

Transport of Cu(II) Ions Through Charged Cation-Exchange Membranes

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ABSTRACT: Transport of Cu(II) ions through polysulfonated cation-exchange membranes under Donnan dialysis conditions was studied as a function of the pH gradient. The used charged membranes are homogeneous (polysulfone composition) and heterogeneous (polysulfone with polyester support) structures which are strongly acidic cation-exchange microporous-type membranes. The flux increases with decreasing of the pH gradient, which is influenced by the transport of copper ions. The quantitative relations were obtained which describe the time dependence of the transport system with the equilibrium distribution and the results were correlated with the flux data as well as with the membrane structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 421–427, 2001

Key words: transport; metal; polysulfone; donnan dialysis; ion exchange membranes.

INTRODUCTION

Ion-exchange membranes have found numerous applications in industrial processes,^{1–9} but many questions regarding their transport behavior is not well understood. In applications of the membranes, it is important to develop as detailed an understanding as possible about the underlying relationships between the membrane structure and the transport properties. Many studies on the diffusion of ions and molecules through ion-exchange membranes have been studied.^{10–16} It has been reported that the transport of metal ions through polymer membranes with a fixed specific functional group of the membrane is selectively possible. The function of specific carriers can be

adjusted as reversible or rapid changes of the chemical structure with the pH gradient. The mechanism of the interaction between ions and a charged group of a polymer chain is an interesting subject in ion-transport phenomena through charged membranes. The composition and the structure of the membrane polymer and the transport of ions may be controlled by the chemical potential gradient, pH gradient, the mobility of the cation through the membrane, ion-exchange sites within the ion-exchange polymer, and solvation/swelling of the polymer.

Donnan dialysis is a membrane-based equilibrium process, which has been proposed for a number of applications in which metal ions need to be recovered using hydrogen ions as a “pumping” ion. Some commercial membranes such as Nafion and DuPont membranes (sulfonated perfluoro polymer membranes) have been applied to recover or transfer cations using the Donnan dialy-

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sis process. Some applications of Donnan dialysis such as the concentration and removal of cations from hard water have been studied.¹⁷⁻²⁰

Polysulfonated ion-exchange membranes are truly microporous with controlled ion-exchange capacities and excellent mechanical wet strength and are particularly patented for the posttreatment process. The membrane also has the necessary chemical stability and ionic-transport properties which need to be designed for various applications. To use these technologies, it is important, first, to characterize the physical and chemical properties of the membrane for solution environments in which it is to be used. This was partly to investigate the transport mechanism of copper ions within a charged membrane and to correlate these results systematically with results based on the Donnan dialysis process. The present experiments are designed for the hydrogen ion to serve as a "pumping" for the process.

Relatively little quantitative data are available concerning the transport of ions through these polysulfonated ion-exchange membranes. An understanding of the parameters which affect ion transport is important in their use in chemical technology as well as in understanding their transport properties. Therefore, in this study, we are interested in obtaining information about the behavior of the Donnan dialysis process for the recovery of metals and the influence of the nature and pH gradient on the flux of copper ions through charged polysulfonated membranes.

EXPERIMENTAL

CuSO₄, standard NaOH, and HCl solutions were from BDH Ltd.; H₂SO₄, from Merck, Hopkin & Williams; and ICE-450 polysulfonated membranes which are of polysulfone composition (homogen, SA₃S) and polysulfone with a polyester support (heterogeneous, SA₃T), from Gelman Sciences, MI. A Spectrapor dialysis membrane was used for comparison and was obtained from Spectrum Medical Industries Inc.: a wet cellulose dialysis tubing in 1% sodium azide which was composed of cotton cellulose, 0.05 mm thick, with a nominal molecular weight cutoff of 3500.

Solutions were prepared using deionized water without further purification by dissolving a weighed quantity of Analar salts. Standard solutions were prepared using standard concentrated solutions.

Polysulfonated ion-exchange membranes are strongly acidic cation-exchange membranes and their ion-exchange capacity, 14 μeq per 47-mm disc, and thickness, δ 152.4 μm, were supplied in the hydrogen-ion form. The polysulfonated membrane discs in the H form were conditioned by a cycle of equilibrations with HCl, distilled water, NaOH, and, finally, distilled water; then, the membrane discs were pretreated with 1.0M H₂SO₄.

