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The Solvent Properties of Water in Desalination Membranes

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ABSTRACT

The solvent properties of water in regular copolyoxamide and cellulose acetate membranes have been investigated. Partition coefficients of chlorides between the water in dense cellulose acetate membranes and a bulk aqueous phase decreased in the order: $Cs^+ > K^+ > Na^+ > Li^+ > Ca^{2+} > Mg^{2+}$. In copolyoxamide membranes, partition coefficients of both chlorides and nitrates showed similar trends. Partition coefficients in methanol appeared to be unity. KCl and CsCl were accumulated into the surface water from extremely low concentrations (0.1 mM) but not from moderate or high concentrations. Partition coefficients of the chlorides of Na^+, Li^+, Ca^{2+}, and Mg^{2+} were all less than unity and decreased with increasing concentration. In explanation of these findings, it is proposed that, when the hydrophobic pores of the membranes are wet by prolonged soaking in water, the high surface energy resulting from unfavorable surface-water interactions leads to an expansion of water out of the pores and a decrease in its macroscopic density. This "stretched" water has anomalously low entropy and high hydrogen-bond energy, which together profoundly change its solvent properties. By generating osmotic pressure gradients of opposite sign, an accumulated solute opposes expansion and stretching of pore water, while

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an excluded solute reinforces it. Infrared spectra supported this hypothesis: spectral characteristics of water in dense cellulose acetate membranes were accentuated by $MgCl_2$ and abolished by KCl.

INTRODUCTION

Living cells use metabolic energy to discriminate with exquisite precision between ions of like charge and similar size. Their ability to separate Na^+ and K^+ ions across thin membranes is unmatched in any laboratory analytical procedure. It has been suggested [1, 2] that this remarkable cation selectivity is achieved by means of transient changes in the hydrating properties of water contained in the clefts of the enzymes which transport the cations. In order to account for the biological data, it is necessary to postulate the existence of small pockets of water in which partition coefficients of cations decrease with increasing degree of hydration: $Cs^+ > K^+ > Na^+ > Li^+ > H_3O^+ \gg Ca^{2+} > Mg^{2+}$, those for Cs^+ and K^+ being greater than unity, and those for the small cations all less than unity. It was further suggested that such changes in free energies of hydration might be expected if the water increased in hydrogen-bond energy and decreased in entropy.

Desalinating membranes contain water which does not freeze at 0°C [3, 4] and which is a poor solvent for electrolytes [5]. This water has been variously described as highly hydrogen-bonded and ice-like [6] and as weakly hydrogen-bonded and more mobile than liquid water [7, 8]. There is no evidence to suggest that such water accumulates K^+ and Cs^+ salts to high concentrations.

Since the polymers from which desalinating membranes are made resemble proteins in that they present to water a mixed hydrophilic-hydrophobic surface, they seemed the most promising models for the biological function proposed for water. Motivated by a strong intuition that water capable of accumulating K^+ salts exists in enzymes, we have sought conditions under which the water in desalinating membranes might show the same preferential solvent properties.

Experiments in which copolyoxamide and cellulose acetate membranes have been equilibrated with electrolyte solutions have shown that the partition coefficients of CsCl and KCl were considerably greater than unity when the external concentration was low enough, but that they rapidly decreased as the concentration increased. Partition coefficients of other chlorides were less than unity and also decreased with increasing concentration. In order to explain these and other findings, it has been proposed that water in the small pores of the desalinating membranes has decreased macroscopic density, which facilitates strong tetrahedral bonding. This "stretched" water has anomalously low entropy and high hydrogen-bond energy which, together, profoundly change its solvent properties.

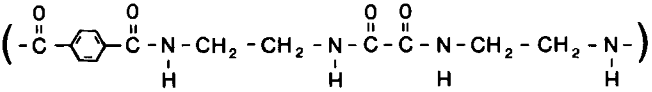

FIG. 1. Structure of the regular copolyoxamide p-222I.

EXPERIMENTAL

Preparation of Membranes for Equilibration

The copolyoxamide membranes (p-222I) used in this study had the structure shown in Fig. 1. Vogl and co-workers have investigated the conditions of preparation of these membranes [9], their water absorption properties [10], ion-binding [11], and morphology [12] in great detail. The dense cellulose acetate membranes had a degree of acetylation between 2 and 3. Both were prepared for equilibration by prolonged washing in many changes of HNO_3 (0.1 M) followed by many changes of distilled water for several days. After a final wash in distilled water, each piece of membrane was blotted with Whatman No. 1 filter paper to remove excess surface water and placed in a large volume (50-100 mL) of equilibrating solution. Preliminary experiments showed that both p-222I and CA membranes took up to 7 days to come to equilibrium with an electrolyte solution at room temperature. Each piece of membrane was therefore soaked for 7 days before being removed, blotted with Whatman No. 1 filter paper placed in a preweighed tube, weighed, dried to constant weight 110°C overnight, and reweighed to obtain wet weight, dry weight, and water content. The dry membrane was then extracted for 7 days in 5-10 mL of distilled water, dry methanol or, usually, HNO_3 (0.1 M). Each membrane was dried and extracted in the same tube, and the volume of extractant was checked by weighing.

In one series of experiments, single p-222I membranes were equilibrated sequentially in 10 mL of extremely dilute solutions (0.1-0.2 mM) of KCl and another chloride. Following equilibration in one solution, 1 mL of the supernatant was removed and kept for analysis. The tube, which had been weighed before the initial equilibration, was reweighed to determine accurately the amount of solution that had been removed, a mL of water added, the tube reweighed, and the membrane left to equilibrate with the new more dilute solution. Following this second equilibration the tube and contents were weighed again so that a (very small) correction could be made for evaporation during the period of equilibration or during the brief time when the lid of the tube was removed. Then, again 1 mL of supernatant was removed, the tube reweighed, 1 mL of water added, and the tube reweighed. Although time-consuming, the repeated weighings were necessary because they enabled a detailed balance sheet of additions and subtractions of ions and water to be made over seven separate equilibrations without removing the membranes from their tubes.

Analyses

Na^+, K^+, and Li^+ were determined on a Perkin-Elmer Coleman 51 flame photometer with external standards made up in HNO_3 (0.1 M); Cs^+, Ca^{2+}, and Mg^{2+} were determined by use of a Varian Techtron AA5 atomic absorption spectrometer, and Cl^- by use of an Aminco-Cotlove chloride titrator. KCl was used as the primary standard, stock solutions of the other chlorides being checked by determining their chloride concentrations relative to that of KCl. When urea was added to the extracting solution, it was also added at appropriate concentrations to the flame photometer and atomic absorption standard solutions. Interference between pairs of cation was only significant with Cs^+ and K^+, which were accordingly not equilibrated together. Urea was determined by the phenol-hypochlorite method, using the Berthelot reaction [13].

Infrared Spectroscopy

Infrared spectra were recorded on a Nicolet 5DX Fourier-transform spectrophotometer equipped with a data acquisition system based on a Nicolet 1280 minicomputer. Typically 100 scans (4 600-400 cm^{-1} at 4 cm^{-1} resolution, 1 s per scan) were averaged. Thin CA membranes, cut to a uniform size to fit the KRS-5 window of the liquid cell, were soaked in water or electrolyte solution for 3 days and blotted gently immediately before mounting in the cell with a 0.25-mm spacer. The cell was sealed to prevent loss of water during spectral measurement. Since the spectrum of a sample was unchanged an hour after being mounted in the cell, it was concluded that water loss was not significant.

RESULTS AND DISCUSSION

Water Contents of Membranes

Following equilibration, the rather dense CA membranes contained 0.208 ± 0.013 g water/g dry weight (mean and standard deviation of 19 determinations on different pieces of membrane). After repeated cycles of soaking, drying, and extracting in HNO_3, membranes which had been exposed to CsCl, KCl, urea, or ethanol absorbed more water in subsequent equilibrations, up to 1.1 g/g dry weight. Those membranes, however, which had come into contact only with NaCl, LiCl, $CaCl_2$, or $MgCl_2$ retained their low water absorption. As long as the water contents of different samples of CA membranes were the same, it was possible to equilibrate different pieces of membrane with a range of electrolyte concentrations and compare their ion contents directly. This practical advantage was not shared by the p-222I membranes which varied in water content from 0.5 to 3 g/g dry weight, so that an experimental result obtained in one membrane could not readily be compared with that on another.

