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ORIGINAL CONTRIBUTION

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Electrodialytic transport properties of anion-exchange membranes in the presence of α-cyclodextrin

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Abstract Electrodialysis of mixed salt solutions, sodium chloride and sodium sulfate, and sodium chloride and sodium nitrate, was carried out in the presence of α-cyclodextrin using commercial anion-exchange membranes. It was confirmed by several methods that the compound existed in the membrane matrix when the membrane had been immersed in its aqueous solution, though the molecular weight of α-cyclodextrin is relatively high. In electrodialysis, sulfate ions, large and strongly hydrated anions, easily permeated through the membranes and nitrate ions, less hydrated anions, permeated with difficulty through the membranes in the presence of α-cyclodextrin. Because α-cyclodextrin is a hydrophilic compound, which has many ether and alcoholic groups, the hydrophilicity of the anion-exchange membranes is thought to increase. Thus, sulfate ions easily permeate and nitrate ions permeate with difficulty. This proves that the hydrophilicity of the anion-exchange membranes controls permselectivity between anions through the membranes.

Key words Transport number of sulfate or nitrate ions relative to chloride ions · α-Cyclodextrin · Anion-exchange membranes · Electrodialysis

Introduction

The most important function of ion-exchange membranes is to separate cations from anions and anions from cations. Today, in the chlor-alkali industry, about 12 mol/dm^3 caustic soda is directly overflowed from an electrolyzer at a current efficiency of more than 95%. Cation-exchange membranes producing 50% caustic soda solution directly have been developed [1], which means that permselectivity between cations and anions almost attains an ideal value. However, the separation of ions with the same charge in these high-performance membranes is ineffective though various methods have been tried from various aspects [2]. Among trials, it was reported that the transport numbers of various anions relative to chloride ions are decided by the balance of the hydrophilicity of anion-exchange membranes with the hydration energies of respective anions [3, 4].

Cyclodextrins are naturally occurring cyclic oligosaccharides and most consists of six, seven and eight D-glucose unite for α-, β- and γ-cyclodextrins, respectively. The doughnut-shaped cyclodextrins have an interior cavity with a diameter of 4.7–5.7 Å (α-cyclodextrin), 6.0–6.4 Å(β-cyclodextrin) and 7.5–8.3 Å(γ-cyclodextrin) [5]. The outer surface of the compounds is hydrophilic and their inner surface is hydrophobic. They are water-soluble and form inclusion complexes with various organic compounds [6] and polymers [7]. Also, cyclodextrins are interesting as a component of separation membranes. For example, membranes containing cyclodextrins were reported to be used in diffusion dialysis and pervaporation to separate isomers [8]. Anion-exchange membranes prepared from poly(vinyl alcohol), poly(*N*-ethyl 4-vinylpyridinium bromide) and β-cyclodextrin, following the cross-linking reaction with formaldehyde, were reported to show different transport numbers of anions relative to chloride ions in electrodialysis, compared with membranes without α-cyclodextrin [9]. Also, it is interesting to electrodialyze mixed salt solutions containing various anions in the presence of cyclodextrins using anion-exchange membranes. However, because the pore size of ion-exchange membranes is generally recognized to be 10 Å [10], it seems to be difficult to make cyclodextrins be adsorbed in the membrane matrix.

In this work, after anion-exchange membranes had been immersed in an aqueous α-cyclodextrin, the smallest among cyclodextrins, solution until equilibrium to adsorb α-cyclodextrin into the membrane matrix, electrodialysis of mixed salt solutions of sodium salts having different anions and sodium chloride was carried out in the presence of α-cyclodextrin in the desalting side solution to feed the compound to the membrane matrix. The change in permselectivity of various anions relative to chloride ions was evaluated in the presence of α-cyclodextrin.

