Molecular Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Self-Diffusion in Some Plastic Crystals

Hiroshi Suga [a], Masayasu Sugisaki [a] & SyÛzô Seki [a]

[a] Department of Chemistry, Osaka University, Toyonaka, Japan

Version of record first published: 21 Mar 2007.

To cite this article: Hiroshi Suga , Masayasu Sugisaki & SyÛzô Seki (1966): Self-Diffusion in Some Plastic Crystals, Molecular Crystals, 1:3, 377-394

To link to this article: http://dx.doi.org/10.1080/15421406608083279

Molecular Crystals. 1966. Vol. 1, pp. 377–394

Printed in Great Britain

Self-Diffusion in some Plastic Crystals

HIROSHI SUGA, MASAYASU SUGISAKI and SYÛZÔ SEKI
Department of Chemistry, Osaka University, Toyonaka, Japan

Received March 28, 1966

Abstract—Self-diffusion phenomena in several plastic crystals were studied by use of high-resolution n.m.r. techniques which have been hitherto applied to pure liquid or solution systems. The pursuit of spectral narrowing processes, with the aid of Kubo–Tomita formula, makes it possible to evaluate the kinetic aspects of diffusional motion. Activation enthalpies for diffusion were obtained for trimethylacetic acid, triethylenediamine, succinonitrile and ammonium nitrate; they were 8.09 ± 0.25, 21.7 ± 1.0, 10.7 ± 0.5 and 11.3 ± 0.5 kcal/mole, respectively. These data, as well as those available for the other plastic crystals, were correlated with the latent heat of fusion in a similar manner to those for cubic metals.

Also, the chemical shift of OH resonance relative to CH_3 resonance line of trimethylacetic acid was measured for the crystal and liquid phases. Temperature coefficient of OH chemical shift is of the order of 1.0×10^{-2} ppm/° C. This observation and the other evidence suggest strongly the validity of the model, by which Muller and Reiter have explained the main origin of temperature variation of OH chemical shift in some hydrogen-bonded systems.

Introduction

The observation of high-resolution nuclear magnetic resonance spectra of fluid systems is possible because of the averaging out of magnetic dipolar interactions between nuclei by random rotational, and translational motions. On the other hand, the relatively strong dipolar interactions in the solid state overlap and obscure the fine structure which arises from different chemical shifts, and electron-coupled interactions.

Some kinds of molecular crystals, which have entropies of fusion less than about 5 e.u., and are miscible with each other regardless of their difference in molecular shape, show a much larger plastic flow than that found in ordinary crystals. Timmermans[1] designated these types of crystals as "plastic crystals". X-ray, thermal, dielectric and broad line n.m.r. studies have shown the existence of an isotropic reorientation of molecular groups, or of the molecule as a whole, as well as self-diffusion[2] in these plastic crystals. Broad line techniques usually give some qualitative information of the nature of the self-diffusion.

This self-diffusion phenomenon in the crystalline state gives rise to a change in the magnetic environment of a given nucleus at the lattice point. As the correlation time at each lattice point becomes shorter compared to the spin–spin relaxation time, phase coherence is progressively lost, and the resonance line is expected to become narrow enough to give high-resolution n.m.r. spectra even for the crystalline state,[3] if the molecule involves chemically different nuclei. We may, therefore, expect high-resolution techniques to be useful for the investigation of molecular motion, as well as chemical shifts of the molecule in plastic crystals.

In the following we should like to report the high-resolution n.m.r. spectra of some plastic crystals. The pursuit of spectral narrowing processes, with the aid of a statistical approach developed by Kubo–Tomita,[4] makes it possible to get some quantitative information on the kinetic aspects of diffusional motion in molecular crystals. This approach seems to be particularly useful for molecular crystals for which direct experimental techniques, such as the tracer method, are rather difficult to apply.

Experimental

Measurements were carried out with a Varian Associates Model V-4311, and VA-60 spectrometers, combined with an attachment for temperature variation. The attachment could control automatically the temperature of the specimen in the range − 100° C to + 200° C. Since the impurities involved in the specimen strongly affect the diffusional process, specimens were purified very carefully.

(a) Trimethylacetic acid (pivalic acid) was synthetized by the method of Puntambecker and Zoellner.[5] The specimen was purified primarily by distillation (b.p. 163.7°–.8° C) and then by fractional sublimation using liquid air under high vacuum (10^{-6}

torr). The purified specimen was transferred into the standard sample tube *in vacuo*. Part of the specimen was used for the measurement of heat capacity of the solid and the liquid phases. Analysis of the enthalpy *vs*. temperature curve around the m.p. (36.5° C) revealed that the present material was approximately 99.8 % pure.

