Ion Movements in Cellulose Acetate Membranes

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Synopsis

The behavior of ions in a cellulose acetate membrane was discussed from the standpoint of mobilities obtained from the membrane potentials. The mobilities of univalent ions larger in radius or divalent ions relative to Na^+ ion mobility in the membrane are much different from those in aqueous solutions. The order of the mobilities of ions in the membrane is shown quantitatively. The mobilities of the ions with radii larger than a certain value in the membrane decrease with increase in their size. This could be explained by the physical friction between the ion and the membrane wall. This friction is of importance as the ionic radius comes close to the intermolecular gaps between polymer chains. The mobilities of Na^+ and I^- ions in the membrane are $(2–3) \times 10^{-7}$ $cm^2/sec \cdot V$ and are about three to four orders of magnitude less than those in aqueous solutions.

INTRODUCTION

Several mechanisms[1,2,3] have been suggested for explaining salt separation by the cellulose acetate membrane which was developed for reverse osmosis membrane. And there are many reports[4] on the relationships between the physicochemical properties of the membrane and its separation characteristics.

Using irreversible thermodynamics and the friction model, Kedem[5] has derived the following equation for uniunivalent salts approximating that volume flow is equal to water flow:

$$\sigma = 1 - K \frac{f_{sw}}{f_{sw} + f_{sm}}$$

In this equation, σ is the reflection coefficient and is usually less than unity; K is the salt distribution per cm^3 of water in the membrane; f_{ij} is the friction coefficient between species i and j; and subscripts w, s, and m represent water, salt, and membrane, respectively.

The above equation indicates that if $K \to 0, f_{sm} \gg f_{sw}$, the reflection coefficient σ is nearly equal to unity, which means an ideal membrane completely rejecting salts.

We have already reported[7] that K, the equilibrium factor of salt separation, of the dense cellulose acetate membrane could nearly be expressed by Grueckauf's equation based on the electrochemical effect. On the other hand, many studies on the kinetic factor of salt separation have been reported, but they are still insufficient to explain the ionic behavior in the membrane.

In this study, the membrane potential of the cellulose acetate membrane was
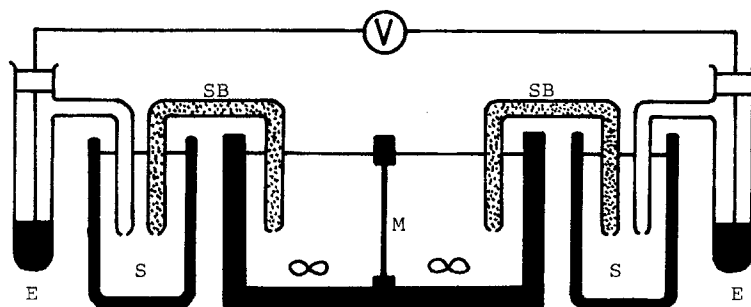
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Fig. 1. Apparatus for membrane potential measurement: M, membrane; SB, agar bridge saturated with KCl; E, calomel electrode; S, saturated KCl solution; V, potentiometer.

measured in order to obtain further information on the ionic behavior in the cellulose acetate membrane.

EXPERIMENTAL

Membrane Potential Measurement

A typical cell for membrane potential measurement is shown in Figure 1. The solutions in both compartments separated by a membrane were well stirred. The volume of the compartments was about 10 cm^3, and the membrane area was 0.7 cm^2. Agar KCl bridges were used as shown in Figure 1 in order to protect the solutions against KCl contamination from the calomel electrodes. The validity of the measurement by this cell was confirmed by the following fact: the transference number of Na$^+$ obtained with the cation exchange membrane (CMV made by Asahi Glass Co.) in NaCl aqueous solution was equal to the datum reported by the membrane maker. The temperature for measurement was 22°C. An Electrometer (TR-8651) made by Takeda Riken Co. Japan was used for the potential measurement.

