

Continuous dialysis of mixture of inorganic acids

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Abstract

The simultaneous transport of sulphuric and phosphoric acids through a polymeric membrane was investigated at steady state in a two-compartment counter-current dialyzer. For this purpose, an anion-exchange membrane Neosepta-AFN (Astom Corporation, Tokyo, Japan) was used. This transport was quantified by four membrane mass transfer coefficients which are dependent upon the concentrations of both acids in the feed. These coefficients were determined by a two-step procedure. In the first step, the basic differential equations describing the dependences of the volumetric liquid flow rates and acid concentrations on the length coordinate in the individual compartments were numerically integrated. In the second step, an objective function was minimised to ensure the best coincidence between the experimental and calculated data.

Keywords: Diffusion dialysis, Anion-exchange membrane, Sulphuric acid, Phosphoric acid, Continuous dialyzer

1. Introduction

Diffusion dialysis, which belongs to a group of promising separation processes, is preferably used to recover inorganic acids from acid waste waters generated in steel, metal-refining and electroplating industries. Its main advantage is a high acid recovery yield, high rejection of metals, low environmental impact and low consumption of energy. The only energy is that ensuring the transport of liquid streams into a dialyzer. On the other hand, diffusion dialysis is a very slow process due to the fact that its controlling step is the transport of components through the membrane by diffusion.

In order to determine process characteristics, two types of equipment are used, i.e., a batch cell [1-10] and continuous dialyzer [11-20]. In the former case, the data on time dependences of the liquid volumes and component concentrations in the individual compartments are treated, while in the latter case, the characteristics are calculated from the volumetric liquid flow rates and concentrations of all streams at steady state.

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 [1]. Xu and Yang [2] prepared a series of anion-exchange membranes from poly(2,6-dimethyl-1,4-phenylene oxide) by bromination, chloromethylation and amination, which were used in the recovery of sulphuric acid from titanium white waste liquor. Palatý and Bendová [3] reported on the separation of aqueous solutions of HCl+FeCl₂ by an anion-exchange membrane Neosepta-AFN. The experiments revealed that this membrane is a good separator for HCl+FeCl₂ mixture — ferrous chloride was efficiently rejected while hydrochloric acid passed well through the membrane. Xu *et al.* [4] investigated the recovery of H₂SO₄ 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. Recently [5], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)-SiO₂ hybrid membranes were synthesised and successfully used in the recovery of hydrochloric acid from its mixture with ferrous chloride. The experiments in a batch cell proved that the separation factor of commercial polymeric membrane DF-120 was much lower than that of hybrid membrane. In literature [6], the same research group presented results on diffusion dialysis of different inorganic acids in the presence of their sodium salts, i.e., HCl+NaCl, H₂SO₄+Na₂SO₄ and H₃PO₄+Na₃PO₄ in a batch dialyzer. For this purpose, a novel

organic/inorganic hybrid membrane was used. The simultaneous transport of nitric acid and sodium nitrate was investigated in a batch cell by Palatý and Bendová [7]. In this paper, the transport of the individual components was quantified by four concentration dependent phenomenological coefficients. Wang *et al.* [8] prepared and tested polyelectrolyte complexes/polyvinyl alcohol membranes. Authors proved that these membranes can be applied for both acid and alkali recovery through the diffusion dialysis process. Luo *et al.* [9] investigated diffusion dialysis of hydrochloric acid in the presence of their different metal salts (systems: HCl+NaCl, HCl+FeCl₂, HCl+NiCl₂, HCl+CuCl₂, HCl+ZnCl₂, and HCl+AlCl₃) using a novel organic/inorganic hybrid membrane. Erosion effects of HCl+FeCl₂ solutions on the membrane structure during the diffusion dialysis process were investigated by Mao *et al.* [10]. The tests were carried out with commercial membranes DF-120 and 9010, and the membranes based on quaternised poly(2,6-dimethyl-1,4-phenylene oxide and polyvinyl alcohol. Oh *et al.* [11] experimentally studied diffusion dialysis to investigate the effect of metal ions on its performance for recovery of acids. It was found that formation of complexes affected the selectivity of this separation due to the existence of complexes bearing negative charges. Xu and Yang [12] experimentally proved that mixed acid (HNO₃+HF) can selectively be separated from the spent liquor containing mainly HNO₃, HF and titanium ions by diffusion dialysis. The results showed that this separation is strongly affected by the membrane water content and ion-exchange capacity. Another experiments with surface cross-linked PPO anion-exchange membranes used in the recovery of sulphuric acid and nickel from electrolysis spent liquor proved that nickel leakage can be controlled within 4 %, whereas the recovery of acid can reach 66-72 % [13]. Literature [14] presents the results on the recovery of hydrochloric acid from HCl+FeCl₂ mixture and real acid waste solution containing hydrochloric acid, Fe²⁺ and Zn²⁺ ions. In the case of real solution, it was proved that the acid recovery yield was higher than 88 %, while that of Fe²⁺ ions was in the limits from 11 % to 23 %. On the other hand, a high leakage of Zn²⁺ ions through the membrane was observed, i.e., over 56 %. Wei *et al.* [15] studied the recovery of sulphuric acid from model solutions (H₂SO₄ + FeSO₄, H₂SO₄ + VOSO₄) and a real acid solution, which is generated from a black shale pressure acid leaching process in the extraction of vanadium from black shale. It was found that more than 80 % of sulphuric acid can be recovered, while V and Fe are effectively rejected. An economic evaluation proved that an investment can be recovered within 27 months. The results on the recovery of nitric acid from acidic effluents discharged by an electro dialysis plant were published by Lan *et al.* [16]. In the diffusion dialysis experiments, an anion-exchange membrane DF-120 was used, and the effects of the concentrations of nitric acid and metal ions (Li, Na, K, Mg, Ca), and the water to acid flow rate ratio on the performance of the dialysis process were investigated. In a two-compartment counter-current dialyzer with single passes, the transport of sulphuric acid in the presence of magnesium sulphate was studied by Palatý and Bendová [17]. The dialysis process was characterised by the recovery yield of acid and rejection of salt. Moreover, the transport of each component was quantified by phenomenological coefficients. The some characteristics of the dialysis process were used to quantify the simultaneous transport of sulphuric acid and zinc sulphate [18]. Diffusion dialysis with anion-exchange membranes was used to recover sulphuric acid from an acid leaching solution generated in the vanadium producing process [19]. The effects of the liquid flow rates of the feed and stripping agent, the flow rate ratio, and ion concentration on the acid recovery and metal rejection were investigated. Wang *et al.* [20] presented results on dynamic behaviour of a continuous dialyzer. From the breakthrough curves obtained for various acid concentrations (HNO₃, H₂SO₄, H₃PO₄), the sorbed amount of the individual acids in the membrane was then calculated.

