Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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L. Fernandez[a]; J. Aparicio[ab]; M. Muhammed[a]
[a] DEPARTMENT OF INORGANIC CHEMISTRY, ROYAL INSTITUTE OF TECHNOLOGY, STOCKHOLM, SWEDEN [b] Kimika Departamendua, Euskal Herriko Unibertsitatea, Bilbo, Spain

To cite this Article Fernandez, L. , Aparicio, J. and Muhammed, M.(1987) 'The Role of Feed Metal Concentration in the Coupled Transport of Zinc through a Bis-(2-ethylhexyl)phosphoric Acid Solid Supported Liquid Membrane from Aqueous Perchlorate Media', Separation Science and Technology, 22: 6, 1577 — 1595

To link to this Article: DOI: 10.1080/01496398708058419

URL: http://dx.doi.org/10.1080/01496398708058419

SEPARATION SCIENCE AND TECHNOLOGY, **22(6)**, pp. 1577-1595, 1987

The Role of Feed Metal Concentration in the Coupled Transport of Zinc through a Bis-(2-ethylhexyl)phosphoric Acid Solid Supported Liquid Membrane from Aqueous Perchlorate Media

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L. FERNANDEZ,* J. APARICIO,* and M. MUHAMMED

DEPARTMENT OF INORGANIC CHEMISTRY
ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM, SWEDEN

Abstract

The coupled transport of Zn(II) macroconcentrations (up to 100 mmol/dm^3) and H$^+$ through a solid supported liquid membrane (SSLM) consisting of bis-(2-ethylhexyl)phosphoric acid (HDEHP) dissolved in the aliphatic kerosene Isopar-H has been investigated as a function of the hydrodynamic characteristics and chemical composition of the system. The results were analyzed in terms of a model considering the aqueous and organic diffusion as well as chemical reaction rates in order to explain the observed zinc transfer rates. The analysis showed the importance of the carrier saturation phenomenon taking place as the metal concentration is increased and the subsequent minimization of the role of chemical reaction kinetics.

INTRODUCTION

Solvent extraction of zinc by di(2-ethylhexyl)phosphoric acid (HDEHP = HR) has been most successfully applied in industrial operations. An example is the Espindesa process which is presently used at an industrial plant scale (*1*). However, the possibility of combining the extraction and stripping stages in a single operation should be considered as an alternative to conventional solvent extraction. This can be achieved by the use of solid supported liquid membranes (SSLM).

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*Permanent address: Kimika Departamendua, Euskal Herriko Unibertsitatea, 48080 Bilbo, Spain.

In a previous study the coupled transport of zinc through a HDEHP SSLM was described (*2*). In that work the influence of both hydrodynamic and chemical conditions was investigated. Permeability equations taking into account the equilibrium and kinetic characteristics of this system (*3*, *4*) were derived and showed to be in fair agreement with the experimental data. In that study the metal concentration was kept at trace level with the purpose of investigating the chemical kinetic contribution to the overall transport rate through the membrane.

In order to test further the potential applicability of SSLM as an alternative process for zinc recovery, more realistic conditions of the feed solutions containing the metal are considered. The higher metal concentration is probably the most significant difference with respect to the study performed in Ref. *2*. For this reason an extension of the previous investigation has been carried out. In the present study the range of metal concentrations investigated has been substantially increased.

At high metal concentration the concentration of unbound carrier available for transport becomes considerably lowered. On the other hand, a decrease in the effective carrier concentration will bring about a considerable increase in the mass transfer resistance due to organic diffusion. Although the role of aqueous diffusion and chemical reaction rates can be expected to diminish in these circumstances, it cannot be disregarded.

Baker et al. (*5*) observed a limiting flux value in the permeation of Cu^{2+} through a SSLM consisting of pure LIX 64N when the metal concentration was increased. This was attributed to the limited solubility of the extracted copper complex. In fact, they isolated a green precipitate, which is characteristic of this copper complex, from the membrane phase. Imato et al. (*6*), while studying the transport of Cu^{2+} with LIX 64N at high copper concentration, did not observe the precipitate. A possible explanation is that they employed LIX 65N diluted with phosphorous esters. In this work the flux equations used did not consider aqueous diffusion and chemical reaction rates. Therefore, deviations of the proposed equation from the results are noticed.

Largman et al. (*7*) proposed that the rates of chemical reaction are the only active resistance in the transport of copper at macroconcentrations (up to 0.1 mol/dm^3) using SSLM consisting of a variety of hydroxyoxime carriers. Organic diffusion is quoted in this work as the main resistance only for fresh membranes. Aqueous diffusion contribution is disregarded. Choy et al. (*8*) reported the existence of an induction time prior to the attainment of steady state in their study of the transport of sodium macroconcentrations using monensine and cholanic acid as carriers. This induction time was explained in the form of an added diffusion resistence in the membrane. No theoretical basis equations were given.

In a review paper by Danesi (*9*) the effect of carrier saturation was treated. Although the theoretical equations derived do not take into account the effect of chemical reaction rates, good agreement with the experimental data presented in this work was observed.

The study presented here aims at obtaining a better understanding of the various phenomena which take place when the metal concentration in SSLM systems is increased. It also serves as a test for the validity of the model previously derived for this coupled transport system.

THEORETICAL CONSIDERATIONS

The transport rate is assumed to be mainly governed by the diffusion and chemical kinetic processes taking place at the aqueous–feed membrane boundaries and interface as well as within the membrane itself (cf. Fig. 10b in Ref. *2*).

The equilibrium study of this system (*3*) shows that the extraction of the metal can be described by the following equations:

$$\mathrm{Zn}^{2+} + \overline{2(\mathrm{HR})_2} \overset{k_{\mathrm{eq1}}}{\rightleftharpoons} \overline{\mathrm{ZnR}_2(\mathrm{HR})_2} + 2\mathrm{H}^+ \tag{1}$$

$$\mathrm{Zn}^{2+} + \overline{\tfrac{3}{2}(\mathrm{HR})_2} \overset{k_{\mathrm{eq2}}}{\rightleftharpoons} \overline{\mathrm{ZnR}_2(\mathrm{HR})} + 2\mathrm{H}^+ \tag{2}$$

On the other hand, a kinetic study of the same system (*4*) in which both extracted species were considered showed that the interfacial flux can be described by

$$J_i = \overrightarrow{J} - \overleftarrow{J} = K_{ao}[\mathrm{Zn}] - k_{oa}\overline{[\mathrm{Zn}]} \tag{3}$$

where k_{ao} and k_{oa} are the pseudofirst-order kinetic constants of the ITSCR mechanism proposed in Ref. *4*, and $\overline{[\mathrm{Zn}]} = \overline{[\mathrm{ZnR}_2(\mathrm{HR})_2]} + \overline{[\mathrm{ZnR}_2(\mathrm{HR})]} = \overline{[\mathrm{Zn}]}_2 + \overline{[\mathrm{Zn}]}_1$.

