EFFECT OF THE HYDROPHILIC CHARACTER
OF THE POLYMERIC BACKBONE ON MEMBRANE PERMEABILITY

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The paper is reporting an investigation of the effect of the hydrophilic character of membranes prepared by the copolymerization of a hydrophilic and a hydrophobic monomer upon the transport of NaCl and H_2O. It follows from the results that the 2-(hydroxyethoxy)ethyl methacrylate-methyl methacrylate copolymer crosslinked with ethylene dimethacrylate has a higher permeability for the above compounds than the copolymer of 2-hydroxyethyl methacrylate and methyl methacrylate crosslinked with ethylene dimethacrylate at the same degree of hydration. This effect has been interpreted in terms of the influence of the difference in the hydrophilic character of the initial monomers on the formation of inhomogeneities in the three-dimensional network. The introduction of ionogenic groups into the copolymers under investigation affects their transport properties.

A membrane suitable for reverse osmosis must fulfil three basis requirements[1]: appropriate separation activity, high permeability, sufficiently long lifetime. The properties of the membrane are affected by both chemical and physical factors. The membranes used so far in reverse osmosis are in most cases made of a single polymer — secondary cellulose acetate — by an extremely complex procedure[2-4]. By this procedure, an asymmetric membrane has been prepared in which the flow rate of water is considerably higher while at the same time a high separation activity is preserved. The selection of an appropriate membrane must be divided into two parts owing to a number of factors influencing the separation. First, the effect of the chemical structure upon the transport properties of the polymer must be studied; then, either an ultrathin or an asymmetric membrane can be prepared from the polymer whose transport characteristic will be similar to that of the secondary cellulose acetate.

Our earlier paper[5] has been dealing with the permeability of membranes based on poly(2-hydroxyethyl methacrylate) modified by the introduction of ionogenic groups. We have found that ampholytic membranes containing the same amounts of weak acidic and weak basic groups have higher diffusion coefficients for inorganic salts compared to neutral membranes. We have also deduced that an approximation of the free volume by the solvent volume does not hold for the poly(2-hydroxyethyl methacrylate) gel. This conclusion has been assumed to be generally valid for all systems swollen in a thermodynamically poor solvent. It has been our aim to verify in more detail the above conclusions in this paper which reports the effect of the hydrophilic character of the basic polymeric backbone on the transport of NaCl and H_2O.

The hydrophilic character of the polymeric backbone has been modified by co-polymerization of 2-hydroxyethyl methacrylate or 2-(hydroxyethoxy)ethyl methacrylate and methyl methacrylate. Methacrylic acid and 2-diethylaminoethyl methacrylate were used as ionogenic comonomers, and ethylene dimethacrylate was used as the crosslinking agent. Besides the objectives pointed out above, the determination of the dependence of the water and sodium chloride permeability ratio on the membrane structure will enable us to choose structures appropriate for the preparation of membranes for reverse osmotic separations.

EXPERIMENTAL

2-Hydroxyethyl methacrylate, ethylene dimethacrylate, methacrylic acid, 2-diethylaminoethyl methacrylate and 2,2′-azo-bis(methyl isobutyrate) were prepared and purified by a method described earlier[5]. 2-(Hydroxyethoxy)ethyl methacrylate was prepared by a method described in ref.[6], b.p. 98°C/1 mm Hg, n_D^{20} 1·4568. Methyl methacrylate was purified by rectification on a 40-plate column in an inert atmosphere under reduced pressure. B.p. 47°C/100 mm Hg. 2,2′-Azobis(2,4-dimethyl-4-methoxyvaleronitrile) was synthesized and reprecipitated several times from toluene with light petroleum, m.p. 59°C.

The procedure of membrane preparation, NaCl permeability measurements, determination of the distribution coefficients and of the equilibrium degree of swelling and the evaluation of results have been described in detail in ref.[5]. The permeability of water was measured in diffusometers made of Perspex and consisting of two cells having the same volume (50 cm^3) using 0·1 cm^{-3} of tritiated water (specific activity = 5 mCi/g). The changes in concentration were followed by taking 25 μl samples. The sample was diluted with 0·5 cm^3 H$_2$O and 7·5 cm^3 of the scintillation mixture. The radioactivity of samples thus obtained was measured on a liquid scintillation Intertechnique spectrometer. The permeability of both water and NaCl were measured at 25°C.