Although diffusion dialysis is mainly used for the separation of liquid mixtures containing

inorganic acids and their salts, the aim of this communication is to investigate simultaneous transport of inorganic acids exhibiting different sorption and diffusivities in a polymeric membrane. For this purpose, a model solution of sulphuric and phosphoric acids was used.

2. Theory

Suppose that a ternary mixture (component A, component B and solvent w) is to be dialyzed. The feed enters the bottom of compartment I, while a stripping agent (mostly water) enters the top of compartment II — see Fig. 1. At the steady state, the concentrations of the components in all the streams are constant. These concentrations depend on the length coordinate in the direction of flow. Due to the hydration effects and osmosis, the volumetric liquid flow rates in the individual compartments are also changed. The changes mentioned can be described by the following differential equations as shown earlier [21]

$$\frac{d\dot{V}^j}{dz} = \frac{A}{z_T} \frac{J_A \left(\frac{\partial \rho^j}{\partial c_A^j} - M_A \right) + J_B \left(\frac{\partial \rho^j}{\partial c_B^j} - M_B \right) - u_w \rho_w}{\rho^j - c_A^j \frac{\partial \rho^j}{\partial c_A^j} - c_B^j \frac{\partial \rho^j}{\partial c_B^j}} \quad j = I, II \quad (1)$$

$$\frac{dc_A^j}{dz} = - \frac{A}{z_T} \frac{J_A (\rho^j - c_A^j M_A) - J_B c_A^j M_B + (c_A^j J_B - c_B^j J_A) \frac{\partial \rho^j}{\partial c_B^j} - u_w \rho_w c_A^j}{V^j \left(\rho^j - c_A^j \frac{\partial \rho^j}{\partial c_A^j} - c_B^j \frac{\partial \rho^j}{\partial c_B^j} \right)} \quad j = I, II \quad (2)$$

$$\frac{dc_B^j}{dz} = - \frac{A}{z_T} \frac{J_B (\rho^j - c_B^j M_B) - J_A c_B^j M_A + (c_B^j J_A - c_A^j J_B) \frac{\partial \rho^j}{\partial c_A^j} - u_w \rho_w c_B^j}{V^j \left(\rho^j - c_A^j \frac{\partial \rho^j}{\partial c_A^j} - c_B^j \frac{\partial \rho^j}{\partial c_B^j} \right)} \quad j = I, II \quad (3)$$

In Eqs (1) – (3), \dot{V}^j ($j = I, II$) are the volumetric liquid flow rates, z is the length coordinate, A is the membrane area, z_T is the total height of the compartment, J_i ($i = A, B$) are the component fluxes, ρ^j ($j = I, II$) are densities of liquid which are a function of the molar concentrations of components A and B, c_i^j ($i = A, B; j = I, II$) are the molar concentrations of the components, M_i ($i = A, B$) are the molar masses, and u_w is the velocity of liquid in the membrane. The superscripts I and II mean the compartment, the subscripts A , B and w then denote the components and water, respectively.

The initial conditions of Eqs (1) – (3) are

$$z = 0 \quad \dot{V}^I = \dot{V}_{in}^I \quad \dot{V}^{II} = \dot{V}_{out}^{II} \quad c_A^I = c_{A,in}^I \quad c_A^{II} = c_{A,out}^{II} \quad c_B^I = c_{B,in}^I \quad c_B^{II} = c_{B,out}^{II} \quad (4)$$

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

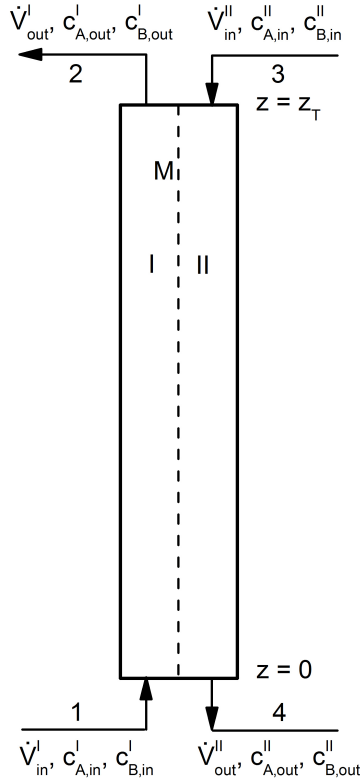


Fig. 1 Scheme of continuous dialyzer: 1 – feed; 2 – dialysate; 3 – stripping agent (water); 4 – diffusate; I – compartment I; II – compartment II; M – membrane

Moreover, the basic differential equations (1) – (3) can also be integrated from $z = z_T$ to $z = 0$. In this case, the right-hand sides of these equations have the opposite signs and the initial conditions are

$$z = z_T \quad \dot{V}^I = \dot{V}_{out}^I \quad \dot{V}^{II} = \dot{V}_{in}^{II} \quad c_A^I = c_{A,out}^I \quad c_A^{II} = c_{A,in}^{II} = 0 \quad c_B^I = c_{B,out}^I \quad c_B^{II} = c_{B,in}^{II} = 0 \quad (5)$$

The fluxes of components A and B, which are needed in the integration of Eqs (1) – (3), are calculated from the following equations

$$J_A = k_{AA}(c_{AM}^I - c_{AM}^{II}) + k_{AB}(c_{BM}^I - c_{BM}^{II}) \quad (6)$$

$$J_B = k_{BA}(c_{AM}^I - c_{AM}^{II}) + k_{BB}(c_{BM}^I - c_{BM}^{II}) \quad (7)$$

where k_{ij} ($i = A, B; j = A, B$) are the membrane mass transfer coefficients defined as ratios of ternary diffusion coefficients in the membrane to the membrane thickness. The subscript M denotes the membrane. These equations represent a phenomenological correlation based on the analogy to diffusion in multicomponent systems, where the flux of one component depends not only on its own concentration gradient but also on the concentration gradients of other components.

In the modelling the dialysis process in a continuous dialyzer, not only the transport of each

component through the membrane but also their transport through liquids films on both the sides of the membrane must be considered — see Fig. 2 in Refs [3,18,22]. Based on the film theory, the fluxes of components A and B can easily be expressed as [3,18,22,23]

$$J_A = k_{LA}^I (c_A^I - c_{Af}^I) \quad (8)$$

$$J_A = k_{LA}^{II} (c_{Af}^{II} - c_A^{II}) \quad (9)$$

$$J_B = k_{LB}^I (c_B^I - c_{Bf}^I) \quad (10)$$

$$J_B = k_{LB}^{II} (c_{Bf}^{II} - c_B^{II}) \quad (11)$$

Contrary to transport of components in the membrane, in the liquid films, it is supposed that each component is transported independently of other. In Eqs (8) – (11), k_{Li}^j ($i = A, B; j = I, II$) are the liquid mass transfer coefficients, subscript f means the solution/membrane interface. The membrane mass transfer coefficients can be estimated from Eq. (12) valid for laminar flow [24]

$$Sh = C Re^{0.5} Sc^{0.33} \quad (12)$$

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 are interrelated with the following equations [23]

$$k_{LB}^j = k_{LA}^j \frac{D_B^j}{D_A^j} \quad j = I, II \quad (13)$$

In Eq. (13), D_i^j ($i = A, B; j = I, II$) are diffusion coefficients.

