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Self-diffusion and the isotope-mass-effect in stearic acid single crystals

R. S. NARANG, J. N. SHERWOOD
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland

Self-diffusion parallel to the molecular axis in melt-grown crystals of the monoclinic "*c*" form of stearic acid has been examined in the temperature range 320 to 340 K using the radiotracer serial-sectioning technique. The results are best described by an expression of the form $D = 4 \times 10^{33} \exp(-314 \pm 4\,\text{kJ mol}^{-1}/RT)\,\text{m}^2\,\text{sec}^{-1}$. The value of the pre-exponential factor and activation energy are similar, relatively, to those obtained previously for other organic solids and are consistent with self-diffusion by a vacancy mechanism. Isotope-mass-effect measurements yielded mass factors $E_{ab} = f\Delta K = 0.3 \pm 0.04$. For vacancy migration in a simple monoclinic lattice $f_v \simeq 0.6$, thus $\Delta K \simeq 0.5$. This is not an unreasonable value of ΔK. It is argued however that values of f for vacancy diffusion in such anisotropic lattices as stearic acid could be significantly lower than expected.

1. Introduction

Recent studies of radiotracer self-diffusion in the linear chain alkane, *n*-eicosane ($C_{20}H_{42}$) [1] have shown that self-diffusion is likely to proceed by a vacancy mechanism. This solid is highly plastic. Consequently, melt-grown crystals contain a high concentration of dislocations and sub-grain boundaries. The simultaneous diffusion of radiotracer along these defects masks the true lattice process and analysis is difficult. In an attempt to define the nature and energy of the self-diffusion process in solids which comprise this type of molecule, we have extended our measurements to the more brittle solid, stearic acid. Since the molecules exist as dimers in the solid state [2] the molecule is effectively linear $C_{17}H_{35}COOH–HOOCC_{17}H_{35}$ i.e. approximately twice the length of *n*-eicosane. Thus it offers the opportunity to examine the influence of chain length on diffusion rate. An isotope-mass-effect study was also carried out in an attempt to confirm the mechanism of diffusion.

2. Experimental

Reagent grade stearic acid (99.29% purity, vapour phase chromatography) was readily purified by zone-refining (50 passes of a 2 cm zone at $1\,\text{cm h}^{-1}$) to yield a sample of 99.995% purity. Vapour phase chromatography (5% FFAP on a Chromosorb column) showed that the initial material contained six major impurities. The final material contained only one impurity (> 1 ppm level) which was identified as palmitic acid.

Single crystals of excellent quality were grown from this material by a Bridgman Technique [3]. These were of the "*c*" form which is monoclinic, space group $P2_1/a$ with $a = 0.936$ nm, $b = 0.496$ nm, $c = 5.075$ nm, $\beta = 128^\circ\,14'$ and $Z = 4$ [2]. The crystals, which cleaved readily on the (0 0 1) basal plane, were cut into pieces 1 cm × 1 cm × 0.5 cm with large faces parallel to the (0 0 1) plane.

Solvent etching using acetone at 283 K followed by a water wash showed that the crystals contained 10^5 to 10^6 dislocations cm^{-2} emergent on both basal and non-basal planes. In spite of the apparent brittleness of this material, slip occurs readily on the basal plane. Microscopic examination of annealed crystals showed that these slip dislocations readily polygonize to yield sub-grain boundaries parallel to the basal plane. Few such boundaries aligned in directions normal to this. The total concentration of these defects was significantly lower than in eicosane, but as a consequence of our experience with that material,

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measurements on stearic acid were restricted to the direction perpendicular to the basal plane, i.e. parallel to the molecular axes.

Tritiated stearic acid (chain labelled) was purchased from the Radiochemical Centre, Amersham. ^{14}C labelled deuterated stearic acid was prepared from the inactive deuterated acid (0.5 g) by a series of reactions involving the preparation of the silver salt, conversion of this to *n*-heptadecyl bromide, exchange of the bromine with K ^{14}CN (250 μCi) and hydrolysis to yield $^{12}C_{18}{}^{2}H_{37}{}^{14}COOH$.

