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Recovery and Concentration of Metal Ions. II Multimembrane Hybrid System

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ABSTRACT

The multimembrane hybrid system (MHS) has been developed and used for the transportation and separation of divalent metal ions from multicomponent solutions. The system consists of three membranes in series

ion-exchange membrane | liquid membrane | ion-exchange membrane

The experiments were performed with liquid membranes composed of di(2-ethylhexyl)phosphoric acid in kerosene and Nafion-120 perfluorosulfonic acid polymer membranes. The fluxes and separation characteristics have been determined for MHS separating a solution of Zn(II), Mn(II), Cu(II), Co(II), and Ni(II) sulfates as the feed phase, and the strip phase containing sulfuric acid. The results of competitive permeation experiments have shown the selectivity order Zn(II) > Mn(II) > Cu(II) $\gg$ Co(II), Ni(II). High separation coefficients were found for Zn(II), Cu(II), and Mn(II) compared to Ni(II) and Co(II).

INTRODUCTION

Liquid membranes (1–6), LMs, in the form of supported, bulk, or emulsion LMs are fast developing as a promising method for the concentration, separation, and recovery of metal ions from wastewaters, industrial effluents, and dilute leach liquors in hydrometallurgical processing of lean ores (7–11). Other applications, such as disposal of radionuclides (12, 13) and the preconcentration of trace metals in analytical chemistry (14, 15), are also possible. On the other hand, ion-exchange membranes (16–18) made of various functionalized polymers are attractive for separation techniques. Their affinity toward ionic species and stability in industrial-scale processes make them useful in dialysis, Donnan dialysis, and electrodialysis as typical membrane processes (19–21).

While looking for effective and stable separation systems of practical importance, we checked the transport properties of a multimembrane hybrid system (MHS):

feed solution	ion-exchange	bulk liquid	ion-exchange	strip solution
MSO_4	membrane	membrane	membrane	H_2SO_4

The system is intended to combine the selectivity of liquid membranes with the stability of ion-exchange membranes by preserving the exchange-diffusion mechanism of transport in the system components. To some degree, MHS returns to the idea of an extraction process as realized by coupling an ion-exchange polymer membrane with a liquid organic extractant. The method was patented by Ho et al. (22) in 1976 and renewed recently by Kedem et al. (23). The same concept applied to both extraction and reextraction assembled in a continuous process leads to the MHS described in this paper. A similar system composed of an LM (hydrooxime reagent LIX64N) and different ion-exchange membranes was used by Kedem et al. (23) for transporting Cu(II) ions. It should also be noted that very promising separation properties of multimembrane systems in the form of composite membranes (three SLMs) or multistage processes for the separation of multivalent cations were reported by Danesi et al. (24–26).

The main advantage of MHSs is the possibility of avoiding some problems caused by the instability of organic liquid membranes in contact with aqueous solutions. Donnan exclusion of the ionic forms of an extractant and the high tortuosity of diffusion pathways are supposed to be practical ways suppress the permeation of a carrier from an LM to feed and strip solutions. Moreover, the ability of IEMs (ion-exchange membranes) to take up cations (or anions, depending on the charge of the ionogenic groups) from dilute solutions should result in high accumulation of reacting species at interfaces, thus probably enhancing the overall transport process.

In this paper the MHS has been tried for recovering, concentrating, and/or separating one or a group of ions from a mixture containing Zn(II), Mn(II), Cu(II), Ni(II), and Co(II) sulfates. For that purpose, di(2-ethylhexyl)phosphoric acid (henceforth D2EHPA) was selected as a carrier because it is a good extractant of divalent transition metals (27–39). In a number of transport experiments D2EHPA has been proved to transport zinc or other metals in relation to the operating conditions, e.g., pH and the concentration of a feed solution. However, information on the selective separation of a specified metal from a mixture of many competing cations is rather limited. Moreover, due to reaction-diffusion coupling, the selectivity of competitive LM transport cannot be predicted exactly from the transport of single metals (40, 41).

EXPERIMENTAL

Materials

The liquid membrane solution was prepared by dissolving D2EHPA (Sigma, USA) in kerosene (product of Maker, Poland). Both components were used as received. The concentration of D2EHPA in all liquid membranes used for our experiments was 0.1 M. The perfluorosulfonic ionomer membranes Nafion-120 (Du Pont de Nemours, USA) were used as intermediate ion-exchanging layers between LM and external solutions. Diffusion phenomena and Donnan dialysis performed with Nafion-120, which are part of the system discussed herein, have been presented in Part 1 of this series (20). Aqueous feed and strip solutions were prepared from analytical grade salts and sulfuric acid (P.O.Ch., Poland) dissolved in distilled water.

