DIFFUSION COEFFICIENTS OF ALIPHATIC ALCOHOLS IN THE POLY(2-HYDROXYETHYL METHACRYLATE) GEL MEASURED BY MEANS OF A DYNAMIC DESORPTION METHOD

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A rapid and sensitive method for measuring the diffusion coefficients of organic compounds in polymers has been described. The amount of the desorbed substance is determined from the time dependence of its concentration in a stream of hydrogen which flows over the surface of the polymeric sample. A flame ionization detector was used in the concentration measurements. To verify the possibilities offered by this method, measurements were made of the concentration dependence of the diffusion coefficients of lower aliphatic alcohols in the poly(2-hydroxyethyl methacrylate) gel at various temperatures. In the region of low alcohol concentrations in the gel, when the swollen sample is below the glass transition temperature, a steep fall of the diffusion coefficients within a range of several logarithmic decades was observed.

The diffusion coefficients of organic compounds in polymers are usually determined by measuring the kinetics of sorption and/or desorption. A sorption balance[1–3] is used for this purpose; the polymer sample is suspended in vacuum on a quartz helix-shaped spring, and the weight changes caused by sorption or desorption of the organic vapours at a given partial pressure are determined by means of a cathetometer from the change in the length of the spring. This method, although sufficiently sensitive (diffusion coefficients having an order of magnitude as low as 10^{-11} cm^2 s^{-1} may be determined in a favourable case[4,5]), has nevertheless a number of drawbacks. The necessity of employing a vacuum line involves considerable time losses at each exchange of the sample (be it the polymer or the solvent under investigation) and the visual following of the length by means of the cathetometer does not make the measurements more effective either. The difficulties connected with the removal of the condensation heat from the sample placed in the vacuum[6,7] impose a lower limit on the thickness of the foils.

The present paper describes a rapid, sufficiently sensitive and accurate method for the investigation of the rate of desorption of organic compounds from a polymeric sample. Its principle may be briefly described as follows: a polymer in the shape of a thin disc swollen in advance to the required degree in the solvent under investigation is rinsed in a through-flow vessel by a stream of thermostated pure hydrogen, which ensures a constant temperature of the sample while at the same time carrying

away the desorbed vapour into the flame ionization detector situated directly behind the desorption cell. The amount of the solvent desorbed from the surface of the foil is then determined from the time dependence of its concentration in the carrier gas. A similar method has been used for measurements of the effective diffusion rate of gases in spherical particles of macroporous catalyst carriers[8]. The method was used for measurements of the diffusion coefficients of aliphatic alcohols in poly(2-hydroxy-ethyl methacrylate-co-ethylene dimethacrylate) having a low network density. The glass transition temperature, T_g, of this sample in the dry state[9,10] is about 100°C, but decreases rapidly with increasing degree of swelling[11], so that already a sample containing 10 to 15% of the solvent is viscoelastic at room temperature. Consequently, measurements of the diffusion coefficients in the copolymer in dependence on the degree of swelling and temperature may give information on the inhibiting effect of the immobilized polymeric network upon the rate of transport of the low-molecular-weight compounds. This effect is also important for the suggested use of the slightly crosslinked poly(2-hydroxyethyl methacrylate) and similar hydrophilic polymers in the glassy state for the encapsulation of volatile or sensitive low-molecular-weight compounds[12,13]. Preliminary measurements of the diffusion of model compounds in the given copolymer have shown[14] that the transport of molecules of a larger size in the glassy polymer is blocked with such efficiency that the corresponding diffusion coefficients are too low to be measured. Therefore, comparatively small molecules of lower aliphatic alcohols have been chosen for the present work; they also offer another advantage, namely, that they are good swelling agents for the copolymer, so that the diffusion coefficients can be measured over a wide concentration range.