The radiotracers (^{3}H labelled for the self-diffusion studies and the mixed tracer for the isotope-effect studies) were dissolved in ether and painted onto one large surface of a pre-annealed crystal. The ether rapidly evaporated to leave a uniform thin (1 to 2 μm) deposit on the crystal surface.

The crystal and deposit were heated for periods of 2 to 10 days in the temperature range 320 to 340 K prior to sectioning on a microtome and assaying of the sections for penetrated radioactivity by scintillation counting. Fuller details of these procedures are given elsewhere [4].

3. Results

3.1. Self-diffussion studies

Under the experimental conditions used, the concentration of diffused activity (A) should vary with depth of penetration (x) and time (t) as [4]

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

where Q is the total activity deposited on the surface of the crystal at the start of the experiment and D is the self-diffusion coefficient.

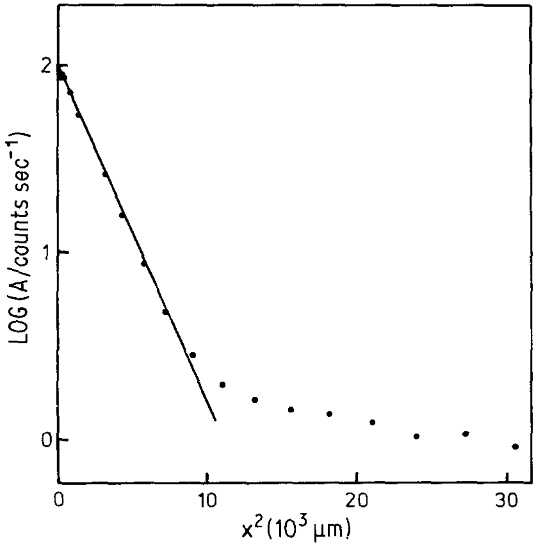

Figure 1 Plot of $\log A$ against x^2 (Equation 1) for self-diffusion parallel to the molecular axis ([0 0 1] direction) in stearic acid. $T = 340.54$ K, $t = 2.43 \times 10^5$ sec.

The experimental diffusion profiles ($\log A$ versus x^2, Fig. 1) show the departure from linearity characteristic of simultaneous lattice and dislocation/grain boundary (pipe) diffusion. The portion of the curve at lower penetrations is dominated by the lattice process. It has been shown [1] for other molecular solids of equivalent defect content, that a satisfactory representation of the lattice self-diffusion coefficient can be obtained from the slope of the initial portion of the curve. Attempts to refine this value by subtraction of the pipe contribution extrapolated from the deep penetration part of the profile or by more detailed analysis using pipe self-diffusion coefficients evaluated from measurements on samples of low quality, yielded little improvement within the overall error [1].

Diffusion coefficients determined in this way are reported in Table 1 and Fig. 2. The latter shows that within experimental error the values exhibit the expected temperature dependence which can best be expressed as

$$D = 4 \times 10^{33}$$
$$\times \exp(-314 \pm 4\,\text{kJ mol}^{-1}/RT)\,\text{m}^2\,\text{sec}^{-1}. \qquad (2)$$

The value of D at the melting point is $D_m = 6.82 \times 10^{-15}\,\text{m}^2\,\text{sec}^{-1}$.

Thermodynamic theories of the diffusion process based on point defect mechanisms lead to an expression for the diffusion coefficient of the form [4]

$$D = \gamma f a^2 \nu \exp(\Delta S_d/R) \exp - (E_d/RT) \qquad (3)$$

γ is a geometrical factor, f, the correlation factor, a, the lattice parameter and ν, the lattice vibrational frequency. ΔS_d and E_d are entropy and energy terms associated with the formation (f) and migration (m) of the defect ($\Delta S_d = \Delta S_f +$

TABLE I Lattice self-diffusion coefficients in stearic acid for diffusion parallel to the [0 0 1] direction

T (K)	K/T ($\times 10^3$)	D (m^2 sec^{-1})
327.32	3.0551	2.73×10^{-17}
333.45	2.9989	2.55×10^{-16}
3335.19	2.9834	4.23×10^{-16}
337.96	2.9589	1.11×10^{-15}
340.54	2.9365	2.27×10^{-15}