Transport Experiments

Experiments with the MHS were carried out by using the experimental arrangement shown in Fig. 1. A glass vessel equipped with a holder and two tubes made of Teflon contained a liquid membrane of the volume $V_{LM} = 15\ cm^3$. The membrane was stirred magnetically (Heidolph MR2000, Germany) at a constant rate of 300 ± 2 rpm. Nafion membranes separating the organic and aqueous solutions were mounted at the bottoms of the tubes. The working area A of each polymer membrane was 1.5 cm^2, and their thickness in its hydrogen form was 0.028 cm. Feed and strip solutions were circulated between cell tubes and reservoirs by running a multichannel peristaltic pump (Zalimp PP1B-05A, Poland).

Transport of ions across the membranes was followed in time by AAS analysis (Varian Spectra-20ABQ) of samples taken from the feed and strip solutions. The pH values of the feed were monitored using a pH electrode and a multifunction computer meter (ELMETRON CX 721, Poland).

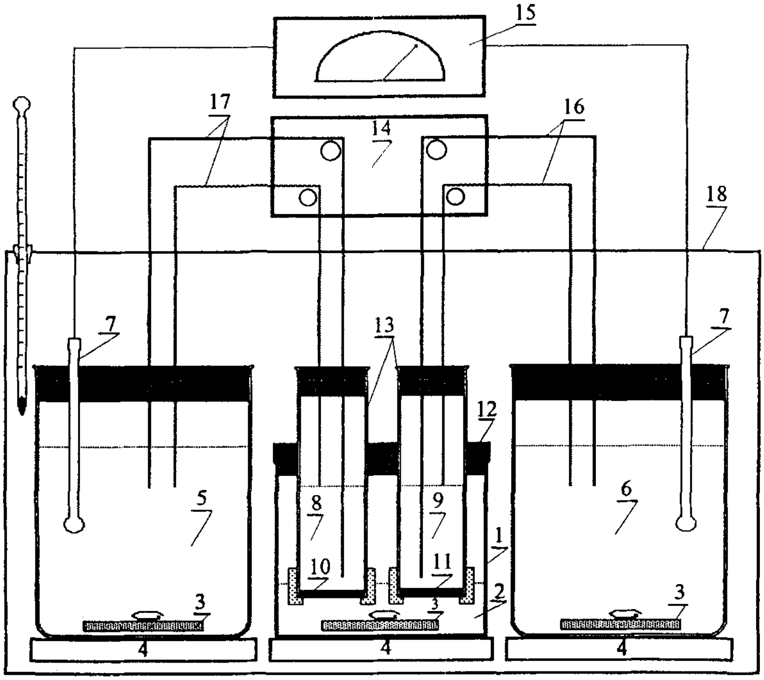

FIG. 1 Experimental arrangement of multimembrane hybrid system: (1) glass vessel, (2) bulk liquid membrane, (3) magnetic stirrer bars, (4) magnetic stirrer, (5, 8) feed solution, (6, 9) strip solution, (7) pH electrodes, (10, 11) Nafion membranes at strip and feed interfaces, (12) holder of Teflon tubes, (13) feed and strip cylinders, (14) multichannel peristaltic pump, (15) multielectrode pH meter, (16, 17) input and output of strip and feed solution.

The investigations were made at 25°C for transport systems A–D. The systems are characterized by the following concentrations and volumes of external solutions:

	Feed (f)	Strip (s)
A	250 mL 0.1 M $ZnSO_4$	150 mL 0.1 M H_2SO_4
B	500 mL 0.001 M $ZnSO_4$	100 mL 0.001 M $ZnSO_4$ + 0.1 M H_2SO_4
C	250 mL 0.02 M MSO_4	150 mL 0.1 M H_2SO_4
D	500 mL 0.001 M MSO_4	100 mL 0.1 M H_2SO_4

The symbol M in Systems C and D denotes Zn(II), Cu(II), Mn(II), Co(II), and Ni(II) in equimolar concentrations.

RESULTS AND DISCUSSION

Selective transport in MHS can be influenced by factors arising from the membranes (carrier and solvent, ionogenic groups in IEM) and external factors due to the medium (kind of ions, concentrations, pH, temperature). In this work, for evaluating the feasibility of MHS in the transport and separation of metal ions, it was only the composition of the feed solution that has been considered as a transport-determining factor. Therefore, some permeation and separation experiments were performed by using nonbuffered solutions of metal sulfates of different concentrations. In this way, metal fluxes, concentration and recovery factors, and separation characteristics were measured or calculated for use in designing new multimembrane systems.

