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Abstract

Full Text

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ON THE PERMEABILITY OF ION-EXCHANGE MEMBRANES WITH RESPECT TO LIGHT AND HEAVY WATER

(Presented by Academician A. N. Frumkin, 24 X 1962)

This work is devoted to determining the relation between the degree of swelling of ion-exchange membranes and their permeability with respect to vapors of deuterium and protium oxides.

Ion-exchange resins and ion-exchange membranes prepared on their basis do not have pores in their structure in the usual sense of the word (*1, 2*). The transfer of water molecules through a membrane occurs as a result of its swelling, which is the result of hydration of the active groups and of the mobile ions neutralizing them (*3*). If a series of adjoining hydrate shells of neighboring groups begins on one side of the membrane and ends on the other, then it is a "channel" through which water penetrates the membrane (*4*). The cross section of the "channels" in the membrane must evidently increase as its swelling increases. The latter depends on the nature of the counterions and increases with increasing temperature and polarity of the solvent molecules (*5-8*). Consequently, the permeability of ion-exchange membranes must also depend on their salt form and temperature and, with respect to H_2O, must be higher than with respect to the less polar D_2O.

Fig. 1. Schematic of the apparatus for studying the permeability of an ion-exchange membrane. **1, 2** –chambers, **3** –ion-exchange membrane, **4** –gaskets of vacuum rubber, **5** –tightening bolts, **6** –mesh metal gasket, **7, 8** –jackets for thermostating, **9-13, 15** –vacuum stopcocks, **14, 16** –reservoirs

Experimental verification of the ideas set forth was carried out using a sulfonated polystyrene cation-exchange membrane DPU-70 in various salt forms. Pure H_2O, D_2O, and their mixtures containing 25, 50, and 75% deuterium ox-

Fig. 2.

Figure 2: Fig. 2.

Fig. 3.

Figure 3: Fig. 3.

ide were used as the initial solutions. The permeability of the membrane was determined by the manometric method (*9*). It should be noted that at present, for measuring the moisture-permeability coefficient of polymer films, methods are used in which water labeled with tritium is employed (*10–13*). However, as follows from the very principle of these methods, it is impossible to use them for the purposes of our investigation.

The study of the permeability of the membrane was carried out in an apparatus whose scheme is shown in Fig. 1. The membrane under investigation was hermetically clamped between two thermostated chambers connected to manometers, each of which was evacuated before the start of the experiment. Chamber **1**

with the aid of a stopcock, it was connected to a reservoir containing 1 ml of depleted water with a definite deuterium concentration. When the stopcock was opened, a rapid rise in pressure was observed in this chamber, whereas in the membrane-separated chamber 2 the pressure increased slowly. When the stopcock was opened, the vapor pressure of water in this chamber reached 7–8 mm Hg (depending on the D_2O content and temperature) within one and a half minutes. In the membrane-separated chamber 2, to attain a pressure amounting to about 92% of the pressure in chamber 1, 18–50 min was required. The quantity τ, the reciprocal of this time, was taken to characterize the permeability of the membrane. The experimental results are presented in Fig. 2.

Fig. 2. Dependence of the permeability of an ion-exchange membrane on the D_2O content in the initial mixture. **1, 2, 3** –membrane in the sodium form; temperature of the experiments respectively 20, 50, and 80° ($±$0.05°). **4, 5** –membrane respectively in the lithium and barium forms; temperature of both experiments 20°.

Fig. 3. Dependence of the permeability and swelling of an ion-exchange membrane on the hydrodynamic radius of the saturating ion. **1** –permeability with respect to pure H_2O; **2** –permeability with respect to a mixture of H_2O and D_2O containing 50% deuterium oxide; **3** –permeability with respect to pure D_2O; **4** –swelling of the membrane.

With increasing D_2O content in the initial mixture, the permeability of the membrane decreases. Consequently, H_2O molecules penetrate through the membrane preferentially, and the diffused fraction of the mixture is partially enriched in protium oxide. With increasing temperature the permeability of the mem-

Fig. 4. Dependence of the permeability and swelling of an ion-exchange membrane on temperature. Designations as in Fig. 3

Figure 4: Fig. 4. Dependence of the permeability and swelling of an ion-exchange membrane on temperature. Designations as in Fig. 3

brane increases (curves 1, 2, 3). At the same time, the difference in permeability with respect to light and heavy water decreases appreciably. For different temperatures, the difference in permeability with respect to pure protium oxide is smaller than with respect to deuterium oxide (and its mixtures with H_2O) at the same temperatures. This indicates an increase in the rate of transfer of heavy-water molecules through the membrane as the temperature rises. A similar regularity is also observed in going from the barium to the sodium and then to the lithium forms of the membrane (curves 1, 4, 5). In the same sequence, the relative swelling of the membrane increases. In this case the cross section of the "channels" increases, and, consequently, so does the total amount of water penetrating through the membrane. The effect of preferential transfer of light-water molecules is weakened in this case.

Thus, the permeability of the ion-exchange membrane is determined by its swelling, which is well confirmed by the curves presented in Figs. 3 and 4. As can be seen from the figures, the permeability and swelling

membranes have almost the same dependence on the hydrodynamic radius of the saturating ion and on temperature.

The results obtained agree with the effect we established earlier^(14) of the nonuniform distribution of deuterium oxide and protium oxide in a swollen ion-exchange resin. This effect, based on the different dissolving capacity of H_2O and D_2O with respect to electrolytes^(15, 16), consists in the fact that in the ion exchanger–water system the hydrate shell of the active groups and their counterions has an increased H_2O content compared with the equilibrium solution of deuterium oxide. The selectivity of sorption of protium oxide by an ion exchanger swelling in a mixture of H_2O and D_2O depends on its salt form and decreases with increasing temperature and deuterium oxide content in the contacting solution. The permeability of ion-exchange membranes, determined by their swelling, must show a similar dependence. The latter is well confirmed by the experimental data obtained in the present work.

Fig. 4. Dependence of the permeability and swelling of an ion-exchange membrane on temperature. Designations as in Fig. 3

Consequently, the preferential permeability of an ion-exchange membrane with respect to light water and the effect of nonuniform distribution of H_2O and D_2O in a swollen ion exchanger are of the same nature.

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