

Continuous ion-exchange membrane electro dialysis of mother liquid discharged from a salt-manufacturing plant and transport of Cl^- ions and SO_4^{2-} ions

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Abstract. Mother liquid discharged from a salt-manufacturing plant was electro dialyzed at 25 and 40°C in a continuous process integrated with SO_4^{2-} ion low-permeable anion-exchange membranes to remove Na_2SO_4 and recover NaCl in the mother liquid. Performance of electro dialysis was evaluated by measuring ion concentration in a concentrated solution, permselectivity coefficient of SO_4^{2-} ions against Cl^- ions, current efficiency, cell voltage, energy consumption to obtain one ton of NaCl and membrane pair characteristics. The permselectivity coefficient of SO_4^{2-} ions against Cl^- ions was low enough particularly at 40°C and SO_4^{2-} transport across anion-exchange membranes was prevented successfully. Applying the overall mass transport equation, Cl^- ion and SO_4^{2-} ion transport across anion-exchange membranes is evaluated. SO_4^{2-} ion transport number is decreased due to the decrease of electro-migration of SO_4^{2-} ions across the anion-exchange membranes. SO_4^{2-} ion concentration in desalting cells becomes higher than that in concentration cells and SO_4^{2-} ion diffusion is accelerated across the anion-exchange membranes from desalting cells toward concentrating cells.

Keywords: ion-exchange membrane; electro dialysis; saline water concentration; ion transport; permselectivity; salt production

1. Introduction

In the process for manufacturing edible salt, raw salt (solar salt) is dissolved in water to produce brine and it is purified by adding Na_2CO_3 and NaOH to remove Ca^{2+} and Mg^{2+} ions. The purified brine is evaporated in a multiple-effect evaporation process. In the final evaporator, NaCl is crystallized, however at the same time SO_4^{2-} ions are accumulated and its concentration is increased. If Na_2SO_4 concentration in the concentrated brine exceeds 40 g/l, Na_2SO_4 is contaminated into NaCl crystals and deteriorates the product quality. Accordingly, the evaporation is suspended before Na_2SO_4 contamination and NaCl crystals are extracted from the evaporator. Next, the NaCl crystals are dehydrated in a dehydrating unit and dried in a drying machine to produce edible salt. In the mother liquid discharged from the final crystallizer, SO_4^{2-} ions are accumulated and they are usually discharged to the outside of the process. The discharged mother liquid dissolves considerable amount of NaCl crystals which deteriorate NaCl recovering ratio of the process. So it is desirable to separate SO_4^{2-}

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ions from NaCl in the concentrated brine and return the brine to the feeding brine. One of the procedures to recovering SO_4^{2-} ions in the concentrated brine is ion-exchange membrane electrodialysis integrated SO_4^{2-} ion low-permeable anion-exchange membranes (Egawa *et al.* 1968, Inamori and Yamamoto 1980, Tsunoda *et al.* 1981, Tanaka and Murakami 1988).

In a seawater concentration process with ion-exchange membranes, it is necessary to reduce the permeation of divalent ions across the membrane to prevent CaSO_4 precipitation in concentrating cells (Tanaka 2010). Because of this reason, permselectivity of ion-exchange membranes had been attracted a great deal of attention and it was investigated extensively. For reducing Ca^{2+} and Mg^{2+} permeation, technology was developed to form polycation layers on the cation-exchange membranes (Mizutani *et al.* 1971a, 1971b, Mihara *et al.* 1972). Anion-exchange membranes are given low SO_4^{2-} ion permselectivity by forming a polyanion layer or developing cross-linking structure on the membranes (Mihara *et al.* 1970, Hani *et al.* 1961). Permselectivity described above is a specific feature of ion-exchange membranes for seawater concentration and it is applied in many fields.

This investigation is carried out to evaluate the fundamental performance of continuous mode electrodialysis of mother liquid incorporated with SO_4^{2-} ion low-permeable anion-exchange membranes which had been developed for concentrating seawater. The main topic in this investigation is the transport of Cl^- ions and SO_4^{2-} ions across an anion-exchange membrane.

2. Experiment

Concentration (NaCl 25 g/100 g and Na_2SO_4 3.7 g/100 g) and temperature (70°C) of the brine discharged from the final evaporator is too high to treat it in an electrodialyzer. So, we assume that the brine is diluted with equivalent volume of water and the concentration is decreased to NaCl: 12.5 g/100g + Na_2SO_4 : 1.85 g/100 g. Further, temperature is assumed to be decreased to 25 or 40°C. The diluted brine was supplied to an electrodialyzer integrated with Aciplex K172 cation-exchange membranes (Asahi Chemical Co., Japan) and A172 anion-exchange membranes, and electrodialed in a continuous (one-pass flow) system (Fig. 1). In this experiment, the diluted brine (concentration C') was prepared in the feeding solution circulation tank and was supplied to desalting cells in the electrodialyzer at the linear velocity $u = 5$ cm/s. Partition cells were incorporated between the electrodialed stack and electrode cells for preventing the influence of electrode reactions to the performance of the electrodialed. The feeding solution was supplied also to the partition cells. A 0.5 eq/dm³ Na_2SO_4 solution was circulated between the electrode cells and electrode solution circulation tank. A constant electric current was passed through the membranes and concentrated solution was extracted from concentrating cells. The concentrated solution was returned to the feeding solution circulation tank with a desalted solution. After the concentration of the extracted concentrated solution C'' became stable constant, the volume flow of concentrated solution Q'' (cm³/s) and cell voltage V (V/pair) were measured intermittently. Further, the solutions were sampled at the inlets and outlets of desalting cells, at the outlets of concentrating cells and concentrations of Cl^- ions (C_{Cl} , equiv/cm³) and SO_4^{2-} ions (C_{SO_4}) were analyzed. Na^+ ion concentration (C_{Na}) was calculated by summing C_{Cl} and C_{SO_4} . Changing current density incrementally the electrodialed was repeated. Tables 1, 2 and 3 give the characteristics of the membranes, specifications of the electrodialyzer and electrodialed conditions respectively.

