

Analysis of Properties of Advanced Ion-Exchange Membranes: Neosepta CIMS and ACS-2

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ABSTRACT

Membrane characteristics such as permeability coefficient of salts and water, electro-osmotic water, and transport numbers were measured for advanced ion-exchange membranes (CIMS, ACS-2) and their characteristics were compared with those of conventional type membranes (CL-25T, AVS-4T). The advanced ion-exchange membranes show some different properties against the conventional membranes. For example, although electro-osmotic water is dependent on current density in the conventional membrane, there is no such dependency in the advanced membrane.

Brine concentration was calculated from the permeability coefficient of salt and water, electro-osmotic water and transport numbers. The calculated brine concentration agrees well with experimental results.

INTRODUCTION

Since 1972, edible salt has been produced by electro-dialytic concentration of seawater in Japan. Two types of ion-exchange membranes — cation-exchange and anion-exchange — are necessary for this purpose. In this process, brine concentration, purity of brine, current efficiency, energy consumption, etc. are mainly dependent on the properties of the ion-exchange membranes used. In this study, membrane characteristics such as permeability coefficient of salts and water, electro-osmotic water, and transport numbers were measured for advanced ion-exchange membranes (CIMS, ACS-2) and their characteristics were compared with those of conventional type membranes (CL-25T, AVS-4T).

THEORETICAL

Brine concentration is calculated from the permeability coefficient of salt and water, electro-osmotic water and transport numbers (Yamane et al., 1967a). The material balance in electro-dialysis of sodium chloride solution is represented by the factors shown in Fig. 1: the amount of ions which are electrically transferred, the amount of water which passes by osmosis accompanying the transfer of ions (electro-osmotic water), the amount of salt which

diffuses under the concentration gradient between both sides of the membrane, and the amount of water which passes by osmosis under the concentration gradient between both sides of the membrane (osmotic water). The transferred amounts of these

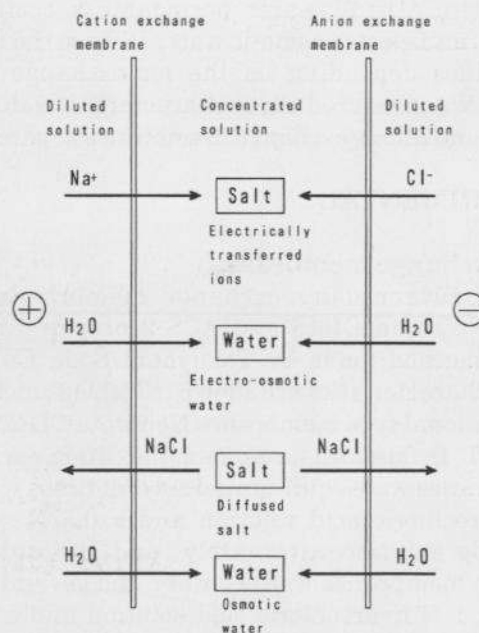


Fig. 1. Mass transfer under electro-dialysis.

materials give the concentration (C wt%) of the concentrated solution through the formula:

$$C = 100 \times (Se - Sd) / (Se - Sd + We + Wd) \quad (1)$$

where Se is the amount of ions transferred electrically in unit time; Sd is the amount of salt diffusing through the membrane by concentration difference in unit time; We is the electro-osmotic water in unit time; and Wd is the osmotic water in unit time.

In the case of sodium chloride, Se , Sd , We and Wd are calculated as follows:

$$Se = 58.5 \times (t^+ + t^- - 1) \times I/F \quad (2)$$

$$Sd = 58.5 \times (Ds/d) \times S \times \Delta C \quad (3)$$

$$We = 18 \times W \times I/F \quad (4)$$

$$Wd = (Dw/d) \times S \times \Delta C \quad (5)$$

where t^+ is the transport number of cation in cation-exchange membrane; t^- is the transport number of anion in anion-exchange membrane; Ds is the diffusion coefficient of salt ($\text{cm}^2 \text{sec}^{-1}$); Dw is the osmotic coefficient of water [$\text{cm}^2 \text{sec}^{-1} \cdot (\text{mol cm}^{-3})^{-1}$]; W is electro-osmotic water (mol F^{-1}); I is the current density (amp cm^{-2}); F is the faraday constant; ΔC is the concentration difference across membrane (mol cm^{-3}); S is the effective membrane area (cm^2); and d is the membrane thickness (cm).

