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Interfacial Mass Transfer in Ligand Accelerated Metal Extraction by Liquid Surfactant Membranes

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Abstract

Interfacial mass transfer rates were determined for the extraction of Co(II), Ni(II), and Cu(II) by di-(2-ethyl hexyl) phosphoric acid by using a modified Lewis cell. This allowed us to elucidate the effect of ligands on liquid surfactant membrane extraction of heavy metal ions by ligand addition to the external aqueous phase. The effects of different ligands on the kinetics of extraction and the influence of surfactant on interfacial resistance to mass transfer were then examined.

INTRODUCTION

Recent studies of metal extraction by liquid surfactant membranes in our laboratory (*1*) have shown that the extraction process is accelerated by introducing certain ligands to the continuous aqueous phase. In order to elucidate this ligand effect, it is necessary to acquire information on the mass transfer process occurring at the liquid membrane–aqueous interfaces. At this time, scant information is available about the rate and mechanism of mass transfer across the liquid membrane–aqueous

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interfaces due to the complexity of the liquid surfactant membrane system.

We studied interfacial mass transfer for the extraction of Co(II), Ni(II), and Cu(II) by di-(2-ethyl hexyl) phosphoric acid (D2EHPA) and stripping by sulfuric acid using a modified Lewis cell. Information about interfacial mass transfer at the liquid membrane–aqueous phase interfaces was obtained in this way.

The effect of some ligands on the extraction rate of metal ions has been found to be significant. For example, in the absence of ligand in the aqueous phase, the interfacial resistance to mass transfer for cobalt(II) extraction by D2EHPA was observed to be as high as 10^4 s/cm, while with the addition of 0.03 *M* of acetate as ligand in the aqueous phase the interfacial mass transfer resistance dropped to approximately zero. This indicates that the ligand effect changes the slow interfacial chemical reaction to a very fast reaction, thus transforming the kinetically controlled process into a diffusion-controlled process for the liquid surfactant membrane extraction of cobalt(II).

The effect of surfactant on the interfacial mass transfer rate in liquid–liquid extraction has been reported previously (*2–5*). For the liquid surfactant membrane system, however, no quantitative description is reported, although some authors have noticed the effect (*6, 7*). Work in our laboratory has shown that the interfacial resistance due to the presence of a surfactant layer at the interface may reach as high as 10^4 s/cm (*14*).

EXPERIMENTAL

Equipment and Procedure

The Lewis cell (Fig. 1) used for our mass transfer study consisted of a cylinder 10 cm in diameter and 8 cm high. The cylinder was constructed of two glass pipes, each 4 cm long and 10 cm in diameter, which were clamped between two flat end plates. These plates, and all other metal parts inside the cell, were made of stainless steel. The two glass sections were separated by a circumferential baffle, and this, together with the central baffle, divided the cell into two identical halves, each having a volume of 250 mL. The interfacial area (the annular gap) was 27.3 cm^2.

The two stirrers of the two phases were driven by two variable speed dc motors (Boding Electric Co.). The stirring speed ranged from 0 to 300 rpm.

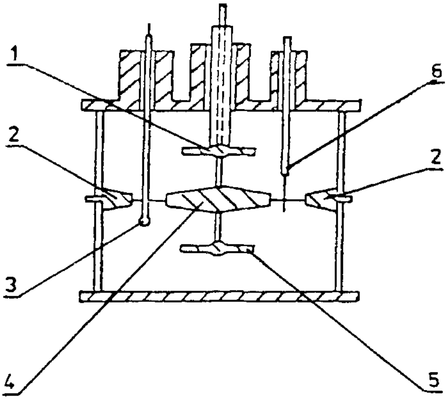

FIG. 1. Modified Lewis cell: (1) Upper stirrer, (2) peripheral baffle, (3) pH sensor, (4) central baffle, (5) lower stirrer, (6) NaOH tip for pH controller.

