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Ascending Water Electrode Studies of Metal Extractants. Role of Kinetic Factors in the Faradaic Ion Transfer of Metal–Phenanthroline Complex Ions across an Aqueous–Organic Solvent Interface

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The mechanism of transfer of metal ions Cd^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} from an aqueous phase to a dichloroethane (DCE) solution of 1,10-phenanthroline (phen) was investigated by current scan polarography at the ascending water electrode. As deduced from analysis of the polarograms, the transfer process involves (a) the diffusion of phen to the aqueous phase, (b) the formation of a 1:1 M^{2+}–phen complex, which, for Co^{2+} and Zn^{2+}, is the slow or rate-determining step, (c) the phase transfer of the 1:1 complex into DCE, and (d) the further reaction of this complex with phen in the DCE. The rates of formation of Co–phen^{2+} and Zn–phen^{2+} in the aqueous phase are calculated from the kinetically controlled limiting currents to be $(5.0 \pm 1.6) \times 10^5$ and $(8.4 \pm 5.6) \times 10^7$ M^{-1} s^{-1}, respectively.

Introduction

Investigations of the Faradaic ion transfer across the externally polarized interface of an aqueous–immiscible organic solvent pair provide powerful insights into the mechanisms of the liquid–liquid mass-transfer processes. In a previous paper,[1] the phase distribution behavior of the protonated 1,10-phenanthroline (phen) and its derivatives between aqueous and 1,2-dichloroethane (DCE) phases was elucidated by means of current scan polarography at the ascending water electrode (AWE) and chronopotentiometry at the stationary water electrode (SWE). Through this study the sequence of events involved in these solvent extraction systems was demonstrated to be (i) distribution of neutral extractant between the two phases, (ii) protonation of the extractant in the aqueous phase, forming phenanthrolinium ion, PH^+, (iii) distribution of PH^+ between the two phases, and (iv) ion-pair formation between PH^+ and tetraphenylborate, TPB^-, in the organic phase. Reaction step iii is the electrochemical ion-transfer process that gives rise to the current observed. Since these reaction steps are sufficiently rapid, the overall extraction rate of such systems is controlled by the diffusion of neutral extractant from the bulk organic phase to the interface. A comparable study of the formally analogous system of potassium ion (K^+) and valinomycin (V) clearly showed that, in this system also, the neutral carrier diffuses to the aqueous phase where the KV^+ forms, which is then electrochemically transferred to the organic phase.[2]

Interesting questions arise in the case of extraction systems such as those involving metal chelation in which chemical reactions rather than diffusion might be rate determining. How would this affect the behavior of such systems at the AWE and the SWE? Can such measurements give useful quantitative information concerning the kinetics and mechanisms of the chelate formation and phase-transfer reactions? In order to examine such questions our polarographic study at the AWE and SWE was extended to solvent extraction systems of metal–phen complexes inasmuch as these systems are well characterized from both equilibrium and kinetic aspects.[3–6]

Experimental Section

The electrolytic cell and the electrochemical procedure were the same as those reported previously.[1] The aqueous supporting electrolyte solution AWE phase was 0.2–1.0 M acetate buffer or citrate buffer, both of which contained sodium salts, over the pH range of 4–7. The oragnic DCE solution contained 0.02 M tetrabutylammonium tetraphenylborate (TBA^+,TPB^-) as supporting electrolyte prepared according to the procedure described earlier.[1] All reagent grade chemicals were employed without further purification.

