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Recovery and Concentration of Metal Ions. III. Concentration and Temperature Effects in Multimembrane Hybrid System

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ABSTRACT

The performance of the multimembrane hybrid system (MHS) made up of ion-exchange membranes and a bulk liquid membrane (D2EHPA in kerosene) has been examined. Fluxes and the separation between Zn(II), Mn(II), Cu(II), Co(II), and Ni(II) sulfates have been studied as dependent on the concentration of aqueous phases and temperature. The results show a saturation of fluxes at increased concentrations of aqueous feed or strip solutions. The total limiting fluxes are ~1 × 10^{-9} mol/cm^2·s whereas the limiting fluxes for specific metal ions vary in the range from 6×10^{-12} to 5×10^{-10} mol/cm^2·s. The effect of temperature on MHS transport results in an activation energy of 16 to 30 kJ/mol depending on the metal species. The optimum conditions for separating metals are determined by the concentration of a feed solution in the range from 0.001 to 0.01 M and the concentration of sulfuric acid in a stripping solution in the range from 0.01 to 0.5 M. Selectivity coefficients $\beta_{Co+Ni}^{Zn+Mn+Cu}$ calculated as the ratio of stationary fluxes amount to 30–40, and are practically constant in the 298 to 328 K temperature interval.

INTRODUCTION

There are numerous industrial processes producing effluents that contain several ions of heavy metals or other substances which should be separated or removed because of proecological legislation and demands for products' purity, nontoxicity, etc. Liquid membranes (LMs) of a high separation ability and adaptability are considered to be a promising

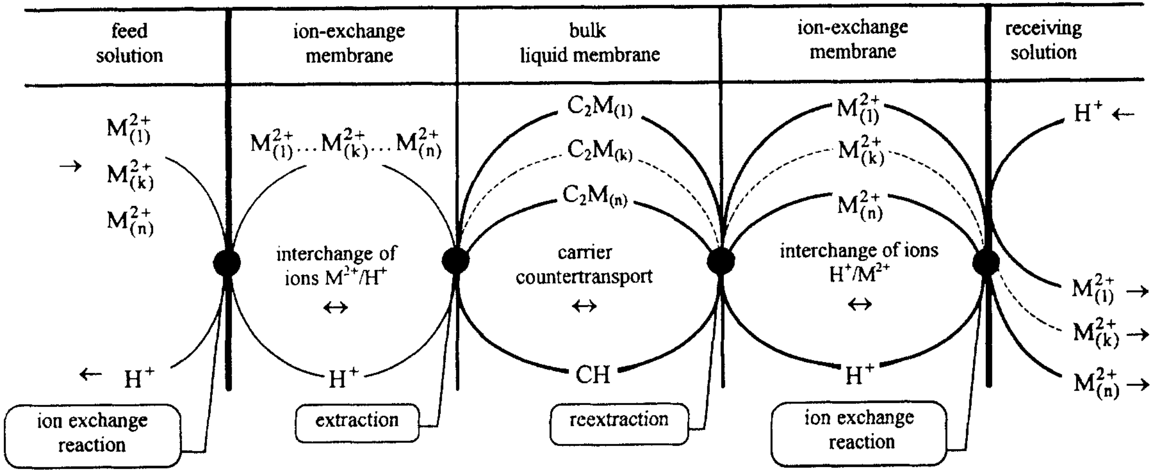

FIG. 1 Schematic representation of the transport mechanism and separation of divalent ions in a multimembrane hybrid system.

method for satisfying requirements of both a technological and economical nature. However, the instability of liquid membrane systems, e.g., emulsion liquid membranes, as well as the uptake of a carrier and an organic solvent into a processed solution, could hamper potential applications of LMs in some industrial areas like the pharmacy and food industries. To some extent these difficulties can be overcome by designing a multimembrane hybrid system (MHS) that combines the performances of solid ion-exchange membranes and liquid membranes containing various ionic carriers (1–3).