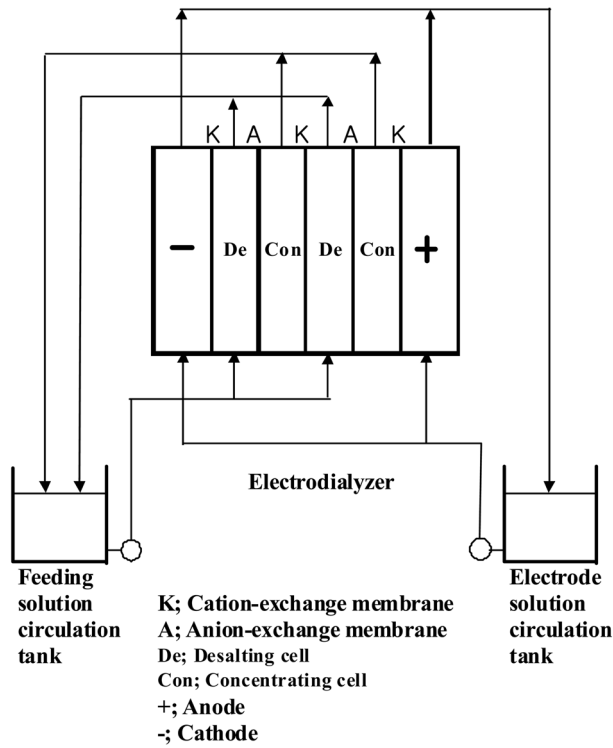


Fig. 1 Continuous electro dialysis process

Table 1 Characteristics of ion-exchange membranes

	Thickness mm	Electric resistance $\Omega \text{ cm}^2$	Transport number	Exchange capacity meq/dry memb.	Water content %	Intensity kg/cm^2
Aciplex K172	0.11-0.13	1.9-2.2	> 0.99	1.5-1.6	20-30	2.6-3.3
A172	0.11-0.15	1.7-2.1	> 0.99	1.8-1.9	24-25	2.2-3.0

Table 2 Specifications of the electro dialyzer

Ion-exchange membrane	Aciplex K172/A172
Number of desalting and concentrating cells	9
Thickness of desalting and concentrating cells	0.075 cm
Material of desalting and concentrating cells	Polypropyrene
Membrane area	172 cm^2 (10 cm width, 18 cm height)
Spacer	Diagonal net, polypropyrene
Anode	Ti (3 mm)/Pt (3 μm thick)
Cathode	SUS-304 (3 mm thick)

Table 3 Electrolysis conditions

Concentration of feeding solutions	NaCl 12.5 g/100 g + Na ₂ SO ₄ 1.85 g/100 g
Concentration of electrode solutions	0.5 eq/dm ³ Na ₂ SO ₄
Linear velocity in desalting cells	5 cm/s
Current density	1, 2, 3, 4, 6 A/dm ²
Solution temperature	25, 40°C

3. Results and discussion

3.1 Performance of electrolysis

Fig. 2 shows concentration of Na⁺ ions (C''_{Na}), Cl⁻ ions (C''_{Cl}) and SO₄²⁻ ions (C''_{SO_4}) in concentrating cells versus current density i . C''_{Na} and C''_{Cl} are increased and C''_{SO_4} is decreased with increasing i . Decreasing range of C''_{SO_4} is larger at $T=40^\circ\text{C}$ than at 25°C . Comparing with SO₄²⁻ ion concentration in desalting cells ($C'_{SO_4} = 28.55 \times 10^{-2}$ eq/dm³ at 25°C and 30.58×10^{-2} eq/dm³ at 40°C ; described in the figure), C''_{SO_4} is considerably less than C'_{SO_4} ($C''_{SO_4} < C'_{SO_4}$). SO₄²⁻ ion transport across SO₄²⁻ ion low-permeable anion-exchange membranes is confirmed to be prevented sufficiently, so far as SO₄²⁻ ions are concentrated in desalting cells. Fig. 3 shows NaCl concentration C''_{NaCl} and Na₂SO₄ concentration $C''_{Na_2SO_4}$ in concentrating cells. $C''_{Na_2SO_4}$ is decreased remarkably at 40°C . Fig. 4 shows the permselectivity coefficient of SO₄²⁻ ions against Cl⁻ ions $T_{Cl}^{SO_4}$, which is decreased drastically at 40°C with increasing i . Current efficiency for total ions ($\eta_{total} = \text{Na}^+$ ion current efficiency η_{Na}), for Cl⁻ ions (η_{Cl}) and for SO₄²⁻ ions (η_{SO_4}) are plotted in Fig. 5. η_{total} and η_{Cl} are not influenced by i and