EXPERIMENTAL

Materials and Apparatus

Methanol and ethanol were of analytical purity grade; propanol (pure, Lachema, Brno) was dried with sodium and distilled on a column (120 cm long, Berl's saddles) (b.p. 97·0 -97·1°C). The sorption material was prepared in the form of foils of various thickness (0·3 mm—0·9 mm) by copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate (crosslinking agent, whose content was 0·11% in the initial mixture) between two plane-parallel glass plates[15]. The samples, cut from the foils with steel punches, were disc-shaped, 2 to 3 cm in diameter; they were purified from the soluble fractions by boiling in several portions of distilled water, dried *in vacuo* at 100°C to constant weight and stored in a desiccator over silicagel. Fig. 1 shows a schematic view of the apparatus used. Hydrogen from a pressure cylinder was purified and dried, and its flow rate was regulated and measured using conventional methods[16]. At A, it entered the thermostating coil of the desorption vessel B thermostated with flowing water from an external thermostat. The polymeric sample C having a known initial uniform concentration of the diffusing substance was put at time $t = 0$ into the cell through the upper ground joint D and placed on a supporting stainless wire coil reposing on the fritted disc E. A stream of hydrogen carried the desorbed vapour into a flame ionization detector F, connected with the desorption

vessel through a ground seal G with a capillary outlet. The signal of this sensitive detector (ref.[16], p. 217) was then amplified and recorded. The deviation of the recorder pen is proportional to the amount of the organic compound entering the detector in unit time over a wide concentration range (comprising several logarithmic decades). The weight of the solvent desorbed from the polymeric sample from the beginning of the experiment to a time t is thus proportional to the area below the recorded curve. The flame ionization detector and the amplifying unit were the same as in the gas chromatograph Chrom II of the firm Laboratorní přístroje, Prague.

Preparation of Samples

Dry membranes were weighed and left to swell to equilibrium in the respective alcohol in closed weighing bottles. The swelling in methanol and ethanol took place at room temperature, and the equilibrium was attained within 30 to 50 h, depending on the thickness of the foil. Samples used in the measurements with 1-propanol were boiled 20 min in the same alcohol, protected against the air moisture, and afterwards kept immersed at room temperature for at least 48 h. The required degree of swelling was attained by partial evaporation of the alcohol from samples swollen to equilibrium, either *in vacuo* or (in the case of samples for which very low initial degrees of swelling were required) directly in the desorption vessel in a stream of hydrogen at 80°C during a time determined by trial and error. To satisfy the necessary condition that the concentration of the sorbate in the sample at the beginning of the experiment must be uniform, the membranes prepared as described above were stored in ampoules closed with perfect ground joints for at least 80 h in the case of samples with methanol and ethanol and for at least 150 h for 1-propanol. The same samples were used many times for repeated determinations of the rate of desorption at various temperatures and with various initial degrees of swelling for the given alcohol. No changes in the equilibrium degree of swelling with time could be observed.

Measuring Procedure

The initial degree of swelling was determined by weighing the membrane in a weighing bottle, and its thickness was then quickly measured with a micrometric screw between two microscopic slides. The sample was then placed in the thermostated desorption cell, and the desorption curve was recorded. The duration of one experiment varied from 20 min (for samples having a high initial degree of swelling at elevated temperatures) to 2 h for samples having the lowest initial concentration of 1-propanol. Immediately after the desorption was completed the sample was weighed again, and the weight difference served for transforming the area below the recorded desorption curve to the time dependence of the amount of the desorbed compound, M_t.
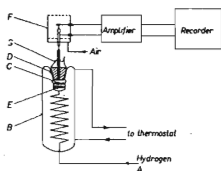

Fig. 1

Schematic Diagram of the Desorption Apparatus Used

A Inlet of purified and dried hydrogen, *B* desorption vessel with a coil for preheating the hydrogen, *C* polymer sample, *D* ground joint for insertion of the sample, *E* supporting fritted disc, *F* flame ionization detector, *G* ground joint with a capillary outlet.