The simplest MHS is based on the idea of countertransport in a liquid membrane coupled to interchanges of ions in two adjacent ion-exchange membranes. The mechanism of permeation and the separation of ions after passing through the stack of membranes is depicted in Fig. 1. According to this scheme, the transport in a liquid membrane is facilitated by a selective carrier whereas the transport in polymer membranes (IEM) is mediated by their ionogenic groups fixed in a polymer backbone. At the interfaces IEM/LM a specific dual ion-exchange process (4) occurs between counterions of a carrier and counterions of ionic groups in ion-exchange membranes. All exchange-diffusion processes underlying the transport system allow an active "up-hill" transport of ions from a feed phase into a strip chamber, whereas the separation should follow the order of selectivity characteristic for a carrier and metal ions in a feed solution.

Previous test experiments (3) made in our laboratory demonstrated the multimembrane hybrid system to be stable over time and to be effective for transporting some divalent ions. However, to implement the MHS as a method of practical importance, more information concerning the dependence of permeation rates and separation characteristics on operating conditions is needed. In this work the variables of interest are the concentration of an aqueous feed, the strip phase, and the temperature. The respective scaling functions for fluxes and the separation ability of MHS are expected to be useful in ascertaining an optimum regime for the transport system investigated.

EXPERIMENTAL

Materials

The bulk liquid membrane was composed of a 0.1 M solution of di-(2-ethylhexyl)-phosphoric acid (D2EHPA purchased from SIGMA USA) dissolved in kerosene (produced by Maker, Poland). The volume of the liquid membrane solution used in each experiment was 15 mL. The ion-exchange membranes Nafion-120 (produced by Du Pont de Nemours, USA) were used as the separators between immiscible liquid phases, i.e., between the liquid membrane and the respective aqueous solutions. The Nafion membrane is composed of a perfluorosulfonic polymer of 0.6 equiv/kg ion-exchange capacity in its dry state (or 1.1 mol H^+/dm^3 in its swollen form). The sorption of salts and their permeation in the Nafion membrane have been reported elsewhere (2).

Transport Experiments

Experimental procedures and the equipment used were essentially the same as these described previously in detail (3). The membrane system consisted of three membranes in series contacted with an external aqueous solution containing a mixture of Zn(II), Cu(II), Mn(II), Ni(II), and Co(II) sulfates, and a solution of sulfuric acid at the opposite interface:

aqueous solution of MSO_4	Nafion-120 polymer membrane	D2EHPA in kerosene 0.1 M	Nafion-120 polymer membrane	aqueous solution of H_2SO_4

A summary of the experimental conditions and the concentrations of solutions used are listed in Table 1. To diminish the number of variables, only experiments under quasi-steady-state conditions were carried out, and they are presented herein.

TABLE 1
Summary of Experimental Operating Conditions

	Stripping solution		Feed solution[a]		
	$[H_2SO_4]_{s,0}$ (mol/dm^3)	volume (V_s) (cm^3)	$[MSO_4]_{f,0}$ (mol/dm^3)	volume (V_f) (cm^3)	Temperature (K)
The effect of stripping agent concentration	0.001–1.0	150	0.002 pH_{start} = 4.5 pH_{end} = 3.3	350	298
The effect of feed concentration	0.5	150	0.0001–0.1 pH_{start} = 6.3–3.0 pH_{end} = 3.6–2.9	350	298
The effect of temperature	0.5	150	0.002	350	298–326

[a] The concentration for each metal species in a solution.

RESULTS AND DISCUSSION

Basic Formulations

Transport in a membrane system, when mediated by a carrier, usually exhibits a hyperbolic relationship between stationary fluxes and the concentration of substrates in a feed solution. Consequently, the fluxes in liquid membranes become asymptotic at their limiting value $J_{\mathrm{M,lim}}$ (5, 6) due to restrictions imposed by the extraction/reextraction efficiency of an ionic carrier. The overall experimentally observed effect is a weak dependence of the fluxes on the concentrations of reagents outside of a liquid membrane. Note that a similar effect was observed by Uragami et al. (7) for ion-exchange membranes during Donnan dialysis. It was also proved for exchange diffusion, i.e., LM countertransport (8, 9), that the saturation of fluxes can be reached both by increasing the concentration of reagents in a feed phase and/or strip phase. This effect can be described quantitatively by using the phenomenological Eq. (1) derived from the Michaelis–Menten kinetics of consecutive reactions:

$$J_{\mathrm{M}} = J_{\mathrm{M,lim}} \times \frac{[C]}{K_{\mathrm{MM}} + [C]} \tag{1}$$

$J_{\mathrm{M,lim}}$ in Eq. (1) denotes the limiting flux, and $[C]$ is the concentration of solutes in a feed or stripping solution. The constant K_{MM} (mol/dm^3) corresponds to the concentration resulting in $J_{\mathrm{M}} = 0.5J_{\mathrm{M,lim}}$.