Experimental

Materials

Commercially available anion-exchange membranes, NEOSEPTA AM-1 and AFN, which were kindly supplied by Tokuyama Corporation, were used in this work. The membranes, which were homogeneous and reinforced with fabric, have quaternary ammonium groups as anion-exchange groups. The characteristics of the membranes are shown in Table 1. The membranes supplied were equilibrated with 1.0 mol/dm^3 hydrochloric acid solution and 0.5 mol/dm^3 ammonia solution alternately several times and stored in 0.5 mol/dm^3 sodium chloride solution after equilibration with 1.0 mol/dm^3 hydrochloric acid solution. Before use, the membranes were equilibrated with the mixed salt solution to be used in electrodialysis. To examine parts of the membranes on which α-cyclodextrin adsorbed, components of the anion-exchange membranes were prepared: reinforcing fabric made of poly(vinyl chloride), Teviron cloth, made by Teijin Co., inert polymer added to the membrane, acrylonitrile–butadiene rubber, from Japan Synthetic Rubber Co., and an anion-exchange resin as a model of the anion-exchange domain in the membrane, Amberlite IRA-400, from Ishizu Seiyaku Co. α-cyclodextrin, which was kindly supplied by Nihon Shokuhin Co. (Celdex A-100), was used without further purification. Sodium chloride, sodium nitrate and sodium sulfate, which were used to prepare mixed salt solutions for electrodialysis, obtained from Ishizu Seiyaku Co., were of reagent grade. Methyl alcohol and other reagents were also obtained from Ishizu Seiyaku Co. Deionized water was used throughout all the experiments.

Adsorption of α-cyclodextrin on the anion-exchange membranes

After a piece of the anion-exchange membranes (4.0 cm × 7.0 cm, Cl$^-$ form) had been dried under reduced pressure for 4.5 h at 40 °C, the membranes were immersed in an aqueous 14.0 wt% α-cyclodextrin solution (solubility of α-cyclodextrin: 14.5 g/100 ml H_2O at 25.0 °C) for 72 h at 60 °C. After immersion, the surfaces of the membranes were rinsed with pure water and were used in the experiments.

Apparatus

Electrodialysis of the mixed salt solutions of sodium chloride and other sodium salts having various anions was carried out using a four-compartment cell with Ag/AgCl electrodes, which was the same as that previously reported [11]. The anion-exchange membrane to be measured (4.0 cm × 7.0 cm) was placed in the middle of the cell and the cation-exchange membranes (NEOSEPTA CM-2, Tokuyama Corporation: the transport number of the sodium ions in the membrane was greater than 0.99 in the electrodialysis of 0.50 mol/dm^3 sodium chloride solution at a current density of 10 mA/cm^2; the electrical resistance measured in 0.500 mol/dm^3 sodium chloride solution with 1000 Hz alternating current at 25.0 °C was 2.8 Ωcm^2) were placed between the two middle compartments and the electrode compartments. The effective membrane area was 10 cm^2 (2.0 cm × 5.0 cm). The capacity of each compartment was 120 cm^3 and solutions of two middle compartments were vigorously agitated with stirrers (1500 ± 100 rpm) to eliminate the effect of diffusion boundary layers on the transport properties of the membrane. The current was supplied by a regulated direct current supply. The amount of current passing through the membrane during electrodialysis was measured with a digital coulometer (NMD-1, Nikko Keisoku). The voltage drop across the membrane during electrodialysis was recorded on an $X - t$ recorder (EPR-2T, Toa Electronics Co.).

Table 1 Characteristics of anion-exchange membranes used in this work

Name	NEOSEPTA AM-1[a]	NEOSEPTA AFN[a]
Backing fabric	Poly(vinyl chloride)	Poly(vinyl chloride)
Electrical resistance (Ωcm^2)[b]	1.23	0.60
Transport number[c]	> 0.98	> 0.98
Ion-exchange capacity (Meq/g Cl$^-$ form)[d]	2.07	3.26
Water content (gH_2O/g Cl$^-$ form)[e]	0.25	0.55
Fixed ion concentration (m)[f]	8.28	5.93
Thickness (mm)	0.134	0.164

[a] Homogeneous membranes with strongly basic anion-exchange groups
[b] Measured with 1000 Hz alternating current at 25.0 °C after equilibrium with 0.500 mol/dm^3 sodium chloride solution
[c] Measured by electrodialysis of 0.500 mol/dm^3 sodium chloride solution at 10 mA/cm^2 for 1 h
[d] Based on the weight of dry membrane
[e] Based on the weight of dry membrane
[f] Molality: (ion-exchange capacity/water content)

Measurements

Examination of adsorption of α-cyclodextrin on anion-exchange membranes

Because the size of α-cyclodextrin and the pore size of the anion-exchange membranes is almost the same, adsorption of α-cyclodextrin on the membrane matrix is thought to be difficult. Thus, the following measurements were performed to confirm adsorption of α-cyclodextrin on the surfaces and inner parts of the membranes.