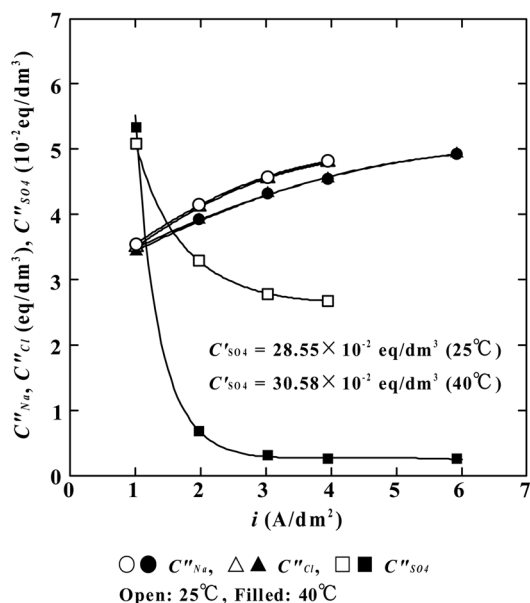


Fig. 2 Concentration of Na⁺ ions, Cl⁻ ions and SO₄²⁻ ions in a concentrated solution

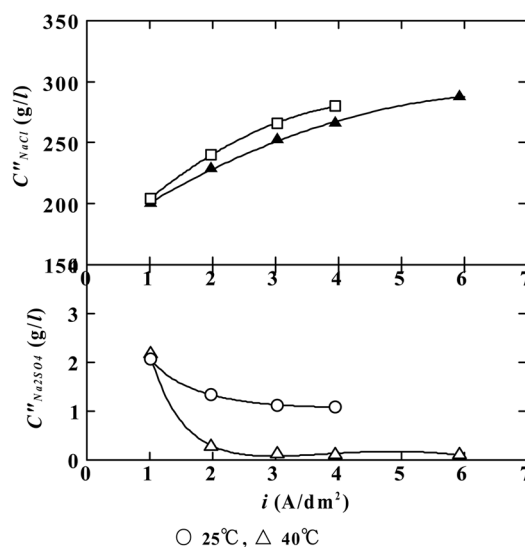


Fig. 3 Concentration of NaCl and Na₂SO₄ in a concentrated solution

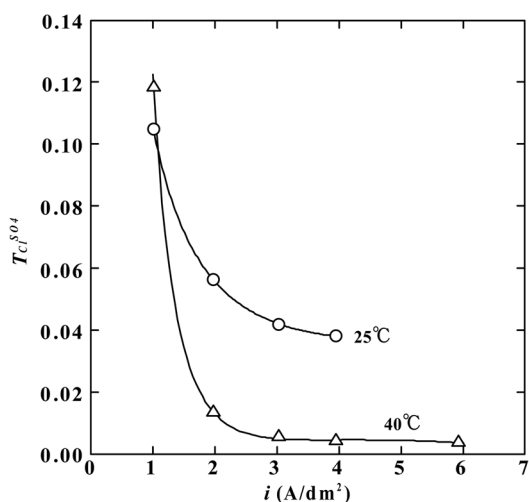


Fig. 4 Permeability coefficient of SO_4^{2-} ions against Cl^- ions

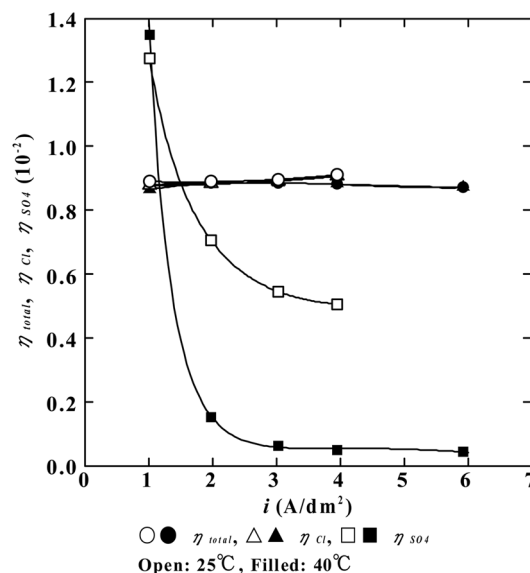


Fig. 5 Current efficiency for total ions, Cl^- ions and SO_4^{2-} ions

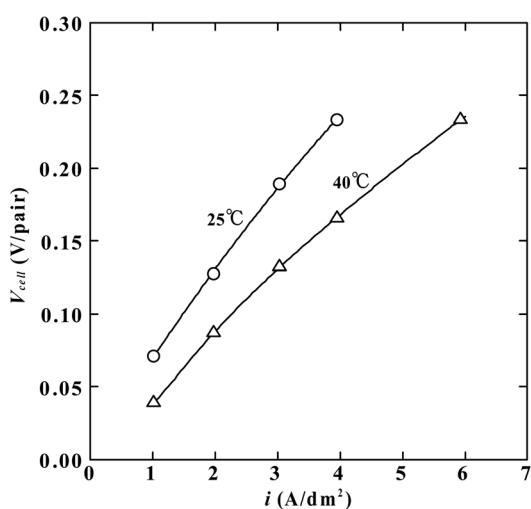


Fig. 6 Cell voltage

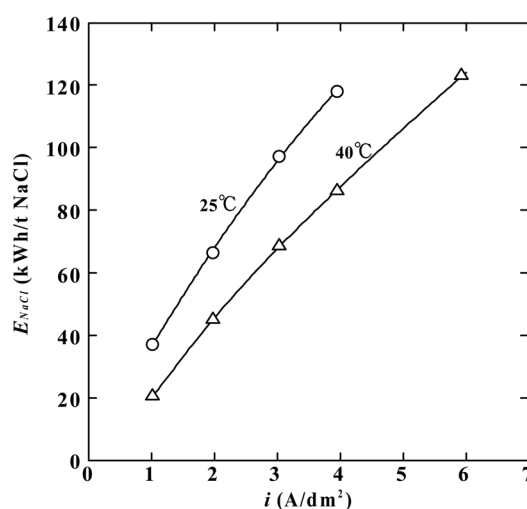


Fig. 7 Energy consumption

almost constant. η_{SO_4} is decreased with increasing i particularly at 40°C. Cell voltage V_{cell} is plotted in Fig. 6. V_{cell} is increased with i , but it is decreased with increasing T due to the decrease of electric resistance of solutions and membranes. Fig. 7 gives energy consumption to concentrate one ton of NaCl in the concentrating cell (E_{NaCl}). E_{NaCl} at 40°C is considerably less than the values at 25°C. This is because of decreased V_{cell} (Fig. 6) and $T_{Cl^{SO_4}}$ (Fig. 4).

