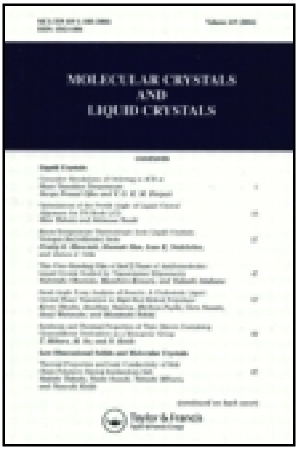

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Self-Diffusion in Single Crystals of Plastic Pivalic Acid

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Self-Diffusion in Single Crystals of Plastic Pivalic Acid

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In rotationally disordered molecular solids such as pivalic acid, the mechanism of diffusion and the point defects involved are still in question. N.m.r. and tracer diffusion results, for example, disagree; it is often supposed that these discrepancies correlate with the perfection of the crystal studied.

Pivalic acid rotator phase is stable between 279.9° K and $T_M = 309.5°$ K. This phase has FCC symmetry, but monomers are linked by hydrogen bonding. The plastic phase is a disordered assembly of dimers stretched along the twofold axes.[1]

1 EXPERIMENTAL PROCEDURE

Tracer self-diffusion was studied using the thin layer method and the serial sectioning technique.[2] The samples used were constituted of single crystals of 99.9999 % purity containing 10^5–10^6 dislocations/cm^2.[3]

The radioactive tracers were composed of either $(CH_3)_3C—^{14}COOH$ or a mixture of $(CD_3)_3C—^{14}COOH$ and $(CH_3)_2(CH_2T)C—COOH$.

The diffusion anneals were performed at temperatures between 281 and 301°K. The anneal period was chosen so that $\sqrt{Dt} \simeq 100\,\mu$m.

2 RESULTS

2.1 Activation energy of self-diffusion

Analysis of the concentration–penetration curves shows that the serial sectioning data fit the Fick's solution characteristic of bulk diffusion:

$$C(x, t) = C_0/(\pi D t)^{1/2} \exp - (x^2/4Dt) \qquad (1)$$

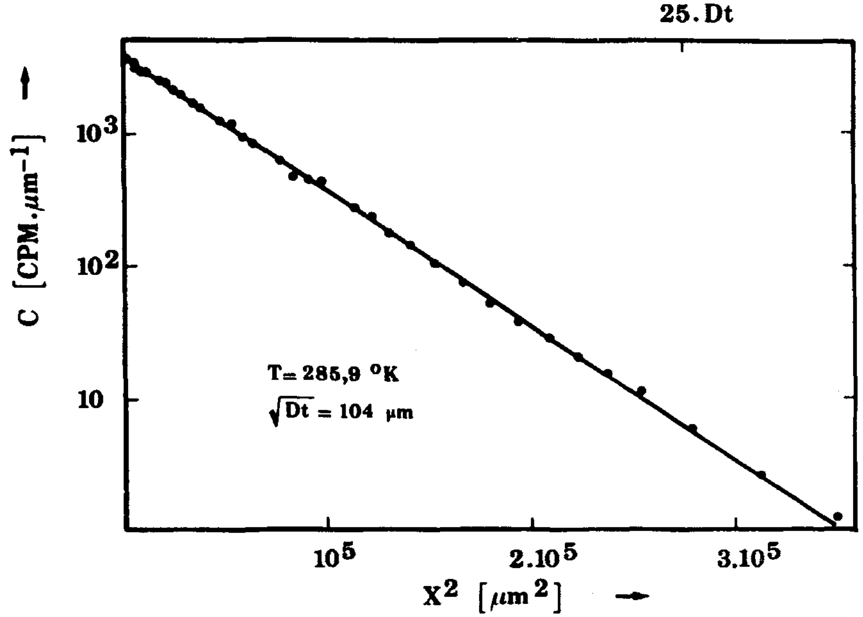

FIGURE 1 Specific activity due to the molecules labelled with ^{14}C versus the square of the penetration depth x. Typical concentration–penetration curve.

C is the concentration of the diffusing material at a distance x into the crystal after time t; C_0 is the amount of tracer per unit of area at $x = 0$ and $t = 0$; D is the self-diffusion coefficient. In the present case $C(x, t)$ can be represented by the specific activities C and T of the slices due to the molecules labelled with ^{14}C or tritium. The activity versus penetration curves are linear over more than two order of magnitude in C (or T) before reaching the background level at a penetration depth of 4 to 6 $\sqrt{Dt}$ (Figure 1).

The diffusion coefficients calculated from Eq. (1) by the least-mean square method are plotted Figure 2. The temperature dependence of D is described by an Arrhenius equation:

$$D(\mathrm{m}^2\,\mathrm{s}^{-1}) = (2.4 \pm 1.5)10^{-4} \exp - \frac{58 \pm 2}{RT}\,(\mathrm{kJ\ mole}^{-1}).$$

2.2 Isotope effect

The two tracers diffusing simultaneously during an experiment have masses of $m_C = 113$ g/mole (molecules labelled with ^{14}C) and $m_T = 104$ g/mole (molecules labelled with ^3H). When the diffusion is described by relation 1,