The flux equations describing the transport process across the membrane are obtained as follows.

First, it is assumed that an unstirred diffusion layer may exist between the bulk feed solution and the membrane–feed interface. Assuming as well that the concentration gradient due to this diffusion layer does not substantially vary with time in the course of the experiments, Fick's first law can be applied to obtain the metal flux across this diffusion layer:

$$J_a = \Delta_a^{-1}([\mathrm{Zn}] - [\mathrm{Zn}]_i) \tag{4}$$

The interfacial flux due to the chemical reaction at the interface will now take the form

$$J_i = k_{ao}[\mathrm{Zn}]_i - k_{oa}\overline{[\mathrm{Zn}]} \tag{5}$$

Finally, the flux due to diffusion of the extracted species through the organic membrane can be described by

$$J_o = J_{o,2} + J_{o,1} = \Delta_{o,2}^{-1}(\overline{[\mathrm{Zn}]}_2 - \overline{[\mathrm{Zn}]}_{2,s}) + \Delta_{o,1}^{-1}(\overline{[\mathrm{Zn}]}_1 - \overline{[\mathrm{Zn}]}_{1,s}) \tag{6}$$

where Fick's first law is again applied.

The following two assumptions are now made:

(1) Steady state is established throughout the system and thus $J_a = J_i = J_o = J$ (*10*).
(2) $\overline{[\mathrm{Zn}]}_2 \gg \overline{[\mathrm{Zn}]}_{2,s}$ and $\overline{[\mathrm{Zn}]}_1 \gg \overline{[\mathrm{Zn}]}_{1,s}$. This is justified as we used high $[\mathrm{H}^+]$ at the membrane-strip interface which causes equilibria (1) and (2) to be almost completely reversed toward the left.

Using the results in Refs. *3* and *4* and solving for the flux, taking into account that

$$\frac{k_{ao}}{k_{oa}} = \frac{\overline{[\mathrm{Zn}]}}{[\mathrm{Zn}]} = k_D \tag{7}$$

the following equation is obtained:

$$J = \frac{[\mathrm{Zn}][(\overline{\mathrm{HR}})_2]^2 F}{\Delta_a[(\overline{\mathrm{HR}})_2]^2 F + \Delta_{o,2} k_{\mathrm{eq1}}^{-1}[\mathrm{H}^+]^2 + k_1^{*-1} F} \tag{8}$$

where

$$F = 1 + \beta[(\overline{\mathrm{HR}})_2]^{-1/2}\chi \tag{9}$$

Nevertheless, some simplifications could be introduced to Eq. (8). First, if we consider that [Zn] in the present study increases up to 0.1 mol/dm^3, the contribution of the chemical reaction rate to the overall flux could be disregarded. This is valid because the high metal concentration will favor the forward reaction as compared to the back reaction rates (cf. Eq. 5). Although this contribution, expressed by the term k_1^{*-1} in the Eq. (8), proved to be of great importance in describing the data at a trace level, it is negligible in the present case. Equation (8) would reduce to

$$J = \frac{[\mathrm{Zn}][\overline{(\mathrm{HR})_2}]^2 F}{\Delta_a[\overline{(\mathrm{HR})_2}]^2 F + \Delta_o k_{\mathrm{eq1}}^{-1}[\mathrm{H}^+]^2} \tag{10}$$

where F is defined as in Eq. (9).

On the other hand, χ may be assumed to be equal to unity because the two extracted species are similar in size and, hence, similar diffusion coefficients may be assumed. In this case

$$J = \frac{[\mathrm{Zn}][\overline{(\mathrm{HR})_2}]^2 F}{\Delta_a[\overline{(\mathrm{HR})_2}]^2 F + \Delta_o k_{\mathrm{eq1}}^{-1}[\mathrm{H}^+]^2} \tag{11}$$

where

$$F = 1 + \beta[\overline{(\mathrm{HR})_2}]^{-1/2} \tag{12}$$

Flux equations derived with the assumption of only one species diffusing in the organic membrane proved to fail to describe the transport behavior observed in the previous study and were not considered in the present work.

EXPERIMENTAL

Reagents and Solutions

Bis-(2-ethylhexyl)phosphoric acid (HDEHP = HR), (BDH), was used as received. Its purity was found to be 96.01% by potentiometric titration with NaOH in ethanol media.

$Zn(ClO_4)_2$ was prepared from ZnO and $HClO_4$ AR grade and recrystallized twice before use. The concentration in the stock solutions was determined by titration with EDTA using Eriochrome Black T as indicator (*11*).

Isopar-H (Esso Chemical Co.), an odorless aliphatic kerosene diluent, was washed with NaOH (0.1 *M*), bidistilled water, HCl (0.1 *M*), and finally bidistilled water until no traces of chloride were detected in the aqueous solution.

The solid support was a hydrophobic Durapore (Millipore Corp., Bedford, Massachusetts) polyvinylidene fluoride flat film of 1.25×10^{-2} cm thickness and 75% porosity ($\varepsilon = 0.75$).

Analytical Technique

A modification of the method used in Ref. *2* for the determination of the [Zn] variation with time was adopted. Due to the limitation of the linear range of the automated FIA method previously developed (*12*) (up to 0.5 mmol/dm^3), it was decided to follow the increase of [Zn] in the strip solution. For that purpose the FIA manifold was modified as described in Fig. 1, allowing linear detection up to 40 ppm [Zn] in 1.0 mol/dm^3 $HClO_4$. The linear range so achieved is high enough to permit a direct recording of the [Zn] variation in the strip solution during the first minutes of the permeation experiment.

