Separation of H_2SO_4 + $CuSO_4$ mixture by diffusion dialysis

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Abstract

Diffusion dialysis of aqueous solution of H_2SO_4 + $CuSO_4$ has been investigated in a two-compartment cell with an anion-exchange membrane Neosepta-AFN. The experiments have proved that sulfuric acid permeates well through the membrane used, while cupric sulfate is efficiently rejected. This operation is very effective at high acid concentrations and low concentrations of cupric sulfate. Furthermore, it has been found that even at the highest concentration of $CuSO_4$, the rejection coefficient is higher than 0.965. The flux of $CuSO_4$ calculated from the time dependences of the $CuSO_4$ concentration is negatively influenced by increasing acid concentration.
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1. Introduction

The separation of mixtures by membrane processes is based on the fact that components of mixtures penetrate through the membrane with different rates as a result of complex interactions between the components transported and the membrane matrix. In the case of diffusion dialysis, which uses an anion-exchange membrane (AEM) (in its structure, positively charged sites are fixed), it is necessary, besides other effects, to consider the interactions between the species transported and electrically charged sites.

Fig. 1 schematically shows an anion-exchange membrane, which separates two solutions of strong electrolytes having the same composition but different concentrations, e.g. aqueous solution of HCl + NaCl—in such a solution, H_3O^+, Na^+ and Cl^- ions are present. Due to the attractive forces, the transport of counter-ions through the membrane is facilitated, while co-ions, i.e. Na^+ ions, are rejected. Hydrated hydrogen ions exhibit high mobility also in the membrane, so that they permeate through the membrane very easily. This phenomenon is not disadvantageous as such a membrane is used in the separation of inorganic acids (namely

HCl, H_2SO_4, HNO_3, H_3PO_4 and HF) from mixtures containing besides acids also their salts [1–7]. The main advantage of diffusion dialysis is the low consumption of energy during the process, which is a consequence of the fact that the separation of mixtures is realized under common pressures and without changing the state. On the other hand, diffusion character of the process results in very low rate, which in some cases can be considered to be a disadvantage.

Inorganic acids are often used as agents in the pickling process, which is one of the key steps in the metal finishing industry. Metal surfaces with oxides are immersed into an acid solution; during this process, the acid concentration decreases with time while the metal is accumulated, so that, after a certain time, a fresh solution must be used. The acid from this exhausted solution can effectively be recovered by diffusion dialysis. Introduction of diffusion dialysis into the acid pickling process leads to some economical merits, e.g. (i) improvement in the productivity and quality of products; (ii) lower cost for chemical used to neutralize waste; and (iii) decrease in the sludge formed, which is very often dangerous to the environment.

The aim of the paper is to obtain basic information on the separation of H_2SO_4 + $CuSO_4$ mixture, which can be encountered in the industrial practice.

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Nomenclature

A	membrane area (m^2)
c	(total) molar concentration ($kmol\,m^{-3}$)
f	general function
J	flux ($kmol\,m^{-2}\,s^{-1}$)
K_H	protonization constant
n	rotational speed of stirrers (s^{-1})
p_1	constant in Eq. (1)
p_2	constant in Eq. (1) ($m^3\,kmol^{-1}$)
p_3	constant in Eq. (1) ($m^6\,kmol^{-2}$)
R	rejection coefficient
t	time (s)
V	volume (m^3)
β_{Cu}	complexity constant
[ ]	actual concentration ($kmol\,m^{-3}$) (in Eqs. (4) and (5) dimensionless)

