NON-FICKIAN DIFFUSION BEHAVIOUR
OF THE 2-HYDROXYETHYL METHACRYLATE–PHENOL–WATER SYSTEM

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The diffusion coefficients D (from a non-stationary diffusion course), permeation coefficients P (from a stationary diffusion course) and partition coefficients k (from the sorption equilibrium) were measured for the system phenol–2-hydroxyethyl methacrylate gel swollen with water to equilibrium. A theoretical analysis of the concentration dependence of the D, P and k values shows that the system exhibits non-Fickian behaviour.

Our previous paper[1] has been devoted to the diffusion of several low-molecular weight compounds in 2-hydroxyethyl methacrylate gels swollen to equilibrium with water. The partition coefficient k_{kin} defined as the ratio of the permeation and diffusion coefficients was compared with the corresponding quantity k_{st} obtained from the equilibrium sorption measurements. The measurements were done on membranes having different apparent porosities; in some systems considerable differences were found between both values of the partition coefficients, even in a gel which was optically quite homogeneous. This fact can be regarded as a consequence of the so-called non-Fickian behaviour of the system; it seems the more interesting in this case since the swollen polymer is undoubtedly much above its glass transition temperature T_g. However, if we want to confirm the existence of the non-Fickian diffusion, we must determine the concentration dependence of both the transport quantities and the partition coefficients and perform a theoretical analysis of the dependences thus found. This has been the objective of the work reported here.

EXPERIMENTAL

The membrane was obtained by polymerizing 2-hydroxyethyl methacrylate (with 1% by wt. of ethylene dimethacrylate as the crosslinking agent) in 2-hydroxyethyl pivalate (30% by wt. in the mixture); 2-hydroxyethyl pivalate as a hydrogenated homologue of the monomer used is a model of the forming polymer and was intentionally used as the polymerization medium (instead of water used formerly[1]) to reduce the tendency of the polymerizing system to microphase separation. The polymerization initiated with diisopropyl percarbonate (0·5%) proceeded at 45°C for 24 h. The membrane was extracted several times in boiling water to remove the low-molecular weight components and to transform it into a polymer swollen with water to equi-

librium. The membrane was optically very homogeneous, which was also confirmed turbidimetrically[2]; its thickness (l) was 0·47 mm. Samples were cut out from the membrane for both the diffusion and equilibrium sorption measurements. Phenol was used as the diffusing compound; preliminary experiments with phenol indicated particularly pronounced differences between the partition coefficients k_{kin} and k_{st}.

The apparatus used and the measuring procedure have been described previously[1,3]. A number of experiments was carried out in which the time dependence of the concentration within the measuring space due to the diffusion of phenol through the membrane was measured with a differential refractometer. The initial phenol concentration in the measuring loop was always zero. The individual experiments differed by the phenol concentration, c, in the space on the other side of the membrane, which was kept constant during each experiment. By using a procedure described earlier[1,3], the permeation coefficient $\overline{P}(c)$ corresponding to a given concentration c was determined from the slope of the straight line corresponding to the stationary course of the diffusion. The diffusion coefficient $\overline{D}_L(c)$ was calculated from the time-lag. From the equilibrium distribution of the phenol concentration between the aqueous and gel phases, the partition coefficient $k_{st}(c)$ was determined as a function of phenol concentration outside the gel by using the same procedure as in ref.[1].

RESULTS AND DISCUSSION

The experimental results are summarized in Fig. 1; it can be seen that the accuracy of determination is very good, particularly in the case of $\overline{D}_L(c)$ and k_{st}. The curve designated by k_{kin} expresses the concentration dependence of the partition coefficient and was obtained as the ratio of the corresponding values, $\overline{P}(c)/\overline{D}_L(c) = k_{kin}(c)$.

The concentration dependence of the transport quantities $\overline{P}(c)$ and $\overline{D}_L(c)$ and the equilibrium partition coefficient $k_{st}(c)$ allow to demonstrate unambiguously whether the given system obeys Fick law. An appropriate procedure suggested by Fujita[4] and using the results by Frisch[5] is based on the following idea.

