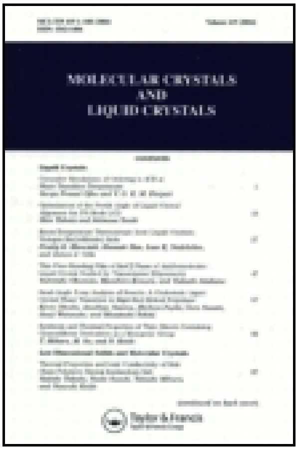

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Self-Diffusion in Eicosane Single Crystals

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Self-Diffusion in Eicosane Single Crystals

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Radiotracer, serial sectioning studies of self-diffusion have been made in ultra-pure single crystals of the triclinic phase of *n*-eicosane ($C_{20}H_{42}$) in the temperature range 295–309 K. The crystals of this solid readily undergo plastic deformation. Consequently, crystals grown from the melt (Bridgman Technique) contain a high concentration of dislocations, slip bands and polygonized boundaries. Diffusion along these defects (pipe-diffusion) contributes significantly to the total penetration of radioactivity and hence decreases the precision with which lattice self-diffusion coefficients can be evaluated. An attempt is made to assess this interference and to correct data.

As might be expected in such anisotropic materials, there is a significant difference in self-diffusion parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the basal (001) planes. The latter can be shown with reasonable precision to follow a temperature dependence.

$D_{\perp} = 9 \times 10^{44} \exp(-341 \pm 18 \text{ kJ mol}^{-1}/RT)$. The former cannot be defined due to the greater interference of pipe diffusion in the basal planes.

Diffusion probably proceeds by vacancy migration.

INTRODUCTION

Up to the present time, studies of self-diffusion in organic molecular solids have been confined to the examination of solids comprising small molecules. The results of these studies[1] show that the dominant mode of self-diffusion is by vacancy migration and that the process is isotropic within the experimental error, even in the most anisotropic lattices examined. In contrast, a small but distinct anisotropy has been detected in highly perfect crystals of the inorganic molecular solid orthorhombic sulphur.[2] In extremely anisotropic organic materials such as the higher *n*-alkanes not only are anisotropic diffusion processes more likely but it has been suggested that the diffusion mechanism may vary in different crystallographic directions; whole molecule or segmental translation occurring as appropriate. This suggestion plus the increasing interest in the nature of point defects in this type of solid, coupled with their influence on such experiments as mechanical relaxation,[3,4] has led us to examine self-diffusion in a typical linear saturated hydrocarbon, *n*-eicosane, using the radiotracer, serial-sectioning technique.[1]

EXPERIMENTAL

Single crystals of ultra-pure, *n*-eicosane (99.998 % purity, vapour phase chromatography) were prepared from zone-refined material[5] using a Bridgman technique.[6] Full details of the preparation and characterization of the crystals are given elsewhere.[5] The resulting boules of the triclinic form,[7] 1.5 cm diameter × 10 cm long were cleaved or cut and polished to yield specimens $1 \times 1 \times 0.5\ \mathrm{cm}^3$ with the large face parallel or perpendicular to the (001) cleavage plane. The cleaved (001) faces were ready for immediate use. Etching of the cleavage surfaces yielded a high concentration of dislocation etch-pits (10^4–$10^5\ \mathrm{cm}^{-2}$) and numerous slip traces.[5] Non-basal surfaces exhibited densely packed slip traces consistent with easy basal slip. We estimate these to be 5–10 times more concentrated than the slip lines on the cleavage plane.

Radioactive *n*-eicosane-1,2-^{3}H was prepared by the catalytic reduction of *n*-1,2-eicosene in dioxan over palladium black using tritium.[8]

The procedure of application of the tracer to the crystal and subsequent annealing, sectioning (18 μm sections) and liquid scintillation counting to determine the penetration profile of diffused radioactivity, have been described in detail elsewhere.[1] Experiments were carried out with the tracer diffusing either parallel or perpendicular to the (001) planes at temperatures in the range 295–309 K. The crystals passed the phase transformation temperature (307 K) without transforming or fracturing.