The transport numbers (t^+ , t^-), salt permeability coefficient (Ds/d), water permeability coefficient (Dw/d), and electro-osmotic water (W) are the intrinsic values depending on the ion-exchange membrane. We measured these characteristic values for cation and anion-exchange membranes separately.

EXPERIMENTAL

Ion-exchange membranes

The advanced ion-exchange membranes used were Neosepta CIMS and ACS-2 prepared by the paste method made by Tokuyama Soda Co., Ltd. Their characteristics are shown in Table 1, including conventional type membranes Neosepta CL-25T and AVS-4T. Before measurements, the cation-exchange membranes were equilibrated several times with a 1 N hydrochloric acid solution and a 0.5 N sodium chloride solution alternately, and the anion-exchange membranes were equilibrated several times with a 1 N hydrochloric acid solution and a 0.5 N ammonia solution alternately. Both membranes were then equilibrated with the salt solution which was used in the measurements.

TABLE 1

Characteristics of ion-exchange membranes

	CIMS	ACS-2	CL-25T	AVS-4T
Electrical resistance (Ωcm^2) ^a	1.7	1.7	2.8	4.0
Ion-exchange capacity (meq g^{-1}) ^b	2.3	2.1	1.8	1.8
Water content ^c	0.38	0.28	0.30	0.28
Thickness (mm)	0.15	0.11	0.16	0.16
Bursting strength (kg cm^{-2})	2.3	1.9	3.6	5.7

^aEquilibrated with 0.5 N NaCl solution and using 1000 Hz AC at 25.0°C.

^bmeq/g Cl^- or Na^+ -form dry membrane.

^cEquilibrated with 0.5 N NaCl solution, $\text{gH}_2\text{O/g}$ Cl^- or Na^+ -form dry membrane.

MEASUREMENT

Ion exchange capacity, water content, electric resistance, transport numbers, salt permeability coefficient, water permeability coefficient and electro-osmotic water have been measured by Stewart and Graydon (1957) and Onoue et al. (1959). Figure 2 shows apparatus for measuring the permeability coefficient of salt and water. Figure 3 shows apparatus for measuring electro-osmotic water. The concentration of the seawater in Tokuyama Bay was carried out by use of an electro-dialyzer (effective membrane area: 1 dm^2).

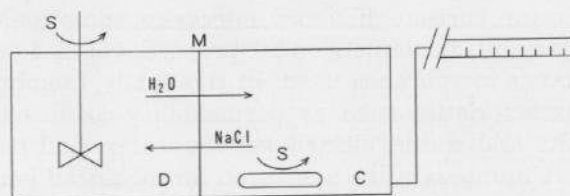


Fig. 2. Apparatus to measure permeability of salt and water. C, concentrated compartment; D, diluted compartment; M, membrane; S, stirrer.

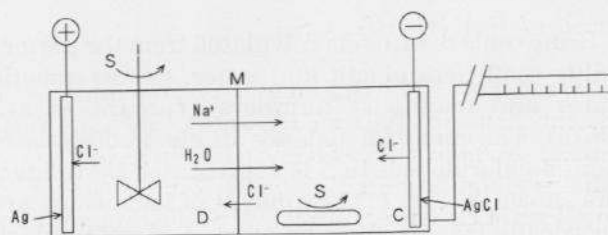


Fig. 3. Apparatus to measure electro-osmotic water. C, concentrated compartment; D, diluted compartment; M, membrane; S, stirrer.

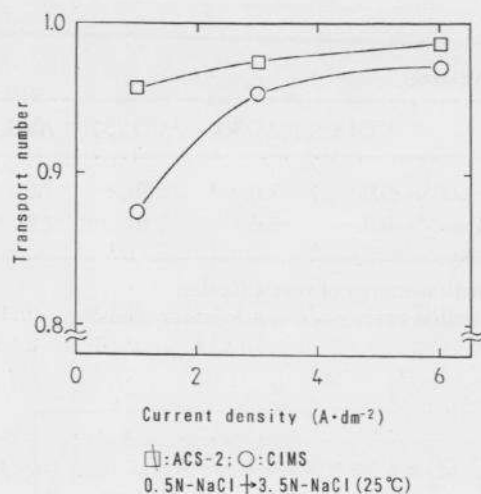


Fig. 4. Effect of current density on transport number.