Transport Measurement

A two-compartment cell was used to measure the transport of ions. At zero time, each compartment, separated by the ion-exchange membrane, contained 20-mL solutions of equal volume; the effective membrane area, *A*, was 2.05 cm² and was maintained at 25 ± 1°C. The donor solution was CuSO₄ and was kept constant (0.1 mol dm⁻³) and the receiver side was of H₂SO₄ solutions applied at different pH ranges of 1.0–4.0. The experiments were repeated using Spectrapor dialysis membranes. The concentration of copper ions was determined by a Py Unicam-929 atomic absorption spectrophotometer. The acid concentration was measured by potentiometric acid–base titration.

THEORETICAL TREATMENT

The system to be discussed here is Donnan dialysis with ion-exchange membranes separating two solutions initially containing a metal salt at cell I and an acidic solution at cell II. In this article, a 2:1 electrolyte system was studied and, therefore, the basic equation for feed (metal) and driving (hydrogen) ions in Donnan dialysis using $z_2 = z_1$ can be expressed in terms of the Nernst-Planck equation:

$$\bar{J}_{\text{Cu}^{2+}} = -\bar{D}_{\text{Cu}^{2+}} \left(\frac{d\bar{C}_{\text{Cu}^{2+}}}{dx} + z_{\text{Cu}^{2+}} \bar{C}_{\text{Cu}^{2+}} \frac{F}{RT} \frac{d\bar{\Psi}}{dx} \right) \quad (1)$$

$$\bar{J}_{\text{H}^+} = -\bar{D}_{\text{H}^+} \left(\frac{d\bar{C}_{\text{H}^+}}{dx} + z_{\text{H}^+} \bar{C}_{\text{H}^+} \frac{F}{RT} \frac{d\bar{\Psi}}{dx} \right) \quad (2)$$

where \bar{J} and \bar{C} are the flux and the concentrations of ions in the membrane, respectively; *F*, the Faraday constant; *R*, the gas constant; *T*, the temperature; $\bar{\Psi}$, the electrical potential; and *x*, the distance in the membrane.

In the experiments described here, two ionic solutions containing copper sulfate and sulfuric acid separated by a cation-permeable membrane and no electric field is enforced externally across the membrane. Here, it is assumed that only cations are able to enter and pass through the membrane. The charge balance within both external solutions and the membrane phase should be equal, so the electric current density I must be zero through a cross section of the membrane:

$$I = 2\bar{J}_{\text{Cu}^{2+}} + \bar{J}_{\text{H}^+} = 0 \quad (3)$$

By electroneutrality, the total concentration of both counterions in the membrane is equal to the fixed charges \bar{C}_x , as eq. (4). Because of the conditions, the electric current is not applied, so the fluxes of the both ions is zero, as in eq. (5):

$$\frac{1}{2}\bar{C}_{\text{Cu}^{2+}} + \bar{C}_{\text{H}^+} = \bar{C}_x \quad (4)$$

$$2\bar{J}_{\text{Cu}^{2+}} = -\bar{J}_{\text{H}^+} \quad (5)$$

Boundary conditions are expressed as

$$x = 0, \quad C_{\text{Cu}^{2+}} = \bar{C}_{\text{Cu}^{2+},\text{I}}$$

$$x = 1, \quad C_{\text{Cu}^{2+}} = \bar{C}_{\text{Cu}^{2+},\text{II}}$$

Integration of eq. (1) by substituting eqs. (2), (4), and (5) yields

$$\begin{aligned} \bar{J}_{\text{Cu}^{2+}} = & \frac{\left(\frac{1}{2} - 1\right)\bar{D}_{\text{Cu}^{2+}}\bar{D}_{\text{H}^+}}{\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)l} (\bar{C}_{\text{Cu}^{2+},\text{I}} - \bar{C}_{\text{Cu}^{2+},\text{II}}) \\ & + \frac{\bar{D}_{\text{Cu}^{2+}}\bar{D}_{\text{H}^+}(\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+})\bar{C}_x}{\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)^2 l} \\ & \times \ln \frac{\frac{1}{2}\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)\bar{C}_{\text{Cu}^{2+},\text{I}} + \bar{D}_{\text{H}^+}\bar{C}_x}{\frac{1}{2}\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)\bar{C}_{\text{Cu}^{2+},\text{II}} + \bar{D}_{\text{H}^+}\bar{C}_x} \quad (6) \end{aligned}$$

where l is the thickness of the membrane and subscripts I and II represent the metal solution and the acidic solution, respectively.

