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Separation of HCl + $NiCl_2$ Mixture by Diffusion Dialysis

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Abstract: Separation of an aqueous solution of HCl + $NiCl_2$ by diffusion dialysis was investigated in a two-compartment mixed cell with an anion-exchange membrane Neosepta-AFN. The experiments proved that this membrane can be considered a good separator for the mixture mentioned, because nickel chloride is efficiently rejected, while hydrochloric acid permeates well through the membrane. The separation is very effective at high acid concentrations and low concentrations of nickel chloride. The separation efficiency of the membrane was evaluated by the partial flux of nickel chloride. The experiments revealed that the partial flux is very low, i.e. below 3.2%—it decreases with increasing acid concentration, but it increases with increasing content of salt in the solution separated. Moreover, the separation process was quantified by the permeability of the membrane based on four phenomenological coefficients which depend on the initial acid and salt concentrations.

Keywords: Diffusion dialysis, batch cell, hydrochloric acid, nickel chloride, Neosepta-AFN membrane

INTRODUCTION

Separation of mixtures by membranes is based on different transport rates of the individual components in the mixture as a consequence of different diffusivities or mobilities in the membrane phase. In the case of diffusion dialysis, which uses ion-exchange membranes, it is necessary to consider besides other

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effects the interactions between the species in the solution and positively charged sites inside the membrane. If an anion-exchange membrane is used for the separation of electrolytes, cations are rejected, while the transport of anions is facilitated. Hydrogen ions (although they are hydrated) are not effectively rejected, because they are very small and their mobility is high not only in aqueous solutions but also in the membrane phase. This phenomenon need not be considered to be a disadvantage if the anion-exchange membrane is used in the separation of acid-salt mixtures (1, 2).

Diffusion dialysis using an anion-exchange membrane was used to recover H_2SO_4 from waste sulfuric acid solutions in the diamond manufacturing process (3). It is reported that about 80% of H_2SO_4 could be recovered from the waste solution, which contained $4.5\,\mathrm{kmol\,m^{-3}}$ H_2SO_4 at the liquid flow rate of $0.26 \times 10^{-3}\,\mathrm{m^3\,h^{-1}\,m^{-2}}$. Under these conditions the concentration of sulfuric acid was $4.3\,\mathrm{kmol\,m^{-3}}$, while that of the total impurity was 2000 ppm. From the economical point of view the dialysis system used is highly attractive, as the payback period is only few months. Also the use of diffusion dialysis in the recovery of sulfuric acid from the waste acid solution of aluminium surface processing plant was found to be very efficient (4). Moreover, a preliminary economic evaluation of the whole process showed that diffusion dialysis is highly viable for sulfuric acid due to its short payback period. 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 communication (5) focused on the examining of the effects of various operating variables on the process performance with an aim to finding optimum operating conditions for both the processes. Xu and Yang dealt with sulfuric acid recovery from titanium white (pigment) waste liquor (6) and the recovery of mixed acid ($HF + HNO_3$) from the titanium spent leaching solution (7) using diffusion dialysis with a new series of anion exchange membranes. The membranes used were prepared from poly(2,6-dimethyl-1,4-phenylene oxide) by bromination in both benzyl and aryl positions and following amination and functionalization. In the case of sulfuric acid, the acid recovery from titanium white waste liquor was improved by benzyl substitution, while the selectivity by aryl substitution. It was reported that the $HF + HNO_3$ mixture can be separated selectively from the spent liquor. The separation was highly affected by the water content in the membrane and the ion-exchange capacity. In another paper (8), the same authors carried out experiments focused on simultaneous recovery of sulfuric acid and nickel from electrolysis spent liquor of relatively low acid concentration. The pilot experiments with surface cross-linked PPO anion-exchange membranes showed that nickel leakage can be controlled within 4%, and the recovery of acid can attain as high as 66–72%. Oh et al. (9) studied the effects of metal ions on the diffusion dialysis of inorganic acids using a continuous dialyzer. It was observed that the formation of complexes affected the selectivity and flux of acid. Out of five metals investigated, Fe, Ni, Cr, and Cu were reasonably rejected by the anion-exchange membrane, while Zn in the HCl solution leaked through the membrane significantly. In reference (10) the recovery and concentration of Zn^{2+} and Cu^{2+} ions from industrial rinse water containing a mixture of Zn^{2+}, Cu^{2+}, Mg^{2+}, K^+, and Na^+ ions were studied in a continuous membrane extraction, where sulfuric acid was used as a stripping agent for metal ions. In order to de-acidify the concentrate solution of Cu^{2+} ions, the diffusion dialysis technique was suggested. The experiments at steady state proved that diffusion dialysis can be evaluated as a very effective process, because its selectivity (defined as an acid flux to copper flux ratio) exhibits a high value of 166. Wisniewska et al. (11) tested the processes of electrodialysis and diffusion dialysis in the separation of model mixtures containing hydrochloric acid and ferric ions. Diffusion dialysis provided acid removal of 56–67% with high retention of ferric ions—up to 98–99%. Besides the investigation of the separation of multicomponent mixtures (ternary and quarternary) by diffusion dialysis as mentioned above, much attention has been paid to the study and the modelling of the dialysis of solutions with one component (12–20).

The aim of this paper is to obtain both basic and quantitative information on dialysis of a $HCl + NiCl_2$ mixture, because this system can be encountered in industrial practice.

EXPERIMENTAL

Membrane Used

An anion-exchange membrane Neosepta-AFN was used in all the experiments. This polymeric strongly basic membrane is produced by Tokuyama Soda Co., Inc. (Japan). Its basic properties were as follows: thickness 165 μm, water content 0.418 g per gram of dry membrane in Cl^- form and concentration of fixed charges (considered as monovalent) 4.7 kmol m^{-3} (see references (18, 21)). The area of the membrane was 62.2 cm^2.