The permeability of water was calculated[7] from the slope of the dependence of log Δc vs t according to $P/\Delta x = V \Delta \ln (\Delta c)/2A \Delta t$, where A is the membrane area, V is the cell volume, Δx is the membrane thickness, and Δc is the concentration (count) difference between two cells at a time t.

RESULTS AND DISCUSSION

In the first part of the work the hydrophilic character of the 2-hydroxyethyl methacrylate backbone was modified by copolymerization with methyl methacrylate at a constant content of the crosslinking agent (Table I, membranes 1—6). A decrease in the hydrophilic character of the polymeric backbone leads to a monotonic decrease in both the diffusion coefficient of the salt and the diffusion coefficient of water (Table II, Fig. 1). An important result is to be seen in an increase in the ratios P_{H_2O}/P_{NaCl} and D_{H_2O}/D_{NaCl} with decreasing hydrophilic character of the polymer, *i.e.* with a decrease in the ratio of the concentrations of 2-hydroxyethyl and methyl methacrylate over the whole range of compositions under investigation. This result agrees well with the results obtained by an investigation of the poly(2-hydroxyethyl methacrylate) membranes crosslinked with different amounts of ethylene dimeth-

Table I

Composition of the Starting Mixture (mol/kg) for the Preparation of Modified Hydrophilic Membranes

Initiators: 2,2′-azo-bis(methyl isobutyrate), $6·1 . 10^{-3}$ mol/kg of the mixture (membranes 1—6, polymerization temperature 60°C), 2,2′-azo-bis(2,4-dimethyl-4-methoxyvaleronitrile), $4·8 . 10^{-3}$ mol/kg of the mixture (the other membranes, 50°C).

Composition of Starting Mixture	mol/kg					
Membrane:	1	2	3	4	5	6
2-Hydroxyethyl methacrylate	6·27	5·74	5·25	4·69	4·11	3·80
Methyl methacrylate	—	0·62	1·25	1·93	2·66	3·00
Ethylene dimethacrylate	0·124	0·131	0·133	0·133	0·134	0·137
Butanol	2·25	2·25	2·25	2·25	2·25	2·25
Membrane:	7	8	9	10	11	12
2-(Hydroxyethoxy)ethyl methacrylate	3·44	3·54	3·47	3·49	3·42	3·47
Methyl methacrylate	2·96	2·14	2·16	2·85	2·97	2·14
Ethylene dimethacrylate	0·216	0·211	0·043	0·128	0·043	0·127
Ethanol	3·50	3·50	3·50	3·50	3·50	3·50
Membrane:	13 (13A)[a]	14	15	16	17	18
2-(Hydroxyethoxy)ethyl methacrylate	3·49	2·64	2·41	2·20	2·08	1·98
Methyl methacrylate	2·14	2·12	2·11	2·87	2·88	2·90
2-Diethylaminoethyl methacrylate	—	0·585	0·606	0·602	0·591	0·571
Methacrylic acid	1·43	0·588	0·586	0·588	0·593	0·583
Ethylene dimethacrylate	0·129	0·051	0·244	0·047	0·146	0·247
Ethanol	3·50	3·50	3·50	3·50	3·50	3·50

[a] The concentrations in the case of membrane 13 A were in the given column as follows: 3·58, 2·28, 1·35, —, 0·134, 3·50.

acrylate both by the dialysis experiments[5] and by a study of reverse osmosis[8]. Jadwin explains this phenomenon in terms of a model of the primary and secondary water in the polymer. The diffusion of water can occur through both the primary (bound) water and through the regions of the secondary (free) water, while the diffusion of salt can proceed in the regions of the secondary water only. A decrease in the water content in the membrane interrupts the connection between the regions of the secondary water, thus rendering the salt transport more difficult. According to Jadwin[8], the effect of a change in the primary to the secondary water ratio in the case of the copolymers of 2-hydroxyethyl methacrylate and hydrophobic monomers is rather unpronounced. Moreover, the fact should be borne in mind that the presence of methyl methacrylate units in the copolymer raises the number of the physical crosslinks, thus reducing the mobility of the polymeric segments[5], which in agreement

with our previous conclusions about the effect of the mobility of segments upon the free volume leads to a decrease in the permeability of salt through the membrane.