$HClO_4$ (1.0 mol/dm^3) was used as the carrier stream in the FIA manifold in order not to disturb the experiments. This stream was later neutralized with another stream of 1.0 mol/dm^3 NaOH at the same flow rate and finally mixed with a stream containing Xylenol Orange in a 0.1 mol/dm^3 HAc–1.0 mol/dm^3 Ac^- buffer at pH = 5.7 in amounts adequate to permit the detection of the red complex formed. This method was also automated as described in Ref. *12*.

Other apparatus and experimental procedures used are described in Ref. *12*.

RESULTS

For all the permeation experiments presented in Figs. 3–7, the flux of zinc ions entering the strip solution,

$$J = \frac{d[\mathrm{Zn}]_s}{dt} \frac{V_s}{Q'} \tag{13}$$

was evaluated from the slope of the linear part of the $[\mathrm{Zn}]_s$ vs time plots. In most cases a progressive change in the slope of these plots was observed during the first seconds from the start of the permeation experiments. A typical $[\mathrm{Zn}^{2+}]_s$ vs time plot is presented in Fig. 2. After this induction time, the slope was constant for at least several minutes. This part was then used to evaluate the flux. This induction time, which may be considered as the time needed to reach a linear concentration gradient through the membrane, is discussed later in more detail.

DISCUSSION AND CONCLUSIONS

In Fig. 3 the effect of the hydrodynamic conditions is presented. The experiments in Fig. 3b were performed at higher pH_f and C_{Zn} than those

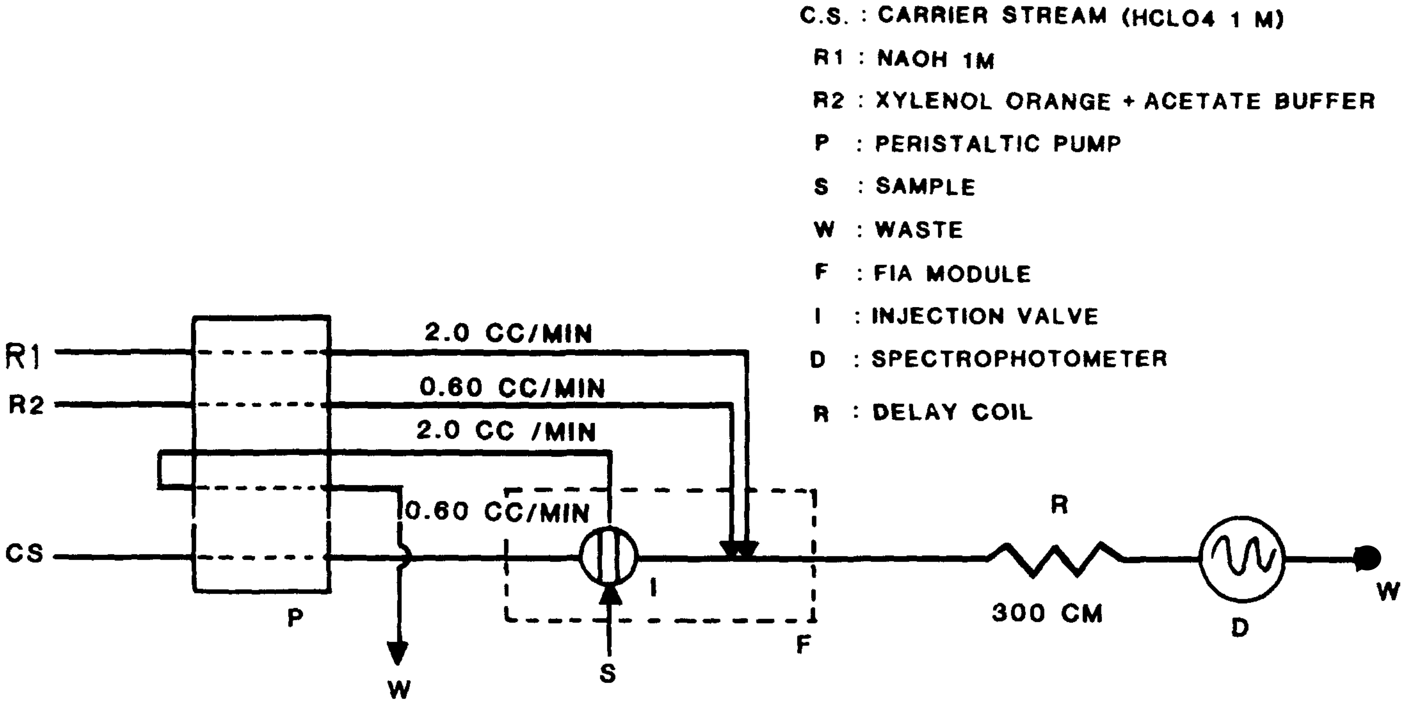

FIG. 1. FIA manifold used for the determination of zinc in $HClO_4$ 1.0 mol/dm^3.