Results and Discussion

Figure 1 includes the polarograms at the AWE observed when the aqueous solution is 0.2 M acetate buffer (pH 5.1) in the absence (curve 1) and presence (curve 2) of 1×10^{-3} M of Co^{2+}, which is in contact with a DCE solution containing 0.02 M TBA^+,TPB^- and 5×10^{-4} M phen. The measurement was carried out with a mean flow rate of the aqueous solution, m, of 0.0250 cm^3 s^{-1}, a drop time, t, of about 1.3 s at zero current, and a current scan from −10 to +80 μA at the rate of 0.5 μA s^{-1}. The background polarogram, obtained when phen is not present in the organic phase, is shown in curve 3. As defined earlier,[1] the flow of the anodic current corresponds to the transfer of positive charge from aqueous to organic phases or negative charge from organic to aqueous phases. The anodic wave in curve 1 is attributable to the ion transfer of PH^+ from the aqueous to the DCE phase. The limiting current, i_1, of this wave is controlled by the diffusion of phen from the bulk organic phase to the interfacial region of the aqueous/DCE phases.[1] When Co^{2+} (or Zn^{2+}) is present in the aqueous phase, a two-step polarogram is observed (curve 2 in Figure 1). The first wave at more negative potential corresponds to the transfer of the Co^{2+}–phen complex ion from the aqueous to the organic phases. The second wave corresponds to the transfer of PH^+ from the aqueous to the organic phases, as is clear from the 60-mV shift observed in the half-wave potential, $\Delta_o^a\phi_{1/2}$, per unit change of the aqueous pH. In a series of polarograms run at varying flow rates of the AWE, accomplished by changing the height of the hydrostatic head of the water level in the aqueous reservoir, the limiting current of the first wave i_1 was totally independent of flow rate while that of the second wave i_2 increased as the square root of the increase of the flow rate. Hence, the first wave (transfer of the complex ion) is kinetically controlled, whereas the second wave (transfer of the PH^+) is diffusion controlled. In fact, the polarograms obtained when the aqueous solution contained Cd^{2+} or Zn^{2+} also exhibited new waves whose limiting currents increase in the order of Co^{2+}

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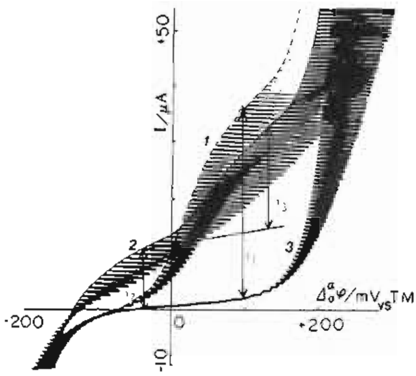

Figure 1. Current scan polarograms at the AWE (current scan rate 5 μA s^{-1}): aqueous phase, 0.2 M acetate buffer (pH 5.1) plus 10^{-3} M Co^{2+} (curve 2) and no Co^{2+} (curves 1 and 3); organic phase (DCE), 0.02 M TBA^+,TPB^- plus 5 × 10^{-4} M phen (curves 1 and 2) and no phen (curve 3).

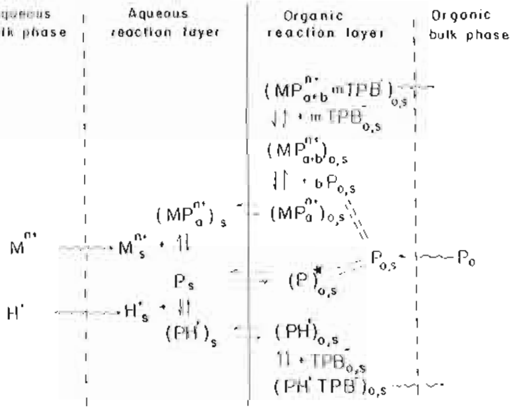

Figure 2. Schematic diagram of the solvent extraction system of the metal (M^{n+})–phen (P) complex.

$< Zn^{2+} < Cd^{2+}$ coinciding with the sequence of the increasing rate constant of the metal–phen complex formation reactions.[3,5] The system, Ni^{2+}–phen, gave no wave characteristic of the metal complex ion transfer, showing rather a polarogram identical with curve 1 in Figure 1 over the experimental conditions of pH 4.5–7.0, concentrations of Ni^{2+} up to 0.1 M, and concentrations of phen up to 10^{-2} M. Thus, under the conditions studied, complex formation of Ni^{2+} with phen did not occur in the time frame of the polarographic measurement. At the other extreme, the system Cd^{2+}–phen gave only the first wave, which was found to be diffusion controlled by the half-order dependence of limiting current on flow rate, indicating that complex formation of Cd^{2+}–phen is so rapid that the overall process is still controlled by the diffusion of phen in the organic phase as was the H^+–phen system. Furthermore, the disappearance of the second wave in this system confirms the conclusion that the second wave in curve 2 corresponds to the transfer of PH^+ formed by the protonation of uncomplexes phen remaining in the aqueous phase.