In order to get meaningful results, mass transfer data of different systems should be compared under the same pH value. Therefore a pH controller (Cole-Parmer Co.) was used to control the pH of the aqueous phase.

In each run the 250-mL organic phase contained LOPS (Low Odor Paraffin Solvent made by Exxon Co.) as solvent, and 5% (v/v) of D2EHPA (Sigma Co.) as extractant. The 250-mL aqueous phase consisted of a $CoCl_2$ solution containing 500 ppm Co^{2+}. The pH value of the aqueous phase was maintained at 4.6 ± 0.1 with a pH controller during the course of experiment. The ligand effect was examined by adding different ligands at various concentrations to the aqueous phase.

The effect of surfactant on interfacial mass transfer was checked using different concentrations of ECA4360, a nonionic polyamine surfactant made by Exxon Co.

The stripping was carried out using 0.5 N H_2SO_4 as the stripping solution. The metal concentration in the aqueous phase was analyzed with an UV spectrophotometer (Beckman Co.).

Mass Transfer Calculations

In order to get data of interfacial mass transfer from the kinetic curves, the resistances to mass transfer in the interfacial zone should be analyzed. For metal extraction from the aqueous phase to the organic phase in the Lewis cell, the metal ions in the bulk of the aqueous phase can be viewed as passing through three stagnant films: water film δ_w, interfacial film δ_i, and oil film δ_o, each contributing their respective resistances r_w, r_i, and r_o. The resistances to mass transfer in the bulk of both the water and oil phases can be neglected because of the mixing in those two regions.

The interfacial resistance, r_i, consists of the resistance of interfacial chemical reaction, r_{ir}, and the resistance to molecular diffusion across the interfacial film, r_{if}, which is usually caused by the adsorption of surfactant molecules at the interface. Now we have

$$r_i = r_{ir} + r_{if} \tag{1}$$

The overall resistance to mass transfer, R_w, is accordingly the sum of r_w, r_i, and r_o:

$$R_w = r_w + r_o + r_i \tag{2}$$

The relationship among the overall mass transfer coefficient, the individual-phase mass transfer coefficients, and the interfacial resistance coefficient due to any chemical reaction and/or surfactant adsorption at the interface between phases may be expressed as

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{1}{Hk_o} + \frac{1}{k_i} \tag{3}$$

where K_w, k_w, k_o, and k_i represent overall, aqueous phase, organic phase, and interfacial mass transfer coefficients in cm/s and H represents the distribution coefficient of metal ions between the aqueous and organic phases,

The mean value of the overall mass transfer coefficient $\bar{K}_w$, for extraction of metal from the aqueous to the organic phase, was obtained experimentally with

$$\bar{K}_w = -\frac{V_w}{A\Delta t}\int_{C_w(t)}^{C_w(t+\Delta t)} \frac{dC_w}{C_w - C_w^*} \tag{4}$$

where V_w represents the aqueous phase volume in cm^3, A represents the interfacial area in cm^2, and C_w and C_w^* are the concentration of metal ions in the aqueous phase and the equilibrium concentration, respectively, in ppm. Because the value of $\bar{K}_w$ varied with concentration when the ligand was added to the aqueous phase, $\bar{K}_w$ was calculated by graphical integration of Eq. (4).