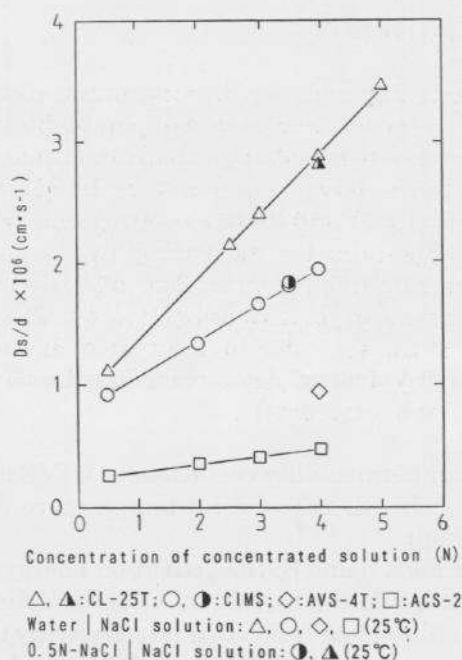


Fig. 5. Effect of concentration of concentrated solution on permeability of salt (NaCl).

RESULTS AND DISCUSSION

In order to save the energy to produce sodium chloride, ion-exchange membranes should permeate cations or anions selectively with little leakage of salt from concentrated solution. Firstly, transport numbers of cation and anion-exchange membranes were measured separately in the presence of a concentration difference across the membrane. Figure 4 shows transport numbers of CIMS and ACS-2

measured with various current densities. The transport numbers are low at the low current density for both CIMS and ACS-2. This is due to the large contribution of the salt diffusion to the transport number in the low current density because the measurement was carried out in the presence of a concentration difference across the membrane. In fact, when the measurement was made without a concentration difference, the current efficiency did not decrease in the same low current density. The amount of salt transferred (Se) can be also calculated from the transport numbers using equation (2). Figure 5 shows the salt permeability coefficient when the concentration of the concentrated compartment was changed. Two types of measurement were made:

- (1) water/membrane/various concentrations of sodium chloride solution,
- (2) 0.5 N sodium chloride solution/membrane/various concentrations of sodium chloride solution.

Figure 5 apparently shows that permeability coefficients of sodium chloride of CIMS and ACS-2 are remarkably lower than those of CL-25T and AVS-4T in spite of low electric resistance of the membranes shown in Table 1. Figure 6 shows the effect of solution temperature on the permeability coefficient. Although the permeability coefficient of sodium chloride increases with the rise of temperature in all membranes, CIMS and ACS-2 show lower values as compared with CL-25T and AVS-4T. This means that salt leakage through the membranes is small for CIMS and ACS-2. The concentration of the

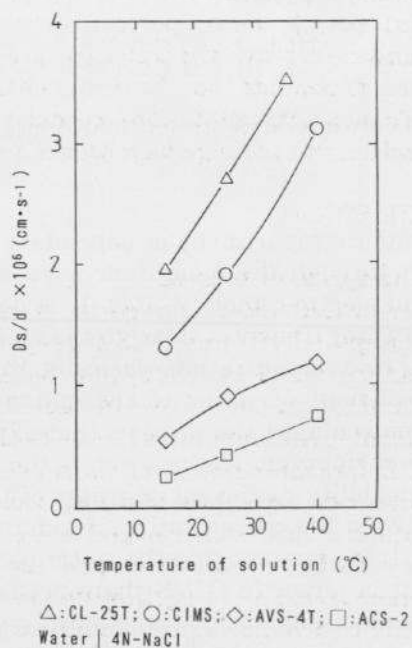


Fig. 6. Effect of temperature of solution on permeability coefficient of salt.

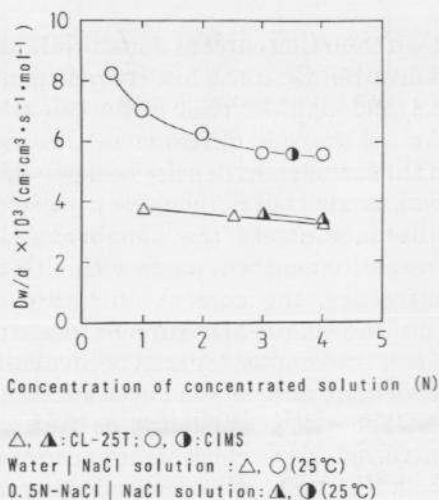


Fig. 7. Effect of concentration of concentrated solution on permeability coefficient of water.

