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SHORT COMMUNICATION

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Electrodialytic separation of potassium ions from sodium ions in the presence of crown ether using a cation-exchange membrane

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Abstract The separation of potassium and sodium ions from their mixture was performed by electrodialyzing a mixed solution of potassium chloride and sodium chloride in the presence of 18-crown-6 using a commercial cation-exchange membrane. After 18-crown-6 had been impregnated in the membrane, the mixed solution containing 18-crown-6 was electrodialyzed as the desalting-side solution. The permeation of potassium ions through the membrane decreased remarkably and the electrical resistance of the membrane increased during electrodialysis with increasing concentration of 18-crown-6 in the solution. Because potassium ions form a more stable complex with 18-crown-6 than sodium ions and because the complex permeated through the membrane with difficulty, sodium ions are thought to selectively permeate through the membrane. The current efficiency in electrodialysis was greater than 97.0%.

Key words Separation of potassium ions from sodium ions · 18-Crown-6 · Cation-exchange membrane · Electrodialysis

Introduction

Because crown ethers form complexes with specific cations, various ion-selective electrodes have been developed and used [1]. At the same time, selective permeation of specific cations was studied using liquid membranes [2] and supported liquid membranes [3] containing various crown ethers to separate cations, to remove harmful cations, etc. However, the flux of the ions permeated through the liquid membranes and supported liquid membranes was low and the membranes were unstable. A cross-linked membrane having benzo-18-crown-6 ether groups was also studied to gain an understanding of the behavior of fixed-site carrier membranes [4].

Electrodialytic transport of ions through ion-exchange membranes is controllable by the current density passing through the membranes; however, ion-exchange membranes are ineffective in separating ions with the same charge due to poor permselectivity for specific ions. Several improved ion-exchange membranes have been reported [5] and improved electrodialysis methods have also been proposed, such as electrodialyzing the mixed-salt solutions of heavy-metal ions in the presence of complexing agents, such as ethylenediaminetetraacetate, oxalic acid, etc. [6].

Though the separation of potassium ions from sodium ions was tried using a charge-mosaic membrane [7], the separation of potassium ions from sodium ions is generally difficult using a cation-exchange membrane by electrodialysis and diffusion dialysis. Their ion-exchange equilibrium constants and migration speeds in the membrane phase are not so different from each other. Thus, it is interesting to electrodialyze a mixed solution of potassium and sodium ions in the presence of crown ethers to separate potassium ions from sodium ions. In this work, electrodialysis of a mixed solution of potassium and sodium ions was performed in the presence of 15-crown-5 ether or 18-crown-6 ether.

Experimental

Materials

A commercially available cation-exchange membrane, NEOSEPTA CM-1 (produced by Tokuyama Corp.; sulfonated styrene–divinylbenzene type) was used. The characteristics of NEOSEPTA CM-1 are shown in Table 1. The 18-crown-6 and 15-crown-5, which were impregnated in the membrane and added to the mixed-salt solution to be electrodialyzed, potassium chloride, sodium chloride and other reagents such as hydrochloric acid (35%), etc., obtained from Ishizu Seiyaku Co., were of reagent grade and were used without further purification.

Measurements

Apparatus

A similar four-compartment cell with two kinds of Ag–AgCl electrodes, which were used for current supply and measurement of voltage drop across the membrane during electrodialysis, to that reported previously [8] was used to measure the transport properties of the cation-exchange membrane in the presence of crown ethers. The effective membrane area was 10 cm^2 (2 × 5 cm), and the capacity of each compartment was 100 cm^3. The area of the Ag–AgCl electrodes for current supply was 4.0 × 10.0 cm, and the electrodes were into a wavelike shape in the cell. Wire probe electrodes of Ag–AgCl were placed close to the membrane surfaces (about 2 mm from the membrane surfaces). Sodium chloride solution 0.50 N was used as an anolyte and a catholyte; these were separated from two middle compartments by two-anion exchange membranes (NEOSEPTA AM-3, made by Tokuyama Corp.: the transport number of chloride ions in the membrane was greater than 0.99 in the electrodialysis of a 0.50 N sodium chloride solution at a current density of 20 mA/cm^2; the electrical resistance was 4.1 Ω cm^2; the fixed ion concentration of the membrane was 10.3 *m*). The anode side of the middle compartments was filled with a 1:1 mixed solution of 0.25 N sodium chloride and 0.25 N potassium chloride (chloride ion concentration: 0.50 N) containing crown ether (18-crown-6 or 15-crown-5) of various concentrations and the cathode side was filled with a mixed solution of 0.25 N sodium chloride and 0.25 N potassium chloride.