Dialysis Experiments

The dialysis of aqueous solutions of $HCl + NiCl_2$ was investigated in a two-compartment cell with stirrers. Its inner dimensions were: 0.12 m × 0.15 m × 0.16 m (length × width × height). A vertical partition, in which the membrane was fastened, divided the cell into two approximately similar compartments (22). In both the compartments the liquid was stirred with laboratory stirrers with electronic rotation rate control. The experimental set-up was the same as that used in previous work (see, e.g., references (18, 21, 23, 24)).

At the beginning of each experiment, compartments I and II were filled with HCl-$NiCl_2$ solution and distilled water, respectively. The initial acid concentration in compartment I was changed in the range from 0.2 to

3.0 kmol m^{-3}, while the salt concentration was in the range from 0.1 to 1.0 kmol m^{-3}. During the experiments, both the compartments were intensively stirred ($n^I = n^{II} = 9.17$ s^{-1}) in order to minimize the effect of liquid films on both sides of the membrane upon the transport of the components through the membrane. In the case of dialysis of single component solutions, the rotational speed of stirrers was also 13.67 s^{-1}. In the course of each experiment, the concentration of components and the height of liquid levels (for the determination of the volume changes) were measured. The acid concentration was determined from the total concentration of Cl^- ions (for that purpose, the samples were titrated with a standard $AgNO_3$ solution—the end-point being determined potentiometrically) and the concentration of Ni^{2+} ions, which was determined by titration with EDTA. In the titration of the samples from compartment I and II, the end-point was indicated visually using an indicator and by voltammetry, respectively. In the latter case, an ECO-TRIBO polarograph (PolaroSensors, The Czech Republic) was used. In all the experiments, the temperature was kept at a constant value of 20 ± 0.5°C.

DATA TREATMENT AND DISCUSSION

Partial Flux of Salt

Figures 1–3 demonstrate the course of dialysis of an $HCl + NiCl_2$ mixture in a two-compartment dialysis cell. In Fig. 1, the dependences of the acid concentration in both the compartments upon time are presented, while Figs. 2 and 3

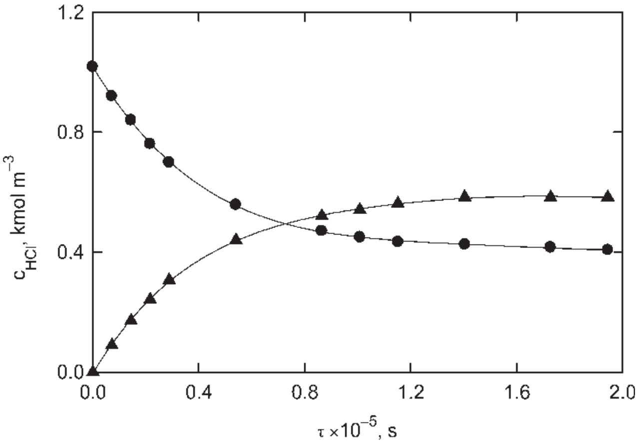

Figure 1. Dependence of HCl concentration in compartment I (●) and II (▲) upon time: $c^I_{HCl,0} = 1.0$ kmol m^{-3}; $c^I_{NiCl_2,0} = 0.25$ kmol m^{-3}.

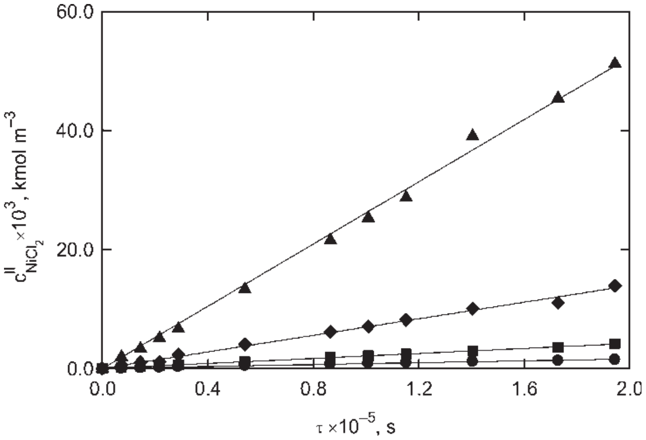

Figure 2. Dependence of NiCl$_2$ concentration in compartment II upon time for $c^I_{HCl,0} = 1.0$ kmol m^{-3}. Effect of initial NiCl$_2$ concentration in compartment I: (●) – $c^I_{NiCl_2,0} = 0.1$ kmol m^{-3}; (■) – $c^I_{NiCl_2,0} = 0.25$ kmol m^{-3}; (◆) – $c^I_{NiCl_2,0} =$ 0.5 kmol m^{-3}; (▲) – $c^I_{NiCl_2,0} = 1.0$ kmol m^{-3}

show the concentration of NiCl$_2$ in the compartment with the stripping agent (water). All three figures show good separation of the HCl + NiCl$_2$ mixture by the anion-exchange membrane Neosepta-AFN, which was specially developed and is manufactured for diffusion dialysis. From the graphical

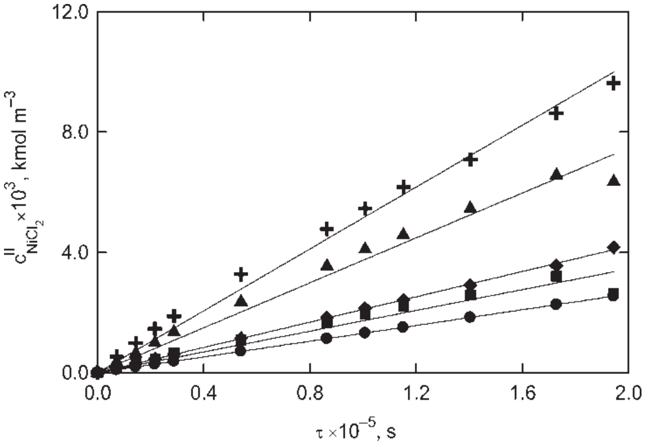

Figure 3. Dependence of NiCl$_2$ concentration in compartment II upon time for $c^I_{NiCl_2,0} = 0.25$ kmol m^{-3}. Effect of initial HCl concentration in compartment I: (●) – $c^I_{HCl,0} = 0.2$ kmol m^{-3}; (■) – $c^I_{HCl,0} = 0.5$ kmol m^{-3}; (◆) – $c^I_{HCl,0} = 1.0$ kmol m^{-3}; (▲) – $c^I_{HCl,0} = 2.0$ kmol m^{-3}; (+) – $c^I_{HCl,0} = 3.0$ kmol m^{-3}.