In order to evaluate the limiting fluxes of metal species in the MHS, the steady-state fluxes were determined as dependent on the respective concentrations $[\mathrm{M(II)}]_{\mathrm{f,0}}$, and $[\mathrm{H_2SO_4}]_{\mathrm{s,0}}$. These fluxes were calculated from the linear experimental relationship

$$\frac{[\mathrm{M(II)}]_{\mathrm{s}} V_{\mathrm{s}}}{1000 A_{\mathrm{s}}} = J_{\mathrm{M}} t \tag{2}$$

where $[\mathrm{M(II)}]_{\mathrm{s}}$ and V_{s} denote the concentration and the volume (cm^3) of the stripping solution, respectively, and A_{s} is the area (cm^2) of the ion-exchange membrane. Thus, all fluxes were calculated as the slope of a plot of $[\mathrm{M(II)}]_{\mathrm{s}}$ against the time of transport by using the least-squares technique. Note that the above formulation requiring $dJ_{\mathrm{M}}/dt = 0$ represents a steady state for the reextraction process only. This means that some accumulation of ions inside a membrane phase can still proceed if the input flux exceeds the output flux. The exact steady-state conditions require $J_{\mathrm{in}} = J_{\mathrm{out}} =$ constant and $d[\mathrm{M(II)}]_{\mathrm{m}}/dt = 0$, where $[\mathrm{M(II)}]_{\mathrm{m}}$ is the concentration of M(II) ions accumulated in each of membranes forming the MHS.

In the case of multicomponent feed solutions, the selectivity of MHS is characterized by selectivity coefficients $\beta^{M_k}_{M_p}$ defined as the ratio of stationary fluxes corresponding with selected metal ions k and p:

$$\beta^{M_k}_{M_p} = J_{M_k}/J_{M_p} \tag{3}$$

Another measure of the MHS quality concerning the separation process is the selectivity coefficient for a group of ions. This coefficient should be applied when separated ions form no less than two distinct groups:

$$\beta^{\Sigma M_k}_{\Sigma M_p} = \frac{\sum_{i=1}^{n} J_{M_{k,i}}}{\sum_{j=1}^{m} J_{M_{p,j}}} \tag{4}$$

where $M_{k,i}$ are preferred metal ions.

Effect of Stripping Agent Concentration

According to the above theoretical predictions, the experimental fluxes reach their limiting value for Mn(II) and Cu(II) or go to saturation in the case of Zn(II) with an increased concentration of sulfuric acid (see Fig. 2). The total flux of divalent metal cations ranges from 2 × 10^{-10} to 1 ×

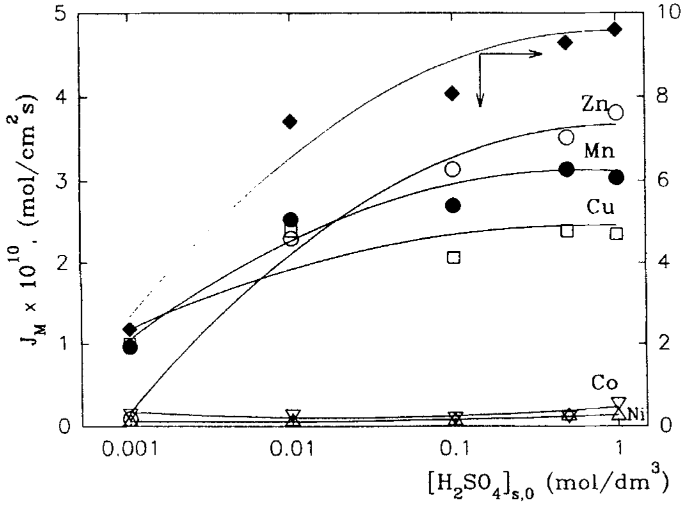

FIG. 2 Effect of sulfuric acid concentration in receiving solution on fluxes in MHS: (○) Zn(II), (●) Mn(II), (□) Cu(II), (▽) Co(II), (△) Ni(II), (◆) total flux.