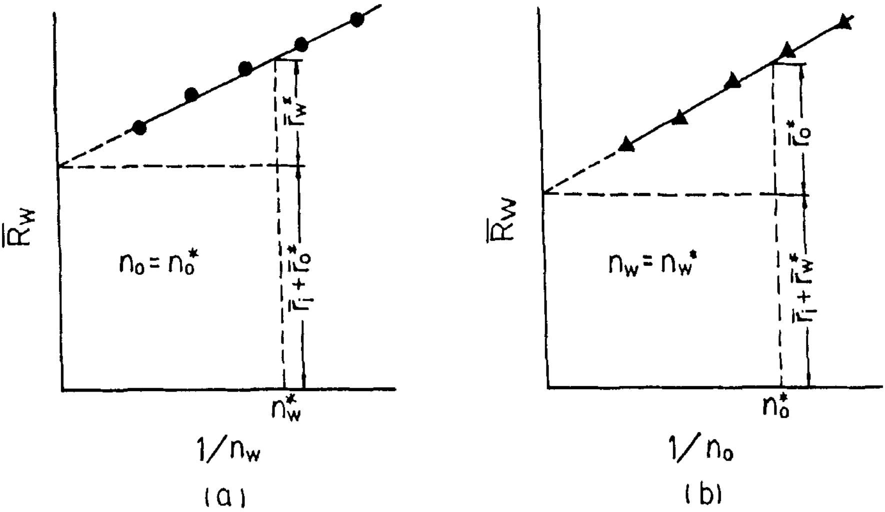

FIG. 2. Illustration of experimental method for estimating the interfacial resistance.

The individual-phase and interfacial resistances to mass transfer were also estimated experimentally by the following means. At the given stirring speed of the organic phase n_o^*, the mean value of overall mass transfer resistance, $\bar{R}_w$, was plotted against the reciprocal of the stirring speed of the aqueous phsae, $1/n_w$, and was extrapolated to the infinite stirring speed of the aqueous phase. At that point the individual-phase resistance of the aqueous phase was assumed to be negligible, i.e., $\bar{r}_w \rightarrow 0$, and the measured value of the overall resistance was regarded as the sum of the individual-phase resistance of the organic phase and the interfacial resistance, i.e., $\bar{R}_w = \bar{r}_o^* + \bar{r}_i$, as illustrated in Fig. 2(a). Using the same method, the sum of the aqueous phase and interfacial resistances $(\bar{r}_w^* + \bar{r}_i)$ was estimated at the fixed stirring speed of the aqueous phase n_w^* as shown in Fig. 2(b). The individual-phase resistances $\bar{r}_w^*$ and $\bar{r}_o^*$ at the specific stirring speed n_o^* and n_w^* and the interfacial resistance $\bar{r}_i$ were thus obtained by a combination of the above two cases.

RESULTS AND DISCUSSION

Ligand Effect on Kinetics of Metal Extraction

Several organic ligands were tested to examine their effects on the kinetics of cobalt extraction by D2EHPA.

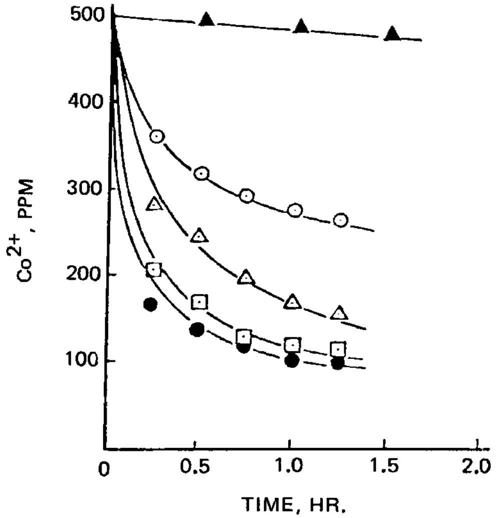

FIG. 3. Effect of different ligands (0.03 *M*) on kinetics of C_0^{2+} extraction: (▲) No ligand, (⊙) salicylate, (△) formate, (⊡) succinate, (•) acetate.

In all cases studied, 0.03 *M* of different ligands were added to the aqueous phase separately. The stirring speed of both phases was 150 rpm. Other conditions were the same as described above.

