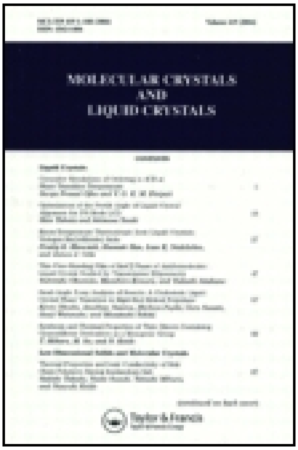

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Pressure Dependence of Translational Molecular Motion in Plastic Crystals

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Pressure Dependence of Translational Molecular Motion in Plastic Crystals

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The measurement of nuclear magnetic resonance (NMR) relaxation times provides a sensitive method for the investigation of molecular dynamics in a wide variety of materials; we report a detailed study of translational molecular self-diffusion as a function of temperature and pressure in the plastic phase of two organic molecular crystals.

The term "plastic" has been used to describe those solids with roughly globular molecules which crystallise in a lattice of high symmetry and exhibit considerable rotational disorder and a low entropy of fusion ($\Delta S_f \lesssim 2.5$ R). It has been found that the molecules execute translational self-diffusion and that the spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, is sensitive to this motion. The measured $T_{1\rho}$ values can be related to the mean molecular jump time τ, and to the self-diffusion coefficient by the use of an appropriate theory.[1–3]

The self-diffusive step is usually regarded as an activated process associated with a free energy ΔG^*:

$$\tau = \tau_0 \exp(\Delta G^*/RT). \tag{1}$$

Studies of the pressure dependence of the motion may be interpreted in terms of an activation volume, ΔV^*, defined by the relation

$$\Delta V^* = (\partial \Delta G^*/\partial P)_T. \tag{2}$$

The ratio of ΔV^* to the molar volume V_m is of particular interest in elucidating the diffusion mechanism. Assuming the pressure dependence of $\ln \tau_0$ to be negligible,[4] Equations (1) and (2) show that

$$\Delta V^* = RT(\partial \ln \tau/\partial P)_T. \tag{3}$$

The activation enthalpy ΔH^* is obtained by substituting $\Delta H^* = \Delta G^* - T\Delta S^*$ and assuming ΔS^* to be independent of temperature. Thus

$$\Delta H^* = R(\partial \ln \tau/\partial[1/T])_P. \tag{4}$$

Previous determinations of activation volumes for self-diffusion in a range of plastic crystals[4] suggest that translational motion in these materials generally proceeds by some sort of vacancy mechanism and indicate that the detailed nature of the motion is correlated with the entropy of fusion. The value of ΔS_f reflects the increase in disorder of the crystal on melting and thus may provide an indication of the relative disorder in the plastic phase. This might therefore be expected to be related to the degree of relaxation around a vacancy. A detailed study of the temperature and pressure dependence of both ΔV^* and ΔH^* has therefore been undertaken in a pair of isostructural b.c.c. plastic crystals with very different entropies of fusion. Hexamethylethane, $(CH_3)_3 \cdot C \cdot C \cdot (CH_3)_3$, hereafter referred to as HME, has $\Delta S_f/R = 2.42$, whereas its silicon analogue hexamethyldisilane (HMDS), $(CH_3)_3 \cdot Si \cdot Si \cdot (CH_3)_3$, has $\Delta S_f/R = 1.26$.

$T_{1\rho}$ measurements have been carried out in HME at five temperatures between 295 and 368°K for hydrostatic pressures up to 2.3 kbar. The variation of $\ln \tau$ with pressure is illustrated in Figure 1. Except at extreme low pressures and high temperatures, the activation volume was found to be independent of both pressure and temperature and of value $(1.12 \pm 0.05)\ V_m$. The activation enthalpy increases approximately linearly with pressure from 69.6 ± 1.1 kJ mol^{-1} at atmospheric pressure to 105.9 ± 1.2 kJ mol^{-1} at 2.07 kbar. As the temperature is increased, a second region corresponding to a higher activation volume of about 1.6 V_m appears at low pressures, suggesting a change in diffusion mechanism. The activation enthalpy associated with this region is also higher (93.0 ± 1.6 kJ mol^{-1}). It has been shown[5] that divacancies will be both stable and mobile at high temperatures and low pressures and that the onset of their participation in the diffusive process would be indicated by an increase in activation volume. The values of ΔV^* observed at high temperatures in HME are thus not inconsistent with a divacancy contribution to the diffusion. Both the BPP and Torrey models have been used to calculate τ. Figure 1 shows that in HME the activation volumes obtained for the two mechanisms are model-independent; however, the apparent change in mechanism occurs at a slightly higher pressure according to the Torrey interpretation.