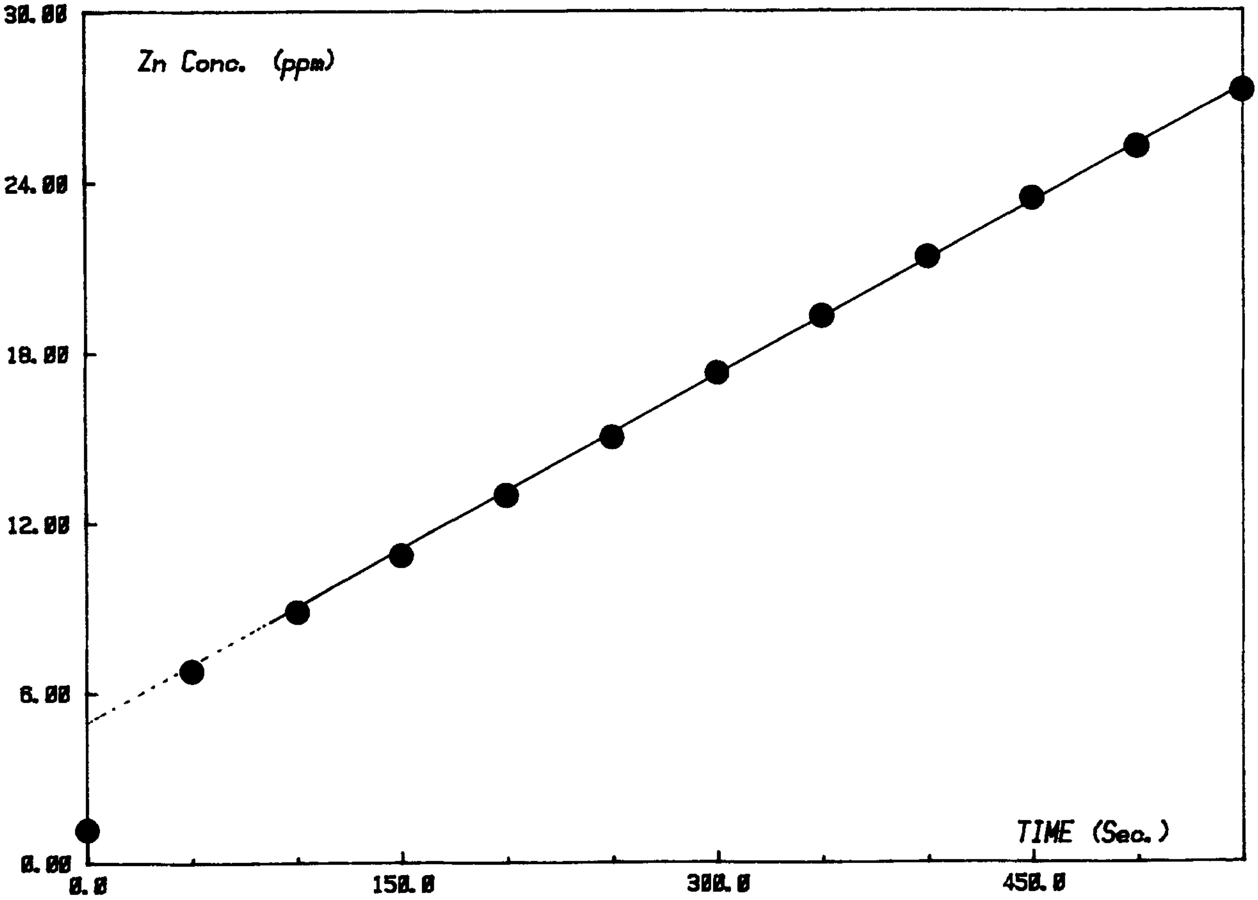

FIG. 2. Typical $[Zn^{2+}]_s$ vs time plot showing the induction time.

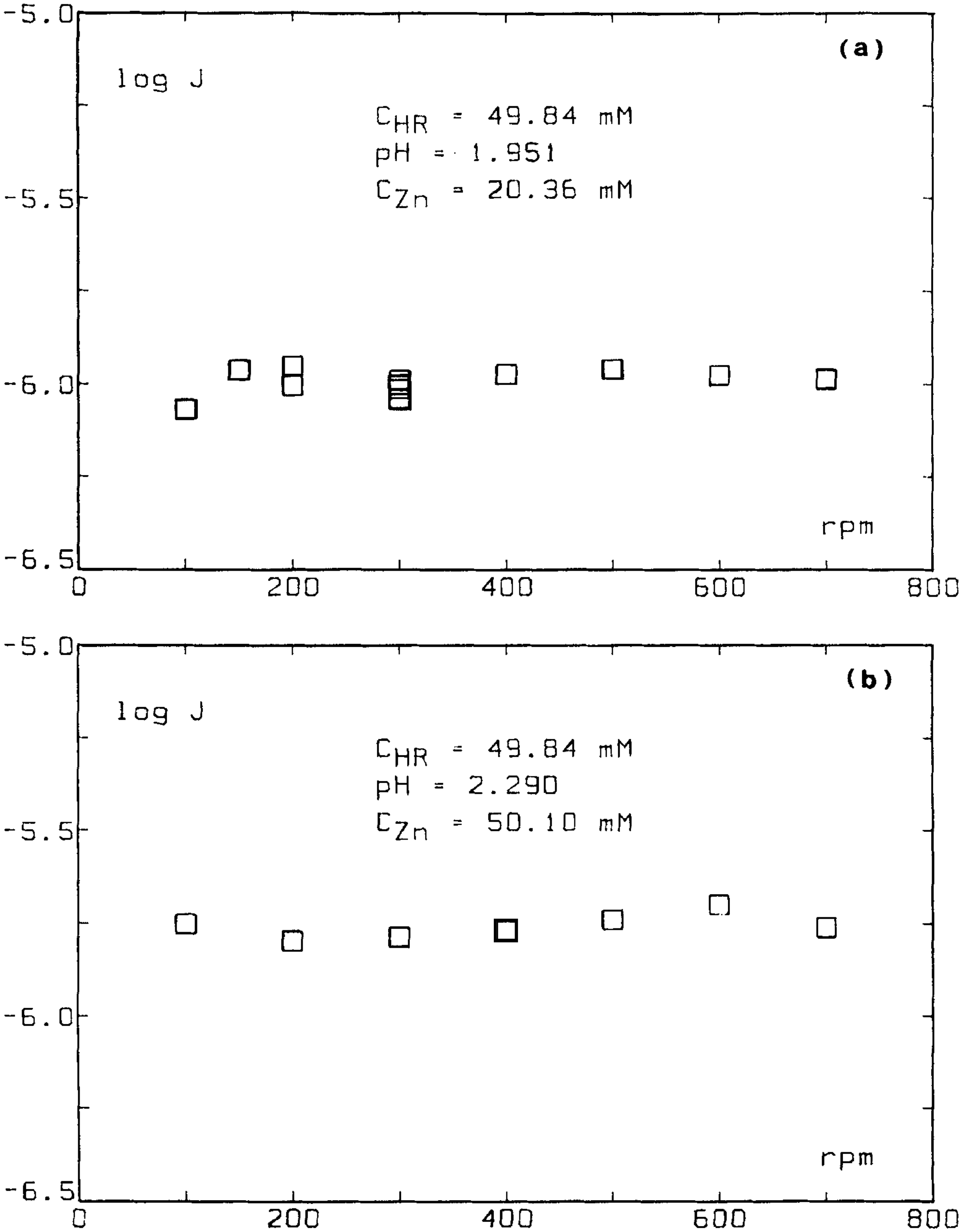

FIG. 3. Variation of the flux as a function of the hydrodynamic conditions for two different chemical compositions of the system. $[H^+]_s$ = 1.0 mol/dm^3 in all cases.

in Fig. 3a. This results in a higher degree of carrier saturation. The difference in chemical composition has some relevance regarding the dependence of J on the hydrodynamic conditions. In fact, a plateau region is obtained in Fig. 3a only for stirring speeds higher than 200 rpm while in Fig. 3b this plateau has begun by 100 rpm. These results can be understood in terms of Eq. (8). As the carrier is progressively saturated, the term $\Delta_{o,2}k_{\mathrm{eq1}}^{-1}[\mathrm{H}^+]^2$, which accounts for the contribution of organic diffusion to the overall flux, becomes more significant and the other terms in the denominator of Eq. (8) become negligible. This leads to the independence of J on the hydrodynamic conditions (the dependence is otherwise established through the term containing Δ_a) as seen in Fig. 3b. If the carrier is not completely saturated, a slight dependence of J on the hydrodynamic conditions might still be expected. This is the case in the experiments in Fig. 3a.