The amount of electrical current passing through the membrane during electrodialysis was measured with a coulometer (Nikko digital coulometer NDCM-4, Nikko Keisoku). The voltage drop across the membrane during electrodialysis was recorded on an *X-t* recorder (Toa Electronics Co., EPR-2T).

Table 1 Characteristics of the cation-exchange membrane, NEOSEPTA CM-1, used in this work

Name	NEOSEPTA CM-1
Backing	Poly(vinyl chloride)
Thickness (mm)	0.145
Electrical resistance[a]	1.43
Transport number[b]	> 0.98
Ion-exchange capacity[c]	2.24
Water content[d]	35.8
Fixed ion concentration[e]	6.26

[a] Ω cm^2, measured with 1000 Hz a.c. at 25.0 °C after equilibration with 0.500 N sodium chloride solution

[b] Measured by electrodialysis of 0.500 N sodium chloride solution at 10 mA/cm^2 at 25.0 °C

[c] Meq/g of Na$^+$-form dry membrane

[d] (g H_2O/g of Na$^+$-form dry membrane) × 100

[e] Molality: (ion-exchange capacity)/(water content) × 100

Measurement of transport properties of the cation-exchange membrane

The transport properties measured were the transport number of potassium ions relative to sodium ions, the current efficiency and the voltage drop across the membrane during electrodialysis. The transport number of potassium ions relative to sodium ions was defined as follows:

$$P_{\mathrm{Na}}^{\mathrm{K}} = \frac{t_{\mathrm{K}}/t_{\mathrm{Na}}}{c_{\mathrm{K}}/c_{\mathrm{Na}}} \quad ,$$

where t_{K} and t_{Na} are the transport numbers of the potassium ions and the sodium ions in the membrane, and c_{K} and c_{Na} are the average concentrations of the potassium ions and the sodium ions in the solution during electrodialysis. $P_{\mathrm{Na}}^{\mathrm{K}}$ means the permeated equivalent of potassium ions when 1 Eq of sodium ions permeates through the membrane.

Procedure of electrodialysis

After a piece of the cation-exchange membrane (3.5 × 7.0 cm, Na$^+$ form) had been dried under reduced pressure for 5 h at room temperature to obtain the dry weight of the membrane, the membrane was immersed in an aqueous 20% crown ether (18-crown-6 or 15-crown-5) solution for 48 h at 60 °C. After immersion, the membrane surfaces were wiped with filter paper and dried under the same conditions to estimate the weight increase by impregnation of the ethers. The cation-exchange membrane to be used in electrodialysis was also dried under the same conditions and was immersed in an aqueous 20% crown ether (18-crown-6 or 15-crown-5) solution for 48 h at 60 °C. Then the membrane surfaces were wiped with filter paper and placed in the middle of the cell. After each compartment of the cell had been filled with the respective solution, electrodialysis of the mixed solution of potassium chloride and sodium chloride was carried out in the presence of the crown ether in the desalting-side solution (anode-side compartment of the middle compartments) at a current density of 10 mA/cm^2 under vigorous agitation (1500 ± 100 rpm, with stirrers) for 1 h at 25.0 °C.

After electrodialysis had been performed, the solutions in the two middle compartments were analyzed by the Mohr method (for Cl$^-$) and by a gravimetric method using tetraphenylborate sodium salt [9] (for K$^+$). The concentration of sodium ions was calculated by subtracting the concentration of potassium ions from the concentration of chloride ions.

Ionic ratio of potassium ions to sodium ions in the membrane just after electrodialysis

After electrodialysis had been carried out under the same conditions as the measurement of the transport number of potassium ions relative to sodium ions, the membrane was instantaneously removed from the cell during electrodialysis (within 10 s after stopping), wiped with filter paper and the ions in the membrane were eluted by 1.0 N hydrochloric acid solution several times. Potassium and sodium ions in the eluant were analyzed by atomic adsorption spectroscopy. The ionic ratio (K/Na) in the membrane was calculated by $K_{\mathrm{Na}}^{\mathrm{K}} = (c_{\mathrm{K}}^{\mathrm{M}}/c_{\mathrm{Na}}^{\mathrm{M}})/(c_{\mathrm{K}}^{\mathrm{S}}/c_{\mathrm{Na}}^{\mathrm{S}})$. $c_{\mathrm{K}}^{\mathrm{M}}$ and $c_{\mathrm{Na}}^{\mathrm{M}}$ are equivalents of sodium ions and potassium ions in the membrane during electrodialysis, and $c_{\mathrm{K}}^{\mathrm{S}}$ and $c_{\mathrm{Na}}^{\mathrm{S}}$ are average concentrations of potassium ions and sodium ions in the solution during electrodialysis.