Superscripts and subscripts

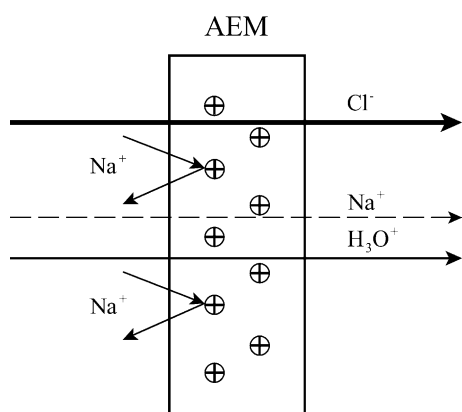|	
Cu^{2+}	referred to Cu^{2+} ions
$CuSO_4$	referred to $CuSO_4$
$(CuSO_4)_{non}$	referred to non-dissociated form of $CuSO_4$
H_2SO_4	referred to H_2SO_4
M	referred to membrane
I, II	referred to compartment I, II, respectively
0	initial
+	referred to fixed charges

Fig. 1. Transport of ions through anion-exchange membrane.

2. Experimental

In order to obtain basic information on dialysis process, a batch dialysis cell is often used with the membrane separating two identical solutions with different concentrations. In the course of the experiment, time dependences of the components concentrations in both the compartments are monitored. It is not possible to evaluate the dialysis process only using these dependences; other data concerning the sorption isotherms must be at disposal because the distribution of the individual ions (or non-dissociated forms) in the membrane can differ from that in the bulk solution.

The experimental results obtained in a batch cell represent only a part of information needed for a design or simulation of industrial dialysis units. In the industrial scale, the separation of mixtures by diffusion dialysis is performed in a continuous dialyzer. For that purpose, other data must be known, e.g. data on mass transfer in liquid films on both sides of the membrane.

2.1. Concentration of H_2SO_4 and $CuSO_4$ in membrane

The concentration of sulfuric acid and cupric sulfate in the membrane equilibrated with the solution of a known composition was determined by the procedure based on the saturation of the membrane with $H_2SO_4 + CuSO_4$ solution followed by an extraction of the components into water. The membrane of 25–40 cm^2 surface area, which was kept in 0.5 M NaCl, was rid of salt by thorough washing in distilled water and then repeatedly saturated with 0.2 M H_2SO_4 to transfer the membrane from its basic Cl^- form into an HSO_4^-/SO_4^{2-} form. The membrane treated in such a way was shaken with the solution of a given composition for 18 h (overnight). Then the membrane was wiped quickly with blotting paper to remove the solution adhering its surface whereupon it was shaken repeatedly for 2 h (three times) in 25 ml distilled water. The concentration of H_2SO_4 in the individual extracts was determined by microtitration with a standard solution of NaOH. In order to find the $CuSO_4$ concentration, the extracts were titrated with 0.005 M EDTA, the end-point being detected by voltammetry.

2.2. Dialysis experiments

Dialysis of aqueous solution of $H_2SO_4 + CuSO_4$ was investigated in a two-compartment cell with stirrers. The description of the cell is given in detail in reference [8]. The experimental set-up is shown in Fig. 2.
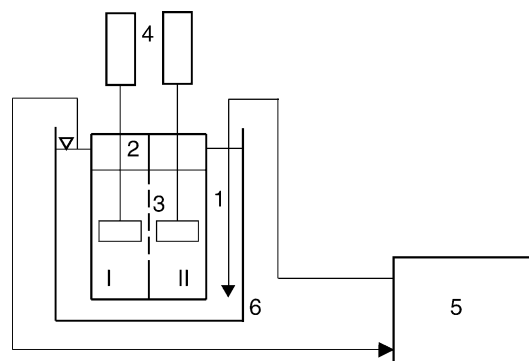

Fig. 2. Experimental set-up: (1) dialysis cell; (2) partition; (3) membrane; (4) stirrers; (5) thermostat; (6) thermostat reservoir; (I, II) compartments.

In all the experiments, an anion-exchange membrane Neosepta-AFN developed by Tokuyama Soda Co., Ltd. was used. The basic physical properties of the membrane used were: thickness 165 μm; water content 0.418 g per gram of dry membrane in Cl^- form; the concentration of fixed charges (considered as monovalent) 4.7 kmol m^{-3} (the concentration referred to the pore volume). The area of the membrane was 62.2 cm^2.