The kinetic curves of cobalt(II) extraction with the addition of different ligands in the aqueous phase are shown in Fig. 3. The mean value of the overall mass transfer coefficients within the first hour of extraction, $\bar{K}_w$, and the related interfacial resistances, $\bar{r}_i$, for different ligands in the

TABLE 1
Mean Value of Overall Mass Transfer Coefficients, $\bar{K}_w$, and the Interfacial Resistance to Mass Transfer, $\bar{r}_i$, within the First Hour of Mass Transfer for Cobalt Extraction by D2EHPA with the Addition of 0.03 mol/dm^3 of Different Ligands to the Aqueous Phase

Ligand	$\bar{K}_w \times 10^3$ (cm/s)	$\bar{r}_i \times 10^{-2}$ (s/cm)
—	0.094	105.70
Salicylate	1.64	5.00
Formate	3.51	1.75
Succinate	5.34	0.77
Acetate	6.09	0.54

aqueous phase are calculated and shown in Table 1. The sequence of the ligand effect for the different ligands is: acetate > succinate > formate > salicylate. This sequence is in good agreement with that found previously in our liquid membrane study of cobalt(II) extraction (*14*). Acetate is confirmed as the best of the ligands tested for accelerating the extraction process.

For the extraction of Ni(II) and Cu(II) by D2EHPA, a similar effect has been found by introducing acetate as a ligand to the aqueous phase as shown in Fig. 4.

It has been found that in the absence of ligand in the aqueous phase, the interfacial resistance to mass transfer due to the interfacial extraction reaction of Co(II), Ni(II), and Cu(II) with D2EHPA is of the order of 10^4 s/cm. (See Table 1.) Obviously, such a high resistance to interfacial chemical reaction defines the extraction process as a kinetically controlled process.

However, in modeling a metal extraction process (such as the extraction of Cu(II) in a liquid surfactant membrane system), some authors have assumed that the process is diffusion controlled. Our experimental results clearly show that this assumption is untenable

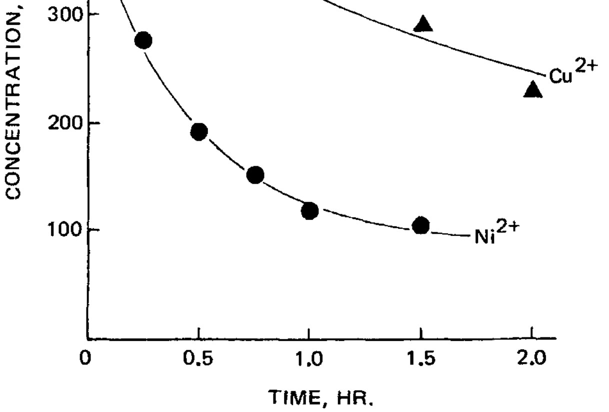

FIG. 4. Effect of 0.03 *M* acetate on kinetics of Cu^{2+}, Ni^{2+} extraction: (- -) No ligand.

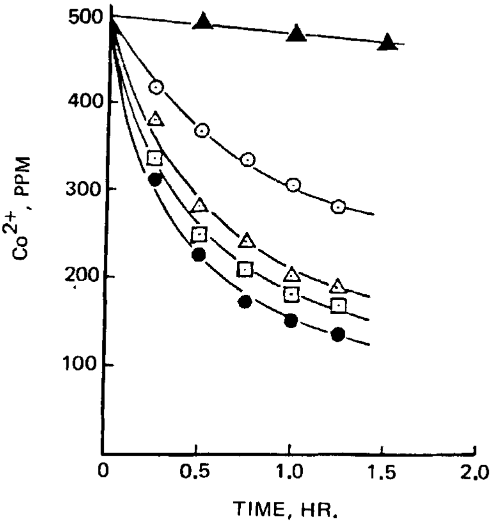

FIG. 5. Combined effect on kinetics of 0.1 *M* different inorganic ligands with 0.015 *M* acetate in aqueous phase: (▲) No ligand, (⊙) SO_4^{2-} + AC^-, (△)) NO_3^- + AC^-, (⊡) Cl^- + AC^-, (•) AC^-.

because of the very slow extraction reaction in the absence of ligand in the aqueous phase.

Several inorganic anion ligands, such as SO_4^{2-}, NO_3^-, and Cl^-, were also tested together with the organic ligand acetate to check their effect on kinetics.