Results and discussion

In general, the ion-exchange equilibrium constant of potassium ions to sodium ions of sulfonated styrene–divinylbenzene-type membranes is more than unity and the mobility of potassium ions to that of sodium ions is slightly high. Accordingly, the transport number of potassium ions relative to sodium ions ($P_{\mathrm{Na}}^{\mathrm{K}}$) is more than unity, for example, 1.73 for commercial sulfonated styrene–divinylbenzene-type membrane under the same conditions [10]. Namely, potassium ions more selectively permeate through the cation-exchange membrane in electrodialysis and also in diffusion dialysis.

The change in the transport number of potassium ions relative to sodium ions with the concentration of 18-crown-6 in the desalting-side solution is shown in Fig. 1. Permeation of potassium ions decreased remarkably with increasing concentration of 18-crown-6. The Stokes radii of potassium and sodium ions are 133 and 195 pm, respectively. On the other hand, the crystal radii of potassium and sodium ions are 133 and 97 pm, respectively [11]. The inner radius of 18-crown-6 is reported to be 130 pm [12]. It is well known that complex formation between 18-crown-6 and alkali-metal cations is directly related to the inner diameter of the ether and the crystal radii of the cations. The complex formation constants of potassium and sodium ions with 18-crown-6, log *K*, were reported to be 2.03 and 0.8, respectively [13]. On the other hand, the weight increase of the membrane by immersing the membrane in an aqueous 20% 18-crown-6 solution was 18.1% (based on a Na^+-form dry membrane). Because 18-crown-6 had existed in the membrane before electrodialysis and was added in the desalting-side of the mixed solution during electrodialysis, the more stable complex of potassium ions with 18-crown-6 than sodium ions is thought to be formed in the desalting-side solution and in the membrane.

The transport number of potassium ions relative to sodium ions is a product of the ion-exchange equilibrium constant of potassium ions to sodium ions by a ratio of the mobility of potassium ions in the membrane to that of sodium ions. Because potassium ions form more stable complexes with 18-crown-6 than sodium ions, potassium ions would be difficult to ion-exchange with the membrane compared with sodium ions. In fact, the ionic ratio of potassium ions to sodium ions in the membrane just after electrodialysis was 2.66 without 18-crown-6 and that was 1.62 of the membrane in the presence of 100 g/l 18-crown-6. Apparently the ratio of potassium ions in the membrane decreased in the presence of the ether.

The change in the voltage drop across the membrane during electrodialysis with the concentration of 18-crown-6 in the desalting-side solution is shown in Fig. 2. The voltage drop across the membrane, which corresponds to the electrical resistance of the membrane, increased during electrodialysis and with increasing concentration of 18-crown-6. Both potassium and sodium ions form complexes with 18-crown-6. The molecular weights of the complexes of 18-crown-6 and potassium and sodium ions are 303.42 and 287.31, respectively, and the complexes have cationic charge, which can permeate through the cation-exchange

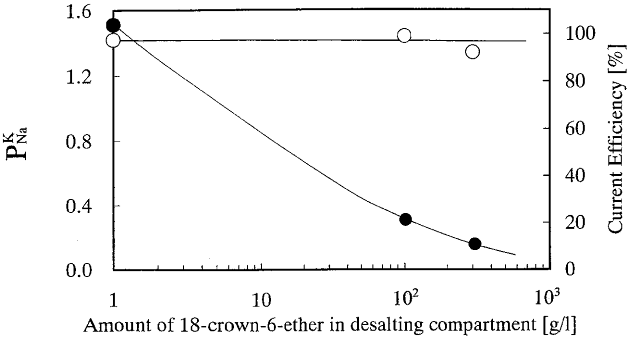

Fig. 1 Change in the transport number of potassium ions relative to sodium ions with the concentration of 18-crown-6 in the desalting-side solution. $P_{\mathrm{Na}}^{\mathrm{K}}$ (●), current efficiency (%) (○). A mixed solution of 0.250 N sodium chloride and 0.250 N potassium chloride containing 18-crown-6 of various concentrations was electrodialyzed as the desalting-side solution using NEOSEPTA CM-1 which had been immersed in an aqueous 20% 18-crown-6 solution for 48 h at 60 °C