3.2 Membrane characteristics

Total solute flow (J_S) and volume flow (J_V) across a membrane pair in saline water electro dialysis are expressed by the following overall mass transport equation in a steady state (Tanaka 2006).

$$J_S = C_S'' J_V = \lambda_S i - \mu_S (C_S'' - C_S') = \lambda_S i - \mu_S \Delta C_S \quad (1)$$

$$J_V = \phi i + \rho (C_S'' - C_S') = \phi i + \rho \Delta C_S \quad (2)$$

where i is the current density; C_S' and C_S'' are total electrolyte ($\text{NaCl} + \text{Na}_2\text{SO}_4$) concentrations in a desalting and a concentrating cell, respectively; the superscripts ' and '' denote a desalting cell and a concentrating cell, respectively; λ_S is the total electrolyte overall transport number and μ_S is the total electrolyte overall solute permeability. Both parameters are given the subscript "s" because they are the values for total electrolytes. ϕ is the overall electro-osmotic permeability and ρ is the overall hydraulic permeability. The above parameters are the overall membrane pair characteristics. The term "overall" means that the coefficients express the contributions of a cation- and an anion-exchange membrane. It means also that the coefficients express the contributions of many types of ions dissolving in an electrolyte solution. Plots of J_S/i and J_V/i versus $(C_S'' - C_S')/i = \Delta C_S/i$ yield straight line, such that λ_S (eq C^{-1}), μ_S (cm s^{-1}), ϕ ($\text{cm}^3 \text{C}^{-1}$), and ρ ($\text{cm}^4 \text{equiv}^{-1} \text{s}^{-1}$) can be determined from the intercepts and the gradients of the lines. Electrolyte concentration C (equiv/cm^3) in Eqs. (1) and (2) is the total electrolyte concentration C_S , so it is equivalent to $C_S = C_{\text{Na}} = C_{\text{Cl}}(C_{\text{NaCl}}) + C_{\text{SO}_4} \cdot (C_{\text{Na}_2\text{SO}_4})$. Fig. 8 gives J_S/i and J_V/i versus $\Delta C_S/i$ plots created by substituting the data measured in the experiment. The plots are presented by the straight lines and Eqs. (3) ~ (6). The overall membrane pair characteristics λ_S , μ_S , ϕ and ρ are appeared in the equations.

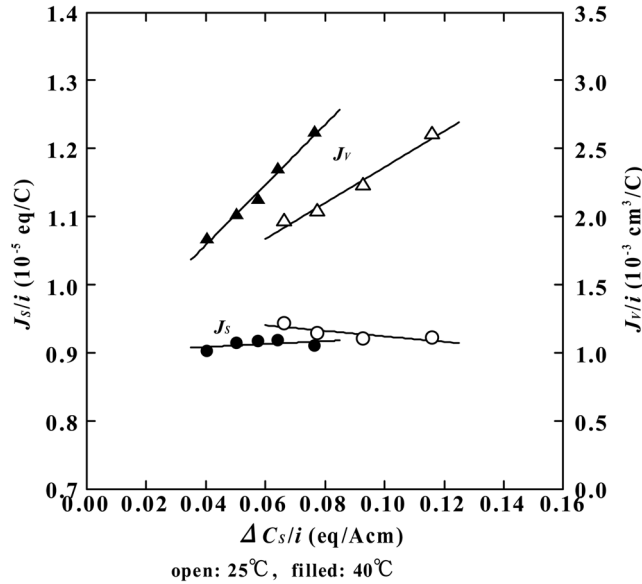


Fig. 8 J_S/i and J_V/i versus $\Delta C_S/i$ plot

at 25°C

$$J_S/i = 9.647 \times 10^{-6} - 4.034 \times 10^{-6} \Delta C_S/i \quad (3)$$

$$J_V/i = 1.0416 \times 10^{-3} + 1.3214 \times 10^{-2} \Delta C_S/i \quad (4)$$

at 40°C

$$J_S/i = 9.005 \times 10^{-6} + 2.0997 \times 10^{-6} \Delta C_S/i \quad (5)$$

$$J_V/i = 9.134 \times 10^{-4} + 2.2026 \times 10^{-2} \Delta C_S/i \quad (6)$$

It should be noticed that the solute permeability at 40°C takes minus value; $\mu_S = -2.0997 \times 10^{-6}$ cm/s (Eq. (5)), thus solutes transfer from desalting cells to concentrating cells against solute concentration gradient formed in the membranes. This phenomenon is estimated to be due to:

(1) Influence of SO_4^{2-} ion diffusion from desalting cells toward concentrating cells (Fig. 15).

(2) Influence of hydraulic osmosis flow $\rho \Delta C_S$ from desalting cells toward concentrating cells (Fig. 10).

Demin and Zabolotskii presented the mass transport equation similar to the overall mass transport equation; Eqs. (1) and (2). They evaluate the membrane pair characteristics of MK-40/MA-40 membranes placed in LiCl and NaCl solutions. The model equations are successfully applied in calculating the operating parameters of the electrodialysis process (Demin and Zabolotskii 2008).

