

PARTITION COEFFICIENTS AND RATES OF DIFFUSION OF SOME MODEL COMPOUNDS IN SWOLLEN POLY(2-HYDROXYETHYL METHACRYLATE) GELS OF VARIOUS POROSITY-

P. ŠPAČEK and M. KUBÍN

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

Received March 6th, 1971

Diffusion (D) and permeation (P) coefficients of potassium chloride, ethanol, 1-propanol and cyclohexanol were measured in poly(2-hydroxyethyl methacrylate) gel swollen to equilibrium in water. From the values of P and D , the partition coefficient k_{kin} was calculated and compared with the partition coefficient k_{st} , obtained from the equilibrium sorption measurements. Both these quantities were found to differ from each other; the difference is explained by the existence of local microheterogeneities in the swollen copolymer. The effect of the content of water and crosslinking agent in the copolymerization mixture on the differences between k_{kin} and k_{st} in the copolymer thus obtained was also investigated.

The results of measurements of light-scattering and rheoptical properties of swollen gels based on poly(2-hydroxyethyl methacrylate)^{1,2} were interpreted in terms of a hypothesis that — although the hydrophilic gel appears to be optically quite homogeneous, and in the swollen state is obviously above its glass transition temperature — it nevertheless contains regions having a higher degree of order of the polymeric network, provided the degree of crosslinking is low and the gel is swollen in not too good a solvent (such as, *e.g.*, water). The assumed volume fraction of these regions is as high as 10%; their dimensions can reach several thousand Å. In a number of other papers³⁻⁵, the method of turbidity ratios was applied to the apparently homogeneous as well as heterogeneous gels obtained by the crosslinking copolymerization of 2-hydroxyethyl methacrylate under various conditions. It follows from these results that also in the so-called homogeneous gel there exist particles of considerable size having different refractive indices. Irrespective of differences in views concerning the character of inhomogeneities, we can regard it as proved that such gel, if swollen with water to equilibrium, represents a heterogeneous system, and this fact should also be reflected in measurements of its transport properties.

From the theoretical viewpoint, measurements of the rate of diffusion of various low-molecular-weight compounds in the gel, along with the knowledge of the respective equilibrium data (equilibrium sorption) enable us to form an idea of the occurrence of the so-called non-Fickian behaviour of the polymer, or the presence

of local inhomogeneities^{6,7}. It has been the aim of the present work to verify the assumed existence of local heterogeneities in swollen poly(2-hydroxyethyl methacrylate) gels by measuring the diffusion and partition coefficients of several low-molecular-weight model compounds.

EXPERIMENTAL

Materials

Membranes. Three gel samples were prepared by copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate (a crosslinking agent) in an aqueous medium: samples A and B, both with 1% by vol. of the crosslinking agent (with respect to the monofunctional monomer) contained 40 and 65% water in the initial mixture, respectively; sample C contained 40% by vol. H₂O and 0.11% by vol. of the crosslinking agent. The system ammonium persulphate-2-(dimethylamino)ethyl acetate was used as the initiator⁸. Foils, approx. 1 mm thick, were obtained by copolymerization between two parallel glasses, whose parallelism was checked by means of a micrometric screw with an accuracy of ± 0.01 mm. The polymerization proceeded at room temperature for about 5 h and was completed by heating to 70°C for additional two hours. The residual low-molecular-weight components of the copolymerization mixture were removed by repeated extraction carried out for several hours in four portions of boiling water. Membranes for the diffusion measurements with required shape were cut from the foil by means of a steel punch; the rest was used for sorption equilibrium measurements in the ternary systems.

Model compounds: potassium chloride, anal. purity grade (Lachema, Brno), ethanol, commercial product of highest purity (96%), 1-propanol, anal. purity grade, redistilled on a column (1 m high, ceramic packing) after drying with sodium (b.p. 97.0–97.2°C), cyclohexanol, anal. purity grade, distilled.