(A) Transport of Zn(II)

D2EHPA is recognised as an efficient carrier of Zn(II) when applied in liquid membranes (30). We carried out experiments aimed at comparing Zn(II) flux in MHS with fluxes reported by other authors (e.g., Ref. 30, 39, 42) and dialytic processes performed with the Nafion-120 ion-exchange membrane (20). Experimental results for the transport of Zn(II) are shown in Fig. 2 as a plot of Zn(II) concentration in the strip solution against the time of transport. The quasi-stationary flux of Zn(II) across the MHS, J_{Zn}, was then calculated from the slope of linear dependence (squared correlation coefficient r^2 equal to 0.995) of the amount of transported Zn(II) (Q_{Zn}) vs time:

$$Q_{\mathrm{Zn}} = [\mathrm{Zn(II)}]_s V_s/1000A = J_{\mathrm{Zn}}t \qquad (\mathrm{mol/cm^2}) \qquad (1)$$

where V_s denotes the volume of the strip solution (cm^3) and A is the area of the ion-exchange membrane (cm^3) in contact with LM. The flux of Zn(II) from 0.1 M solution J_{Zn} calculated by a linear regression technique is $6.4 \pm 0.1 \times 10^{-9}$ mol/cm^2·s. Considering that the diffusion coefficients of D2EHPA are reported to range from 1×10^{-6} to 9×10^{-6} cm^2/s (30, 33), the order of magnitude of J_{Zn} seems to be typical for LMs containing that carrier. On the other hand, comparing the flux of Zn(II) in MHS with fluxes reported elsewhere for Donnan dialysis (20) ($\sim 10^{-8}$ mol/cm^2·s) it can be concluded that transport through IEMs does not limit the transport rates in MHS.

(B) Recovery and Concentration of Zn(II)

In order to check MHS performance in recovering and concentrating Zn(II) simultaneously, an experiment with a more dilute (0.001 M) feed

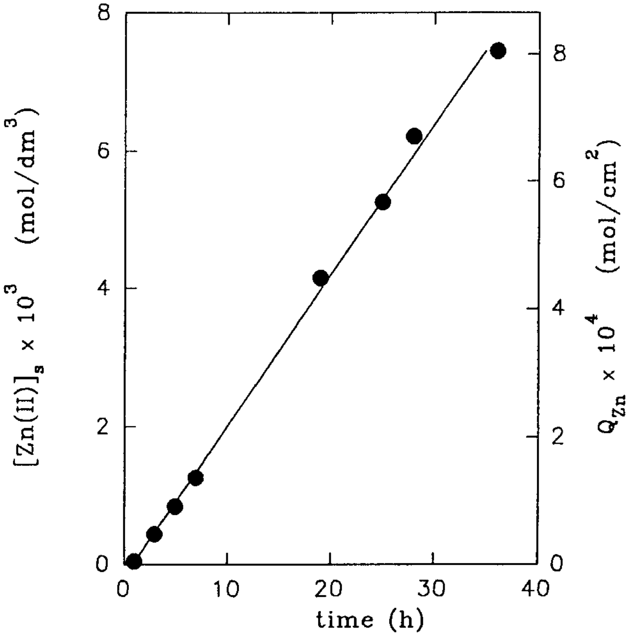

FIG. 2 Steady-state transport of Zn(II) ions from 0.1 M solution of $ZnSO_4$.

solution has been carried out. In order to reveal the effect of "up-hill" transport, the strip solution was composed of a 0.1 M solution of sulfuric acid with 0.001 M $ZnSO_4$ added. The results of the experiment are presented in Fig. 3(a–c). From the plot of $[Zn(II)]_s$ against the time of transport, the flux of Zn(II) was calculated to be 7.8×10^{-10} mol/cm^2·s. This value corresponds to the initial quasi-stationary conditions (up to 50 hours; the broken line in Fig. 3) characterized by a linear correlation between $[Zn(II)]_s$ and *t*. However, due to the flow and progressive depletion of metal ions in the feed solution, the flux decreases over time to a value of 4×10^{-11} mol/cm^2·s ($t = 120$ hours).