Equilibrium Ion Contents of Membranes

As previously reported [5], the water in CA membranes was a poor solvent for electrolytes. Figure 2 shows the cations extracted from membranes which had been equilibrated with graded concentrations of the chlorides of Cs^+, K^+, Na^+, Li^+, Ca^{2+}, and Mg^{2+}. They are expressed as mmol/kg membrane water, so that no assumption has yet been made about the amount of water accessible as a solvent. While the Cs^+ and K^+ points lie on an identical straight line, the relative quantities of the other cations decreased markedly with increasing concentration, in the order $Mg^{2+} < Ca^{2+} < Li^+ < Na^+$. The CA membranes were slightly negatively charged, presumably with residual free COO^- groups. For the univalent salts, the average difference between cations

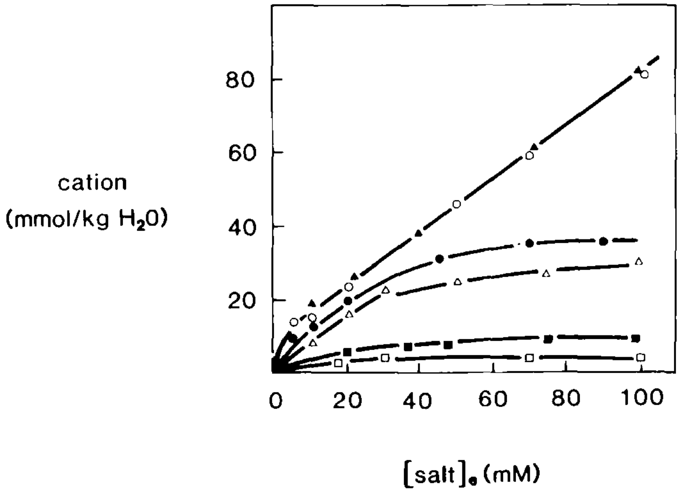

FIG. 2. Concentrations of cations in the water of CA membranes equilibrated with graded concentrations of (○) CsCl, (▲) KCl, (●) NaCl, (△) LiCl, (■) $CaCl_2$, and (□) $MgCl_2$.

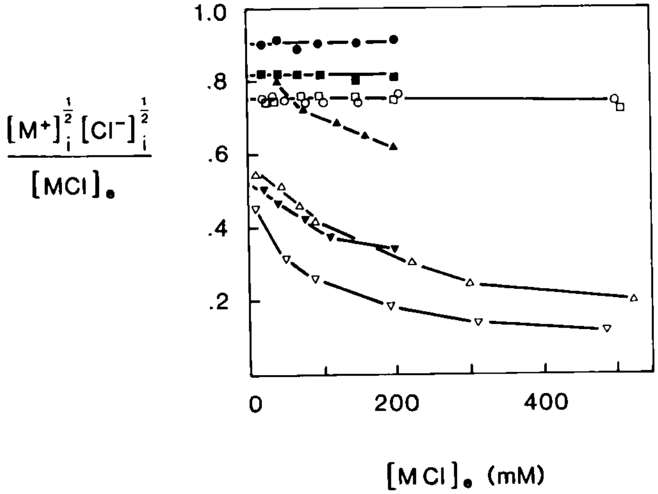

FIG. 3. Apparent partition coefficients of the chlorides of univalent cations in the water of dense (○,□,△,▽) or swollen (●,■,▲,▼) CA membranes: (○,●) CsCl, (□,■) KCl, (△,▲) NaCl, (▽,▼) LiCl. The water contents of the membranes in g/g dry weight of membrane were: (○,□,△,▽) 0.21, (●) 1.0-1.3, (■) 0.6-0.8, (▲) 1.1-1.3, (▼) 0.3-0.45.

and chlorides amounted to 13.90 ± 2.85 mmol/kg water (mean and standard deviation of 22 determinations). The chloride content of membranes equilibrated with $CaCl_2$ or $MgCl_2$ was too low to measure.

Figure 3 shows data on the chlorides of the univalent cations plotted as the quantity $[M^+]_i^{\frac{1}{2}}[Cl^-]_i^{\frac{1}{2}}/[MCl]_e$ against $[MCl]_e$, where the subscripts i and e denote inside and outside the membrane, respectively. These apparent partition coefficients of the salts were constant and equal for CsCl and KCl in the normal membranes and constant but unequal in swollen membranes. NaCl and LiCl, however, behaved very differently: their apparent partition coefficients decreased considerably with increasing concentration, both in normal and in swollen membranes. Since association of the ions with the surface of CA does not appear to be important, the decrease in partition coefficients with increasing concentration is probably real; it is evident in Fig. 2 from the curvature of the plots and was clearly most drastic for Ca^{2+} and Mg^{2+}. Only CsCl and KCl, with their near-linear and equal plots, were different.

Figure 4 shows similar results of equilibrations of p-222I membranes with chlorides in either water or methanol and with nitrates in water. Each curve was obtained from a single membrane, so that an individual curve is internally consistent, but because of the vari-

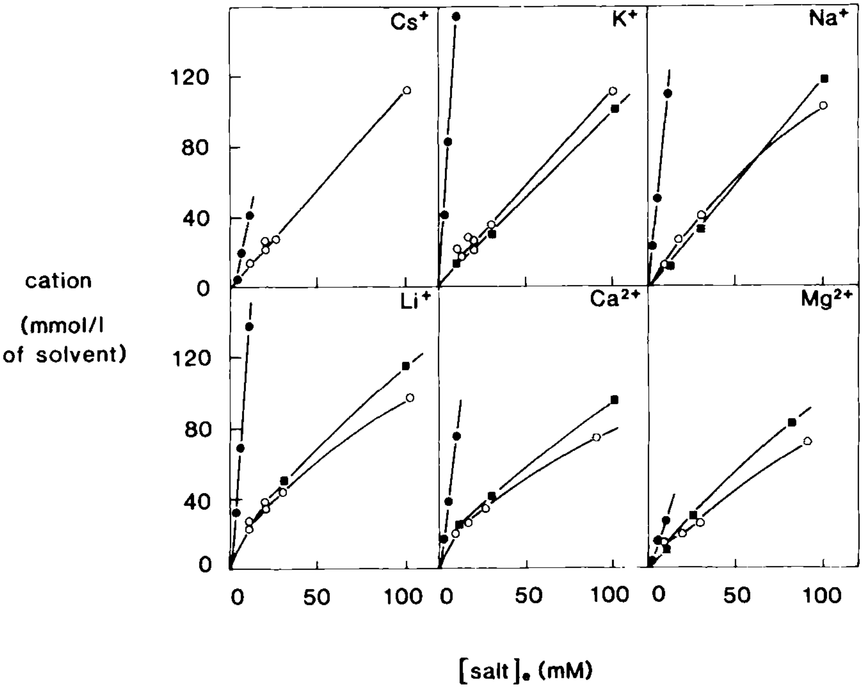

FIG. 4. Cation contents in mmol/L membrane solvent of p-222I membranes equilibrated with graded concentrations of salts of Cs^+, K^+, Na^+, Li^+, Ca^{2+}, and Mg^{2+}. (○) Chlorides in water, (●) chlorides in methanol, (■) nitrates in water. The solvent contents of the membranes in mL/g dry weight, assuming normal density, were: Cs^+, 2.96-3.35; K^+, 1.2-1.5; Na^+, 2.43-2.65; Li^+, 0.74-0.75; Ca^{2+}, 0.98-1.33; Mg^{2+}, 1.18-2.21.

ability of solvent contents from membrane to membrane, one curve cannot be directly compared with another. Chlorides in methanol gave simple linear plots for all salts and showed a high level of direct ion-binding to the surface. CsCl, KCl, KNO_3, and $NaNO_3$ in water also gave simple linear plots resembling those of the methanolic solutions of Fig. 3 and the aqueous equilibrations of CsCl and KCl in Fig. 2. The main difference is that there was appreciable binding to the p-222I membranes. However, NaCl, LiCl, $LiNO_3$, $CaCl_2$, $Ca(NO_3)_2$, $MgCl_2$, and $Mg(NO_3)_2$ showed the same curvature with increasing concentration that appeared in Fig. 2. These curves are less dramatic than those of Fig. 2 because the membranes contained variable amounts of normal liquid water with normal solvent properties. Moreover, binding of ions to the membranes would obscure the decrease in partition coefficient with increasing concentration that was so obvious in Figs. 2 and 3. It seems unlikely that the curvature in Fig. 4 is due to saturation of binding sites because the curves for methanolic equilibrations, which showed much more binding, are all linear.