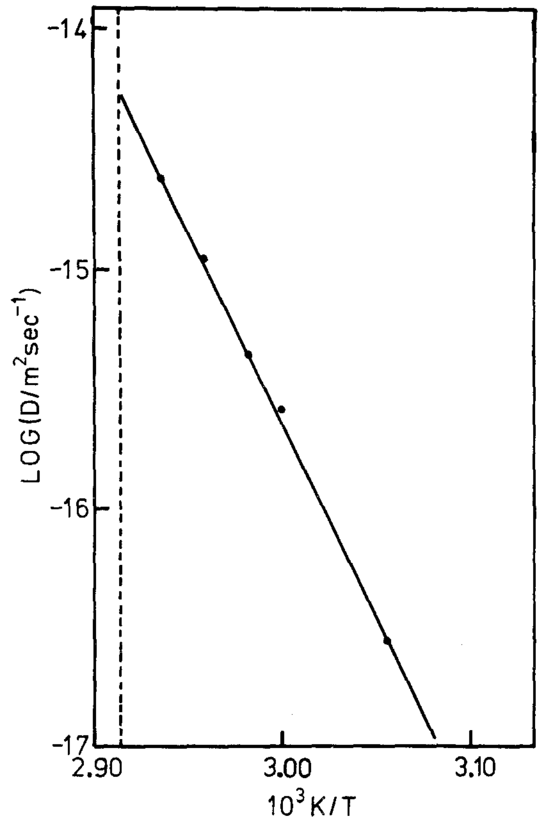

Figure 2 Arrhenius plot for self-diffusion parallel to the (0 0 1) direction in stearic acid.

ΔS_m, $E_d = E_f + E_m$). Insertion of reasonable values for γ, f, a and ν leads to the evaluation of $\Delta S_d \simeq 700\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

The correlation factor f noted above arises as a consequence of the non-random nature of the tracer diffusion process. f has a specific value which depends only on the nature of the lattice and the mechanism of diffusion. Its evaluation and comparison with theoretical values for different mechanisms has been successfully used to define or at least indicate likely mechanisms [5].

It can be shown [5] that for two tracers of different mass, m_C and m_T, the diffusion coefficients are related to the mass by

$$\left(\frac{D_C}{D_T} - 1\right) = E_{ab}\left[\sqrt{\left(\frac{m_T}{m_C}\right)} - 1\right] \qquad (4)$$

The mass factor $E_{ab} = f\Delta K$ where ΔK is a factor, $\leqslant 1$, related to the distribution of kinetic energy amongst surrounding molecules during the diffusion step. Evaluation of D_C/D_T allows the definition of E_{ab}.

This can be carried out experimentally by the simultaneous diffusion of two differently labelled tracers of different mass [5]. In the present case $({}^{12}C_{17}{}^{2}H_{27}{}^{14}COOH)_2$–$m_C$ and $({}^{12}C_{17}{}^{1}H_{34}{}^{3}H_1{}^{12}COOH)_2$–$m_T$. The distribution of activity in the crystal following diffusion is then given by the two logarithmic forms of Equation 1

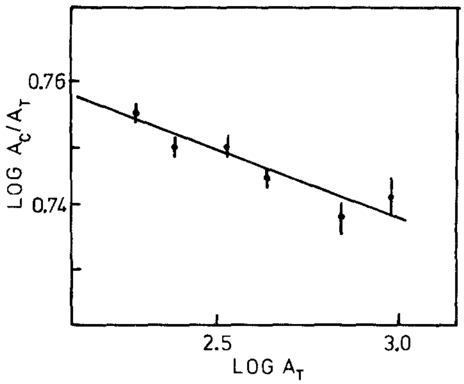

Figure 3 Plot of $\log A_C/A_T$ against $\log A_T$ (Equation 5) for stearic acid.

$$\ln A_C = \text{const.} - x^2/4D_C t$$

$$\ln A_T = \text{const.} - x^2/4D_T t$$

Combining these equations we have

$$\ln A_C/A_T = \ln A_T(D_T/D_C - 1) + \text{const.} \qquad (5)$$

Fig. 3 shows a plot of $\log A_C/A_T$ against $\log A_T$ for one experiment. Two such experiments yielded values of $E_{ab} = 0.30 \pm 0.04$ (337.9 K) and 0.33 ± 0.05 (334.5 K).