10^{-9} mol·cm^{-2}·s^{-1}, with the main contribution of Zn(II), Mn(II), and Cu(II). Ni(II) and Co(II) ions are transported in small amounts only.

The experimental data presented in Fig. 2 were fitted to the linear equation, derived from Eq. (1), for relating the reciprocities of J_M and $[H_2SO_4]_s$. The calculated limiting fluxes $J_{M,lim}$ and the constants K_{MM} are collected in Table 2. The 2–4 × 10^{-10} mol·cm^{-2}·s^{-1} values of $J_{M,lim}$ for Zn(II), Mn(II), and Cu(II) are much higher than those of Ni(II) and Co(II) ($J_{M,lim} < 10^{-11}$ mol·cm^{-2}·s^{-1}). However, in the respective subgroups the fluxes are not differentiated to the degree which would enable their effective separation, e.g., between Zn(II) and Cu(II) or Mn(II). The selectivity order resulting from $J_{M,lim}$ is Zn(II) > Mn(II) > Cu(II) ≫ Ni(II) and remains unchanged after dilution of sulfuric acid from 1.0 to ~0.01 M.

It can be also concluded through regression analysis (see the squared correlation coefficients in Table 2) that the effect of sulfuric acid concentration on the transport properties of the MHS is described fairly well by Eq. (1). Some divergence of the experimental points and the general relationship was observed only for very diluted stripping solutions, i.e., when $[H_2SO_4]_s < [M(II)]_f$.

Effect of Feed Concentration

The concentrations of feeds originating from industrial effluents can be very different. Therefore, it is important to recognize the performance of the MHS in processing different feed phases and to evaluate any limiting fluxes that may appear. The experimental results that illustrate the relation between steady-state fluxes and initial concentrations $[M(II)]_{f,0}$ are presented in Fig. 3. As expected, an increase of $[M(II)]_{f,0}$ in subsequent trans-

TABLE 2

Concentration and Temperature Parameters of Transport in the Multimembrane Hybrid System[a]

	$1/J_M = f(1/[H_2SO_4]_{s,0})$			$1/J_M = f(1/[M(II)]_{f,0})$			$\ln(J_M) = f(1/T)$	
Ion	$J_{M,lim}$ (mol·cm^{-2}·s^{-1})	K_{MM} (mol/dm^3)	r^2	$J_{M,lim}$ (mol·cm^{-2}·s^{-1})	K_{MM} (mol/dm^3)	r^2	E_a (kJ/mol)	r^2
Zn(II)	3.6×10^{-10}	5.5×10^{-3}	0.95	5.1×10^{-10}	8.7×10^{-4}	0.88	21 ± 4	0.98
Mn(II)	3.0×10^{-10}	2.1×10^{-3}	0.99	—	—	—	16 ± 3	0.95
Cu(II)	2.4×10^{-10}	1.1×10^{-3}	0.97	—	—	—	19 ± 8	0.81
Co(II)	—	—	—	2.3×10^{-11}	2.2×10^{-3}	0.94	31 ± 5	0.97
Ni(II)	6.6×10^{-12}	6.1×10^{-4}	0.88	1.3×10^{-11}	3.7×10^{-4}	0.86	—	—
Total M(II)	9.2×10^{-10}	2.9×10^{-3}	0.99	1.1×10^{-9}	2.5×10^{-3}	0.84	19 ± 5	0.93

[a] r^2 = squared correlation coefficient for the specified relationship; — = no suitable experimental data.

