RADIOACTIVE STUDIES OF DIFFUSION IN POLYMER SYSTEMS

PART 2.—THE SYSTEM *ISO*PENTANE + POLY*ISO*BUTENE

BY G. S. PARK
Courtaulds Ltd., Research Laboratory, Maidenhead, Berks.

Received 27*th July*, 1956

A method for measuring the self-diffusion coefficient in mixtures of polymer with volatile liquids is given. The synthesis of tritio*iso*pentane is described. The self-diffusion coefficients of *iso*pentane in poly*iso*butene + *iso*pentane mixtures at 25° C and 35° C have been obtained at a few concentrations of the *iso*pentane. These coefficients are much larger than the integrated mean of the chemical diffusion coefficient but agree well with the intrinsic diffusion coefficient. The experiments are not accurate enough to indicate whether a thermodynamic correction should be applied.

In recent years there have been many studies of the diffusion of liquids or vapours into polymers from which the so-called chemical diffusion coefficients D have been obtained. It has been shown that in many cases this coefficient increases rapidly with increase in the concentration of the small molecular species.[1] To correlate these concentration-dependent diffusion coefficients with molecular motions it is necessary to obtain an independent measure of these motions in the absence of the complicating factors due to the gradient in chemical composition.

In part 1 [2] of this series a technique was described for using a radioactive tracer to measure diffusion coefficients in polymer systems in the absence of changes in chemical composition. It is convenient to call this the self-diffusion coefficient, $\mathscr{D}^*$, though strictly this term should be used only for single component systems. The technique involved the welding together of two slabs of polymer + solvent mixtures of the same chemical composition. Radioactive labelled solvent was used in one slab and its migration to the other slab was obtained from the change in β radiation strength at the face of the second slab.

Unfortunately this method is only suitable for non-volatile substances. A new method had to be developed for measuring $\mathscr{D}^*$ in polymer + volatile solvent mixtures and for this work it was decided to investigate the poly*iso*butene + *iso*pentane system. The chemical diffusion coefficients [3, 4] and the vapour pressure-composition curves [5] had already been determined and this provided data helpful to the planning of the self-diffusion experiments as well as being useful for the interpretation of the results obtained. *iso*Pentane was chosen rather than one of the other hydrocarbons because its boiling point is reasonably low (28° C) which makes experimentation easier by enabling vapour pressures of the order of $\frac{1}{2}$ atm to be used.

EXPERIMENTAL

MATERIALS

POLY*ISO*BUTENE.—This was a specimen obtained from I.C.I., Billingham. Its quoted molecular weight was 92,000. It was dissolved in a mixture of benzene and carbon tetrachloride and precipitated in the form of a fine filament in cold acetone to remove low molecular weight impurities. Films were made by casting a solution in the benzene + carbon tetrachloride mixture on a mercury surface.

TRITIO*iso*PENTANE.—*iso*Pentane labelled with tritium was prepared by reaction of tritiated water, obtained from Harwell, with *iso*amyl magnesium bromide. About 40 g of this Grignard compound was made in ether solution. The ether was removed by heating at 120° C for 2 h in a 3-l. vessel connected to the vacuum system. 2 cm^3 of tritiated water having an activity of about 20 millicuries were distilled into the vessel which was next closed off and heated at 120° C for a further period of 2 h. This gave a 70 % yield of tritio*iso*pentane based on the water. It was purified from *iso*pentene, ether and water by treatment with concentrated sulphuric acid, acid potassium permanganate, and alkali. The final product, after outgassing had a vapour pressure against temperature relationship in good agreement with that given by the American Petroleum Institute.[6] Less active samples of *iso*pentane were made by dilution with inactive *iso*pentane.

INACTIVE *iso*PENTANE.—This was made by a similar method to the above but an excess of dilute acid was used instead of tritiated water to decompose the Grignard compound.

ARGON.—Cylinder argon obtained from the British Oxygen Company was dried but no further purification was attempted.

THE DIFFUSION APPARATUS

The apparatus is shown diagrammatically in fig. 1. The principle of the apparatus is simple. A polymer specimen S, cemented to a glass plate P, is equilibrated with a fixed pressure of radioactive vapour in the chamber C. The vapour in C is then replaced with " chemically identical " inactive vapour at the same pressure. The rate at which this vapour becomes radioactive by diffusional exchange is then obtained by taking samples of the vapour as it is circulated through the sampling tap T_1. Three features of the apparatus require special mention.