The salts examined in this study are listed in Table I. It was impossible to

TABLE I
Membrane Potentials and Transference Numbers in Asymmetric CA Membrane and Aqueous Solution

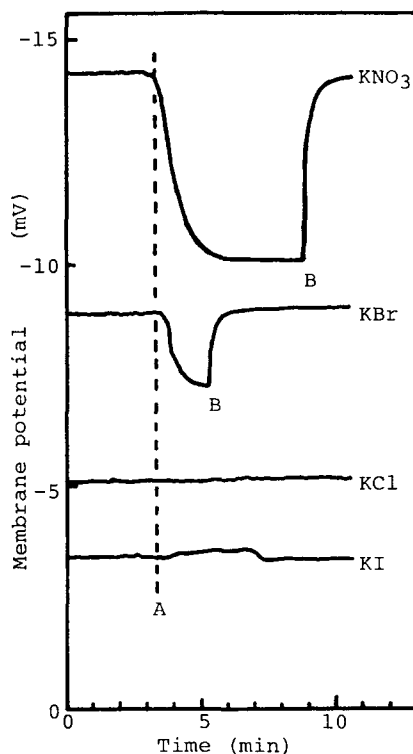| Salt	Membrane potential, mV	Transference numbers of positive ions	
		In membrane	In aq. solution
NaCl	−6.7	0.41	0.385
LiCl	−10.1	0.37	0.317
KCl	−5.0	0.44	0.490
H$_2$SO$_4$	+30.0	0.94	0.742
Na$_2$SO$_4$	+19.0	0.80	0.383
MgCl$_2$	−23.0	0.23	0.410
NaI	−4.8	0.44	0.395
MgSO$_4$	+6.0	0.71	0.398
KNO$_3$	−14.4	0.31	0.510
KI	−3.3	0.46	0.488
KBr	−9.0	0.38	0.483

Fig. 2. Typical membrane potentials measured with the asymmetric CA membrane: A, the time to stop stirring; B, the time to start stirring.

estimate the mobilities of ions for salts that are composed of a strong acid and a weak base, or vice versa.   Because the aqueous solutions of such salts are acidic or basic, the H^+ or OH^- ion in the aqueous solution is much more mobile compared with other ions due to the particular transport process called the chain mechanism of conduction.   The concentrations in the compartments were 0.1 and 0.02 mole/l., and the concentration ratio was 5.0.

When there exists a concentration difference of the same salt across the membrane having no electric charge, the membrane potential can be observed if the transport velocity of the cations differs from that of the anions.   Generally, this membrane potential g_m can be described by the following equation, assuming that T_i is independent of concentration, and further assuming Guggenheim's hypothesis:

$$g_m = \frac{RT}{F} \sum_i \frac{T_i}{Z_i} \ln \frac{a_{\pm}^{II}}{a_{\pm}^{I}}$$

(1)

where R is the gas constant, T is temperature, F is the faraday, Z_i is the valence of ion i, T_i is the transference number for ion i through the membrane; and $a_{\pm}^{I}$ and $a_{\pm}^{II}$ are the mean activities of the electrolyte in solutions I and II and related to the mean ionic activity coefficient $f_{\pm}$ by the following relationship:

$$a_{\pm} = f_{\pm} m_{\pm}$$

TABLE II
Membrane Potentials and Transference Numbers in Dense CA Membrane

Salt	Membrane potential, mV	Transference numbers of positive ions in membrane
NaCl	−8.1	0.40
Na_2SO_4	+20.6	0.84

In this case, $m_\pm$ is the mean ionic concentration. The mean ionic concentration is proportional to the molar concentration, but the proportionality constant depends on the type of electrolyte. However, in the case of the same salt, the ratio of the molar concentration is equal to that of the mean ionic concentration. The value of $f_\pm$, which depends on concentration, was quoted from the literature.[8]

Thus, the transference numbers of ions can be calculated from the membrane potentials using eq. (1). In the case of an asymmetric membrane, the membrane potential under thorough stirring was higher than that under no stirring, as shown in Figure 2. It is apparent from this figure that the higher the permeability of the salt such as KNO_3 or KBr, the larger is the potential difference.