Measuring Procedure

The apparatus used was described in detail elsewhere⁹; let us only note here that it combines a diffusion cell with a twin membrane pump; the oscillatory movement of both teflon membranes, T, is derived from a common eccentric wheel. The membrane pumps provide circulation of the measured solutions on both sides of the gel membrane, M. The apparatus (without the driving eccentric) is schematically represented in Fig. 1. The apparatus is designed so as to make the volume of the diffusion cell as small as possible, because a large measuring volume is the common drawback of similar instruments used in this kind of measurements^{10–14}. Large volume of the diffusion cell reduces the sensitivity, since the concentration changes caused by diffusion through the membrane are indirectly proportional to it; in the *in situ* measurements, the minimal size of the measuring cell is usually determined by the necessity of a thorough stirring and by the presence of the sensing element of the concentration detector.

The experiment was so arranged (Fig. 1) that in one closed loop a dilute aqueous solution of the diffusing compound was circulating, whose concentration (c_1) could be regarded as constant throughout the measurement (the volume of the storage tank V inserted into this loop was comparatively large (50 ml) in relation to the very low total amount of the substance that passed through the membrane during the experiment). To follow the time dependence of the concentration of the measured compound, the measuring cell of a flow differential refractometer (Waters Associates, model R 4) was introduced into the second loop. Such arrangement avoids the necessity of stirring the solutions near the surface of the membrane, so that the volume of the

measuring loop could be relatively small (5 ml), which together with the high sensitivity of the refractometer used allowed accurate and comparatively little time-consuming measurement of the diffusion and permeation coefficients, even with low concentration differences of the diffusing compound across the membrane. (This turned out to be important in our case where changes in the equilibrium degree of swelling had to be avoided.) The flow of the liquid through the diffusion cell must be sufficiently fast in order to suppress the effect of stagnant laminar films of the liquid at the membrane surface¹⁵; a flow rate of 6 ml/min proved to be adequate.

The output of the refractometer was connected to a recorder (EZ 4, Laboratorní přístroje, Prague, full scale deflection 5 mV); the output of the refractometer (100 mV) was adjusted to this purpose with the aid of a precise helical potentiometer Aripot (Aritma, Prague, resistance 10 kΩ). To exploit the full sensitivity of the differential refractometer, it was necessary to improve the function of the external ultrathermostat by adjusting the contact thermometer according to Becsey and Bierlein¹⁶. The adjustment is based on a forced swinging motion of the controlling magnet around its equilibrium position; the vertical shift of the contact in our arrangement corresponds to approx. 0.25°C, the frequency being one oscillation in two seconds; the temperature fluctuations are thus reduced almost ten times, *i.e.* to $\pm 0.002^\circ\text{C}$ (measured with a miniature thermistor in the outlet of the ultrathermostat).

The diffusion coefficient D ($\text{cm}^2 \text{s}^{-1}$), was calculated according to⁷

$$D = l^2/6L; \quad (1)$$

here, l is the membrane thickness (cm) and L (s) is the so-called "time lag". L is determined by extrapolating the linear part of the dependence of the concentration $c_2(t)$ back to the original zero line. This method, originally suggested by Barrer¹⁷ for the diffusion of gases in solid polymers, may be applied also to condensed systems, if the concentration on one side of the membrane, c_1 , is constant, and the time-dependent concentration of the diffusing compound on the other side is negligibly small in comparison with c_1 throughout the experiment.

The permeability coefficient, P ($\text{cm}^2 \text{s}^{-1}$), was determined from an equation which follows directly from the first Fick's law applied to the stationary flow of the compound through the membrane. If $c_2 = 0$ at $t = 0$, then

$$P = (V_2 l / F c_1) dc_2 / dt, \quad (2)$$

where V_2 (cm^3) is the volume of the measuring loop, F is the effective area of the membrane (cm^2),

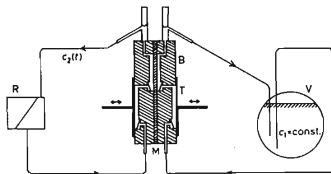


FIG. 1

Experimental Arrangement (Schematically)