presentations given in Figs. 1–3, it is evident that hydrochloric acid permeates well through this membrane, while nickel chloride is efficiently rejected. Generally, the concentration of nickel chloride in compartment II increases with increasing concentration of both HCl and $NiCl_2$ in compartment I and with the duration of the experiment. From the comparison of $NiCl_2$ concentrations in both compartments it follows that the concentration of $NiCl_2$ in compartment II is much lower than that in compartment I.

The separation ability of the membrane studied in the separation of the $HCl + NiCl_2$ mixture can be evaluated not only on the basis of the concentration of $NiCl_2$ in compartment II, but also using the partial flux of $NiCl_2$ through the membrane. As the fluxes of salt and acid change with time, it is necessary to refer them to the reference time, e.g., $\tau = 0$.

$$\bar{J}_{\mathrm{NiCl_2}}, 0 = \frac{J_{\mathrm{NiCl_2,0}}}{J_{\mathrm{NiCl_2,0}} + J_{\mathrm{HCl,0}}} \times 100 \tag{1}$$

where

$$J_{i,0} = \frac{1}{A}\frac{dn_i^{II}}{d\tau}\bigg|_{\tau=0} \qquad i = \mathrm{HCl, NiCl_2} \tag{2}$$

In the calculation of the flux of hydrochloric acid, the dependences $n_{\mathrm{HCl}}^{II} = f(\tau)$, which were obtained from the dependences $c_{\mathrm{HCl}}^{II} = f(\tau)$ multiplied by V^{II}, were approximated by the empirical equation (3)(where the constants a and b were determined by a non-linear regression), from which the derivation $dn_{\mathrm{HCl}}^{\mathrm{II}}/d\tau|_{\tau=0}$ can easily be calculated.

$$n_{\mathrm{HCl}}^{II} = \frac{\tau}{a + b\tau} \tag{3}$$

In the case of nickel chloride, the dependences $c_{\mathrm{NiCl_2}}^{II} = f(\tau)$ were approximated by straight lines with zero intercept

$$c_{\mathrm{NiCl_2}}^{II} = B\tau \tag{4}$$

whose slopes were used in the calculation of the flux of nickel chloride

$$J_{\mathrm{NiCl_2,0}} = \frac{1}{A}\frac{dn_{\mathrm{NiCl_2}}^{II}}{d\tau}\bigg|_{\tau=0} = \frac{V^{II}}{A}\frac{dc_{\mathrm{NiCl_2}}^{II}}{d\tau}\bigg|_{\tau=0} + \frac{c_{\mathrm{NiCl_2}}^{II}}{A}\frac{dV^{II}}{d\tau}\bigg|_{\tau=0} = \frac{V^{II}}{A}B \tag{5}$$

(Note that $c_{\mathrm{NiCl_{2,0}}}^{II} = 0$)

The dependence of the partial $NiCl_2$ flux at a reference time $\tau = 0$ upon the initial acid concentration in compartment I of the dialysis cell is presented in Fig. 4, the initial salt concentration in the same compartment being the parameter of the individual curves. From this figure it can be seen that the partial flux of $NiCl_2$ increases with increasing salt content in the mixture dialyzed. On the other hand, if the acid concentration increases, the partial $NiCl_2$ flux decreases. For example, at the highest $NiCl_2$ concentration used the $NiCl_2$ partial flux decreases from approx. 3.15% (at the initial acid concentration of 0.2 kmol m^{-3}) to 0.37% (at the initial acid concentration of 3.0 kmol m^{-3}). Based on the dependences given in Fig. 4, it can be concluded that, in the case of separation of the $HCl + NiCl_2$ mixture, the anion-exchange membrane Neosepta-AFN can be considered a good separator for the mixture mentioned.

Species in HCl + $NiCl_2$ Mixture

In the separation of mixtures of electrolytes by an ion-exchange membrane, ions and other species are transported owing to their concentration gradients. In order to analyze this complex transport, other pieces of information on the composition of the solution dialyzed must be known. According to reference (25), the following species exist in aqueous solution of $HCl + NiCl_2$: Cl^-, H_3O^+, Ni^{2+} and $NiCl^+$. The concentration of the individual ions can be found by solving the set of equations describing the ionic equilibrium ($Ni^{2+} + Cl^- \rightleftarrows NiCl^+$) (Eq. 6), the electro-neutrality

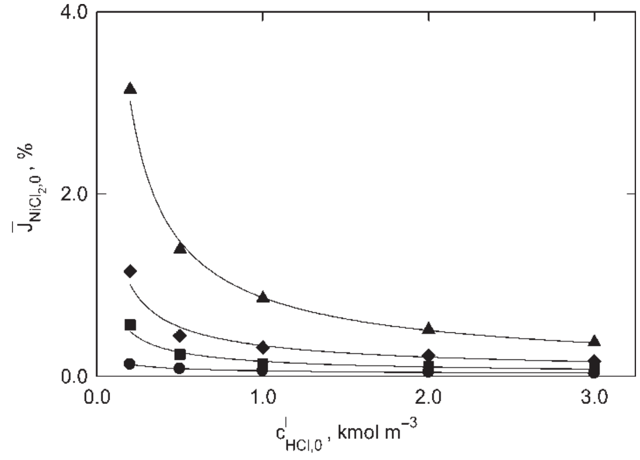

Figure 4. Dependence of partial $NiCl_2$ flux upon initial acid concentration in compartment I: (●) – $c^I_{NiCl_2,0} = 0.1$ kmol m^{-3}; (■) – $c^I_{NiCl_2,0} = 0.25$ kmol m^{-3}; (◆) – $c^I_{NiCl_2,0} = 0.5$ kmol m^{-3}; (▲) – $c^I_{NiCl_2,0} = 1.0$ kmol m^{-3}.