These results can be expressed for the mean flux Cu^{2+} at the thickness direction in the membrane. The metal ion transferred from cell I to cell II is equal to that of the H^+ ion transferred from cell II to I by the mass balance. As the steady state is constant at all points within the membrane, the flux of Cu^{2+} is, therefore, obtained as time-dependent. The total concentration of each solution in cell I (C_{IT}) or cell II (C_{IIT}) can be expressed as

$$\frac{1}{2}C_{\text{Cu}^{2+},\text{I}} + C_{\text{H}^+,\text{I}} = C_{\text{IT}} \quad (7)$$

$$\frac{1}{2}C_{\text{Cu}^{2+},\text{II}} + C_{\text{H}^+,\text{II}} = C_{\text{IIT}} \quad (8)$$

where the subscript T represents the total concentration. In this work, the volume of the both cells is equal and either metal ions or hydrogen ions remain constant as in the following equation:

$$C_{\text{Cu}^{2+},\text{I}} + C_{\text{Cu}^{2+},\text{II}} = C_{\text{Cu}^{2+},T} \quad (9)$$

$$C_{\text{H}^+,\text{I}} + C_{\text{H}^+,\text{II}} = C_{\text{H}^+,\text{T}} \quad (10)$$

During the experiment, the concentration of metal ion is decreased in cell I and increased in cell II and can be written as

$$\bar{J}_{\text{Cu}^{2+}} = -\frac{V_{\text{I}}}{A} \frac{d\bar{C}_{\text{Cu}^{2+},\text{I}}}{dt} \quad (11)$$

$$\bar{J}_{\text{Cu}^{2+}} = \frac{V_{\text{II}}}{A} \frac{d\bar{C}_{\text{Cu}^{2+},\text{II}}}{dt} \quad (12)$$

where A is the exposed membrane area. The problem is the fact that the concentration involved in the above equations is that in the membrane and usually we know only the concentrations outside the membrane. To solve this problem, the selectivity coefficients on the surface of the membrane have to be considered. So, in this Experimental section, the selectivity was used and it was assumed that the selectivity at cell I ($x = 0$) and that at cell II ($x = 1$) are defined as

$$K_{\text{Cu},\text{I}}^{\text{H}} = \frac{\bar{C}_{\text{H}^+,\text{I}}}{\bar{C}_{\text{Cu}^{2+},\text{I}}} \frac{C_{\text{H}^+,\text{I}}}{C_{\text{Cu}^{2+},\text{I}}} \quad \text{at } x = 0 \quad (13)$$

$$K_{\text{Cu},\text{II}}^{\text{H}} = \frac{\bar{C}_{\text{H}^+, \text{II}}}{\bar{C}_{\text{Cu}^{2+}, \text{II}}} \frac{C_{\text{H}^+, \text{II}}}{C_{\text{Cu}^{2+}, \text{II}}} \quad \text{at } x = 1 \quad (14)$$

The value of the selectivity substituted by eqs. (4), (7), and (8) is represented by eq. (15):

$$K_{\text{Cu}^{2+}, \text{I}}^{\text{H}^+} = \frac{\left(\bar{C}_x - \frac{1}{2}\bar{C}_{\text{Cu}^{2+}, \text{I}}\right)^{1/2}}{(\bar{C}_{\text{Cu}^{2+}, \text{I}})} \frac{C_{\text{Cu}^{2+}, \text{I}}}{\left(C_{\text{I}^{\text{T}}} - \frac{1}{2}C_{\text{Cu}^{2+}, \text{I}}\right)^{1/2}} \quad \text{at } x = 0 \quad (15)$$

$$K_{\text{Cu}^{2+}, \text{II}}^{\text{H}^+} = \frac{\left(\bar{C}_x - \frac{1}{2}\bar{C}_{\text{Cu}^{2+}, \text{II}}\right)^{1/2}}{(\bar{C}_{\text{Cu}^{2+}, \text{II}})} \frac{C_{\text{Cu}^{2+}, \text{II}}}{\left(C_{\text{II}^{\text{T}}} - \frac{1}{2}C_{\text{Cu}^{2+}, \text{II}}\right)^{1/2}} \quad \text{at } x = 1 \quad (16)$$