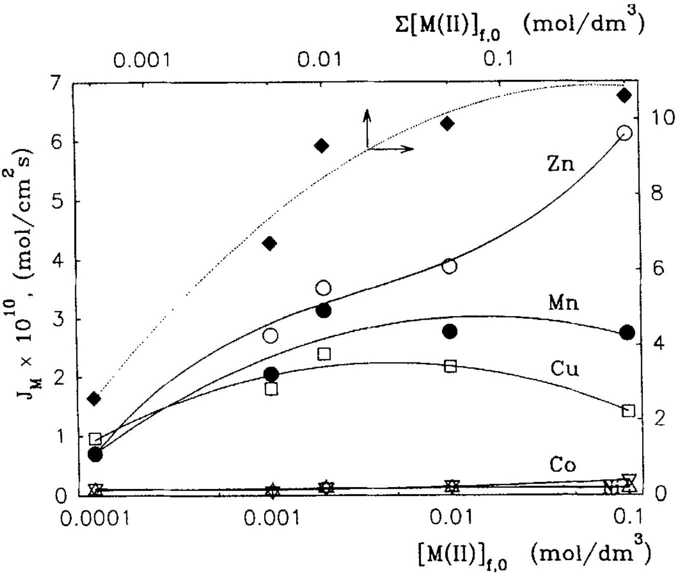

FIG. 3 Effect of feed concentration on fluxes in MHS: (○) Zn(II), (●) Mn(II), (□) Cu(II), (▽) Co(II), (△) Ni(II), (◆) total flux.

port runs causes a rise in the total flux up to its limiting value (~1 × 10^{-10} mol·cm^{-2}·s^{-1}, Table 2) as predicted by Eq. (1). It is noteworthy that the total limiting flux for $J_M = f(\Sigma[\mathrm{M(II)}]_{\mathrm{f,0}})$ is nearly the same as for $J_M = f([\mathrm{H_2SO_4})]_s)$, which indicates that the concentration of D2EHPA is the transport limiting factor. An additional evaluation can be made through K_{MM} constants which are 2.5 × 10^{-3} M for $J_M = f(\Sigma[\mathrm{M(II)}]_{\mathrm{f,0}})$ and 2.9 × 10^{-3} M for $J_M = f([\mathrm{H_2SO_4}]_s)$. These rather low values prove that the ion-exchange membranes stabilize interfacial processes involved in MHS transport. This stabilization probably results from a high ion-exchange sorption of transported and antitransported ions from the aqueous phases into the Nafion membranes.

A comparison of the curves in Fig. 3 corresponding to particular metal species shows that the effect of feed concentration can be qualitatively different. Over the experimental conditions evaluated, the fluxes of Mn(II) and Cu(II) exhibit a weak maximum at a concentration of 5 × 10^{-3} M. An increased selectivity toward Zn(II) ions can be seen above this concentration. The origin of this phenomenon is not clear. However, one can postulate that it results from a peculiarity of the competitive dual ion-exchange reactions in the multiionic system. These reactions should be considered as coupled processes, especially when the concentration of metal ions becomes comparable or higher than that of mediating species like the carrier in a liquid membrane. Therefore, Eq. (1) describes the overall transport in the multiionic systems satisfactorily but not the specific fluxes.

Effect of Temperature

Some transport runs were conducted in order to investigate the effect of temperature on the steady-state fluxes in the MHS. The experiments, made over the temperature range from 298 to 338 K under selected conditions, yielded the saturation of fluxes. The resulting fluxes (see Fig. 4A), plotted as a function of $\ln(J_M)$ versus $1/T$ (see Fig. 4B), show a typical Arrhenius relationship as represented by

$$\ln(J_{\mathrm{M}}) = \text{constant} + \frac{E_{\mathrm{a}}}{RT} \tag{5}$$

where R is the gas constant, T is the temperature in K, and E_a is the effective activation energy for the MHS transport.

The activation energies were calculated from the plots presented in Fig. 4(B) and are summarized in Table 2. The overall activation energy for the MHS transport is 19 ± 0.5 kJ/mol whereas for particular metals E_a ranges from 16 ± 3 to ~30 kJ/mol for Mn(II) and Co(II), respectively. The lowest E_a found for Mn(II) is close to that reported by Mohapatra et al. (6), i.e., 12 kJ/mol, for Mn(II) transported by D2EHPA in a supported liquid membrane. In general, the activation energies found in our study are comparable or lower than those for diffusion phenomena in the perfluorosulfonic ion-exchange membranes, i.e., 20–30 kJ/mol, reported by other authors (10–12). On the other hand, Dreisinger and Cooper (13), in their study of D2EHPA extraction rates, found the following activation energy for Zn(II), Co(II), and Ni(II): 14.8, 18.0, and 13.2 kJ/mol, respectively. They concluded that increased values of E_a indicate the kinetics of interfacial chemical reactions as the process limiting factor. Their observation on the largest activation energy for an interfacial transport of Co(II) agrees with our results. Thus, it is reasonable to assume that both factors, i.e., diffusion phenomena in the ion-exchange membranes and interfacial dual ion-exchange processes, determine the overall activation energy for the transport in MHS.

