# Competitive Transport of Hydrochloric Acid and Zinc Chloride through Polymeric Anion-Exchange Membrane

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**ABSTRACT:** Competitive transport of hydrochloric acid and zinc chloride has been investigated in a two-compartment mixed cell with an anion-exchange membrane Neosepta-AFN developed and produced by Tokuyama Soda Co. These experiments have proved that hydrochloric acid permeates well through the membrane used but, on the other hand, zinc chloride is not effectively rejected. The flux of zinc chloride has been found to be increasing with increasing acid and salt concentrations. Furthermore, it has been found that it is approximately one order of magnitude higher than that found in the case of simultaneous transport of sulfuric acid and zinc sulfate through the same membrane. The further calculations concerning the ionic equilibria with sorption isotherms for the HCl–ZnCl<sub>2</sub> system, which have been measured experimentally, have revealed that high flux of ZnCl<sub>2</sub> is due to the fact that a considerable amount of zinc chloride in the membrane is in the form of ZnCl<sub>3</sub><sup>-</sup> complex, which is relatively small and passes well through this membrane. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1391–1397, 2006

**Key words:** diffusion; diffusion dialysis; membranes; separation techniques; hydrochloric acid

#### INTRODUCTION

The basic element of the membrane process called diffusion dialysis is an ion-exchange membrane having in its structure electrically charged sites, which facilitate the transport of counter-ions while cions are rejected. If an anion-exchange membrane is used in such a process, then a high proton leakage exists (hydrogen ions are very small and they exhibit high mobility not only in aqueous solutions but also in membranes), so that this process is predominantly used in the separation of mixtures containing inorganic or organic acids and their salts.<sup>1,2</sup> Another interesting applications of diffusion dialysis are separation of sulfuric acid and glucose in the process of manufacturing glucose from wood and desalination of low-molecular-weight organic substances, such as sugars, alcohols, organic acids, low amino acids, etc.<sup>3</sup> Wódzki and Szczepanski<sup>4</sup> reported the use of diffusion dialysis unit as a part of the integrated process for recovery and concentration of  $Zn^{2+}$  and  $Cu^{2+}$  ions from industrial rinse water containing a mixture of  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ , and  $Na^+$  ions. The results proved

that this integrated process can be considered to be a part of a technology for the efficient recovery of Zn<sup>2+</sup> and Cu<sup>2+</sup> ions in metal-finishing plants. An extensive study on the recovery of formic acid from pickling solution in the leather industry using diffusion dialysis and electro-electro dialysis was a subject of the study.<sup>5</sup> Xu and Yang<sup>6</sup> carried out experiments focused on the simultaneous recovery of sulfuric acid and nickel from electrolysis spent liquor of relatively low acid concentration. The pilot experiments with surface crosslinked PPO anion-exchange membranes showed that nickel leakage can be controlled within 4%, and the acid recovery can attain as high as 66-72%. In another study,<sup>7</sup> the same authors dealt with the recovery of mixed acid (HF +  $HNO_3$ ) from the titanium spent leaching solution by diffusion dialysis with a new series of anion-exchange membranes. It was reported that acid mixture can selectively be separated from the spent liquor. Effects of metal ions on diffusion dialysis of inorganic acids were studied using a continuous dialyzer by Oh et al.<sup>8</sup> It was observed that the formation of complexes affected the selectivity and flux of the acid. Besides the investigation of the separation of multicomponent mixtures (ternary and quarternary) by diffusion dialysis, much work has been done in the area of studying and modeling the dialysis of binary mixtures (acid-water mixtures).<sup>9,10</sup>

The aim of this study is to present basic information on the transport of hydrochloric acid in the presence of zinc chloride through an anion-exchange mem-

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brane, as a  $HCl-ZnCl_2$  system can be encountered in the practice.

# **EXPERIMENTAL**

To study the dialysis process, a two-compartment mixed cell is often used with the membrane, which separates two identical solutions, but with different concentrations. During the experiment, time dependencies of the components concentrations in both the compartments are recorded. To correctly evaluate this process, not only these data but also other data on the sorption of the components in the membrane must be known, because the concentration of the individual species (ions, complexes, and nondissociated forms) in the membrane can differ from that in the bulk solution.