At any rate, the independence of the flux on the stirring speed of the aqueous solutions does not necessarily mean the complete elimination of the aqueous diffusion layer adjacent to the feed–membrane interface. Although the value of the aqueous diffusion resistance can be expected to be lower than that of the organic, a minimized and constant value can still be assumed for the former. This lower value of the aqueous diffusion resistance can be explained, without assuming $\delta_a \approx 0$, if we consider the increasing value of the difference $[\mathrm{Zn}] - [\mathrm{Zn}]_i$ in Eq. (4) as the metal bulk feed concentration is increased.

The variation of the initial flux with the unbound carrier concentration (total concentrations were varied from 6.5 to 200 mmol/dm^3) is presented in Fig. 4 in the form of $\log J$ vs $\log [\overline{(\mathrm{HR})_2}]$. The concentration of HDEHP unbound was calculated with the SOLGASWATER program (*13*) by assuming that $[\mathrm{Zn}] \approx C_{\mathrm{Zn}}$ and $[\mathrm{H}^+] \approx [\mathrm{H}^+]_{\mathrm{init}}$ because of the high V_f/V_o ratio used in the experiments. Zinc hydrolysis under the chemical conditions used is negligible (*14*).

Assuming that the carrier molecules are totally bound to zinc as C_{Zn} is increased, Eq. (8) reduces to

$$J = \frac{[\mathrm{Zn}][\overline{(\mathrm{HR})_2}]^2 F}{\Delta_{o,2}k_{\mathrm{eq1}}^{-1}[\mathrm{H}^+]^2} \tag{14}$$

Equation [14] allows a preliminary estimation of the value $\Delta_{o,2}$. If the above assumption is valid, plotting $\log J + 2 \log [\mathrm{H}^+] - \log C_{\mathrm{Zn}}$ vs $2 \log [\overline{(\mathrm{HR})_2}] + \log F$ should yield a straight line with a slope of unity. In Fig. 5 the plot was made using the data given in Fig. 4. A straight line of slope 1.03 is obtained, and from the intercept the value $\log \Delta_{o,2} = 3.88$ ($\Delta_{o,2} = 7.6 \times 10^3$) is obtained. This result seems to support the assumption made.

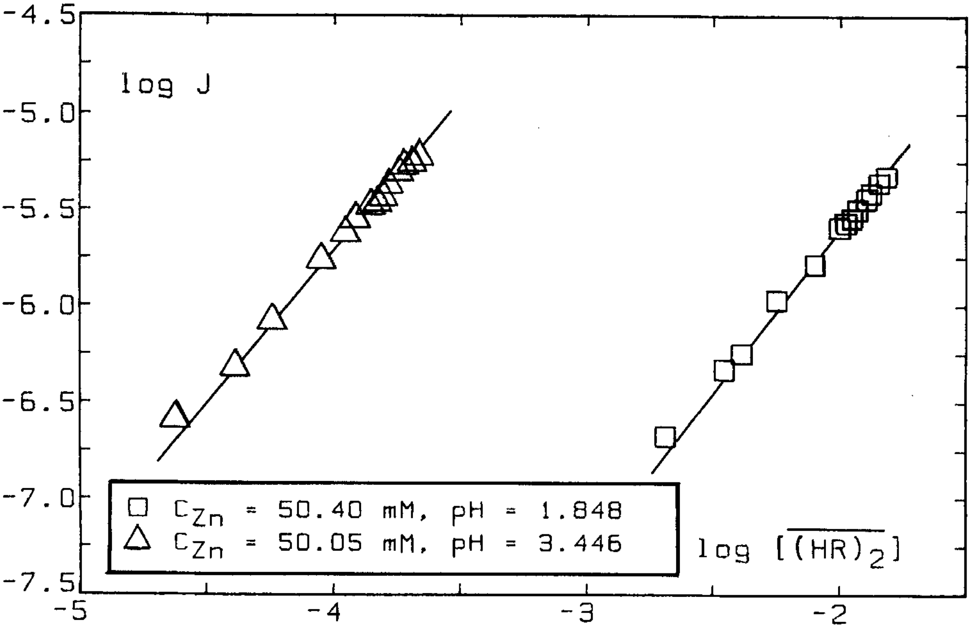

FIG. 4. Variation of the flux as a function of the free HDEHP dimer concentration. $[H^+]_s$ = 1.0 mol/dm^3 and stirring speed of 500 rpm were kept constant in all cases.