This difference might be attributed to the asymmetrical structure of the membrane. Moreover, the potential when the active layer of the asymmetric membrane faced the concentrated solution differed from that when the active layer faced the dilute solution. The difference, however, was eliminated by thorough stirring of the solutions on both sides of the membrane. On the other hand, the potential difference due to the stirring condition described above was not observed with the dense membrane. Unlike in reverse osmosis experiments, the concentration polarization did not seem so effective in the case of the membrane potential measurement; in measuring the membrane potential, permeation of water and salt through the membrane was not so large that, by stirring, the concentration in the porous layer of the asymmetric membrane could be made nearly equal to the one in the external solution. This could be confirmed by the fact that the potential difference between the asymmetric and the dense membranes was small, as shown in Tables I and II.

The time necessary to attain a stationary membrane potential since providing the concentration gradient was 10–30 min for the dense membrane and 3–15 min for the asymmetric membrane, although it depended on the kind of salt. In this measurement, attention should be given to the fact that the transport of water through the membrane during the measurement had an effect on the salt concentration on both sides and consequently on the membrane potential. This effect was expected to be greater particularly for the asymmetric membrane. However, a measuring time within 60 min could confine the concentration change to a few per cent, even for the asymmetric membrane.

Electrical Resistance Measurement

The electrical resistance measurement at a frequency of 1 KHz was made with a conductance cell containing an NaCl aqueous solution of 0.217 mole/l. in the two compartments separated by the membrane. Letting the resistances of the

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TABLE III

Electrical Resistance of Cellulose Acetate Membranes

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Membrane	Resistance without membrane, Ω	Resistance with membrane, Ω
Asymetric membrane	26.0	30.0
Dense membrane	26.0	1600

cell equipped with the membrane and without the membrane be R_1 and R_2, respectively, the specific resistance of the membrane ρ_m can be obtained using the following equation:

$$\rho_m = (R_1/R_2 - 1) \, SR_2/d \tag{2}$$

where S is the membrane area and d is the membrane thickness. Equation (2) was derived assuming that the resistance of the cell with a membrane is equal to the sum of the membrane resistance and that of the NaCl aqueous solution. Here, S was 12.6 cm^2.

Membrane Preparation

The membranes used were the asymmetric membrane of Eastman Chemical Products KP-98, whose salt rejection was about 98% for NaCl solution, and the dense membrane made from the binary solution consisting of acetone and cellulose acetate (Eastman 398-3).[6] The dense membrane was 50-μ thick. All the salts used here were reagent grade.

RESULTS

The sign of the membrane potential of the diluted solution side to that of the concentrated solution side was adopted as the sign of the membrane potential. The membrane potentials measured here for the various salts and the transference numbers of the ions in the membrane calculated from the membrane potential using eq. (1) are listed together with those[8] for aqueous solutions in Tables I and II. The scatter of the data was within $\pm 10\%$. It was found that the transference numbers of the ions measured with the asymmetric membrane were somewhat larger than those with the dense membrane. The pH of aqueous FeCl$_3$ solution of 0.1 mole/l. was 1.7, and the sign of the membrane potential for the FeCl$_3$ solution was positive. In this case, very mobile H$^+$ ion seemed to be related to this result, because the transference number of Fe^{3+} in the membrane could not be larger than that of Cl$^-$ ion. Therefore, as mentioned above, it is impossible to obtain the correct transference numbers of ions in the case of salts that produce H$^+$ ion or OH$^-$ ion in aqueous solutions. The electrical resistances of the membranes are given in Table III.