While CsCl and KCl behaved differently from the chlorides of the smaller cations in both membranes, there is nothing in the results of Figs. 2-4 to suggest that either salt was accumulated to higher concentrations in the modified aqueous phase. Indeed, in CA membranes the apparent partition coefficient was 0.75. Luck, Schioberg, and Siemann [7] estimated that a monolayer amounted to approximately one-fifth of the total equilibrium water in similar homogeneous CA membranes. An apparent partition coefficient of 0.75, therefore, is consistent with a real partition coefficient of unity in 75% of the water, the other 25% being water of surface hydration and unavailable as solvent.

In some early experiments, ions had been extracted in 10 mL water or methanol in case repeated extraction in HNO_3 might prove harmful to the membranes. Figure 4 shows that extraction in methanol was not satisfactory for p-222I membranes because of the high ion binding from that solvent. It also seemed probable that extraction in water might be incomplete if a new equilibrium in which some salts were selectively retained in the nonfreezing water were set up. To investigate this possibility, we equilibrated five p-222I membranes with a solution which was 10 mM in KCl and 10 mM in LiCl. Ions were then extracted in 10 mL water for 7 days, 1 mL of the supernatant removed for analysis, and solid urea added to the remaining 9 mL of supernatant to a final concentration of 5 molal.

Table 1 lists concentrations of KCl and LiCl in the two extracting solutions, each of which was in equilibrium with residual ions in the membrane. When urea was added to the initial extracting solution, more KCl was extracted from each membrane, but some LiCl diffused back into the membrane from 5 molal urea. Presumably the nonfreezing water with modified solvent properties which excluded LiCl was disrupted by the high urea concentrations, so that more water in the membrane was accessible as solvent for Li^+. At the same time, the loss of K^+ from the membrane when that water was disrupted suggested that KCl was indeed accumulated into the surface water of the membranes when the external concentration was low enough.

Accumulation of KCl from Extremely Low External Concentrations

To investigate further the possibility that KCl had a partition coefficient greater than unity, we equilibrated single p-222I membranes in pairs of 10 mM salts, one of which was always KCl. Following equilibration, wet and dry weights of the membranes were obtained, and 10 mL water weighed on to each dry membrane. After a new

TABLE 1. Extraction of Ions into Water and Urea Solution[a]

Membrane	First extraction K^+ mM	First extraction Li^+ mM	Second extraction K^+ mM	Second extraction Li^+ mM	Difference K^+ mM	Difference Li^+ mM
22	0.084	0.097	0.089	0.090	0.005	-0.007
32	0.145	0.163	0.155	0.156	0.010	-0.007
33	0.100	0.116	0.109	0.110	0.009	-0.006
42	0.173	0.190	0.191	0.180	0.018	-0.010
71	0.115	0.128	0.130	0.119	0.015	-0.009

[a] Concentrations of ions extracted into 10 mL water and then into 9 mL of that water to which 2.7 g urea had been added.

equilibrium was reached, 1 mL supernatant was removed for analysis and replaced with 1 mL water. A series of seven new equilibria with extremely low external concentrations of ions was obtained by repeating this procedure as described in the Experimental section.

The results of this experiment are shown in Fig. 5. Each time 1 mL solution was replaced with 1 mL water, the final concentration decreased. Starting from the top of Fig. 5, as the concentration of the external solution decreased, the quantity of Na^+ extracted from the membranes increased. Similarly more Li^+, more Ca^{2+}, and more Mg^{2+} were extracted into lower external concentrations. This, of course, is to be expected. K^+, however, behaved differently. At very low external concentrations, the amount of K^+ did not change significantly with decreasing external concentration. At higher external concentrations, the amount of K^+ extracted from a membrane actually decreased with decreasing external concentration; i.e., as the external concentration of K^+ decreased, K^+ went back into the membrane from which it had been extracted. This suggests, again, that at low enough external concentrations, KCl was accumulated into the nonfreezing water, but that as the external concentration increased, its partition coefficient tended toward unity. Only KCl and CsCl were reaccumulated from low concentrations in this manner.

The results of experiments described in Table 1 and Fig. 5 have been combined in Fig. 6, making the following approximations and assumptions. Grossman, Tirrell, and Vogl [4] found an approximately linear relationship between nonfreezing water and surface area in p-222I membranes given by bound water: (g/g dry weight) = 0.32 + 0.26A, where A was the specific area in m^2/g. They also found an almost linear relationship between surface area and total water content

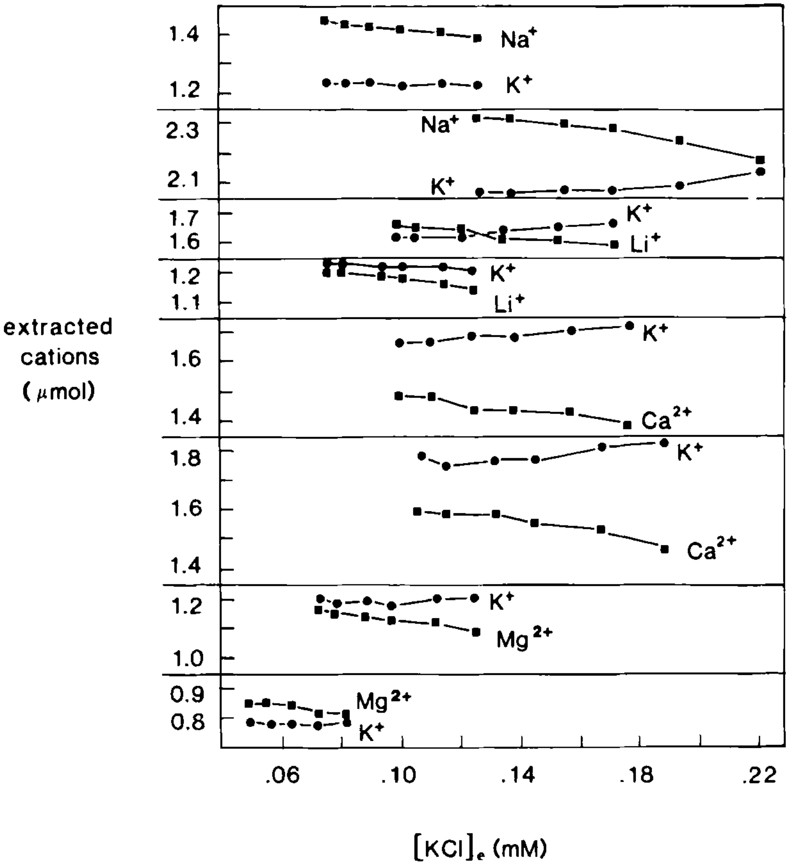

FIG. 5. The quantities of cations in μmol extracted into solutions of varying concentration of KCl from membranes previously equilibrated with 10 mM KCl together with 10 mM of the chloride of a second cation.

(%). Using these relationships, we have estimated from the measured water contents of the membranes their contents of nonfreezing water. We have further assumed that 0.32 g/g dry weight of this water was bound directly to the matrix of the membrane and was not accessible as solvent for any ions [4]; the remainder, which we have called "surface solvent water," dissolved solutes but had solvent properties which differed from those of a normal liquid aqueous phase. To estimate the quantity of K^+ remaining in a membrane in equilibrium with each external concentration, the data of Table 1 were used. For example, for the first membrane [22], when the external concentration of KCl was 0.084 mM, 0.43 mmol/kg water remained in the membrane and was subsequently extracted by urea. This same membrane [22] was used in the experiment of Fig. 4 (top). Accordingly, it was assumed that the K^+ content of the membrane when it was in equilibrium with an external concentration of 0.082 mM was also 0.43 mmol/kg water. With one point fixed, the K^+ contents of the other membranes were calculated for each external concentration.

The concentration of KCl in the solvent surface water was then calculated from the equation

$$Q = W_{nl}[\mathrm{KCl}]_e + (W - W_{nl} - 0.32)\,[\mathrm{KCl}]_{sw},$$

where Q is the total amount of KCl in the membrane in μmol, W_{nl} the weight of normal liquid water in g, $[\mathrm{KCl}]_e$ the concentration of KCl in the external solution (mM), W the total amount of water in g, and $[\mathrm{KCl}]_{sw}$ the concentration of KCl in the solvent surface water. Binding of KCl to the surface has been neglected.

Figure 6 shows that, as the external concentration of KCl increased, the derived partition coefficients decreased from a value of approximately 35 at 0.08 mM to approximately 4 at 0.18 mM. Inclusion of a term for ion binding decreases the absolute values of the partition coefficient without changing their trend with concentration.

The State of the Surface Water Phase

Figures 2-6 showed that partition coefficients of all salts changed with concentration. When they were less than unity at low concentrations (NaCl, LiCl, $CaCl_2$, $MgCl_2$), they decreased with increasing external concentration; when they were greater than unity at low concentrations (KCl and CsCl), they decreased rapidly to unity with increasing external concentration. In explanation of these observations, it is proposed that the surface solvent water in both p-222I and CA membranes is "stretched" [14].