RESULTS AND DISCUSSION

For the chosen geometry of the diffusion couple, the concentration of diffused radioactivity A will vary with depth x, into the crystal and time, t, according to the expression[1]

$$A = \frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \qquad (1)$$

Q is the total activity applied to the crystal surface at $t = 0$. D is the diffusion coefficient. As can be seen from Figure 1, log A against x^2 plots are nonlinear and have the shape characteristic of mixed lattice and dislocation/

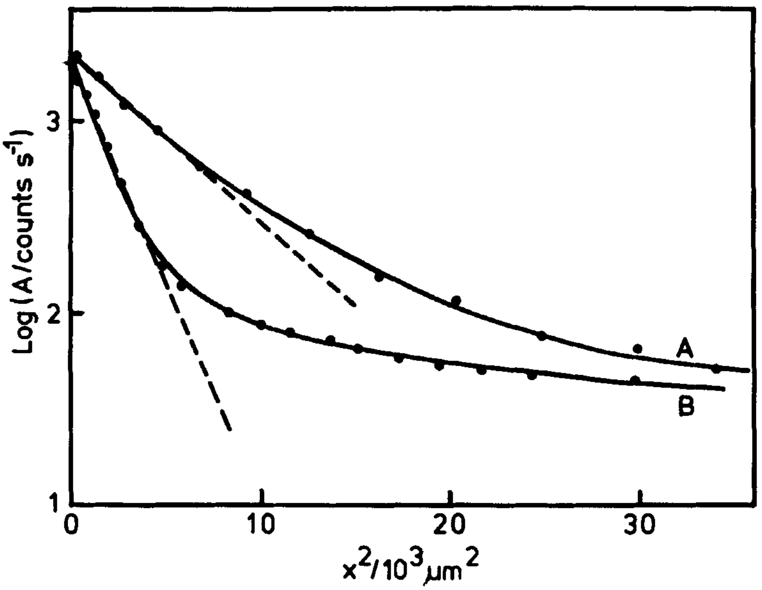

FIGURE 1 Log A against x^2 plots for self-diffusion parallel (A) and perpendicular (B) to the (001) plane in n-eicosane A. 4.97 × 10^5 s, 303.3 K, B. 2.08 × 10^5 s, 305.2 K.

grain-boundary (pipe) diffusion.[1] It is usually accepted that the initial linear portion of the curve satisfactorily represents lattice self-diffusion. On this basis we have evaluated the self-diffusion coefficients parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the basal (001) plane. These are quoted in Table I and are plotted as a function of reciprocal temperature in Figure 2. The two lines are adequately represented by the equations:

$$D_{\perp} = 9 \times 10^{44} \exp(-342 \pm 18 \text{ kJ mol}^{-1}/\text{RT}) \tag{2}$$

$$D_{\parallel} = 8 \times 10^{13} \exp(-161 + 5 \text{ kJ mol}^{-1}/\text{RT}) \tag{3}$$

At first sight, it would appear that there is a distinct anisotropy of self-diffusion with, understandably, diffusion in the basal plane being faster and of lower energy than non-basal diffusion. That this relative differential is correct is confirmed by reference to Figure 1 which demonstrates that more rapid penetration of radioactivity occurs in basal directions than in non-basal directions under similar conditions. Before concluding that Figure 2 represents the absolute situation however, it is necessary to recall that the influence of pipe-diffusion in each case is significant and to question its contribution to overall penetration in the near surface regions.

Hart[9] has shown that, where the concentration of defect pipes in the crystal is high, then one may evaluate from the near surface regions of the log A

TABLE I

Evaluated self-diffusion coefficients for non-basal ($D_\perp$) and basal ($D_\parallel$) self-diffusion in crystalline *n*-eicosane.

Diffusion perpendicular to the basal plane

T/K	10^{-3} K/T	$D_\perp/\mathrm{m}^2\,\mathrm{s}^{-1}$
296.1	3.378	2.22×10^{-17}
299.5	3.339	1.84×10^{-16}
303.3	3.297	8.59×10^{-16}
306.2	3.265	3.61×10^{-15}
307.9	3.248	5.61×10^{-15}

$D_\perp$ (melting point) = $1.45 \times 10^{-14}\,\mathrm{m}^2\mathrm{s}^{-1}$

Diffusion parallel to the basal plane

T/K	10^{-3} K/T	$D_\parallel/\mathrm{m}^2\,\mathrm{s}^{-1}$
296.7	3.371	9.71×10^{-16}
298.3	3.352	1.55×10^{-15}
305.2	3.277	8.32×10^{-15}
307.2	3.255	1.08×10^{-14}
309.2	3.234	1.95×10^{-14}