In order to complete the mathematical model, the equilibrium relations (Eqs (14)) must be added to equations given above

$$c_{iM}^j = \Psi_i^j c_{iM}^j \quad i = A, B; \quad j = I, II \quad (14)$$

The membrane mass transfer coefficients k_{ij} ($i = A, B; j = A, B$) are process characteristics which quantify simultaneous transport of components A and B through the membrane. They are a complex function of the concentrations of both the components. For simplicity, suppose that they are functions of the component concentrations in the feed, e.g.

$$k_{ij} = k_{ij,0} \left[1 + A_{ij,1} c_{A,in}^I + A_{ij,2} (c_{A,in}^I)^2 + A_{ij,3} c_{B,in}^I + A_{ij,4} (c_{B,in}^I)^2 \right] \quad i = A, B; \quad j = A, B \quad (15)$$

The coefficients $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B; k = 1, 2, \dots, 4$) in Eqs (15) can be determined using the procedure consisting of the numerical integration of the basic

differential equations (1) – (3) and a suitable optimisation procedure which ensures the best coincidence between the experimental and calculated volumetric liquid flow rates and concentrations of components in all the streams connected with the dialyzer. Some of these coefficients, i.e., $k_{AA,0}$, $A_{AA,1}$, $A_{AA,2}$, $k_{BB,0}$, $A_{BB,3}$ and $A_{BB,3}$ can be determined independently from data on dialysis of single component solutions.

The correlation represented by Eqs (6), (7) and (15) is very similar to those used in Refs [3,7,18,22], but the meaning of the constants therein is quite different as these coefficients were applied to approximate the dependences of ternary diffusion coefficients upon the concentrations of two components in the membrane [7] or to approximate ternary permeability coefficients of the membrane upon the concentrations of both the components in the feed [3,18,22]

3. Experimental

Two series of experiments were carried out. The aim of the first one was to get equilibrium data, i.e., the concentrations of sulphuric and phosphoric acids in the membrane as functions of their concentrations in the bulk solution. The second series was aimed at obtaining data on dialysis of an $H_2SO_4+H_3PO_4$ solution at steady state in a continuous dialyzer. In both the cases, an anion-exchange membrane Neosepta-AFN (Astom Corporation, Tokyo, Japan) was used.

3.1. Sorption experiments

The concentrations of sulphuric and phosphoric acids in the membrane were determined by the procedure consisting of the saturation of the membrane with a mixture of acids followed by an extraction of the components into distilled water of known volume. The details of this procedure are given elsewhere [3,21,25,26]. The concentrations of both acids were changed in the limits from 0 to 1.0 kmol m^{-3} . The temperature was $25 \pm 0.5 \text{ }^\circ\text{C}$. The content of the individual acids in the acid mixture was determined by titration with a standard NaOH solution, the equivalence points being indicated potentiometrically. Due to the high difference between the dissociation constants, it was possible to determine both the acids from only one potentiometric curve.

3.2. Dialysis experiments

Dialysis of an $H_2SO_4 + H_3PO_4$ mixture was investigated in a continuous two-compartment counter-current dialyzer. The description of the experimental set-up used and experiments is given in detail elsewhere [17,18,21,22]. The concentrations of both acids in the feed were changed in the limits from 0.2 to 1.0 kmol m^{-3} . Moreover, the dialysis experiments were carried out with only one component, i.e., sulphuric acid and phosphoric acid. The concentrations of acids in the feed, dialysate and diffusate were determined in the same way as in the case of sorption experiments. The temperature was constant, i.e., $25 \pm 0.5 \text{ }^\circ\text{C}$.

4. Data treatment and discussion

4.1. Sorption experiments

The concentrations of acids in the membrane (referred to the volume of the swollen membrane) were calculated from their amounts released from the membrane into the individual extracts. Figure 2 presents the dependence of the phosphoric acid concentration in the membrane upon that in the bulk solution. From this graphical presentation, it is evident that the acid concentration in the membrane is always higher than that in the bulk solution. Moreover, this dependence is very similar to that found for sulphuric acid. But, the H_2SO_4 concentration in the membrane is lower than that of H_3PO_4 — see Ref. [21].

For the further calculations, the dependence in Fig. 2 was approximated by the empirical equation

$$c_{BM} = \frac{c_B}{a_0 + a_1 c_B + a_2 c_B^2} \quad (16)$$

where the constants a_i ($i = 0, 1, 2$) were determined by a nonlinear regression $a_0 = 0.116$; $a_1 = 0.640 \text{ m}^3 \text{ kmol}^{-1}$; $a_2 = -0.155 \text{ m}^6 \text{ kmol}^{-2}$

The results of the sorption experiments concerning the ternary solutions are presented in Figs 3 and 4, where the concentration of one acid in the membrane is plotted against the concentration of other acid in the bulk solution. Generally, a decrease in the acid concentration in

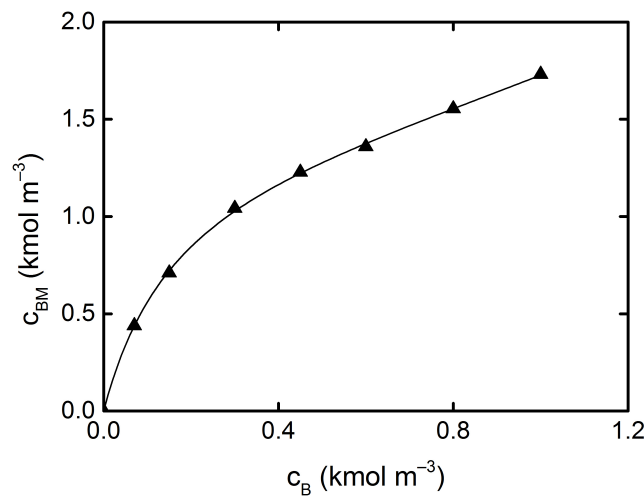


Fig. 2 Dependence of H_3PO_4 concentration in membrane upon acid concentration in bulk solution

the membrane with an increasing acid content of other acid in the bulk solution can be observed throughout the concentration range investigated. Moreover, an increase in the acid concentration in the bulk solution causes an increase in the same acid concentration in the membrane. For the further utilisation, the dependences in Figs 3 and 4 were approximated by the following equations (logistic functions)