After immersing the anion-exchange membrane, NEOSEPTA AFN, of which the dry weight had been previously measured (dried under reduced pressure for 4.5 h at 60 °C), into an aqueous 14.0% α-cyclodextrin solution for 72 h at 60 °C, the membrane was removed from the solution, wiped with filter paper, dried under the same conditions and weighed to measure the weight increase by adsorption of the compound.

IR spectra (transmission) of the anion-exchange membrane, NEOSEPTA AFN, were measured using a Fourier transform IR spectrometer (FT-8100, Shimadzu Corporation). After immersing the membrane in an aqueous 14.0% α-cyclodextrin solution for 72 h at 60 °C, the membrane surfaces were rinsed with pure water, dried under reduced pressure for 4.5 h at 40 °C and were used in the measurement. The same membrane was also analyzed by X-ray photoelectron spectroscopy (XPS).

To make clear components of the anion-exchange membranes on which α-cyclodextrin mainly adsorbed, poly(vinyl chloride) cloth, acrylonitrile–butadiene rubber and anion-exchange resin (as a model of the anion-exchange domain in the membrane), Amberlite IRA-400 (Cl^- form), were immersed in the same 14.0% α-cyclodextrin solution for 72 h at 60 °C and the weight increase of the respective components was measured.

Measurements of basic electrochemical properties of anion-exchange membranes

The electrical resistance of the anion-exchange membranes was measured at 1000 Hz alternating current (Hewlett-Packard LCR meter 4263A) at 25.0 °C using a two-compartment cell with platinized platinum electrodes after equilibration with 0.500 mol/dm^3 sodium chloride solution. To evaluate the change in the ratio of the mobility of sulfate ions to that of chloride ion and that of nitrate to chloride ions in the anion-exchange membranes, NEOSEPTA AM-1 and AFN, in the presence of α-cyclodextrin, the electrical resistance of the membranes was measured using 0.500 mol/dm^3 sodium chloride solution, 0.500 mol/dm^3 sodium nitrate solution and 0.500 mol/dm^3 sodium sulfate solution in the absence of α-cyclodextrin and then in the presence of the compound. Namely, after immersing the membranes in aqueous 14.0wt% α-cyclodextrin solution for 72 h at 60 °C, the electrical resistance of the membranes was measured using the respective salt solution containing 50 g/l α-cyclodextrin. The transport number of the anion-exchange membranes was evaluated by electrodialyzing 0.50 mol/dm^3 sodium chloride solution at 25.0 °C at a current density of 10 mA/cm^2 for 60 min (Hittorf transport number). The ion-exchange capacity and the water content of the membranes were measured according to conventional methods (based on dry weight of the membrane) [12].

Evaluation of transport properties of the anion-exchange membranes

The transport properties of the anion-exchange membranes measured were the transport numbers of various anions relative to chloride ions, the current efficiency and the voltage drop across the membrane during electrodialysis in the absence and in the presence of cyclodextrins. The transport number of anion A relative to chloride ions was defined as follows:

$$P_{\mathrm{Cl}}^{\mathrm{A}} = \frac{t_{\mathrm{A}}/t_{\mathrm{Cl}}}{c_{\mathrm{A}}/c_{\mathrm{Cl}}} \quad , \tag{1}$$

where t_{A} and t_{Cl} are the transport numbers of anion A and chloride ions in the membrane and c_{A} and c_{Cl} are the average concentrations of anion A and chloride ions before and after electrodialysis. $P_{\mathrm{Cl}}^{\mathrm{A}}$ means the permeated equivalent of anion A through the membrane when 1 Eq chloride ions permeates through the membrane (because a 1:1 mixed salt solution is used throughout all the experiments).