(b) The sample of triethylenediamine, 1.4-diazabicyclo-(2,2,2,)-octane, used for the present research was kindly offered us by Houdry Process Corporation, Pa., U.S.A. This material is quite hygroscopic and has a strong tendency to form the monohydrate.[6] The method of purification of this material was the same as that for trimethylacetic acid crystal. Some thermal properties as well as the preliminary investigation of structural analysis were already reported in a previous paper.[7]

(c) The specimens of succinonitrile, cyclohexanol and ammonium nitrate were commercially obtained (Nakarai Chem., Ltd.; guaranteed reagent). These materials were more or less hygroscopic and therefore always treated *in vacuo* or under a stream of dry nitrogen gas.

(d) In the case of ammonium nitrate, an excitation of the diffusional process of the constitutent ions should affect the conductive properties of the crystal remarkably. So, d.c. conductivity was also measured in parallel with the experiment of high-resolution n.m.r. in order to clarify the mechanism of the diffusional process more in detail. Parallel platinum electrodes, 0.28 cm^2 of cross-section with 4.5 mm gap, were fixed within a glass tube by use of metal-glass seals. Powdered specimen, purified twice by recrystallizations from distilled water, was packed into this glass tube. The apparatus was sealed via a side-arm into a vacuum line (10^{-6} torr), dried at 130° C for 10 hr, and then sealed off after introduction of dry nitrogen. The whole system was heated up to 170° C (just above the m.p.) in an oil bath, the temperature of which was measured by a calibrated Cu-constantan thermocouple. The melt was allowed to crystallize at a temperature *ca.* 3° C below the m.p. It was confirmed that the crystallization started from the environment of electrodes and fairly transparent crystal grew over the whole system. After annealing at this temperature, resistance was measured using a Wheatstone bridge (Ando Denki Co. WP-4 type) with an electronic amplifier which served as null detector. In order to diminish spurious polarization effects, pulse voltages with opposite signs were applied alternately.

Experimental Results

I. TRIMETHYLACETIC ACID

This crystal has quite a small entropy of fusion (1.56 e.u. at 36.5° C) compared with that of the transition (6.07 e.u. at 6.9° C), and is face-centered cubic[8] above the transition point. Below the transition point the proton n.m.r. line width is of the order of several gauss, so that no significant spectrum appears on the high-resolution n.m.r. chart. The high-resolution n.m.r. spectrum of the cubic phase is composed of two peaks; a rather broad one located at about 1.2 ppm, and a relatively sharp one located at about 12.7 ppm, referred to the standard TMS signal, as is shown in Fig. 1. These two peaks can be assigned to the nine methyl proton and single carboxyl proton resonances, as is evidenced by the approximate intensity ratio of 9:1. The high field side spectrum at 34.5° C seems to consist of two components. Although the temperature measurement in the present study is not as accurate as in the heat capacity measurement, qualitative analysis of the melting curve showed that a minute amount of liquid phase co-exists with the solid at this temperature. Therefore, the sharp component of the spectrum will be ascribed to the co-existing liquid.

The differences in chemical shifts between the two types of protons were measured in both solid and liquid phases as a function of temperature. They are plotted in Fig. 2. The separation of the two peaks narrows gradually in the solid state, and more rapidly in the liquid state, when the temperature is raised. There seems to be no discernible change in the separation of the two peaks at the melting point.

A gradual reduction in the line width of each peak is observed with the rise of temperature. Temperature variation of half width

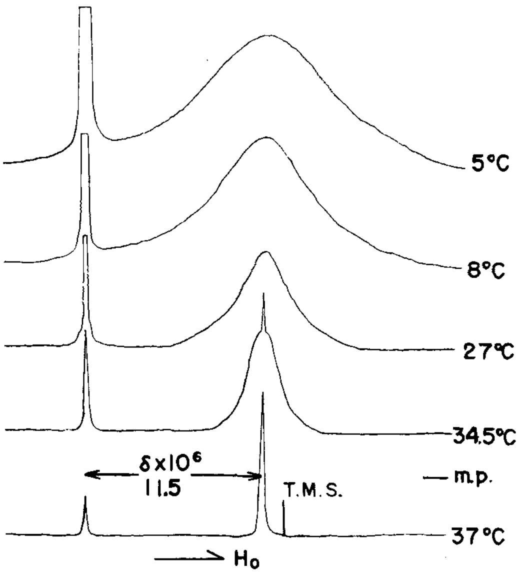

Figure 1. High-resolution n.m.r. spectra of trimethylacetic acid at various temperatures.