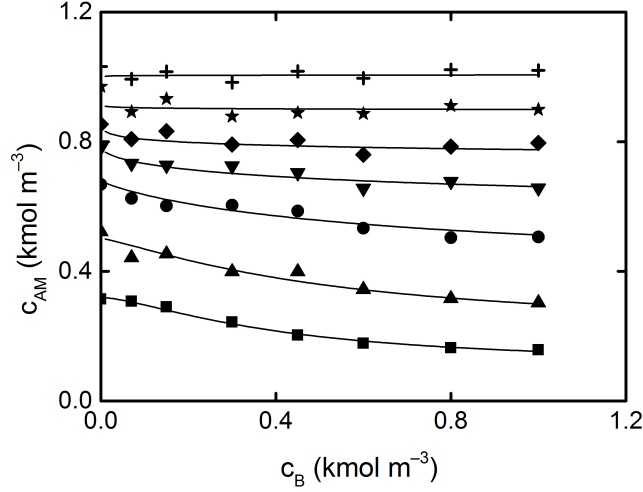


Fig. 3 Dependence of H_2SO_4 concentration in membrane upon H_3PO_4 concentration in bulk solution. c_A [kmol m^{-3}]: ■ – 0.07; ▲ – 0.15; ● – 0.30; ▼ – 0.45; ◆ – 0.60; ★ – 0.80; + – 1.00; — Eq. (17)

$$c_{iM} = A_{i2} + \frac{A_{i1} - A_{i2}}{1 + \left(\frac{c_j}{x_{i0}}\right)^{p_i}} \quad i = A, B; j = B, A \quad (17)$$

where c_j is the molar concentration of other acid. The parameters A_{i1} , A_{i2} , x_{i0} and p_i ($i = A, B$) are dependent upon the concentration of the i -th acid. The parameters A_{i1} ($i = A, B$) were approximated by Eq. (16), the constants a_0 , a_1 and a_2 for sulphuric acid being taken from Ref. [21]. In order to describe the concentration dependences of the remaining parameters, the following empirical equations were suggested

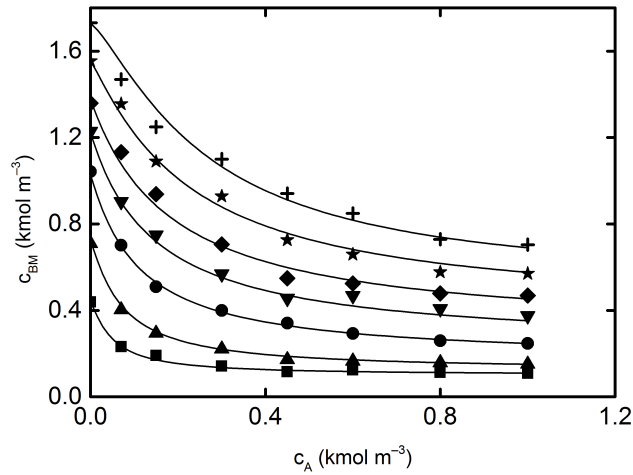


Fig. 4 Dependence of H_3PO_4 concentration in membrane upon H_2SO_4 concentration in bulk solution. c_B [kmol m^{-3}]: ■ – 0.07; ▲ – 0.15; ● – 0.30; ▼ – 0.45; ◆ – 0.60; ★ – 0.80; + – 1.00; — Eq. (17)

$$A_{i2} = b_{i1} + b_{i2}c_i + b_{i3}c_i^2 \quad i = A, B \quad (18)$$

$$x_{i0} = b_{i4} + b_{i5}c_i + b_{i6}c_i^2 \quad i = A, B \quad (19)$$

$$p_i = b_{i7} + b_{i8}c_i + b_{i9}c_i^2 \quad i = A, B \quad (20)$$

The constants b_{ik} ($i = A, B$; $k = 1, 2, \dots, 9$) were determined by a nonlinear regression and are summarised in Tables 1 and 2.

Table 1 Constants b_{Ak} ($k = 1, 2, \dots, 9$) of polynomials (18) – (20) for sulphuric acid

Constant	Value	Unit
b_{A1}	1.64×10^{-2}	kmol m^{-3}
b_{A2}	1.33	–
b_{A3}	-3.70×10^{-1}	$\text{kmol}^{-1} \text{m}^3$
b_{A4}	3.07×10^{-1}	kmol m^{-3}
b_{A5}	1.50	–
b_{A6}	-4.43×10^{-2}	$\text{kmol}^{-1} \text{m}^3$
b_{A7}	1.67	–
b_{A8}	-3.04	$\text{kmol}^{-1} \text{m}^3$
b_{A9}	1.31	$\text{kmol}^{-2} \text{m}^6$

Table 2 Constants b_{Bk} ($k = 1, 2, \dots, 9$) of polynomials (18) – (20) for phosphoric acid

Constant	Value	jednotka
b_{B1}	8.50×10^{-2}	kmol m^{-3}
b_{B2}	2.18×10^{-1}	–
b_{B3}	2.09×10^{-1}	$\text{kmol}^{-1} \text{m}^3$
b_{B4}	2.99×10^{-2}	kmol m^{-3}
b_{B5}	2.82×10^{-1}	–
b_{B6}	-4.98×10^{-2}	$\text{kmol}^{-1} \text{m}^3$
b_{B7}	1.28	–
b_{B8}	-1.16	$\text{kmol}^{-1} \text{m}^3$
b_{B9}	1.19	$\text{kmol}^{-2} \text{m}^6$

Figures 5 and 6, where the calculated acid concentrations in the membrane are compared with the experimental ones, demonstrate a good agreement between the calculated and experimental concentrations.

