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Modeling of continuous diffusion dialysis of aqueous solutions of sulphuric acid and nickel sulphate

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Abstract. At steady state, the simultaneous transport of sulphuric acid and nickel sulphate through an anion-exchange membrane Neosepta-AFN (Astom Corporation, Tokyo, Japan) was investigated in a two-compartment counter-current dialyzer with single passes. The transport was quantified by the recovery yield of acid, rejection of salt and four phenomenological coefficients, which were correlated with the acid and salt concentrations in the feed. The phenomenological coefficients were determined by the numerical integration of the basic differential equations describing the concentration profiles of the components in the dialyzer. This integration was combined with an optimizing procedure. The experiments proved that the acid recovery yield is in the limits from 63 to 91 %, while salt rejection is in the limits from 79 to 97 % in the dependence on the volumetric liquid flow rate and composition of the feed.

Keywords: dialysis; anion-exchange membrane; sulphuric acid; nickel sulphate; continuous dialyzer

1. Introduction

Polymeric anion-exchange membranes are utilized to recover acids with the process commonly referred to as diffusion dialysis. Generally, diffusion dialysis techniques are used to remove metal contamination from concentrated solutions. The process units are an alternative for the conventional industrial wastewater treatment and discharge of strongly acidic and basic solutions used in metal preparation processes. At present, diffusion dialysis is intensively studied by many researchers to obtain basic transport characteristics of systems consisting of membranes and solutions to be treated.

Narębska and Warszawski (1992) examined selected anion-exchange membranes to highlight the relationship between the membrane composition and the ability to separate acid + salt mixtures by diffusion dialysis. Elmidaoui *et al.* (1995), which studied the competitive transport between sulphuric acid and sodium and zinc sulphates, found that the presence of sodium and zinc sulphates in solutions dialyzed had no significant effect on the acid flux. Narębska and Staniszewski (1997) used Neosepta-AFN and Selemion DSV membranes to separate lactic acid from sodium lactate. Effects of metal ions on diffusion dialysis of inorganic acids (HCl, H_2SO_4, HNO_3) in a continuous dialyzer was investigated by Oh *et al.* (2000). Out of five metals studied, Fe, Ni, Cr and Cu were reasonably rejected by anion-exchange membrane, while Zn in HCl leaked through the membrane significantly. In the case of the H_2SO_4 + $NiSO_4$ system (3.96 M H_2SO_4, 2.56×10^{-2} – 17.0×10^{-2} M Ni), the nickel leakage was less than 2 %, while the acid recovery yield was in the limits from approx. 65 to 72 %.

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Xu and Yang (2001, 2003) presented results on the sulphuric acid recovery from titanium white waste liquor and the recovery of mixed acid (HF + HNO_3) from the titanium spent leaching solution using diffusion dialysis with a series of anion-exchange membranes prepared from poly(2,6-dimethyl-1,4-phenylene oxide) by bromination. Xu and Yang (2004) aimed at the recovery of sulphuric acid and nickel from electrolysis spent liquor with a relatively low acid concentration. They investigated the effect of the surface-cross-linking degree of PPO anion-exchange membranes upon the apparent water osmosis coefficient, the acid recovery ratio and the nickel leakage ratio. In all the experiments, the composition of the feed was constant, i.e., 47 g l^{-1} H_2SO_4 and 72 g l^{-1} Ni. The experiments proved that the best membrane is that cross-linked at least 8 h. Palatý and Žáková (2004a, 2004b, 2006, 2007a) and Palatý and Bendová (2009, 2011a, 2011b, 2011c) published a series of papers dealing with dialysis of acid + salt mixtures in batch and continuous dialyzers. Diffusion dialysis was used to recover H_2SO_4 from waste sulphuric acid solutions in the diamond manufacturing process (Jeong *et al.* 2005). The anion-exchange membranes Neosepta-AFN and Selemion DSV were used in the separation of acetic and propionic acids from their sodium salts by Narębska and Staniszewski (2008). Xu *et al.* (2009a) investigated the recovery of H_2SO_4 from waste anodic aluminium oxidation solutions using the diffusion dialysis process both in a batch and continuous dialyzer equipped with a commercial polymeric membrane DF-120. In their next paper, Xu *et al.* (2009b) presented the results on the recovery of hydrochloric acid from HCl + $FeCl_2$ mixture and real acid waste solution containing hydrochloric acid, Fe^{2+} and Zn^{2+} ions. Wei *et al.* (2010) applied diffusion dialysis to recover sulphuric acid from an acid leach solution produced in the vanadium manufacturing process. New poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-SiO_2 hybrid membranes were synthesized and tested for diffusion dialysis of HCl + $FeCl_2$ model mixtures by Luo *et al.* (2010). The same authors (Luo *et al.* 2011a) presented results on diffusion dialysis of various inorganic acids in the presence of their sodium salts, i.e., HCl + NaCl, H_2SO_4 + Na_2SO_4 and H_3PO_4 + Na_3PO_4, in a batch dialyzer. Besides the papers mentioned above, a series of other papers can be found in the extensive review paper published lately (Luo *et al.* 2011b).