Calculation of the Diffusion Coefficients

The solution of the second Fick's law for the desorption from a foil of a thickness l at a constant diffusion coefficient D has the form (ref.[7], p. 45)

$$M_t/M_\infty = 4[(Dt)^{1/2}/l] \, [\pi^{-1/2} + f(t)] \, ; \qquad (1)$$

here, M_t is the total amount of the diffusing substance desorbed from the sample from the beginning of the experiment until a time t, and M_∞ is the corresponding amount after an infinite time (in our case, where the vapour concentration in the carrier gas is virtually zero, M_∞ is obviously equal to the total amount of the substance in the sample at the onset of desorption); the function f does not significantly contribute to the sum in the brackets until higher values of t are reached. If, therefore, the ratio M_t/M_∞ is plotted against $t^{1/2}$, it is possible to determine D from the slope s of the initial straight part according to

$$D = (\pi/16) \, l^2 s^2 \, . \qquad (2)$$

If the diffusion coefficient is not constant, $i.e.$, if it depends on the concentration of the diffusing substance in the polymer, the value $\bar{D}$ determined according to (2) from the first stages of desorption from the membrane with an initial concentration of the diffusing substance c_0 is a good approximation to the average diffusion coefficient within the investigated concentration range $0 - c_0$,

$$\bar{D} = (1/c_0) \int_0^{c_0} D(c) \, \mathrm{d}c \, , \qquad (3)$$

where $D(c)$ is the actual value of the (concentration-dependent) diffusion coefficient at a concentration c.

RESULTS AND DISCUSSION

The shape of the dependences M_t/M_∞ on $t^{1/2}$ ($cf.$ Eq. (1)) for the three alcohols under investigation at 25°C is shown in Figs 2$a-c$. The areas below the recorded experimental curves (proportional to M_t) were calculated by numerical integration using the trapezoidal rule. (A small integration step was chosen so as to prevent the numerical error from affecting the accuracy of determination of $\bar{D}$.) The samples were not preheated to the temperature of desorption before placing them into the apparatus. As a consequence (and also due to the necessary short manipulation with the sample during weighing and the thickness measurements before the desorption), a short initial region (usually about 20 to 80 s) appeared at the beginning of all experimental curves, when the rate of desorption was lower than predicted by Eq. (1); since, however, the diffusion coefficients were calculated from the slope of the linear part of the dependence of the ratio M_t/M_∞ on $t^{1/2}$, this initial region will not affect the results[17].

The average diffusion coefficients $\bar{D}$ were measured for three aliphatic alcohols at different temperatures. Reproducibility and sensitivity of the method can be seen from Table I. The agreement between the obtained values of the diffusion coefficients at virtually identical initial degrees of swelling and identical temperatures is very good,

although the polymeric samples had different geometric sizes. Also the rate of hydrogen flow within the range of 50 to 85 ml/min does not affect the values of $\bar{D}$, although the sensitivity of the flame ionization detector increases considerably with the increasing flow of hydrogen in this region, as was demonstrated by a preliminary calibration. The last column in Table I documents the reserve in the sensitivity of the flame ionization detector during these measurements. The lowest values of $\bar{D}$, determined for the system copolymer–propanol were approximately $3 . 10^{-10}$ cm^2 s^{-1}; neither in this case, however, was it necessary to employ the highest sensitivity of the flame ionization detector, which would allow to measure values of the diffusion coefficients lower by at least one order of magnitude with the same accuracy. The steep fall of $\bar{D}$ in the region of low degrees of swelling (Figs 3 and 4) makes virtually impossible
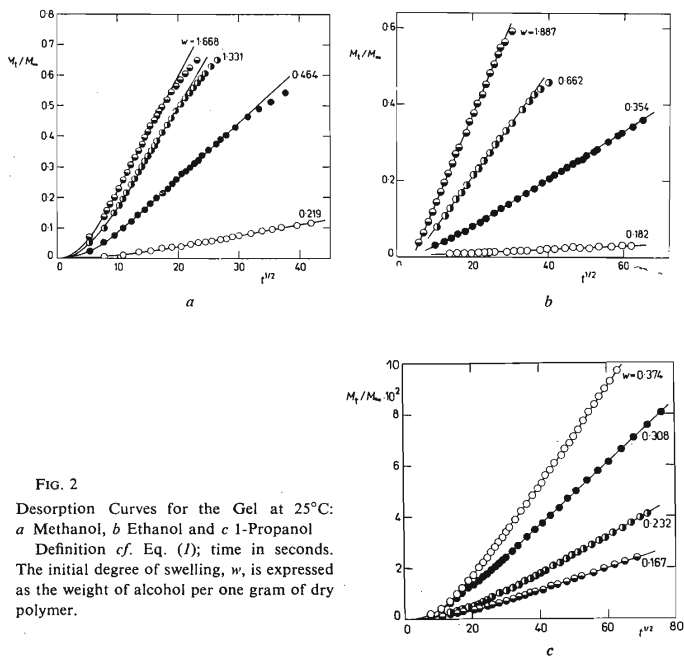