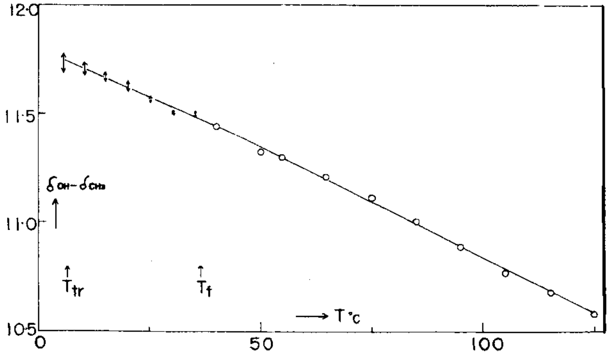

Figure 2. Temperature variation of chemical shift for carboxylic proton in trimethylacetic acid.

of the line due to methyl groups is given in Fig. 3. The smooth decrease in the spectral width can be explained by postulating self-diffusion of molecules in the crystal lattice which is most likely to occur by the movement of the molecules through the neighbouring vacancies formed increasingly as the temperature approaches the melting point. A sudden decrease in the spectral width at the melting transition presumably is associated with increased motional averaging of the dipolar broadening. The line-width data for the other crystals investigated in the present study display similar behaviour at the melting point.

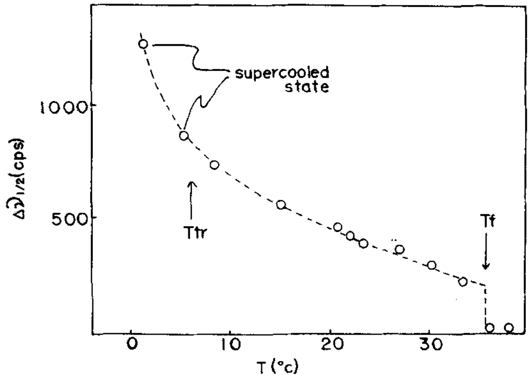

Figure 3. Temperature variation of the line width of the methyl proton resonance.

A few measurements of the spin lattice relaxation time T_1 were made in the cubic phase by the use of spin-echo techniques. The measured values of T_1 fall into a region between 0.1 and 1.0 sec and these values are much larger than the inverse of the observed spectral width. Therefore, we may safely attribute the observed line width to the secular contribution of dipolar interactions, as in the usual cases.[10,11] From the temperature dependence of the line width of methyl protons, the analysis of the kinetic properties associated with a plausible self-diffusion mechanism was made by using the Kubo-Tomita formula.[4] They discussed the general problem of motional effects on dipolar broadening, and derived the following formula in the adiabatic limit:

$$(1/T_2)^2 = \frac{4\ln 2}{\pi} a^2 \tan^{-1}\left\{\frac{\pi\tau_c}{(4\ln 2)T_2}\right\}$$

where $1/T_2$ stands for the half width of the resonance line, a^2, the second moment of the rigid lattice, and τ_c, the correlation time. Here the second moment of the rigid lattice was replaced by the intermolecular contributions in the cubic phase for the present purposes. The lattice sum of r^{-6} was calculated with the known lattice type (f.c.c.) and the cell constant ($a = 8.82$ Å), based on the model that all the ten protons lie on the centre of gravity of

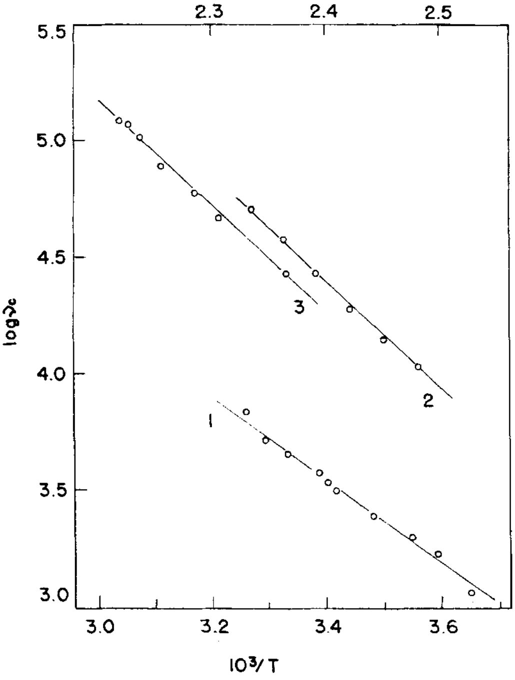

Figure 4. Correlation frequency data plotted against inverse temperature. 1, trimethylacetic acid; 2, triethylenediamine (upper scale for $1/T$); 3, succinonitrile.

individual molecule. The correlation frequency ν_c, defined as $\nu_c = 1/(2\pi\tau_c)$, derived from this equation is inversely proportional to the temperature over the full range of the cubic phase. The results are summarized in Fig. 4 with those for the other crystals. Thus, it seems reasonable to assume that diffusional motion in this crystal is described by a single correlation time. A least-squares fit of the activation plot gives 8.09 ± 0.25 kcal/mole as an activation enthalpy for self-diffusion.