$D_\parallel$ (melting point) = $2.40 \times 10^{-14}\,\mathrm{m}^2\,\mathrm{s}^{-1}$

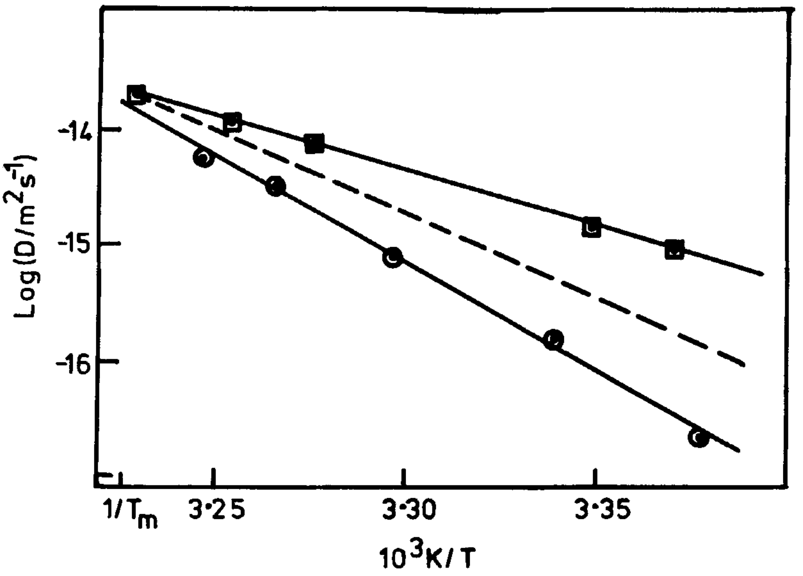

FIGURE 2 Log D against $1/T$ for self-diffusion in *n*-eicosane perpendicular ○ and parallel ☐ to the (001) plane—data uncorrected for pipe-diffusion. The dotted line represents the estimated upper limit of values of $D_\parallel$ for true lattice self-diffusion.

against x^2 plot an overall D related to the lattice diffusion coefficient D_l and pipe-diffusion coefficient D_p as follows:

$$D = gD_p + (1 - g)D_l \tag{4}$$

where g is the fraction of diffusing activity in the pipes. Thus, since $D_p > D_l$,[1] D will also be greater than D_l. Also since the corresponding activation energies $E_p < E_l$,[1] the evaluated activation energy will be less than the true lattice value. In order to determine the overestimates, if any, values of D_p are required.

Methods of analysis of mixed lattice and pipe diffusion using the deep penetration portions of the diffusion penetration curve have been proposed by Whipple[10] and Suzuoka.[11] Both yield a relationship of the form

$$D_p\delta = \left[\frac{\mathrm{d}(\ln A)}{\mathrm{d}x^{6/5}}\right]^{-5/3} \cdot \left[\frac{4D_l}{t}\right]^{1/2} \cdot A^{5/3} \tag{5}$$

where δ is the average width of the pipe. In regions beyond the direct range of lattice diffusion, the parameter $A = 0.78$ for both solutions.[12] From plots