FIG. 2

Desorption Curves for the Gel at 25°C: a Methanol, b Ethanol and c 1-Propanol

Definition cf. Eq. (1); time in seconds. The initial degree of swelling, w, is expressed as the weight of alcohol per one gram of dry polymer.

TABLE I

Diffusion Coefficients of Ethanol and Propanol in the Case of Comparable Degrees of Swelling of the Polymeric Membrane

Membrane[a]	w^b	t °C	H_2 ml/min	$\bar{D} \cdot 10^9$ cm^2 s^{-1}	Detector attenuation
			Ethanol		
27·0 × 0·35	0·690	35	65	115·4	1/500
28·5 × 0·43	0·686	35	85	121·5	1/500
25·2 × 0·40	0·265	45	85	18·7	1/200
28·6 × 0·75	0·267	45	85	16·9	1/200
21·3 × 0·29	0·270	45	50	18·3	1/200
19·8 × 0·33	0·230	55	85	22·4	1/200
27·3 × 0·38	0·231	55	50	24·2	1/200
			1-Propanol		
27·5 × 0·83	0·511	25	50	9·4	1/100
25·6 × 0·75	0·499	25	85	9·1	1/100
26·1 × 0·79	0·515	25	50	9·3	1/100
28·4 × 0·85	0·702	35	85	48·5	1/500
25·5 × 0·71	0·705	35	85	46·8	1/500
24·3 × 0·75	0·507	45	85	35·9	1/500
28·1 × 0·81	0·503	45	85	31·4	1/500

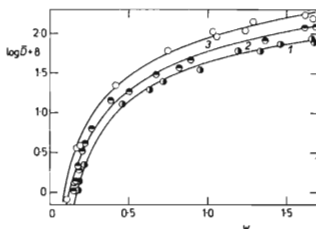[a] Dimensions are given in mm (diameter × thickness). [b] Weight of solvent per one gram of dry polymer.

FIG. 3

Dependence of the Average Diffusion Coefficients ($\bar{D}$, cm^2 s^{-1}) of Methanol on the Initial Degree of Swelling (w)

1 25°C; 2 35°C; 3 45°C.

both the direct extrapolation to $D_0 \equiv D_{w=0}$ and the use of a method for determination of D_0 based on another solution of Fick's law, valid in the region of high t (ref.[17,18]). We have found, however, that if $\log \bar{D}$ is plotted against $(1 - v_{\mathrm{P}}^3)$, where v_{P} is the volume fraction of the polymer in the swollen sample, approximately linear dependences are obtained; they may be used for a more reliable extrapolation to $v_{\mathrm{P}} = 1$ (corresponding to $w = 0$). Both values, w and v_{P}, are related with each other through $v_{\mathrm{P}} = 1/(1 + w\varrho_{\mathrm{P}}/\varrho_{\mathrm{L}})$ where ϱ_{P} and ϱ_{L} are densities of the dry polymer and the respective solvent. Although the nature of this extrapolation procedure is purely empirical, it cannot introduce any serious error into the calculations with respect to the narrow concentration range used for the extrapolation $(w < 0.15$ in most cases).