Water and Hydrophobic Surfaces

When liquid water is in contact with a nonpolar surface, it tends to minimize the area of contact. Thus liquid droplets in air are spherical; water in contact with an oily surface forms a near-spherical droplet rather than spread across the surface; amphiphilic molecules in aqueous systems form micelles or bilayers in which the hydrocarbon tails aggregate, thus minimizing their contact with water [15].

All these phenomena are manifestations of the high free energy of water molecules in contact with such surfaces and of their tendency

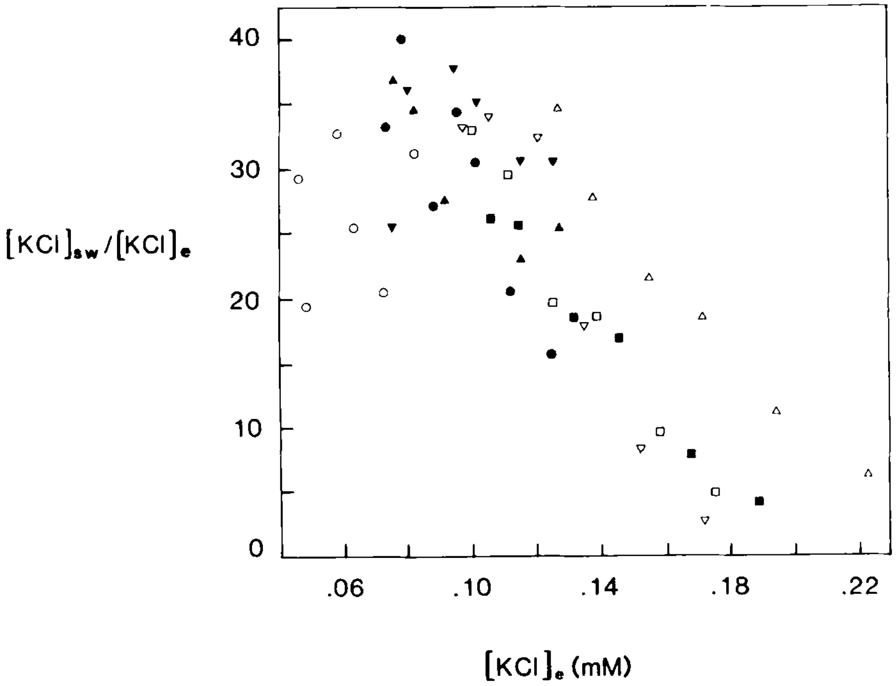

FIG. 6. Calculated partition coefficients for KCl partitioned between the surface solvent water of p-222I membranes and a normal aqueous phase. Each symbol represents values for a single membrane from Fig. 4. Water contents ranged from 0.65 to 3.6 g/g dry weight.

to leave the surface in favor of the bulk aqueous phase with its strong cohesive forces. In the water droplet, this tendency appears as a pressure difference across the surface given by $\Delta P = \gamma_{lv}/R$, where γ_{lv} is the surface tension between water and air, and R is the radius of the droplet [15]. In a pore of a synthetic polymer membrane of predominantly hydrophobic character, water is forced to wet the surface (either by prolonged soaking or by the application of pressure). Those molecules in contact with the surface have the same tendency to move from their state of high free energy to a lower state in a bulk aqueous phase as they had in the water droplet or in the solution of amphiphiles. As Adamson [16] has pointed out, entropy changes accompanying structural perturbation of a soft interfacial region probably contribute to this high free energy. If such a pore were filled with water at normal temperature and pressure and sealed at both ends, the tendency of water molecules to minimize their contact with the surfaces would also be expressed as an excess pressure inside the pore given by

$$\Delta P = \gamma_{1s}(1/R_1 + 1/R_2),$$

where γ_{1s} is the surface tension between water and the solid surface, and R_1 and R_2 are the radii of curvature. When the pore is open to a normal aqueous phase, the pressures in the two compartments must equalize. Since the walls are relatively rigid, this can be achieved mainly by movement of water out of the pore with a resultant decrease in its density. The extent to which its density decreases is also a function of $\gamma_{1s}(1/R_1 + 1/R_2)$, i.e., the smaller the radii of curvature of the pore and the larger the surface tension, the lower the density of the pore water. With a normal liquid, expansion results merely in an increase in average intermolecular separation and a decrease in the energy of interaction. But the anomalous properties of water seem to be accentuated by expansion.

The macroscopic density of water decreases when it is supercooled [17] or subjected to negative pressures [14]. Stillinger [18] attributed this decrease to aggregation of bulky polyhedral clusters of water molecules which have a net attraction for one another. If the same kind of water exists in narrow hydrophobic pores, the change of state must be induced by the decrease in macroscopic density per se. It seems likely that the preferred tetrahedral bonding of water molecules, which is geometrically impossible when they are too close together, becomes dominant when, for whatever reason, they move further apart. Thus, expansion of water at constant pressure and temperature might be another way of increasing the incidence of tetrahedrally bonded clusters with stronger hydrogen bonds and more hydrogen bonds per water molecule than are found in a normal liquid phase at the same temperature and pressure.

It is suggested that water in small pores of desalinating membranes is in this sense stretched, the average number of hydrogen bonds per molecule and the average bond energy increasing with increasing γ and with decreasing pore radius. The changed solvent properties of the water in small pores can then be attributed to the changes in hydrogen-bond energy and in entropy that accompany stretching. Whether or not CA and p-222I membranes have sufficiently dominant hydrophobic domains for this mechanism to operate is a matter for experiment to decide. Infrared spectra of water adsorbed to CA membranes suggest that the interaction is very weak [7, 8].

Although p-222I polymers are rich in both hydrogen-bond donors and acceptors, it is probable that, as with proteins [19], many of these potential hydrogen bonds are made internally between NH and CO groups, which are equal in number. If this were true, hydrophobic domains would predominate. Siggia, Beeber, and Vogl [11] found that p-222I films bound fewer divalent cations than did p-222I particles, in spite of the fact that the film had a higher specific surface area. They suggested that complexation took place only on the outside surface of a film. This is an interesting possibility, which is consistent with predominantly hydrophobic pores. In the present experiments, also, there was no correlation at all between the estimated surface area of a film and its capacity to bind ions. Tirrell, Grossman, and Vogl [10] showed that the water regain at 93% relative humidity was essentially the same for p-222I films (14.7%) and CA films (14.5%); this is consistent with similar surface-water interactions in the two polymers. Like CA films, p-222I allows rapid water flux with rejection of NaCl up to 90% [12].

Osmotic Pressure Gradients

Figure 7 illustrates schematically the effects of equilibrating such hypothetical water with two classes of aqueous solution. Figure 7(a) represents a cross section of a small cylindrical pore in a membrane equilibrated with a low concentration of a KCl-like solute; i.e., a solute with a partition coefficient greater than unity. The low concentration in the external solution (c_e) is in equilibrium with a high concentration (c_s) in the stretched water. This results in an osmotic pressure difference across the interface given approximately by

$$\Pi_s - \Pi_e = RT(c_e - c_s) = RTc_e(1 - \lambda),$$

where λ is the partition coefficient. Since $\lambda > 1$ in this case, water tends to move into the pore, opposing the outward expansion of water which has stretched it. If $c_e = 0.08$ mM (see Fig. 6), the osmotic pressure difference is small enough to be overcome by the expansive forces, the water remains stretched, and KCl is accumulated. If, however, c_e is high enough, the tendency for water to move into the pore because of the osmotic pressure difference is greater than the tendency of water to move out of the pore because of unfavorable water-surface interactions. Then the water is not stretched, its solvent properties are normal, and the partition coefficient of KCl is unity (Fig. 7b). Figure 7(c) represents equilibration of a pore containing stretched water with a solute of partition coefficient less than unity. Now the tendency of water to expand out of the pores in response to the unfavorable water-surface interactions is reinforced by the osmotic pressure difference across the interface: the pore water is stretched more than it was in the absence of the excluded solute, and the partition coefficient of this solute decreases as its increasing external concentration increases the osmotic pressure difference.