It has been found that for cobalt extraction accelerated by 0.015 *M* acetate in the aqueous phase, the extraction rate was slowed somewhat by the addition of 0.1 *M* of SO_4^{2-}, NO_3^-, or Cl^- to the aqueous phase as shown in Fig. 5. The sequence of the inorganic ligands which lower the extraction process is $SO_4^{2-} > NO_3^- > Cl^-$. This sequence is very similar to that observed by Eccles et al. (8) in their kinetic study of copper extraction. The result shown in Fig. 5 indicates that the chloride system is preferred kinetically over the sulfate or nitrate system for the extraction of cobalt.

Effect of Acetate Concentration

The effect of ligand concentration on the kinetics of cobalt(II) extraction by D2EHPA is shown in Fig. 6. Here the average interfacial resistance $\bar{r}_i$, calculated within the first hour of mass transfer, is plotted as

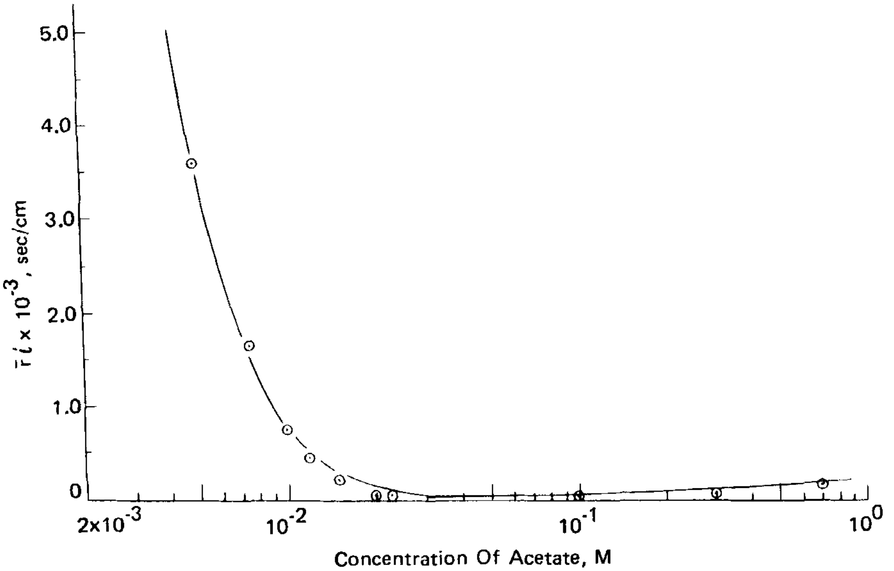

FIG. 6. Interfacial resistance as a function of sodium acetate concentration.

the function of the concentration of sodium acetate which acts as a ligand.

In the present system there is no surfactant other than D2EHPA (extractant) in the organic phase and acetate (ligand) in the aqueous phase. Both D2EHPA and acetate exhibit weak surface activity, and their relative concentrations at the water-oil interface is favorable for cobalt extraction. Therefore, the estimated interfacial resistance is attributed to the extraction reaction occurring at the interface.

In the absence of ligand in the aqueous phase, the $\bar{r}_i$ is as high as 10.57 × 10^3 s/cm (Table 1). It decreases to approximately zero after more than 0.025 *M* acetate is added to the aqueous phase, as shown in Fig. 6. This result indicates that the ligand effect changes the slow interfacial chemical reaction to a very fast reaction.

From Fig. 6 it can be seen that the ligand effect increases sharply when the acetate concentration in the aqueous phase is below 0.01 *M*. The ligand effect reaches a maximum (i.e., the minimum value of interfacial resistance) near a concentration of 0.025 *M* acetate, and then remains constant in a substantially wide range of acetate concentrations.