To calculate the concentration dependence $D(c)$, a slightly modified method suggested by Park[19] was used. The concentration of the diffusing compound was expressed in terms of its volume fraction, $v_{\mathrm{L}} = 1 - v_{\mathrm{P}}$. With this choice of variables, it holds for the diffusion coefficient

$$\bar{D} = \left(1/v_{\mathrm{L}}^0\right) \int_0^{v_{\mathrm{L}}^0} D(v_{\mathrm{L}})\, dv_{\mathrm{L}} , \qquad (3b)$$

where v_{L}^0 is the initial volume fraction of the diffusing component in the polymeric sample. By multiplying Eq. $(3b)$ by v_{L}^0 and taking logarithms we obtain

$$\log\left(\bar{D} v_{\mathrm{L}}^0\right) = \log I , \qquad (4)$$

where

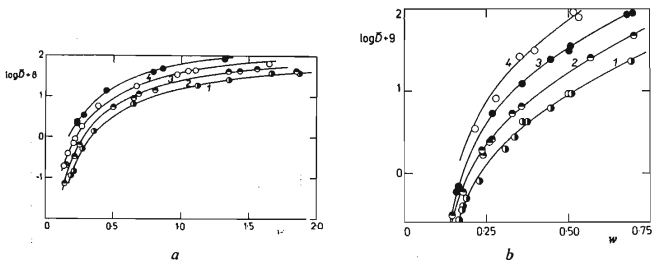$$I = \int_0^{v_{\mathrm{L}}^0} D(v_{\mathrm{L}})\, dv_{\mathrm{L}} . \qquad (5)$$

FIG. 4

Dependence of $\bar{D}$ (cm^2 s^{-1}) on the Initial Degree of Swelling (w) of Gel for (a) Ethanol and (b) 1-Propanol

1 25°C; 2 35°C; 3 45°C; 4 55°C.

By differentiating Eq. (4), an expression for the diffusion coefficient at a degree of swelling characterized by the volume fraction of the solvent, v_L, is obtained:

$$D(v_L) = 2 \cdot 303 . I . \frac{d \log I}{dv_L} . \tag{6}$$

For the numerical differentiation of smoothed experimental data (*cf.* Figs 3 and 4), the five-point polynomic formula was used[20].

The diffusion coefficients of the individual alcohols in the copolymer under investigation calculated using the above procedure are plotted in Fig. 5 against the volume fraction of the solvent. With the increasing degree of swelling the logarithms of the diffusion coefficients first decrease almost linearly; in the region of low v_L, however, the rate of diffusion drops very steeply within several logarithmic decades. This region (approximately for $v_L < 0 \cdot 1$) of a steep decrease in the rate of transport coincides with the concentration range in which the glass transition temperature
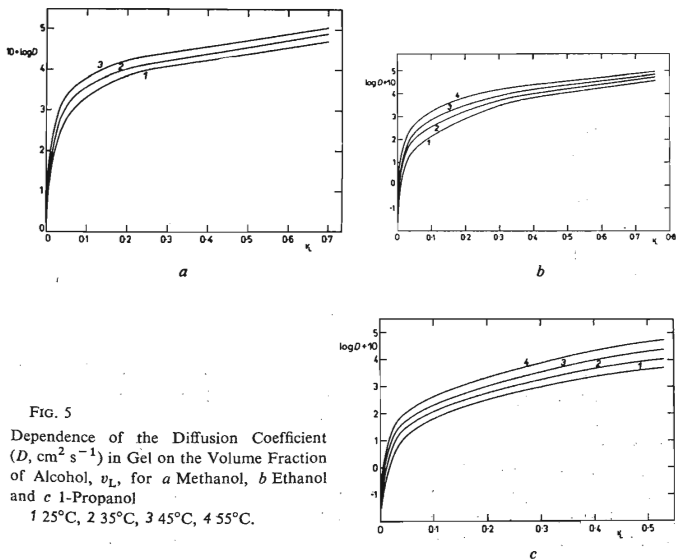