In the literature dealing with dialysis of the H_2SO_4 + $NiSO_4$ system (Oh *et al.* 2000, Xu and Yang 2004), one can only find the acid recovery ratio and metal leakage ratio in the limited concentration range — no other quantifying data reflecting the effect of the feed composition on the mass transfer rate are presented. The aim of this paper is to present qualitative and quantitative characteristics of the system mentioned above in broad ranges of the concentrations of both components in the feed.

2. Theory

Fig. 1 depicts the balance scheme of a counter-current continuous dialyzer with two identical compartments I and II, whose cross-section and height are S and z_T, respectively. The feed, which consists of sulphuric acid (component A) and nickel sulphate (component B), enters the bottom of compartment I, while the stripping agent (distilled water) enters the top of compartment II. Under these conditions, the transport of the components in the direction from compartment I to compartment II takes place. At steady state, the basic differential equations (Eq. (1)) describing the concentration profiles of both the components in the individual compartments can be derived from the balances of each component over the differential volumes $S\mathrm{d}z$ in compartments I and II

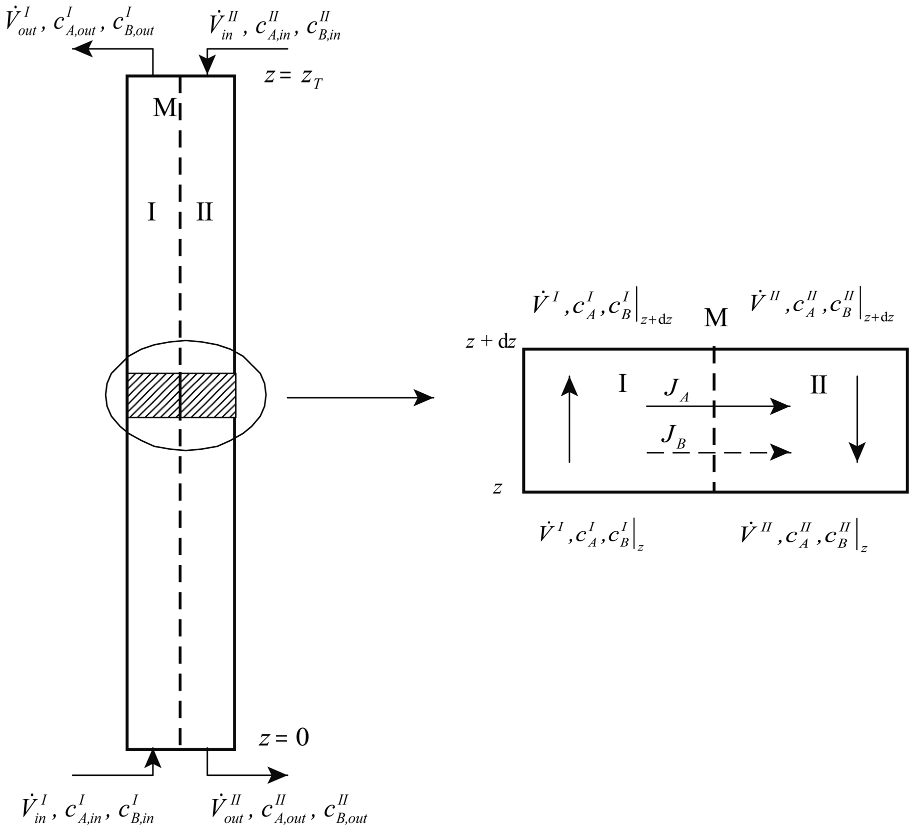

Fig. 1 Balance scheme of counter-current continuous dialyzer

$$\frac{\mathrm{d}c_i^j}{\mathrm{d}z} = -J_i \frac{A}{\dot{V}^j z_T} - \frac{c_i^j}{\dot{V}^j} \frac{\mathrm{d}\dot{V}^j}{\mathrm{d}z} \qquad i = A, B; j = I, II \tag{1}$$

In Eq. (1), c_i is the molar concentration of component i ($i = A$, B), z is the length coordinate, J_i is the flux of the component through the membrane, A is the membrane area and $\dot{V}$ is the volumetric flow rate of liquid. The superscript j ($j = I$, II) indicates the compartment.

The initial conditions for Eq. (1) are

$$z = 0 \quad c_i^I = c_{i,\,in}^I \quad c_i^{II} = c_{i,out}^{II} \quad i = A, B \tag{2}$$

where subscripts *in* and *out* mean the inlet and outlet, respectively.

In ternary mixtures consisting of component A, component B and solvent, the diffusion flux of one component is affected not only by its own concentration gradient but also by the concentration gradient of other component. Based on this fact, a phenomenological correlation represented by Eqs. (3) and (4) was used to describe the flux of each component through the membrane. Here, the concentration gradients are replaced with the concentration differences

$$J_A = P_{AA}(c_{Af}^I - c_{Af}^{II}) + P_{AB}(c_{Bf}^I - c_{Bf}^{II}) \tag{3}$$

$$J_B = P_{BA}(c^I_{Af} - c^{II}_{Af}) + P_{BB}(c^I_{Bf} - c^{II}_{Bf}) \tag{4}$$

In Eqs. (3) and (4), P_{ij} ($i = A, B$; $j = A, B$) are the phenomenological coefficients and subscript f means the solution/membrane interface.