At the beginning of each experiment, compartments I and II were filled with H_2SO_4 + $CuSO_4$ solution and distilled water, respectively. The initial acid concentration in the compartment I was changed in the limits from 0.1 to 2.0 M, while the salt concentration was in the range from 0.1 to 0.75 M. During the experiments, both compartments were intensively mixed ($n^I = n^{II} = 9.17\,s^{-1}$). The initial volume of liquid in both compartments was 1 l. In the course of each experiment, the concentration of the components (acid and salt) in both compartments and the height of liquid levels (for the determination of the volumetric changes) were measured. The acid concentration was determined by titration with 0.1 M NaOH. The concentration of cupric sulfate was determined by titration with EDTA—the samples from the compartments I and II were titrated with 0.02 and 0.005 M EDTA, respectively. The end-points were detected visually using an indicator and by voltammetry. The changes in the levels of liquid were measured with the help of a modified micrometer screw with a needle. The temperature was kept at a constant value of 20 ± 0.5 °C.

3. Data treatment and discussion

3.1. Concentration of H_2SO_4 and $CuSO_4$ in membrane

The acid concentration and that of cupric sulfate in the membrane were calculated from the concentrations of these components in the individual extracts and the volume of the solution in the membrane, which was calculated from density of H_2SO_4 + $CuSO_4$ solution, weight of the membrane saturated with the solution and that of dry membrane. For this purpose, the membrane was dried under vacuum at 60 °C.

Fig. 3 shows the dependence of the concentration of $CuSO_4$ in the membrane upon the acid concentration in the external solution—the $CuSO_4$ concentration in the external solution being the parameter of the individual lines. From this graphical presentation, it is evident that, except for the case when the acid concentration in the external solution is equal to zero, the concentration of $CuSO_4$ in the membrane is always lower than that in the external solution. The course of the lines indicates that the concentration of $CuSO_4$ in the membrane is affected by both acid concentration and salt concentration. After the initial decrease in the concentration of $CuSO_4$ with increasing H_2SO_4 concentration, the concentration of $CuSO_4$ in the membrane approaches practically constant value (at the concentrations over 0.25 kmol m^{-3} H_2SO_4)—this con-
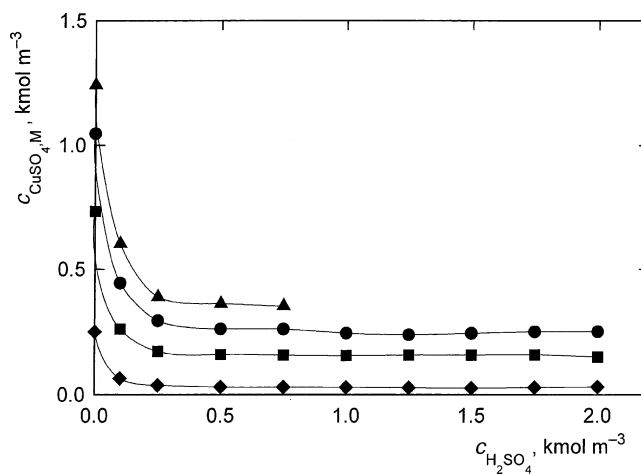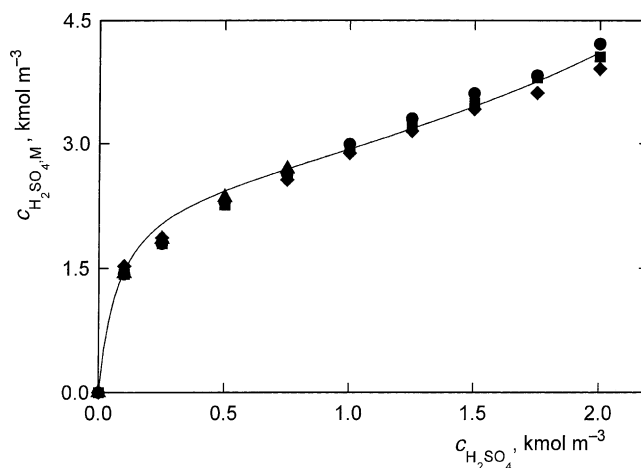