II. TRIETHYLENEDIAMINE

The globular cage structure of this molecule is somewhat reminiscent of that of hexamethylenetetramine. At 79.8° C, this crystal changes from the hexagonal[7] to the f.c.c.[12] system with $a = 9.03$ Å (130° C). The relatively low entropy of fusion[13] as well as the high crystallographic symmetry suggest strongly that this material belongs to the category of plastic crystals. The high-resolution n.m.r. spectrum of the cubic crystal shows only a single peak with the following spectral half-width; 460 cps at 130° C, 356 cps at 135° C, 262 cps at 140° C, 184 cps at 145° C, 132 cps at 150° C and 98 cps at 155° C. The line width decreases smoothly as the temperature approaches the melting point (161° C).[9] The source of this intermolecular averaging will be accounted for by self-diffusion, as in the case of trimethylacetic acid crystal. In this case the contributions from the nitrogen nuclei to the resultant second moment were taken into account. The best fit of the activation plot data gives 21.7 ± 1.0 kcal/mole as an activation enthalpy for self-diffusion. Recently, Smith[14] has studied broad line n.m.r. spectra of this material in the temperature range from 77° K to 420° K. From the analysis of temperature dependence of spectral width above the transition point, he gave 16.2 kcal/mole as the activation enthalpy for self-diffusion. The reason of discrepancy between them is not clear at the present stage. Perhaps a trace of water left behind in the specimen will strongly affect the diffusional process.

III. SUCCINONITRILE

Early dielectric-constant[15] and heat capacity measurements[16] indicated a rotational transition at −40° C. X-ray investigation[17] confirmed that the crystal above the transition point belongs to the b.c.c. system. Infrared spectra[18] taken below and above the transition point were explained by the model that succinonitrile molecule below the transition point exists entirely in the C_2(*gauche*) rather than C_{2h}(*trans*) configuration, and also that it is present in an equilibrium mixture of the two rotational isomers above the transition point. The high-resolution n.m.r. spectra were taken in the hope that the kinetic aspects of internal rotation as well as self-diffusion which might occur would be clarified.

The high-resolution n.m.r. spectrum shows only a single peak in both solid and liquid phases. The spectral width varies continuously from 121 cps at 25° C to 19.5 cps at 56° C. The logarithm of correlation frequency plotted against inverse temperature in the cubic phase gives a straight line, whose slope leads to 10.7 ± 0.5 kcal/mole as an activation enthalpy for self-diffusion.[9] Quite independently, Petrakis and Rao[19] have investigated narrowing process of spectral width above the transition point, by the use of broad-line techniques. Their reported value 9.7 kcal/mole for the activation enthalpy of self-diffusion is in reasonable agreement with our value.

IV. CYCLOHEXANOL

This crystal is known to be a plastic crystal, as suggested by its small entropy of fusion.[20] Averbuch[21] has pointed out the possibility of occurrence of self-diffusion above the transition point (at −9.7° C).

The line width above the transition point is sufficiently narrow to give well-separated peaks, which arise from different protons in the molecule. These spectra are given in Fig. 5. The spectrum at −9° C consists of three main peaks located at about 5.4, 3.5, and 1.5 ppm, respectively, referred to the TMS signal. The areas under the peaks stand roughly in the ratio 1 : 1 : 10, as would be expected if each peak, in the order of increasing field, corresponds to the chemically different OH, H_α, and remaining ring protons. As the temperature is raised, and the line width of each peak is narrowed by the self-diffusion process, the main peak shows further splitting, whose components have an approximate intensity ratio of 2:3, and have a distance of 0.4 ppm. This splitting seems to be due to the difference in chemical shifts between the two types of ring protons (β-protons, and γ- plus δ-protons). The rate at which cyclohexanol isomers change from axial to equatorial conformations will be faster than the inverse of the difference of chemical shifts between the axial, and equatorial protons. The difference of chemical shifts between the axial and the equatorial protons of

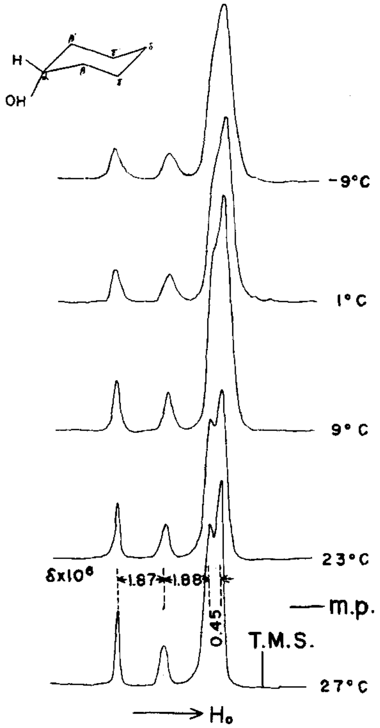

Figure 5. High-resolution n.m.r. spectra of cyclohexanol crystal and liquid.

several cyclohexane derivatives[22] amounts to approximately 0.7 ppm. Since the spectra at 280°K display a fine structure separated by 0.4 ppm, mean life-time τ of a- and e-conformations of cyclohexanol molecule in the crystalline state must be shorter than the inverse of 0.4 ppm or 24 cps. By using the absolute-rate scheme, this consideration gives 14.5 kcal/mole as an upper limit of activation enthalpy for the axial-equatorial conversion.

