

A Fundamental Study on the Production of Highly Concentrated Sea Water by Ion Exchange Membranes

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The effective charge density and the mobility of ions in the membrane would decrease with the decrease of dielectric constant. It is normally postulated that the counter-ions prefer to make ion pairs with the fixed charge groups in the medium of low dielectric constant field. If, however, the medium has a large number of -OH groups the effective charge density and the mobility of the counter-ions will not decrease in spite of the relatively low dielectric field. This evidence has significant meaning for the production of highly concentrated sea water by ion exchange membranes

1. Introduction

In the salt production process sea water concentration is increased by about 5 times through ion-exchange membrane before evaporation. If the salt should be obtained in the higher efficiency it is necessary to concentrate the sea water by 8 or 9 times. We, however, have following problems to be solved before completing this project.

(1) How can we increase the counter-ion concentration in the membrane?

(2) How can we prevent the water volume flux caused by the osmotic pressure difference?

Reducing the water content in the membrane is one of the solutions for this problems. However, it decreases the effective fixed charge density and the ionic mobility in the membrane. In this study, the effect of ion pairing between fixed charge groups and counter-ions on the effective charge density and the ionic mobility in the low water content, theoretically and experimentally.

2. Theory

The formal relationship between the ionic activity coefficients in the membrane and the membrane effective charge density is established by comparing the results obtained from a model based on the ideal Donnan equilibrium extended to account for the ion pairing effect with the results obtained

from a thermodynamic formalism including ionic activities instead of concentrations. We calculate¹ the membrane effective charge density and the ionic activity coefficients by using a simple model of ion pairing based on the Fuoss approach for contact ion pairs in electrolyte solutions with a correction term for the entropy change of the counter-ion undergoing ion pairing. Membrane effective charge density, QC_x , is given by the product of net charge density, C_x , and charge effectiveness, Q .

Application of the Fuoss formalism to the ion pair in a membrane would lead to the association constant, K_A ,

$$K_A = (4\pi N_A / 3 \times 10^{-3}) a^3 \exp(b) \quad (1)$$

$$b = e^2 / 4\pi \epsilon_0 \epsilon_s a kT \quad (2)$$

where N_A is Avogadro's number, e is the electronic charge, ϵ_s is the local dielectric constant, ϵ_0 is the vacuum permittivity, k is the Boltzmann constant, T is the absolute temperature, and a is the contact distance. The charge effectiveness, Q , is shown by the following equation.

$$Q = \frac{1}{k' K_A + 1} \quad (3)$$

According to the diffusion theory with chemical reaction, the relationship between the counterion

mobility in the membrane, $\bar{\omega}_{\text{counterion}}$, and the association constant, βK_A , is as follows².

$$\bar{\omega}_{\text{counterion}} = \frac{1}{\beta K_A + 1} \frac{\omega_{\text{counterion}}}{q^2} \quad (4)$$

where q is the tortuosity factor and $\omega_{\text{counterion}}$ is the mobility of a counterion in an external solution. Clearly the charge effectiveness and ionic mobility in the membrane decrease with increase of the association constant and are the function of local dielectric constant.

3. Experimental

Two cation-exchange membranes, respectively composed of poly (divinylbenzene-co-styrene) and poly (vinyl alcohol) containing sulfonic acid groups, and an anion-exchange membrane, composed of poly(butadiene-co-styrene) containing quaternary amine groups in a polymer matrix, were used for the measurements. Membranes were immersed in ion-exchanged water, dimethyl sulfoxide, ethylene glycol, methanol or n-propanol for a week to ensure that the solvents were sorbed in the membrane phase.

A membrane was installed at the center of the measuring cell, which had two glass containers, one on either side of the membrane. Electrolyte solutions of different concentrations were poured into the left container; the concentration was varied from 0.001 to 4.0 mol/l and that in the right was kept constant at 0.001 mol/l. KCl, LiCl or LiBr was used to measure the membrane potential.

4. Results and Discussion

The charge effectiveness, Q , is shown in Fig.1 as a function of the local dielectric constant, ϵ_s ³. The theoretical results indicate that Q decreases with decrease of ϵ_s , which correspond with the experimental results except ethylene glycol. The effective charge density and the mobility of ions in the membrane would decrease with the decrease of dielectric constant. In Fig.2 the effective charge density, QC_x , is plotted as a function of weight fractions of methanol for charged PVA membrane containing sulfonic acid groups. QC_x increases with

increase of methanol fraction, which corresponds with decrease of ϵ_s . It is normally postulated that the counter-ions prefer to make ion pairs with the fixed charge groups in the medium of low dielectric constant field. However, if the medium has a large number of -OH groups the effective charge density and the mobility of the counter-ions will not decrease in spite of the relatively low dielectric field. This evidence has significant meaning for the production of highly concentrated sea water by ion exchange membranes

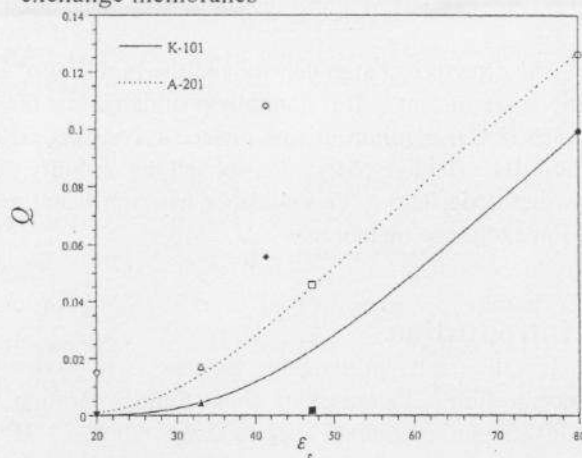


Fig.1 Charge effectiveness, Q , as a function of local dielectric constant

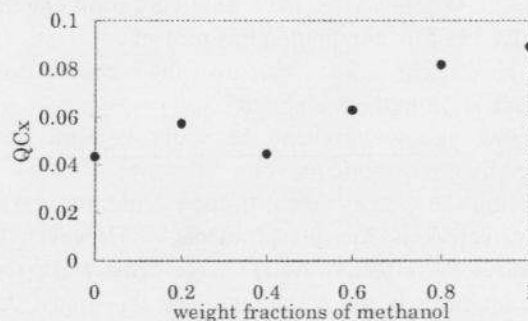


Fig.2 Effective charge density, QC_x , as a function of methanol weight fraction

REFERENCES

1. S. Mafé, P. Ramírez, A. Tanioka and J. Pellicer, J. Phys. Chem. B, 101 (1997) 1851
2. T.-J. Chou and A. Tanioka, J. Phys. Chem. B, 102 (1998) 129
3. T.-J. Chou and A. Tanioka, J. Phys. Chem. B, 102 (1998) 7198