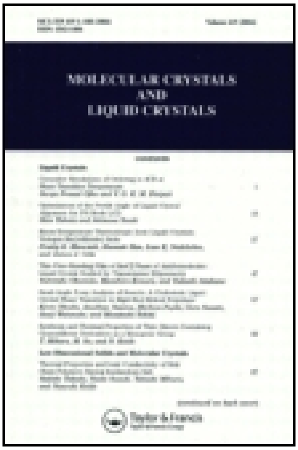

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Isotope Exchange Studies of Self-Diffusion in Organic Plastic Crystals

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INTRODUCTION

A technique that has been fairly extensively used in the study of self-diffusion in ionic[1] and rare gas crystals[2,3] is the isotopic vapour exchange technique. In these experiments the kinetics by which isotopically labelled molecules exchange between the bulk solid and vapour phases is monitored. The rate determining step in this process is the diffusion rate in the solid since the exchange of molecules at the interface and diffusion in the vapour are both relatively fast. Provided that the surface area involved in exchange, A, can be determined then self-diffusion coefficients in the solid, D, can be evaluated. Compared to the conventional serial sectioning technique of determining diffusion coefficients this technique requires considerably less "handling" of the specimen and is ideally suited for the study of solids with low melting points and volatile solids. Organic plastic crystals have relatively high vapour pressures and in some cases present handling problems. There is considerable interest in diffusion in these crystals[4] and we have developed apparatus for their study by the isotopic vapour exchange technique.

Several methods can be employed to study the isotopic vapour exchange; the isotopically labelled molecules (tracers) can be initially in the vapour or solid phase, dependent on the type of labelling the tracer can be monitored mass spectrometrically or with radiotracer detectors. When radiotracers are used the usual experimental arrangement is to follow the exchange of labelled solid with a roughly equal mass of unlabelled vapour and monitor the tracer concentration in the vapour. If mass spectrometric detection is employed then the tracer concentration of labelled vapour is monitored as it exchanges with unlabelled solid. The boundary conditions for the solution of the diffusion equation are different in the two experiments, however, in both cases the exchange kinetics are governed by A^2D and it is this product which is evaluated.

The kinetics for the radiotracer experiment is relatively simple and is given in Ref. 5.

$$N_t^2 = \left(\frac{2AC_0}{\pi^{1/2}}\right)^2 Dt \tag{1}$$

where N_t is the number of tracer atoms in the vapour at time t and C_0 is the initial tracer concentration of the solid. If the exchange is followed at a seres of temperatures then[5]

$$N^2_{(t_1+t_2\cdots t_i)} = \left(\frac{2AC_0}{\pi^{1/2}}\right)^2 (D_1t_1 + D_2t_2 \cdots D_it_i) \tag{2}$$

where D_i and t_i are the diffusion coefficient and time at temperature i.

EXPERIMENTAL

Two separate sets of apparatus have been constructed; one to perform radiotracer experiments above 243K (system 1) and one to perform radiotracer and mass spectrometric experiments above 63 K (system 2). The upper temperature limit in both systems is room temperature and the major difference is in the cell which holds the crystal. In system 1 the cell was constructed of glass and crystals could be visually inspected. The mass spectrometer used was a Vacuum Generators Micromass 6 and the counter operated with a CaF_2–Eu doped scintillation detector. The counter was constructed in our laboratory and had the advantage of a reasonably high gas phase efficiency e.g. 4 percent (^3H), 35 percent (^{14}C), and was not contaminated by organic vapours.

The essentials of the radiotracer system are shown in Figure 1. The lowest temperature that can be studied for any system is governed by the fact that the circulating pump will only operate at pressures above 10 Torr. There is a

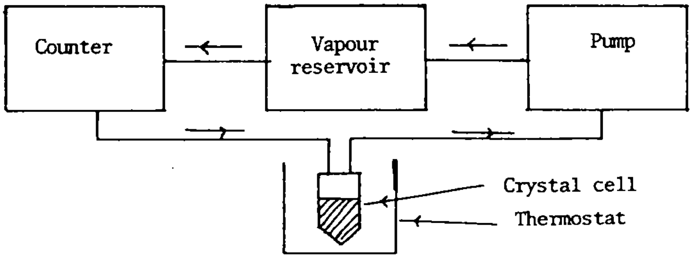

FIGURE 1

similar limit for the mass spectrometer experiment set by the sensitivity of the spectrometer.

Preliminary radiotracer measurements were made on tertbutyl thiol and more extensive measurements on norbornylene in system 1. The tracers used were ^{35}S-thiol and ^{3}H-norbornylene. Mass spectrometric measurements were made on methane using ^{13}C tracer.

RESULTS

The radiotracer experiments that were made on *tert*-butyl thiol confirmed the feasibility of these experiments. Tracer containing material was condensed into the cell as a liquid and a crystal grown by the Stockbarger technique. The exchange was followed in a number of crystals close to the melting point (274.6 K). The observed exchange was fitted by Equation 1 which proved the mixing of the vapour was efficient and the temperature control was adequate. The diffusion coefficients agreed roughly with those evaluated from NMR measurements.

The norbornylene crystals were grown from the vapour and contained at most three grains. Experiments were performed on as-grown crystals, still visibly attached to the cell walls, and on crystals that were detached from the walls by slight evaporation. For each crystal measurements were made at three temperatures between 273 and 290 K and the results fitted to Equation 2. In the case of "attached" crystals A was taken as the top, exposed crystal area whereas for "detached" crystals it was assumed to be the total crystal area. D from the first temperature runs of attached crystals was in fair agreement with the value from sectioning measurements,[6] being about 50 percent higher. The activation energy, Q, for attached crystals was abnormally high which suggests that on increasing the temperature the crystal is becoming detached and A has increased. For the detached crystals Q agreed well with the sectioning data but D was too high by a factor of 10. We concluded that in the process of detaching the crystal grain boundaries were opened up and A, although constant in each experiment, was larger than expected.

The mass spectrometric measurements on methane followed by the procedure developed by Bernè *et al.*[7] which uses thin films. We found it impossible to evaluate D and concluded that the grain size was too small to make the usual assumption that the film was semi-infinite. It appears that the assumption was also invalid in the work on rare gas crystals.[3, 7]

From our work it would appear that the isotopic vapour exchange technique is useful for the determination of D and Q in plastic crystals provided both attached and detached crystals are studied.

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