#### Concentration of HCl and ZnCl<sub>2</sub> in the membrane

The concentrations of hydrochloric acid and zinc chloride in the membrane, which is equilibrated with the solution of a known composition, were determined by the procedure based on the saturation of the membrane with HCl–ZnCl<sub>2</sub> solution, followed by an extraction of the components into water. The membrane of 25–40  $\text{cm}^2$  surface area, which was kept in 0.5M NaCl, was rid of salt by thorough washing in distilled water and shaken with the solution of a given composition for 18 h (overnight). Then, the membrane was wiped quickly with blotting paper to remove the solution adhering to its surface whereupon it was shaken repeatedly for 2 h (three times) in 25 mL distilled water. The concentration of HCl in the individual extracts was determined by microtitration with a standard solution of NaOH. To find the ZnCl<sub>2</sub> concentration, the extracts were titrated with 0.005M EDTA, the end-point being detected by voltammetry. For that purpose, an ECO-TRIBO polarograph (Polaro-Sensors, the Czech Republic) was used.

#### **Dialysis experiments**

Dialysis of aqueous solutions of HCl–ZnCl<sub>2</sub> was investigated in a two-compartment cell with stirrers. The description of the cell is given in detail elsewhere.<sup>11</sup> The experimental set-up was the same as that used formerly (see e.g., Ref. 12). In all the experiments, we used an anion-exchange membrane Neosepta-AFN produced by Tokuyama Soda Co., whose basic physical properties have already been published.<sup>12</sup>

At the beginning of each experiment, compartments I and II were filled with the HCl–ZnCl<sub>2</sub> solution and distilled water, respectively. The initial acid concentration in the compartment I was changed in the limits from 0.2 to 3.0 kmol m<sup>-3</sup>, while the salt concentration was in the range from 0.1 to 1.0 kmol m<sup>-3</sup>. During the

experiments, both compartments were intensively mixed ( $n^{I} = n^{II} = 9.17 \text{ s}^{-1}$ ). The initial volume of liquid in both compartments was always  $10^{-3}$  m<sup>3</sup>. In the course of each experiment, the concentration of the components and the liquid height of liquid levels (for the determination of the volume changes) were measured. The acid concentration was determined by titration with 0.1M NaOH. The concentration of zinc chloride was determined by titration with EDTAthe samples from the compartment I and II were titrated with 0.02M and 0.005M EDTA, respectively, and the end points were indicated visually using an indicator and by voltammetry. The changes in the levels of liquid were measured with the help of a modified micrometer screw with a needle. The temperature was kept at a constant value of  $(20 \pm 0.5)^{\circ}$ C.

# DATA TREATMENT AND DISCUSSION

#### Concentration of HCl and ZnCl<sub>2</sub> in membrane

The concentrations of acid and zinc chloride in the membrane were calculated from the amount of these components in the individual extracts and the volume of the solution in the membrane, which was calculated from density of HCl–ZnCl<sub>2</sub> solution, weight of the membrane saturated with the solution and that of dry membrane. For this purpose, the membrane was dried at vacuum at 60°C. In the calculation of the acid and zinc chloride concentrations in the membrane, the following relations were used

$$c_{j} = \frac{25 \times 10^{-6} \sum_{i=1}^{3} c_{ji}^{\text{extract}}}{V_{\text{SM}}}$$
(1)  
$$j = \text{HCl}, \text{ZnCl}_{2}$$

where

$$V_{\rm SM} = \frac{m_{\rm WM} - m_{\rm DM}}{\rho_{\rm s}} \tag{2}$$

Figure 1 presents the dependence of the ZnCl<sub>2</sub> concentration in the membrane upon the HCl concentration in the external solution—the ZnCl<sub>2</sub> concentration in the external solution being the parameter of the individual curves. From this figure, it is evident that this membrane exhibits high affinity to zinc chloride. Even at zero HCl concentration, the ZnCl<sub>2</sub> concentration in the membrane reaches high values and is higher than that in the external solution. At all ZnCl<sub>2</sub> concentrations in the external solution, the ZnCl<sub>2</sub> concentration in the membrane gradually increases until it reaches a practically constant value.