THE SAMPLING TAP T_1.—A tap is arranged so that the contents of the bore (about 2 cm^3) can be isolated and distilled into a sampling tube J. While this is occurring all the ports of the tap are closed and so vapour circulation is continued through the by-pass tap T_2. After taking a sample, T_8 can be closed and the bore of the tap can be refilled with inactive vapour from G. On turning the tap back to the open position the pressure of vapour in the circulating system is maintained by the inactive vapour and allowance can be made for the slight change in specific activity that this causes. With T_1 in the open position another tube J can be evacuated through the barrel of the tap ready for the next sample.

THE CIRCULATING PUMP E.—The vapour is circulated through the specimen chamber and sampling tap by means of an all-glass circulating pump. The design of this pump is not very different from the one given by Brenschede.[7] The soft iron core is, however, shorter and fatter and only one coil working against gravity is used for oscillating the piston. The coil is made of P.V.C. insulated flexible wire so that the whole pump can be immersed in the thermostat bath without fear of electrical shortage. Forced cooling of the pump is provided by drawing a current of thermostat water through the annulus between the coil and the glass tube which forms the barrel of the pump.

THE SPECIMEN CHAMBER C.—This is so arranged that mercury from the bulb B can be used to cut off the lower end by closing the valve O. By letting more mercury in the whole gaseous contents of the chamber can be pushed out through the two-way tap T_3. On lowering the mercury level either active or inactive vapour can be drawn in through T_3 and by lowering the mercury right out of the U-tube an open path for the circulation of vapour can be provided. It is necessary to break down the barrier to diffusion caused by the stagnant layer of vapour above the polymer surface and so the polymer specimen S which is cemented to the glass plate P can be rotated rapidly by suitable rapid switching of the 3 electromagnets, M, from a multiple commutator driven by an electric motor.

RADIOACTIVE ASSAY

The radioactive assay of tritium is made difficult by the low energy of the β particles that are given off. A method based on the filling of a special Geiger tube (20th Century Electronics Tube, GA. 10/M) with tritiobutane has been developed by Glascock.[8] We have tried these tubes with fillings of tritio*iso*pentane but though we could get results the high voltages needed (about 3,500 V) often caused electrical leakages leading, amongst other things, to Geiger plateaux with very steep slopes. Since we did not need to put as much hydrocarbon as possible into the tubes, we found that in our work satisfactory results could be obtained from a normal argon filling using about 5 % addition of the active hydrocarbon which also acts as a quenching agent. As an example of the action of such a filling 160 mm of argon with 6 mm of *iso*pentane counted at about 1100 V and gave a plateau longer than 200 V with a slope of less than 4 % per 100 V. Pressures of these magnitudes were easily obtained by transferring the whole of the contents of the sampling tap into the Geiger tube and letting the argon expand in from a bulb.

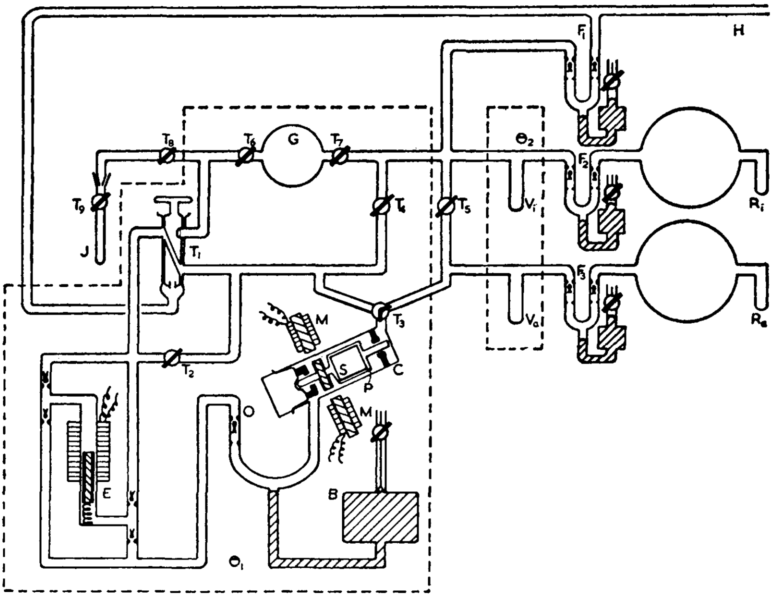

FIG. 1.—The diffusion apparatus.