B Stainless steel block, M measured membrane, R refractometric cell, V vessel with stock solution, T teflon membrane of the pump.

and dc_2/dt is the slope of the linear part of the time dependence of c_2 . If we follow, in a single experiment, both the initial non-stationary course of diffusion and the rate of the transport in the steady state, we obtain the "kinetic" partition coefficient from the relation⁷

$$k_{\text{kin}} = P/D. \quad (3)$$

To meet the initial conditions necessary for the application of the above relations, the experiment was arranged so that at first pure water was flowing in both circulation circuits, and was at the moment $t = 0$ replaced by a solution with the known concentration c_1 in the circuit containing the storage tank. (When L is being determined, the transportation lag in the connecting capillary tubes between the membrane and the refractometer might play a role; however, in our arrangement the correction was about 20 s, a value quite negligible in comparison with the usual values of L which amounted to hours.) The experiment proceeded until a sufficiently long linear part of the time dependence of c_2 was obtained. The final value of c_2 was not higher than several hundredths per cent, which in comparison with c_1 (1 to 2%) ensures a satisfactory fulfilment of the required boundary conditions.

At the end of each experiment, the refractometer deflection was independently calibrated by a solution with known concentration of the diffusing compound; F and l were obtained by direct measurements with a micrometric screw. To determine V_2 , the measuring loop was filled with a carefully prepared solution of an appropriate compound; the solution was then transferred quantitatively into a volumetric flask, and concentration was determined by the differential refractometer; V_2 was then calculated from the material balance. These measurements were carried out, on the one hand, using a solution of potassium chloride, with the gel membrane replaced by a polyethylene film, and on the other, with a solution of sucrose, for which the gel membranes based on poly(2-hydroxyethyl methacrylate) are practically impermeable.

The partition coefficient can be obtained independently from the results of an equilibrium measurement. If a sample of water-swollen gel having a volume V_g is immersed into a solution of a known concentration c_0 and volume V_0 , the concentration equilibrium attained after a certain time will yield a concentration c' in the solution and c_g in the gel. Let us designate the partition coefficient thus obtained by k_{st} ; it may be calculated using the relation

$$k_{st} = c_g/c' = (V_0/V_g) [\Delta c/(c_0 - \Delta c)], \quad (4)$$

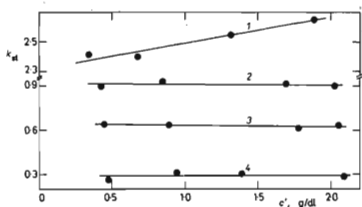


FIG. 2

Concentration Dependence of k_{st} as Determined by Equilibrium Measurements in a System Water-Gel-Sorbate

Sorbate: 1 cyclohexanol, 2 1-propanol, 3 ethanol, 4 potassium chloride.

where Δc is the concentration difference $c_0 - c'$. The volume of the gel, V_g , was calculated from its geometric dimensions; it was found that within the used concentration range of the compounds under investigation the changes in the degree of swelling against the equilibrium degree of swelling in pure water were virtually negligible (the differences did not exceed 3%). The concentration changes were again measured with the refractometer, and a mean value from three independent determinations was taken as the resulting k_{st} (the individual determinations did not differ from each other by more than $\pm 1\%$ rel.).

