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A linear representation of the diffusion of solvents into insoluble polymers

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The amount, q, of a solvent taken up by a sample of an insoluble polymer during a time, t, can be represented accurately by the relation $q = t/(at + b)$, which has a very simple linear equivalent: $(t/q) = at + b$, where a and b are constants. The same behaviour is also shown by the exchange of ions in an ion-exchange resin and in the case of a swell process, where q may be measured as a volume increase. The kinetic relation $\dot{q} = k(Q - q)^2$, where $Q = a^{-1}$ and $k = Q^{-2}b^{-1}$, is compared with Fick's first law of diffusion and the dependence of the diffusion coefficient and the concentration gradient on q is discussed.

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1. Introduction

In this article two points will be considered:

(a) The diffusion of a solvent into an insoluble polymer, shown in Fig. 1, can be expressed as a linear function, shown in Fig. 2. This will be outlined in Section 2.

(b) The above relation leads to a kinetic expression which can be compared with Fick's first law of diffusion. For the case where the amount q of the solvent in the polymer approaches its limiting value, Q, it can be shown accurately that the diffusion coefficient and the concentration gradient are proportional to the amount, $Q - q$, of solvent which can be taken up by the solvent during further diffusion. Particularly in the case of the diffusion coefficient this proportionality seems to be reasonable and can be expected also for ranges of q far from Q because $(Q - q)$ is a measure of the space open for further diffusion. These points will be considered in Section 3.

2. The diffusion of a solvent into an insoluble polymer

The measurement of the amount of the solvent in the polymer can be performed either by mass or by volume measurements. A mass, $M(0)$, or volume, $V(0)$ is selected from a piece of the polymer. Then this sample is plunged into the solvent. After a time, t, the mass $M(t)$ or the volume $V(t)$ of the sample is measured. Provided that the polymer is insoluble in the solvent the amount $m(t)$ of the solvent within the polymer is

$$m(t) = M(t) - M(0). \qquad (1)$$

However, $m(t)$ depends on the size of the polymer. A size independent parameter is

$$q(t) = \frac{m(t)}{M(0)}. \qquad (2)$$

In the case that the volume $V(t)$ of the polymer sample is measured, it is assumed that the volume change is proportional to $m(t)$:

$$m(t) = v(V(t) - V(0)), \qquad (3)$$

where v is a proportionality factor.

A measure independent of the size of the polymer sample is

$$q_v(t) = v\frac{V(t) - V(0)}{V(0)}. \qquad (4)$$

Measured values of $q(t)$ are shown in Figs 1 and 2. They are compared with the functions

$$q = \frac{t}{at + b}; \qquad (5)$$

$$(t/q) = at + b. \qquad (6)$$

The constants a and b are easily derived from Fig. 2 by the linear expression, Equation 6.

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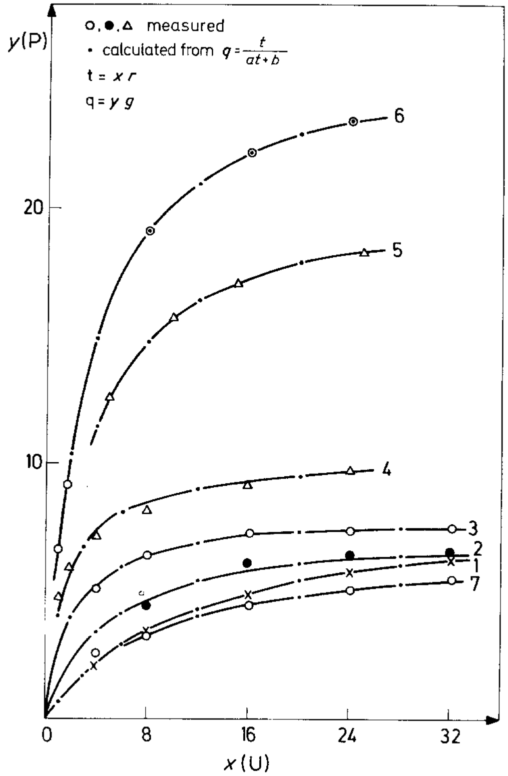

Figure 1 Up-take $q(t)$ of solvents by samples of insoluble polymers during a time, t. The explanation of the numbers and symbols is given in Table I.

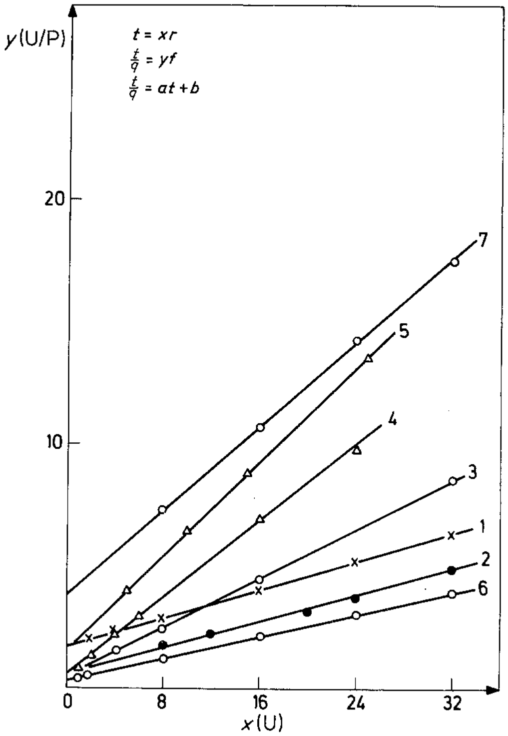

Figure 2 The relation $q = q(t)$ shown in Fig. 1 represented as a linear expression $(t/g(t)) = at + b$. The constants a and b as well as the explanation of the other numbers and symbols are given in Table I.