The phenomenological coefficients are complex functions of the component concentrations. For simplicity, the following approximations were suggested

$$P_{ij} = P_{ij,0}[1 + A_{ij,1}c^I_{A,in} + A_{ij,2}(c^I_{A,in})^2 + A_{ij,3}c^I_{B,in} + A_{ij,4}(c^I_{B,in})^2] \quad i = A, B; j = A, B \tag{5}$$

The forms of Eq. (5) are supported by the fact that — in the case of a batch dialyzer — not only the permeability coefficients of the membrane but also the phenomenological coefficients P_{ij} ($i = A$, B; $j = A$, B) are functions of the initial acid and salt concentrations in the compartment initially filled with a solution containing acid and salt (Palatý and Žáková 2007).

The total number of the constants in Eq. (5) is 20. Fortunately, the constants $P_{AA,0}$, $A_{AA,1}$, $A_{AA,2}$ (they concern sulphuric acid), $P_{BB,0}$, $A_{BB,3}$ and $A_{BB,4}$ (they concern nickel sulphate) can be obtained from independent dialysis experiments with only one component.

Due to low liquid rates in both the compartment of the dialyzer the mass transfer resistances in liquid films must be considered, i.e., the component concentrations in liquid at the solution/membrane interfaces can not be replaced with the bulk concentrations. In order to determine the concentrations c^j_{if} ($i = A$, B; $j = I$, II), mass transfer in the membrane must be solved simultaneously with that in the liquid films (see Fig. 2). For simplicity, it is supposed that both the components are transported through the liquid films independently. This simplification, which is in the contradiction with the fact above mentioned, does not cause large errors in the final results because the mass transfer resistance in the membrane is much higher than those in the liquid films. For known component concentrations in the bulk solutions, the component concentrations in liquid at the solution/membrane interfaces can be obtained by solving Eqs. (3) and (4), to which the following equations are added

$$J_A = k^I_{LA}(c^I_A - c^I_{Af}) \tag{6}$$

$$J_A = k^{II}_{LA}(c^{II}_{Af} - c^{II}_A) \tag{7}$$

$$J_B = k^I_{LB}(c^I_B - c^I_{Bf}) \tag{8}$$

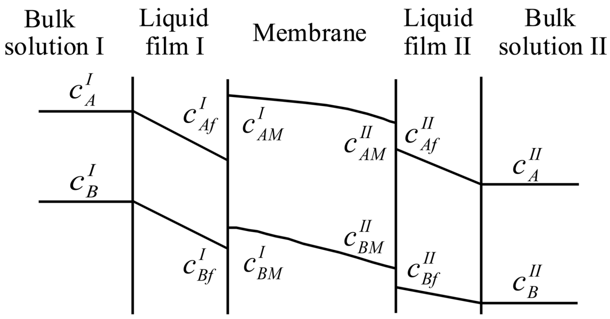

Fig. 2 Concentration profiles of acid (A) and salt (B) in membrane and liquid films

$$J_B = k_{LB}^{II}(c_{Bf}^{II} - c_B^{II}) \tag{9}$$

Mass transfer coefficients, k_{Li}^{j} ($i = A, B$; $j = I, II$), in Eqs. (6) – (9) can be estimated from the following equation

$$Sh = CRe^{0.5}Sc^{0.33} \tag{10}$$

where Sh is the Sherwood number, C is a constant, Re is the Reynolds number and Sc is the Schmidt number. Moreover, according to the film theory, the mass transfer coefficients of the individual components are interrelated with the following relation

$$k_{LB}^{j} = k_{LA}^{j}\frac{D_B}{D_A} \quad j = I, II \tag{11}$$

where D_i is the diffusion coefficient of component i ($i = A, B$).

In the experiments performed with a continuous dialyzer, the volumetric flow rates and concentrations of both the components in the streams entering and leaving the dialyzer are known. Under these conditions, the basic differential equations (Eq. (1)) can be numerically integrated. If this integration is followed by an optimizing procedure searching for a minimum of a suitable objective function, the coefficients $P_{ij,0}$, $A_{ij,k}$ ($i = A, B$; $j = A, B$; $k = 1, 2, ... 4$) can be determined.

3. Experimental

The simultaneous transport of sulphuric acid and nickel sulphate was investigated in a two-compartment counter-current dialyzer with single passes. The compartments were separated by an anion-exchange membrane Neosepta-AFN (Astom Corporation, Tokyo, Japan), whose area was 331 cm^2. The dimensions (height × width × thickness) of two identical compartments were 0.92 m × 0.036 m × 0.0011 m. The thickness of the compartments was adjusted with net-type spacers made of PVC. The dialyzer was placed in a Plexiglas® box, where the temperature was kept constant — 25.0 ± 0.5 °C. The description of the set-up used including the experiments is given in detail elsewhere (Palatý *et al.* 2007, 2008, Palatý and Bendová 2011a).