Further part of this work was devoted to the copolymers of 2-(hydroxyethoxy)ethyl methacrylate (I) and methyl methacrylate (II). The hydrophilic character of such backbone compared with that of 2-hydroxyethyl methacrylate is higher (the polymer–water interaction parameter depending on the degree of croslinking lies in the former case within the range $0.50-0.55$ (ref.[6]) and in the latter case between $0.7-0.8$ (ref.[9])). By investigating the copolymers of a more hydrophilic monomer (I) with (II) we wished to verify the possibility of generalization of the conclusions obtained by the study of polymers based on 2-hydroxyethyl methacrylate (IV) to include more hydrophilic systems. Apart from neutral copolymers I(II)ethylene dimethacrylate (III), we also studied membranes modified by introducing ionogenic groups of methacrylic acid and/or 2-diethylaminoethyl methacrylate. As follows from a comparison of the permeabilities of membranes 12 (neutral), 13 (acidic) and 13A (basic), there occurs (as expected) a decrease in the permeability of NaCl through membranes containing methacrylic acid only or dimethylaminoethyl methacrylate only owing to a permanent charge on these membranes which gives rise to the Donnan potential.

TABLE II
Transport Properties and the Equilibrium Degree of Swelling of Membranes Studied at 25°C

Membrane	v_2	$P_{NaCl} \cdot 10^8$ cm^2 s^{-1}	$D_{NaCl} \cdot 10^7$ cm^2 s^{-1}	$P_{H_2O} \cdot 10^7$ cm^2 s^{-1}	$D_{H_2O} \cdot 10^7$ cm^2 s^{-1}	P_{H_2O}/P_{NaCl}
1	0·586	7·97	4·55	4·57	11·0	5·73
2	0·670	5·14	2·96	2·97	8·99	5·78
3	0·715	1·62	1·89	1·88	6·60	11·6
4	0·762	1·46	2·26	1·42	6·00	9·73
5	0·797	0·348	1·01	1·07	5·27	30·7
6	0·809	0·057	0·218	0·535	2·80	93·8
7	0·739	4·87	5·70	2·59	9·94	5·32
8	0·662	13·5	11·4	—	—	—
9	0·563	30·1	17·3	—	—	—
10	0·669	6·41	7·82	2·76	8·34	4·31
11	0·681	8·43	9·81	3·11	9·75	3·69
12	0·577	27·0	15·1	—	—	—
13	0·790	1·44	—	—	—	—
13A	0·823	3·54	—	—	—	—
14	0·422	84·5	—	—	—	—
15	0·527	27·6	—	—	—	—
16	0·520	32·2	—	6·44	13·4	2·00
17	0·586	18·2	—	4·29	10·4	2·36
18	0·603	11·5	—	3·94	9·9	3·43

A comparison of the permeability of NaCl through neutral (7, 10, 11) and ampholytic membranes (16—18) is represented in Fig. 2. In this case too (*cf.* also the comparison between membranes 8 and 9, on the one hand, and 14 and 15, on the other), the permeability of NaCl is accelerated with respect to the formation of an internal salt in this copolymer and the coulombic interactions ensuing therefrom[5].
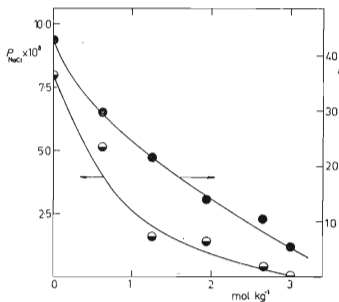

FIG. 1

Dependence of the Permeability Coefficients (cm^2 s^{-1}) of the Copolymers 2-Hydroxyethyl Methacrylate/Methyl Methacrylate/Ethylene Dimethacrylate on the Concentration of Methyl Methacrylate