HMDS has been studied at six temperatures between 253 and 339°K, from atmospheric pressure to 2.7 kbar. Plots of $\ln \tau$ vs pressure are non-linear at all temperatures, as illustrated in Figure 2. At low pressures, the activation volume is approximately independent of pressure and temperature, and of value $(0.55 \pm 0.03)V_m$. In this region, the activation enthalpy is (42.4 ± 2.2)

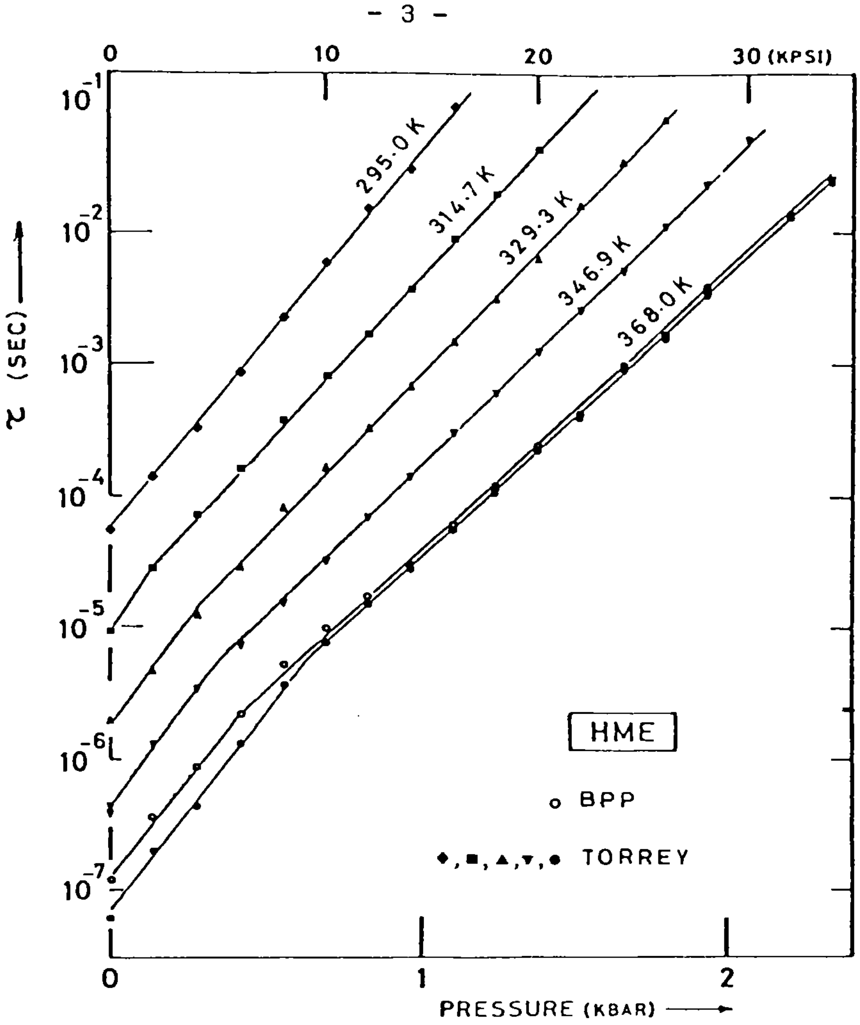

FIGURE 1

kJ mol^{-1} in the temperature range covered, a value which is only weakly, if at all, dependent on the pressure. As the pressure is increased, two further regions may be distinguished, corresponding to successively lower values of both ΔH^* and ΔV^*, and in which ΔV^* apparently decreases with increasing temperature. In the intermediate pressure region the activation volume ranges from $(0.44 \pm 0.02)V_m$ at 271°K to $(0.26 \pm 0.01)V_m$ at 339°K. In the high pressure region, it decreases from $(0.30 \pm 0.01)V_m$ at 253°K to $(0.17 \pm 0.01)V_m$ at 339°K. These results can be interpreted in terms of changes in