RESULTS AND DISCUSSION

The partition coefficients k_{st} calculated from the equilibrium measurements with potassium chloride, ethanol, 1-propanol and cyclohexanol are plotted in Fig. 2 against the equilibrium outer concentration c' . Only the partition coefficient of cyclohexanol is slightly concentration-dependent within the investigated concentration range. For a dissolved compound, which is not preferentially sorbed by the polymeric network, the equilibrium concentration in the outer solution should be identical with its concentration inside the gel related to the water present in the swollen gel. Thus, from the degree of swelling of the membrane and from the density of the dry copolymer it is possible (assuming the additivity of volumes during swelling) to calculate a value of 0.43 for the partition coefficient of the compound which is not preferentially sorbed on the polymer matrix. By comparing the obtained values of k_{st} with this hypothetical value, we can see that the strong electrolyte (KCl) is partially excluded from the gel phase, whereas all three alcohols under investigation are preferentially sorbed by the polymer; the magnitude of this effect increases with the decreasing polarity of the compound sorbed^{18,19}. This fact seems to be at variance with the behaviour of the binary system gel-alcohol, where the equilibrium degree of swelling decreases in the series ethanol-1-propanol-cyclohexanol²⁰. However, in the case of the ternary systems under investigation, the less polar higher alcohols obviously prefer the less polar gel phase to the highly polar phase of pure water, in contrast with the hydrated ions of the strong electrolyte.

The results of the diffusion experiments evaluated by means of Eqs (1)–(3) are summarized in Table I, which also includes the values of k_{st} corresponding to the mean concentration of solutions on both sides of the membrane during the diffusion run. As seen from the Table, the reproducibility of determination of P and D (and thus also k_{kin}) is good.

The diffusion coefficients which are immediately related to the mobility of molecules inside the membrane decrease with the size of the diffusing molecules as expected (Table I). The permeation coefficients, which determine the amount of the compound passing through the membrane at a certain concentration difference outside the gel, are not as unambiguously dependent on the size of the molecule as D are. Thus, for instance, the values of P for potassium chloride are almost the

same as for a comparatively large molecule of cyclohexanol. This is due to the fact that P is proportional not only to D , but to the partition coefficient as well.

The existence of local microheterogeneities in the membrane under investigation (*i.e.*, regions in which the diffusion and/or partition coefficient assume values other than those in their surroundings) can manifest itself by different values of the quantities k_{st} and k_{kin} , determined by both independent methods. So far, no exact theoretical analysis of diffusion in a heterogeneous medium has been suggested; however, during experimental study of the stationary and non-stationary diffusion in the heterogeneous system polymer-filler²¹, relevant differences were found between the respective diffusion coefficients (which in this case correspond to differences between k_{st} and k_{kin}).

A comparison between the values of the partition coefficients k_{st} , determined from the equilibrium sorption, and k_{kin} , calculated from the transport quantities P and D , shows that there actually exist considerable differences between these two values and that these differences increase with the size of the diffusing molecules. In the case of KCl, k_{kin} and k_{st} are equal within limits of experimental error; in the case

TABLE I
Diffusion (D , $\text{cm}^2 \text{s}^{-1}$), Permeation (P , $\text{cm}^2 \text{s}^{-1}$) and Partition Coefficients in Membrane C Equilibrated in Water at 25°C

$P \cdot 10^7$	$D \cdot 10^7$	k_{kin}	k_{st}	$P \cdot 10^7$	$D \cdot 10^7$	k_{kin}	k_{st}
KCl, $c_1 = 1 \text{ g/dl}^a$				1-Propanol, $c_1 = 2 \text{ g/dl}^a$			
3.53	13.8	0.26	0.29	4.85	6.32	0.77	0.91
3.67	12.1	0.30	0.29	5.18	6.43	0.81	0.91
3.67	12.9	0.28	0.29	4.88	6.36	0.77	0.91
3.90	12.9	0.30	0.29	5.21	6.67	0.78	0.91
				5.08	6.63	0.77	0.91
				4.95	6.52	0.76	0.91
Ethanol, $c_1 = 2 \text{ g/dl}^a$				Cyclohexanol, $c_1 = 2 \text{ g/dl}^a$			
5.88	10.7	0.55	0.63	2.82	2.64	1.07	2.49
6.20	10.5	0.59	0.63	2.93	2.66	1.10	2.49
6.35	10.9	0.58	0.63	2.87	2.60	1.10	2.49
5.87	10.6	0.55	0.63	2.82	2.47	1.14	2.49
				3.07 ^b	2.62	1.17	2.49
				2.86 ^c	2.48	1.15	2.49