Fig. 3. Dependence of $CuSO_4$ concentration in membrane upon H_2SO_4 concentration in external solution: ($\blacklozenge$) $c_{CuSO_4} = 0.1$ kmol m^{-3}; ($\blacksquare$) $c_{CuSO_4} = 0.5$ kmol m^{-3}; ($\bullet$) $c_{CuSO_4} = 0.75$ kmol m^{-3}; ($\blacktriangle$) $c_{CuSO_4} = 1.0$ kmol m^{-3}.

centration increases with increasing salt concentration in the external solution.

As can be seen from Fig. 4, where the acid concentration in the membrane is plotted versus the acid concentration in the solution at various concentrations of $CuSO_4$, the acid concentration in the membrane is not affected by $CuSO_4$ concentration and it can be approximated with a sufficient accuracy by the following empirical equation:

$$c_{H_2SO_4,M} = \frac{c_{H_2SO_4}}{p_1 + p_2 c_{H_2SO_4} + p_3 c_{H_2SO_4}^2} \tag{1}$$

whose constants were determined using non-linear regression of experimental data on acid concentration in the membrane obtained by the same experimental technique as in the case of H_2SO_4 + $CuSO_4$ solution/membrane equilibrium—$p_1 = 0.0297$; $p_2 = 0.394$ m^3 kmol^{-1}; $p_3 = -0.0829$ m^6 kmol^{-2}.

Fig. 4. Dependence of H_2SO_4 concentration in membrane upon H_2SO_4 concentration in external solution: ($\blacklozenge$) $c_{CuSO_4} = 0.1$ kmol m^{-3}; ($\blacksquare$) $c_{CuSO_4} = 0.5$ kmol m^{-3}; ($\bullet$) $c_{CuSO_4} = 0.75$ kmol m^{-3}; ($\blacktriangle$) $c_{CuSO_4} = 1.0$ kmol m^{-3}; (—) calculated from Eq. (1).
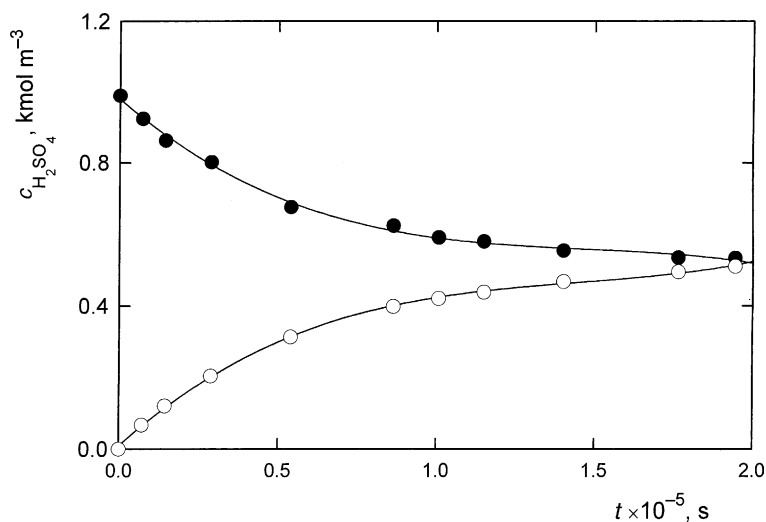
Fig. 5. Dependence of H$_2$SO$_4$ concentration in compartment I (●) and II (○) upon time: $c_{H_2SO_4,0}^I = 1.0 \, \text{kmol m}^{-3}$; $c_{CuSO_4,0}^I = 0.5 \, \text{kmol m}^{-3}$.