In order to deduce the detailed mechanism of the process responsible for the kinetically controlled wave, it is convenient to assume a thin reaction layer in the vicinity of the interface present in both the aqueous and organic phases (Figure 2). The possible reaction components included in this overall electrochemical reaction are shown in this diagram. The subscripts s and o denote the interfacial reaction layer and the organic phase, respectively. The reaction steps are as follows: (i) mass transport of phen and M^{n+} by diffusion from their respective bulk solution phases to the reaction layers, (ii) equilibrium distribution of phen between organic and aqueous phase characterized by the distribution constant K_{DR}, (iii) successive complex formation reactions in the aqueous phase

$$M^{n+} + aP \rightleftharpoons MP_a^{n+} \tag{1}$$

(iv) the distribution of the cationic complex MP_a^{n+} from aqueous to organic phases, (v) successive complex formation reactions in the organic phase

$$MP_a^{n+} + bP \rightleftharpoons MP_{a+bn}^{+} \tag{2}$$

(vi) ion-pair formation between the cationic complex MP_{a+b}^{n+} and the TPB^- anion in the organic reaction layer, and (vii) the diffusion of product from organic reaction layer to the bulk organic phase. Reaction step iv gives rise to the anodic current. For simplicity, any ion-pair formation in the aqueous phase is neglected in this formation.

The reaction pathway, that which determines the composition of the complex ion MP_a^{n+} that transfers across the interface, is affected both by the rate at which subsequent ligands would add to MP_a^{n+} in the aqueous phase as well as by the extractability of this complex ion into the organic phase. At one extreme, if the 1:1 complex ion MP^{n+} is sufficiently extractable and if the rates of the successive complex formation steps in the aqueous phase are sufficiently slow, then MP^{n+} transfers into the organic phase where successive additions of phen occur, to form MP_2^{n+} and then MP_3^{n+}. In this connection, a mechanism involving the transfer of the hydrated metal ion itself, followed by complex formation with phen only in the organic phase, is very unlikely in view of the demonstration that this pathway does not occur with the singly charged proton.[1]

Prediction of the Reaction Path. The reaction pathway may proceed either (a) by complex formation occurring completely in the aqueous phase, namely the transferring ion is the fully formed complex ion or (b) by complex formation taking place both in the aqueous and organic phases. In the latter, the partially formed complex becomes sufficiently lipophilic to transfer to the organic phase where the additional phen molecules are attached.

Regardless of the site of metal–phen complex formation, the competitive protonation of phen in the aqueous phase is coupled with it. That is, if complex formation occurs in the aqueous phase, the amount of PH^+ will be decreased by the amount consumed in complex formation. Correspondingly, if complex formation occurs in the organic phase, this decreases the amount of neutral phen, which in turn governs the amount that distributes into the aqueous phase, and hence also decreases the amount of PH^+.

As described in detail previously,[1] in the absence of metal ion in the aqueous solution, $\Delta_o^a\phi_{1/2}$ for PH^+ transfer can be expressed by

$$\Delta_o^a\phi_{1/2,PH^+} = \Delta_o^a\phi_{1/2,PH^+} + (RT/F)\ln(K_{DR}K_a/K_{IP}) - (RT/F)\ln[H^+][TPB^-]_o \tag{3}$$