4. Discussion

No calculations have been made of the correlation factors for self-diffusion in monoclinic systems. Reasonable estimates can be made for the simple mechanisms.

Interstitial and exchange processes occur by random migration [5]. Thus $f = 1$, a value considerably in excess of the present experimental E_{ab}. Furthermore, interstitial molecules are not energetically favoured in such close-packed lattices [4], an argument which can also be used to eliminate the possibility of interstitial type processes. This leaves vacancy migration as the most probable mechanism.

For vacancy migration in an isotropic lattice, a satisfactory upper limit to the correlation factor has been shown to be $f_v = (1 - 2/X)$ where X is the coordination number of the lattice. The coordination of stearic acid is similar to that of naphthalene (also monoclinic, $P2_{1/a}$) where we have argued that the most probable molecule-vacancy exchanges will occur with the four neighbouring molecules lying in $\frac{1}{2}$ [1 1 0] and $\frac{1}{2}$ [1 $\bar{1}$ 0] directions or with the two molecules in the [0 0 1] directions. Thus $Z = 6$ and $f_v \leqslant 0.66$. For naphthalene [6] experimental values of $E_{ab} = 0.6$ were obtained to confirm this analysis i.e. $\Delta K \simeq 1$.

The present value of $E_{ab} = f \Delta K = 0.30$ is considerably lower than this estimate. The difference can be interpreted in several ways. It could be taken to imply that the vacancy motion occurred with a significant involvement of the surrounding lattice molecules; $\Delta K \simeq 0.5$. Such a conclusion would not be unreasonable and values of this order have been both experimentally observed and theoretically confirmed in some b c c solids [5]. In general, however, ΔK values are higher in the close-packed solids [5]. With one exception, hexamethylethane, all organic materials so far examined have yielded values of $E_{ab} \simeq f_v$ [7]. In the case of hexamethylethane, [8] on the basis of accumulated evidence from several types of measurement, the lower value of E_{ab} (= 0.52) could be best ascribed to a contribution from divacancy motion ($f_{\text{vacancy}} = 0.72$, $f_{\text{divacancy}} = 0.48$). There is no additional evidence to support a similar suggestion in the present case.

Before accepting that $\Delta K \simeq 0.5$, it seems appropriate to question whether or not the estimate of f_v is satisfactory for the present material. Naphthalene is a rigid molecule and the lattice has a relatively low anisotropy ($\frac{1}{2}$ [1 1 0]/$c = 0.6$). Stearic acid is a flexible molecule and the lattice anisotropy is 0.1. This must have a significant influence on the various jump probabilities and on the effective coordination number. If so this could yield a marked reduction in f_v particularly since diffusion is being examined in the direction of greatest anisotropy. It would require that $X \rightarrow 3$ for $f_v \rightarrow 0.3$. It could be argued that this was not unreasonable.

Until more calculations of correlation factors appropriate to such anisotropic lattices are performed, we can only conclude that a vacancy mechanism of diffusion is most likely and that the process may be accompanied by some lattice disordering.

This conclusion is confirmed by the direct diffusion measurements which yield an activation enthalpy of diffusion 314 kJ mol^{-1} equal to 1.9 L_s (the latent heat of sublimation $L_s = 166$ kJ mol^{-1}) an equivalence which also can best be interpreted as reflecting vacancy diffusion. The extremely high value of ΔS_d can be similarly interpreted since, accepting that the vacancy concentration will reach 10^{-3} of the vacancy fraction at the melting point and that $E_v = L_s$ yields $\Delta S_v \simeq 400$ J mol^{-1} K^{-1}.

Finally we note with interest that $D_m = 6.82 \times 10^{-15}$ m^2 sec^{-1} a value not significantly different to that found for other brittle solids of lower molecular weight. We conclude that increasing chain length has little influence on self diffusion rate.

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