The overall mass transport equation is related to the irreversible thermodynamics. The phenomenological coefficients (transport number t , solute permeability ω , electro-osmotic permeability, hydraulic permeability L_P) appeared in the irreversible thermodynamics are expressed by the following functions of the membrane pair characteristics λ , μ , ϕ and ρ (Tanaka 2006).

$$t_K + t_A = \lambda F + 1 \quad (7)$$

$$\omega_K + \omega_A = \frac{\mu}{RT} \quad (8)$$

$$\beta_K + \beta_A = \phi \quad (9)$$

$$L_{P,K} + L_{P,A} = \frac{\rho}{RT} \quad (10)$$

Table 4 Phenomenological coefficients

Transport number and solute permeability

T	°C	NaCl + Na ₂ SO ₄		NaCl	Na ₂ SO ₄
		25	40	25	25
$t_K + t_A$		1.931	1.869	1.929	1.002
$\omega^K + \omega^A$	mol cm J ⁻¹ s ⁻¹	1.627×10^{-9}	-8.470×10^{-10}	1.657×10^{-9}	1.930×10^{-9}

Electro-osmotic permeability and hydraulic permeability

T	°C	25	40
$\beta_K + \beta_A$	cm ³ C ⁻¹	1.042×10^{-3}	9.134×10^{-4}
$L_{P,K} + L_{P,A}$	mol cm ⁴ eq ⁻¹ J ⁻¹ s ⁻¹	5.331×10^{-6}	8.885×10^{-6}

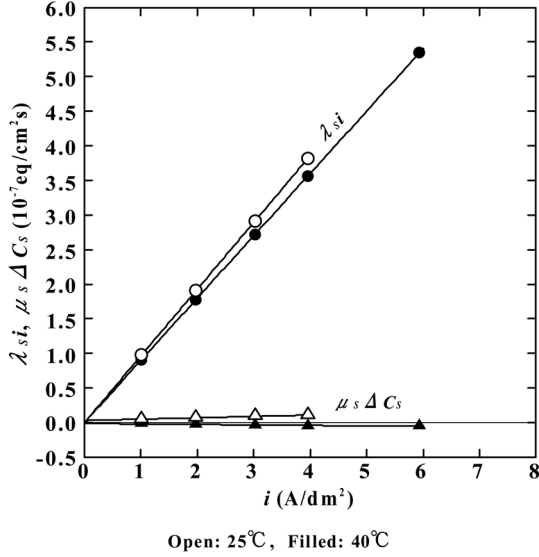


Fig. 9 Electro-migration and diffusion

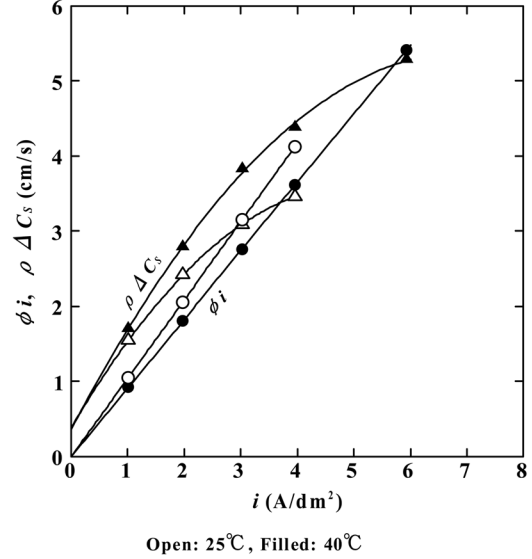


Fig. 10 Electro-osmosis and hydraulic osmosis

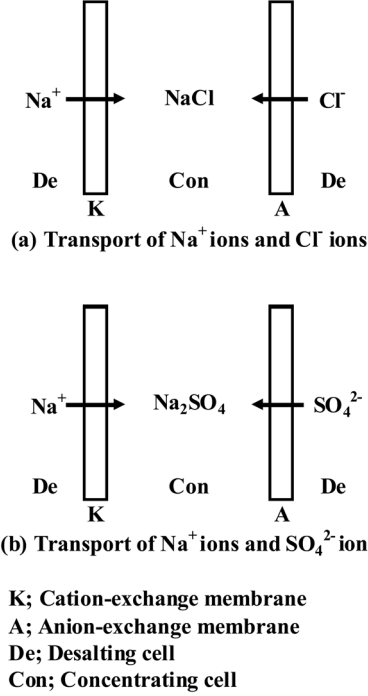
The above phenomenological coefficients are calculated using Eqs. (7) ~ (10) and given in Table 4 for total electrolytes ($\text{NaCl} + \text{Na}_2\text{SO}_4$) flow and volume flow. Irreversible thermodynamics is believed to be held in the circumstance being apart to some extent from equilibrium state (Dunlop 1957, Dunlop and Gosting 1959). Eqs. (7) ~ (10) mean that the overall mass transport equation (Eqs. (1) ~ (6)) holds in the irreversible state in the range of current density applied in this experiment (Section 2).

In Eqs. (1) and (2), parameters $\lambda_s i$ and $\mu_s \Delta C_s$ stand for the electro-migration and solute diffusion, respectively. ϕi and $\rho \Delta C_s$ correspond to the electro-osmosis and hydraulic osmosis, respectively. These parameters are plotted against i and shown in Figs. 9 and 10. Solute diffusion $\mu_s \Delta C_s$ is very small compared to electro-migration $\lambda_s i$ and takes minus value at 40°C because $\mu_s = -2.0997 \times 10^{-6} \text{ cm/s} < 0$.