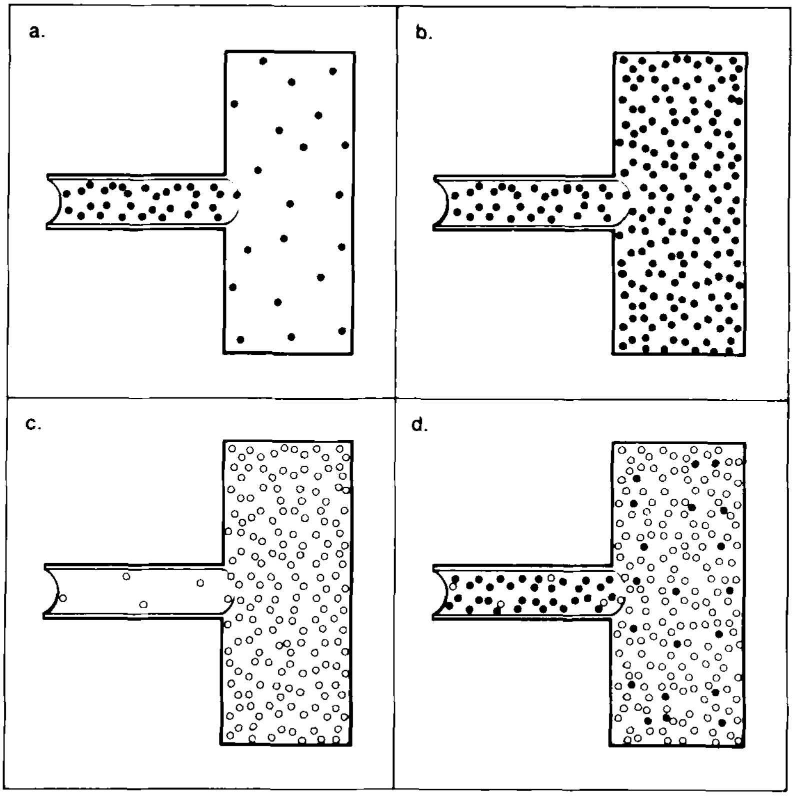

FIG. 7. Diagrammatic representation of the osmotic pressure gradient hypothesis. A small cylindrical hydrophobic pore is equilibrated with a normal aqueous phase containing (a) an extremely low concentration of a solute with partition coefficient 10, (b) a high concentration of the same solute, (c) a high concentration of a solute with partition coefficient 0.1, and (d) an intermediate concentration of the solute of (a) with partition coefficient 10 and a high concentration of a solute with partition coefficient 0.1.

This hypothesis has been tested by means of experiments of the kind illustrated in Fig. 7(d). Since osmotic pressure is principally a colligative property of solutions, the chemical identity of the species responsible for lowering the chemical potential of water is relatively unimportant. Therefore, it should be possible to combine the two equilibria illustrated in Figs. 7(a) and 7(c) as shown in Fig. 7(d). Here, the excess concentration of the KCl-like solute in the stretched water is balanced by an excess concentration of a $MgCl_2$-like solute in the bulk water; the osmotic pressure is the same in both compart-

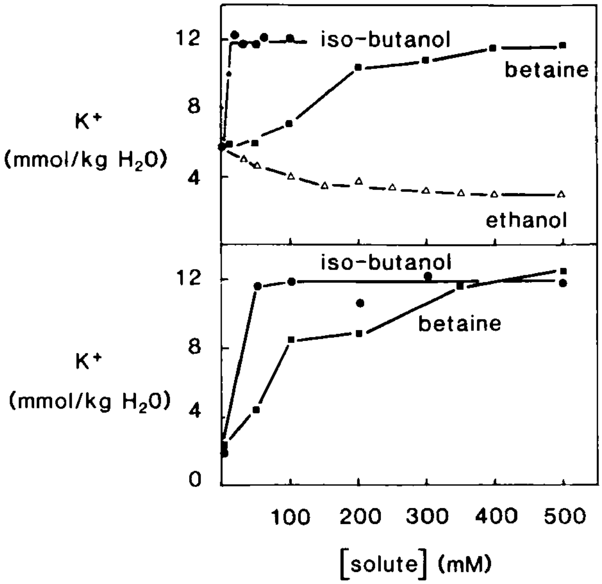

FIG. 8. The effect of added solutes upon the concentration of K^+ in membranes equilibrated with 1 mM KCl. Top: CA membranes; the K^+ concentration is that in all the membrane water. Bottom: p-222I membranes; the K^+ concentration is that calculated for the surface solvent water.

ments. Even if this were a concentration of the accumulated solute that by itself prevented stretching of the pore water, its accumulation into that water is now possible. The lower the partition coefficient of the excluded solute, the lower the concentration at which it allows maximal accumulation of the second solute.

Figures 8-12 show representative results of such experiments. When either p-222I or CA membranes were equilibrated with 1 mM KCl and graded concentrations of isobutanol or betaine, the concentration of KCl in the stretched water increased to a maximal level of approximately 12 mM (Fig. 8). The maximum was reached at a lower concentration of isobutanol than of betaine, suggesting that isobutanol was more strongly excluded from the stretched water than was betaine. Ethanol in CA membranes decreased the concentration of KCl. Presumably it was accumulated into the stretched water, and opposed its stretching by generating an osmotic pressure gradient of opposite sign.

Figure 9 shows the effects on the K^+/Na^+ ratio in the total membrane water when swollen CA membranes were equilibrated with 1 mM NaCl, 1 mM KCl, and graded concentrations of propanol, glycerol, or

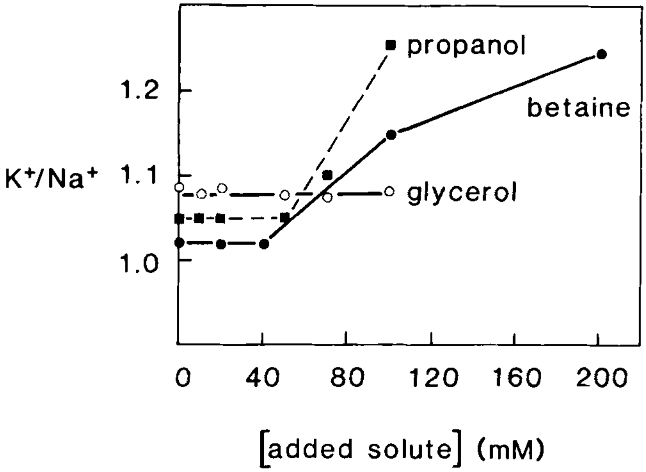

FIG. 9. The effect of added solutes on the K^+/Na^+ ratio in swollen CA membranes equilibrated with 1 mM NaCl and 1 mM KCl.

betaine. Since much of the membrane water in these swollen membranes had normal solvent properties, the ratio was not high. It began to increase, however, in the presence of 40 mM betaine and 50 mM propanol, but remained constant in the presence of up to 100 mM glycerol. Figure 10 shows the effects of two sugars on the K^+ distribution in CA membranes. Ribose very slightly increased the concentration of K^+, while glucose decreased it. These results, together with those of Fig. 8, suggest that the rank order of partition coefficients of the solutes was: glucose > ethanol > glycerol > ribose > propanol > betaine > isobutanol, with that of glycerol approximately unity.

When p-222I membranes were equilibrated with 1 mM KCl in the presence of increasing concentrations of $MgCl_2$, each cation affected the distribution of the other (Fig. 11). At each external concentration of $MgCl_2$ its concentration in the membrane water was higher than it was in the absence of KCl. The concentration of K^+ in the membrane water decreased at first and then increased at higher concentrations of $MgCl_2$. Figure 12 shows the result of a similar experiment with CA membranes. The initial drop in K^+ concentration in the presence of low concentrations of $MgCl_2$ was probably due to an increase in the activity of KCl with increasing concentration of Cl^-. Influx of KCl and water opposed the stretching of water, and the partition coefficient of K^+ decreased. At higher concentrations of $MgCl_2$, exclusion of Mg^{2+} reinforced the stretching of water and the partition coefficient of K^+ increased again. Figure 12 also shows the effect of urea upon the parti-

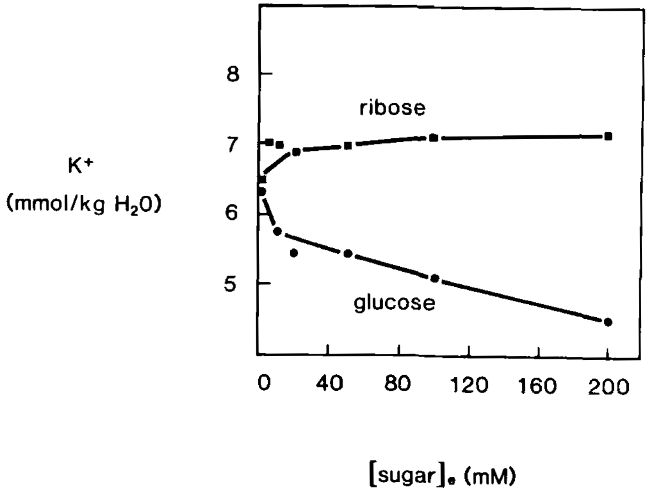

FIG. 10. The effect of increasing concentrations of glucose or ribose upon the concentration of K^+ in the water of a CA membrane when its external concentration was 1 mM.

