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Molecular Rotational Relaxation in Liquids and Solids

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The rotation of molecules in the solid state presents a number of features of particular interest. Timmermans [1] has summarized the properties of organic materials showing this molecular rotation—they form plastic crystals with low heats of melting and of sublimation and the molecules concerned are of a “globular” or quasi-spherical form. Smyth [2] and coworkers amongst others, have shown that the dielectric properties of such solids approximate to those of the corresponding liquids, whilst Dr. Nora Hill [3] has given a very clear representation of the differences in the viscous and dielectric behaviour of the two classes of liquids whose molecules do and do not rotate in the crystal lattice.

The present study is concerned with such quasi-spherical molecules having a rigid dipole element. The dielectric properties of the liquids and solids have been measured principally in the region 250-920 Mc/s using the General Radio slotted-line apparatus (Williams [4]). The solids were prepared by carefully freezing the purified liquids, into which the coaxial line was immersed to a known depth. Frequently the liquids froze to a clear glass-like specimen, possibly forming essentially a single crystal. Repetition of such measurements led to satisfactorily reproducible dielectric constants and absorption: their internal consistency was further checked by temperature variation. For the liquid measurements a temperature range up to 100° C was used: for the solids the range was limited by the difference between the melting-point and the transition temperature at which “rotational freezing” occurs.

2 Chloro-2 nitropropane ($\text{CH}_3\cdot\text{C}(\text{NO}_2)\text{Cl}\cdot\text{CH}_3$) is a typical example of these compounds. At its m.p. (-22°C) there is virtually no change in the dielectric constant ($\epsilon'_0 = 29.0$) and this increases gradually until the transition point at -60°C is reached when it abruptly falls to 3.0.

Data for the solid are given in Table 1.

TABLE 1.

2 chloro-2 nitropropane. Dielectric properties of the solid.

| $t^\circ \text{C}$ | Mc/s | ϵ' | ϵ'' | $10^{10} \epsilon''/f$ | |
|----------------------|------|-------------|--------------|------------------------|---|
| — $25^\circ \pm 0.5$ | 897 | 28.7 | 3.48 | 38.7 | $(\epsilon_0 - \epsilon_\infty) = 26.3$ $\tau = 23.5 \times 10^{-12} \text{ sec.}$ |
| | 500 | 28.8 | 1.87 | 37.4 | |
| | 250 | 29.3 | 0.97 | 38.8 | |
| — 41.5 ± 0.5 | 897 | 30.2 | 4.56 | 50.8 | $(\epsilon_0 - \epsilon_\infty) = 27.5$ $\tau = 30.3 \times 10^{-12} \text{ sec.}$ |
| | 500 | 30.4 | 2.56 | 51.2 | |
| | 250 | 30.5 | 1.31 | 52.4 | |
| — $56 \pm 1^\circ$ | 897 | 30.0 | 6.03 | 67.2 | $(\epsilon_0 - \epsilon_\infty) = 28.2$ $\tau = 39.3 \times 10^{-12} \text{ sec.}$ |
| | 500 | 30.7 | 3.40 | 68.0 | |
| | 250 | 31.2 | 1.74 | 69.6 | |

These data have been evaluated in terms of the Eyring relation:

$$\tau = (h/kT) \exp [\Delta H/RT - \Delta S/R].$$

In this, it is best to regard $[\exp (\Delta S/R)]$ as an empirical correction term (P) to the frequency factor (kT/h) . The values thus found are:

for the solid: $\Delta H = 1.31 \text{ kcal/mole}$; $\Delta S = -4.2 \text{ c.u.}$; $P = 0.12$
 for the liquid: $\Delta H = 1.46 \text{ kcal/mole}$; $\Delta S = -3.5_5 \text{ c.u.}$; $P = 0.16$.

Although, as the dielectric constants indicate, there is the same range of rotational motion in the solid as in the liquid, in this case, the restriction on rotation in the solid is, if anything, slightly less than in the liquid. The activation energy for the viscosity process in the liquid $\Delta H (\eta) = 3.25 \text{ kcal/mole}$ is appreciably larger than for the molecular re-orientation and serves to emphasize the difference in the molecular mechanisms of rotational relaxation and viscosity for this type of liquid, i.e. the difference established by Dr. Hill.

Another example is methyl chloroform, CH_3CCl_3 whose m.p. is -33°C and "rotational freezing-point" -50°C . This means that the dipole rotation in the solid occurs over a range of only 17°C : however, if the relaxation times calculated for the supercooled liquid (τ_l) are compared with those observed for the solid (τ_s) at -38° and -48°C , the ratio τ_s/τ_l is 1.16 ± 0.01 at both temperatures. Thus, whilst no difference can be established between the dielectric activation energies for liquid

and solid at 1.12 kcal/mole, this is again less than half that for the viscosity of the liquid, $\Delta H(\eta) = 2.55$ kcal/mole.

Some of the other data are summarized in Table 2.