Fig. 5

Dependence of the Diffusion Coefficient (D, cm^2 s^{-1}) in Gel on the Volume Fraction of Alcohol, v_L, for *a* Methanol, *b* Ethanol and *c* 1-Propanol

1 25°C, *2* 35°C, *3* 45°C, *4* 55°C.

of the swollen copolymer rapidly decreases from about 100°C (corresponding to the pure polymer) to room temperature, regardless of the chemical nature of the swelling agent. Thus, the freezing of the degrees of freedom of the polymeric network in the glassy state strongly hinders the diffusion.

The rate of diffusion decreases with the increasing length of the alcohol chain. Also in this case it holds, therefore[17], that the diffusion coefficients in polymers depend not only on the cross-section, but also on the length of the diffusing molecules. At 25°C the diffusion coefficients of ethanol and propanol differ by a factor of about 2 to 3, the difference being greater at lower v_L. However, the difference between the diffusion coefficients of methanol and ethanol depends on concentration much more markedly: their ratio increases from about 2 at $v_L = 0.6$ up to 15 at $v_L = 0.1$. (The diffusion coefficient of methanol obtained by extrapolation to zero concentration is even a hundred times higher than the corresponding extrapolated value for ethanol, but may be considerably affected by the uncertainty originating in the empirical extrapolation method employed.) In comparison with both higher homologs, the diffusion of a small molecule of methanol is less hindered by the immobilization of the polymeric network during the transition into the glassy state.

The curves corresponding to different temperatures are almost parallel within the whole concentration range, so that the activation energy of diffusion is independent of the degree of swelling. (Curves in Fig. 5 cover the whole accessible range of the volume fractions from $v_L = 0$ to the value corresponding to the equilibrium degree of swelling of our samples in the respective alcohol.)

In conclusion, a comparison may be made between the diffusion coefficients of ethanol and propanol in the binary system alcohol–copolymer with values determined by an independent method[21,22] for the above alcohols in the same copolymer swollen in water to equlibrion. According to Fujita's free volume[5] theory, the decisive parameter for the rate of diffusion in polymers is the free volume of the system. This quantity depends on the degree of swelling (the volume fraction of the solvent, v_L) according to

$$f(v_L, T) = f(0, T) + v_L \cdot \beta(T) ; \tag{7}$$

here, $f(v_L, T)$ is the fractional free volume at a temperature T and at the volume fraction of the swelling agent v_L, $f(0, T)$ is the fractional free volume of the pure polymer at the same temperature, and $\beta(T)$ is a quantity characterizing the increase in free volume due to an addition of the given solvent. Since there are no experimental data at disposal on the values $\beta(T)$ for the systems copolymer–water or copolymer–aliphatic alcohol, our comparison is based on the assumption that the quantities $\beta(T)$ will be virtually the same in these systems; in which case, it is possible to compare directly the diffusion coefficients of ethanol and propanol in a gel swollen to equilibrium in water (when $v_p = 0.53$) with the diffusion coefficients in the corresponding binary

systems investigated in the present work at the same value of the volume fraction of the solvent. From the curve in Fig. 5b, we may read off at $v_L = (1 - v_P) = 0.47$ the diffusion coefficient of ethanol, $9 . 10^{-7}\,cm^2\,s^{-1}$, whereas the direct measurement in the gel based on poly(2-hydroxyethyl methacrylate) swollen in water[22] yielded the value $10.5 . 10^{-7}\,cm^2\,s^{-1}$. The corresponding pair of the diffusion coefficients for propanol is $4 . 10^{-7}$ (read off from the graph in Fig. 5c) and $6.4 . 10^{-7}\,cm^2\,s^{-1}$ (determined directly[22]). With respect to approximations and assumptions involved in this comparison, the agreement may be considered satisfactory.

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