The "up-hill" transport of Zn(II) resulting from the imposed experimental conditions can be evaluated by calculating the concentration (CF) and efficiency (EF) factors:

$$CF = [M(II)]_{s,t}/[M(II)]_{s,o} \quad (2)$$

$$EF = [M(II)]_{s,t}/[M(II)]_{f,t} \quad (3)$$

where [M(II)] denotes the concentration of divalent metal ions in a strip

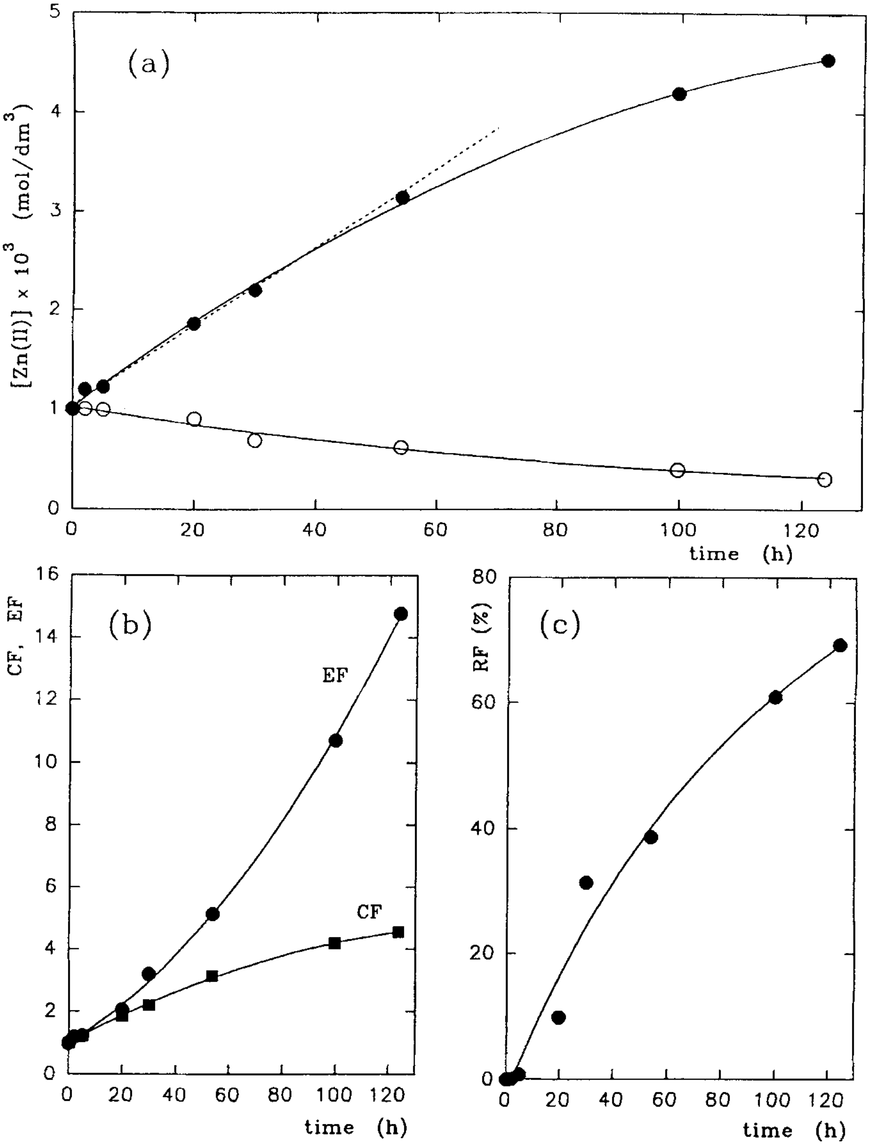

FIG. 3 Transport, concentration, and recovery of Zn(II) from 0.001 M solution of $ZnSO_4$: (a) concentration of Zn(II) in the strip (●) and feed (○) solution, (b) concentration CF (●) and efficiency EF (■) factor, (c) recovery factor RF.