^a See Fig. 1 for definition. ^{b,c} Two identical experiments with reversed position of the membrane with respect to the diffusion flux.

of ethanol, however, the difference between the mean value of k_{kin} (0.569) and the corresponding equilibrium k_{st} (0.63) is statistically significant: the probability that k_{kin} might attain the value 0.63 only as a consequence of random fluctuations caused by experimental error is only 0.3%, as follows from the calculation of the one-sided confidence interval based on Student's statistics t . The difference between both quantities is even more pronounced in the case of 1-propanol; for cyclohexanol, both partition coefficients differ by a factor greater than 2.

However, to have some ground for the assumption that the differences between k_{kin} and k_{st} can really be attributed to local heterogeneities in the gel, we have to preclude all known influences having similar effects. One of the causes of the difference between k_{kin} and k_{st} could consist in the considerable concentration dependence of k_{kin} , due to the considerable concentration dependence of the diffusion and/or permeation coefficient. Although this influence is rather unlikely within the concentration range under investigation, it cannot be excluded *a priori*; it is therefore desirable to measure both k_{kin} and k_{st} in the same range of concentrations. However, the error in determination of k_{st} by the method used increases with decreasing concentration c' in such a way that it is not possible to determine k_{st} directly for c' lower than 0.5% with sufficient accuracy. To be able to exclude the effect of the possible steep concentration dependence of the quantities under investigation in the low-concentration range (which was experimentally established²², *e.g.*, for the partition coefficient of some salts in swollen poly(2-hydroxyethyl methacrylate) gel), the diffusion coefficients of 1-propanol and cyclohexanol were measured so that the concentration of the diffusing compound on both sides of the gel membrane would not fall below 0.5%. The gel was first put into equilibrium with the solution of the corresponding alcohol having the concentration $c_0 = 0.5\%$; this was accomplished by replacing the distilled water circulating on both sides of the membrane by this solution. At the time $t = 0$, the concentration on one side was increased jumpwise

TABLE II
Diffusion (D , $\text{cm}^2 \text{s}^{-1}$), Permeation (P , $\text{cm}^2 \text{s}^{-1}$) and Partition Coefficients in Membrane C Equilibrated in a 0.5% Solution at 25°C

$P \cdot 10^7$	$D \cdot 10^7$	k_{kin}	k_{st}	$P \cdot 10^7$	$D \cdot 10^7$	k_{kin}	k_{st}
1-Propanol, $c_1 = 2 \text{ g/dl}^a$				Cyclohexanol, $c_1 = 2 \text{ g/dl}^a$			
5.28	6.27	0.84	0.91	3.06	2.30	1.33	2.54
5.02	6.26	0.80	0.91	3.07	2.29	1.34	2.54
				3.12	2.26	1.38	2.54

^a $c_2 = 0.5 \text{ g/dl}$ at $t = 0$; see Fig. 1 for definition.

to c_1 . To calculate D and P , Eqs (1) and (2) may be used in this case, if in Eq. (2) c_1 in the denominator is replaced by the difference ($c_1 - c_0$).

The results of these experiments are summarized in Table II. The value of k_{kin} has somewhat increased (especially for cyclohexanol), but the difference between the two partition coefficients still remains significant (particularly with respect to the fact that k_{st} , too, slightly increases with concentration). It is evident, therefore, that the differences found between the partition coefficients cannot be explained in terms of the concentration dependence of the diffusion or partition coefficients.

With respect to the fact that the diffusion coefficients of the low-molecular-weight compounds in a gel of this type are lower by more than an order of magnitude than in pure water, it is also not possible to explain the difference between k_{kin} and k_{st} by an error due to the stagnant laminar films on the surfaces of the membrane under investigation¹⁵.