condition (Eq.7) and the balance of hydroxonium ion (Eq. 8) and the chloride ion (Eq. 9)

$$\frac{[\mathrm{NiCl}^+]}{[\mathrm{Ni}^{2+}][\mathrm{Cl}^-]} - \beta_1 = 0 \tag{6}$$

$$[\mathrm{H_3O}^+] + 2[\mathrm{Ni}^{2+}] + [\mathrm{NiCl}^+] - [\mathrm{Cl}^-] = 0 \tag{7}$$

$$[\mathrm{H_3O}^+] - \mathrm{c_{HCl}} = 0 \tag{8}$$

$$[\mathrm{Cl}^-] + [\mathrm{NiCl}^+] - c_{\mathrm{Cl}^-} = 0 \tag{9}$$

(Note that $c_{\mathrm{Cl}^-} = c_{\mathrm{HCl}} + 2c_{\mathrm{NiCl_2}}$)

In the set of equations (6)–(9), the complete dissociation of hydrochloric acid was presumed.

The set of Eqs (6) – (9) was solved by the Newton–Raphson method. The results are presented in Figs. 5 and 6 as dependences of the Ni^{2+} and NiCl^+ concentrations upon the acid and salt concentrations. The concentration limits for hydrochloric acid and nickel chloride correspond to those in the experiments.

In reference (25) only three values of β_1 are given at the temperature of 25°C, at the ionic strength equal to 1.0, 2.0 and 3.0 kmol m^{-3}. First, these data were extrapolated to obtain the complexity constant at zero ionic strength. Then all the data were approximated by the empirical exponential function (10) in order to enable the interpolation and extrapolation of the data. As we did not succeed in finding data enabling the calculation of ΔH_r for the

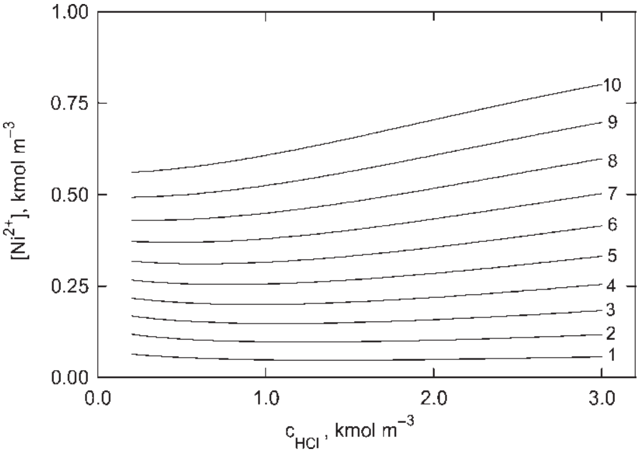

Figure 5. Dependence of concentration of Ni^{2+} ions upon HCl concentration in aqueous solution: 1 – $c_{\mathrm{NiCl_2}} = 0.1$ kmol m^{-3}; 2 – $c_{\mathrm{NiCl_2}} = 0.2$ kmol m^{-3}; 3 – $c_{\mathrm{NiCl_2}} = 0.3$ kmol m^{-3}; 4 – $c_{\mathrm{NiCl_2}} = 0.4$ kmol m^{-3}; 5 – $c_{\mathrm{NiCl_2}} = 0.5$ kmol m^{-3}; 6 – $c_{\mathrm{NiCl_2}} = 0.6$ kmol m^{-3}; 7 – $c_{\mathrm{NiCl_2}} = 0.7$ kmol m^{-3}; 8 – $c_{\mathrm{NiCl_2}} = 0.8$ kmol m^{-3}; 9 – $c_{\mathrm{NiCl_2}} = 0.9$ kmol m^{-3}; 10 – $c_{\mathrm{NiCl_2}} = 1.0$ kmol m^{-3}.

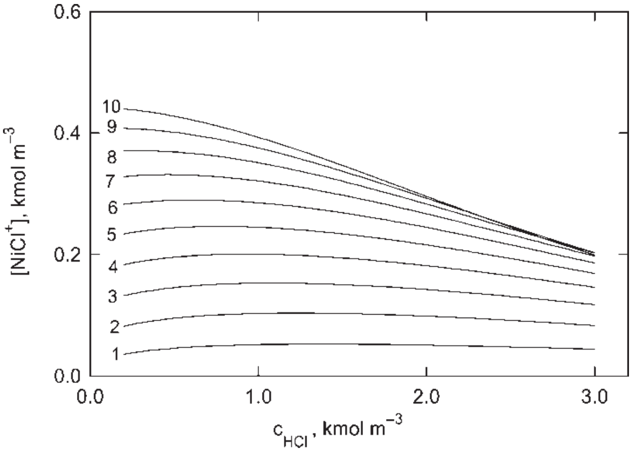

Figure 6. Dependence of concentration of NiCl$^+$ ions upon HCl concentration in aqueous solution. Parameter of individual lines is the same as that in Fig. 5.

reaction between Cl$^-$ and Ni^{2+} ions, which is needed for the recalculation of β_1 to the temperature of 20°C, the complexity constant at 25°C was used.

$$\beta_1 = 2.042 \exp[-0.656I] \tag{10}$$

Beside the partial flux of NiCl$_2$, the flux of NiCl$_2$ through the membrane at a reference time $\tau = 0$ (see Eq. 5) was analyzed, too. The dependence of the NiCl$_2$ flux upon the initial acid concentration in compartment I at various initial salt concentration is shown in Fig. 7. It is evident from this graphical presentation that the NiCl$_2$ flux exhibits low values—it is in the range from 0.3×10^{-9} kmol m^{-2} s^{-1} to 43.0×10^{-9} kmol m^{-2} s^{-1}. This low flux is due to the fact that no ions or complexes with negative charge, whose transport through the anion-exchange membrane is facilitated, are present in the solution.