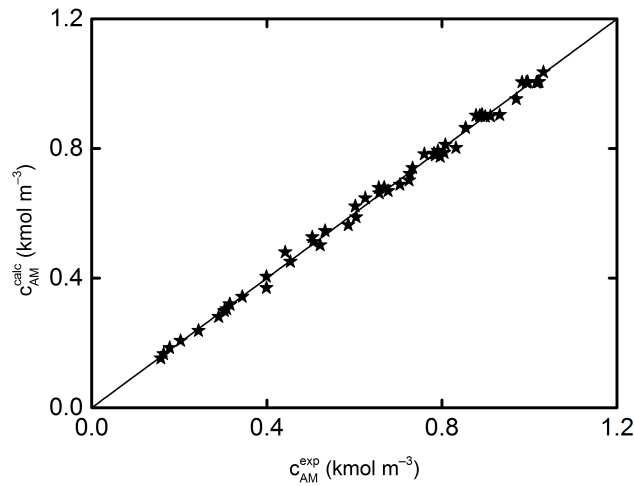


Fig. 5 Comparison of experimental and calculated H_2SO_4 concentrations in membrane

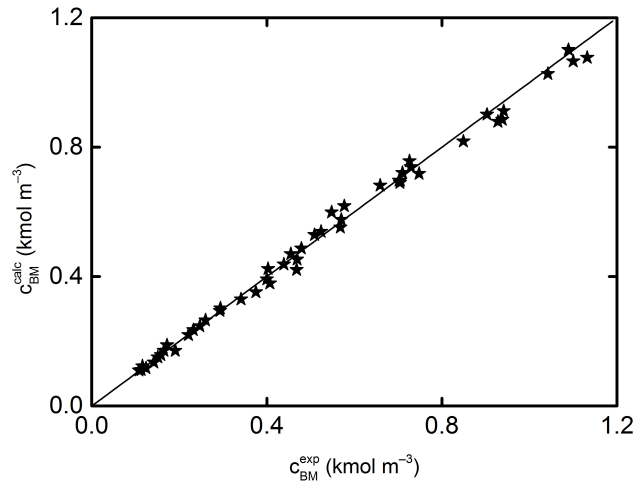


Fig. 6 Comparison of experimental and calculated H_3PO_4 concentrations in membrane

4.2. Dialysis experiments

The simultaneous transport of sulphuric and phosphoric acids through an anion-exchange membrane was quantified by four membrane mass transfer coefficients k_{ij} ($i = A, B; j = A, B$) which are functions of the concentrations of both acids in the feed — see Eqs (15). The coefficients of Eqs (15) were determined by the numerical integration of the basic differential equations (1) – (3) combined with an optimisation procedure. The whole procedure consisted of the following steps:

1. The calculation of the flow velocity of solvent

$$u_w = J_{w,in}^I \bar{v}_{w,in}^I - J_{w,out}^I \bar{v}_{w,out}^I = J_{w,out}^{II} \bar{v}_{w,out}^{II} - J_{w,in}^{II} \bar{v}_{w,in}^{II} \quad (21)$$

where \bar{v} is the partial molar volume. Using the relation

$$\dot{V} = A(J_A \bar{v}_A + J_B \bar{v}_B + J_w \bar{v}_w) \quad (22)$$

Eq. (21) can be transformed into the form

$$\begin{aligned} u_w &= \frac{1}{A} \left[\dot{V}_{in}^I \left(1 - c_{A,in}^I \bar{v}_{A,in}^I - c_{B,in}^I \bar{v}_{B,in}^I \right) - \dot{V}_{out}^I \left(1 - c_{A,out}^I \bar{v}_{A,out}^I - c_{B,out}^I \bar{v}_{B,out}^I \right) \right] = \\ &= \frac{1}{A} \left[\dot{V}_{out}^{II} \left(1 - c_{A,out}^{II} \bar{v}_{A,out}^{II} - c_{B,out}^{II} \bar{v}_{B,out}^{II} \right) - \dot{V}_{in}^{II} \right] \end{aligned} \quad (23)$$

In the calculation of the flow velocity of solvent, it was assumed that the partial molar volumes in the ternary systems do not significantly differ from those in the corresponding binary systems, i.e., $H_2SO_4 - H_2O$ and $H_3PO_4 - H_2O$. The partial molar volumes in the binary systems were calculated from density data of these systems.

2. The initial estimate of the coefficients $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B; k = 1, 2, \dots, 4$).
3. The integration of Eqs (1) – (3) in the direction from $z = z_T$ to $z = 0$. In such a way, the volumetric liquid flow rates and concentration of acids in the streams entering compartment I and leaving compartment II are obtained. In each integration step, several partial steps had to be done.
 - a) The initial estimate of the partition coefficients Ψ_i^j ($i = A, B; j = A, B$).
 - b) The solution to the set of Eqs (6) – (11) and (14).
 - c) The calculation of c_{iM}^j ($i = A, B; j = A, B$) from the sorption isotherms (17).
 - d) The calculation of the corrected partial coefficients.
 - e) The procedure from b) to d) was repeated until relative errors in Ψ_i^j ($i = A, B; j = A, B$) in two subsequent iterations were below 0.1 %.
4. The calculation of the objective function

$$F = \sum_{k=1}^n \left[\left(\frac{\dot{V}_{in,k}^{I,exp} - \dot{V}_{in,k}^{I,calc}}{\dot{V}_{in,k}^{I,exp}} \right)^2 + \left(\frac{\dot{V}_{out,k}^{II,exp} - \dot{V}_{out,k}^{II,calc}}{\dot{V}_{out,k}^{II,exp}} \right)^2 + \sum_{i=A}^B \left(\frac{c_{i,in,k}^{I,exp} - c_{i,in,k}^{I,calc}}{c_{i,in,k}^{I,exp}} \right)^2 + \sum_{i=A}^B \left(\frac{c_{i,out,k}^{II,exp} - c_{i,out,k}^{II,calc}}{c_{i,out,k}^{II,exp}} \right)^2 \right] \quad (24)$$

where n is the number of experiments. Moreover, the following constraints were considered

$$k_{AA} > 0 \quad (25)$$

$$k_{BB} > 0 \quad (26)$$

Note: The objective function (24) was considered to be a function not only the coefficients $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B; k = 1, 2, \dots, 4$) but also the constant C in Eq. (12).

5. The calculation of the corrected values of $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B;$

$k = 1, 2, \dots, 4$). For this purpose, one step of an optimisation procedure (a simplex method) was realised.

6. The procedure from 3) to 5) was repeated until reaching a minimum of the objective function (24).

Note: First, the coefficients $k_{AA,0}$, $A_{AA,1}$, $A_{AA,2}$, $k_{BB,0}$, $A_{BB,3}$ and $A_{BB,3}$ were calculated. For this purpose, the procedure described above was applied to the transport of only one acid through the membrane. Here, only one flux Eq. (6) or (7) with only one coefficient (k_{AA} or k_{BB}) was needed. Besides, the differential equations (1) – (3) and the objective function (24) were simplified.

In order to verify the mathematical model and procedure suggested, the calculated concentrations of both acids in the feed and in the stream leaving compartment II are plotted against the experimental ones in Fig. 7. This comparison and finding the small differences between the experimental and calculated volumetric liquid flow rates of the streams mentioned above reveal that the model represented by Eqs (1) – (3) and (5) – (15) is adequate.