Both the acid and salt concentrations in the feed were changed in the limits from 0.1 to 1.0 kmol m^{-3}. The volumetric liquid flow rates of the feed and stripping agent (distilled water) were in the limits from 8×10^{-9} to 24×10^{-9} $\text{m}^3\ \text{s}^{-1}$. Beside the dialysis experiments with $H_2SO_4 + NiSO_4$ solutions, also experiments with $NiSO_4$ solutions were carried out. The concentration of sulphuric acid was determined by titration with a standard NaOH solution, while that of nickel sulphate was determined in the same way using a standard EDTA solution.

4. Data treatment and discussion

4.1 Acid recovery yield and rejection of salt

The acid recovery yield, R_A, and rejection of salt, R_B, can be used to preliminary evaluate the separation of liquid mixtures containing acid and salt

$$R_A = \frac{\dot{V}^I_{in} c^I_{A,in} - \dot{V}^I_{out} c^I_{A,out}}{\dot{V}^I_{in} c^I_{A,in}} \times 100 = \frac{\dot{V}^{II}_{out} c^{II}_{A,out}}{\dot{V}^I_{in} c^I_{A,in}} \times 100 \quad (12)$$

$$R_B = \frac{\dot{V}^I_{in} c^I_{B,in} - \dot{V}^{II}_{out} c^{II}_{B,out}}{\dot{V}^I_{in} c^I_{B,in}} \times 100 \quad (13)$$

The dependences of the acid recovery yield upon the volumetric liquid flow rate of the feed are presented in Figs. 3 and 4. Fig. 3 concerns the lowest acid concentration, i.e., 0.1 kmol m^{-3}, while Fig. 4 concerns the highest acid concentration in the feed, i.e., 1.0 kmol m^{-3}. The salt concentrations

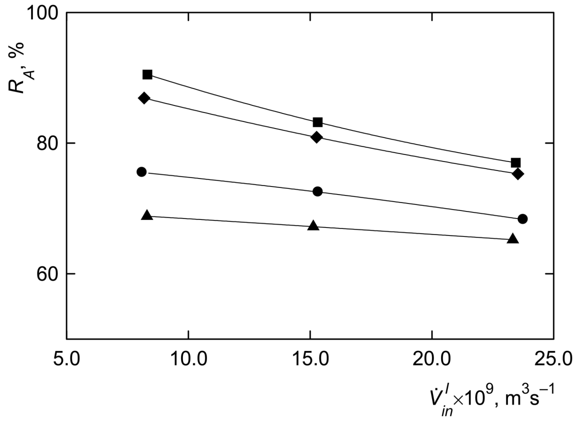

Fig. 3 Dependence of acid recovery yield upon volumetric liquid flow rate of feed for acid concentration of 0.1 kmol m^{-3}: $c^I_{B,in}$ [kmol m^{-3}] : ■ – 0.0; ◆ – 0.1; ● – 0.5; ▲ – 1.0

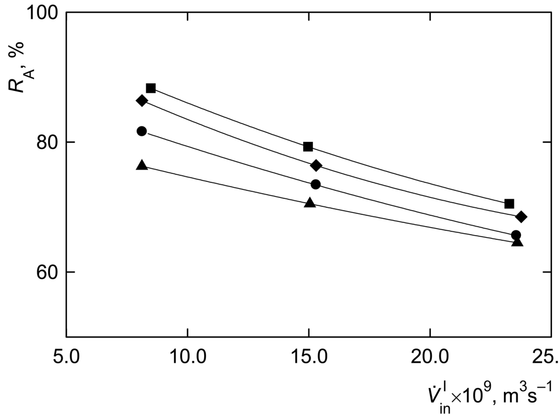

Fig. 4 Dependence of acid recovery yield upon volumetric liquid flow rate of feed for acid concentration of 1.0 kmol m^{-3}: For meaning of symbols, see Fig. 3

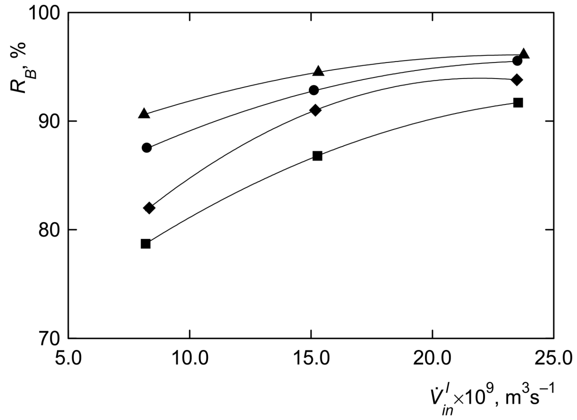

Fig. 5 Dependence of rejection of salt upon volumetric liquid flow rate of feed for salt concentration of 0.1 kmol m^{-3}: $c^I_{A,in}$ [kmol m^{-3}] : ■ – 0.1; ◆ – 0.2; ● – 0.5; ▲ – 1.0

