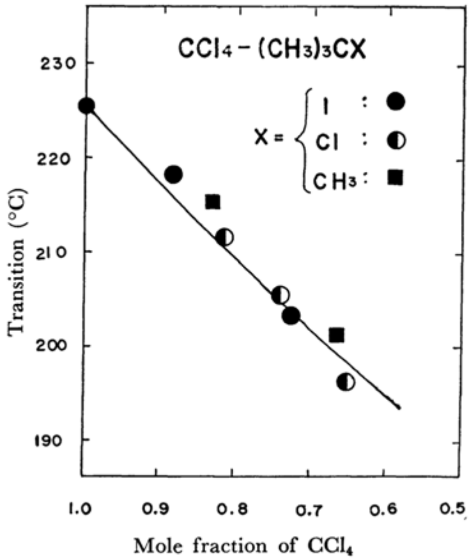

Fig. 12. Transition point lowering of CCl_4.
The solid line corresponds to a theoretical prediction for a regular solution case with $w=350$ cal./mol.

$$\boldsymbol{R}T_0 \ln x + w(1-x)^2 = \Delta H\left(1-\frac{T_0}{T}\right)$$

and

$$w = 350 \text{ cal./mol.}$$

where x is the mole fraction of carbon tetrachloride, T_0 is the transition temperature of pure carbon tetrachloride, ΔH is its heat of transition, and T is the observed transition temperature. The parameter w is related to the heat of mixing of the two components. The deviation of the observed points from the solid line is small, which fact shows that the plastic crystals are good solid solvents and they are 'liquids' at least with regard to the molecular orientation.²⁰⁾ Similar finding has also been obtained for the solid system, CO-N_2.²¹⁾

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Dedication

This paper is dedicated to Professor Masao Kotani of Osaka University in celebration of his sixtieth birthday, who has a world-wide reputation for his scientific activity in so many different branches of physics and chemistry.

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