Procedure

Electrodialysis was carried out in the absence of α-cyclodextrin and then in the presence of α-cyclodextrin using the same membrane. After electrodialysis without α-cyclodextrin, the same anion-exchange membrane was immersed in 14.0% α-cyclodextrin solution for 72 h at 60 °C and was placed in the middle of the four-compartment cell. After the cathode side of the middle compartments had been filled with a 1:1 mixed salt solution (concentration of sodium ion: 0.10 mol/dm^3) containing 50 g/l α-cyclodextrin, the anode side with the same mixed salt solution without α-cyclodextrin and anolyte and catholyte with 0.10 mol/dm^3 sodium chloride solution, electrodialysis was carried out in the presence of α-cyclodextrin at a current density of 2.0 mA/cm^2 for 60 min at 25.0 °C. The 1:1 mixed salt solutions used were sodium sulfate and sodium chloride or sodium nitrate and sodium chloride. After electrodialysis, the solutions of the two middle compartments were analyzed by the Mohr method (for Cl^-), conventional chelate back titration (for SO_4^{2-}) or ion chromatography (TOSOH CCPD, IC-8010, Chromatocorder 21). The transport number of anion A relative to chloride ions was calculated from the change in the concentration of each anion using Eq. (1), and the current efficiency was calculated from the change in the concentration of anions in the two middle compartments and the amount of electricity passed through the membrane during electrodialysis, which was measured using a coulometer.

Determination of the ratio of sulfate ions or nitrate ions to chloride ions in the membrane during electrodialysis

To determine the ratio of nitrate or sulfate ions to chloride ions in the membrane phase during electrodialysis, the anion-exchange membrane was instantaneously removed from the cell (within 10 s after stopping the electrodialysis) during electrodialysis, which had been performed under the same conditions as the measurement of the transport properties, and wiped with filter paper. The membrane part (2 cm × 5 cm) through which current had been passed was cut from the membrane and immersed in 0.02 mol/dm^3 sodium nitrate solution repeatedly renewing the solution to elute anions from the membranes. The concentrations of chloride and sulfate ions in the eluent were determined by the Mohr method and chelate back titration. The concentration of nitrate ions was calculated by subtracting the number of chloride ions from the ion-exchange capacity of the membranes. The ratio of anions in the membrane phase during electrodialysis, which corresponds to the ion-exchange equilibrium constant, was calculated using the following equation:

$$K_{\mathrm{Cl}}^{\mathrm{A}} = \frac{c_{\mathrm{A}}^{\mathrm{M}}/c_{\mathrm{Cl}}^{\mathrm{M}}}{c_{\mathrm{A}}^{\mathrm{S}}/c_{\mathrm{Cl}}^{\mathrm{S}}} \quad , \tag{2}$$

where $c_{\mathrm{A}}^{\mathrm{M}}$ and $c_{\mathrm{Cl}}^{\mathrm{M}}$ are equivalent concentrations of sulfate or nitrate ions and that of chloride ions ion-exchanged with the membrane, and $c_{\mathrm{A}}^{\mathrm{S}}$ and $c_{\mathrm{Cl}}^{\mathrm{S}}$ are average concentrations of sulfate or nitrate ions and chloride ions in the solution during electrodialysis.