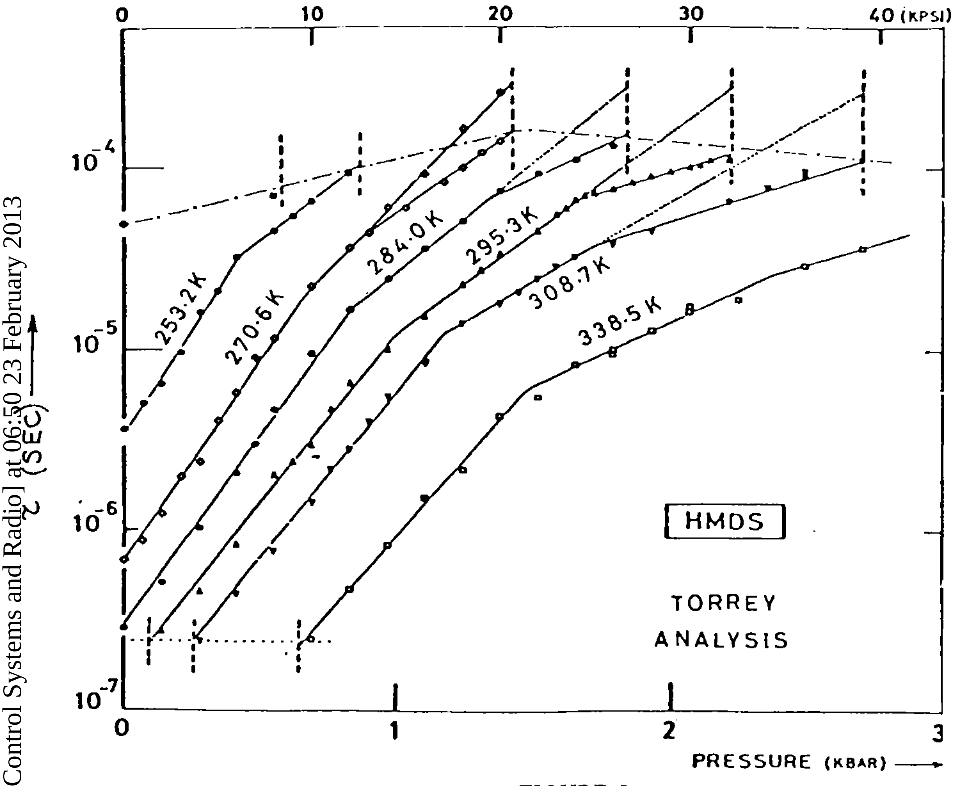

FIGURE 2

the self-diffusion mechanism with pressure, which might be associated with structural modifications of the plastic phase. Figure 2 also shows that the correlation time for self-diffusion at the melting temperature (2.4 or 4.0 × 10^{-7} sec, depending on the model used) is independent of pressure within experimental uncertainty. Similar behaviour has been found in another plastic crystal, cyclohexane.[6]

In conclusion, it would appear that the high entropy of fusion compound HME has a large activation volume which is independent of pressure and temperature over most of the range covered; it is possible that there may be a divacancy contribution to the diffusion at low pressures and high temperatures. The smaller activation volume observed in the low ΔS_f compound HMDS suggests that the vacancies are more highly relaxed. The diffusional behaviour is much more complex in this material than in HME and there is evidence to suggest that self-diffusion may proceed by more than one mechanism, a phenomenon which may indicate the existence of high pressure structural modifications within the plastic phase.

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