The intermolecular dipolar interaction is almost entirely averaged out in the cubic phase and the line width of each peak changes continuously from the solid to the liquid phase. Therefore, the activation enthalpy for self-diffusion is not obtained.

V. AMMONIUM NITRATE

Although ammonium nitrate is usually classified as an ionic crystal, its thermodynamic properties such as low m.p. or small entropy of fusion[23] (2.94 e.u.) quite resemble those of a plastic crystal. Previous broad-line n.m.r. and d.c. conductivity experiments[24] show, in rather qualitative manner, the occurrence of self-diffusion in the cubic phase (125°–169.3° C).

A plot of correlation frequency data obtained from n.m.r. spectra is given in Fig. 6 as a function of $1/T$.[9] The figure also includes $\log \sigma$ *vs.* $1/T$ plot for both cubic and tetragonal phases, where σ is the specific conductivity in ohm^{-1} cm^{-1}. A linear relationship holds for $\log \nu_c$ data against $1/T$ over the entire cubic phase, whereas significant deviations from linearity are observed near the m.p. for the $\log \sigma$ *vs.* $1/T$ plot. Least-squares fit of correlation frequency data gives 11.3 ± 0.5 kcal/mole as an activation enthalpy for diffusion, while the linear part of ($\log \sigma$ *vs.* $1/T$) plot gives 16.0 ± 0.3 kcal/mole for the same quantity. This appreciable difference indicates that species playing an important role in the d.c. conductivity are not presumably the same as those observed in n.m.r. spectra.

It is well known that correlation time τ_c obtained from n.m.r. data is connected with diffusion coefficient $D(\tau)$.

$$D(\tau) = \langle r^2 \rangle / 6\tau_c$$

where $\langle r^2 \rangle$ is the mean squared jump distance. If the cube-edge parameter[27] is taken as r, we can obtain, for example, $D(\tau) = 6.19 \times 10^{-11}$ cm²/sec at 416°K ($1/T = 2.4 \times 10^{-3}$ K^{-1}).

On the other hand, Nernst–Einstein's equation[26] gives a relation between conductivity σ and diffusion constant $D(\sigma)$ in electrolytic solution;

$$D_i(\sigma) = \frac{kT\lambda_i \sigma}{Z_i e^2 N_i}$$

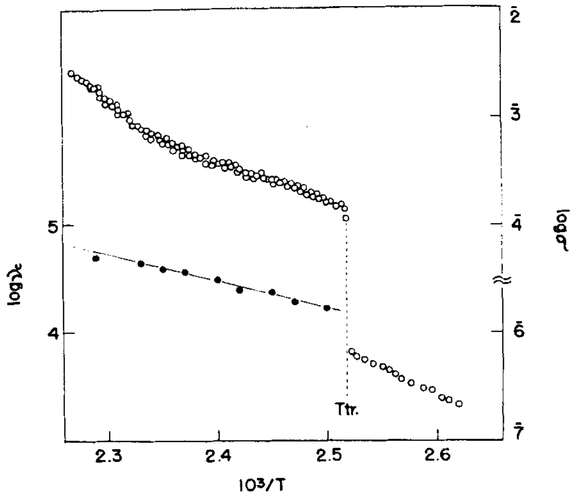

Figure 6. ● correlation frequency ν_c (cps) and ○ specific conductivity σ (ohm^{-1} cm^{-1}) of ammonium nitrate.

where σ denotes specific conductivity, λ_i transport number of the constituent ion, Z_i ion charge, N_i number of ions per unit volume, and the other constants have usual meanings. This equation was established to hold also for ionic crystals. As a first approximation, we may tentatively assume that dominant charge carriers in cubic NH_4NO_3 crystal are NH_4^+ ions. This assumption led us to calculate diffusion constant of ammonium ion from the observed conductivity data through the use of Nernst–Einstein's equation. The result is, for example, $D(\sigma) = 7.24 \times 10^{-9}$ cm²/sec at 416°K. Admitting the validity of these equations, the appreciable disagreement between the two D values as well as the two activation enthalpies obtained from n.m.r. and conductivity data suggests that conductive charges are transported mainly by NO_3^- ions in the cubic phase. The predominant anion conduction was also reported for the case of CsCl crystal.[25]

Alternatively, the conduction currents are transported by quite another species. Concerning the latter possibility, Staveley and his coworker[28] have recently proposed a proton switch model for a conductive mechanism of ammonium chloride crystal. This illustration is plausible because of the thermal instability of this material at relatively high temperatures. The detailed properties of d.c. conductivity of the ammonium nitrate crystal will be clarified by more comprehensive studies.