(s) or feed (f) solution at the beginning (0) or after time t of the transport run. Because the maximum concentration of M(II) in a strip solution is given by Eq. (4) (43), the CF should become asymptotic at a value close to 5:

$$[\mathrm{M(II)}]_{\mathrm{s,max}} \approx [\mathrm{M(II)}]_{\mathrm{f,0}} V_{\mathrm{f}}/V_{\mathrm{s}} \tag{4}$$

Pumping of Zn(II) from the feed into strip chamber is alternatively characterized by the recovery factor RF:

$$\mathrm{RF} = 100([\mathrm{M(II)}]_{\mathrm{f,0}} - [\mathrm{M(II)}]_{\mathrm{f,t}})/[\mathrm{M(II)}]_{\mathrm{f,0}} \tag{5}$$

RF values found in this experiment reach 60% (see Fig. 3c) and, similarly to other factors (CF, EF, Fig. 3b), they can be augmented by prolonging the time of transport. Nevertheless, all the results presented (see plots of CF and EF in Fig. 3b and RF in Fig. 3c) confirm the usefulness of MHS for actively transporting and recovering Zn(II) ions from their dilute solutions. In practice, the effectiveness of MHS for concentrating metal ions ($\mathrm{CF} \gg 4$) can be significantly improved by making the volume of the acid solution as small as possible. Contrary to the concentration process, effective recovery requires only that an equivalent number of moles of a species be transported and antiported. This results from the fact that the recovery factor (Eq. 5) is independent of system volumes.

(C) Transport and Separation of Ions in Multiionic System

The MHS was tested for the competitive transport of five metal cations from a feed phase containing Zn(II), Mn(II), Cu(II), Co(II), and Ni(II), each of 0.02 M concentration, into a receiving phase containing 0.1 M H_2SO_4. Experimental curves for $[\mathrm{M(II)}]_\mathrm{s}$ vs t for each ion are presented in Fig. 4a. The respective plots show little transport of nickel and cobalt ions from the multiionic solution. The stationary fluxes (Table 1) calculated from data in Fig. 4(a) cover a broad range of values from 1.8×10^{-9} to $\sim 1 \times 10^{-11}$ mol/cm^2·s for Zn(II) and Ni(II), respectively. The total flux of metals is 3.1×10^{-9} mol/cm^2·s, i.e., half that of Zn(II) observed for the system described in Section A.

The separation properties of MHS are generally characterized by the overall separation coefficients $\alpha_{\mathrm{M_k}}$ calculated from the time-dependent concentrations of the feed (f) and strip (s) solutions:

$$\alpha_{\mathrm{M_k}} = \frac{[\mathrm{M}]_{\mathrm{k,s}}/\sum[\mathrm{M}]_{j\neq\mathrm{k,s}}}{[\mathrm{M}]_{\mathrm{k,f}}/\sum[\mathrm{M}]_{j\neq\mathrm{k,f}}} \tag{6}$$

In case of stationary transports, the separation ability of any membrane

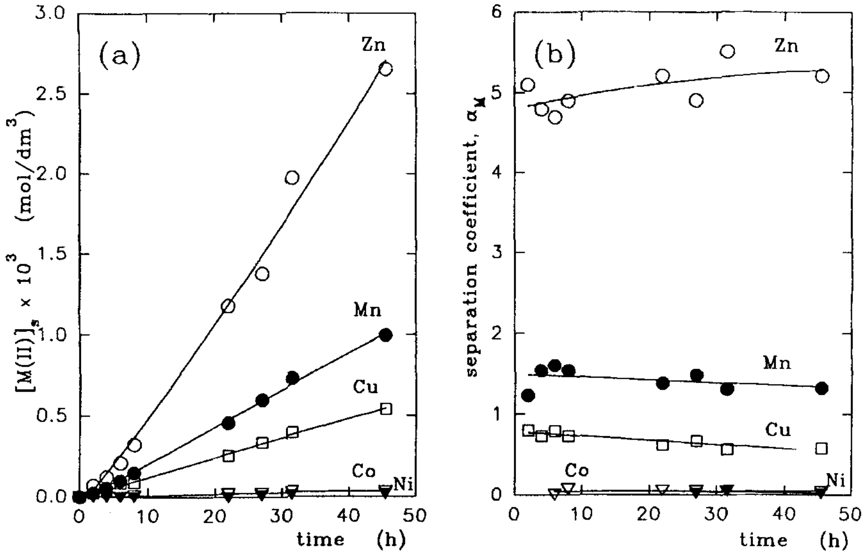

FIG. 4 Competitive transport and separation of divalent metal ions in MHS: (a) concentration of metal ions in the strip solution, (b) separation factor α_{M_k}. (○) Zn(II), (●) Mn(II), (□) Cu(II), (△) Co(II), (▲) Ni(II).