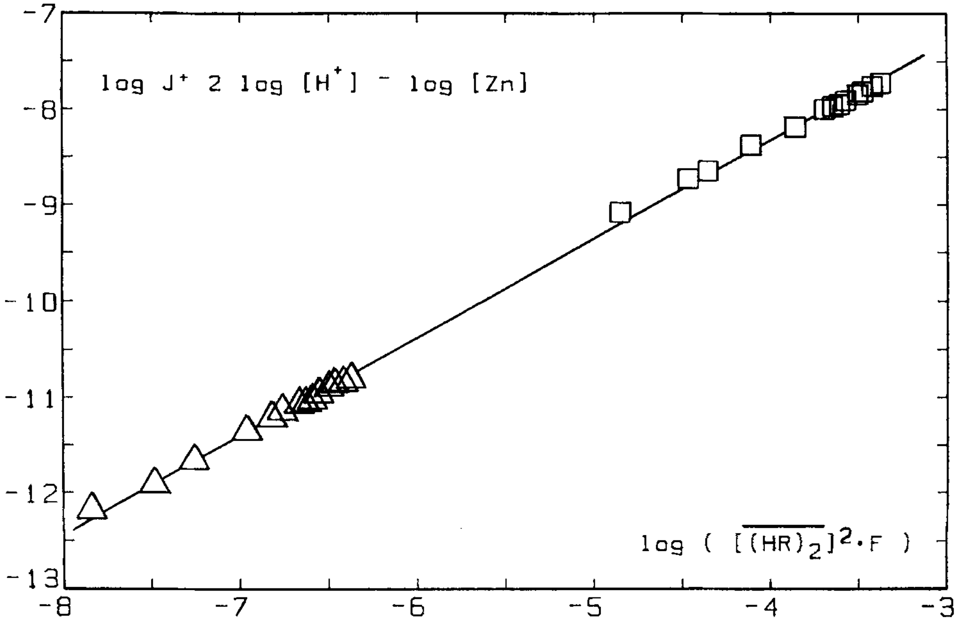

FIG. 5. Plot of log J + 2 log $[H^+]$ − log C_{Zn} vs log $[\overline{(HR)_2}]$ + log F using the data in Fig. 4. The symbols are the same as in Fig. 4.

Nevertheless, the $\Delta_{o,2}$ value obtained must be considered as tentative because equilibrium calculations show that the carrier does not fully exist as the Zn-HDEHP species.

The variation of log J as a function of pH_f and log C_{Zn} is presented in Figs. 6 and 7, respectively. As it can be appreciated in these figures, the initial flux tends to a limiting value, $J(\lim)$, for each C_{HR} used as pH_f and C_{Zn} increase, and thus the amount of carrier saturated. Following a similar argument, Eq. (14) can be transformed to

$$J(\lim) = \frac{[\overline{ZnR_2(HR)_2}] + [\overline{ZnR_2(HR)}]}{\Delta_{o,2}} \approx \frac{C_{HR}}{3.5\Delta_{o,2}} \qquad (15)$$

This value depends only on C_{HR}, in agreement with the experimental results. From these limiting values a new estimation of $\Delta_{o,2}$ can be made. Plotting log $J(\lim)$ (obtained from the data in Figs. 6 and 7) as a function of log C_{HR} (Fig. 8) yields a straight line of slope 0.95, sufficiently close to 1 to give support to the above argument. From the intercept, the value log $\Delta_{o,2} = 4.02$ ($D_{o,2} = 1.0 \times 10^4$) is deduced.

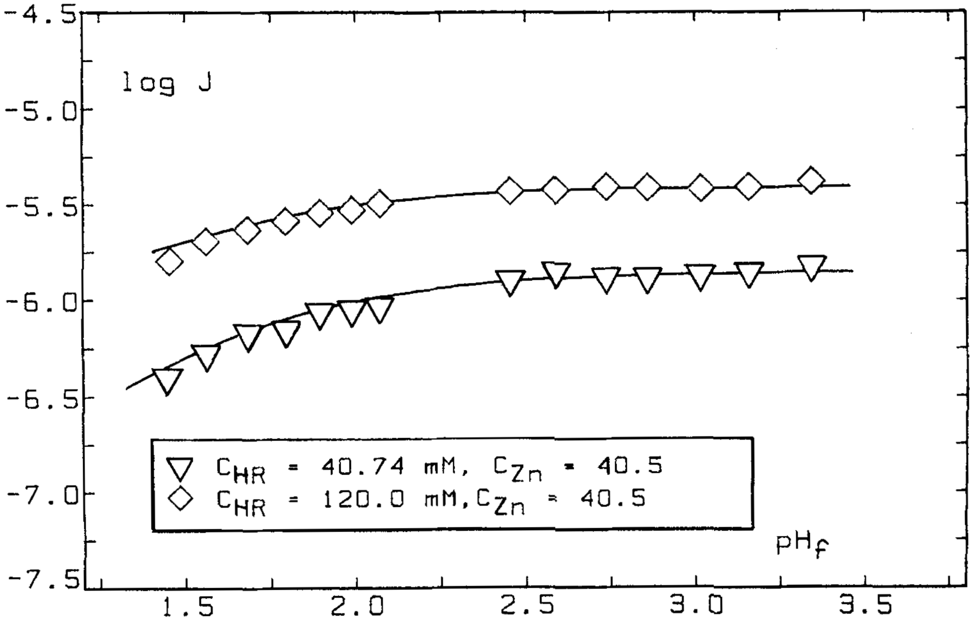

FIG. 6. Variation of the flux as a function of the aqueous feed pH. Other conditions as for Fig. 4.

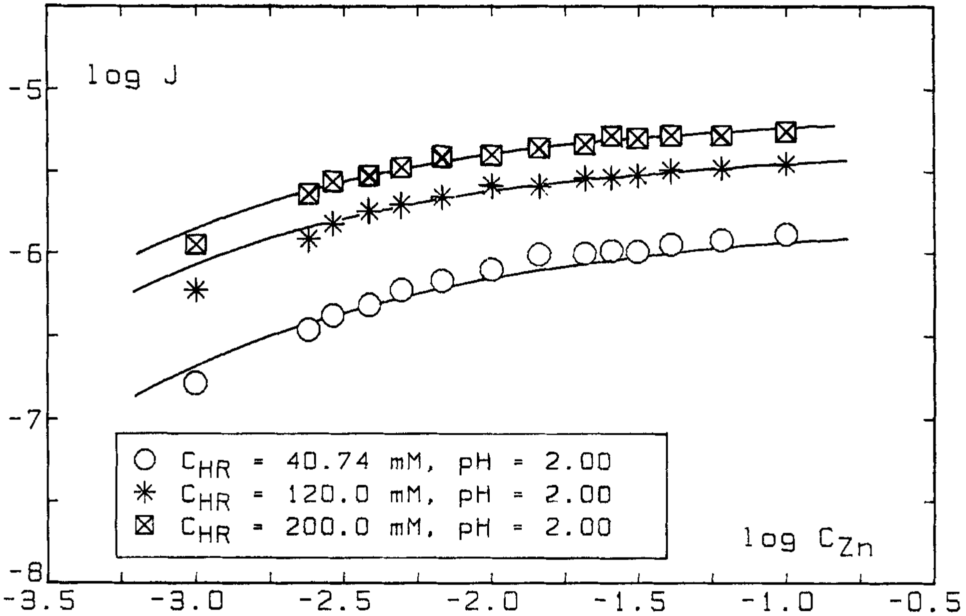

FIG. 7. Variation of the flux as a function of the total zinc concentration in the feed solution. Other conditions as for Fig. 4.