Discussion

I. CHEMICAL SHIFTS OF ACID

The chemical shift for carboxyl proton relative to that for methyl proton in trimethylacetic acid changes significantly in the solid as well as in the liquid phases when the temperature is raised. The temperature coefficient, $\Delta\delta/\Delta T$, of the OH shift is 1.0×10^{-2} ppm/°C in the liquid state and somewhat smaller than this in the solid state. This value is comparable in its magnitude with the cases of benzoic acid[29] (0.6×10^{-2} ppm/°C), of acetic acid[29] (1.3×10^{-2} ppm/°C) and of decanoic acid[30] (1.2×10^{-2} ppm/°C). Since it has been established that formation of a hydrogen bond results in a downfield shift of OH resonance signal, the observed shift to higher field on heating for hydrogen bonded systems has hitherto been explained by a shift in the association equilibrium that favors destruction of the hydrogen bond with increasing temperature.

Recently, Muller and Reiter[31] have interpreted the main origin of such a temperature variation in terms of thermal excitation of vibrational levels of associating, dimeric species. The chemical shift for the associated species depends quite strongly on the degree of excitation of hydrogen-bond-stretching vibrational mode with low frequency and, therefore, suffers a significant temperature variation when an appropriate average over these vibrational levels is used to evaluate the shift. By using the Morse potential function for the dimeric interaction, they have calculated $\Delta\delta/\Delta T$ values which lie between 0.2 and 0.8×10^{-2} ppm/°C for a number of potential constants. Although these values seem to be somewhat smaller than the average of the observed values for hydrogen-bonded substances cited above, $\Delta\delta/\Delta T$ value of the order of 1.0×10^{-2} ppm/°C will probably be ascribed to the dimeric species without taking into account association equilibria. In the case of trimethylacetic acid, the dielectric constant[32] of the solid and liquid phases is comparable in its magnitude with those for non-polar substances (2.63 at 20° C and 2.55 at 40° C). Also, the d.c. conductivity[32] of trimethylacetic acid crystal is of the order of 10^{-12} ohm^{-1} cm^{-1} and remains unchanged on melting. These observations as well as a small entropy of fusion of this material lead us to conclude that only dimeric species will probably exist in the solid and liquid phases not far above the melting point. Therefore, the new proposal concerning the temperature variation of chemical shift seems to be justified as far as trimethylacetic acid and similar hydrogen-bonded systems are concerned.

II. Self-diffusion in Plastic Crystals

Atomic diffusion phenomena in simple metals have been extensively studied with various methods by many investigators. In these cases, data obtained from n.m.r. and from radioactive tracer methods were generally in good agreement, and some attempts were made in correlating the activation enthalpy with various thermodynamic properties. In particular, Nachtrieb and his coworkers[33] have proposed the following, semi-empirical equation for body- and face-centered cubic metals:

$$\Delta H_D = 16.5 \Delta H_f$$

where ΔH_D is the activation enthalpy for diffusion, ΔH_f, the latent heat of fusion of the metal. This equation suggests that diffusion in cubic metals is in some way related to fusion. Based on this relationship they arrived at a mechanism for diffusion in which the elementary acts are not the creation and movement of a simple vacancy, but rather the creation of a small region of disorder (relaxion) whose movement through the crystal is the origin of positional exchange. In contrast to this viewpoint, the simple vacancy model would lead one to expect a connection with heat of sublimation.