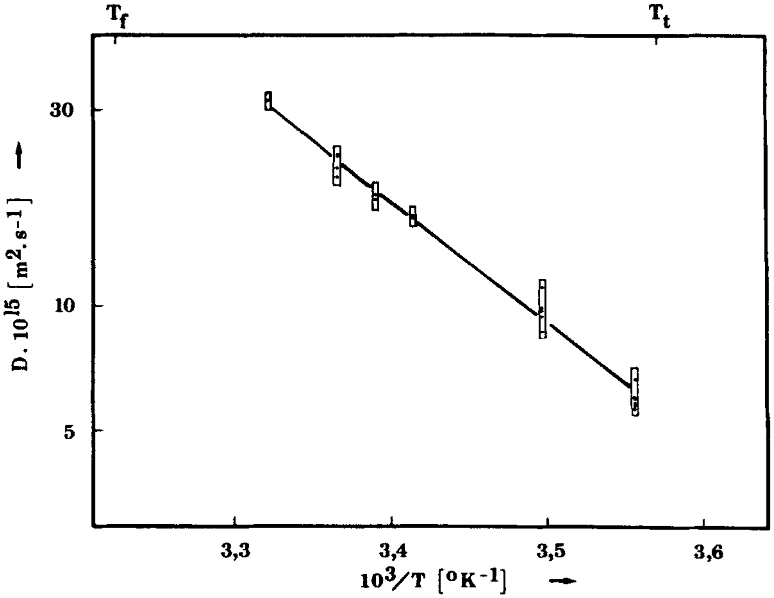

FIGURE 2 Temperature dependence of the lattice self-diffusion coefficient T_t = transition point; T_f = melting point.

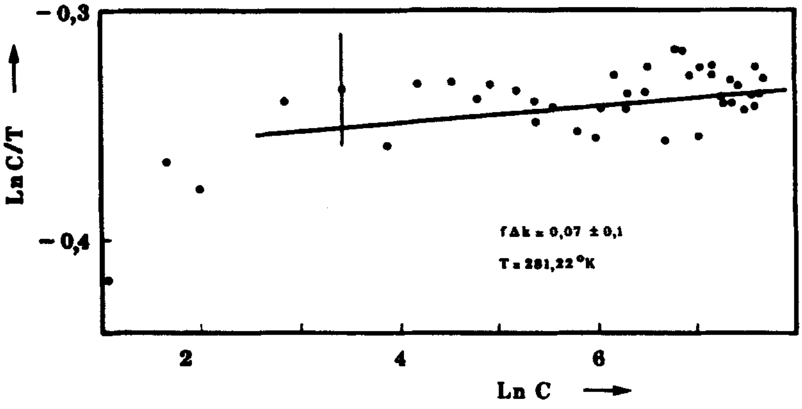

FIGURE 3 Typical Ln C/T against LnC for isotope-effect experiments.

the specific activities C and T of the two tracers are related by:[4]

$$
\begin{aligned}
LnC/T &= \text{const.} - [D_C/D_T - 1]LnC \\
&= \text{const.} - f\Delta k[(m_T/m_C)^{1/2} - 1]LnC \qquad (2)
\end{aligned}
$$

where D_C and D_T are the diffusion coefficients of the two tracers of masses m_C and m_T respectively; f is the correlation factor characteristic of the lattice symmetry and of the diffusion mechanism; Δk is related to the distribution of the kinetic energy among surrounding molecules or to the molecular displacements during the diffusive step. Figure 3 shows a typical result plotted in the form of Eq. (2). The mass factor $E = f\Delta k$ calculated by the least-mean square method for each experiment has a mean value of:

$$E = 0.13 \pm 0.13.$$

3 DISCUSSION

The activation-penetration curves are characteristic of a diffusion mechanism controlled by bulk-diffusion. In such materials, even at high temperature ($>0.9\ T_M$), some authors consider the possibility of an enhancement of the diffusion process by the dislocations.[5,6] This effect could be analysed[4] in these experiments, given the pipe diffusivity in pivalic acid using the Hart analysis. If we extrapolate to pivalic acid the results obtained in adamantane rotator phase,[6] we conclude that a dislocation density of 10^8 cm^{-2} would be necessary to enhance the lattice self-diffusion coefficient by a few per cent at the lowest temperature (281°K). Therefore, the activation energy and the mass factor measured are certainly characteristic of bulk self-diffusion in plastic pivalic acid. The agreement between the activation energies obtained during this work and those measured previously by n.m.r. ($E_D = (63 \pm 5)$ kJ mole^{-1},[7] $E_D = 54.8$ kJ mole^{-1})[8] confirm this conclusion. In the case of pivalic acid there is no discrepancy between n.m.r. and our tracers measurements.

The difference between the former tracer diffusion study which yields $E = (91.24 \pm 0.42)$ kJ mole^{-1} [9] and the present result may be attributed to the difference in the impurity contents of the samples (99.98 % instead of 99.9999 %).

The value of the activation energy is roughly equal to the latent heat of sublimation. Extrapolating the rare gas models to the other molecular solids, such a low value of E_D is generally interpreted in term of a diffusion process involving a relaxed molecular vacancy defect. A vacancy type defect agrees with all previous point defect studies in molecular crystals.[5] The hypothesis of a relaxed vacancy defect has been pointed out previously in n.m.r. studies of plastic solids with low entropies of fusion.[10,11] This hypothesis agrees with a low value of the mass factor.

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