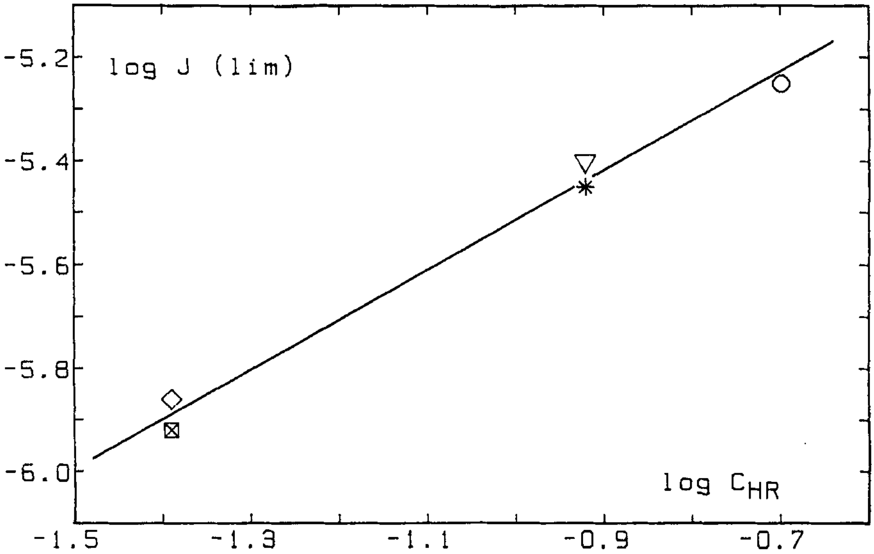

FIG. 8. Plot of the limiting flux values in Figs. 6 and 7 as a function of the total HDEHP concentration. The symbols are the same as in Figs. 6 and 7.

In order to get information about the Δ_a value, the simplified flux Eq. (11) was subjected to normalization methods. This analysis cannot be applied to the more general Eq. (8). Equation (11) can be written as

$$\frac{J^{-1}[\mathrm{Zn}]}{\Delta_a} = 1 + \frac{\Delta_o k_{\mathrm{eq1}}^{-1}}{\Delta_a} \frac{[\mathrm{H}^+]^2}{[\overline{(\mathrm{HR})_2}]^2 F} \tag{16}$$

Defining the normalized variables

$$Y = \frac{J^{-1}[\mathrm{Zn}]}{\Delta_a} \tag{17}$$

and

$$X = (\Delta_o k_{\mathrm{eq1}}^{-1}/\Delta_a)^{1/2} \frac{[\mathrm{H}^+]}{[\overline{(\mathrm{HR})_2}]F^{1/2}} \tag{18}$$

and comparing the experimental data in Figs. 4, 6, and 7 in the form log J^{-1} + log [Zn] vs log $[\mathrm{H}^+]$ − log $[\overline{(\mathrm{HR})_2}]$ − ½ log F with the theoretical function log $(1 + X^2)$ vs log X, a position can be found by translation along the x and y axes in which the best fit is obtained. In this position (cf. Fig. 9) the values

$$\log \Delta_a = 2.40\ (\Delta_a = 2.51 \times 10^2 \text{ s/cm})$$
$$\log \Delta_o = 3.96\ (\Delta_o = 9.12 \times 10^3 \text{ s/cm})$$

can be read off from the differences between the experimental and theoretical functions in the y and x axes, respectively. The value of log Δ_o so obtained is an average mass transfer coefficient for the organic membrane due to the assumption of $\chi = 1$ made in the derivation of Eq. (11).

Finally, the data were treated numerically using the general minimizing program MLAB (*15*). This program was used to fit the model flux Eqs. (8), (10), and (11) to the whole set of experimental data in Figs. 4, 6, and 7. The results of these calculations are summarized in Table 1. From these calculations it is concluded that the best description of the experimental data is obtained using Eq. (8). From the fitted parameters the values

$$\Delta_a = 2.40 \times 10^2 \text{ s/cm}$$
$$\Delta_{o,2} = 9.78 \times 10^3 \text{ s/cm}$$

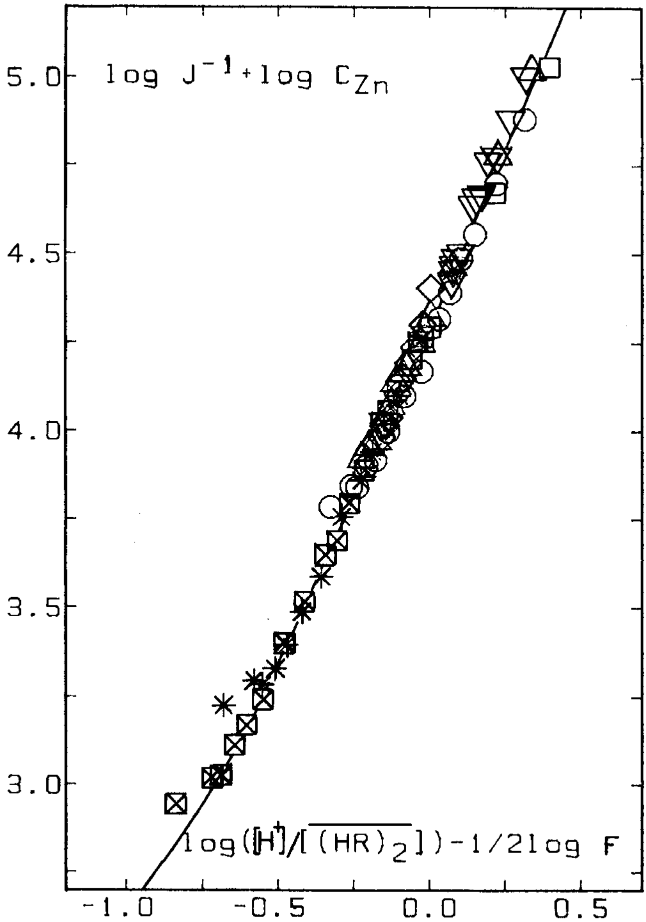

FIG. 9. Comparison of the experimental data in Figs. 4, 6, and 7 in the form $\log J^{-1} + \log C_{Zn}$ vs $\log([H^+]/[\overline{(HR)_2}]) - 1/2 \log F$ with the theoretical function $\log(1 + X^2)$ vs $\log X$ in the best fit position. The symbols are the same as in Figs. 4, 6, and 7.

$$k_1^* = 4.10 \times 10^4 \ [(\text{cm/s})/(\text{molec/Å}^2)^2]$$

$$\chi = 1.12$$

are obtained. The values of Δ_a and $\Delta_{o,2}$ compare favorably with those reported by us earlier (*2*). This agreement indicates that the diffusion layers are of similar thickness for both studies, independent on the degree of carrier saturation. This is reasonable since the hydrodynamic conditions used in both cases are the same.