For a unidirectional diffusion through a membrane of thickness l and obeying Fick law

$$\partial c_g / \partial t = (\partial/\partial x) [D(c_g) (\partial c_g/\partial x)] \qquad (1)$$

(where c_g denotes concentration of the diffusing compound in the membrane, x is coordinate, t is time and $D(c_g)$ is concentration-dependent differential diffusion coefficient) it holds in the stationary state $\partial c_g/\partial t = 0$; hence

$$(d/dx) [D(c_g^*) (dc_g^*/dx)] = 0 , \qquad (2)$$

where c_g^* is the concentration of the diffusing compound in the membrane in the stationary state, $c_g^*(x) = \lim_{t \to \infty} c_g(x, t)$. Integration of Eq. (2) gives (with respect to the boundary conditions $c_g(0, t) = = c_g^0, c_g(l, t) = 0$ valid for the experimental arrangement used) the relationship

$$D(c_g^*) (dc_g^*/dx) = - J^* ; \qquad (3)$$

the integration constant J^* (independent of x) has according to the first Fick law, the physical

meaning of a stationary diffusion flux through the membrane. Further integration of Eq. (3) between $x = 0$ and $x = l$ leads to

$$J^* = (1/l) \int_0^{c^0_g} D(u) \, du \, , \tag{4a}$$

so that J^* is obviously a function of the concentration c^0_g only, $J^* = J^*(c^0_g)$. If the integral diffusion coefficient within the concentration range from 0 to c^0_g is defined in the usual way as

$$\overline{D}(c^0_g) = (1/c^0_g) \int_0^{c^0_g} D(u) \, du \, , \tag{4b}$$

it follows from Eq. (4a) that

$$\overline{D}(c^0_g) = J^*(c^0_g) \cdot l/c^0_g \, . \tag{5}$$

In accordance with the definition of the permeation coefficient measured within the concentration interval of the diffusing compound from 0 to c^0 (corresponding to the equilibrium concentration in the membrane from 0 to c^0_g) we have

$$\overline{P}(c^0_g) = J^*(c^0_g) \, l/c^0 \, ; \tag{6}$$

the equilibrium partition coefficient k_{st} is given by

$$k_{st}(c^0_g) = c^0_g/c^0 \, . \tag{7}$$

By combining Eqs (4)—(7) one obtains

$$\overline{D}(c^0_g) = (1/c^0_g) \int_0^{c^0_g} D(u) \, du = \overline{P}(c^0_g)/k_{st}(c^0_g) \, , \tag{8}$$

so that the ratio of the permeation and the equilibrium partition coefficient (if both quantities are expressed as functions of concentration in the membrane c^0_g) directly defines the integral diffusion coefficient for the concentration range from 0 to c^0_g. The quantity $\overline{D}(c^0_g)$ thus defined includes an extrapolation to $t \to \infty$, and is therefore insensitive to any time-dependent properties of the system, which are often responsible for its non-Fickian behaviour. The concentration dependence of the respective differential diffusion coefficient $D(c)_g$ can then be obtained by differentiation according to the equation

$$(d/dc_g) \, [(\overline{P}(c_g) \cdot c_g)/k_{st}(c_g)] = D(c_g) \, . \tag{9}$$

On the other hand, Frisch[5] has derived for a diffusion obeying Fick law with the diffusion coefficient $D(c)$ depending only on concentration that the quantity $\overline{D}_L(c^0_g)$ determined by the time-lag method (if the concentration of the diffusing compound in the inlet membrane surface is equal to c^0_g) is given by

$$\overline{D}_L(c^0_g) = (1/6) \left\{ \int_0^{c^0_g} D(c) \, dc \right\}^3 \Big/ \int_0^{c^0_g} c D(c) \left[\int_c^{c^0_g} D(u) \, du \right] dc \, . \tag{10}$$

In principle, on the basis of the experimentally determined concentration dependence $\bar{D}_L(c_g)$, Eq. (10) can be solved for $D(c_g)$ and compared with the corresponding quantity determined from the stationary course of diffusion according to Eq. (9). However, the solution of the integral Eq. (10) is rather difficult even by numerical methods and an equivalent reverse procedure has therefore been chosen here: The concentration dependence of the diffusion coefficient $D(c_g)$ determined according to Eq. (9) (i.e. an experimentally obtained value of $D(c_g)$ corresponding to purely Fickian diffusion) was introduced into Eq. (10) and the theoretical concentration dependence of the diffusion coefficient $\bar{D}_L$ thus obtained was compared with the curve corresponding to $\bar{D}_L$ actually determined from the "time lag" experimental data (which of course includes the possible non-Fickian behaviour of the system).
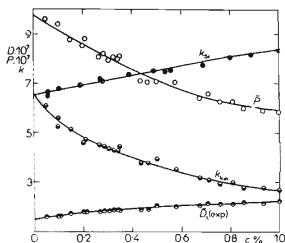