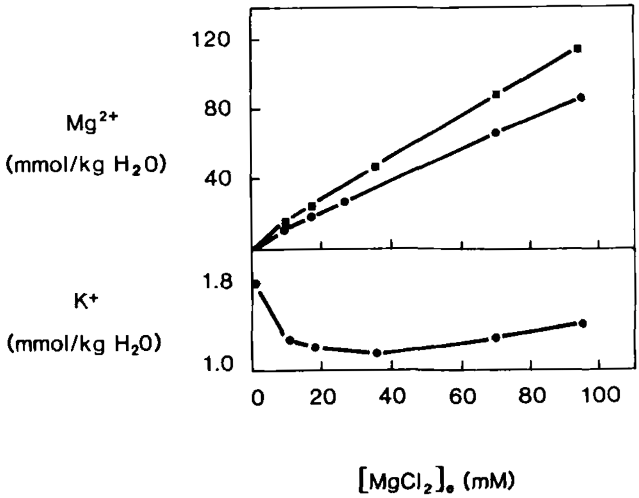

FIG. 11. The concentrations of Mg^{2+} and K^+ in the water of p-222I membranes equilibrated with increasing concentrations of $MgCl_2$ in the presence and absence of 1 mM KCl. Top: (■) With KCl, (●) without KCl.

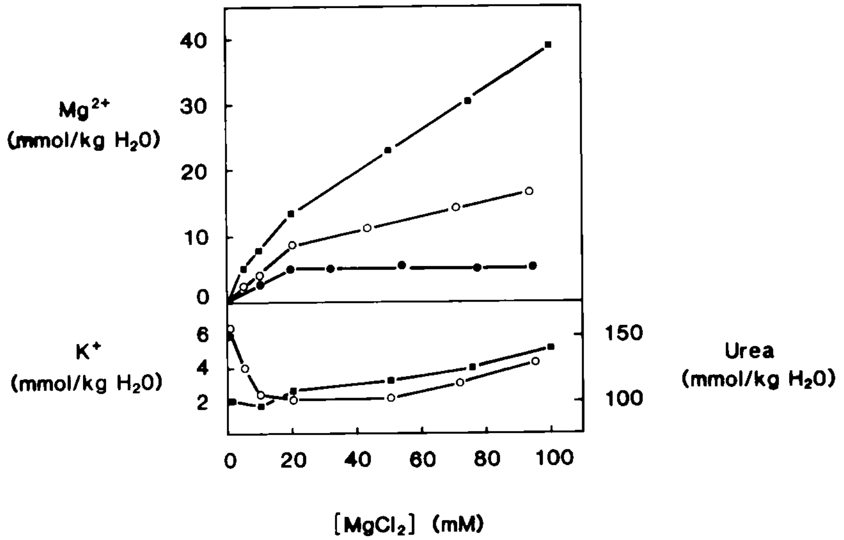

FIG. 12. The concentrations of Mg^{2+}, K^+, and urea in the water of CA membranes equilibrated with increasing concentrations of $MgCl_2$ and constant or zero concentrations of KCl or urea. Top: (■) With urea (100 mM), (○) with KCl (1 mM), (●) with no added solute. Bottom: (○) K^+, (■) urea.

tion coefficient of $MgCl_2$. Urea increased the concentration of Mg^{2+} in the membranes at each external concentration and was itself increased in concentration at higher $MgCl_2$ concentrations.

Infrared Spectra of CA Membranes

The hypothesis that water in dense CA membranes is stretched was also tested by measuring the infrared spectrum of water in the membranes in the presence and absence of added electrolytes.

The infrared spectrum of a dry CA membrane showed an OH stretch band at 3 486 cm^{-1}. The spectrum of water in the membranes was obtained by subtracting the spectrum of the anhydrous membrane from that of the membrane equilibrated by soaking. This subtraction is valid only if the position of the OH stretch of the dry membrane is unchanged upon hydration. Figure 13(a) shows the difference spectrum of water adsorbed from the atmosphere (0.094 g/g dry weight). It is similar to that obtained by Toprak and co-workers [8], with bands at 3 610 and 3 429 cm^{-1}. When the same membrane was soaked in water for 3 days and blotted using our standard technique, its water

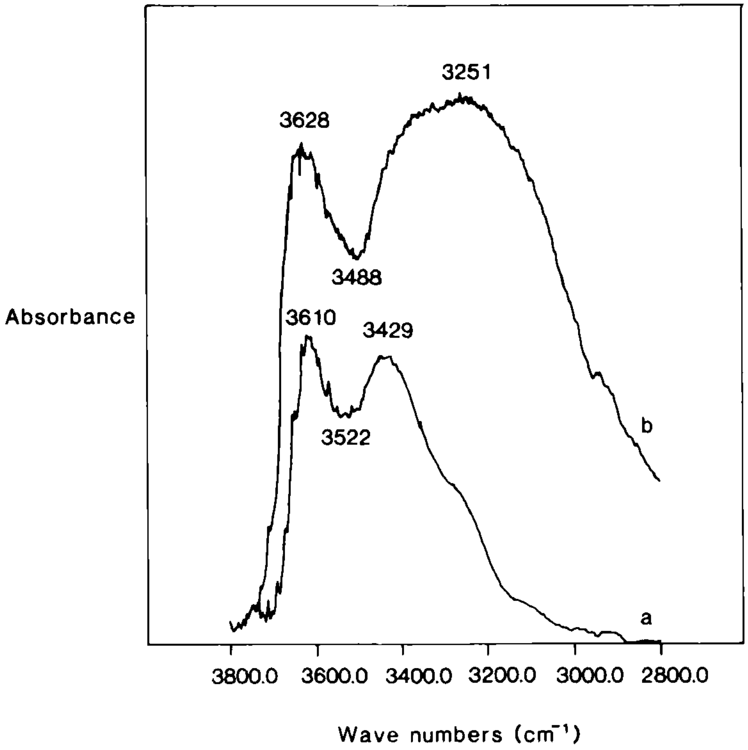

FIG. 13. Difference spectra of water in dense CA membranes. (a) A membrane exposed to atmospheric water vapor; (b) a membrane soaked in water and blotted. The spectrum of the dry membrane was subtracted from that of the wet membrane.

content was 0.21 g/g dry weight, and its difference spectrum was that of Fig. 13(b). Absorbance increased absolutely, the band at 3 610 intensified and moved to slightly higher wavenumber, and the band at 3 429 disappeared and was replaced by a strong band with a maximum at 3 251, where there had been a slight shoulder in the vapor-adsorbed water spectrum.

Figure 14 shows representative difference spectra for membranes equilibrated with 10-100 mM KCl or CsCl (Fig. 14a) or 10-1000 mM $MgCl_2$, $CaCl_2$, LiCl, or NaCl (Fig. 14b). These membranes contained approximately the same water content as that of Fig. 13(b), and their absorbances were of similar magnitude. In the presence of 10 mM KCl, however, the spectral features characteristic of membrane water equilibrated with liquid water disappeared, while in the presence of 100 mM LiCl, they were accentuated.

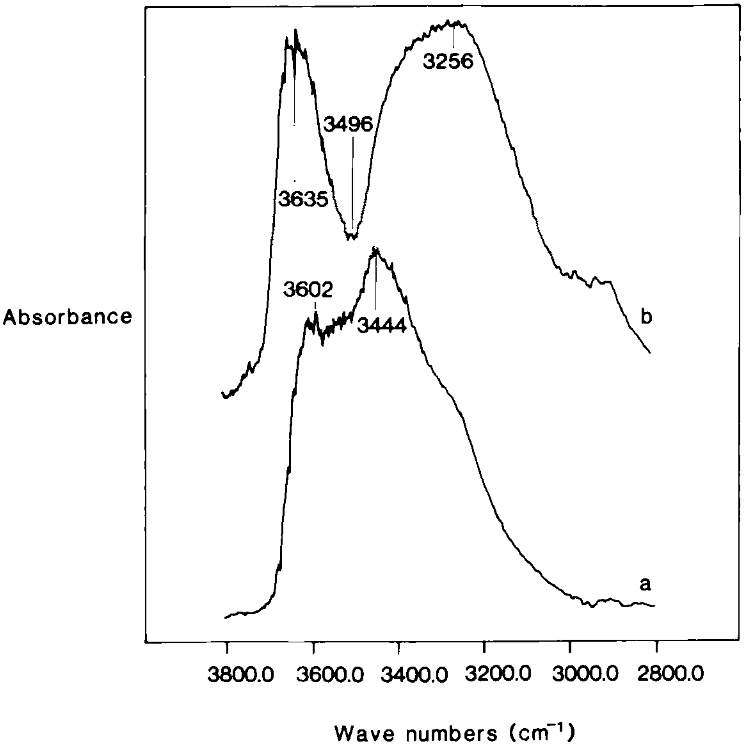

FIG. 14. Difference spectra of membranes soaked in electrolyte solutions. (a) 10 mM KCl; (b) 100 mM LiCl. The method of subtraction was the same as for Fig. 13.