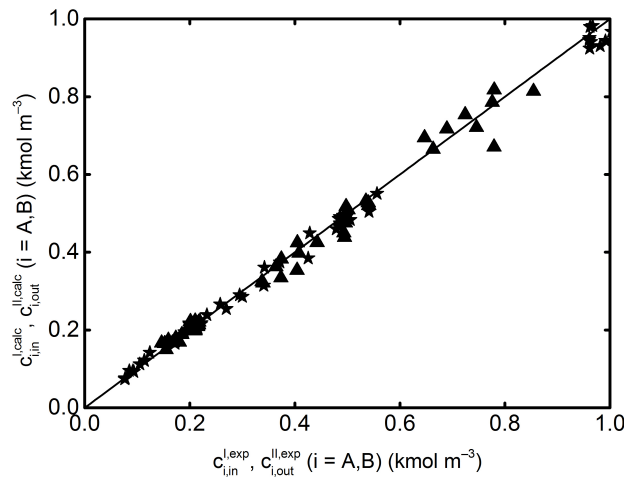


Fig. 7 Comparison of experimental and calculated H_2SO_4 (\blacktriangle) and H_3PO_4 (\star) concentrations in feed and in stream leaving compartment II

The calculated constants $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B; k = 1, 2, \dots, 4$) of the second degree polynomials (15) are summarised in Table 3. The dependences of the membrane mass transfer coefficients k_{ij} ($i = A, B; j = A, B$) upon the sulphuric acid concentration in the feed are presented in Figs (9) – (12), the phosphoric acid concentrations in the feed being the parameters of the individual dependences.

Table 3 Constants $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B; k = 1, 2, \dots, 4$) of polynomials (15)

k_{ij}	$k_{ij,0}$ m s^{-1}	$A_{ij,1}$ $\text{m}^3 \text{ kmol}^{-1}$	$A_{ij,2}$ $\text{m}^6 \text{ kmol}^{-2}$	$A_{ij,3}$ $\text{m}^3 \text{ kmol}^{-1}$	$A_{ij,4}$ $\text{m}^6 \text{ kmol}^{-2}$
k_{AA}	1.34×10^{-6}	2.18	-2.71×10^{-1}	1.10	-2.20
k_{AB}	8.75×10^{-7}	1.43	-5.45×10^{-1}	-1.60	6.09×10^{-1}
k_{BA}	1.78×10^{-8}	1.36	-8.41	1.11×10^2	-93.8
k_{BB}	5.50×10^{-7}	-7.53×10^{-1}	5.79×10^{-1}	1.03×10^{-1}	2.55×10^{-2}

$C = 0.893$

The different values of the membrane mass transfer coefficients and their dependences upon the concentrations of both acids in the feed are the consequence of strong interactions between species, between the species and solvent, and between the species and membrane matrix. Unfortunately, the values of the coefficients k_{ij} ($i = A, B; j = A, B$) and their dependences can hardly be explained on the basis of the membrane structure and ion concentrations in the membrane. In aqueous solutions of electrolytes, the interactions between the individual species, and between the species and solvent are included into activity coefficients, which can be predicted with the help of, e.g., the Pitzer theory [27]. No reliable models exist for predicting activity coefficients in ion-exchange polymers [28].

The coefficient k_{AA} , which quantifies the effect of the concentration difference of sulphuric acid upon the sulphuric acid flux through the membrane, is in the limits from approx. 0.4×10^{-6} to $4.0 \times 10^{-6} \text{ m s}^{-1}$ — see Fig. 8. This coefficient practically linearly increases with an increasing H_2SO_4 concentration in the feed. The sequence of the individual lines reveals the existence of a minimum on the dependences $k_{AA} = f(c_{B,in}^I)$. Its first coordinate can easily be calculated from the data in Table 3 ($c_{B,in}^I = 0.25 \text{ kmol m}^{-3}$). Under the experimental conditions, the coefficient k_{AB} is much lower than the coefficient k_{AA} — it is in the limits from approx. 0.3×10^{-6} to $1.4 \times 10^{-6} \text{ m s}^{-1}$ — see Fig. 9. The coefficient k_{AB} increases with an increasing H_2SO_4 concentration and decreasing H_3PO_4 concentration throughout the concentration range investigated. On the basis of the dependences given in Figs 8 and 9, it can be stated that the total flux of sulphuric acid through the membrane increases with a decreasing H_3PO_4 concentration in the feed.

From the graphical presentations in Fig. 10, it is evident that the coefficient k_{BA} decreases with an increasing H_2SO_4 concentration, while on the dependences $k_{BA} = f(c_{B,in}^I)$ a minimum can be identified at the H_3PO_4 concentration of 0.59 kmol m^{-3} . This coefficient, which reflects a contribution to the total flux of phosphoric acid due to the concentration difference of H_2SO_4 , exhibits relatively low values — it is in the range from approx. 0.2×10^{-6} to $0.6 \times 10^{-6} \text{ m s}^{-1}$. The

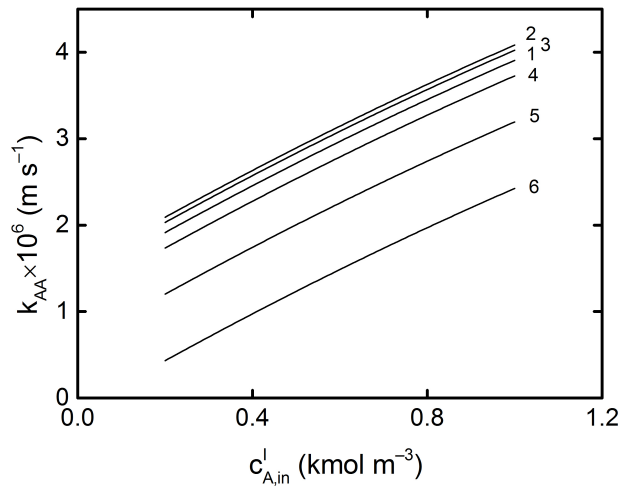


Fig. 8 Dependence of membrane mass transfer coefficient k_{AA} upon H_2SO_4 concentration in feed. $c_{B,in}^I$ [kmol m^{-3}]: 1 – 0; 2 – 0.2; 3 – 0.4; 4 – 0.6; 5 – 0.8; 6 – 1.0;