FIG. 1

Measured Concentration Dependences of the Transport Quantities and of the Equilibrium Sorption of Phenol in 2-Hydroxyethyl Methacrylate Gel Swollen with Water to Equilibrium
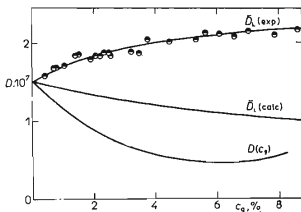

FIG. 2

Comparison of the Experimental and Theoretically Calculated Concentration Dependence of the Diffusion Coefficient D_L

The lowest curve represents the calculated concentration dependence of the differential diffusion coefficient assuming Fickian diffusion.

To facilitate the calculations, the following procedure was adopted. First, the least squares method was used to approximate the reciprocal value $(1/k_{st})$ by a polynomial in c_g; the degree of the polynomial was determined[6] so as to make the coefficient of the leading term statistically significant at the significance level 1%. The second-degree polynomial $(1/k_{st}) = 0.153 - 0.00649c_g + 0.000299c_g^2$ fulfilled these requirements within the given scatter of the experimental points. Next, a least-squares polynomial was used to smooth the $\bar{P}(c_g)$ data at the same significance level; the resulting approximation (again of the second degree) can be written as $\bar{P}(c_g) = (9.808 - 0.901c_g + 0.05212c_g^2) \cdot 10^{-7}$. (The two curves plotted through the experimental

points k_{st} and $\bar{P}$ in Fig. 1 correspond to the approximating polynomials determined in this way; only the independent variable c_g was replaced by the concentration in the external solution c according to the relation $c = c_g/k_{st}$.) By this procedure, we obtained the approximate expression for $\bar{D}(c_g)$ ($= \bar{P}(c_g)/k_{st}$) again in the form of a polynomial (this time of the fourth degree), so that both the differentiation in Eq. (9) and the integration in Eq. (10) could be performed analytically.

The results of the theoretical procedure outlined are represented graphically in Fig. 2. We can see that the courses of both curves, $\bar{D}_L(\exp)$ and $\bar{D}_L(\text{calc.})$ differ considerably; the former is an increasing function while the latter decreases with the concentration of phenol. With respect to the assumptions involved in the theoretical analysis used, this fact cannot be explained merely by the concentration dependence of the diffusion coefficient, but the cause should be looked for in an effect which is usually called "non-Fickian diffusion". It is known[4] that such anomalous behaviour can be observed only if the diffusion proceeds in a non-stationary way, that is, if the concentration at any site of the polymer varies with time (e.g. when the kinetics of sorption is measured or if the "time lag" method is used). The cause proper of the "non-Fickian" behaviour can consist in certain local fluctuations of the properties of the polymer (the existence of heterogeneities or considerable relaxation times of some parts of polymer chains). If these effects are not included in the mathematical description of the system, the relevant forms of integrated Fick law do not describe the actual diffusion process and the behaviour of the system seems to be "non-Fickian". In fact, however, Fick laws are always valid, so that e.g. in the case where the anomalous behaviour is due to a finite rate in establishing the equilibrium surface concentration, the system ceases to behave in a "non-Fickian" way if this fact is taken into consideration in the boundary conditions. A more complex situation arises if some parts of the polymer chains inside the membrane are not in a mechanical equilibrium. The concentration of the diffusing compound in these places does not immediately correspond to Fick law, and the diffusion in such a system ceases to be the only process controlling its distribution. (It should be noted, however, that the equilibrium data and the data obtained from the stationary diffusion — k_{st} or $\bar{P}(c_g)$ and $\bar{D}(c_g)$ in our case — are not affected by this anomalous behaviour of the polymer.)

It can be concluded that even a simple system, such as water–glycol methacrylate–phenol in our case, in which the polymer as a whole is obviously above T_g, need not obey Fick law. With respect to the optical homogeneity of the membrane[2] it can be assumed that long relaxation times of some chains in the polymer phase are responsible for the observed anomaly.

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