3.3 Transport of Cl^- ions and SO_4^{2-} ions across an anion-exchange membrane

When two types of ions having the same charged sign are dissolved in a solution, the permeation of these ions through an ion-exchange membrane is not equivalent each other. This phenomenon is termed “the permselectivity of ions having the same charged sign”, and investigated widely (McClintock *et al.* 1960, Oren and Litan 1974, Rubinstein 1990, Quemeneur *et al.* 2002, Sata 1997, 2004, Kabay *et al.* 2006, 2006, Koter *et al.* 2011). The permselectivity was applied for industrial use to separate or to purify ionic species in a solution (Mohamadi *et al.* 2004, Sadrzadeh *et al.* 2007, Turek *et al.* 2007, Amara and Kerdjoudj 2007).

We discuss here the transport of Cl^- ions and SO_4^{2-} ions across an anion-exchange membrane applying the overall mass transport equation; Eqs. (1) and (2). Ion transport across a membrane pair is shown by the transport of electrolytes as illustrated in Fig. 11. In this system, the overall mass transport equation expresses the transport of electrolytes (NaCl and Na_2SO_4) across a membrane


 Fig. 11 Transport of Na⁺ ions, Cl⁻ ions and SO₄²⁻ ions across a membrane pair (illustration)

pair as follows.

$$J_{NaCl} = \lambda_{NaCl}i - \mu_{NaCl}(C''_{NaCl} - C'_{NaCl}) = \lambda_{NaCl}i - \mu_{NaCl}\Delta C_{NaCl} \quad (11)$$

$$J_{Na_2SO_4} = \lambda_{Na_2SO_4}i - \mu_{Na_2SO_4}(C''_{Na_2SO_4} - C'_{Na_2SO_4}) = \lambda_{Na_2SO_4}i - \mu_{Na_2SO_4}\Delta C_{Na_2SO_4} \quad (12)$$

in which

$$C_{NaCl} = C_{Cl}, \quad C_{Na_2SO_4} = C_{SO_4} \quad (13)$$

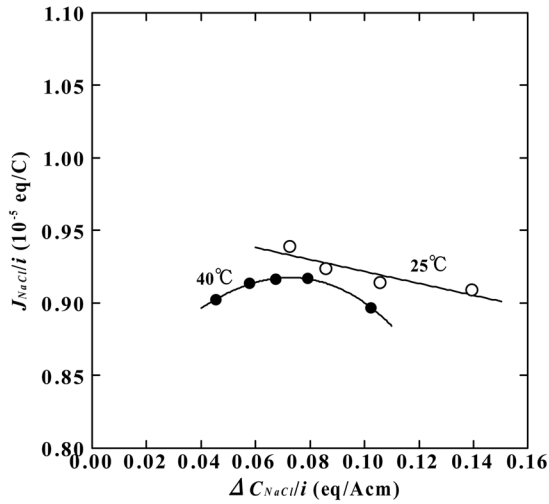
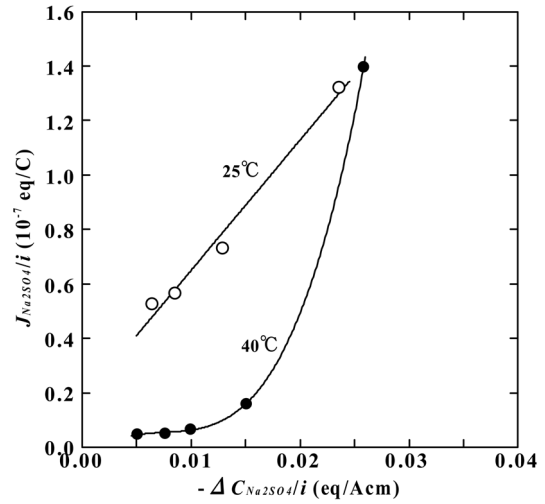
We discuss the transport of Cl⁻ ions and SO₄²⁻ ion across an anion-exchange membrane using Eqs. (11) ~ (13). Permselectivity coefficient $T_{Cl}^{SO_4}$ is defined as

$$T_{Cl}^{SO_4} = \frac{J_{Na_2SO_4}/J_{NaCl}}{C'_{Na_2SO_4}/C'_{NaCl}} = \frac{J_{SO_4}/J_{Cl}}{C'_{SO_4}/C'_{Cl}} \quad (14)$$

In order to measure the overall transport number and solute permeability (λ_{NaCl} , $\lambda_{Na_2SO_4}$, μ_{NaCl} , $\mu_{Na_2SO_4}$) in Eqs. (11) and (12), J_{NaCl}/i and $J_{Na_2SO_4}/i$ are plotted against respectively $\Delta C_{NaCl}/i$ and $\Delta C_{Na_2SO_4}/i$ and shown in Figs. 12 (J_{NaCl}/i) and 13 ($J_{Na_2SO_4}/i$). The plots are presented by the following equations at 25°C.