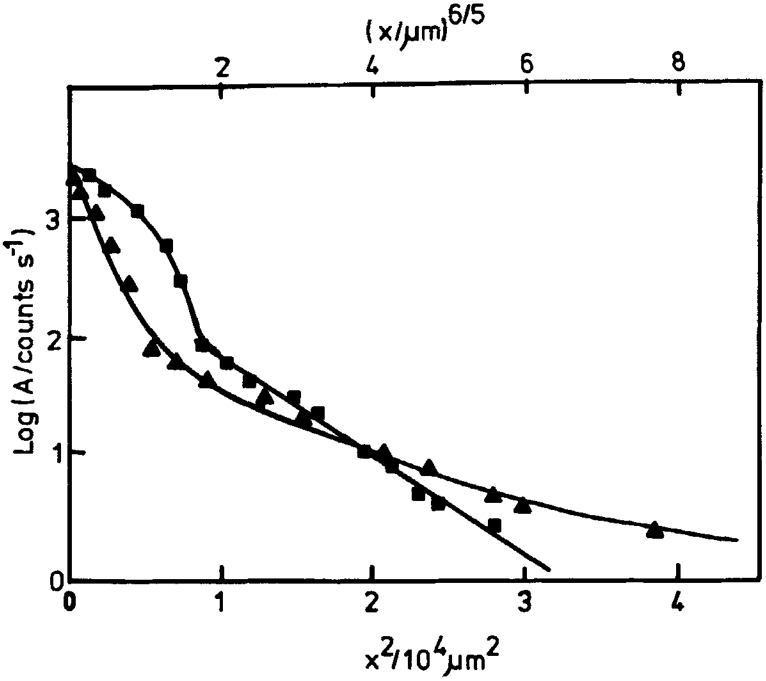

FIGURE 3 Log A against x^2 (▲) and log A against $x^{6/5}$ (■) plots for self-diffusion perpendicular to the (001) plane in polycrystalline n-eicosane (3.2×10^5s, 298.3 K).

of ln A against $x^{6/5}$ (Figure 3) under reasonable conditions of penetration and accepting a value of $\delta = 5$ nm (10 molecular diameters) we evaluate that D_p lies in the range 10^{-10}–10^{-11} m^2 s^{-1} over the temperature range used in the initial experiments.

For self-diffusion in the [001] direction we have identified two types of pipe defect: dislocations in concentrations of 10^4–10^5 cm^{-2} and slip traces.[5] We estimate that the former will contribute a fraction $g \simeq 5 \times 10^{-9}$ (5×10^4 dislocations cm^{-2} $\times$ 10 molecules per dislocation $\times$ 10^{-14} cm^2 molecule^{-1}). From the measured width and density of the slip traces we assess that the contribution from this source will be no greater than that due to the dislocations. Using this sum ($g = 10^{-8}$) and the maximum value of $D_p \simeq 10^{-10}$ m^2 s^{-1} we find (Eq. 4) that the overestimate of D_l due to this cause will vary from zero at the maximum temperature to, at most, 10% at the minimum. Thus, within the experimental error, the evaluated values of $D_\perp$ represent lattice self-diffusion.

For basal diffusion, similar values were obtained for D_p. We have no estimates of the basal dislocation content but the observation of densely packed slip traces as noted above suggest values of $g \simeq 10^{-7}$ which could result in over-estimates of D at the lower temperatures by 50% or more and parallel underestimates of the activation energy. Thus we must conclude that although there are strong indications of anisotropy in self-diffusion, crystals of the present quality are inadequate to define this distinction, other than perhaps close to the melting temperature where the overestimate will be smaller.

Accepting that the estimates of the pre-exponential factor (D_0) and activation energy (E_d) (Eq. (2)) for non-basal diffusion are more correctly descriptive of lattice self-diffusion in this direction, we can speculate on the possible mechanism.

The activation energy $E_d = 2.1L_s$(L_s = lattice energy, 164 kJ mol^{-1}), an equivalence noted previously[1] as corresponding to the expected activation energy for self-diffusion by vacancy migration in molecular solids. The pre-exponential factor appears to be high in comparison with data for other types of solid[1] and yields a correspondingly high entropy factor: $\Delta S_d = 874$ J mol^{-1} K^{-1}. ($D_0 = \gamma a^2 \nu \exp \Delta S_d/R$ where γ is a geometrical factor, a the mean jump distances and ν a lattice vibrational frequency). This is considerably higher than values for other anisotropic molecular crystals (300–400 J mol^{-1} K^{-1}) but not unreasonably so if we consider the increased molecular and structural complexity of the system. In fact, invoking a vacancy mechanism and accepting that E (vacancy formation) $\simeq L_s$ and that the vacancy fraction N_v at the melting point will be 10^{-3} yields $\Delta S_v = 471$ J mol^{-1} K^{-1} ($N_v = \exp - G_v/RT$ where G_v is the free energy of vacancy formation) a figure in satisfactory relationship to that for self-diffusion. We conclude that, as for other organic molecular solids, non-basal self-diffusion in *n*-eicosane proceeds via a whole molecule vacancy migration mechanism. Further experiments are in course to test this speculation.

Acknowledgements

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