Results and discussion

Adsorption of α-cyclodextrin on the anion-exchange membranes

As mentioned before, the pore size of the ion-exchange membranes, which is generally recognized, is nearly equal to the diameter of cyclodextrins, which are hydrated in water. To change the transport properties of the anion-exchange membranes, it is desirable to adsorb α-cyclodextrin into the membrane matrix as much as possible. Thus, NEOSEPTA AFN, which has a high water content as shown in Table 1, and α-cyclodextrin, which is the smallest among the cyclodetrins, were used in the measurement. The weight increase of NEOSEPTA AFN was 4.7% and that of NEOSEPTA AM-1 was 1.5% after the anion-exchange membranes had been immersed in an aqueous 14% α-cyclodextrin solution for 72 h at 60 °C. To clarify the parts on which α-cyclodextrin adsorbed, each component of the membranes was immersed in the same 14.0% α-cyclodextrin solution under the same conditions. Though the fabric made of poly(vinyl chloride) and acrylonitrile–butadiene rubber did not show any appreciable weight increase, the weight increase in the anion-exchange resin, Amberlite IRA-400, was 38%. The remarkable weight increase in the anion-exchange resin is thought to be due to interaction between cationic charge, anion-exchange groups and the negatively polarized oxygen of α-cyclodextrin such as ether and alcohol groups. The analysis of the same membrane by XPS also revealed that though ether bands (C_{1s}, 286.6 eV) exist in the anion-exchange membrane, NEOSEPTA AFN, the intensity of the bands increased about 2.5 times after immersing the membrane in aqueous 14.0% α-cyclodextrin solution. The intensity of N_{1s} (398 eV) on the basis of anion-exchange groups remarkably decreased after immersing the membrane in the α-cyclodextrin solution because of dilution with adsorbed α-cyclodextrin. This proves that α-cyclodextrin exists on the membrane surfaces.

IR spectra were measured after drying the membrane without and with α-cyclodextrin. Figure 1 shows IR spectra of α-cyclodextrin (curve a), NEOSEPTA AFN membrane (curve b), the membrane immersed in aqueous 14.0 wt% α-cyclodextrin solution for 72 h at 60 °C (curve c), the membrane used in electrodialysis of 0.10 mol/dm^3 sodium chloride solution after immersing the membrane in 14.0 wt% α-cyclodextrin solution in the absence of α-cyclodextrin in the desalting side solution (curve d) and the membrane used in electrodialysis of 0.10 mol/dm^3 sodium chloride solution containing 50 g/l α-cyclodextrin after immersing the membrane in 14.0 wt% α-cyclodextrin under the same conditions as for curve c (curve e). Figure 1 suggests that though α-cyclodextrin is adsorbed on the anion-exchange membrane, the compound desorbs from the membrane during electrodialysis. However, when electrodialysis was carried out using the mixed salt solution containing α-cyclodextrin after adsorption of the compound on the membrane, the spectra suggest that the compound was fed from the solution to the membrane matrix. The concentration of α-cyclodextrin in the membrane could be kept high.

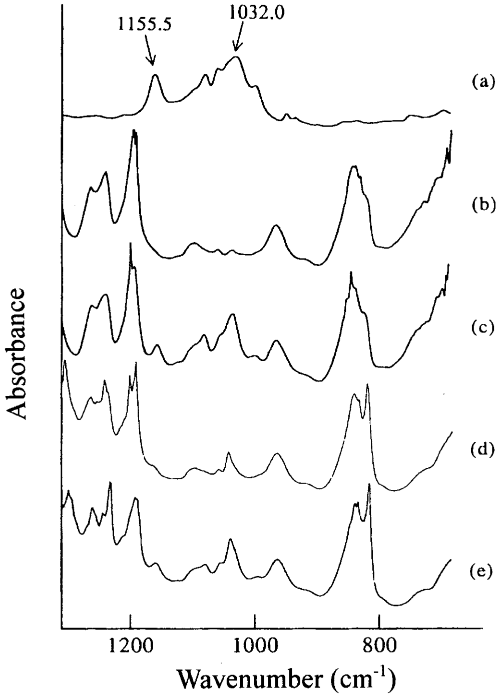

Fig. 1 IR spectra of α-cyclodextrin (α-CD), anion-exchange membrane and anion-exchange membrane adsorbed with α-CD. (*a*) α-CD; (*b*) anion-exchange membrane NEOSEPTA AFN; (*c*) anion-exchange membrane NEOSEPTA AFN on which α-CD was adsorbed; (*d*) anion-exchange membrane NEOSEPTA AFN after electrodialysis of mixed salt solution without α-CD. α-CD was previously adsorbed, (*e*) anion-exchange membrane NEOSEPTA AFN after electrodialysis in the presence of α-CD (50 g/l) using the membrane on which α-CD was previously adsorbed. Adsorption of α-CD was carried out by immersing the membrane in aqueous 14.0 wt% α-CD solution for 72 h at 60 °C. Electrodialysis was carried out using 0.10 mol/dm^3 sodium chloride solution without and with 50 g/l α-CD

Change in the transport properties of anion-exchange membranes in the presence of α-cyclodextrin