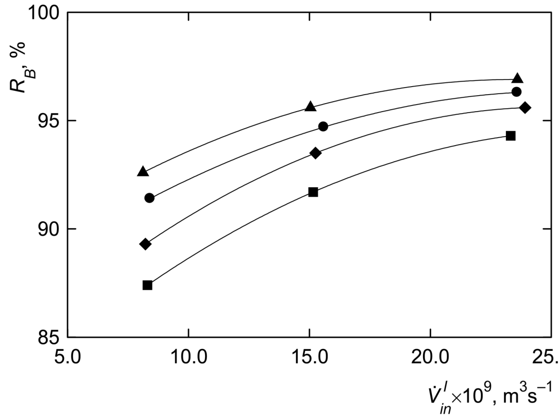

Fig. 6 Dependence of rejection coefficient of salt upon volumetric liquid flow rate of feed for salt concentration of 1.0 kmol m^{-3}. For meaning of symbols, see Fig. 5

in the feed are the parameters of the individual lines. From these graphical presentations it is evident that the acid recovery yield decreases with the increasing volumetric flow rate of the feed. Moreover, the separation ability of the membrane is negatively influenced by the increasing salt concentration in the feed. The recovery yield of acid is in the limits from 63 % to 91 % as found experimentally.

In Figs. 5 and 6, the rejection of salt is plotted against the volumetric flow rate of the feed for the lowest (Fig. 5) and highest (Fig. 6) salt concentration in the feed. In both the cases, the sulphuric acid concentrations in the feed are the parameters of the individual dependences. From the dependences presented it can be seen that the salt rejection increases with the increasing volumetric flow rate and the acid concentration in the feed. Moreover, the rejection of salt is somewhat higher if the salt content in the feed is increased. It was proved experimentally that the salt rejection is in the limits from 79 % to 97 %.

4.2 Permeability of membrane for acid + salt mixture

If acid and salt are simultaneously transported through the membrane, then the permeability of the membrane can be quantified by four phenomenological coefficients, whose dependences upon the acid and salt concentrations in the feed are approximated by polynomials (5). As the cofficients $P_{AA,0}$, $A_{AA,1}$ and $A_{AA,2}$ are available in the literature (Palatý and Bendová, 2011a, 2011b) ($P_{AA,0}$ = 3.126×10^{-6} m s^{-1}; $A_{AA,1}$ = –1.005 m^3 kmol^{-1}; $A_{AA,2}$ = 0.537 m^6 kmol^{-2}), the following procedure is used to determine the remaining coefficients. It consists of two steps:

(i) the determination of coefficients $P_{BB,0}$, $A_{BB,3}$ and $A_{BB,4}$;

(ii) the determination of coefficients $A_{AA,3}$, $A_{AA,4}$, $P_{AB,0}$, $A_{AB,k}$ (k = 1, 2, ..., 4), $P_{BA,0}$, $A_{BA,k}$ (k = 1, 2, ..., 4), $A_{BB,1}$ and $A_{BB,2}$.

In order to calculate the coefficients $P_{BB,0}$, $A_{BB,3}$ and $A_{BB,4}$, the basic differential equation (Eq. 1)) for $i = B$, in which the salt flux, J_B, is expressed by Eq. (4) for $P_{BA} = 0$ and $c^{I}_{A,in} = 0$, is numerically integrated. For this purpose, the fourth order Runge–Kutta method is used. In such a way, the calculated salt concentrations in the streams leaving compartment I and entering compartment II are obtained, i.e., $c^{I,calc}_{B,out}$ and $c^{II,calc}_{B,in}$. The numerical integration is combined with an optimizing procedure, which searches for a minimum of the objective function (14), the simplex method by Nelder and Mead being used.

$$F(P_{BB,0}, A_{BB,3}, A_{BB,4}, C) = \sum_{k=1}^{n} \left[\left(\frac{c_{B,out}^{I,k,exp} - c_{B,out}^{I,k,calc}}{c_{B,out}^{I,k,exp}} \right)^2 + (c_{B,in}^{II,k,calc})^2 \right] \tag{14}$$

In Eq. (14), n is the number of the experimental points.

The salt concentrations in liquid at the solution/membrane interfaces, i.e., c^{I}_{Bf} and c^{II}_{Bf}, must be known to calculate the flux of nickel sulphate through the membrane. These concentrations are obtained by solving the set of Eqs. (4), (8) and (9). Physico-chemical data (density and viscosity), which are needed in the calculation of the liquid mass transfer coefficients, are taken from literature (Andrussow and Schramm 1969). As no data on diffusivity of $NiSO_4$ are found, diffusivity of $CuSO_4$ is used in the calculation of k^{j}_{LB} ($j = I, II$).