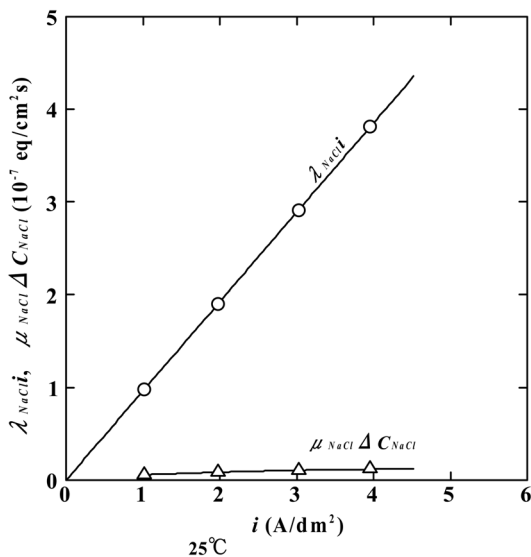
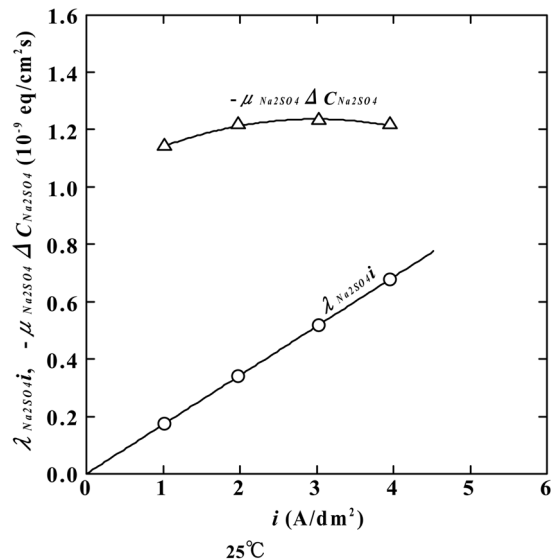
$$J_{NaCl}/i = 9.628 \times 10^{-6} - 4.108 \times 10^{-6} \Delta C_{NaCl}/i \quad (15)$$

$$J_{Na_2SO_4}/i = 1.7156 \times 10^{-8} - 4.785 \times 10^{-6} \Delta C_{Na_2SO_4}/i \quad (16)$$

Fig. 12 J_{NaCl}/i versus $\Delta C_{NaCl}/i$ plotFig. 13 $J_{Na_2SO_4}/i$ versus $-\Delta C_{Na_2SO_4}/i$ plot

The plots at 40°C are presented by curved lines. This phenomenon is estimated to be due to changing membrane pair characteristics (λ and μ), however the mechanism of the phenomenon is not understandable.

Electro-migration and solute diffusion for NaCl (Cl^- ions) across an anion-exchange membrane ($\lambda_{NaCl}i$ and $\mu_{NaCl}\Delta C_{NaCl}$) at 25°C are plotted against current density i and shown in Fig. 14. $\lambda_{NaCl}i$ is extremely larger than $\mu_{NaCl}\Delta C_{NaCl}$ and this phenomenon is fundamentally the same to Fig. 9. Fig. 15 gives the changes of $\lambda_{Na_2SO_4}i$ and $\mu_{Na_2SO_4}\Delta C_{Na_2SO_4}$ at 25°C. $\lambda_{Na_2SO_4}i$ is found to be suppressed

Fig. 14 Electro-migration and diffusion of NaCl (Cl^- ions)Fig. 15 Electro-migration and diffusion of Na_2SO_4 (SO_4^{2-} ions)

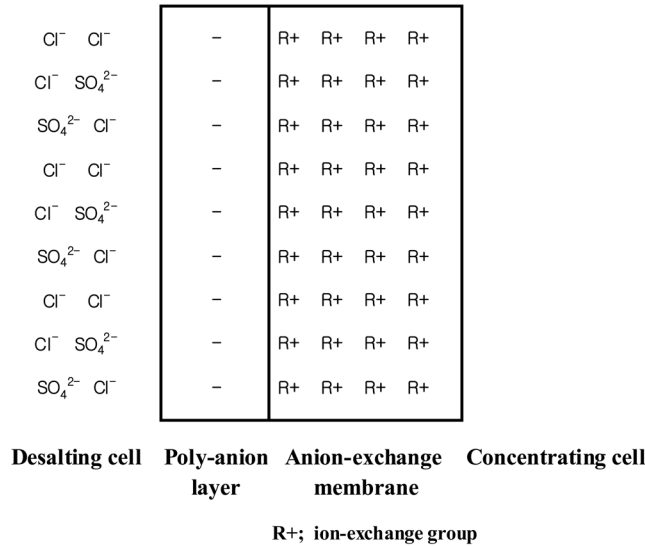


Fig. 16 Poly-anion layer formed on an anion-exchange membrane (illustration)

considerably and $-\mu_{\text{Na}_2\text{SO}_4} \Delta C_{\text{Na}_2\text{SO}_4}$ is increased simultaneously. This phenomenon shows that Na_2SO_4 (SO_4^{2-} ion) transfer across an anion-exchange membrane is prevented by decreasing $\lambda_{\text{Na}_2\text{SO}_4}$ at 25°C . Further transfer decrease of SO_4^{2-} ions at 40°C (Figs. 2 ~ 5) is estimated to be due to further decrease of $\lambda_{\text{Na}_2\text{SO}_4}$ across anion-exchange membranes. Na_2SO_4 (SO_4^{2-} ion) concentration in desalting cells ($C'_{\text{Na}_2\text{SO}_4} = C'_{\text{SO}_4}$) becomes larger than that in concentrating cells ($C''_{\text{Na}_2\text{SO}_4} = C''_{\text{SO}_4}$). This phenomenon induces the increase of $-\mu_{\text{Na}_2\text{SO}_4} \Delta C_{\text{Na}_2\text{SO}_4}$ i.e., the increase of Na_2SO_4 (SO_4^{2-} ion) diffusion across anion-exchange membranes from desalting cells toward concentrating cells.