From the equation, the concentration of ions on both surfaces of the membrane at cells I and II can be defined as

$$\bar{C}_{\text{Cu}^{2+}, \text{I}} = \frac{\sqrt{Z_1^2 - 16Z_1\bar{C}_x} - Z_1}{4} \quad \text{at } x = 0 \quad (17)$$

$$\bar{C}_{\text{Cu}^{2+}, \text{II}} = \frac{\sqrt{Z_2^2 - 16Z_2\bar{C}_x} - Z_2}{4} \quad \text{at } x = 1 \quad (18)$$

where Z_1 and Z_2 are described as

$$Z_1 = \frac{\bar{C}_{\text{Cu}^{2+}, \text{I}}^2}{(K_{\text{Cu}^{2+}, \text{I}}^{\text{H}^+})^2 \left(C_{\text{I}^{\text{T}}} - \frac{1}{2}\bar{C}_{\text{Cu}^{2+}, \text{I}}\right)} \quad (19)$$

$$Z_2 = \frac{\bar{C}_{\text{Cu}^{2+}, \text{II}}^2}{(K_{\text{Cu}^{2+}, \text{II}}^{\text{H}^+})^2 \left(C_{\text{II}^{\text{T}}} - \frac{1}{2}\bar{C}_{\text{Cu}^{2+}, \text{II}}\right)} \quad (20)$$

Equation (6) can be rewritten using eq. (17):

$$\begin{aligned} \bar{J}_{\text{Cu}^{2+}} = \frac{1}{4} \frac{\left(\frac{1}{2} - 1\right)\bar{D}_{\text{Cu}^{2+}}\bar{D}_{\text{H}^+}}{\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)l} & [(Z_1^2 - 16Z_1\bar{C}_x)^{1/2} - Z_1][(Z_2^2 - 16Z_2\bar{C}_x)^{1/2} - Z_2] + \frac{\bar{D}_{\text{Cu}^{2+}}\bar{D}_{\text{H}^+}(\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+})}{\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)^2 l} \\ & \times \ln \frac{\frac{1}{2}\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)[(Z_1^2 - 16Z_1\bar{C}_x)^{1/2} - Z_1] + 4\bar{D}_{\text{H}^+}\bar{C}_x}{\frac{1}{2}\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)[(Z_2^2 - 16Z_2\bar{C}_x)^{1/2} - Z_2] + 4\bar{D}_{\text{H}^+}\bar{C}_x} \quad (21) \end{aligned}$$

By substituting eq. (21) into eq. (11), the following equation can be found:

$$\begin{aligned} \frac{d\bar{C}_{\text{Cu}^{2+}, \text{I}}}{dt} = \frac{1}{8} \frac{\left(\frac{1}{2} - 1\right)\bar{D}_{\text{Cu}^{2+}}\bar{D}_{\text{H}^+}A(V_{\text{I}} + V_{\text{II}})}{\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)lV_{\text{I}}V_{\text{II}}} & \left[\{(Z_2^2 - 16Z_2\bar{C}_x)^{1/2} - Z_2\} - \{(Z_1^2 - 16Z_1\bar{C}_x)^{1/2} - Z_1\}\right] \\ & + \frac{1}{2} \frac{\bar{D}_{\text{Cu}^{2+}}\bar{D}_{\text{H}^+}(\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+})\bar{C}_xA(V_{\text{I}} + V_{\text{II}})}{\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)^2 lV_{\text{I}}V_{\text{II}}} \times \ln \frac{\frac{1}{2}\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)[(Z_2^2 - 16Z_2\bar{C}_x)^{1/2} - Z_2] + 4\bar{D}_{\text{H}^+}\bar{C}_x}{\frac{1}{2}\left(\frac{1}{2}\bar{D}_{\text{Cu}^{2+}} - \bar{D}_{\text{H}^+}\right)[(Z_1^2 - 16Z_1\bar{C}_x)^{1/2} - Z_1] + 4\bar{D}_{\text{H}^+}\bar{C}_x} \quad (22) \end{aligned}$$

Only the concentrations of two external solutions are known during the experiment. In this Experimental section, two electrolyte solutions

containing copper nitrate and an acid solution are separated by a cation-exchange membrane. Both solutions were stirred at the same rotational

speed with a magnetic stirrer to prevent the formation of significant boundary layers and also to ensure that the concentration of Cu^{2+} was uniform throughout in both solutions.