system is usually measured by selectivity coefficients $\beta_{M_p}^{M_k}$ defined as the ratio of fluxes of two different cations k and p:

$$\beta_{M_p}^{M_k} = J_{M_k}/J_{M_p} \tag{7}$$

The separation coefficients α_{M_k} (see Fig. 4b) and other separation characteristics of MHS, including $\beta_{M_p}^{M_k}$ in Table 1, show the following separation order:

$$\mathrm{Zn} > \mathrm{Mn} > \mathrm{Cu} >> \mathrm{Co} \geq \mathrm{Ni} \tag{8}$$

The separation properties of MHS must come directly from the properties of the carrier in a liquid membrane because ion-exchange membranes Nafion-120 do not separate these metals satisfactorily (20). Considering the known extraction properties of D2EHPA, the separation of Zn(II) against Ni(II) and Co(II) can be expected. Additionally, the results presented indicate that the system is efficient for the separation of two groups of ions, i.e., Zn(II), Mn(II), and Cu(II) against Co(II) and Ni(II). The separation coefficient for the group of metals $\alpha_{\mathrm{Zn+Mn+Cu}}$ is 44 whereas the selectivity coefficient $\beta_{\mathrm{Co+Ni}}^{\mathrm{Zn+Mn+Cu}}$ is 102. The mutual selectivity coeffi-

TABLE 1
Separation Characteristics of Divalent Metal Ions in the Multimembrane Hybrid System (MHS)

Specification		System C						System D				
Concentration of MSO_4 in the feed solution				0.02 M						0.001 M		
M(II)		Zn	Mn	Cu	Co	Ni		Zn	Mn	Cu	Co	Ni
Flux $J_M \times 10^{10}$ (mol/cm²·s)		18.4	8.7	3.6	0.20	~0.1		7.6	4.4	3.4	0.18	~0.08
Total flux × 10^9 (mol/cm²·s)				3.1						1.6		
Group selectivity coefficient $\beta_{Co+Ni}^{Zn+Mn+Cu}$				102						59		
Starting and final pH of the feed solution				4.3 → 3.3						4.9 → 2.9		
		M_k						M_k				
	M_p	Zn	Mn	Cu	Co	Ni	M_p	Zn	Mn	Cu	Co	Ni
Selectivity coefficients												
$\beta_{M_p}^{M_k}$	Zn	1	0.47	0.19	0.01	~0.005	Zn	1	0.58	0.44	0.02	~0.01
	Mn	2.1	1	0.41	0.02	~0.01	Mn	1.7	1	0.77	0.04	~0.02
	Cu	5.1	2.4	1	0.06	~0.03	Cu	2.2	1.3	1	0.05	~0.02
	Co	92	43.5	18	1	~0.5	Co	42	24	19	1	0.44
	Ni	~184	~87	36	2	1	Ni	~55	~55	~43	~2.3	1

cients $\beta_{M_p}^{M_k}$ for Zn, Mn, and Cu are much lower and vary from 2.1 to 5.1 (see Table 1).

(D) Separation, Concentration, and Recovery of Divalent Metals

In order to find the characteristics of simultaneous separation, concentration, and recovery of ions in MHS, an experiment has been carried out using a more dilute feed solution (0.001 M). The separation properties of MHS found in this experiment are similar to those observed in System C (see Fig. 5 and Table 1). However, the separation and selectivity coefficients referred to Zn(II) are slightly lower. The separation coefficients of Zn(II) and Mn(II) increase remarkably over time (see Fig. 5a). This effect is a consequence of decreasing the pH of the feed solution from 4.9 to 2.9 due to the equivalent countertransport of protons. The dependence of the separation process in the liquid membrane on the pH of the feed solution is expected because liquid membrane separation and reactivity are governed by phenomena similar to these in solvent extraction. The lowered pH of the feed phase favors the extraction of Zn(II) (36), and probably Mn(II), in comparison to Cu(II), Co(II), and Ni(II) ions which require a higher pH to be effectively transported by D2EHPA. However, in the case of MHS it is difficult to discuss the influence of pH on transport because its value at the interface between the ion-exchange and liquid membrane may be quite different from the pH of the bulk solution.