Since the initial concentration of Co^{2+} in the aqueous phase is 500 ppm (i.e., 0.0083 *M* in molar concentration), the 0.025 *M* acetate in the aqueous phase is about three times as high as the molar concentration of Co^{2+} ions. This implies that the extraction reaction of cobalt(II) by D2EHPA at the water–oil interface is greatly accelerated after 2 or 3 coordinated water molecules surrounding the Co^{2+} ions are replaced by acetate ions.

The further increase of sodium acetate concentration (>0.2 *M*) slightly decreases the ligand effect. This can be plausibly explained by the competitive extraction of sodium with cobalt.

Stripping

The average overall mass transfer coefficient for stripping of Co^{2+} by 0.5 *N* sulfuric acid was calculated as 0.22×10^{-4} cm/s. This value is lower than that of extraction even in the absence of ligand in the aqueous phase.

The fact that the mass transfer coefficient for stripping is so low gives rise to the following question: Why does the overall mass transfer rate for liquid surfactant membranes increase solely with the acceleration of the extraction step through the ligand effect? The answer lies in the fact that, for a liquid surfactant membrane system, the interfacial area for stripping is much larger than that of extraction as analyzed previously (*1*). Even though the stripping reaction is slow, the total flux of stripping is still higher than that of extraction due to the larger contacting area used in the stripping process. From this point of view, it can be said that the ligand effect in the continuous aqueous phase takes advantage of the liquid surfactant membranes by fully tapping the potential of the large stripping area of the system.

Effect of Surfactant

The effect of surfactant on interfacial mass transfer has been reported to be significant in many cases (*9–12*). In our previous study of liquid surfactant membrane extraction (*14*), ECA4360, a nonionic polyamine, was used as a surfactant to stabilize the liquid membranes. Here the influence of this surfactant on cobalt extraction was studied.

With the presence of surfactant in the organic phase, it is possible that, for the extraction process at the water–oil interface, the interfacial resistance to mass transfer comes from both the extraction reaction and the interfacial barrier caused by the surfactant orientation at the interface, which hinders the passage of solute across the interface. Also, it has been shown in Fig. 6 that with the addition of more than 0.025 *M* acetate to the aqueous phase, the interfacial resistance to mass transfer due to chemical reaction may be neglected by means of the ligand effect.

In this work, when the effect of the surfactant on interfacial mass transfer was studied, 0.1 *M* acetate was added to the aqueous phase. By doing this, the interfacial resistance to mass transfer may be regarded as the result of the surfactant layer at the interface by excluding the resistance of chemical reaction. The interfacial resistance $\bar{r}_i$ due to ECA436 is now plotted against the concentration of ECA4360 as shown by the upper curve in Fig. 7. It is seen from Fig. 7 that in the range of low ECA4360 concentration ($<5 \times 10^{-3}$ *M*) the $\bar{r}_i$ increases slowly with the increase of ECA4360 concentration. When ECA4360 in the oil phase is greater than 5.0×10^{-3} *M*, the $\bar{r}_i$ rises sharply and then remains approximately constant. This can be interpreted as follows: In the range of low ECA4360 concentration (5×10^{-3} *M*), ECA4360 adsorbed at the interface is far from saturation and there exists no rigid surfactant film at interface, therefore $\bar{r}_i$ in this region rises slowly with ECA4360 concentration. In the region from 5.0×10^{-3} to 1.0×10^{-2} *M* of ECA4360 concentration, the interface is packed with ECA4360 molecules more and more closely, thereby forming a dense, rigid interfacial barrier for the solute to pass through. Therefore the $\bar{r}_i$ rises sharply in this region.

Once a densely packed monolayer (or multilayer) of surfactant at the interface is formed, the $\bar{r}_i$ reaches a maximum and the further increase of ECA4360 concentration does not significantly contribute to the rigidity of the interfacial film. Therefore, a substantially constant value of $\bar{r}_i$ is maintained.