DISCUSSION

A cellulose acetate membrane is consdered to have no electric charge. Therefore, it is not the Donnan membrane potential observed with an ion ex-

Ion	Relative mobility in membrane	Relative mobility in aq. solution
Na^+	1.00	1.00
H^+	4.00	6.80
K^+	1.10	1.43
Li^+	0.82	0.75
Mg^{2+}	0.42	1.05
NO_3^-	2.41	1.42
Br^-	1.76	1.53
Cl^-	1.43	1.50
I^-	1.28	1.50
SO_4^{2-}	0.30	1.60

change membrane, but the diffusion potential that has to be taken into consideration. In a previous paper,[6] we suggested that there would be a size distribution of the gap between the cellulose acetate molecular chains in the membrane. The gaps could be grouped into three types depending on the size. Gap A which cannot accommodate any ion except water molecules does not give rise to the membrane potential. Gap B is narrow to such an extent that the salt distribution coefficient K predicted by Glueckauf is less than unity due to the electrochemical excluding effect. Gap C is a somewhat large hole rather than the intermolecular gap, and thus the solution within gap C has the same salt concentration as the external solution. In the case of B and C, the membrane potential is expressed by eq. (1). Gap C gives rise to the same potential as the liquid junction potential corresponding to the difference between the transference numbers of ions in an aqueous solution. However, it was considered that holes like gap C would not exist in the membrane used in this study from the measurements of the NaCl permeability, electrical resistance, and membrane potential. Assuming that the electrical neutrality is valid in the membrane, the transference numbers of ions are expressed as below in terms of their mobilities u_i; thus,

$$T_+ = \frac{u_+}{u_+ + u_-}, \qquad T_- = \frac{u_-}{u_+ + u_-}$$

The mobility of each ion relative to that of Na^+ ion in the membrane calculated from the data in Table I is shown along with that in an aqueous solution in Table IV. It is apparent from this result that the mobilities of univalent ions larger in radius or divalent ions relative to Na^+ ion mobility in the membrane are much different from those in aqueous solution. It is particularly noteworthy that Mg^{2+} and SO_4^{2-} ions in the membrane are less mobile, but that NO_3^- is more mobile in the membrane. Further, the order of relative ionic mobilities in the membrane seems to be very similar to those obtained from the salt separation by the reverse osmosis process. However, the orders so far reported in the literature are quantitative ones of cations for a given anion or those of anions for a given cation.

The mobility of SO_4^{2-} ion is larger than that of Na^+ ion in aqueous solution, and thus the liquid junction potential across the membrane with only holes like gap C must be negative. However, the positive sign of the membrane potential

TABLE V
Ionic Mobilities in Membranes and Aqueous Solutions

Ion	Cellulose acetate membrane, $\times 10^{-7}$ cm^2/sec-V	Ion exchange membrane,[11] $\times 10^{-5}$ cm^2/sec-V	Aqueous solution, $\times 10^{-4}$ cm^2/sec·V
Na$^+$	2.0	4.4	5.3
Cl$^-$	2.8	5.0	6.8
NO$_3^-$	...	3.9	...
SO$_4^{2-}$	...	3.5	...

for the aqueous Na$_2$SO$_4$ solution shows that the SO$_4^{2-}$ ion is less mobile than the Na$^+$ ion in the membrane.

The relationship of relative ionic mobility $u_i/u_{\mathrm{Na^+}}$ to the ionic radii is shown in Figure 3. This figure shows that the mobilities of univalent ions increase with the increase in their ionic radii, but this relationship is inverse for the ions with larger radii than that of the NO$_3^-$ ion. The same relationship for divalent ions Mg^{2+} and SO$_4^{2-}$ as for univalent ions is expected from Figure 3. It is well known in aqueous solutions that the higher the charge density of an ion, the stronger is the interaction between the ion and the water molecules, resulting in small ionic mobility. On the other hand, the mobility of an ion is proportional to its valence, and hence ions with high valences are considered to have larger mobility if their charge densities are the same. The trend of the ionic mobilities in aqueous solutions could be explained by taking into consideration the above-mentioned facts. This effect seems to be more emphasized in the membrane. It is expected that the water which exists as bound water[6,9] in the membrane might make the ions less mobile compared with free water in an aqueous solution. The latter trend, i.e., that the mobilities of the ions with larger radius than NO$_3^-$ decrease with increase in their ionic radii, could not be explained only by the effect of the valence and electric charge density.