Separation Characteristics

It can be seen in Fig. 5 that the MHS containing the liquid membrane with D2EHPA is efficient for the separation of Zn(II), Mn(II), and Cu(II)

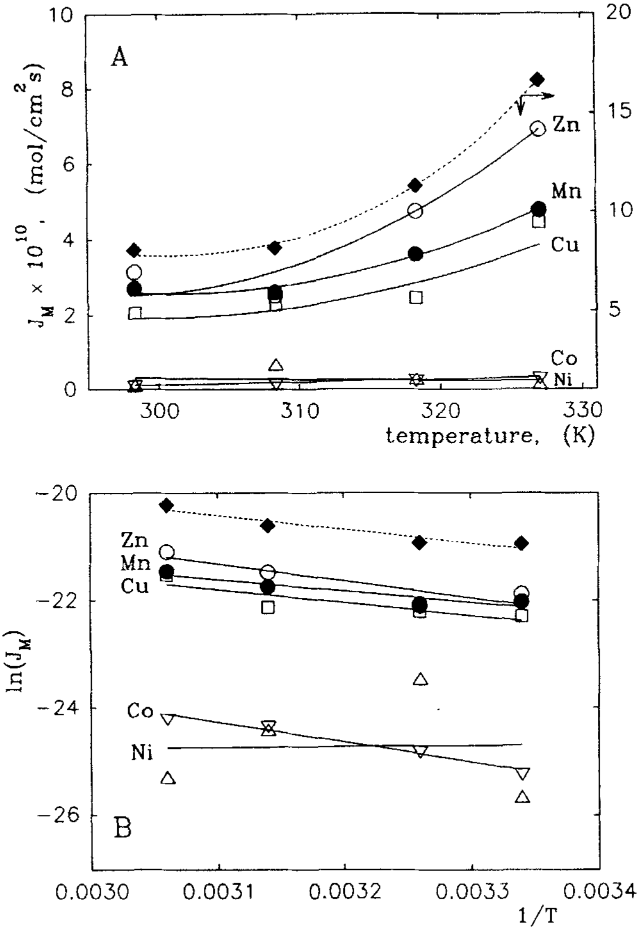

FIG. 4 Effect of temperature on fluxes in MHS: (A) experimental results, (B) Arrhenius plots; (○) Zn(II), (●) Mn(II), (□) Cu(II), (▽) Co(II), (△) Ni(II), (◆) total flux.

over Ni(II), and Co(II) from their mixtures of an equimolar concentration. The selectivity coefficient $\beta^{M_k}_{M_p}$ reaches a value of 40 at the maximum of $\beta^{M_k}_{M_p} = f([H_2SO_4]_{s,o})$, and $f([M(II)]_{f,o})$ curves (see Figs. 5A, 5B). The optimum conditions for the separation are then limited by the concentration of sulfuric acid in a stripping solution from 0.01 to 0.5 M and a concentration of the feed solution not below 0.001 M. From the $\beta^{M_k}_{M_p} = f(T)$ plots presented in Fig. 5(C) it can also be concluded that the separation is practically independent of temperature in the 298 to 328 K range.