B	bulb of mercury used to displace vapour from C,
C	specimen chamber,
E	electromagnetic glass circulating pump,
G	bulb of inactive vapour for filling bore of T_1,
H	high vacuum line,
J	sample tube for removing specimens of radioactive vapour,
M	system of three electromagnets for rotating the plate P,
O	cut-off valve to enable sealing of lower end of specimen chamber,
P	glass plate with soft iron bar for rotation,
R_a	storage reservoir for active liquid,
R_i	storage reservoir for inactive liquid,
S	polymer specimen with one face exposed to vapour,
T_1	sampling tap for isolating samples of circulating vapour,
T_2	by-pass tap for T_1,
V_a	vapour source for active vapour,
V_i	vapour source for inactive vapour,
θ_1	all within the dotted line maintained at θ_1 °C by water thermostat,
θ_2	all within the dotted line maintained at θ_2 °C by water thermostat.

GENERAL PROCEDURE

A sheet of poly*iso*butene of suitable thickness was cemented to the glass plate P by gentle pressure. Care was taken to avoid the inclusion of air bubbles between the film and the plate and film projecting beyond the edge of the plate was removed with moist scissors. Traces of casting solvent were removed by heating in a vacuum oven overnight and the thickness of the polymer was obtained by weight and area measurement. The whole plate and film were then mounted in the chamber C which was next evacuated and O was closed with the mercury from B. The temperatures θ_1 and θ_2 were adjusted to give the required equilibrium of *iso*pentane in the poly*iso*butene and T_3 was turned to the active *iso*pentane in V_a. The time for equilibrium to be established in the polymer was calculated from the data of Prager, Bagley and Long,[3, 4] and after this time the rest of the apparatus was filled with inactive vapour from V_i. The active vapour was displaced with mercury, T_3 was turned and inactive vapour drawn in by lowering the mercury with T_4 open. When all the mercury had run out T_4 was closed and the rotation of P and the pumping by E were started. At known intervals from the start, samples were withdrawn into J and their activities were determined. An average experiment continued for 24 h after closing T_4, most of the readings being taken in the first 4-5 h.

RESULTS

ACTIVITY AGAINST TIME RELATIONSHIP

In fig. 2 the activities of the *iso*pentane in the diffusion apparatus during two experiments at the same vapour pressure are plotted against the square root of time. Allowance has been made for the slight dilution of activity which occurs when each sample is taken. The first part of the curve can be represented very nearly by a straight line. This line has a positive intercept on the activity axis. A blank experiment in the absence of polymer showed that the intercept represents the amount of radioactive *iso*pentane left in the specimen chamber (but not dissolved in the polymer) when the bulk of this vapour is displaced by the rising mercury. To give the true measure of the amount of radioactive vapour diffused out of the polymer at any time during the experiment the intercept was subtracted from the observed activity.

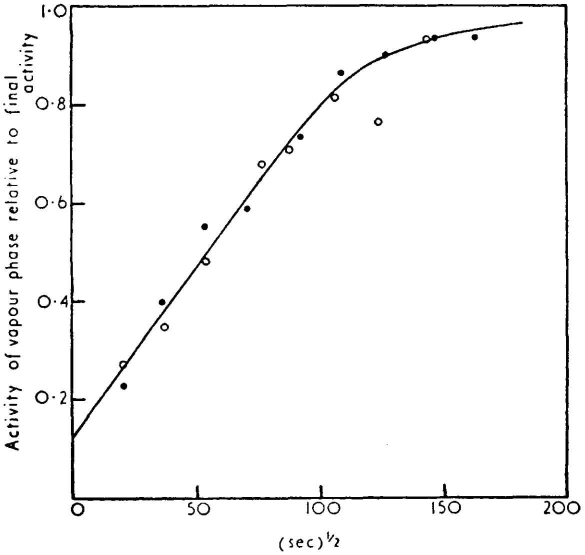

FIG. 2.—Tritiopentane desorption plot.

○ high-activity *iso*pentane used (~1 mcurie mole^{-1}),
● low-activity *iso*pentane used ~ 100 μcurie mole^{-1}),
thickness of P.I.B. specimen initially = 0·077 cm,

vapour pressure of *iso*pentane = 665 mm,
regain of *iso*pentane = 18 %,
*iso*pentane in specimen/*iso*pentane in vapour phase = 0·2,
specimen temperature = 35° C.