The change in the transport number of sulfate ions relative to chloride ions in the absence or in the presence of α-cyclodextrin when anion-exchange membranes, NEOSEPTA AM-1 and AFN, were used is shown in Fig. 2. Because sulfate ions are bulkier than chloride ions (the Stokes radii of sulfate and chloride ions are

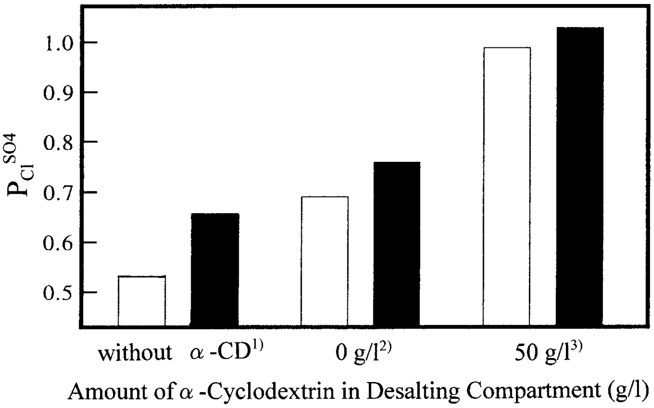

Fig. 2 Change in $P_{\mathrm{Cl}}^{\mathrm{SO_4}}$ of anion exchange membranes, NEOSEPTA AM-1 and AFN in the absence and in the presence of α-CD. □: NEOSEPTA AM-1; ■: NEOSEPTA AFN. Without α-CD: electrodialysis without α-CD; 0 g/l: electrodialysis of a 1:1 mixed salt solution without α-CD (concentration of sodium ions, 0.10 mol/dm^3) using the membranes on which α-CD was previously adsorbed; 50 g/l: electrodialysis of a 1:1 mixed salt solution containing 50 g/l α-CD (concentration of sodium ions, 0.10 mol/dm^3) using the membrane on which α-CD was previously adsorbed

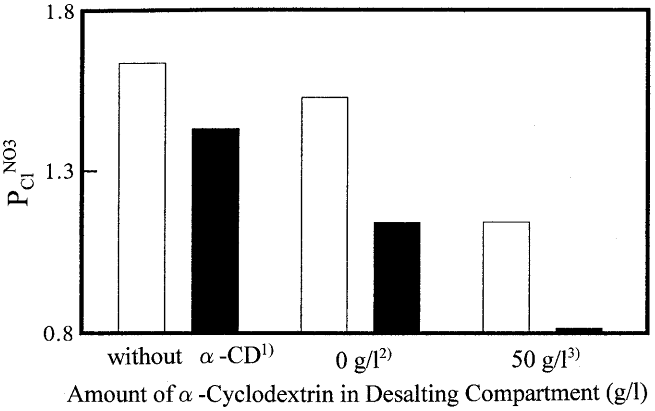

Fig. 3 Change in $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ of anion-exchange membranes NEOSEPTA AM-1 and AFN in the absence and in the presence of α-CD. □: NEOSEPTA AM-1; ■: NEOSEPTA AFN. Without α-CD: electrodialysis without α-CD; 0 g/l: electrodialysis of a 1:1 mixed salt solution without α-CD (concentration of sodium ions, 0.10 mol/dm^3) using the membranes on which α-CD was previously adsorbed; 50 g/l: electrodialysis of a 1:1 mixed salt solution containing 50 g/l α-CD (concentration of sodium ions, 0.10 mol/dm^3) using the membrane on which α-CD was previously adsorbed