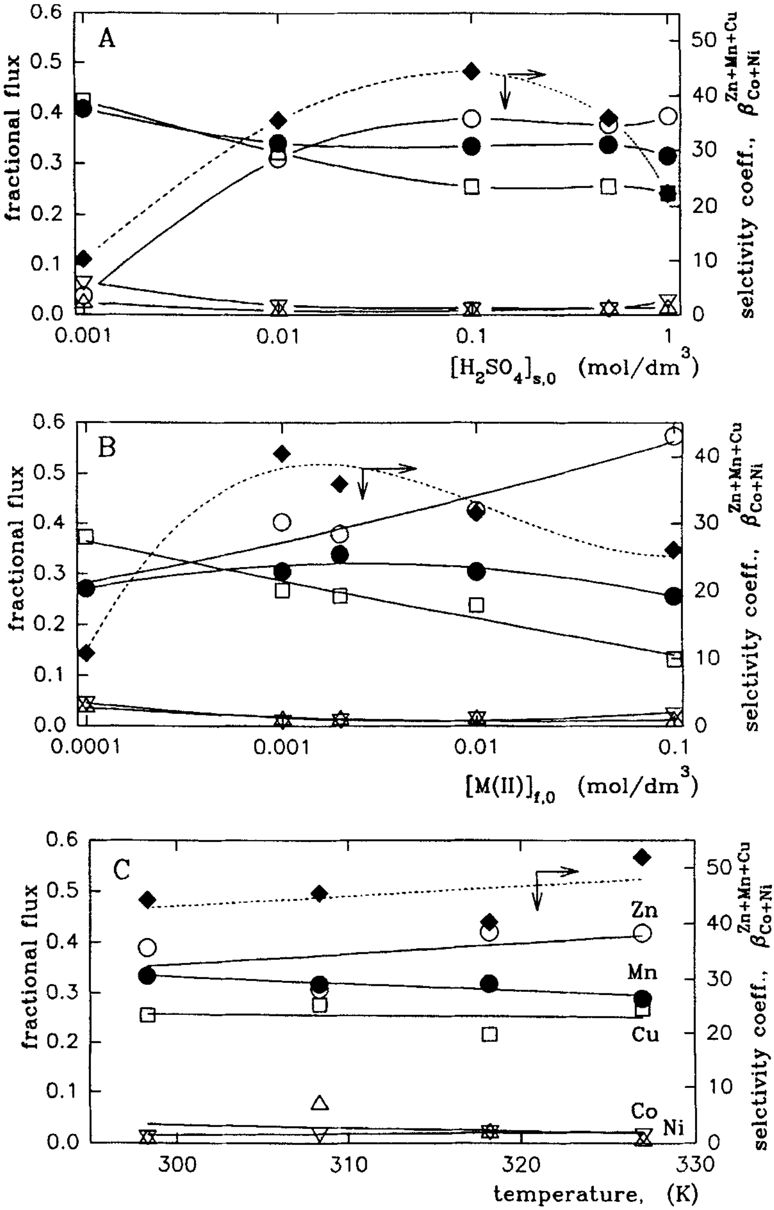

FIG. 5 Separation characteristics: fractional fluxes of (●) Mn(II), (□) Cu(II), (▽) Co(II), (△) Ni(II), and (◆) selectivity coefficients. Effect of acid concentration (A), feed concentration (B), and temperature (C).

The dominant metal species Zn(II), Mn(II), and Cu(II) are characterized by comparable selectivity coefficients and fractional fluxes F:

$$F = \frac{J_{M_k}}{\sum J_M} \tag{6}$$

However, all the results shown in Fig. 5 prove that these fluxes mainly form the following selectivity order: Zn(II) > Mn(II) > Cu(II). Decreasing the strip and the feed concentrations to 0.01 M and 5×10^{-4} M, respectively, changes the selectivity order to Cu(II), Mn(II) > Zn(II) or Cu(II) > Mn(II), Zn(II), respectively. A similar sequence was reported by Mohapatra et al. (14) in respect to the separation of Zn(II) and Mn(II) from solutions of higher pH. Therefore, this different result can be explained by an insufficiently low pH (at the liquid and ion-exchange membrane interface) favoring the reaction of preferential complexing of Mn(II) or Cu(II) ions instead of Zn(II).

CONCLUSIONS

The following practical conclusions, based upon the stationary fluxes and separation characteristics of the multimembrane hybrid system, and related to the feed and strip concentrations and temperature, can be drawn.

- The MHS containing D2EHPA is effective for separating Zn(II), Mn(II), and Co(II) over Ni(II) and Co(II) over the broad range of their concentrations.
- The optimum feed concentrations for the system evaluated are above 0.001 M for each of metals whereas the optimum concentration of sulfuric acid in the receiving solution is between 0.1 and 0.5 M.
- Despite the differences in the activation energies for specific metal fluxes, the separation characteristics do not depend on temperature in the 295 to 325 K range.
- Further development of the MHS toward an advanced transport system could be made by introducing additional ion-exchange polymer membranes and liquid membranes containing more sophisticated and efficient carriers.

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