Technical Paper

The Membrane Potential and Reverse Osmosis Property of Cellulose Acetate Membrane

Norio YUI*, Yoichi KUROKAWA* and Kazuo WAKAKUWA*

The membrane potential and reverse osmosis property of cellulose acetate membrane have been investigated. Membrane potentials were measured in the resin cell using two calomel electrodes with aqueous solutions of NaCl, KCl, NH_4Cl , CaCl_2 , MgCl_2 and Na_2SO_4 . Reverse osmosis experiments were made with these solutions under an applied pressure of 30~100 atm. It was found that the order of permeability ratio determined from the potential measurements agreed well with that of salt rejection observed in reverse osmosis performance. No evidence of asymmetric character of membrane potential has been observed.

1 Introduction

The cellulose acetate membrane is generally recognized to be applicable in the reverse osmosis process, and the researches to find a superior membrane have been carried out^{1),2)}. The study of the process of reverse osmosis has been made progressively. However, no work has been found in the literature dealing with the relationship between the membrane potential and salt rejection or asymmetric property of reverse osmosis membrane. The authors performed this work in order to obtain some information on this relationship.

2 Experimental

2.1 Preparation of membrane

The procedure of preparation of cellulose acetate membrane used was the same as that developed by Loeb and Sourirajan^{1),2)}. The casting solution was prepared by mixing 38.8%-acetyl cellulose acetate (Wakōjyunkyo Co.), formamide and acetone in a proportion of 25 : 30 : 45 by weight. This solution was cast on a glass plate at room temperature, by using the casting knife used in the thin layer chromatography. The exposed surface to air was allowed to evaporate the solvent for one minute. After evaporation, the membrane together with the glass plate was immersed in an ice water bath for two hours. Then, the membranes were annealed in hot water at 80°C for 5 minutes.

2.2 Measurements of membrane potential

The membrane potential was measured by using the following cell,

The cell used is shown in Fig. 1, which is made from resin and is composed of two half cells held together by four rods running through the entire cell. It has inlet and outlet for exchanging or bubbling the solution. For the investigation of asymmetric character of membrane, the solution (1) was placed on the rightside of the membrane and the solution (2) on the leftside, and then potential was measured. Next the solution (2) on the rightside of the membrane and the solution (1) on the leftside were placed and the potential was measured.

Fig. 1 Cell for measurement for membrane potential

The potential values were almost reproducible to within 0.1 mV over periods of at least 30 minutes. The electrolyte solutions were of NaCl, KCl, NH_4Cl , CaCl_2 , MgCl_2 and Na_2SO_4 with varying the concentration ratios from 2 to 10. A dilute solution was taken as reference solution throughout experiments.

2.3 Reverse osmosis performance

The apparatus and experimental procedure used

* Department of Applied Science, Faculty of Engineering, Tohoku Univ. (Aoba, Aramaki, Sendai)

were the same as those employed previously³⁾. The feed solution is injected into a desalination cell by a pressure pump, through a surge tank and a filter³⁾. The water permeated through the membrane is collected by flowing through a spiral path to the center of the cell. The membrane is supported on a porous disk of stainless steel. Salt rejection R is calculated by

$$R(\%) = \frac{C_1 - C_2}{C_1} \times 100,$$

where suffixes 1 and 2 refer to the concentration of the feed and that of the permeated solution, respectively. The concentration of chloride ions was determined by Mohr titration method.

3 Results and Discussion

Membrane prepared in this way has the thickness of ca. 200 μ , and is shown to be consisted of a very thin dense surface layer and a porous structure^{(1),(2)}. The dense layer was estimated to be about 0.3~0.5 μ thick from the electron micrography and the relation of water flux vs. applied pressure, and the porous substructure to have a pore size of the order of 0.1 μ . Thus, the membrane has the asymmetric characteristic which is reflected in both water flux through the membrane and salt rejection³⁾. Desalination can be achieved only when the dense layer is in contact with the feed solution under pressure. The definite water flux and salt rejection may probably arise as a result of the asymmetric structure of the membrane^{(2),(3)}. The observed membrane potentials are represented in Table 1.

The observed values are lower than those of theoretical potential (*e. g.* 33 mV for a membrane separating 0.1 N and 0.5 N NaCl solutions). This deviation increases with an increase of concentration ratio. Therefore, it is considered that the osmotic flow of water plays a role in the potential observed⁽⁷⁾. The potential values for a given membrane were generally reproducible, although the membrane exhibited some variation. This would probably come from some change in membrane structure, such as the pore size and thickness of membrane⁽⁷⁾. This variation might partly be explained by the random orientation of the cellulose molecules similar to that of nitrocellulose membrane⁽⁸⁾. This orientation would produce varying quantities of active carboxyl groups, which extend into the pores of the membrane and are responsible for the membrane potential. With an increase in thickness, the average pore length in the membrane would increase and the probability that each pore has an active dissociable group would increase. Consequently, the membrane potential would