Phenomenological coefficients ($t_K + t_A$ and $\omega_K + \omega_A$ at 25°C) in Eqs. (7) and (8) for NaCl and Na_2SO_4 are also given in Table 4. $t_K + t_A = 1.002$ means that SO_4^{2-} ion transport number t_A in anion-exchange membranes is decreased drastically, and $t_K + t_A$ almost depend to the contribution of Na^+ ion transport number t_K in cation-exchange membranes. This phenomenon corresponds to the extreme decrease in electro-migration of SO_4^{2-} ions $\lambda_{\text{Na}_2\text{SO}_4}$ across anion-exchange membranes (Fig. 15).

The Aciplex K172 anion-exchange membrane is given low SO_4^{2-} ion permselectivity by forming a poly-anion layer on the desalting surface of the membrane (Mihara *et al.* 1970). Structure of the membrane surface is depicted by the two layered membrane consist from an anion-exchange membrane and a poly-anion layer as illustrated in Fig. 16. The permselectivity between Cl^- ions and SO_4^{2-} ions is caused by repulsive forces generated between poly-anions and anions (Cl^- ions and SO_4^{2-} ions) dissolved in the solution. Repulsive force of poly-anions against double charged SO_4^{2-} ions is larger than that against single charged Cl^- ions. SO_4^{2-} ions require greater energy to pass over the potential barrier formed in the poly-anion layer than do Cl^- ions (Tanaka and Seno 1981).

3.4 Influence of concentration polarization.

In the previous investigation, a NaCl solution was supplied to a model electrodialysis unit incorporated with an Aciplex A172 anion-exchange membrane. The structure of this unit was equivalent to Fig. 1. Passing an electric current, limiting current density was observed from a current-voltage relationship.

The influence of NaCl concentration C and linear velocity u in a desalting cell on the limiting current density i_{lim} was expressed in the following equation (Tanaka 2005).

$$i_{lim} = mC^n \quad (17)$$

$$m = 66.36 + 14.72u \quad (18)$$

$$n = 0.7404 + 3.585 \times 10^{-3}u \quad (19)$$

Substituting $C = C_{Na} = 2.28 \times 10^{-3}$ eq/cm³ and $u = 5$ cm/s at $T = 25^\circ\text{C}$ in this study into Eqs. (17)~(19), the limiting current density of the anion-exchange membrane at 25°C is obtained as

$$i_{lim} = 1.39 \text{ A/cm}^2 = 139 \text{ A/dm}^2 \quad (20)$$

Ion transport across the membrane is known to be influenced by concentration polarization (Huang *et al.* 1986, Rubinstein 1990, Zabolotsky *et al.* 1998, Grigorochuk *et al.* 2003, Nikonenko *et al.* 2010). However, ion transport observed in this study is assumed not to be influenced by concentration polarization because the limiting current density (Eq. (20)) is very high due to larger electrolyte concentration $C_S = C_{Na}$ in desalting cells. The influence of concentration polarization on the overall membrane pair characteristics were discussed in the previous investigation (Tanaka 2006), and concluded that the membrane pair characteristics are not influenced by the concentration polarization.

4. Conclusions

Mother liquid discharged from a salt-manufacturing plant is electrodialed. Transport of Na⁺ ions, Cl⁻ ions and SO₄²⁻ ions dissolving in the mother liquid is discussed based on the overall mass transport equation. SO₄²⁻ ion transport is prevented successfully by divalent low-permeable anion exchange membranes integrated in the electrodialed.

The overall mass transport equation has simple form and it is developed from electrodialed experiments. It elucidates the mechanism of mass transport across the membrane and available for discussing electrodialed performance without contradictions. It expresses in principle the flux of all types of ions altogether dissolving in the solution. However, in this investigation, the flux of a specific type of ions is expressed separately by the equation for discussing the permselectivity of the membrane.

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CC

Nomenclature

C_i	concentration of electrolytes i or ion i (eq cm ⁻³ , eq dm ⁻³)
C_S	concentration of total electrolytes (eq cm ⁻³ , eq dm ⁻³)
E_{NaCl}	energy consumption (kWh t ⁻¹ NaCl)
F	Faraday constant (A s eq ⁻¹)
i	current density (A cm ⁻² , A dm ⁻²)
i_{lim}	limiting current density (A cm ⁻² , A dm ⁻²)
J_i	flux of electrolytes i or ion i across a membrane pair (eq cm ⁻² s ⁻¹)
J_S	total electrolyte flux across a membrane pair (eq cm ⁻² s ⁻¹)
J_V	volume flux across a membrane pair (cm ³ cm ⁻² s ⁻¹)
L_P	hydraulic permeability (mol cm ⁴ equiv ⁻¹ J ⁻¹ s ⁻¹)
R	gas constant (J K ⁻¹ mol ⁻¹)
t	transport number of ions in a membrane
T	temperature (°C, K)
u	linear velocity in desalting cells (cm s ⁻¹)
V_{cell}	cell voltage (V pair ⁻¹)

Greek letters

β	electro-osmotic permeability (cm ³ C ⁻¹)
η_i	current efficiency for ion i
λ	overall transport number of a membrane pair (eq C ⁻¹)
μ	overall solute permeability of a membrane pair (cm ³ s ⁻¹)
ΔC	$C'' - C'$
ρ	overall hydraulic permeability of a membrane pair (cm ⁴ eq ⁻¹ s ⁻¹)
ϕ	overall electro-osmotic permeability of a membrane pair (cm ³ C ⁻¹)
ω	solute permeability (mol cm J ⁻¹ s ⁻¹)

Subscript

A	anion-exchange membrane
K	cation-exchange membrane

Super script

'	desalting cell
"	concentrating cell