The results shown in Figs 1 and 2 for caoutchouc synthetic rubber display a swell-process. Instead of q, q_v was used and it is seen that the linear relation is obeyed very well. The example of an ion-exchange resin shows that in this case also the linear relation may hold accurately.

3. Comparison of the diffusion rate with Fick's first law of diffusion

Equation 6 leads to the following rate expression for the up-take of solvent:

$$\dot{q} = k(Q-q)^2; \tag{7}$$

where

$$Q = \lim_{t\to\infty} q(t), \tag{8}$$

$$k = b^{-1}Q^{-2} \tag{9}$$

and $Q = a^{-1}$.

Fick's first law of diffusion [1] reads

$$\mathrm{d}\dot{n} = -D.\nabla c.\mathrm{d}A; \tag{10}$$

integration of the whole surface, asssuming a mean concentration gradient, gives

$$\dot{n} = -D\overline{\nabla c}A, \tag{11}$$

where n is the amount of solvent (mol) through absorbtion into the polymer specimen, and A is the surface area of the specimen. If the molecular weight of the solvent is S, then n and q are related by

$$q = -\frac{nS}{M(0)}. \tag{12}$$

Hence, Fick's diffusion law, expressed in terms of q, becomes

$$\dot{q} = D_0\overline{\nabla c}A \tag{13}$$

where

$$D_0 = \frac{DS}{\mathrm{M}(0)}. \tag{14}$$

Comparison with Equation 7 gives

$$D_0\overline{\nabla c} = k(Q-q)^2/A. \tag{15}$$

For some polymer samples the surface area, A, is a constant. The concentration gradient may be developed into a Taylor series expansion at some point $Q' < Q$:

$$\overline{\nabla c}(q) = \overline{\nabla c}(Q') + \frac{\mathrm{d}}{\mathrm{d}q}\overline{\nabla c}(Q')\cdot(q-Q') + \ldots \tag{16}$$

TABLE I Explanation of the numbers, constants and symbols given in Figs 1 and 2

Number in Figs 1 and 2	Polymer	Solvent	Scaling factors			Units (see key below)		Constants of linear expression		Reference number
			r	*g*	*f*	U	P	*a*	*b*	
1	Polysterene	Chloroform	1.25	1.0	1.0	A	D	0.115	1.75	[2, 3]
2	Phenolresine (pressed)	Water	1.0	1.0	1.0	B	D	0.134	0.62	[4]
3	Phenolresine (hard paper)	Water	1.0	1.0	0.5	B	D	0.250	0.50	[4]
4	Vinylbutynal	Water	4.0	1.0	1.0	B	D	0.0979	0.60	[4]
5	Amberlite	100 mmol l^{-1} trideconoicacid	1.0	1.0	0.1	C	E	0.0480	0.156	[5]
6	Anion-exchange-resin	Hydrocarbon oil								
6	Neopren	Mineral oil at 100° C	3.0	1.0	1.0	C	F	0.0378	0.362	[6]
7	Perbunan	Water at 50° C	3.0	1.0	1.0	C	F	0.144	3.82	[6]

A: $l^{-2}\,10^{-9}$ sec cm^{-2}, where l is the thickness of the polysterene sheet sample [2].
B: weeks
C: h
D: wt%
E: microequivalents of tridecanoicacid per gram exchange resin.
F: vol%

For Q' approaching Q the first term vanishes because

$$\lim_{Q' \to Q} \overline{\nabla c}(Q') = \lim_{q \to Q} \overline{\nabla c} = \lim_{t \to \infty} \overline{\nabla c} = 0. \tag{17}$$

For q nearly equal to Q only the first term of the Taylor series is significant:

$$\overline{\nabla c} \approx C_1 \cdot (Q - q); \text{ as } q \to Q, \tag{18}$$

where

$$C_1 = -\lim_{Q' \to Q} \frac{\mathrm{d}}{\mathrm{d}q} \overline{\nabla c}(Q') \geqslant 0.$$

This means that for q approaching Q for a sample of a polymer with a given surface, $\overline{\nabla c}$, and because of Equation 15, D_0 is proportional to $(Q - q)$.

This result seems also to be reasonable for $q \ll Q$. $(Q - q)$ is a measure of the empty volume which may take up further solvent. It should be expected that the diffusion coefficient is proportional to this free volume open for diffusion. One may imagine that the intermolecular space within the polymer is filled more and more with solvent molecules and that the number of molecules entering subsequently is proportional to the magnitude of the empty space.

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