2.31 and 1.21 Å, respectively) [13] and strongly hydrated (the Gibbs hydration energies of sulfate and chloride ions are −1000 and −317 kJ/mol, respectively) [13]. Because the water content of the AFN membrane is higher than that of the AM-1 membrane (which means it is more porous and more hydrophilic than the AM-1 membrane), the AFN membrane was more permeable to sulfate ions than the AM-1 membrane. $P_{\mathrm{Cl}}^{\mathrm{SO_4}}$ increased slightly in both membranes after immersing the membranes in the α-cyclodextrin solution; however, $P_{\mathrm{Cl}}^{\mathrm{SO_4}}$ increased further when electrodialysis was carried out in the presence of α-cyclodextrin after adsorption of the compound on the membranes. Though α-cyclodextrin adsorbed on the membrane desorbs from the membrane during electrodialysis, it is apparent from curves d and e of Fig. 1 that α-cyclodextrin was fed from the solution to the membrane matrix during electrodialysis and then permeation of sulfate ions increased further. When 50 g/l α-cyclodextrin was added in the desalting side solution, $P_{\mathrm{Cl}}^{\mathrm{SO_4}}$ attained almost unity, which means that sulfate ions, bulky anions, permeate equally through the membrane against chloride ions in both membranes though sulfate ions generally permeate with difficulty through the membrane [14].

The change in the transport number of nitrate ions relative to chloride ions in the absence or in the presence of α-cyclodextrin is shown in Fig. 3. Basically, nitrate ions selectively permeate through anion-exchange membranes compared with chloride ions. Though nitrate ions are larger than chloride ions (Stokes radius of nitrate ions, 1.29 Å) [13], the AM-1 membrane (low water content) is more permeable to nitrate ions than the AFN membrane. It was reported that permselectivity between anions is governed by the degree of hydrophilicity of the anion-exchange membranes [3]. Because the AFN membrane has a high water content, the permeation of less hydrophilic anions, nitrate ions, was low (Gibbs hydration energy in water of nitrate ions is −270 kJ/mol) [13]. The more hydrophobic the membrane, the higher the selectivity for nitrate ions [15]. After adsorption of α-cyclodextrin, $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ decreased in both membranes, especially, in the AFN membrane owing to the higher weight increase than the AM-1 membrane by adsorption of α-cyclodextrin. $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ decreased further in electrodialysis of the mixed salt solution containing 50 g/l α-cyclodextrin after its adsorption on the membrane. $P_{\mathrm{Cl}}^{\mathrm{NO_3}}$ of the AFN membrane decreased to about half the value compared with that without α-cyclodextrin. The transport numbers of sulfate ions and nitrate ions, which are multiatomic anions, relative to chloride ions show completely opposite behavior in the presence of α-cyclodextrin.

As mentioned previously, sulfate ions are strongly hydrated and nitrate ions are less hydrated. It was reported that anion-exchange groups exist in the anion-exchange membranes forming microdomains because of less compatibility of the copolymer of vinylpyridine and divinylbenzene and that of chloromethylstyrene and divinylbenzene with added inert polymer and backing fabric [16,17]. The α-cyclodextrin has many ether and alcohol groups, which are negatively polarized. It is expected that α-cyclodextrin exists in the microdomain, especially, around anion-exchange groups owing to interaction of anion-exchange groups, positive charge, and negatively polarized oxygen. Namely, the hydrophilicity around anion-exchange groups is thought to increase by the adsorption of α-cyclodextrin. Thus, strongly hydrated anions easily ion-exchanged with the membrane and less hydrated anions become difficult to ion-exchange with the membrane. At the same time, migration of anions through the membranes is thought to be affected by the adsorbed α-cyclodextrin.

The transport number of anion A relative to chloride ions is the product of the ratio of the mobility of anion A in the membrane phase to that of chloride ions and the ion-exchange equilibrium constant between anion A and chloride ions. Table 2 shows the ratio of the reversal of electrical resistance measured in sodium sulfate solution to that measured in sodium chloride solution and the ratio between the reversal of electrical resistances measured with sodium nitrate and sodium chloride solution using AM-1 and AFN membranes, which correspond to the mobility ratio in the membrane phase, in the absence and in the presence of α-cyclodextrin (the thickness of the anion-exchange membranes did not appreciably change with anion species). The ratio of the mobility of sulfate ions to that of chloride ions increased in the presence of α-cyclodextrin in both AM-1 and AFN membranes (1.04 for AM-1; 1.07 for AFN), which means that sulfate ions easily migrate through the membrane. On the other hand, the ratio between nitrate ions and chloride ions decreased (0.89 for AM-1; 0.89 for AFN) in the presence of α-cyclodextrin. Table 3 shows the ionic composition in the membranes during electrodialysis, which corresponds to the ion-exchange equilibrium constant, in the absence of α-cyclodextrin, that of the membrane after electrodialysis without the compound using the membrane on which α-cyclodextrin had been adsorbed and that of the membrane after electrodialysis in the presence of α-cyclodextrin using the membrane on which α-cyclodextrin had been adsorbed. The ratio of sulfate ions to chloride ions in the membranes increased by adsorption, especially, in the case of electrodialysis in the presence of α-cyclodextrin (1.18 for AM-1; 1.07 for AFN). On the other hand, the ratio of nitrate ions to chloride ions decreased in the presence of α-cyclodextrin (0.90 for AM-1; 0.83 for AFN). Namely, both the mobility change of anions in the membranes and the change in the uptake of anions in the membranes affected the increase or decrease in the transport numbers between anions. Thus, the transport numbers of sulfate ions and nitrate ions relative to chloride ions changed in the presence of α-cyclodextrin.