On the other hand, very little is known about diffusion in molecular crystals owing to difficulties encountered in experimental techniques. Most of the diffusion data for molecular crystals were obtained by using n.m.r. techniques when applied to plastic crystals. We have already pointed out that a relation similar to the above equation holds for a hexamethyldisilane crystal[34] which was found to be plastic by calorimetric measurements.[35] It seems, therefore, to be of some interest to examine the transferability of this relation to other plastic crystals. The result of the plot of ΔH_D against ΔH_f shows a linear relationship for about ten plastic crystals (see Fig. 7). The proportional constant seems to lie between 12.5 and 13, being somewhat smaller than Nachtrieb's equation. It is interesting to note that no systematic relationship exists between ΔH_D and ΔH_s, the latent heat of sublimation. For example, xenon and cyclohexane crystals have similar values of ΔH_D in spite of the large difference in their latent heats of sublimation (3.8 and 8.5 kcal/mole, respectively), while the latent heats of fusion are quite similar in its magnitude (550 and 640 cal/mole). Data of ΔH_D, ΔH_f and ΔH_s of these plastic crystals are summarized in Table 1. The fact that crystals composed of monatomic molecules and plastic crystals fall on the same line in the ΔH_D–ΔH_f plot is expected from Nachtrieb's scheme and from our experimental knowledge of the general nature of plastic crystals. Plastic crystals generally have transition points where the constituting molecules gain freedom of pseudo-spherical rotation, and therefore have as small an entropy of fusion as those for monatomic crystals (2–3 e.u.). The situation that apparently, a similar mechanism is responsible for the diffusional process in plastic crystals as well as in cubic metals, in spite of their essential difference in cohesive forces, seems to be intimately connected with the fact that the cubic metals have entropies of fusion comparable with those of plastic crystals. In either event, more accurate data concerning the activation enthalpy for diffusion as well as thermodynamic properties for the other plastic crystals are required in order to draw a more definite conclusion.

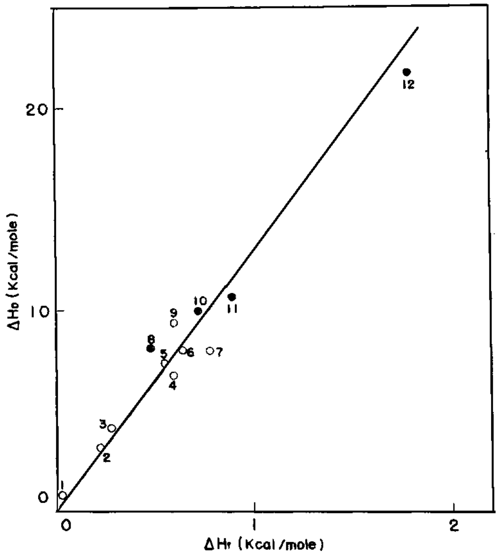

Figure 7. Activation enthalpy for diffusion plotted against latent heat of fusion for several plastic crystals. 1, H_2; 2, CH_4; 3, Ar; 4, CCl_4; 5, Xe; 6, C_6H_{12}; 7, $C(CH_3)_4$; 8, $C(CH_3)_3COOH$; 9, P_4; 10, $Si_2(CH_3)_6$; 11, $(CH_2CN)_2$; 12, $N(CH_2CH_2)_3N$.

Acknowledgement

The authors wish to express their sincere thanks to Dr. K. Asayama for the measurements of T_1, and to Mr. T. Ban for his technical assistance.

Table 1 ΔH_D, ΔH_f and ΔH_s for Various Plastic Crystals

No. in Fig. 7	Substance	Lattice	ΔH_D	ΔH_f	ΔH_s
			(kcal/mole)		
1	H_2	h.c.p.	0.79[a]	0.028	0.25
2	CH_4	f.c.c.	3.2[b]	0.225	2.18
3	Ar	f.c.c.	4.15[c]	0.28	1.85
4	CCl_4	f.c.c.	6.8[d]	0.60	7.8
5	Xe	f.c.c.	7.4[e]	0.55	3.6
6	C_6H_{12}	f.c.c.	8[f]	0.64	8.5
7	$C(CH_3)_4$	f.c.c.	8[g]	0.78	6.0
8	$C(CH_3)_3COOH$	f.c.c.	8.1	0.48[j]	14.1[j]
9	P_4	(b.c.c.)	9.4[h]	0.60	12.4
10	$Si_2(CH_3)_6$	b.c.c.	10[i]	0.72[k]	9.65[k]
11	$(CH_2CN)_2$	b.c.c.	10.7	0.885[l]	16.7[l]
12	$N(CH_2CH_2)_3N$	f.c.c.	21.7	1.775[m]	12.5[n]

ΔH_f and ΔH_s are based on data from the following books: *Selected Values of Chemical Thermodynamic Properties*, F. D. Rossini, ed., (U.S. Government Printing Office, Washington, 1952); J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds* (Elsevier Publ. Co., New York, 1950).

[a] Ref. 36. [b] Ref. 37. [c] Ref. 38. [d] Ref. 39. [e] Ref. 11. [f] Ref. 40. [g] Ref. 41. [h] Ref. 42. [i] Ref. 34. [j] Ref. 43. [k] Ref. 35. [l] Ref. 16. [m] Ref. 13. [n] Ref. 7.

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.

REFERENCES

1. Timmermans, J., *J. Phys. Chem. Solids* **18**, 1 (1961).
2. Andrew, E. R., *J. Phys. Chem. Solids* **18**, 9 (1961).
3. Suga, H. and Seki, S., *J. Phys. Chem. Solids* **24**, 330 (1963); *Bull. Chem. Soc. Japan* **35**, 1905 (1962).
4. Kubo, R. and Tomita, K., *J. Phys. Soc. Japan* **9**, 888 (1954).
5. Puntambecker, S. V. and Zoeller, E. A., "Organic Syntheses", Coll. Vol. I, John Wiley & Sons, Inc., New York, 1947, p. 524.