3.2. Dialysis experiments

The course of dialysis of H$_2$SO$_4$ + CuSO$_4$ mixture is graphically demonstrated in Figs. 5–7 . In Fig. 5, the dependences of the acid concentration in both the compartments upon time are presented, while Figs. 6 and 7 concern the concentration of CuSO$_4$ in the compartment II. All these figures show good separation of H$_2$SO$_4$ + CuSO$_4$ mixture using an anion-exchange membrane Neosepta-AFN, which has been specially developed for diffusion dialysis. While sulfuric acid permeates well through this membrane, cupric sulfate is efficiently rejected. Generally, concentration of cupric sulfate in the compartment II increases with increasing concentration of CuSO$_4$ in the compartment I and with duration of the experiment and it decreases with increasing acid concentration in the compartment I—as compared with that in the compartment I, it is much lower.

The quality of the separation of H$_2$SO$_4$ + CuSO$_4$ mixture can be evaluated not only on the basis of the CuSO$_4$ concentration in the compartment II, but also using the rejection coefficient for CuSO$_4$ defined by equation

$$R_{CuSO_4} = 1 - \frac{V^{II} c_{CuSO_4}^{II}}{V_0^I c_{CuSO_4,0}^I} \tag{2}$$

From Fig. 8, where rejection coefficient for the highest concentration of CuSO$_4$ (i.e. 0.75 kmol m^{-3}) is plotted versus time, it is evident that, under these conditions, rejection coefficient exhibits high values, i.e. $R_{CuSO_4} > 0.965$.
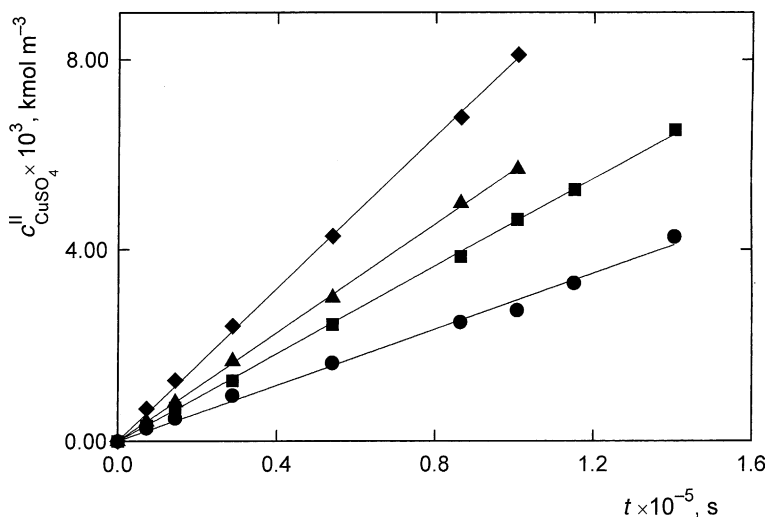

Fig. 6. Dependence of CuSO$_4$ concentration in compartment II upon time for $c_{CuSO_4,0}^I = 0.5 \, \text{kmol m}^{-3}$. Effect of initial H$_2SO_4$ concentration in compartment I: (♦) $c_{H_2SO_4,0}^I = 0.1 \, \text{kmol m}^{-3}$; (▲) $c_{H_2SO_4,0}^I = 0.5 \, \text{kmol m}^{-3}$; (■) $c_{H_2SO_4,0}^I = 1.0 \, \text{kmol m}^{-3}$; (●) $c_{H_2SO_4,0}^I = 2.0 \, \text{kmol m}^{-3}$.
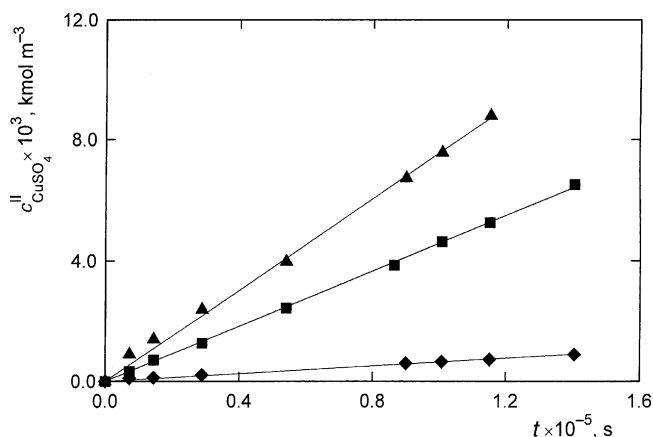
Fig. 7. Dependence of $CuSO_4$ concentration in compartment II upon time for $c_{H_2SO_4,0}^{I} = 1.0\,\text{kmol m}^{-3}$. Effect of initial $CuSO_4$ concentration in compartment I: (♦) $c_{CuSO_4,0}^{I} = 0.1\,\text{kmol m}^{-3}$; (■) $c_{CuSO_4,0}^{I} = 0.5\,\text{kmol m}^{-3}$; (▲) $c_{CuSO_4,0}^{I} = 0.75\,\text{kmol m}^{-3}$.