It is informative to compare the performance of MHS for separations of Co/Mn and Zn/Mn reported elsewhere by Mohapatra et al. (39). The selectivity coefficients β_{Co}^{Zn} published by these authors are 5.2 and 5.1, and they depend on the pH of the feed solution (3.35–4.5). For MHS, these coefficients are 92 and 43 for Systems C and D, respectively. Also, better results in respect to Mn(II)/Co(II) separation were found for MHS, i.e., $\beta_{Co}^{Mn} = 40$ and 25 compared to $\beta_{Co}^{Mn} = 3.7$ (pH 3.5) and 3.1 (pH 4.5) reported by Mohapatra (39). In both cases the selectivity order Mn(II) > Co(II) agrees with extraction data published by Sixiu et al. (29). Some discrepancies are seen, however, for the separation of Zn(II) over Mn(II). Our results indicate the preference of D2EHPA toward Zn(II) with a relatively low selectivity coefficient β_{Mn}^{Zn} ranging from 1.7 to 2.3 for 0.001 and 0.02 M feed solutions. Different results were found by Mohapatra et al. who reported fluxes leading to $\beta_{Mn}^{Zn} = 0.32$ and 0.34. Further studies in this direction made in our laboratory (44) pointed out the dependence of β_{Mn}^{Zn} on the concentration of the strip solution, and a reversed selectivity order, i.e., Mn(II) > Zn(II) ($\beta_{Mn}^{Zn} < 1$), has been observed after dilution of the sulfuric acid to a concentration of $\sim 1 \times 10^{-3}$ M.

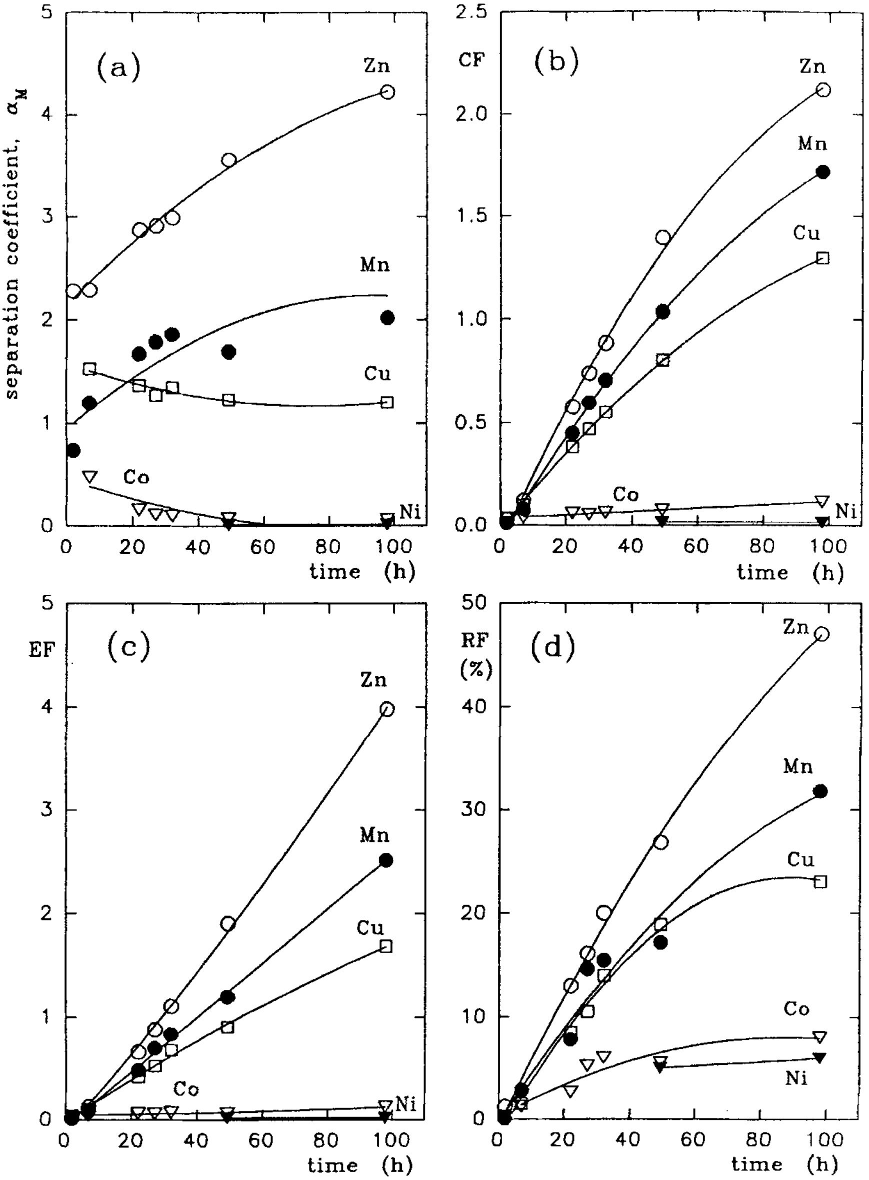

FIG. 5 Separation, concentration, and recovery of divalent metal ions in MHS: (a) separation coefficient α_{M_k}, (b) concentration factor CF, (c) efficiency factor EF, (d) recovery factor RF. (○) Zn(II), (●) Mn(II), (□) Cu(II), (△) Co(II), (▲) Ni(II).