In that case, the fluxes of the ion can be determined experimentally, and an interpretation of the experimental results, the influence of the H^+ concentration for metal-ion fluxes, and other factors can be shown in eq. (21). The following assumptions are made to derive the basic equation, which describes the transport process in Donnan dialysis:

- (i) The system is assumed as membrane-diffusion-controlled;
- (ii) The process is in the pseudo-steady state;
- (iii) The diffusion coefficient is independent of the concentration inside the membrane;
- (iv) The osmotic flow of water through the membrane has been ignored;
- (v) The amount of the co-ion in the membrane is negligible due to its ion-exchange capacity and no co-ion can permeate the membrane according to Donnan co-ion exclusion.

RESULTS AND DISCUSSION

The fluxes of the Cu^{2+} ions passing through the membranes were estimated by monitoring their

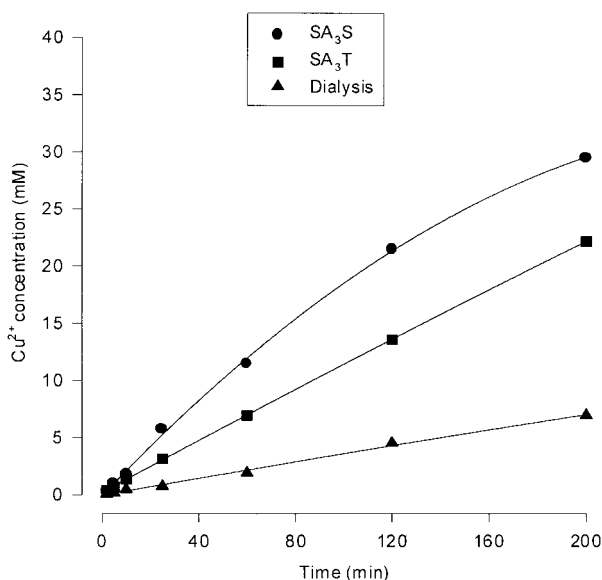


Figure 1 Time dependence of the concentration of $\text{Cu}(\text{II})$ through membranes when the initial pH in the receiver phase is 1.0.

Table I Flux and Diffusion Coefficient of the Membranes for Copper(II) Ion as a Function of pH

Membrane	pH	Flux ($\text{mol cm}^{-2} \text{s}^{-1}$)	Diffusion Coefficient ($\text{cm}^2 \text{s}^{-1}$)
SA ₃ S	1.0	1.792×10^{-4}	7.54×10^{-6}
	2.0	1.35×10^{-4}	5.71×10^{-6}
	4.0	8.85×10^{-5}	2.874×10^{-6}
SA ₃ T	1.0	1.104×10^{-4}	8.422×10^{-6}
	2.0	8.63×10^{-5}	5.74×10^{-6}
	4.0	2.28×10^{-5}	1.925×10^{-6}
Dialysis	1.0	3.713×10^{-5}	3.607×10^{-7}
	2.0	4.42×10^{-5}	4.35×10^{-7}
	4.0	5.15×10^{-5}	6.72×10^{-7}

concentration in the acidic solution as a function of time. The time-dependence concentration of Cu^{2+} ions through the polysulfonated ion exchange (SA₃S and SA₃T) and the dialysis membranes is given in Figure 1 at pH was 1.0. The diffusion coefficients of the copper ions were obtained by curve fitting eq. (22) to the experimental values. The results obtained for the flux and diffusion coefficients of the copper ion are listed in Table I.

The total number of moving ions in the membrane at any time is limited by a fixed charge. The analysis usually begins with the assumption that at either side of the membrane a Donnan equilibrium exists between the solution and membrane face. Within the membrane, an ion (pH) gradient then exists that will attempt to redistribute toward equilibrium by diffusion.

Two opposing effects are imposed by extremes in the membrane structure. If the pore channels are very large, the possibility exists for a co-ion to diffuse across the membrane without being repelled by fixed charges. This would be a leakage flow and would dissipate the Donnan flux. Contrarily, if the pore channels are indeed very small, so that no leakage flow occurs, the diffusion rates may be very low. The studied membranes are a microporous structure, so the metal diffusion rates have been found to be low.

Many studies concerning ion-transport phenomena in membrane–electrolyte solution systems have been done. There may be several factors controlling the membrane phenomena such as the ion flux through the membrane, partition coefficients at the interface between the mem-

brane and the electrolyte solution, the ionic concentration within the membrane, and polymer swelling. Of these, the ions within the membrane may play an important role in the transport phenomena. The ions may exist in two different states, that is, due to ion exchange within sites and Donnan adsorption.²¹ It would be interesting to separate the two states experimentally and, in particular, to compare the behavior of the Donnan salt with that of the free ion in solution.