Table 1 Membrane potentials of cellulose acetate membrane

	Membrane potential mV					
	1.0 : 0.5	0.5 : 1.0	0.5 : 0.1	0.1 : 0.5	1.0 : 0.1	0.1 : 1.0
KCl	1	3.0	3.2	9.0	12.0	14.8
	2	3.7	4.2	13.1	15.3	20.0
	3	3.4	3.7	11.5	12.6	13.0
	4	4.0	4.5	14.2	15.8	16.8
	5	1.9	2.8	8.4	12.2	7.8
	av.	3.2	3.7	11.3	13.6	12.6
NaCl	1	3.3	4.4	10.8	13.7	11.4
	2	4.0	3.6	14.6	15.4	15.6
	3	3.6	3.8	13.4	13.0	12.0
	4	4.1	3.6	15.2	15.4	17.2
	5	3.1	2.8	11.0	13.6	11.5
	av.	3.6	3.6	13.0	14.2	13.5
NH ₄ Cl	1	0.8	1.2	3.6	5.5	3.3
	2	0.9	0.6	3.5	3.1	5.0
	3	0.6	0.9	3.0	5.6	2.2
	4	2.1	2.1	7.6	7.0	10.1
	5	1.0	0.1	5.2	2.4	6.8
	av.	1.1	1.0	4.6	4.7	5.5
CaCl ₂	1	7.4	8.6	22.8	24.5	25.2
	2	6.9	5.9	20.0	18.2	25.7
	3	4.3	7.1	20.0	24.0	21.8
	4	6.6	8.4	27.0	28.5	34.0
	5	7.0	6.2	24.0	20.5	30.0
	av.	6.4	7.2	22.8	23.2	27.4
MgCl ₂	1	6.8	6.0	25.5	21.5	29.5
	2	8.0	7.3	26.5	19.0	31.5
	3	6.8	6.8	22.5	18.7	28.0
	4	8.5	7.3	26.3	27.0	31.5
	5	7.0	5.8	21.0	23.5	24.0
	av.	7.4	6.6	24.4	21.9	28.9
Na ₂ SO ₄	1	-7.4	-3.6	-14.4	-20.0	-17.5
	2	-18.3	-6.8	-19.0	-10.6	-31.0
	3	-8.0	-3.2	-19.2	-16.0	-24.0
	4	-14.6	-8.0	-26.0	-25.5	-33.5
	5	-6.2	-6.4	-20.5	-23.0	-20.0
	av.	-10.9	-5.6	-19.8	-19.0	-25.2

Each potential of different membrane number (1~5) is the value for different samples of the same membrane. 0.1, 0.5 and 1.0 represent normalities of salt solution.

increase. No evidence of membrane asymmetry has been observed as shown in Table 1. The ion selectivity, which is expressed in terms of selectivity constant, is related to the ability of the membrane to reject ions and is reflected in the membrane potential. The authors evaluated the permeability ratios from the membrane potential data by using the equation of Hodgkin and Katz, assuming the Cl⁻ permeability to be unity⁹⁾. The equation for uni-univalent elec-

trolyte:

$$E_m = \frac{RT}{F} \ln \frac{P_+ \cdot C'_+ + P_- \cdot C_-}{P_+ \cdot C_+ + P_- \cdot C'_-}$$

where P , C and C' refer to permeability coefficient and concentrations on both sides of the membrane, respectively. The equation for divalent electrolytes can be derived similarly. The calculated permeability constants are represented in Table 2, by using the average of five readings for 0.5 N : 1.0 N salt solution ratio, because the contribution of water transfer to membrane potential is least in this case. However, this order does not change in the case of other concentration ratio.

Table 2 Permeability constants for various ions

Ion	Cl ⁻	NH ₄ ⁺	K ⁺	Na ⁺	Ca ⁺⁺	Mg ⁺⁺	SO ₄ ⁻⁻
Permeability	1.00	0.981	0.691	0.654	0.626	0.587	0.304

Next, reverse osmosis experiments were performed for the same membrane as that used in membrane potential measurements, with the feed solutions of NaCl, CaCl₂, MgCl₂ and Na₂SO₄ under pressure ranging from 30 to 100 atm, respectively. The same membrane was used throughout the entire performance. The relation of salt rejection R vs. applied pressure are shown in Fig. 2, where R of NaCl increases steply with an increase of applied pressure. This

Fig. 2 Salt rejection vs. applied pressure for 0.5 N salt solution (operation temp. : 25°C)

A : Na₂SO₄, B : MgCl₂, C : CaCl₂, D : NaCl

trend is consistent with the prediction based on the solution-diffusion theory by Lonsdale et al.¹⁰. Salt rejection was found to be in the order of NaCl < CaCl₂ < MgCl₂ < Na₂SO₄, as shown in the figure. This order is consistent with the observations made by other investigators and the order of permeability ratio determined from the membrane potential described before. The semipermeability of cellulose acetate membrane to various solutes of aqueous solution decreases in accordance with the order in the lyotropic series. In other words, the order of rejection increases with an increase in valence of ion and decreases with an increase of radius of the hydrated ion. Since the lyotropic series are frequently found in the fields of physical chemistry, the above order appears significant in relation to the physico-chemical properties of membrane.

Thus it is considered that the size and charge of solute are the most important parameters affecting to its rejection, and the physical structure of the membrane determines the behavior of reverse osmosis. The results for glass electrode membrane by Hair, indicate that the pore geometry (pore radius and pore volume) plays an important role in the selective behavior of the membrane¹¹. That is, membranes with smaller porosity give rise to higher concentration potentials and exhibit better selectivity. Considering these results and non-existence of membrane potential asymmetry, it might be considered that a thin dense layer of the cellulose acetate membrane would contribute to permeability of ions.

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