In order to determine the coefficients $A_{AA,3}$, $A_{AA,4}$, $P_{AB,0}$, $A_{AB,k}$ (k = 1, 2, ..., 4), $P_{BA,0}$, $A_{BA,k}$ (k = 1, 2, ..., 4), $A_{BB,1}$ and $A_{BB,2}$, the procedure described above is modified and used. The modifications are as follows:

(i) the concentrations of both the components in liquid at the solution/membrane interfaces are obtained by solving the set of Eqs. (3), (4) and (6) – (9);

(ii) the fluxes of sulphuric acid and nickel sulphate are calculated from Eqs. (3) and (4) without simplification;

(iii) the mass transfer coefficient in liquid for H_2SO_4 is calculated from Eq. (10), while that for $NiSO_4$ is calculated from Eq. (11);

(iv) the physico-chemical properties of the H_2SO_4 + $NiSO_4$ solutions are determined experimentally;

(v) the objective function is based on the concentrations of both the components, i.e.,

$$F=\sum_{i=A}^{B}\sum_{k=1}^{n}\left[\left(\frac{c_{i,out}^{I,k,exp}-c_{i,out}^{I,k,calc}}{c_{i,out}^{I,k,exp}}\right)^2+\left(c_{i,in}^{II,k,calc}\right)^2\right] \tag{15}$$

(Note: The objective function depends on the coefficients $A_{AA,3}$, $A_{AA,4}$, $P_{AB,0}$, $A_{AB,k}$ (k = 1, 2, ..., 4), $P_{BA,0}$, $A_{BA,k}$ (k = 1, 2, ..., 4), $A_{BB,1}$ and $A_{BB,2}$, and constant C in Eq. (10).)

In order to verify the procedure used, the calculated concentrations of sulphuric acid and nickel sulphate in the streams leaving compartment I are plotted against the experimental concentrations in Fig. 7. This graphical presentation reveals that there is a good agreement between the calculated and experimental concentrations. Based on these findings, it can be stated that the model represented by Eqs. (1) – (11) is adequate.

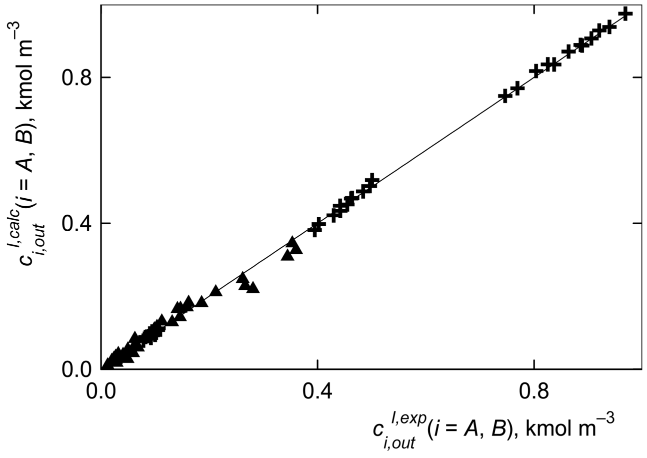

Fig. 7 Comparison of experimental and calculated concentrations of sulphuric acid (▲) and nickel sulphate (+)

Table 1 Coefficients of polynomials (5)

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}	3.126×10^{-6}*)	–1.005*)	0.537*)	0.141	–8.353×10^{-2}
P_{AB}	–3.908×10^{-9}	22.45	–20.87	44.85	–36.03
P_{BA}	–5.283×10^{-7}	–2.772	1.798	0.424	–0.438
P_{BB}	1.361×10^{-7}	–0.848	0.539	–0.944	0.403

*) Taken from literature (Palatý and Bendová 2011a, 2011b)

The constant C in Eq. (10) is determined simultaneously with the constants in Eq. (5). The following values are obtained: $C = 0.430$ for nickel sulphate and $C = 1.862$ for the $H_2SO_4 + NiSO_4$ mixture.

The determined coefficients $A_{AA,3}$, $A_{AA,4}$, $P_{AB,0}$, $A_{AB,k}$ ($k = 1, 2, ..., 4$), $P_{BA,0}$, $A_{BA,k}$ ($k = 1, 2, ..., 4$), $A_{BB,1}$ and $A_{BB,2}$ are summarized in Table 1. Moreover, the phenomenological coefficients P_{ij} ($i = A, B$; $j = A, B$) are presented in Figs. 8 – 12.

Fig. 8 shows the dependence of the permeability coefficient of the membrane for nickel sulphate upon the salt concentration in the feed. In addition, the dependence of the permeability coefficient for sulphuric acid calculated from the data taken from literature (Palatý and Bendová 2011a, 2011b), is presented here. The comparison of both the dependences reveals that the permeability of the anion-exchange membrane Neosepta-AFN for $NiSO_4$ is about one order of magnitude lower than that for sulphuric acid. Both these quantities decrease with the increasing component concentration

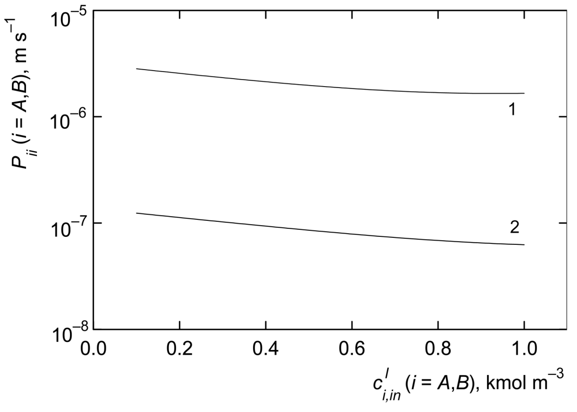

Fig. 8 Dependence of permeability coefficient of membrane for H_2SO_4 (1) and $NiSO_4$ (2) upon acid and salt concentration in feed