It is suggested here that the reduction of mobility of these ions is mainly attributable to their ionic sizes. In other words, the friction between the ion and
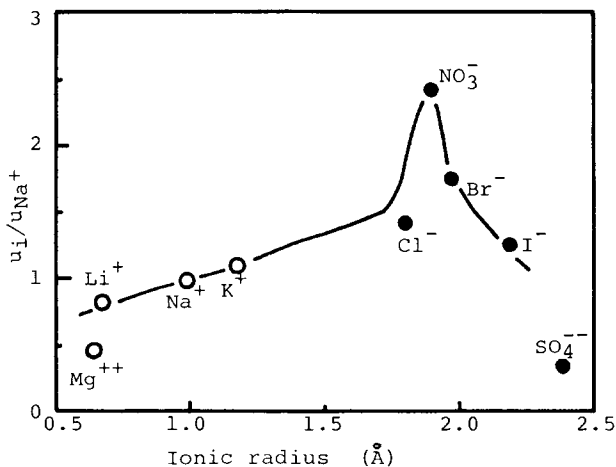

Fig. 3. Relationship between relative ionic mobilities ($u_i/u_{\mathrm{Na^+}}$) and ionic radii.

the membrane wall increases because the ionic size is close to the gap size between the polymer chains. This suggestion may be consistent with the facts, reported by Sarbolouki et al.,[10] that there would exist intermolecular gaps of approximately 3 Å in radius in the active layer of the asymmetric cellulose acetate membrane.

The mobilities of Na^+ and Cl^- ions in the membrane could be calculated from the following data obtained with the dense membrane: the specific resistance $\sigma_m = 4.0 \times 10^6 \Omega\cdot cm$, $u_{Cl^-}/u_{Na^+} = 1.42$ obtained from the membrane potential, and the concentration of NaCl in the membrane which was calculated from the water content and the distribution coefficient of NaCl between the membrane and the external solution $K = 0.25$.[7]

The calculated values are listed in Table V together with their mobilities in aqueous solutions and those in the ion exchange membrane obtained by Yamamoto.[11] It is noticed from the result that the ionic mobilities in the dense cellulose acetate membrane are three to four orders of magnitude less than those in aqueous solutions and about one hundredth of those in an ion exchange membrane. It seems probable that the ion exchange membrane has relatively larger holes compared with the cellulose acetate membrane, because ions are affected by Coulomb's force, a relatively long-range force, due to the electric charge of the membrane. This is also supported by the fact that there are no mobility differences between Cl^-, NO_3^-, and SO_4^{2-} in an ion exchange membrane.[11]

CONCLUSIONS

1. The mobilities of univalent ions larger in radius or divalent ions relative to Na^+ ion mobility in the cellulose acetate membrane are much different from those in aqueous solutions. It is noteworthy that divalent ions such as Mg^{2+} and SO_4^{2-} are less mobile and NO_3^- ion is more mobile in the membrane.

2. The order of ionic mobility in the cellulose acetate membrane could be shown quantitatively and is in agreement with the order obtained from the salt rejection by the reverse osmosis process.

3. The mobility of an ion in the membrane increases with increase in ionic radius, holding its valence constant. However, if the ionic radius is larger than a certain value, the mobility of an ion decreases with increase in its size. The above phenomena can be explained by both the effects of its charge density and the physical friction between the ion and the membrane wall when the ionic radius is close to the intermolecular gaps between polymer chains.

4. The mobilities of Na^+ and Cl^- ions in the membrane are $(2–3) \times 10^{-7}$ cm²/sec·V and three to four orders of magnitude less than those in aqueous solutions.

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