THE SELF-DIFFUSION COEFFICIENT

Since there is no overall change in *iso*pentane concentration in the polymer during a diffusion experiment the motion of radioactive *iso*pentane out of the polymer sheet is governed by a constant diffusion coefficient. The conditions of the experiment are that the concentration of tritio*iso*pentane is initially constant throughout the polymer sheet and at the start of the experiment it is dropped to zero at the exposed surface. If we further assume that the amount of *iso*pentane in the vapour phase is so large that the equilibrium concentration of tritio*iso*pentane at the surface remains at zero then at any time t the amount M_t of tritio*iso*pentane diffused into the vapour phase is given by the well-known equation,

$$\frac{M_t}{M_\infty} = 2\frac{(\mathscr{D}^*t)^{\frac{1}{2}}}{l}\left[\frac{1}{\pi^{\frac{1}{2}}} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\frac{nl}{(\mathscr{D}^*t)^{\frac{1}{2}}}\right]. \qquad (1)$$

Here ierfc x is related to the error function and is given by

$$\frac{2}{\pi^{\frac{1}{2}}}\int_x^\infty\int_y^\infty \exp(-z^2)\,dz\,dy.$$

$\mathscr{D}^*$ is the diffusion coefficient, M_∞ is the amount of tritio*iso*pentane lost from the sheet after infinite time, l is the thickness of the sheet of *iso*pentane + poly*iso*butene mixture and n is an integer.[9] Eqn. (1) leads to the initial linear plots of fig. 2 with no significant deviation from linearity up to $M_t/M_\infty = 0{\cdot}7$. In our experiments where the vapour phase is not infinite in extent the concentration of tritio*iso*pentane at the sheet surface increases with time eventually reaching a steady value at equilibrium. This leads to deviation from the behaviour predicted by eqn. (1) and the consequences of this finite bath behaviour have been worked out by several authors (e.g. ref. (9)). In the experiments reported here the ratio of the capacity of the vapour phase to that of the specimen is between 5 and 20. The main effects are to make the plots against $t^{\frac{1}{2}}$ somewhat curved and to cause the half-way point to be reached up to 20 % earlier. We have calculated our diffusion coefficients from the linear part using eqn. (1) and have corrected for the finite bath effects using the tables given by Berthier.[10] The concentrations of *iso*pentane in the polymer have been obtained from the vapour pressures using the data of Prager, Bagley and Long.[5] These concentrations have been used in calculating l from the thickness of the polymer when free from *iso*pentane (assuming no volume change on mixing and all swelling at right-angles to sheet surface) and in working out the deviations from infinite bath conditions. The vapour pressures were obtained from the temperatures of the liquid *iso*pentane using the figures of the American Petroleum Institute.[6] In fig. 3 the diffusion coefficients obtained have been plotted against concentrations.

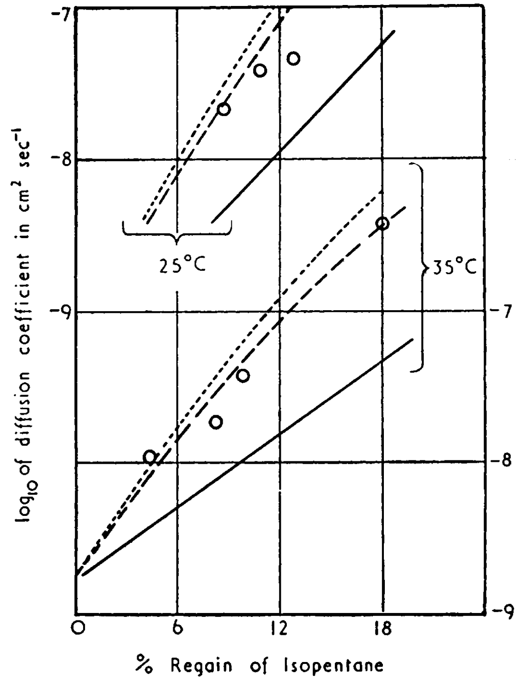

FIG. 3.—Diffusion coefficients at 25 and 35° C
Ordinates: left-hand numerals refer to diffusion coefficients at 25°; right-hand numerals to 35°.

○ self-diffusion coefficient, $\mathscr{D}^*$
——— integral diffusion coefficient D_{av},
— — — intrinsic diffusion coefficient $\mathscr{D}_p$,
.... thermodynamic diffusion coefficient $\mathscr{D}_T$.