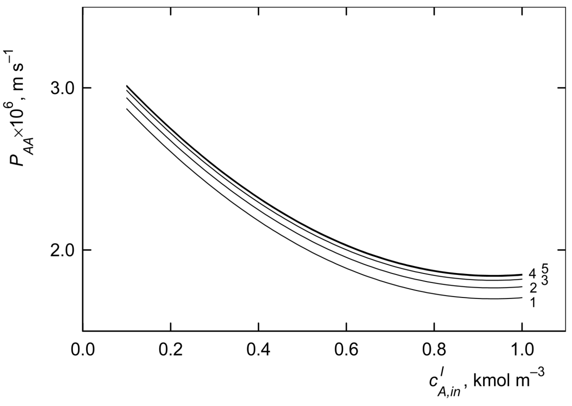

Fig. 9 Dependence of phenomenological coefficient P_{AA} upon acid concentration in feed. $c^I_{B,in}$ [kmol m^{-3}]: 1 – 0.1; 2 – 0.3; 3 – 0.5; 4 – 0.7, 1,0; 5 – 0.9

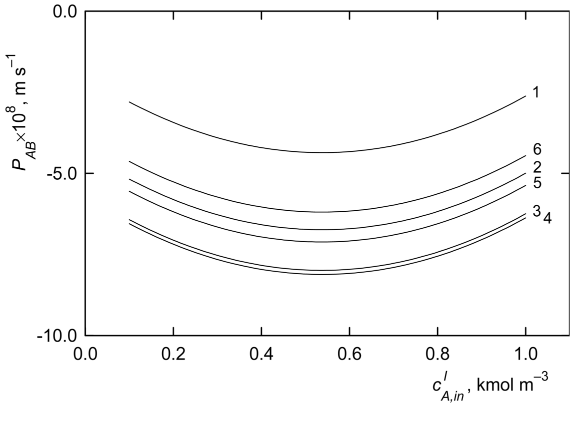

Fig. 10 Dependence of phenomenological coefficient P_{AB} upon acid concentration in feed. $c^I_{B,in}$ [kmol m^{-3}]: 1 – 0.1; 2 – 0.3; 3 – 0.5; 4 – 0.7; 5 – 0.9; 6 – 1.0

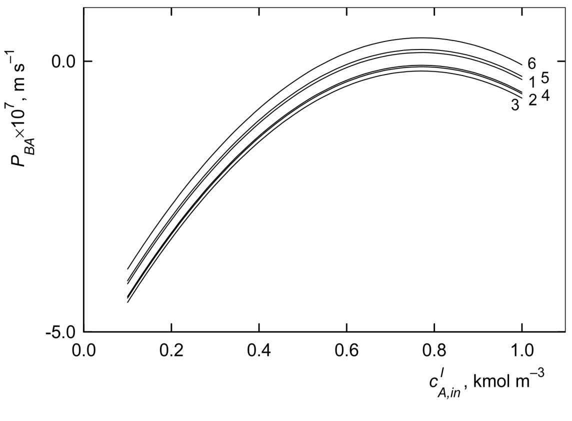

Fig. 11 Dependence of phenomenological coefficient P_{BA} upon acid concentration in feed. Parameters of individual curves are the same as those in Fig. 10

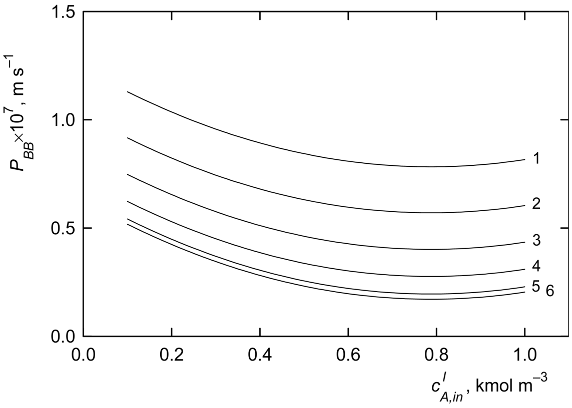

Fig. 12 Dependence of phenomenological coefficient P_{BB} upon acid concentration in feed. Parameters of individual curves are the same as those in Fig. 10