Figure 15(a) shows the difference spectrum obtained by subtracting from the spectrum of a membrane equilibrated with liquid water the spectrum shown in Fig. 13(a) for a membrane equilibrated with atmospheric water. The alternative method of subtraction gives results which show similar trends. Compared with the spectrum of liquid water in the same range (Fig. 15b), the membrane water lacks the absorbance from 3 400 to 3 600 and has a peak at 3 255 which is at a lower wavenumber than the average for liquid water.

Figure 16 shows the effects of 10 mM CsCl (Fig. 16a) and 100 mM $MgCl_2$ (Fig. 16b) upon the difference spectrum of Fig. 15(a). CsCl again abolished the peak at 3 255 cm^{-1} while $MgCl_2$ most dramatically increased it.

Finally, Fig. 17 compares the difference spectrum of a membrane equilibrated with 50 mM $MgCl_2$, which shows its characteristic band

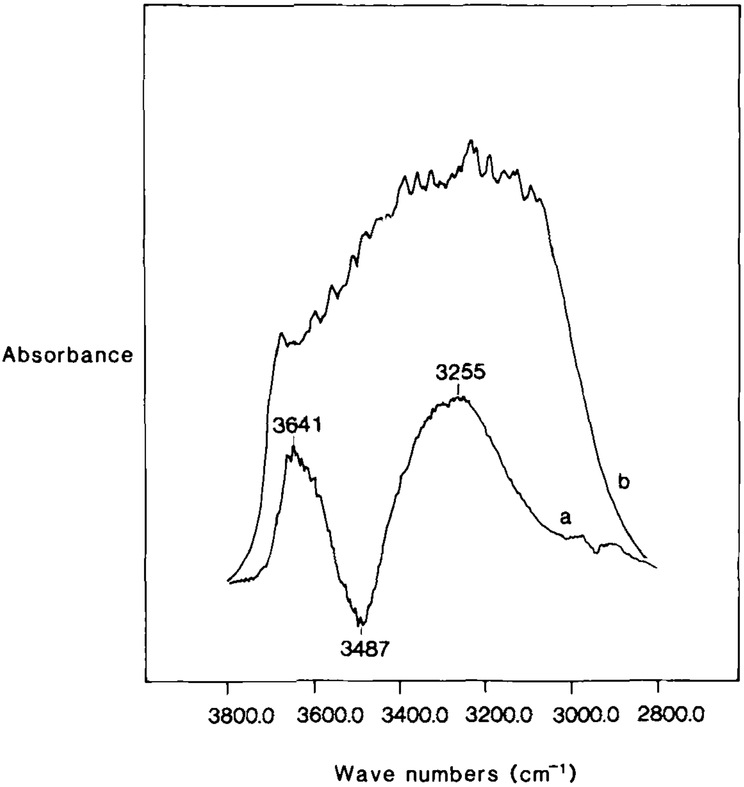

FIG. 15. (a) Difference spectrum for water in a CA membrane. The spectrum of a membrane equilibrated with atmospheric water vapor (Fig. 13a) was subtracted from that of the soaked membrane. (b) Spectrum of liquid water.

at 3 266 cm^{-1}, with the difference spectrum of a piece of the same membrane equilibrated with 50 mM $MgCl_2$ and 1 mM KCl. The band at 3 266 has decreased to a shoulder, and a peak has appeared at 3 341 cm^{-1}, intermediate between the 3 266 band and that of 3 437 cm^{-1} characteristic of a membrane equilibrated with KCl (Fig. 14a). Evidently, the spectral properties of this water are intermediate between those of Fig. 14(a) and those of Fig. 17(b). Figure 12 showed that its solvent properties were also intermediate. Mg^{2+} was at a higher concentration than it was with 50 mM $MgCl_2$ alone, and K^+ was at a lower concentration than with 1 mM KCl alone.

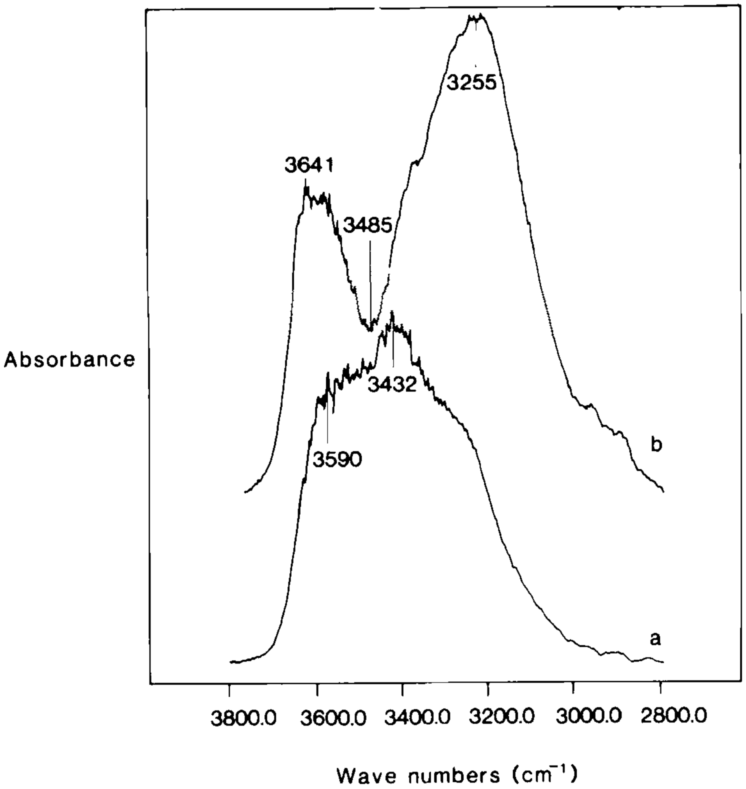

FIG. 16. Difference spectra for water in CA membranes equilibrated with electrolyte solutions. (a) 10 mM CsCl; (b) 100 mM $MgCl_2$. The method of subtraction was the same as for Fig. 15(a).

The State of Water in Membranes Equilibrated with Vapor or Liquid

When membranes with predominantly hydrophobic pores of small radius are equilibrated with water vapor, capillary condensation into the pores should not occur at a presumably convex meniscus. Therefore, most water adsorbed from the vapor phase, even up to saturated vapor pressure, is adsorbed vapor and would be expected to exist as monomers and dimers. Only when a membrane undergoes prolonged soaking are its pores filled. Then, surface water molecules, which had been in equilibrium with the vapor, are in a state of higher free