**Figure 1** Dependence of ZnCl<sub>2</sub> concentration in membrane upon HCl concentration in external solution: ( $\blacklozenge$ ),  $c_{ZnCI_2} = 0.1$  kmol m<sup>-3</sup>; ( $\blacklozenge$ ),  $c_{ZnCI_2} = 0.25$  kmol m<sup>-3</sup>; ( $\blacktriangle$ ),  $c_{ZnCI_2} = 0.5$  kmol m<sup>-3</sup>; ( $\blacksquare$ )  $c_{ZnCI_2} = 1.0$  kmol m<sup>-3</sup>.

As can be seen from Figure 2, where the HCl concentration in the membrane is plotted versus that in the external solution, the acid concentration in the membrane is still increasing with increasing HCl concentration in the external solution in the concentration range investigated. Because of a high data scattering, it is not possible to identify any effect of the ZnCl<sub>2</sub> concentration upon the HCl content in the membrane. All the experimental data obtained at various ZnCl<sub>2</sub> concentrations in the external solution (0.1–1.0 kmol m<sup>-3</sup>) can be fitted by the following empirical equation

$$c_{\mathrm{HCI},M} = a_1 c_{\mathrm{HCI}} + a_2 c_{\mathrm{HCI}}^2 \tag{3}$$

where  $a_1 = 0.844$ ,  $a_2 = 0.0257 \text{ m}^3 \text{ kmol}^{-1}$ .



**Figure 2** Dependence of HCl concentration in membrane upon HCl concentration in external solution: ( $\blacklozenge$ ),  $c_{ZnCI_2} = 0.1$  kmol m<sup>-3</sup>; ( $\blacklozenge$ ),  $c_{ZnCI_2} = 0.25$  kmol m<sup>-3</sup>; ( $\blacklozenge$ ),  $c_{ZnCI_2} = 0.5$  kmol m<sup>-3</sup>; ( $\blacklozenge$ ),  $c_{ZnCI_2} = 1.0$  kmol m<sup>-3</sup>.



**Figure 3** Dependence of HCl concentration in compartment I ( $\bullet$ ) and II ( $\bigcirc$ ) upon time:  $c_{HCL,0}^1 = 2.0 \text{ kmol m}^{-3}$ ,  $c_{ZnCL_2,0}^1 = 0.1 \text{ kmol m}^{-3}$ .

# **Dialysis experiments**

The course of dialysis of the HCl–ZnCl<sub>2</sub> mixture in a two-compartment cell is shown in Figures 3–6. The dependencies of the HCl concentration in both the compartments of the dialysis cell upon time are presented in Figures 3 and 4, while Figures 5 and 6 concern the HCl and ZnCl<sub>2</sub> concentration in the compartment II. If the mixture separated is characterized by a high acid to salt ratio, then the dependencies of acid concentrations upon time in both compartments are very similar to those recorded in dialysis of the solutions containing only one component, i.e., inorganic acid.<sup>11,12</sup> In the case of a high content of ZnCl<sub>2</sub> in the mixture, after a certain time, the HCl concentration in the compartment II becomes higher than that in the compartment I. This phenomenon was also observed in dialysis of HCl-FeCl<sub>3</sub> system.<sup>13</sup> Figures 3–5 demonstrate a good permeability of hydrochloric acid through an anion-exchange membrane Neosepta-AFN in the presence of  $ZnCl_2$ .

From Figure 6, where the ZnCl<sub>2</sub> concentration in the compartment II is plotted versus time, it is evident that this membrane is not able to effectively reject zinc chloride. The concentrations of zinc chloride in the compartment II are relatively high as compared with those in the compartment I. Generally, the ZnCl<sub>2</sub> concentration in the compartment II increases with increasing both salt and acid concentrations and with duration of the experiment.

