

Pressure dependence of self diffusion in the plastic crystals hexamethylethane, norbornylene and cyclohexane

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Abstract. Translational self diffusion in three molecular crystals has been studied as a function of pressure using nuclear spin-lattice relaxation time measurements. Activation volumes are obtained which are consistent with a vacancy diffusion mechanism.

Molecular crystals exhibiting a plastic crystalline phase are generally composed of globular molecules which are undergoing rapid reorientational motion. A consequence of this is that the entropies of fusion are low ($\Delta S_f \lesssim 20 \text{ eu}^\dagger$). It has been noted (eg Bladon *et al* 1971) for plastic crystals with relatively high entropies of fusion ($\Delta S_f > 17 \text{ eu}$) that the activation enthalpy for self diffusion, ΔH^* , is approximately twice the latent heat of sublimation, L_s . For these plastic crystals the activation enthalpies obtained by nuclear magnetic resonance (NMR) techniques are in good agreement with those obtained by radiotracer and creep measurements. Agreement between these techniques for materials with lower ΔS_f is not so good (Bladon *et al* 1971) and discrepancies have been tentatively attributed to relaxation around vacancies. It has been suggested (Jost 1960, Hood and Sherwood 1966a) that since L_s is a measure of the lattice energy, the observation that $\Delta H^* \simeq 2L_s$ implies a single vacancy mechanism for self diffusion. Plastic crystals with relatively low entropies of fusion ($\Delta S_f < 17 \text{ eu}$) have revealed self diffusion activation enthalpies, as determined by NMR, which are in the range $L_s < \Delta H^* \lesssim 2L_s$. This is consistent with vacancy formation parameters obtained by Baughman and Turnbull (1971) from analysis of excess heat capacity in similar systems. These authors suggest considerable vacancy relaxation may be responsible for the low vacancy formation enthalpies in the low ΔS_f materials. In the case of cyclohexane ($\Delta S_f = 9.2 \text{ eu}$) radiotracer measurements of the isotope effect have suggested that many neighbouring atoms (about twelve) are cooperatively involved in the microscopic diffusion step (Chadwick and Sherwood 1972.)

The temperature dependence of the proton spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, for hexamethylethane (Chezeau *et al* 1971), norbornylene (Folland *et al*, to be published) and cyclohexane (Roeder and Douglass 1970) has been measured under their equilibrium vapour pressures. The correlation times for translational self diffusion have been deduced for the plastic phase in each case. Self diffusion coefficients have also been determined by radiotracer studies in hexamethylethane (Lockhart and Sherwood, to be published) and cyclohexane (Hood and Sherwood 1966b). In the case of hexamethylethane ($\Delta S_f = 20 \text{ eu}$) results obtained by the two methods are in good agreement. However, for cyclohexane ($\Delta S_f = 9.2 \text{ eu}$) the activation enthalpy from radiotracer measurements ($\Delta H^* = 68.2 \text{ kJ mol}^{-1}$) differs significantly from the NMR

$\dagger 1 \text{ eu} \equiv 1 \text{ J K}^{-1} \text{ mol}^{-1}$

result ($\Delta H^* = 41.4 \text{ kJ mol}^{-1}$). At temperatures near the melting point the NMR relaxation measurements, interpreted using a vacancy diffusion model (Roeder and Douglass 1970), give values for the diffusion coefficient which are more than two orders of magnitude lower than radiotracer measurements. Tanner (private communication) has recently measured the self diffusion coefficient in cyclohexane using the pulsed field gradient NMR technique which shows good agreement with values calculated from the NMR relaxation results.

A powerful method with which to investigate the nature of the defect responsible for self diffusion in solids is to study the pressure dependence of a diffusion controlled process. Such measurements can be interpreted in terms of an activation volume, ΔV^* , for the diffusion process. In the case of metals, activation volumes are frequently found to be less than their respective molar volumes, V_m . This is taken to indicate inward relaxation of the surrounding atoms into a vacancy. Only one experimental investigation of the pressure dependence of self diffusion in organic molecular crystals has been reported previously (Anderson and Slichter 1966b). Very small activation volumes were found, with $\Delta V^*/V_m \approx 0.08-0.15$.

We have measured $T_{1\rho}$ for hexamethylethane and norbornylene at 296 K and for cyclohexane at 270 K, for hydrostatic pressures up to 2.8 kbar. Over most of this range $T_{1\rho}$ is entirely determined by modulation of intermolecular dipolar interactions by the relative translational motion of molecules. Impurity levels, estimated by vapour phase chromatography, for cyclohexane and norbornylene were less than 1000 ppm and 500 ppm respectively. The sample of hexamethylethane was that used previously (Chezeau *et al* 1971). Samples were degassed and contained in a glass cylinder sealed with a Kel-F plunger to transmit the pressure. Measurements were made at a Larmor frequency of 14.3 MHz and RF field strengths, H_1 , of 2.0 and 10.0 G. The spin-lattice relaxation times T_1 were also measured. T_1 is controlled by endospherical molecular reorientation over most of the pressure range investigated. Results for cyclohexane are shown in figure 1. The three substances chosen have different crystal structures as shown in table 1.

Table 1. Comparison of activation volumes ΔV^* with molar volumes V_m

	Crystal structure	ΔV^* ml mol ⁻¹	V_m ml mol ⁻¹	$\frac{\Delta V^*}{V_m}$	ΔH^* kJ mol ⁻¹	ΔS_f J K ⁻¹ mol ⁻¹
Hexamethylethane	BCC ^a $a_0 = 7.69 \text{ \AA}$	164	137	1.20	82.0 ^d	20.0 ^e
Norbornylene	HCP ^b $a = 6.08 \text{ \AA}$ $c = 9.81 \text{ \AA}$	86.4	94.6	0.90	48.9 ^e	10.1 ^h
Cyclohexane	FCC ^c $a_0 = 8.76 \text{ \AA}$	71.1	101	0.70	41.4 ^f	9.2 ⁱ

^a West (1934)

^b Jackson and Strange (1972)

^c Hassel and Sommerfeldt (1938)

^d Chezeau *et al* (1971)

^e Folland *et al* (1972, to be published)

^f Roeder and Douglass (1970)

^g Scott *et al* (1952)

^h Westrum (1969)

ⁱ Staveley (1962)