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Self-diffusion in Phenanthrene Single Crystals

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Abstract—Studies have been made of self-diffusion in phenanthrene single crystals at temperatures above the motional transition. The results show that, in spite of the increased molecular mobility at these temperatures, the self-diffusion proceeds with characteristics similar to those found for other polycyclic aromatic hydrocarbon solids.

Studies of self-diffusion in single crystals of the polycyclic aromatic hydrocarbons,[1-3] benzoic acid[4] and imidazole[5] have yielded similar relative values for the energies and entropies of the diffusion process. More recent experiments on single crystalline benzene[6] gave similar relative energies but significantly lower entropies. This difference could be associated with the difference in crystal structure between benzene (orthorhombic) and the other solids (monoclinic) or alternatively with the difference in molecular freedom in the lattice. In order to investigate more fully the influence of molecular freedom on the diffusion process we have extended our studies to include other mobile systems. The present note describes the results of an investigation of self-diffusion in phenanthrene.

Phenanthrene is a polycyclic hydrocarbon which at room temperature forms monoclinic crystals.[7] At 345 K it undergoes an endothermic transition[8] which, according to the present evidence, seems more associable with the onset of a limited molecular motion in the solid rather than with a gross crystallographic change.[9] This solid therefore presents an opportunity for the study of self-diffusion in a monoclinic system in which there is an excessive molecular motion.

1. Experimental

Diffusion experiments were carried out in the usual manner[1-4] using single crystals of phenanthrene (total impurity content < 1 p.p.m., dislocation content 10^4–10^5 cm^{-2}.[10] Full details of the purification and crystal growth procedures are given elsewhere.[11] The crystals were pre-annealed for 10 days at 369 K prior to the diffusion experiments. The radiotracer, phenanthrene-9-^{14}C (specific activity 1 μCi mg^{-1})[12] was applied to (001) faces from acetone solution. No effect of solvent penetration was observed. Crystals with the deposits were heated in nitrogen at temperatures in the range 336 K to 369 K for periods of up to 600 h. Great care was taken during the heating and cooling periods, both in the pre-annealing and diffusion experiments, to ensure that the temperature did not change rapidly in the transition region. No obvious physical consequences of the transition were discernible on subsequent examination.

2. Results and Discussion

The results were analysed using the solution of Fick's equation for diffusion from a thin source of total activity Q into a semi-infinite solid, namely

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

where A is the specific activity of the radiotracer at a depth x into the crystal after time t. D is the diffusion coefficient. Plots of $\log A$ against x^2 were linear over the full measured range ($x > (4Dt)^{1/2}$). Values of the diffusion coefficient evaluated from the slopes of the plots are shown plotted as a function of temperature in the usual way in Fig. 1.

The temperature dependence of the five high temperature points are adequately described by the equation:

$$D = 3 \times 10^{13} \exp - (202/RT) m^2 s^{-1}$$

where $R = 8.314$ kJ mol^{-1} k^{-1}.

The linearity of the ($\log A$, x^2) plots implies that interference from diffusion along sub-grain boundaries in the solid is negligible. It does not rule out the possibility of enhancement from diffusion along

dislocations.[1] For a crystal containing $\sim 10^5$ dislocations cm^{-2}, it can be shown that such effects become important when the ratio of the lattice diffusion coefficient to that in the dislocation is less than 10^{-7}. Assuming a similar relationship between the two processes for phenanthrene as for the solids naphthalene[1] and anthracene,[3] this ratio will not be exceeded until 346 K ($1/T = 2.89 \times 10^{-3}$). Below this temperature the measured diffusion coefficients may be higher than the true values. This is more probably the true cause of the final high point on Fig. 1, rather than the alternative possibility; that it represents the behaviour of the low temperature form.

As found for other organic solids,[13] the activation energy for diffusion is approximately double the latent heat of sublimation of the solid (88 kJ mol^{-1}). Evaluation of the entropy of diffusion from

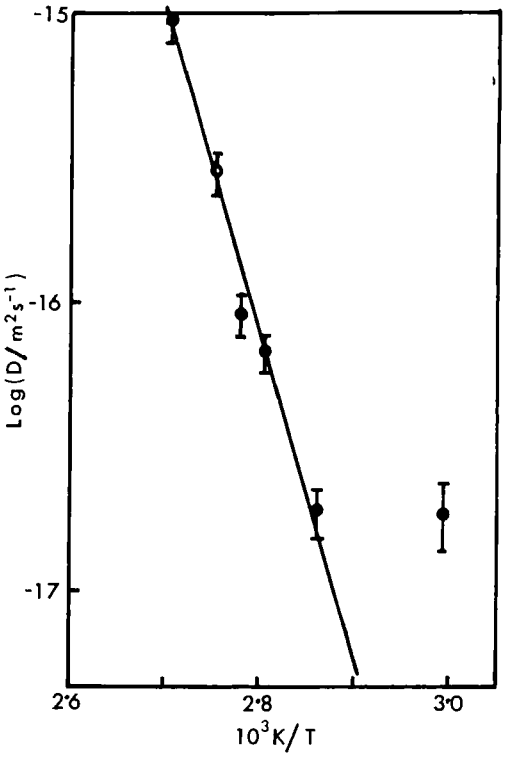

Figure 1. Plot of log D against $1/T$ for self-diffusion in phenanthrene in the ⟨001⟩ direction.

the pre-exponential factor[13] yields a value of $S_d = 368$ J mol^{-1} k^{-1} in agreement with the range of 280 to 334 kJ mol^{-1} k^{-1} found for the other polycyclic hydrocarbon crystals. This similarity indicates that, in spite of the increased molecular motion in the solid, the self-diffusion process maintains similar characteristics to those found in systems with less mobile molecules.

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