To eliminate the effect of a possible gradient of some property across the membrane^{6,7} on the value of the diffusion coefficient thus determined (and therefore also on k_{kin}), the last two experiments listed in Table I were carried out in such a way (under otherwise similar conditions) that the membrane was each time oriented in the direction opposite to that of the diffusion flux. It could be demonstrated⁷ that in the case of a membrane with structure in which the properties affecting the diffusion coefficient are not symmetrically distributed with respect to the plane passing through its centre, the values L (and thus also D) must be different in these two experiments. The results show, however, that the effect of a possible gradient in the membrane does not play any important role.

Therefore, the differences between k_{kin} and k_{st} can be attributed to the existence of local microheterogeneities in a swollen poly(2-hydroxyethyl methacrylate) gel. To explain the effect of the conditions of preparation of the gel on the presence and nature of these heterogeneities, several diffusion experiments and sorption equilibrium measurements were made on membranes which differed by the content of the crosslinking agent, on the one hand, and by the water concentration in the copolymerization mixture, on the other. Both these factors are known to affect the optical homogeneity of the gels^{10,23}. The mean values of D , P , and k_{kin} for these membranes, along with the corresponding values of k_{st} are summarized in Table III which for reasons of clarity also includes the mean values from Table I (that is, the part corresponding to membrane C). Membranes A and C were quite transparent; membrane B, owing to a larger amount of water in the copolymerization mixture, was strongly turbid.

A comparison of the experimental values for membranes A and C shows that the higher content of the crosslinking agent somewhat lowers the diffusion coefficients of both alcohols under investigation. For membrane A with a higher degree of crosslinking, a smaller difference between k_{st} and k_{kin} was found (in the case of 1-propanol, both partition coefficients coincide within limits of experimental error). If we assume

that the system in question is a microheterogeneous one of the type water-gel³, this experimental fact means that separation of water during the crosslinking copolymerization is apparently suppressed by the addition of the crosslinking agent. Similar effect was observed also in papers^{1,2}; it was, however, explained by a negative influence of the crosslinking agent upon the formation of oriented regions in the copolymer.

TABLE III

Diffusion (D , $\text{cm}^2 \text{s}^{-1}$), Permeation (P , $\text{cm}^2 \text{s}^{-1}$) and Partition Coefficients in Membranes of Different Composition

Membrane	Compound	$D \cdot 10^7$	$P \cdot 10^7$	k_{kin}	k_{st}
A	1-propanol	6.39	5.08	0.80	0.83
	cyclohexanol	2.18	2.86	1.31	2.26
B	1-propanol	18.02	15.62	0.87	0.87
	cyclohexanol	8.43	9.13	1.08	1.88
C	1-propanol	6.49	5.03	0.78	0.91
	cyclohexanol	2.58	2.89	1.12	2.49

Membrane B represents an interesting and morphologically not as yet fully investigated system. Although its turbidity is obviously a consequence of the phase separation during crosslinking copolymerization in the presence of a poor solvent (water), no unambiguous description has so far been offered for the nature of these phases (*e.g.*, their continuous character, size distribution of the individual regions, their composition, *etc.*).

The diffusion and permeation coefficients of both alcohols in membrane B are considerably larger than in both transparent membranes. If we assume that what occurs during phase separation, is essentially a syneresis of excess water and monomer, the membrane obtained has a heterogeneous structure which contains continuous or non-continuous regions in which the diffusion coefficient is higher than in the surrounding continuous gel. In consistence with this assumption, the values of k_{st} in membrane B for propanol and cyclohexanol are shifted toward unity, which according to definition represents their value in an infinitely diluted polymeric network.