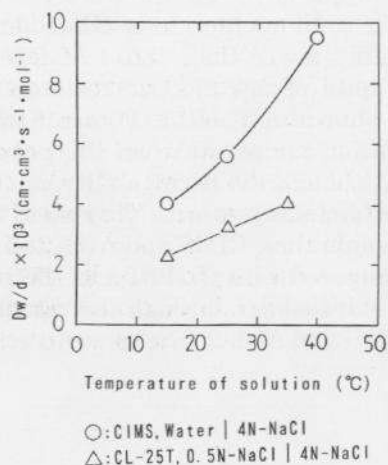


Fig. 8. Effect of temperature of solution on permeability coefficient of water.

concentrated compartment is dependent on water transport through the membrane such as osmotic water and electro-osmotic water. It is desirable to decrease water transport through the membrane to get high brine concentration. Basically, the permeability coefficient of water of the cation-exchange membrane is almost the same as that of the anion-exchange membrane. Figure 7 shows the change in the permeability coefficient of water of CIMS and CL-25T when the concentration of sodium chloride changes. It is apparent that the water permeability coefficient is larger in CIMS than in CL-25T. The water permeability coefficient is hardly influenced by a concentration of the dilute side (between water and 0.5 N NaCl). Figure 8 shows the effect of solution temperature on the permeability coefficient of water.

TABLE 2

Activation energy

	CIMS	ACS-2	CL-25T	AVS-4T
ΔE_s (kcal mol ⁻¹)	6.0	7.0	5.0	7.2
ΔE_w (kcal mol ⁻¹)	6.3	5.6	5.0	4.0

ΔE_s : Activation energy of salt diffusion.

ΔE_w : Activation energy of osmotic water transfer.

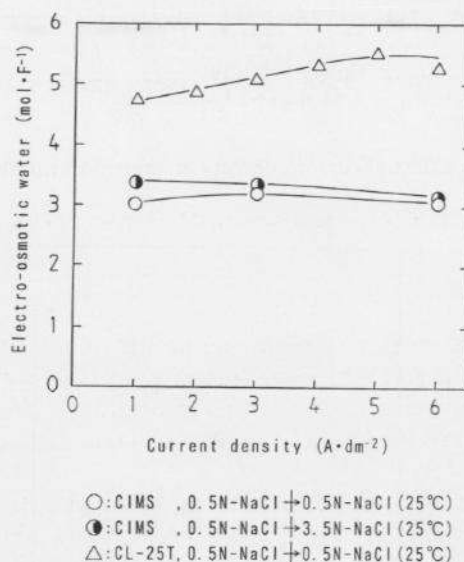


Fig. 9. Effect of current density on electro-osmotic water.

The water permeability coefficient in CIMS is larger than that in CL-25T and its temperature dependence is high.

From Figs. 6 and 8, the activation energy for the diffusion inside the membranes can be determined by Arrhenius' plot (Table 2). It is noteworthy that the activation energy for CIMS is much higher than that for CL-25T in both salt diffusion and osmotic water, although the electric resistance of CL-25T is much higher than that of CIMS. This suggests that the structure of CIMS is much more homogeneous than that of CL-25T.

Figure 9 shows the effect of the current density on electro-osmotic water. It is apparent from this figure that the electro-osmotic water of CIMS is remarkably low as compared with CL-25T and the electro-osmotic water is not influenced so much by the current density or the concentration of solution in the case of CIMS. These facts suggest that the structure of CIMS is tighter than that of CL-25T. Figure 10 shows the effect of solution temperature on electro-osmotic water. The electro-osmotic water apparently