The dependences $c_{CuSO_4}^{II} = f(t)$ given in Figs. 6 and 7 can be approximated with a sufficient accuracy by straight lines from which the derivative $dc_{CuSO_4}^{II}/dt$ at time $t = 0$ can be determined, so that using Eq. (3), one can easily calculate the flux of cupric sulfate through the membrane.

$$J_{CuSO_4,0} = \frac{V^{II}}{A}\frac{dc_{CuSO_4}^{II}}{dt} \tag{3}$$

The flux of cupric sulfate, $J_{CuSO_4,0}$, in Eq. (3) must be understood as a sum of two contributions, i.e. the flux of Cu^{2+} ions and that of the non-dissociated form. The total flux is then dependent upon the mutual ratio of these contributions.

Suppose that in dialysis of the $H_2SO_4 + CuSO_4$ system, the following species are present in the membrane: H_3O^+, Cu^{2+}, SO_4^{2-}, HSO_4^- and the non-dissociated form, i.e. $(CuSO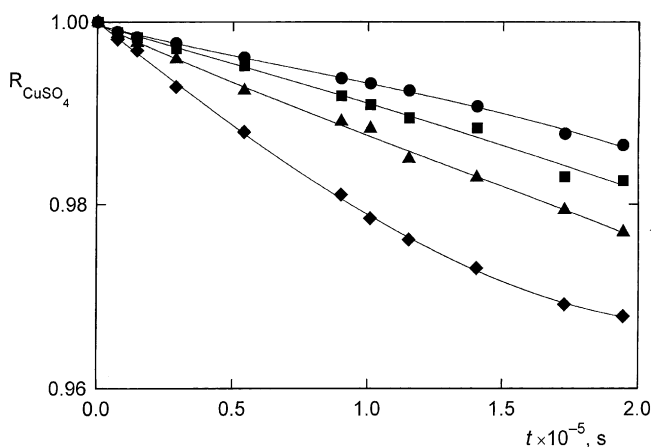_4)_{non}$. The concentration of the individual ions and the non-dissociated form can be found from the solution of the set of equations describing ionic equilibria, the electroneutrality condition and balance of hydrogen and copper, i.e.

$$\frac{[HSO_4^-]_M}{[H_3O^+]_M[SO_4^{2-}]_M} - K_H = 0 \tag{4}$$

$$\frac{[(CuSO_4)_{non}]_M}{[Cu^{2+}]_M[SO_4^{2-}]_M} - \beta_{Cu} = 0 \tag{5}$$

$$c_M^+ + [H_3O^+]_M + 2[Cu^{2+}]_M - [HSO_4^-]_M$$
$$-2[SO_4^{2-}]_M = 0 \tag{6}$$

$$2c_{H_2SO_4,M} - [H_3O^+]_M - [HSO_4^-]_M = 0 \tag{7}$$

$$c_{CuSO_4,M} - [Cu^{2+}]_M - [(CuSO_4)_{non}]_M = 0 \tag{8}$$

Using the protonization constant, K_H, and the complexity constant, β_{Cu}, taken from reference [9], the set of Eqs. (4)–(8) was solved by the Newton–Raphson method—the results are graphically given in Figs. 9 and 10 (the dependence of Cu^{2+} concentration and that of the non-dissociated form upon the H_2SO_4 concentration). (Note: The curves are drawn without considering limiting solubility of $CuSO_4$ in H_2SO_4.)