From this shift, the volume fraction of the excluded aqueous phase may be estimated. It follows from the material balance for the observed apparent partition coefficient.

cient k_{st} in a two-phase system that

$$\bar{k}_{st} = k_I v_1 + k_{II}(1 - v_1), \quad (5)$$

where index I corresponds to the aqueous and index II to the gel phase; v and k designate the volume fraction and the partition coefficient, respectively. If we substitute into Eq. (5) $k_I = 1$ (as corresponds to water) and for k_{II} the value k_{st} found for membrane C, we can calculate the volume fraction of the assumed aqueous phase in the turbid membrane B. We then have $v_1 = 0.30$ from measurements with cyclohexanol (in good agreement with the results obtained in¹⁹), and $v_1 = 0.24$ from measurements with propanol. However, the latter value is subjected to a considerable error, which is a consequence of a small difference between two large numbers. Thus, *e.g.*, if we substitute 0.88 instead of 0.87 for k_{st} of propanol in membrane B (which is still within limits of experimental error), the volume fraction of water, v_1 , will be practically the same as that found with cyclohexanol.

Diffusimetry alone cannot give a definitive answer to the question concerning the morphology of heterogeneities formed as a consequence of phase separation, but a better agreement between values of k_{st} and k_{kin} found for membrane B suggests a plausible hypothesis that the excluded (aqueous) phase is more or less continuous. With respect to a considerable difference between the diffusion coefficients in the gel and in water (the diffusion coefficient of 1-propanol in water²⁴ at 25°C is $1.15 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and also to the comparatively large volume fraction of the excluded phase in membrane B, the transport in such a system will prevalingly occur in the continuous aqueous phase. The effect of heterogeneities (mentioned above) on the total flow of matter through the membrane will thus play a comparatively smaller part. This effect decreases with the size of the diffusing molecule (in the case of 1-propanol, the values of k_{st} and k_{kin} for membrane B are identical).

The authors are indebted to Mrs J. Hromádková for careful technical assistance in the experiments performed in the present work.

REFERENCES

1. Ilavský M., Prins W.: *Macromolecules* 3, 415 (1970).
2. Ilavský M., Prins W.: *Macromolecules* 3, 425 (1970).
3. Sedláček B.: *This Journal* 32, 1595 (1967).
4. Sedláček B.: *This Journal* 32, 1398 (1967).
5. Sedláček B.: *This Journal* 32, 1599 (1967).
6. Petropoulos J. H., Roussis P. P.: *J. Chem. Phys.* 49, 1496 (1967).
7. Crank J., Park G. S.: *Diffusion in Polymers*, p. 165. Academic Press, London 1968.
8. Wichterle O., Lím D.: *Czechoslov. Pat.* 91918.
9. Špaček P., Kubín M.: *Rev. Sci. Instr.* 42, 284 (1971).
10. Špaček P., Kubín M.: *J. Polymer Sci. C16*, 705 (1967).
11. Erdős E., Jirů Z.: *Chem. listy* 49, 1579 (1953).

12. Rius A., Tordesillas M. I.: *Anales Real. Soc. Espan. Fis. Quím. (Madrid)* 51B, 593 (1955).
13. Northrup J. H., Anson M. L.: *J. Gen. Physiol.* 12, 543 (1929).
14. Kubín M., Špaček P.: *This Journal* 30, 3294 (1965).
15. Kubín M., Špaček P.: *This Journal* 32, 2733 (1967).
16. Becsey J. G., Bierlein J. A.: *Rev. Sci. Instr.* 38, 556 (1967).
17. Barrer R. M.: *Diffusion in and through Solids*. Cambridge Univ. Press, London 1951.
18. Tuzar Z., Bohdanecký M.: *This Journal* 34, 289 (1969).
19. Dušek K., Sedláček B.: *European Polymer J.*, in press.
20. Wichterle O., Chomeček R.: *Symposium on Macromolecular Chemistry, Prague 1965*, P 620.
21. Barrer R. M., Barrie J. A., Rogers M. G.: *J. Polymer Sci. A1*, 2565 (1963).
22. Dušek K., Bohdanecký M., Vošický V., Sedláček B.: *International Symposium on Macromolecules, Leiden 1970*, p. 141.
23. Kopeček J., Jokl J., Lim D.: *J. Polymer Sci. C16*, 3877 (1968).
24. Gary-Bobo C. M., Weber H. W.: *J. Phys. Chem.* 73, 1155 (1969).

Translated by L. Kopecká.