6. Farkas, A., Mills, G. A., Erner, W. E., and Maerker, J. B., *J. Chem. Eng. Data* **4**, 334 (1959); *Ind. Eng. Chem.* **51**, 1299 (1959).
7. Wada, T., Kishida, E., Tomiie, Y., Suga, H., Seki, S., and Nitta, I., *Bull. Chem. Soc. Japan* **33**, 1317 (1960).
8. Namba, H. and Oda, T., *Bull. Chem. Soc. Japan* **25**, 225 (1952).
9. Suga, H., Ban, T. and Seki, S. Read before "The Third Symposium on N.M.R.", under the auspices of Kinki Branch of Chemical Society of Japan, held at Osaka (1963).
10. Resing, H. A., *J. Chem. Phys.* **37**, 2575 (1962).
11. Yen, W. M. and Norberg, R. E., *Phys. Rev.* **131**, 269 (1963).
12. Kishida, E., Private communication.
13. Trowbridge, J. C. and Westrum, E. F., Jr., *J. Phys. Chem.* **67**, 2381 (1963).
14. Smith, G. W., *J. Chem. Phys.* **43**, 4325 (1965).
15. White, A. H. and Morgan, S. O., *J. Chem. Phys.* **5**, 655 (1937).
16. Wulff, C. A. and Westrum, E. F., Jr., *J. Phys. Chem.* **67**, 2376 (1963).
17. Finbak, C. and Viervoll, H., *Tidsskr. Kjemi Bergvesen* **2**, 35 (1942).
18. Fitzgerald, W. E. and Yanz, G. J., *J. Mol. Spectry.* **1**, 49 (1957).
19. Petrakis, L. and Rao, A., *J. Chem. Phys.* **39**, 1633 (1963).
20. Kelley, K. K., *J. Am. Chem. Soc.* **51**, 1400 (1929).
21. Averbuch, P., *C. R. Acad. Sci. Paris* **2**, 3147 (1957).
22. Reeves, L. W. and Stromme, K. O., *Can. J. Chem.* **38**, 1241 (1960).
23. Kelley, K. K., *U.S. Bur. Mines Bull.* 393 (1963).
24. Brown, R. N. and Mclaren, A. C., *Proc. Roy. Soc.* **266**, 329 (1962).
25. Laurent, J. F. and Bénard, J., *J. Phys. Chem. Solids* **3**, 7 (1957).
26. Barrer, R. M., *Diffusion in and through Solids* (Cambridge Univ. Press, London, 1951), p. 239.
27. Kracek, F. C., Hendricks, S. B., and Posnjak, E., *J. Am. Chem. Soc.* **54**, 2766 (1932).
28. Herrington, T. M. and Staveley, L. A. K., *J. Phys. Chem. Solids* **25**, 921 (1964).
29. Davis, J. C., Jr. and Pitzer, K. S., *J. Phys. Chem.* **64**, 886 (1960).
30. Reeves, L. W., *Trans. Faraday Soc.* **55**, 1684 (1959).
31. Muller, N. and Reiter, R. C., *J. Chem. Phys.* **42**, 3265 (1965).
32. Kondo, S. and Oda, T., *J. Chem. Soc. Japan* **27**, 565 (1954).
33. Nachtrieb, N. H. and Handler, G. S., *Acta Metallurgica* **2**, 797 (1954).
34. Yukitoshi, T., Suga, H., Seki, S., and Itoh, J., *J. Phys. Soc. Japan* **12**, 1189 (1957).
35. Suga, H. and Seki, S., *Bull. Chem. Soc. Japan* **32**, 1088 (1959).
36. Cremer, E., *Z. physik. Chem.* **B39**, 445 (1938).
37. de Wit, G. A. and Bloom, M., *Can. J. Phys.* **43**, 986 (1965).
38. Merné, A., Boato, G. and DePaz, M., *Nuovo Cimento* **24**, 1179 (1962).
39. Chihara, H., Otsuru, M., and Seki, S., *Bull. Chem. Soc. Japan* (in press).
40. Andrew, E. R. and Eades, R. G., *Proc. Roy. Soc.* **216A**, 398 (1953).
41. Powles, J. G. and Gutowsky, H. S., *J. Chem. Phys.* **21**, 1695 (1953).
42. Nachtrieb, N. H. and Handler, G. S., *J. Chem. Phys.* **23**, 1187 (1955).
43. Suga, H., Koide, T. and Seki, S., unpublished data.