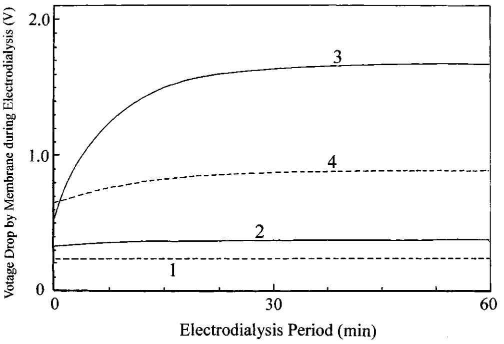

Fig. 2 Change in the voltage drop across a cation-exchange membrane during electrodialysis with concentration of 18-crown-6 or 15-crown-5. Without crown ether (1), 100 g/l 18-crown-6 (2), 300 g/l 18-crown-6 (3), 300 g/l 15-crown-5 (4). A mixed solution of 0.250 N sodium chloride and 0.250 N potassium chloride containing 18-crown-6 or 15-crown-5 of various concentrations was electrodialyzed as the desalting-side solution using NEOSEPTA CM-1 which had been immersed in an aqueous 20% 18-crown-6 or 15-crown-5 solution for 48 h at 60 °C

membrane. Sodium, potassium, complex ions composed of 18-crown-6 and potassium and the ions formed from the ether and sodium ions could permeate through the membranes. The fact that the electrical resistance of the membrane increased during electrodialysis suggests that the complexes of 18-crown-6 and potassium and sodium ions, which are of high molecular weight, permeate through the membrane. Because it is apparent from the complex formation constant that the complex of 18-crown-6 and potassium ions is more stable in this system, sodium ions are thought to selectively permeate through the membrane instead of the complex of potassium ions and 18-crown-6. The increase in the voltage drop across the membrane during electrodialysis is similar to that in organic fouling of the membrane, in which the voltage drop remarkably increases during electrodialysis when the salt solution containing organic ions with high molecular weight, such as ionic surface-active agents, was electrodialyzed [14]. For example, the electrical resistance of the membrane without the ether during electrodialysis was $1.0\ \Omega\ \mathrm{cm}^2$ and that in the presence of 300 g/l 18-crown-6 was $8.3\ \Omega\ \mathrm{cm}^2$; the ratio of the average mobility of all cations through the membrane with 300 g/l 18-crown-6 to that of the membrane without the ether is 0.12. On the other hand, the ratio of the mobility of potassium ions to that of sodium ions in the same membrane without the ether was 1.77. The remarkable decrease in average mobility is thought to be due to the permeation of the complex of the ether and potassium ions through the membrane. Accordingly, the remarkable decrease in $P^{\mathrm{K}}_{\mathrm{Na}}$ in Fig. 1 was due to the marked decrease in the mobility of the potassium ions in the membrane phase because of the formation of the stable complex of potassium ions with 18-crown-6. NEOSEPTA CM-1 used in this work has low electrical resistance, which means that the membrane has a relatively loose structure. Accordingly, if a tighter membrane were used in the same measurement, the separation of potassium ions from sodium ions would be achieved completely with high efficiency because the current efficiency in all electrodialysis was greater than 97.0% and did not decrease in the range studied in this work.

On other hand, when 15-crown-5 was added to the desalting-side solution, the voltage drop across the membrane during electrodialysis was not so high as shown in Fig. 2. The complex formation constants between potassium and sodium ions and 15-crown-5 were 0.74 and 0.70, respectively [15], which are not so different from each other. $P^{\mathrm{K}}_{\mathrm{Na}}$ did not change remarkably.

Conclusions

Potassium ions and sodium ions can be separated by electrodialysis of a mixed solution of potassium ions and sodium ions in the presence of 18-crown-6 using a commercial cation-exchange membrane. The current efficiency was greater than 97% and the transport number of the potassium ions relative to the sodium ions reached 0.15 in spite of 1.75 of the membrane without 18-crown-6. The decrease in $P^{\mathrm{K}}_{\mathrm{Na}}$ is thought to be caused by the decrease in the mobility of the potassium ions in the membrane phase due to the formation of a more stable complex than sodium ions, which was suggested by the increase in the electrical resistance of the membrane during electrodialysis.

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