FIG. 2
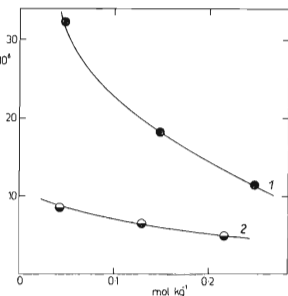
Dependence of the Permeability Coefficient P_{NaCl} (cm^2 s^{-1}) on Network Density (Concentration of Ethylene Dimethacrylate)

Copolymers: 1 2-(hydroxyethoxy)ethyl methacrylate (*I*)/methyl methacrylate (*II*)/ethylene dimethacrylate (*III*)/methacrylic acid-2-diethylaminoethyl methacrylate, 2 copolymer (*I*)/(*II*)/(*III*).
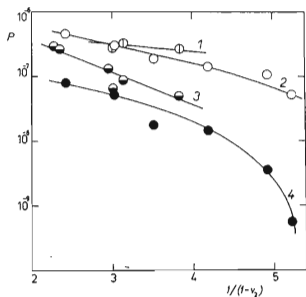

FIG. 3

Dependence of the Permeability Coefficients (cm^2 s^{-1}) on the Degree of Hydration of Copolymers

Copolymer 2-(hydroxyethoxy)ethyl methacrylate/ethylene dimethacrylate/methyl methacrylate: 1 for P_{H_2O}, 3 for P_{NaCl}. Copolymer 2-hydroxyethyl methacrylate/ethylene dimethacrylate/methyl methacrylate: 2 for P_{H_2O}, 4 for P_{NaCl}.

A comparison between the copolymers (*IV* with *II*, *I* with *II*) can give us an idea about the effect of the hydrophilic character on the behaviour of the systems. By plotting the dependence[10] of log *P* vs $1/(1 - v_2)$ (where v_2 is the volume fraction of the polymer) we obtain the dependence of permeability on the inverted degree of the membrane hydration. In contrast with membranes investigated by Yasuda and coworkers[10], the individual points of this curve do not lie on the same straight line; the cause is seen in the low degree of the equilibrium degree of swelling of the polymers investigated here (and thus in an enhanced interaction of the polymer with the diffusing particle), and also in the effect of the mobility of the polymeric segments upon the free volume in the membrane. However, for the individual groups of polymers it is possible to carry out a comparison of the course of these dependences on the degree of hydration. From this comparison, a mild but evident effect of the hydrophilic character of the polymeric backbone on the transport properties of the membranes can be deduced. The salt transport is accelerated in the case of copolymerization of the more hydrophilic monomer (2-(hydroxyethoxy)ethyl methacrylate) with methyl methacrylate compared with poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) having the same degree of hydration, as can be seen from Fig. 3 and also from the dependence of D_{NaCl} vs $1/(1 - v_2)$; a slight increase in the rate of water transport (Fig. 3) can also be observed in the former of the two cases.

This phenomenon can be interpreted in terms of our previous results obtained by studying the polymerization mechanism of hydrophilic methacrylates. We have found[11] that inhomogeneities are formed in a three-dimensional network, and that during polymerization there occurs non-uniform distribution of components in the reaction mixture. If there is a great difference between the hydrophilic characters of the initial monomers, *i.e.* in the case of the copolymer of 2-(hydroxyethoxy)ethyl methacrylate and methyl methacrylate, we can expect, even in the case of equal reactivities of the initial monomers, an increased tendency to the formation of inhomogeneities, particularly at higher conversions. With respect to the hydrophobic character of the crosslinking agent (ethylene dimethacrylate), the more crosslinked regions will be more hydrophobic, while in the more hydrophilic regions a lower network density can be expected. This will result in a non-uniform distribution of the monomer concentrations in the reaction mixture and thus in the polymer. Such an inhomogeneity both in the crosslinking density and in the distribution of the copolymerization components is regarded as the cause of the differences observed in the transport properties of the above copolymers at the same degree of hydration.

In conclusion, it can be summarized that the copolymerization of hydrophilic and hydrophobic monomers or a modification of structure of these copolymers due to the introduction of ionogenic groups permits to vary over a wide range the transport characteristic (ratio of the H_2O and NaCl permeabilities) of the resulting polymers. The systems investigated here are therefore suited for a development of the separation barriers both for dialysis and for the reverse osmotic separations. The transport properties of these copolymers under elevated pressure will be reported in a separate paper.

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