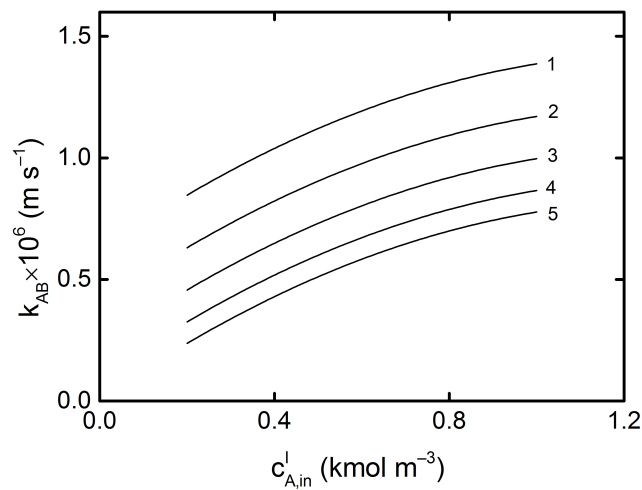


Fig. 9 Dependence of membrane mass transfer coefficient k_{AB} upon H_2SO_4 concentration in feed. $c_{B,in}^I$ [kmol m^{-3}]: 1 – 0.2; 2 – 0.4; 3 – 0.6; 4 – 0.8; 5 – 1.0

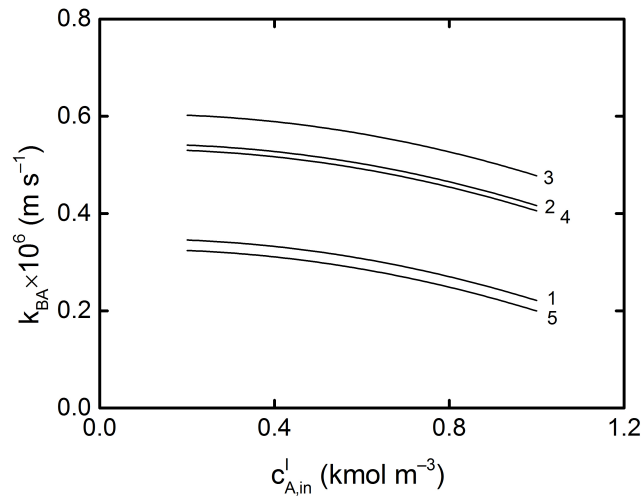


Fig. 10 Dependence of membrane mass transfer coefficient k_{BA} upon H_2SO_4 concentration in feed. For meaning of individual lines, see Fig. 9

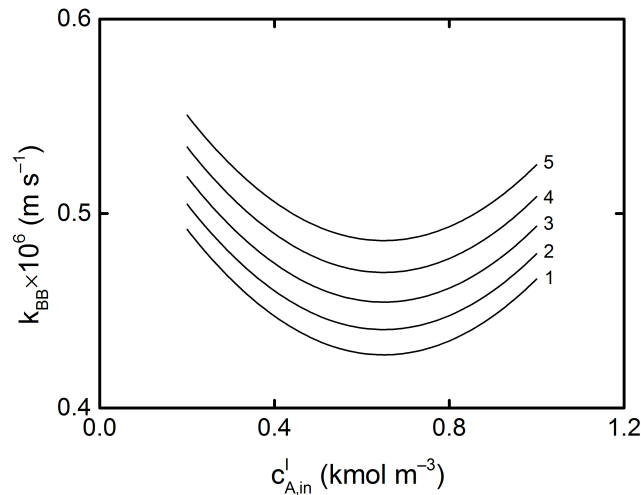


Fig. 11 Dependence of membrane mass transfer coefficient k_{BB} upon H_2SO_4 concentration in feed. For meaning of individual lines, see Fig. 9

values of the last coefficient, i.e., k_{BB} are comparable with those of the coefficient k_{BA} — see Fig. 11. Moreover, they lie in a narrow range, i.e., from approx. 0.40×10^{-6} to $0.55 \times 10^{-6} \text{ m s}^{-1}$. The coefficient k_{BB} first decreases with an increasing H_2SO_4 concentration until reaching a minimum at the acid concentration of 0.65 kmol m^{-3} , then it increases again. An increase in the H_3PO_4 content in the feed results in an increased H_3PO_4 flux due to the fact that not only concentration difference of phosphoric acid but also the coefficient k_{BB} increases.

The analysis of the dependences in Figs 8 – 11 and data in Table 3 enables to estimate the effect of one acid upon the transport rate of other acid. For example, as discussed above, the membrane mass transfer coefficient k_{AA} exhibits maximum at the phosphoric acid concentration of 0.25 kmol m^{-3} . If the H_3PO_4 concentration in the feed does not exceed this value, then the flux of H_2SO_4 in the presence of H_3PO_4 will be higher than that in the absence of H_3PO_4 . Under these

conditions, the flux of H_2SO_4 will be composed of two contributions — the first one due to the concentration difference of H_2SO_4 , the second one due to a non-zero concentration difference of H_3PO_4 . As the values of k_{AB} are comparable with those of k_{AA} (see Figs 8 and 9), the second contribution can be significant. The detailed information can be obtained using a numerical analysis.

5. Conclusion

The simultaneous transport of sulphuric and phosphoric acid through a polymeric membrane was studied. For this purpose, a two-compartment counter-current dialyzer equipped with an anion-exchange membrane Neosepta-AFN (Astom Corporation, Tokyo, Japan) was used. This transport was characterised by four membrane mass transfer coefficients which were correlated with the concentrations of both acids in the feed. The results obtained are presented in tabular and graphical forms. Moreover, the equilibrium concentration of each acid in the membrane was experimentally determined. In this case, the concentration of one acid in the membrane was correlated with the concentrations of both acids in the bulk solution. **The membrane mass transfer coefficients and their dependences upon the concentration of acids in the feed can be used in a design of other dialysis unit for the separation of the same mixture using the same membrane. In this case, reliable data on mass transport in the individual compartments must be at disposal.**

Acknowledgement

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6. Symbols

A	membrane area, m^2
A_{ik}	($i = A, B; k = 1, 2$) coefficients in Eqs (17), kmol m^{-3}
$A_{ij,k}$	($i = A, B; j = A, B; k = 1, 3$) constants in Eqs (15), $\text{m}^3 \text{kmol}^{-1}$
$A_{ij,k}$	($i = A, B; j = A, B; k = 2, 4$) constants in Eqs (15), $\text{m}^6 \text{kmol}^{-2}$
a_0	constant in Eq. (16)
a_1	constant in Eq. (16), $\text{m}^3 \text{kmol}^{-1}$
a_2	constant in Eq. (16), $\text{m}^6 \text{kmol}^{-2}$
b_{i1}	constants in Eqs (18), kmol m^{-3}
b_{i2}	constants in Eqs (18)
b_{i3}	constants in Eqs (18), $\text{m}^3 \text{kmol}^{-1}$
b_{i4}	constants in Eqs (19), kmol m^{-3}
b_{i5}	constants in Eqs (19)
b_{i6}	constants in Eqs (19), $\text{m}^3 \text{kmol}^{-1}$
b_{i7}	constants in Eqs (20)
b_{i8}	constants in Eqs (20), $\text{m}^3 \text{kmol}^{-1}$
b_{i9}	constants in Eqs (20), $\text{m}^6 \text{kmol}^{-2}$
C	constant in Eq. (12)