TABLE 1
Results Obtained in the Fit of the Experimental Data to the Model Functions defined by Eqs. (8), (10), and (11)

Model function	Parameter values[a]	RMS[b]	U[c]
Eq. (8)	$\Delta_a = (2.40 \pm 0.03) \times 10^2$		
	$\Delta_{o,2}k_{eq1}^{-1} = (2.14 \pm 0.07) \times 10^5$		
	$k_1^{*-1} = (2.44 \pm 0.70) \times 10^{-5}$	1.348×10^{-7}	1.691×10^{-12}
	$\chi = (1.12 \pm 6.01) \times 10^{-3}$		
Eq. (10)	$\Delta_a = (2.71 \pm 0.03) \times 10^2$		
	$\Delta_{o,2}k_{eq1}^{-1} = (1.97 \pm 0.04) \times 10^5$	1.412×10^{-7}	1.897×10^{-12}
	$\chi = (0.93 \pm 2.65) \times 10^{-2}$		
Eq. (11)	$\Delta_a = (2.45 \pm 0.03) \times 10^2$	1.459×10^{-7}	2.021×10^{-12}
	$\Delta_o k_{eq1}^{-1} = (2.06 \pm 0.01) \times 10^5$		

[a] The error given is the value of the standard deviation for the parameter.

[b] $\mathrm{RMS} = (U/(m - n))^{1/2}$, where m = number of data points, n = number of fitted parameters.

[c] $U = \Sigma(J_{\mathrm{exp}} - J_{\mathrm{calc}})^2$.

From the above parameters, the values

$$\delta_a = 1.78 \times 10^{-3}\ \mathrm{cm}$$

$$D_{o,2} = 1.70 \times 10^{-6}\ \mathrm{cm^2/s}$$

$$D_{o,1} = 1.91 \times 10^{-6}\ \mathrm{cm^2/s}$$

can be estimated if the typical $D_a = 7.2 \times 10^{-6}$ cm^2/s (*16*) and the nominal $\delta_o = 1.25 \times 10^{-2}$ cm and $\varepsilon = 0.75$ are taken into account. These values are also in agreement with the values found for similar systems (*9*).

It is interesting to notice the high value of k_1^* obtained in this study as compared to the corresponding one in Ref. *2* ($k_1^* = 15.77$ (cm/s)/(molec/Å^2)^2). Recalling that

$$k_1^* = k_1/[(\mathrm{HR})_i]^2 \tag{19}$$

the difference could be explained by a possible decrease of $[(\mathrm{HR})_i]$. In the previous work, $[(\mathrm{HR})_i]$ was assumed to be constant. As the total metal concentration was very low, the amount of metal extracted would not decrease the free carrier concentration to any considerable extent. Thus the bulk organic HDEHP concentration would be sufficient to saturate the interface. However, in the present study it was expected that the loading of the membrane by the zinc complexes would reduce the C_{HR} in the bulk of the membrane to the extent that the unbound carrier concentration would not be enough to keep the interface saturated with HR molecules. A certain time lag is thus needed until steady-state diffusion can be attained in the organic membrane. This would, in turn, explain the induction time experimentally observed (cf. Fig. 2).

Interfacial tension studies have shown that the formation of extractable metal complexes reduces the interfacial activity of the extractant (*17*, *18*). Paatero (*19*) and Cox et al. (*17*) calculated the bulk concentrations of $\mathrm{Cu(LIX\ 65N)_2}$ needed to produce interfacial saturation of the complex to be in the range of 10^{-2} mol/dm^3. Equilibrium calculations show that, in our case, this range of concentrations is obtained for the extracted Zn–HDEHP complexes. Accordingly, interfacial saturation of these complexes instead of HR molecules could be expected.

The lines in Figs. 4, 6, and 7 have been plotted using the fitted parameters of Eq. (8) and show good agreement between the model and the experimental data.

The results of this study emphasize the necessity of an adequate knowledge of the equilibrium and kinetic characteristics of the system under consideration. The use of normalized functions, classical tools in equilibrium analysis, has also proved to be useful for obtaining primary estimates of the physicochemical parameters involved in SSLM processes.

SYMBOLS

k_{eq1}, k_{eq2}	equilibrium constants corresponding to equations (1) and (2), respectively
J	initial flux; mol cm^{-2} s^{-1}
V	volume of the aqueous or organic solutions; cm^3
Q'	area of contact between membrane and aqueous solutions; cm^2
Δ	$\delta/D\varepsilon$: mass transfer coefficient; s/cm
δ	thickness of diffusion layers; cm
D	diffusion coefficients; cm^2/s
k_D	$[\overline{\mathrm{Zn}}]/[\mathrm{Zn}]$: Distribution coefficient of zinc between organic and aqueous solutions
k_1^*	$k_1/[(\mathrm{HR})_i]^2$; [(cm/s)/(molec/Å^2)^2]

k_1	forward rate constant for the ITSCR kinetic mechanism (*4*)
β	k_{eq2}/k_{eq1}
χ	$\Delta_{o,1}/\Delta_{o,2}$
P	permeability; cm/s
ε	porosity
C_{HR}, C_{Zn}	total HDEHP and zinc concentrations, respectively

Indexes *a*, *o*, and *i* refer to aqueous, organic, and interface species or solutions, respectively
Indexes *f* and *s* refer to feed and strip solutions, respectively
Indexes 1 and 2 refer to $ZnR_2(HR)_2$ and $ZnR_2(HR)$ species, respectively
Index 0 refers to time zero
Bars indicates species present in the organic phase

Acknowledgments

L. Fernandez and J. Aparicio wish to acknowledge the financial support received through scholarships from the Basque Government.

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Received by editor August 21, 1986