To quantify the simultaneous transport of hydrochloric acid and zinc chloride, the normalized  $ZnCl_2$ flux at a reference time  $\tau = 0$  defined by eq. (4) was used

$$\hat{J}_{ZnCI_{2,0}} = \frac{J_{ZnCI_{2,0}}}{J_{ZnCI_{2,0}} + J_{HCI,0}} \times 100$$
(4)



**Figure 4** Dependence of HCl concentration in compartment I ( $\bullet$ ) and II ( $\bigcirc$ ) upon time:  $c_{HCL,0}^1 = 2.0 \text{ kmol m}^{-3}$ ,  $c_{ZnCL_{2,0}}^1 = 0.5 \text{ kmol m}^{-3}$ .

where

1.2

0.8

0.4

0.0

0.0

0.4

c<sup>II</sup> , kmol m<sup>-3</sup>

$$J_{i,0} = \frac{1}{A} \frac{dn_i^{ll}}{d\tau}|_{r=0}| \quad i = \text{HCI}, \text{ZnCl}_2$$
(5)

In the calculation of both fluxes from eq. (5), the dependencies  $n^{II} = f(\tau)$ , which were obtained from the dependencies ( $i = \text{HCl}, \text{ZnCl}_2$ ) multiplied by  $V^{II}$ , were approximated by the empirical eq. (6) (here, constants *a* and *b* were determined by nonlinear regression), from which the derivatives

$$\frac{dn_i^{II}}{d\tau}\Big|_{\tau=0}\Big| \quad i = \text{HCI}, \text{ ZnCl}_2$$

at a reference time  $\tau = 0$  can easily be calculated



0.8

1.2

1.6

2.0



**Figure 6** Dependence of ZnCl<sub>2</sub> concentration in compartment II for  $c_{ZnCl_{2,0}}^1 = 0.5 \text{ kmol m}^{-3}$ : ( $\blacklozenge$ ),  $c_{HCL,0}^1 = 0.2 \text{ kmol m}^{-3}$ ; ( $\blacklozenge$ ),  $c_{HCL,0}^1 = 1.0 \text{ kmol m}^{-3}$ ; ( $\blacklozenge$ ),  $c_{HCL,0}^1 = 2.0 \text{ kmol m}^{-3}$ ; ( $\blacklozenge$ ),  $c_{HCL,0}^1 = 3.0 \text{ kmol m}^{-3}$ ; ( $\blacklozenge$ ),  $c_{HCL,0}^1 = 3.0 \text{ kmol m}^{-3}$ .

$$n_i^{II} = \frac{\tau}{a + b\tau} \quad i = \text{HCI}, \text{ZnCl}_2 \tag{6}$$

The dependence of the normalized  $\text{ZnCl}_2$  flux (at a reference time  $\tau = 0$ ) upon the initial acid concentration in compartment I of the cell is shown in Figure 7, the initial salt concentration in the same compartment being the parameter of the individual curves. From this graphical presentation, it is evident that the normalized  $\text{ZnCl}_2$  flux increases with increasing salt content. On the other hand, if the acid concentration increases, then the normalized  $\text{ZnCl}_2$  flux somewhat decreases. On the basis of the dependencies given in Figure 7, it can be concluded that diffusion dialysis of HCl–ZnCl<sub>2</sub> mixture can serve as a pretreatment separation stage only.



**Figure 7** Dependence of normalized flux of ZnCl<sub>2</sub> at time  $\tau$  = 0 upon initial HCl concentration in compartment I: ( $\blacklozenge$ ),  $c_{\text{ZnCl}_{2,0}}^1 = 0.1 \text{ kmol m}^{-3}$ ; ( $\blacktriangle$ )  $c_{\text{ZnCl}_{2,0}}^1 = 0.5 \text{ kmol m}^{-3}$ ; ( $\blacksquare$ ),  $c_{\text{ZnCl}_{2,0}}^1 = 1.0 \text{ kmol m}^{-3}$ .