Metal ions are actively concentrated in the strip solution or removed from the feed solution following the selectivity order (see Figs. 5b and 5d). Thus, MHS can be a useful tool for the simultaneous separation, recovery, and concentration of these metals.

Remarks on the Mechanism of Transport in Multimembrane Hybrid System

The transport of ions in MHS involves a number of reaction–diffusion phenomena contributing to the transport rate and selectivity. According to the scheme presented in Fig. 6, two mechanisms are of prime importance: carrier countertransport in a liquid membrane and the interchange of ions within ion-exchange membranes. These processes are coupled by interfacial ion-exchange reactions. The unidirectional (passive) flow of salts or acid through IEMs (dashed lines in Fig. 6) resulting from the sorption of some amounts of free electrolytes into the membrane phase (20) can also influence transport. However, due to the lack of significant differences in the affinity of sulfonic groups toward the cations studied, the selective extraction of a preferred ion, or a group of ions, by D2EHPA from IEM seems to be the key process for the separation effects. It is known that reactions between D2EHPA and divalent metals in solution have a complex and multistage character, including dissociation of the acid and complexation of M(II) ions. The overall stoichiometry of this reaction depends on the resulting complex. Nevertheless, taking into account the data published by Golovanov et al. (32), it can be assumed that the selectivity order Zn(II) > Cu(II) ≫ Ni(II) observed for MHS is typical for the simple

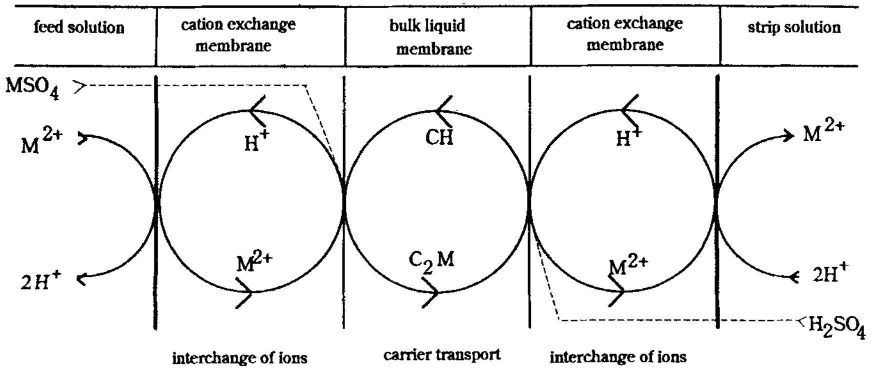

FIG. 6 Schematic representation of the transport mechanism in a multimembrane hybrid system.

reaction of ion exchange between D2EHPA (HR) and metal ions $\overline{M^{2+}}$ associated with the sulfonic groups of IEM:

$$2HR + \overline{M^{2+}} \rightleftarrows MR_2 + 2\overline{H^+}$$

where R denotes the anion of D2EHPA.

CONCLUSIONS

The results presented in this paper show that the properties of MHSs are promissing in view of their stability and possible applications in typical liquid membrane separation techniques. The stationary experiments (A, C) demonstrated the stable performance of MHSs in the transport and separation of M(II). Thus, as expected, ion-exchange membranes prevent the elution of a carrier from the organic phase and stabilize the system interfaces. Some other studies (45) made in our laboratory have indicated the usefulness of MHSs for employing special carriers that are soluble in both water and the organic phase, e.g., poly[poly(ethylene glycol) phosphate] (46). MHSs can be regarded as useful in prolonged transport, especially when the contamination of aqueous solutions is undesirable e.g., in processing products for the food industry or pharmaceuticals.

An effective MHS needs a proper selection of IEMs resistant to the corrosive action of an organic solvent. In our test experiments we did not find any changes in perfluorosulfonic Nafion membranes when they had been in contact with a kerosene solution of D2EHPA for over 400 hours.

The separation properties of MHSs are determined by the selectivity of LMs and the properties of the carrier used. Under the applied experimental conditions, the selectivity order typical of D2EHPA was Zn > Cu > Co ≥ Ni. Mn(II) is located between zinc and cupric ions, although this order can be disturbed by changing the concentration of the feed and/or strip solution.

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