Examples of the results of the metal-interchange fluxes and the membrane-diffusion coefficients, which were obtained across polysulfonated membranes which are symmetric and asymmetric structures, and the dialysis membrane are given in Table I. Polysulfonated membranes have the same nominal exchange capacity and crosslinking, but the difference is their structure.

The transport of Co(II), Ni(II), Mg(II), and Fe(III) ions through a sulfonated styrene-grafted or an acrylic acid-grafted membrane were studied and it was reported that the transport of metal ions increases with increasing of the membrane ion-exchange capacity and that the styrene-grafted membrane showed a higher transport fraction than that of the acrylic acid-grafted one.²² The transfer of copper ion through sulfonated ion-exchange membranes prepared by the paste method were studied by Sudoh et al.^{23,24} They used a ratio such as the ion-exchange capacity, self-diffusion coefficients of the copper ion, and membrane thickness as a criteria for the ionic flux through the membrane. Some workers studied the active and selective transport of alkali metal ions through copolymer ion-exchange membranes and the metal's transport rate was found to depend considerably on the membrane composition.^{25,26}

Transport data were obtained for the copper ion and each experiment was utilized at 0.1M against of various pH's of the H₂SO₄ solutions. Compared with the Nafion 117 (E.W. 100) membrane, the diffusion coefficients are of similar magnitude.¹¹ The diffusion coefficients for the Nafion 117 membrane as a function of pH 1, 2, and 3 are 3.17×10^{-6} , 6.73×10^{-7} , and 8.86×10^{-7} cm² s⁻¹, respectively. A comparison shows that the data obtained by polysulfonated ion-exchange membranes seem to be in good agreement with the Nafion and CMS membranes. The diffusion coefficients of the H⁺ and copper ions in the Neosepta CMS membrane were found to be 2.67×10^{-4} and 7.04×10^{-6} cm² s⁻¹, respectively. When compared, the mobility ratios

for the H⁺ ion over the copper ion in water and in the membrane phase are 13.8 and 37.9, respectively.²⁷ This difference can be interpreted as due to the stronger interaction of the copper ion with the charged polymer matrix which causes a decrease of the activity coefficient of the copper ion with respect to the H⁺ ion. When the diffusion coefficient of the dialysis membrane was compared with data found in the literature, the diffusion coefficient was found to be 3.607×10^{-7} cm² s⁻¹ when the acidic side pH was 1.0. The dialysis membrane is a weak acidic cation exchanger, so in acidic pH, its diffusion coefficients are expected to be lower. The obtained diffusion coefficient was in the reverse order of the polysulfonated charged membranes. When the acidic pH is higher, the diffusion coefficients and also the mass-transfer rates increase. The obtained results are of a similar magnitude as those in the literature.²⁸ The copper transport decreases with decrease of the pH in the receiver solution. It can be supposed that the fixed groups in the membrane are not dissociated, so the transport rate is found to be of a lower degree.

The metal-transfer rates observed for the homogeneous polysulfone membrane were found to be nearly twice higher than those of the supported one. On the other hand, the metal was transported most rapidly through the homogeneous (unsupported) membrane. It can be supposed that the H⁺ flux drives the transport of the metal ion through the membrane. The transport rate is related to the proton activity. The flux of H⁺ ions from the receiver to the feed solution governs the metal transport, meaning that a larger pH difference between the feed and receiver solutions is necessary to obtain a higher metal transport. In our earlier work, the flux of HCl was obtained to be much greater than that of the alkali salts, owing to the higher value of the activity coefficients of HCl than those of the salts.²⁹⁻³¹ This fact is due, to a certain extent, to a higher value of the activity coefficient of HCl in water, and also in water, the mobility of H is more than three times higher than is the mobility of the alkali cations. The larger value for HCl is due more to the more swollen state of the membrane than to the high mobility of the proton. It can be concluded that the metal transport rates were affected mainly by the membrane composition, the pH difference between the feed and the receiver solutions, and other factors such as crosslinking of the polymer and hydration.

For our goal, it is interesting to note that the largest flux of the copper ions was measured with a pH around 1. A much higher flux of the copper ion could, however, be achieved by applying an electrical field with inserting electrodes to chambers and enforcing the migration of the copper ion through the polysulfonated charged membranes.

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