TABLE 2.
Dielectric Relaxations in Liquid and Solid States.

| | $t^\circ \text{ C}$ | $(\epsilon_0 - \epsilon_\infty)$ | $10^{12} \tau$ (sec) | | $t^\circ \text{ C}$ | $(\epsilon_0 - \epsilon_\infty)$ | $10^{12} \tau$ (sec) |
|----------------------------|---------------------|--|-------------------------|-------------------------|---------------------|---|-------------------------|
| Succinonitrile Liquid | 59 | 51.8 | 18.5 | t-Nitrobutane Liquid | 29.3 | 22.1 | 7.4 ₆ |
| | 65 | 50.5 | 16.4 | | 43.3 | 20.5 | 6.6 ₁ |
| | 74 | 48.4 | 14.3 | | 59.0 | 19.1 | 5.8 ₆ |
| | | ΔH (dielectric) = 3.2; ΔH (viscosity) = 3.9 | | | | ΔH (dielectric) = 0.9 ₇ ; ΔH (viscosity) = 3.36 | |
| Succinonitrile Solid | 25.5 | 62.1 | 61 | t-Nitrobutane Solid | -10 | 22.5 | 12.4 |
| | 39.8 | 57.8 | 49 | | +3 | 23.2 | 11.3 |
| | 50.0 | 55.0 | 43 | | 20 | 22.5 | 10.0 |
| | | ΔH (dielectric) = 2.0 ₈ | | | | ΔH (dielectric) = 0.5 ₅ | |
| ΔH 's in kcal/mole | | | | | | | |

Succinonitrile ($\text{NC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$) is not a good approximation to a spherical molecule and is a somewhat surprising example of rotation in the solid state. Its behaviour is possibly related to the fact that the solid, down to the transition temperature (-44°) consists of a mixture of trans and gauche isomers. The special circumstances of this case may account for the liquid ΔH (dielectric) being not very different from ΔH (viscosity). For *t*-nitrobutane ($(\text{CH}_3)_3\text{CNO}_2$) the dipole rotation has exceptionally low activation energies.

It is of some interest to assess the adequacy of simple absolute rate expressions for the rotational relaxation times. In addition to Eyring's well-known version

$$1/\tau = kT/h \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) = P_E kT/h \exp\left(-\frac{\Delta H_E}{RT}\right)$$

Bauer has deduced [5] an expression which can be written

$$1/\tau = \sqrt{\frac{kT}{2\pi I}} \cdot \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) = P_B \sqrt{\frac{kT}{2\pi I}} \exp\left(-\frac{\Delta H_B}{RT}\right)$$

Bauer's deduction gives a formal expression for $(\Delta S/R)$ and a similar pre-exponential factor has been used by Hoffman for a free-rotator. I is a molecular moment of inertia about an axis perpendicular to the dipole. As $(\Delta S/R)$ is essentially a configurational term, it has been replaced above by the numerical factor P : $\Delta S = 0$ would mean $P = 1$. The approach to this very simple condition is shown in Table 3.

TABLE 3.
Dielectric data for « spherical » liquids.

| | $(\text{CH}_3)_3\text{CCl}^a$ | $(\text{CH}_3)_3\text{CNO}_2^b$ | $(\text{CH}_3)_2\text{CCl}_2^a$ | $\text{CH}_3\text{CCl}_3^a$ | $(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{Cl}^b$ |
|--|-------------------------------|---------------------------------|---------------------------------|-----------------------------|---|
| ΔH (E) | 0.67 | 1.0 | 1.14 | 1.21 | 1.46 |
| P (E) | 0.11 | 0.11 | 0.18 | 0.25 | 0.16 |
| ΔH (B) | 0.96 | 1.3 | 1.45 | 1.49 | 1.56 |
| P (B) | 2.0 | 2.4 | 2.7 | 3.8 | 2.7 |
| <i>a</i> Data of Smyth and coworkers. <i>b</i> Data of Clemett. ΔH in kcal/mole. | | | | | |

It is clear that the P values all approximate to 1.0 far more closely than the similar factors in chemical reaction rate processes. This may be an expression of the simplicity of the molecular rotation processes in these instances—a simplicity which is perhaps measured by the strikingly small values of ΔH : that is, the process is almost a completely free rotation.

On average the Bauer expression gives a slightly better approach to $P = 1$ than does the Eyring relation and it may be physically significant that the departures from $P = 1$ expressed as $\log P$ or as ΔS , show this departure to be linearly related to ΔH —and somewhat more consistently so by the Bauer expression than by Eyring's.

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6. HOFFMAN and PFEIFFER, *J. Chem. Physics*, 22, 132, 1954.

DISCUSSION

M. B. Szigeti. — Why is the activation energy higher in the liquid than in the solid ?

MM. Clemett et Davies. — In calculating the relaxation times for the solids it was necessary to assume that the data fitted a simple Debye-type absorption, and though this may result in errors in the absolute magnitudes of the τ 's, the temperature dependence should not be markedly affected. The smaller values of ΔH found in the solids may result from the high symmetry of the crystal lattice in the rotator phase, which is cubic in all the cases discussed. When the crystals melt this symmetry is destroyed, thus possibly increasing the restriction to rotation, even though the free volume is slightly greater in the liquid.