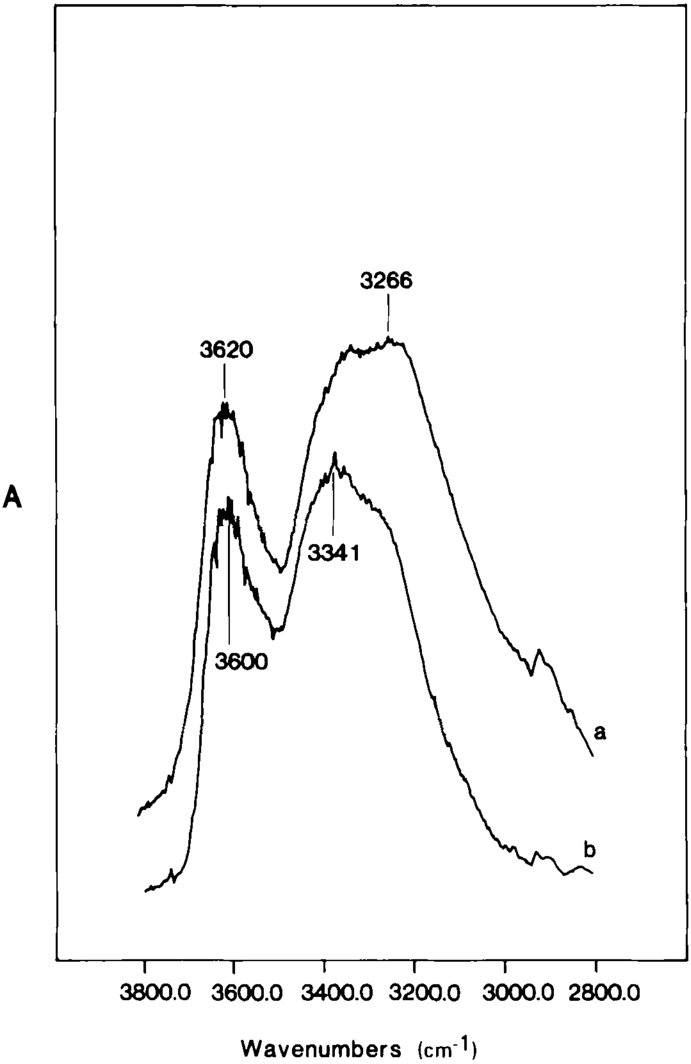

FIG. 17. Difference spectra for water in CA membranes equilibrated with electrolyte solutions. (a) 50 mM $MgCl_2$; (b) 50 mM $MgCl_2$ plus 1 mM KCl. The method of subtraction was the same as that in Fig. 13.

energy than molecules in the bulk of the liquid; water expands out of the pores and the water is stretched. Of course, the mechanism of desalination depends upon the properties of the water in membranes equilibrated with liquid water. If that water is indeed stretched, then it should have anomalously high viscosity, hydrogen bond energy, and heat capacity as well as anomalously low entropy and density [18].

Viscosity

The self-diffusion coefficient of water in CA membranes has been found to be of the order of 10^{-7} cm^2s^{-1} [20]. This is very high compared with that of ice ($\sim 2 \times 10^{-11}$ cm^2s^{-1}), but low compared with that of liquid water ($\sim 2.2 \times 10^{-5} cm^2s^{-1}$) [21], suggesting that the membrane water is more viscous and less mobile than liquid water. The long times required for complete equilibration of both CA and p-222I membranes with electrolyte solutions also suggest a higher viscosity of the membrane water.

Hydrogen Bond Energy

Infrared spectra of water adsorbed from the vapor phase on to CA membranes have shown that normal liquidlike structures do not form [7, 8]. The spectrum of Fig. 13(a) illustrates these findings. The band at 3 610 has been assigned by Toprak and co-workers [8] to the symmetric and asymmetric stretch of water molecules engaging in only weak hydrogen-bonding to acetyl groups on the surface. They assigned the band at 3 429 to the appearance of water dimers, and the shoulder at approximately 3 250 to the overtone of the H_2O bending vibration of dimers, pointing out that these last two bands increased in intensity together as the water content of the membranes increased. When, however, membranes were soaked in water (Fig. 13b), the band at 3 429 disappeared and the shoulder increased to an extremely dominant band centered at 3 251. These changes are incompatible with the assignment of both bands to dimers, and suggest, instead, that with equilibration of the membranes with liquid water, dimers were replaced by larger clusters with stronger hydrogen bonds. The spectrum is still unlike that of liquid water, but is consistent with the existence of molecules weakly associated with the surface (3 628 cm^{-1}) and larger clusters of water molecules joined by hydrogen bonds, which at 3 251 cm^{-1} are stronger than the average in liquid water (3 375 cm^{-1}, Fig. 15b). Figures 14(b) and 16(b) show that, in the presence of a solute which was excluded by the membrane water, this band intensified and sharpened, i.e., apparently the population of molecules engaged in this type of hydrogen bonding increased at the expense of dimers. In the presence of KCl (Fig. 14a) or CsCl (Fig. 16a), the band at 3 255 disappeared and a band at 3 437 was restored. In terms of our working hypothesis, solutes with partition coefficients less than unity reinforced the stretching of the water, while solutes with partition coefficients greater than unity eliminated it.

The spectrum of membrane water in equilibrium with KCl (Fig. 14a) or CsCl (Fig. 16a) is still quite unlike that of liquid water. It suggests that the water consists of small, weakly bonded clusters, similar to those adsorbed from the vapor phase. Since it appears that larger clusters can form inside the pores (Figs. 13b, 14b, 15a, and 16b), their absence is not due to lack of space. An extension of the argument that led to the proposal of stretched water offers an explanation. In the presence of a solute which overcomes the tendency of water to stretch, the concentration of that solute is the same inside the pore and in the external solution. If the water inside the pore had a normal liquid structure, it would again be at a higher chemical potential than the external water because of the unfavorable surface-water interactions. The pore water cannot stretch in the presence of the accumulated solute and must, therefore, adopt some other strategy to lower its chemical potential.

Enthalpy-Entropy Compensation

For many processes in aqueous solution, there is an approximately linear relationship between the enthalpy and entropy changes [22]: they increase or decrease together. Inspection of the equation for the chemical potential of water,

$$\Delta\overline{G} = \Delta\overline{H} - T\Delta\overline{S},$$

shows that a relatively slight change in $\Delta\overline{G}$ can be realized only if there are much larger changes in $\Delta\overline{H}$ and $\Delta\overline{S}$. When water stretched out of the hydrophobic pores, it achieved a lower chemical potential by decreasing $\Delta\overline{H}$. That decrease had to be very large, however, because most of it was compensated by a simultaneous decrease in $\Delta\overline{S}$. The only other method of lowering $\Delta\overline{G}$ requires an increase in $\Delta\overline{S}$, but again, this increase must be large because most of it is compensated by an increase in $\Delta\overline{H}$. Perhaps the water in the hydrophobic pores responds to the presence of a solute which opposes stretching in this manner. The continuous hydrogen-bonded network of water molecules is broken down into a collection of small clusters of water molecules. There is a large increase in entropy, which is mostly compensated by a decrease in the number and strength of hydrogen bonds.

Solvent Properties of Pore Water

Luck, Schioberg, and Siemann [7] ascribed the low partition coefficients of electrolytes in the CA water to the absence of enough water molecules in the very small pores to hydrate ions. Figure 12, however, shows that the concentration of $MgCl_2$ in this water could be increased by the presence of either KCl or of urea, both of which solutes would themselves require hydration. Moreover, one of the most remarkable properties of p-222I membranes soaked in water is that nonfreezing water appears to reach depths of up to 25 nm on the surfaces [4]. When they were equilibrated in methanolic solutions, the distributions of ions appeared normal, i.e., there must have been enough methanol molecules to solvate ions. An alternative explanation is that, in the stretched water, more and stronger hydrogen bonds have to be broken in order to hydrate the ions, so that as the degree of hydration of an ion increases, its enthalpy of hydration increases more in the stretched water than in normal water.

If, like supercooled water, the pore water has anomalously low entropy, then the redistribution of water molecules which takes place when an ion is hydrated, involves a larger increase in entropy when the water is stretched than when it is normal. Thus the free energy of transfer of an ion from a normal aqueous phase into stretched water has the form

$$\Delta G_T = \Delta\Delta H_{hyd} - T\Delta\Delta S_{hyd},$$

where $\Delta\Delta H_{hyd}$ is the increase in enthalpy and $\Delta\Delta S$ is the increase in entropy of hydration in stretched water, both terms being positive. Clearly, ΔG_T may be either positive or negative, depending upon the relative contributions of enthalpy and entropy to the free energy of transfer. Thus it was found (Figs. 2-6) that it was positive for the chlorides of of Na^+, Li^+, Ca^+, and Mg^{2+} and negative for the chlorides of K^+ and Cs^+. Similarly, it was positive for some nonelectrolytes and negative for others. When equilibrations were carried out in methanolic solutions, all partition coefficients appeared to be close to unity and independent of concentration. While methanol might have expanded out of the pores to some degree, it was presumably structurally unchanged, and therefore, its solvent properties were not affected.

CONCLUSIONS

The hypothesis that water in small pores of CA and p-222I membranes is stretched has received support from the properties of the water as a solvent and from features of its infrared spectrum. If this hypothesis is correct, it should help to elucidate the mechanism of desalination by some synthetic polymer membranes. Moreover, the biological function that has been proposed for water [1] becomes more plausible. The enzymes which transport cations across biological membranes bind both the cation to be transported and adenosine triphosphate in a hydrophobic cleft which closes somewhat during transport [23]. According to the stretched-water hypothesis, partial closure of a hydrophobic cleft, by increasing its surface area relative to its volume, increases the chemical potential of its contained water. Stretching of the water then endows it with the solvent properties that have been shown to be necessary to generate the forces for transport.

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