As shown in Fig. 11, where the flux of $CuSO_4$ through the membrane is plotted versus the initial acid concentration in compartment I, in dialysis of the $CuSO_4 + H_2SO_4$ system, a decrease in the flux of $CuSO_4$ with increasing acid concentration can be observed. On the other hand, at a constant acid concentration, the flux of $CuSO_4$ increases with increasing content of salt in the solution dialyzed—these dependences seem to be linear. The decrease in the flux of $CuSO_4$ with increasing acid concentration must be understood as a result of several phenomena. As sorption experiments show, the $CuSO_4$ concentration in the membrane decreases with increasing H_2SO_4 concentration, so that driving force for the transport of $CuSO_4$ is negatively influenced. At the same
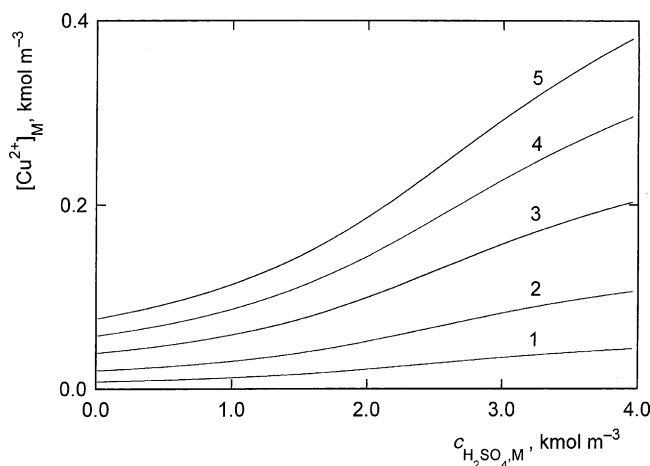

Fig. 8. Dependence of rejection coefficient for $CuSO_4$ upon time for $c_{CuSO_4,0}^{I} = 0.75\,\text{kmol m}^{-3}$: (♦) $c_{H_2SO_4,0}^{I} = 0.1\,\text{kmol m}^{-3}$; (▲) $c_{H_2SO_4,0}^{I} = 0.5\,\text{kmol m}^{-3}$; (■) $c_{H_2SO_4,0}^{I} = 1.0\,\text{kmol m}^{-3}$; (●) $c_{H_2SO_4,0}^{I} = 1.5\,\text{kmol m}^{-3}$.