The flux of nickel chloride through the membrane is a sum of the Ni^{2+} and NiCl$^+$ fluxes. Inside the anion-exchange membrane, repulsive forces between Ni^{2+} ions and fixed charges in the membrane are higher than those between NiCl$^+$ ions and fixed charges. However, on the other hand, NiCl$^+$ ions are larger than Ni^{2+} ions, so that their transport through the membrane is retarded. As can be seen in Fig. 7, the flux of NiCl$_2$ moderately increases with increasing acid concentration in the solution. At the same time, the increase in the acid concentration causes an increase in the Ni^{2+} concentration (Fig. 5), while the concentration of NiCl$^+$ ions decreases (Fig. 6). These graphical presentations indicate that the increase in the nickel flux through the membrane can be ascribed to Ni^{2+} ions.

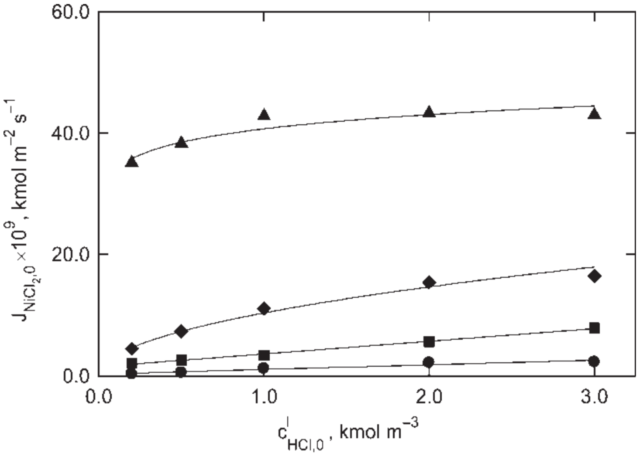

Figure 7. Dependence of $NiCl_2$ flux at reference time $\tau = 0$ upon initial HCl concentration in compartment I: (●) – $c^I_{NiCl_2,0} = 0.1$ kmol m^{-3}; (■) – $c^I_{NiCl_2,0} = 0.25$ kmol m^{-3} (◆) – $c^I_{NiCl_2,0} = 0.5$ kmol m^{-3}; (▲) – $c^I_{NiCl_2,0} = 1.0$ kmol m^{-3}.

Permeability of Membrane

In the case of a binary system, i.e. a system consisting of solvent and component A, permeability the of the membrane for component A is interrelated with the flux by the following equation

$$J_A = P_A(c^I_{Af} - c^{II}_{Af}) \tag{11}$$

where c^I_{Af} and c^{II}_{Af} are the concentrations of the component A at the solution/membrane interface.

The flux of component A can easily be determined from the change in the concentration of component A in compartment I or II, i.e.

$$J_A = -\frac{1}{A}\frac{dn^I_A}{d\tau} = \frac{1}{A}\frac{dn^{II}_A}{d\tau} = -\frac{V^I}{A}\frac{dc^I_A}{d\tau} - \frac{c^I_A}{A}\frac{dV^I}{d\tau} = \frac{V^{II}}{A}\frac{dc^{II}_A}{d\tau} + \frac{c^{II}_A}{A}\frac{dV^{II}}{d\tau} \tag{12}$$

A combination of Eqs (11) and (12) leads to Eqs (13) and (14), which describe the time dependences of the concentration of component A in compartments I and II, respectively.

$$\frac{dc^I_A}{d\tau} = -\frac{A}{V^I}P_A(c^I_{Af} - c^{II}_{Af}) - \frac{c^I_A}{V^I}\frac{dV^I}{d\tau} \tag{13}$$

$$\frac{dc^{II}_A}{d\tau} = \frac{A}{V^{II}}P_A(c^I_{Af} - c^{II}_{Af}) - \frac{c^{II}_A}{V^{II}}\frac{dV^{II}}{d\tau} \tag{14}$$

The initial conditions for Eqs 13 and 14 are

$$\tau = 0 \qquad c_A^I = c_{A0}^I \qquad c_A^{II} = c_{A0}^{II} = 0 \tag{15}$$

If the $c_A - \tau$ dependences in both the compartments and the volume changes are known, then the set of Eqs (13) and (14) can be numerically integrated. If this integration is followed by a suitable optimizing procedure, which searches for a minimum of the objective function (16), then it is possible to determine the permeability of the membrane for component A

$$F(P_A) = \sum_{i=1}^{n} \left(\frac{c_{A,exp}^{II,i} - c_{A,calc}^{II,i}}{c_{A,exp}^{II,i}} \right)^2 \tag{16}$$

(Note: n is the number of the experimental points in one time series)

Generally, the transport of component A through the membrane (Eqs (13) and (14)) must be solved simultaneously with that in liquid films, whose existence is supposed on both sides of the membrane. If the effect of liquid films can be neglected (no effect of increase in the intensity of mixing upon the permeability coefficient is observed), the concentrations c_{Af}^I and c_A^{II} are equal to c_A^I and c_A^{II}, respectively.