**Figure 8** Dependence of  $Zn^{2+}$  concentration upon HCl concentration in membrane: 1,  $c_{ZnCl_2M} = 1.0$  kmol m<sup>-3</sup>; 2,  $c_{ZnCl_2M} = 2.0$  kmol m<sup>-3</sup>; 3,  $c_{ZnCl_2M} = 3.0$  kmol m<sup>-3</sup>; 4,  $c_{ZnCl_2M} = 4.0$  kmol m<sup>-3</sup>.

The flux of zinc chloride,  $J_{ZnCI_2,0}$ , calculated from eq. (5) must be understood as a sum of several contributions, because bivalent  $Zn^{2+}$  ions form with  $Cl^{-}$  ions, a series of complexes, i.e., ZnCl<sup>+</sup>, ZnCl<sub>2</sub>, ZnCl<sub>3</sub><sup>-</sup>, and  $ZnCl_4^{2-}$  (see Ref. 14). The resulting total flux of  $ZnCl_2$  is then dependent upon the mutual ratios of these contributions. In dialysis of HCl–ZnCl<sub>2</sub> mixture, overall mass transfer is controlled by the membrane phase, so that the transport in liquids films at both the sides of the membrane need not be solved. Thus, overall mass transfer is dependent upon the concentrations of the individual species at both boundaries in the membrane. For that reason, we calculated the species concentrations in the membrane in the limits of the HCl and ZnCl<sub>2</sub> concentrations found by the sorption experiments.



**Figure 9** Dependence of ZnCl<sup>+</sup> concentration upon HCl concentration in membrane: 1,  $c_{ZnCl_2M} = 1.0$  kmol m<sup>-3</sup>; 2,  $c_{ZnCl_2M} = 2.0$  kmol m<sup>-3</sup>; 3,  $c_{ZnCl_2M} = 3.0$  kmol m<sup>-3</sup>; 4,  $c_{ZnCl_2M} = 4.0$  kmol m<sup>-3</sup>.



**Figure 10** Dependence of ZnCl<sub>2</sub> concentration upon HCl concentration in membrane: 1,  $c_{ZnCl_2M} = 0.5$  kmol m<sup>-3</sup>; 2,  $c_{ZnCl_2M} = 1.0$  kmol m<sup>-3</sup>; 3,  $c_{ZnCl_2M} = 2.0$  kmol m<sup>-3</sup>; 4,  $c_{ZnCl_2M} = 3.0$  kmol m<sup>-3</sup>; 5,  $c_{ZnCl_2M} = 4.0$  kmol m<sup>-3</sup>.

In aqueous solutions of HCl–ZnCl<sub>2</sub>, except for the complexes mentioned earlier, other species exists, i.e.,  $H_3O^+$ ,  $Zn^{2+}$ , and Cl<sup>-</sup>. The concentration of the individual ions and the nondissociated form (considered to be a complex) can be calculated from the set of equations describing ionic equilibria, the electro-neutrality condition, and balance of zinc and hydrogen.

$$\frac{[ZnCl^+]_M}{[Zn^{2+}]_M[Cl^-]_M} - \beta_1 = 0$$
(7)

$$\frac{[ZnCl_2]_M}{[Zn^{2+}]_M[Cl^{-}]_M^2} - \beta_2 = 0$$
(8)

$$\frac{[ZnCl_3^-]_M}{[Zn^{2+}]_M[Cl^-]_M^3} - \beta_3 = 0$$
(9)

$$\frac{[ZnCl_4^-]_M}{[Zn^{2+}]_M [Cl^-]_M^4} - \beta_4 = 0$$
(10)

$$[H_{3}O^{+}]_{M} + 2[Zn^{2+}]_{M} + [ZnCl^{+}]_{M} + c_{M}^{+} - [Cl^{-}]_{M}$$
$$-[ZnCl_{3}^{-}]_{M} - 2[ZnCl_{4}^{2-}]_{M} = 0 \quad (11)$$

$$C_{Zn,M} - [ZnCl^{2}]_{M} - [ZnCl^{2}]_{M} - [ZnCl_{2}]_{M} - [ZnCl_{3}^{2}]_{M} - [ZnCl_{4}^{2}]_{M} = 0 \quad (12)$$

$$c_{\mathrm{H},M} - c_{\mathrm{HCI},M} = 0 \tag{13}$$

Using the complexity constants  $\beta_i$  (i = 1, 2, ...4) taken from literature,<sup>14</sup> the set of eqs. (7)–(13) was solved by the Newton Raphson method—-the results are graphically presented in Figures 8–12.