Fig. 9. Dependence of Cu^{2+} concentration upon H_2SO_4 concentration in membrane: (1) $c_{CuSO_4,M} = 0.1\,\text{kmol m}^{-3}$; (2) $c_{CuSO_4,M} = 0.25\,\text{kmol m}^{-3}$; (3) $c_{CuSO_4,M} = 0.5\,\text{kmol m}^{-3}$; (4) $c_{CuSO_4,M} = 0.75\,\text{kmol m}^{-3}$; (5) $c_{CuSO_4,M} = 1.0\,\text{kmol m}^{-3}$.
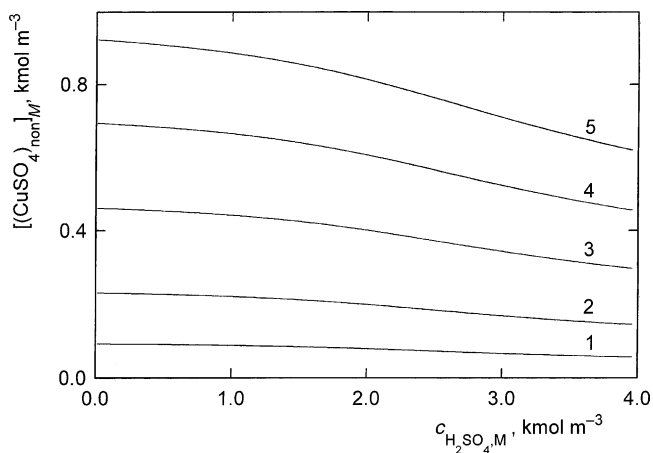
Fig. 10. Dependence of non-dissociated form of $CuSO_4$ upon H_2SO_4 concentration in membrane: (1) $c_{CuSO_4,M} = 0.1\,kmol\,m^{-3}$; (2) $c_{CuSO_4,M} = 0.25\,kmol\,m^{-3}$; (3) $c_{CuSO_4,M} = 0.5\,kmol\,m^{-3}$; (4) $c_{CuSO_4,M} = 0.75\,kmol\,m^{-3}$; (5) $c_{CuSO_4,M} = 1.0\,kmol\,m^{-3}$.
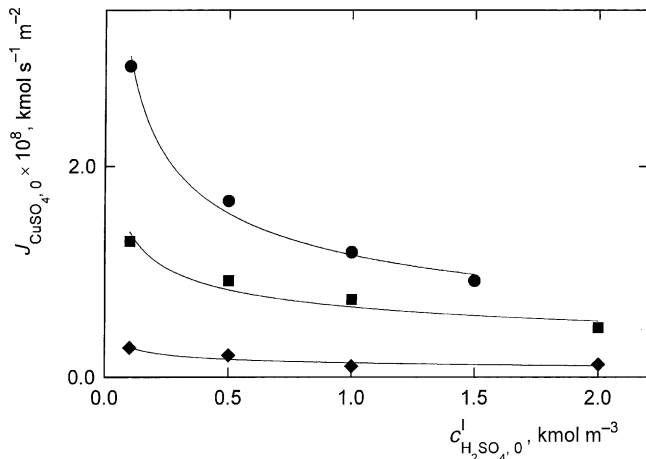

Fig. 11. Dependence of total flux of $CuSO_4$ in time $\tau = 0$ upon initial H_2SO_4 concentration in compartment I: ($\blacklozenge$) $c_{CuSO_4,0}^I = 0.1\,kmol\,m^{-3}$; ($\blacksquare$) $c_{CuSO_4,0}^I = 0.5\,kmol\,m^{-3}$; ($\bullet$) $c_{CuSO_4,0}^I = 0.75\,kmol\,m^{-3}$.

time, the concentration of the non-dissociated form decreases too. On the other hand, the concentration of Cu^{2+} ions is increasing, but these ions are repulsed by charged sites, while the non-dissociated molecules (even though they are larger than Cu^{2+} ions) permeate through the membrane more easily. Thus, the decrease in the total concentration of cupric sulfate and that in its non-dissociated form are controlling steps in this dialysis process. Moreover, the dependences given in Figs. 9 and 10, used here to explain the decrease in the $CuSO_4$ flux, are consistent with the data on sorption of $CuSO_4$ in the presence of H_2SO_4 in the membrane studied.

4. Conclusion

Dialysis of the $H_2SO_4 + CuSO_4$ system was investigated in a two-compartment batch cell with stirrers using an anion-exchange membrane Neosepta-AFN (Tokuyama Soda Co., Ltd.). On the basis of the time dependences of the H_2SO_4 and $CuSO_4$ concentrations in both the compartments, it was found that sulfuric acid permeates well through the membrane used, while cupric sulfate is efficiently rejected. The quality of the separation process was evaluated with the help of the rejection coefficient for $CuSO_4$. It was found that even at the highest $CuSO_4$ concentration ($0.75\,kmol\,m^{-3}$), the rejection coefficient is higher than 0.965. With respect to the low values of $CuSO_4$ fluxes through the membrane studied, the fluxes seem to be adequate for a practical application.

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