Resistance in Oil Phase

We plotted the resistance of the oil phase against the stirring speed of the oil phase (shown by the lower curve in Fig. 7) in order to acquire information about the resistance to molecular diffusion in the oil membrane phase for the liquid surfactant membrane system. We can see from Fig. 7 that the resistance of the oil phase gradually increases with a decrease of the stirring speed in the oil phase. When the stirring speed in the oil phase is lower than 20 rpm, the oil phase can be considered stationary (especially near the interfacial zone); therefore, the resistance to diffusion in oil phase remains unchanged within this region of stirring speeds.

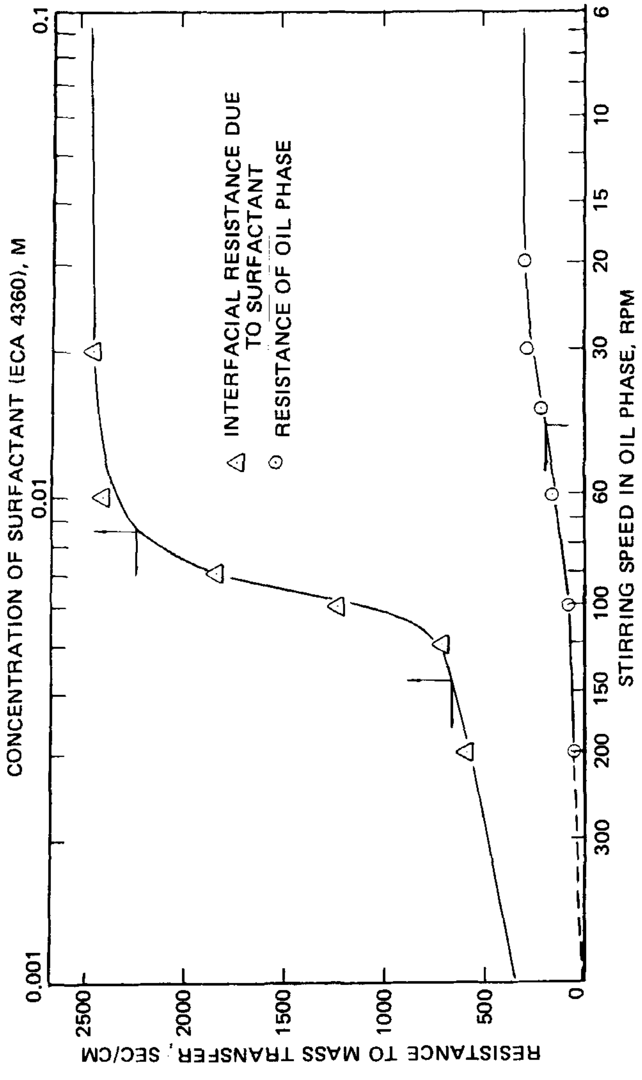

FIG. 7. Comparison between the resistance of the oil phase and the interfacial resistance due to surfactant.

At a zero rpm stirring speed in the oil phase, the measured resistance to mass transfer is the resistance of the metal complex to molecular diffusion through the oil phase. This value can be used to estimate the resistance to molecular diffusion of the metal complex across the membrane phase in a liquid surfactant membrane system. The resistance in the inner core of the emulsion globules should be somewhat smaller than that in the oil membrane phase because of solute consumption due to the stripping reaction.

Comparing the two curves in Fig. 7, we find that the interfacial resistance due to the surfactant is as high as 2500 s/cm when the interface is saturated with the surfactant molecules, while the resistance to molecular diffusion through the oil phase is lower than 500 s/cm. This allows us to assume that for the liquid membrane metal extraction which is accelerated by the ligand effect, the major resistance to mass transfer is concentrated on the peripheral surfactant layers of the emulsion globules, i.e., the interfacial surfactant layer should be the predominant barrier to mass transfer for the liquid surfactant system.

Based on this experimental finding, we have developed a model of diffusion-controlled mass transfer for the liquid surfactant membrane system in which the extraction reaction is speeded up by means of the ligand effect. The details of this model are discussed elsewhere (*13*).

Acknowledgment

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