In dialysis of the  $HCl-ZnCl_2$  system, we found an increase in the  $ZnCl_2$  flux through the membrane with



**Figure 11** Dependence of  $\text{ZnCl}_3^-$  concentration upon HCl concentration in membrane: 1,  $c_{\text{ZnCl}_2\mathcal{M}} = 0.1$  kmol m<sup>-3</sup>; 2,  $c_{\text{ZnCl}_2\mathcal{M}} = 0.5$  kmol m<sup>-3</sup>; 3,  $c_{\text{ZnCl}_2\mathcal{M}} = 1.0$  kmol m<sup>-3</sup>; 4,  $c_{\text{ZnCl}_2\mathcal{M}} = 2.0$  kmol m<sup>-3</sup>; 5,  $c_{\text{ZnCl}_2\mathcal{M}} = 3.0$  kmol m<sup>-3</sup>; 6,  $c_{\text{ZnCl}_2\mathcal{M}} = 4.0$  kmol m<sup>-3</sup>.

increasing both acid and salt concentration (see Fig. 13)—this can be understood as a result of the combination of several phenomena acting in the same direction. From the sorption isotherms shown in Figure 1, it is evident that the  $ZnCl_2$  concentration in the membrane generally increases by increasing both HCl and  $ZnCl_2$  concentration, and consequently, the driving force for the transport of  $ZnCl_2$  is increasing, too.

Moreover, from the solution of the set of eqs. (7)–(13), it can be seen that the concentrations of the species bearing positive charges (i.e.,  $Zn^{2+}$ ,  $ZnCl^+$  and that of the neutral complex are relatively low, and beside this, they decrease with increasing HCl concentration (Figs. 8–10). Zinc in the HCl–ZnCl<sub>2</sub> mixture is



**Figure 12** Dependence of  $ZnCl_4^2$  concentration upon HCl concentration in membrane: 1,  $c_{ZnCl_2M} = 0.1$  kmol m<sup>-3</sup>; 2,  $c_{ZnCl_2M} = 0.5$  kmol m<sup>-3</sup>; 3,  $c_{ZnCl_2M} = 1.0$  kmol m<sup>-3</sup>; 4,  $c_{ZnCl_2M} = 2.0$  kmol m<sup>-3</sup>; 5,  $c_{ZnCl_2M} = 3.0$  kmol m<sup>-3</sup>; 6,  $c_{ZnCl_2M} = 4.0$  kmol m<sup>-3</sup>.



**Figure 13** Dependence of  $\text{ZnCl}_2$  flux at time  $\tau = 0$  upon initial HCl concentration in compartment I: ( $\blacklozenge$ ),  $c_{\text{ZnCl}_2,0}^1 = 0.1$  kmol m<sup>-3</sup>; ( $\blacktriangle$ ),  $c_{\text{ZnCl}_2,0}^1 = 0.5$  kmol m<sup>-3</sup>; ( $\blacksquare$ ),  $c_{\text{ZnCl}_2,0}^1 = 1.0$  kmol m<sup>-3</sup>.

mostly in the form of the  $ZnCl_3^-$  complex (Fig. 11), while the other complex bearing negative charges,  $ZnCl_4^{2-}$ , is present at low concentration in the membrane (Fig. 12). As can be seen from Figure 14, the molar fraction of the  $ZnCl_3^-$  complex (defined as a fraction of all species containing zinc) reaches high values—it is higher than 0.85 throughout the range of acid concentration investigated.