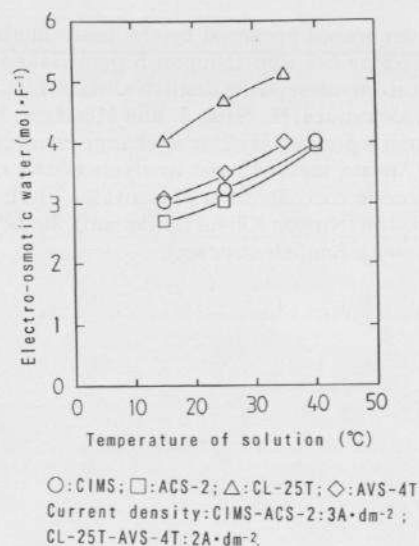


Fig. 10. Effect of temperature of solution on electro-osmotic water.

increases as the solution temperature raised in all ion-exchange membranes. However, CIMS showed extremely small amount electro-osmotic water as compared with CL-25T, though electric resistance of CIMS is low.

In the above experiments, a sodium chloride solution was used in the measurement. Seawater, however, is a multicomponent solution containing many ions in addition to NaCl. We, therefore, expanded our experiment to include other types of salt. Table 3 shows permeability coefficients of various salts, i.e., sodium chloride, potassium chloride, magnesium chloride, and calcium chloride, for CIMS or ACS-2 membranes. Permeability coefficients of salt with a divalent cation are found to be relatively smaller in both CIMS and ACS-2. In particular,

TABLE 3
 Permeability coefficient of various salts

		NaCl	KCl	MgCl ₂	CaCl ₂
CIMS	$D_s/d \times 10^{6a}$	1.81	4.74	0.62	1.41
	$D_w/d \times 10^{3b}$	5.64	7.69	2.42	3.48
	W^c	3.30	3.40	7.29	5.33
ACS-2	$D_s/d \times 10^{6a}$	0.43	0.41	0.03	0.04
	$D_w/d \times 10^{3b}$	6.03	5.95	4.29	3.69

^aPermeability coefficient of salt ($cm \cdot s^{-1}$): Water | 3.5 N.

^bPermeability coefficient of osmotic water ($cm \cdot s^{-1} \cdot cm^3 \cdot mol^{-1}$): Water | 3.5 N.

^cElectro-osmotic water ($mol \cdot F^{-1}$): 0.5 N \rightarrow 3.5 N.

ACS-2 is an anion-exchange membrane through which CaCl₂ or MgCl₂ hardly diffuse. This is due to the effect of Donnan Exclusion of divalent cations such as Ca²⁺ or Mg²⁺ on permeability. Table 3 also shows water permeability coefficient of CIMS and ACS-2 when various kinds of salts were used. Permeability coefficients of both CIMS and ACS-2 are relatively small, especially, that of CIMS. It is thought that this is related to the low water content of divalent ion-form cation-exchange membrane. However, electro-osmotic water in a divalent cation solution is extremely large as compared with a monovalent cation solution. This is also related to hydration of divalent cations. From the above results, we tried to predict the concentration of the concentrated solution in the case of CIMS and ACS-2 according to equation (1).

CONCLUSIONS

The concentration of the concentrated solution in the case of CIMS and ACS-2 were calculated according to equation (1). Figure 11 shows the calculated and the observed values of the concentrations of the concentrated solutions at different current densities. There is a good agreement between the calculated and the experimental values. This result clarifies that the concentrations of the concentrated solutions by electro-dialysis can be predicted by the properties of the ion-exchange membranes, i.e. transport numbers, permeability coefficients of salts and water, and electro-osmotic water.

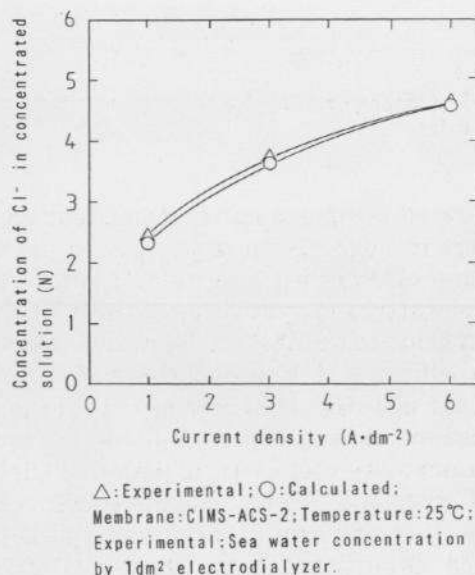


Fig. 11. Comparison of concentration of concentrated solution between experimental and calculated values.

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