In Fig. 8 the permeability coefficient for hydrochloric acid is plotted against the initial acid concentration in compartment I. It is evident that the permeability of the Neosepta-AFN membrane for HCl (A = HCl) exhibits high values, i.e. it is in the range from approx. 0.84×10^{-6} to $2.4 \times 10^{-6}\ \mathrm{m\,s^{-1}}$. Moreover, no effect of increase in the intensity of

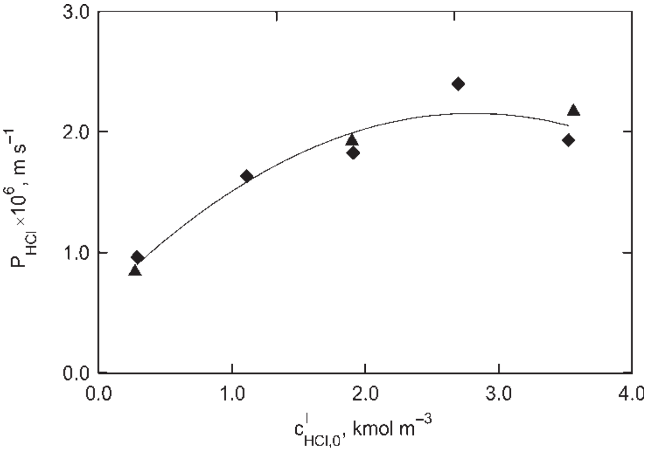

Figure 8. Dependence of permeability coefficient of HCl upon initial acid concentration in compartment I — dialysis of single component solutions: (▲) – $n^I = n^{II} = 9.13\ \mathrm{s^{-1}}$; (◆) – $n^I = n^{II} = 13.67\ \mathrm{s^{-1}}$.

mixing upon P_A can be identified in Fig. 8. As the transport characteristics of the solution/membrane system are usually referred to the initial acid concentration in compartment I, we modified the procedure given above in such a way that the objective function (16) was considered a function of the coefficients a_0, a_1 and a_2 of the polynomial (17) used for the approximation of the dependence $P_A = f(c^I_{A0})$. For that purpose, the experimental data at $n^I = n^{II} = 9.17$ and $13.67\ \mathrm{s}^{-1}$ were used.

$$P_A = a_0 + a_1 c^I_{A0} + a_2 (c^I_{A0})^2 \qquad (17)$$

Using a simplex optimizing method (the algorithm by Nelder and Mead), the following values of a_i ($i = 0, 1, 2$) were found: $a_0 = 5.96 \times 10^{-7}\ \mathrm{m\ s^{-1}}$; $a_1 = 1.11 \times 10^{-6}\ \mathrm{m^4\ s^{-1}\ kmol^{-1}}$; $a_2 = -1.98 \times 10^{-8}\ \mathrm{m^7\ s^{-1}\ kmol^{-2}}$. In Fig. 8, the values of P_A calculated from polynomial (17) are drawn by the solid line.

In a similar way, the permeability coefficient and the constants of polynomial (17) for nickel chloride ($A = NiCl_2$) were determined, too. (see Fig. 9). In this case: $a_0 = 6.27 \times 10^{-11}\ \mathrm{m\ s^{-1}}$; $a_1 = 1.53 \times 10^{-8}\ \mathrm{m^4\ s^{-1}\ kmol^{-1}}$; $a_2 = 7.15 \times 10^{-9}\ \mathrm{m^7\ s^{-1}\ kmol^{-2}}$. The results graphically presented in Fig. 9 show that the permeability coefficient for $NiCl_2$ is about two orders of magnitude lower than that for HCl. These results are consistent with those obtained before.

Equations (18) and (19) were used in order to express the fluxes of the individual components through the membrane in the case of dialysis of a HCl (A) + $NiCl_2$ (B) mixture. It is a convenient phenomenological correlation which is loosely founded on the analogy to diffusion in ternary mixtures,

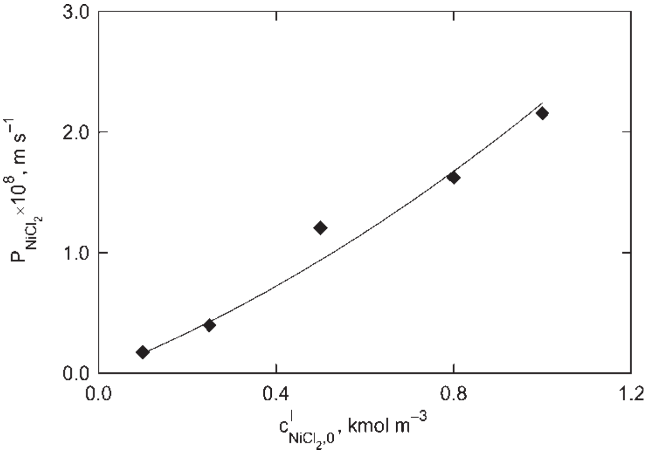

Figure 9. Dependence of permeability coefficient of $NiCl_2$ upon initial salt concentration in compartment I — dialysis of single component solutions.

where the flux of one component is affected not only by its own concentration gradient but also by the concentration gradient of the other component.

$$J_A = P_{AA}(c_A^I - c_A^{II}) + P_{AB}(c_B^I - c_B^{II}) \tag{18}$$

$$J_B = P_{BA}(c_A^I - c_A^{II}) + P_{BB}(c_B^I - c_B^{II}) \tag{19}$$

As shown above, the permeability coefficient for hydrochloric acid and nickel chloride can be expressed as a function of the initial concentration in compartment I. For the same reason, it can be supposed that the coefficients P_{ij} (i = A, B; j = A, B) are functions of both the initial acid and salt concentrations in compartment I, i.e.

$$P_{ij} = P_{ij,0}[1 + A_{ij,1}c_{A0}^I + A_{ij,2}(c_{A0}^I)^2 + A_{ij,3}c_{B0}^I + A_{ij,4}(c_{B0}^I)^2] \tag{20}$$

The total number of the parameters in Eq. (20) is 20, but fortunately, some of them can be determined by independent calculations, i.e. $P_{AA,0}$, $A_{AA,1}$, $A_{AA,2}$, $P_{BB,0}$, $A_{BB,3}$ and $A_{BB,4}$.