Thus, the phenomena mentioned earlier create good conditions, under which the high total flux of zinc through the membrane exists. From Figure 13, it is evident that the maximum  $\text{ZnCl}_2$  flux is about 2  $\times 10^{-7}$  kmol m<sup>-2</sup> s<sup>-1</sup>, which is approximately one order of magnitude higher than that found in the case of dialysis of H<sub>2</sub>SO<sub>4</sub>–ZnSO<sub>4</sub> mixture.<sup>15</sup>



**Figure 14** Dependence of molar fraction of  $ZnCl_3^-$  complex upon HCl concentration in membrane: 1,  $c_{ZnCl_2M} = 0.1$  kmol m<sup>-3</sup>; 2,  $c_{ZnCl_2M} = 0.5$  kmol m<sup>-3</sup>; 3,  $c_{ZnCl_2M} = 1.0$  kmol m<sup>-3</sup>; 4,  $c_{ZnCl_2M} = 2.0$  kmol m<sup>-3</sup>; 5,  $c_{ZnCl_2M} = 3.0$  kmol m<sup>-3</sup>; 6,  $c_{ZnCl_2M} = 4.0$  kmol m<sup>-3</sup>.

Our results are consistent with those published by other authors. Aouad et al.<sup>16</sup> compared the transport properties of anion-exchange membranes in contact with aqueous solutions containing zinc chloride complexes and with uncomplexed metal chloride solution. They measured transport numbers of protons and zinc through the anion-exchange membranes, and the results obtained showed a strong influence of the complexed species on the loss of permselectivity of the membranes studied. These results were analyzed on the basis of Raman spectra of the membranes, which proved that considerable amount of zinc is in the form of the  $ZnCl_3^-$  complex.

# CONCLUSIONS

Dialysis of the HCl–ZnCl<sub>2</sub> system was investigated in a two-compartment batch mixed cell with an anionexchange membrane Neosepta-AFN developed and produced by Tokuyama Soda Co. The analysis of the time dependencies of hydrochloric acid and zinc chloride showed that hydrochloric acid permeates through this membrane well, but on the other hand, zinc chloride is not rejected efficiently. The quality of the separation process was evaluated with the help of the ZnCl<sub>2</sub> partial flux at the beginning of the experiment. It was found that this flux increases with increasing salt concentration and it somewhat decreases with increasing acid concentration. This is a consequence of the fact that zinc is predominantly in the form of the ZnCl<sub>3</sub><sup>-</sup> complex, which is relatively small and permeates through this membrane well. On the basis of the results obtained, it can be concluded that the separation of HCl–ZnCl<sub>2</sub> mixture by diffusion dialysis exhibits low efficiency.

# NOMENCLATURE

#### Symbols

Abbreviation Description

- A Membrane area  $(m^2)$
- a Constant in eq. (4) (s  $\text{kmol}^{-1}$ )
- $a_1$  Constant in eq. (1)
- $a_2$  Constant in eq. (1) (m<sup>3</sup> kmol<sup>-1</sup>)
- *b* Constant in eq. (4)  $(\text{kmol}^{-1})$
- c (Total) molar concentration (kmol  $m^{-3}$ )
- *f* General function
- J Flux (kmol  $m^{-2} s^{-1}$ )
- $\hat{J}$  Normalized flux (%)

- *m* Mass (kg)
- *n* Rotational speed of stirrers  $(s^{-1})$
- *n* Amount of component (kmol)
- V Volume (m<sup>3</sup>)
- *x* Molar fraction
- $\beta_i$  (*i* = 1, 2, ... 4) Complexity constant
- $\rho$  Density (kg m<sup>-3</sup>)
- au Time (s)
- [] Actual concentration (kmol m<sup>-3</sup>) (in eqs. (5)–(8) dimensionless)

#### Superscripts and subscripts

DM	Dry membrane
extract	Referred to extract
Η	Referred to hydrogen
HCl	Referred to hydrochloric acid
M	Referred to membrane
I, II	Referred to compartment I, II, respectively
S	Referred to solution
Zn	Referred to zinc
$ZnCl_2$	Referred to ZnCl <sub>2</sub>
$ZnCI_3^-$	Referred to ZnCI <sub>3</sub> <sup>-</sup> complex
$ZnCI_4^{2-}$	Referred to $ZnCI_4^{2-}$ complex
WM	Wet membrane
0	Initial
+	Referred to fixed charges

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