Table 2 Ratio of reversal of electrical resistance of anion-exchange membranes measured in sodium nitrate or sodium sulfate solution to that in sodium chloride solution. The concentration of salt solutions used in the measurement was 0.500 mol/dm^3

Membrane	NEOSEPTA AM-1		NEOSEPTA AFN	
Amount of α-cyclodextrin in salt solution (g/l)	0[a]	50[b]	0[a]	50[b]
$\frac{R_{NaCl}}{R_{NaNO_3}}$	0.74	0.66	0.94	0.84
$\frac{R_{NaCl}}{R_{Na_2SO_4}}$	0.56	0.58	0.75	0.80

[a] The anion-exchange membranes were previously immersed in an aqueous 14 wt% α-cyclodextrin solution for 72 h at 60 °C and the electrical resistance was measured using salt solutions without α-cyclodextrin. Then the ratio of the reciprocal of the electrical resistance measured with sodium nitrate or sodium sulfate solution to that measured with sodium chloride solution was calculated

[b] The anion-exchange membranes were previously immersed in an aqueous 14 wt% α-cyclodextrin solution for 72 h at 60 °C and the electrical resistance was measured using salt solutions containing 50 g/l α-cyclodextrin

Conclusions

Though the size of α-cyclodextrin is comparable to the pore size of the membrane, α-cyclodextrin is adsorbed in the commercial anion-exchange membranes. Consequently, permeation of strongly hydrated anion, sulfate ions, increased and that of less hydrated anions, nitrate ions, decreased compared with that without α-cyclodextrin when electrodialysis of a mixed solution was carried out in the presence of α-cyclodextrin. This is due to the change in the balance of the hydrophilicity of anion-exchange membranes to the hydration energy of permeated anions by α-cyclodextrin.

Table 3 Ionic ratio in anion-exchange membranes during electrodialysis ($K_{Cl}{}^{A}$). After electrodialysis of a 1:1 mixed salt solution (concentration of sodium ions: 0.10 mol/dm^3) for 1 h at 2.0 mA/cm^2, the membrane was instantaneously removed from the cell during electrodialysis and wiped with filter paper. Then the ionic composition in the membrane was determined

Membrane	NEOSEPTA AM-1			NEOSEPTA AFN		
α-Cyclodextrin	Without[a]	Adsorbed[b]	Adsorbed and added[c]	Without[a]	Adsorbed[b]	Adsorbed and added[c]
$K_{Cl}^{NO_3}$	3.04	3.04	2.72	2.71	2.69	2.24
$K_{Cl}^{SO_4}$	0.40	0.41	0.47	0.87	0.89	0.95

[a] Electrodialysis was carried out without α-cyclodextrin

[b] Before electrodialysis, the anion-exchange membranes was immersed in 14 wt% α-cyclodextrin solution for 72 h at 60 °C and electrodialysis was carried out using the mixed salt solution without α-cyclodextrin

[c] After the anion-exchange membranes had been immersed in 14 wt% α-cyclodextrin solution for 72 h at 60 °C, the membranes were used in electrodialysis of 1:1 mixed salt solutions (concentration of sodium ions, 0.10 mol/dm^3) containing 50 g/l α-cyclodextrin

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