In order to calculate the coefficients $P_{ij,0}$ and $A_{\mathrm{ij},k}$ ($i = A, B$; $j = A, B$; $k = 1, 2, \ldots 4$) except for $P_{AA,0}$, $A_{AA,1}$, $A_{AA,2}$, $P_{BB,0}$, $A_{BB,3}$ and $A_{BB,4}$, the following set of differential equations was numerically solved

$$\frac{dc_A^{II}}{d\tau} = \frac{A}{V^{II}}[P_{AA}(c_A^I - c_A^{II}) + P_{AB}(c_B^I - c_B^{II})] - \frac{c_A^{II}}{V^{II}}\frac{dV^{II}}{d\tau} \tag{21}$$

$$\frac{dc_B^{II}}{d\tau} = \frac{A}{V^{II}}[P_{BA}(c_A^I - c_A^{II}) + P_{BB}(c_B^I - c_B^{II})] - \frac{c_B^{II}}{V^{II}}\frac{dV^{II}}{d\tau} \tag{22}$$

The initial conditions for Eqs 21 and 22 are

$$\tau = 0 \qquad c_A^{II} = c_{A0}^{II} = 0 \qquad c_B^{II} = c_{B0}^{II} = 0 \tag{23}$$

Equation (21) is a combination of Eqs (12) and (18), while Eq. (22) is a combination of Eq. (12) written for the component B (NiCl$_2$) and Eq. (19). This integration was followed by the optimizing procedure searching for a minimum of the objective function (24)

$$F = \sum_{i=1}^{n}\left[\left(\frac{c_{A,exp}^{II,i} - c_{A,calc}^{II,i}}{c_{A,exp}^{II,i}}\right)^2 + \left(\frac{c_{B,exp}^{II,i} - c_{B,calc}^{II,i}}{c_{B,exp}^{II,i}}\right)^2\right] \tag{24}$$

The calculated values of the coefficients of polynomials (20) are summarized in Table 1 Moreover, the coefficients P_{ij} ($i = A, B$; $j = A, B$) are plotted against the initial acid concentration in compartment I in Figs. 10–13. In all the figures, the initial concentration of nickel chloride in compartment I is a parameter of the individual curves. The graphical presentation in Fig. 10 indicates that the phenomenological coefficient P_{AA} is of the same order of magnitude as the coefficient P_A. Moreover, it is influenced not only by the initial acid concentration but also the initial concentration of nickel chloride in compartment I. The value of P_{AA} increases with increasing both the acid

Table 1. Coefficients of polynomials (20)

P_{ij}	$P_{ij,0}$ m s^{-1}	$A_{ij,1}$ m^3 kmol^{-1}	$A_{ij,2}$ m^6 kmol^{-2}	$A_{ij,3}$ m^3 kmol^{-1}	$A_{ij,4}$ m^6 kmol^{-2}
P_{AA}	5.959×10^{-7}	1.863	-3.316×10^{-1}	3.301	−1.560
P_{AB}	-2.329×10^{-8}	−47.62	7.608	−58.53	49.25
P_{BA}	5.212×10^{-12}	1.797×10^2	−55.09	−67.79	22.62
P_{BB}	6.273×10^{-11}	1.272×10^2	8.402	2.437×10^2	1.139×10^2

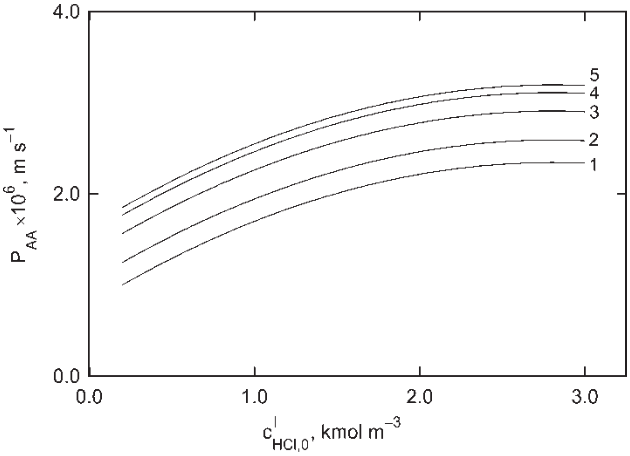

Figure 10. Dependence of coefficient P_{AA} upon initial acid concentration in compartment I: 1 – $c^I_{B0} = 0.1$ kmol m^{-3}; 2 – $c^I_{B0} = 0.25$ kmol m^{-3}; 3 – $c^I_{B0} = 0.5$ kmol m^{-3}; 4 – $c^I_{B0} = 0.75$ kmol m^{-3}; 5 – $c^I_{B0} = 1.0$ kmol m^{-3}.

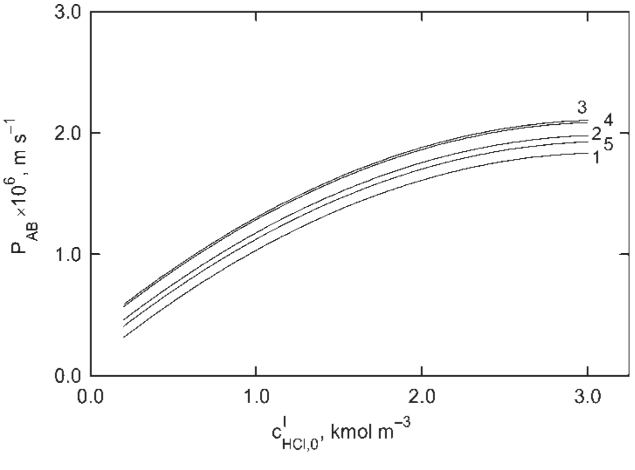

Figure 11. Dependence of coefficient P_{AB} upon initial acid concentration in compartment I. Parameter of individual lines is the same as that in Fig. 10.