DISCUSSION

THE INTEGRAL DIFFUSION COEFFICIENT

Prager and Long [3] suggested that in systems where the diffusion coefficient D varies with concentration the integral diffusion coefficient is more closely related than is D to the frequency ν with which molecules in a region at concentration C jump to a neighbouring region. Here by integral diffusion coefficient is meant D_{av} as defined by

$$D_{av} = \frac{1}{c}\int_0^c D\mathrm{d}C, \tag{2}$$

where D is the diffusion coefficient at concentration C obtained from concentration-gradient experiments. As a consequence of this there has been a tendency to express diffusion data for polymer + small molecule systems in terms of D_{av} and to calculate activation energies for diffusion from D_{av} rather than from D. The self-diffusion coefficient $\mathscr{D}^*$ gives a direct measure of the jumping frequency ν and so if Prager and Long's suggestion were correct $\mathscr{D}^*$ should be equal to D_{av}.

In fig. 3 we have plotted the values given by Prager and Long [3] and by Prager, Bagley and Long [4] for the coefficient D_{av} as obtained from measurements on the rate of sorption of vapour. Both at 25° C and 35° C the $\mathscr{D}^*$ values are much larger than D_{av} and at 35° C the 18 % regain value is greater by about 10 times. It should be pointed out that there are possibilities of systematic experimental error in the tracer experiments due to a stagnant vapour layer on the polymer surface and to a finite rate of circulation of the vapour. Allowance for such errors if they occurred would, however, increase the difference between D_{av} and $\mathscr{D}^*$.

THE THERMODYNAMIC DIFFUSION COEFFICIENT

The relationship between D_{av} and $\mathscr{D}^*$ suggested by Prager and Long is obtained when one assumes that the frequency of jumping of molecules from a region at concentration C_1 to a neighbouring region at concentration C_2 is a function of C_1 only. Prager [11] has considered the situation arising from a jump frequency depending on both C_1 and C_2. His conclusion can be expressed in the form,

$$\mathscr{D}^* = \mathscr{D}_p \,\mathrm{d}\ln C/\mathrm{d}\ln a \equiv \mathscr{D}_T, \tag{3}$$

where $\mathscr{D}_p$ is the intrinsic diffusion coefficient as defined by Hartley and Crank,[12] a is the penetrant activity and C is the penetrant concentration. D_T can be called the thermodynamic diffusion coefficient.

We have calculated $\mathscr{D}_p$ and $\mathscr{D}_T$ from D_{av} using the data of Prager, Bagley and Long [9] and assuming no volume change on mixing. The resultant plots are given in fig. 3. It will be seen that $\mathscr{D}_T$ is in reasonable agreement with $\mathscr{D}^*$. Though the values are somewhat closer to $\mathscr{D}_p$ than to $\mathscr{D}_T$ we consider that, owing to the systematic errors already mentioned and to the general scatter of the results this is not significant.

The author's thanks are due to Dr. B. A. Toms for suggestions leading to the design of the sampling tap, to Dr. R. F. Glascock for discussion on the gas counting of tritium and to Mr. R. E. Hester for experimental assistance.

---

[1] see, for instance, King, *Trans. Faraday Soc.*, 1945, **41,** 479. Park, *Trans. Faraday Soc.*, 1950, **46,** 684. Kokes and Long, *J. Amer. Chem. Soc.*, 1953, **75,** 6142.

[2] Park, *Radioisotope Conference*, 1954 (Butterworths), vol. 2, p. 11.

[3] Prager and Long, *J. Amer. Chem. Soc.*, 1951, **73,** 4072.

[4] Prager, Bagley and Long, *J. Amer. Chem. Soc.*, 1953, **75,** 1255.

[5] Prager, Bagley and Long, *J. Amer. Chem. Soc.*, 1953, **75,** 2742.

[6] *American Petroleum Institute Research Project* 44 (Selected values of properties of hydrocarbons and related compounds), table 1*k*. (Dec. 31, 1952. Carnegie Institute of Technology, Dept. of Chemistry, Pittsburg, Pennsylvania.)

[7] Brenschede, *Z. physik. Chem. A*, 1936, **178,** 74.

[8] Glascock, *Isotopic Gas Analysis for Biochemists* (Academic Press, New York, 1954).

[9] Crank, *The Mathematics of Diffusion* (Oxford, 1956).

[10] Berthier, *J. Chim. Phys.*, 1952, **49,** 527.

[11] Prager, *J. Chem. Physics*, 1953, **21,** 1344.

[12] Hartley and Crank, *Trans. Faraday Soc.*, 1949, **45,** 801.