c	molar concentration, kmol m^{-3}
D	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
d	width of compartment, m
d_e	$(= 2d\delta/(d + \delta))$ equivalent diameter, m
F	objective function
f	general function
J	flux, $\text{kmol m}^{-2} \text{s}^{-1}$
k_{ij}	$(i = A, B; j = A, B)$ membrane mass transfer coefficients, m s^{-1}
$k_{ij,0}$	$(i = A, B; j = A, B)$ constants in Eqs (15), m s^{-1}
k_L	liquid mass transfer coefficient, m s^{-1}
M	molar mass, kg kmol^{-1}
n	number of experiments
p_i	$(i = A, B)$ coefficients in Eqs (17)
Re	$(= ud_e/\nu)$ Reynolds number
Sc	(ν/D) Schmidt number
Sh	$(= k_L d_e/D)$ Sherwood number
u	liquid flow rate, m s^{-1}
\dot{V}	volumetric liquid flow rate, $\text{m}^3 \text{s}^{-1}$
x_{i0}	$(i = A, B)$ coefficients in Eqs (17), kmol m^{-3}
z	length coordinate, m
z_T	total height of compartment, m
δ	thickness, m
ν	kinematic viscosity, $\text{m}^2 \text{s}^{-1}$
ρ	density, kg m^{-3}
Ψ	partition coefficient

Superscripts and subscripts

A	referred to component A, i.e., H_2SO_4
B	referred to component B, i.e., H_3PO_4
$calc$	calculated
exp	experimental
f	solution/membrane interface
in	inlet
M	referred to membrane
out	outlet
w	referred to solvent
I	referred to compartment I
II	referred to compartment II

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Figures

Fig. 1 Scheme of continuous dialyzer: 1 – feed; 2 – dialysate; 3 – stripping agent (water); 4 – diffusate; I – compartment I; II – compartment II; M – membrane

Fig. 2 Dependence of H_3PO_4 concentration in membrane upon acid concentration in bulk solution

Fig. 3 Dependence of H_2SO_4 concentration in membrane upon H_3PO_4 concentration in bulk solution. c_A [kmol m^{-3}]: ■ – 0.07; ▲ – 0.15; ● – 0.30; ▼ – 0.45; ◆ – 0.60; ★ – 0.80; † – 1.00; — Eq. (17)

Fig. 4 Dependence of H_3PO_4 concentration in membrane upon H_2SO_4 concentration in bulk solution. c_B [kmol m^{-3}]: ■ – 0.07; ▲ – 0.15; ● – 0.30; ▼ – 0.45; ◆ – 0.60; ★ – 0.80; † – 1.00; — Eq. (17)

Fig. 5 Comparison of experimental and calculated H_2SO_4 concentrations in membrane

Fig. 6 Comparison of experimental and calculated H_3PO_4 concentrations in membrane

Fig. 7 Comparison of experimental and calculated H_2SO_4 (+) and H_3PO_4 (*) concentrations in feed and in stream leaving compartment II

Fig. 8 Dependence of membrane mass transfer coefficient k_{AA} upon H_2SO_4 concentration in feed. $c_{B,in}^I$ [kmol m^{-3}]: 1 – 0.0; 2 – 0.2; 3 – 0.4; 4 – 0.6; 5 – 0.8; 6 – 1.0

Fig. 9 Dependence of membrane mass transfer coefficient k_{AB} upon H_2SO_4 concentration in feed. $c_{B,in}^I$ [kmol m^{-3}]: 1 – 0.2; 2 – 0.4; 3 – 0.6; 4 – 0.8; 5 – 1.0

Fig. 10 Dependence of membrane mass transfer coefficient k_{BA} upon H_2SO_4 concentration in feed. For meaning of individual lines, see Fig. 9

Fig. 11 Dependence of membrane mass transfer coefficient k_{BB} upon H_2SO_4 concentration in feed. For meaning of individual lines, see Fig. 9

Tables

Table 1 Constants b_{Ak} ($k = 1, 2, \dots, 9$) of polynomials (18) – (20) for sulphuric acid

Constant	Value	Unit
b_{A1}	1.64×10^{-2}	kmol m^{-3}
b_{A2}	1.33	–
b_{A3}	-3.70×10^{-1}	$\text{kmol}^{-1} \text{m}^3$
b_{A4}	3.07×10^{-1}	kmol m^{-3}
b_{A5}	1.50	–
b_{A6}	-4.43×10^{-2}	$\text{kmol}^{-1} \text{m}^3$
b_{A7}	1.67	–
b_{A8}	-3.04	$\text{kmol}^{-1} \text{m}^3$
b_{A9}	1.31	$\text{kmol}^{-2} \text{m}^6$

Table 2 Constants b_{Bk} ($k = 1, 2, \dots, 9$) of polynomials (18) – (20) for phosphoric acid

Constant	Value	jednotka
b_{B1}	8.50×10^{-2}	kmol m^{-3}
b_{B2}	2.18×10^{-1}	–
b_{B3}	2.09×10^{-1}	$\text{kmol}^{-1} \text{m}^3$
b_{B4}	2.99×10^{-2}	kmol m^{-3}
b_{B5}	2.82×10^{-1}	–
b_{B6}	-4.98×10^{-2}	$\text{kmol}^{-1} \text{m}^3$
b_{B7}	1.28	–
b_{B8}	-1.16	$\text{kmol}^{-1} \text{m}^3$
b_{B9}	1.19	$\text{kmol}^{-2} \text{m}^6$

Table 3 Constants $k_{ij,0}$ ($i = A, B; j = A, B$) and $A_{ij,k}$ ($i = A, B; j = A, B; k = 1, 2, \dots, 4$) of polynomials (15)

k_{ij}	$k_{ij,0}$ m s^{-1}	$A_{ij,1}$ $\text{m}^3 \text{kmol}^{-1}$	$A_{ij,2}$ $\text{m}^6 \text{kmol}^{-2}$	$A_{ij,3}$ $\text{m}^3 \text{kmol}^{-1}$	$A_{ij,4}$ $\text{m}^6 \text{kmol}^{-2}$
k_{AA}	1.34×10^{-6}	2.18	-2.71×10^{-1}	1.10	-2.20
k_{AB}	8.75×10^{-7}	1.43	-5.45×10^{-1}	-1.60	6.09×10^{-1}
k_{BA}	1.78×10^{-8}	1.36	-8.41	1.11×10^2	-93.8
k_{BB}	5.50×10^{-7}	-7.53×10^{-1}	5.79×10^{-1}	1.03×10^{-1}	2.55×10^{-2}

$C = 0.893$