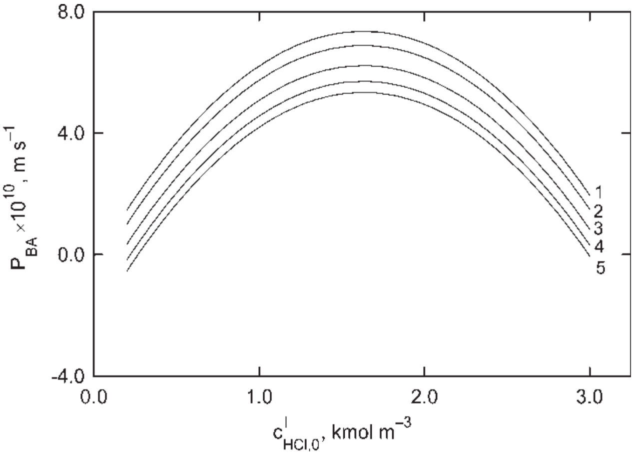

Figure 12. Dependence of coefficient P_{BA} upon initial acid concentration in compartment I. Parameter of individual lines is the same as that in Fig. 10.

and salt concentration at $\tau = 0$ in compartment I. This means that the flux of acid caused by its own concentration difference is positively influenced by c^{I}_{A0} and c^{I}_{B0}. Also the coefficient P_{AB} is of the same order of magnitude as the coefficients P_A and P_{AA}, but on the other hand, it is somewhat lower than P_A or P_{AA} (see Fig. 11). The coefficient P_{AB} gradually increases with increasing initial acid concentration, but the dependence $P_{AB} = f(c^{I}_{B0})$ at a constant c^{I}_{A0} exhibits a maximum, namely at a concentration $c^{I}_{B0} = 0.594$ kmol m^{-3}. The phenomenological coefficient P_{BA} exhibits very low values, as shown in

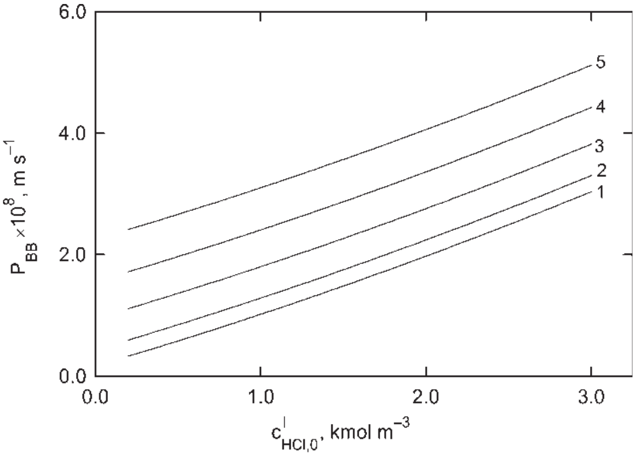

Figure 13. Dependence of coefficient P_{BB} upon initial acid concentration in compartment I. Parameter of individual lines is the same as that in Fig. 10.

Fig. 12. It is about four orders of magnitude lower than the coefficients discussed before, i.e. P_A, P_{AA} and P_{AB}. This coefficient is negatively influenced by increasing initial acid concentration of nickel chloride, while the dependence $P_{BA} = f(c^I_{A0})$ at a constant c^I_{B0} shows a maximum at the initial acid concentration of 1.63 kmol m^{-3}. The coeficient P_{BA} with the coeffcient P_{BB}, which is approx. two orders of magnitude higher than P_{BA} (see Fig. 13), indicate very low flux of nickel chloride through the Neosepta-AFN membrane. As the concentration differences of both the acid and the salt are of the same order of magnitude, the coefficient P_{BB} plays a dominant role in the transport of nickel chloride through the membrane. The last phenomenological coefficient P_{BB} increases with increasing initial concentrations of both the acid and the salt, so the $NiCl_2$ flux increases with increasing initial acid and salt concentrations in compartment I. This conclusion is in a qualitative accordance with the graphical presentations given in Fig. 5.

CONCLUSION

Simultaneous transport of hydrochloric acid and nickel chloride through the anion-exchange membrane Neosepta-AFN (Tokuyama Soda Co., Japan) was investigated using a two-compartment cell with stirrers. The following parameters characterizing the separation process were determined from the time dependences of acid and salt concentrations in the compartment initially filled with distilled water: the partial flux of nickel chloride at a reference time $\tau = 0$ and permeability of the membrane based on four phenomenlogical coefficients in analogy with the description of diffusion in ternary mixtures. The results obtained showed that the Neosepta-AFN membrane can be considered a good separator for $HCl + NiCl_2$ mixture.

SYMBOLS

A	membrane area, m^2
$A_{ij,1}$	(i = A, B; j = A, B) constants in Eq. (20), $m^3\ kmol^{-1}$
$A_{ij,2}$	(i = A, B; j = A, B) constants in Eq. (20), $m^6\ kmol^{-2}$
$A_{ij,3}$	(i = A, B; j = A, B) constants in Eq. (20), $m^3\ kmol^{-1}$
$A_{ij,4}$	(i = A, B; j = A, B) constants in Eq. (20), $m^6\ kmol^{-2}$
a	constant in Eq. (3), s $kmol^{-1}$
a_0	constant in Eq. (17), m s^{-1}
a_1	constant in Eq. (17), $m^4\ s^{-1}\ kmol^{-1}$
a_2	constant in Eq. (17), $m^7\ s^{-1}\ kmol^{-2}$
B	constant in Eq. (4), kmol $m^{-3}\ s^{-1}$
b	constant in Eq. (3), $kmol^{-1}$
c	molar concentration, kmol m^{-3}
F	objective function

f	general function
ΔH_r	reaction enthalpy, kJ $kmol^{-1}$
I	ionic strength, kmol m^{-3}
J	molar flux, kmol m^{-2} s^{-1}
$\bar{J}$	partial flux, %
n	amount of component, kmol
n	rotational speed of stirrer, s^{-1}
P	permeability of membrane, m s^{-1}
P_{ij}	(i = A, B; j = A, B) phenomenological coefficients, m s^{-1}
$P_{ij,0}$	(i = A, B; j = A, B) constants in Eqs (20), m s^{-1}
V	volume, m^3
β_1	complexity constant
τ	time, s
[ ]	actual concentration, kmol m^{-3} (in Eq. (6) dimensionless)

Superscripts and Subscripts

A	referred to component A
B	referred to component B
Cl^-	referred to chlorides
f	referred to solution/membrane interface
HCl	referred to hydrochloric acid
$NiCl_2$	referred to nickel chloride
I, *II*	referred to compartment I and II, resp.
0	referred to time $\tau = 0$

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