in the feed. Figs. 9 – 12 present the dependences of the phenomenological coefficients upon the sulphuric acid concentration in the feed. In all these figures, the nickel sulphate concentrations in the feed are the parameters of the individual dependences. The phenomenological coefficient P_{AA}, which is presented in Fig. 9, is of the same order of magnitude as the permeability coefficient of the Neosepta-AFN membrane for sulphuric acid. It can be found in the limits from 1.698×10^{-6} to 3.015×10^{-6} m s^{-1}. On the dependence $P_{AA} = f(c^I_{A,in})$, a weak minimum at the acid concentration of 0.936 kmol m^{-3} can be identified, while on the dependence $P_{AA} = f(c^I_{B,in})$ a maximum at the salt concentration of 0.846 kmol m^{-3} exists. The first coordinates of both the extremes can be determined from the coefficients in Table 1. The flux of sulphuric acid through the membrane is negatively influenced by the difference of the salt concentrations on both sides of the membrane as it follows from the values of the phenomenological coefficient P_{AB} (Fig. 10) — this coefficient is less than zero throughout the concentration range investigated. First, the coefficient P_{AB} gradually decreases with the increasing acid concentration and after reaching a minimum at the acid concentration of 0.537 kmol m^{-3} it increases. The sequence of the individual curves in Fig. 10 indicates a minimum on the dependence $P_{AB} = f(c^I_{B,in})$, whose first coordinate is 0.622 — as determined from coefficients in Table 1. The phenomenological coefficient P_{BA}, which quantifies the effect of the concentration difference of sulphuric acid on the flux of nickel sulphate, is mostly less than zero (Fig. 11). This coefficient can be found in the limits from -4.456×10^{-7} to 4.345×10^{-8} m s^{-1}. First, the dependence $P_{BA} = f(c^I_{A,in})$ follows an increasing trend and then goes through a maximum at the acid concentration of 0.771 kmol m^{-3}. On the other hand, on the dependence $P_{BA} = f(c^I_{B,in})$ a minimum at the salt concentration of 0.484 kmol m^{-3} exists. The last phenomenological coefficient P_{BB} (Fig. 12) is of the same order of magnitude as the coefficient P_{AA} — but it is somewhat lower than the coefficient P_{AA}. As seen from the dependences in Fig. 12, this coefficient decreases with the increasing acid concentration in the feed and goes through a minimum at the acid concentration of 0.787 kmol m^{-3}. The values of the coefficients $A_{AA,3}$ and $A_{AA,4}$ given in Table 1 reveal that also on the dependence $P_{BB} = f(c^I_{B,in})$ a minimum exists — it is out of the concentration range investigated.

All the dependences presented in Figs. 9 – 12 are qualitatively very similar to those found in the case of dialysis of H_2SO_4 + $ZnSO_4$ solutions (Palatý and Bendová 2011b).

Note: During dialysis, changes in the volumetric flow rates — as a concequence of osmotic flow of water — were observed. They were dependent upon the volumetric flow rate and composition of the feed. The maximum change was about 16 %. The phenomenological coefficients implicitely reflect these facts as the volume changes were considered in their calculation — see the second terms in Eq. (1).

5. Conclusions

Diffusion dialysis of aqueous solutions of sulphuric acid and nickel sulphate was investigated in a two-compartment counter current dialyzer at steady state. For this purpose, an anion-exchange membrane Neosepta-AFN was used. Experiments proved that sulphuric acid permeates well through this membrane, while nickel sulphate is reasonable rejected. The separation process was quantified by the acid recovery yield, salt rejection and four phenomenological coefficients, which are dependent upon the acid and salt concentrations in the feed.

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Symbols

A	membrane area, m^2
$A_{ij,k}$	($i = A,B$; $j = A,B$; k = 1, 3) coefficients in Eq. (5), m^3 $kmol^{-1}$
$A_{ij,k}$	($i = A,B$; $j = A,B$; k = 2, 4) coefficients in Eq. (5), m^6 $kmol^{-2}$
C	constant in Eq. (10)
c	molar concentration, kmol m^{-3}
D	diffusivity, m^2 s^{-1}
d_c	width of compartment, m
d_e	($= 2d_c\delta_c/(d_c + \delta_c)$) equivalent diameter, m
F	objective function
f	general function
J	flux, kmol m^{-2} s^{-1}
k_L	liquid mass transfer coefficient, m s^{-1}
n	number of experimental points
P_{ij}	($i = A,B$; $j = A,B$) phenomenological coefficients, m s^{-1}

$P_{ij,0}$	($i = A,B$; $j = A,B$) coefficients in Eqs (5), m s^{-1}
R_A	acid recovery yield, %
R_B	rejection of salt, %
Re	($= ud_e/\nu$) Reynolds number
S	cross-section of compartment, m^2
Sc	(ν/D) Schmidt number
Sh	($= k_L d_e/D$) Sherwood number
u	($= \dot{V}/S$) liquid flow rate, m s^{-1}
$\dot{V}$	volumetric liquid flow rate, m^3 s^{-1}
z	length coordinate, m
z_T	total height of compartment, m
δ_c	thickness of compartment, m
ν	kinematic viscosity, m^2 s^{-1}

Superscripts and subscripts

A	referred to component A, i.e., H_2SO_4
B	referred to component B, i.e., $NiSO_4$
calc	calculated
exp	experimental
f	solution/membrane interface
i	referred to component *i*
in	inlet
out	outlet
I	referred to compartment I
II	referred to compartment II