where, $\Delta_o^a\phi^o_{PH^+}$, K_a, and K_{IP} are the standard electrical potential difference established by the distribution of PH^+ between aqueous/DCE phases, acid dissociation constant of phen, and ion-pair formation constant between PH^+ and TPB^- in the DCE phase, respectively. Under fixed experimental conditions, i.e. with fixed aqueous pH and fixed TPB^- concentration in the organic phase, a constant value of the half-wave potential, $\Delta_o^a\phi_{1/2,PH^+}$ should be observed. This $\Delta_o^a\phi_{1/2,PH^+}$ was shown to be independent of the amount of PH^+ in the aqueous phase.[1] Hence, variation of PH^+ with the extent of the competitive aqueous complex formation will not affect the half-wave potential. If, however, the amount of phen disributed into the aqueous phase decreases by virtue of complex formation in the organic phase, $\Delta_o^a\phi_{1/2,PH^+}$ might shift more positively, which is equivalent to saying that the apparent distribution constant or ratio in eq 3 increases. When the concentrations of phen in the organic reaction layer in both the absence and in the presence of complex formation in the organic phase

Table I. Characteristics of Kinetically Controlled Ion Transfer in Co^{2+}- and Zn^{2+}-phen Systems

compn		exptl conditions					calcd values				
				limiting currents, μA			$\Delta(\Delta_o^a\phi_{1/2,PH^+})$, mV				
aqueous pH	organic[a] $[phen]_o$, mM	flow rate (m), $cm^3\ s^{-1}$	drop time (t), s	i_2	i_3	i_1	obsd	calcd[b]	obsd/calcd	$(a + b)/n$	k_f, $M^{-1}\ s^{-1}$
						Cobalt (1 mM) in 1 M Acetate Buffer					
4.8	0.5	0.0247	0.89	$17._9$	$27._4$	$51._1$	48	9	5.3	1.32	3.4×10^5
5.4	1	0.0247	0.89	$48._2$		$97._1$[g]					6.9×10^5 [h]
5.4	0.5	0.0247	0.89	$21._1$	$22._5$	$52._9$	46	12	3.8	1.44	4.3×10^5
5.4	0.25	0.0247	0.89	$11._4$	$10._1$	$26._5$	44	13	3.4	1.44	4.9×10^5
5.9	0.5	0.0247	1.05	$22._6$	$20._0$	$54._7$	32	15	2.1	1.54	4.6×10^5
5.9	0.25	0.0247	1.05	$9._5$	$9._7$	$23._6$	36	13	2.8	1.46	4.2×10^5
5.1[c]	0.37	0.0250	1.06	$18._9$	$24._5$	$50._6$	29	8	3.6	1.38	3.5×10^5
5.8[c,d]	0.5	0.0253	1.61	$11._1$	$17._8$	$34._7$	34	10	3.4	1.52	7.8×10^5
									3.1 ± 1.5[i]		$(5.0 \pm 1.6) \times 10^5$ [i]
						Zinc (1 mM) in 1 M Citrate Buffer					
5.8	0.25	0.0179	2.87	$4._2$	$12._4$	$20._8$	18	9	2.0	2.00	1.1×10^8
5.9	0.5	0.0192	1.20	$10._5$	$30._8$	$42._4$	20	4	5.0	1.10	1.5×10^8
5.9[e]	0.25	0.0179	2.87	$3._9$	$17._4$	$23._4$	20	5	4.0	1.54	5.4×10^7
4.8[f]	0.5	0.0242	1.15	$19._7$	$26._9$	$55._3$	25	11	2.3	1.44	2.5×10^7
									3.3 ± 1.4[i]		$(8.4 \pm 5.6) \times 10^7$ [i]

[a] DCE containing 0.02 M TBA^+,TPB^-. [b] Calculated by eq 9 ($n = 2$, $a = 1$). [c] 0.2 M acetate buffer. [d] 0.2 mM Co^{2+}. [e] 0.5 M citrate buffer. [f] 0.2 M citrate buffer. [g] Calculated from data with 0.5 mM of $[phen]_o$. [h] Calculated on the assumption that $(a + b)/n$ is 1.5. [i] Average with standard deviation.

phase are defined to be $[P]_{o,s}$ and $[P]_{o,s}{}^*$, respectively, the shift in $\Delta_o^a\phi_{1/2,PH^+}$, $\Delta(\Delta_o^a\phi_{1/2,PH^+})$, can be described by

$$\Delta(\Delta_o^a\phi_{1/2,PH^+}) = (RT/F) \ln ([P]_{o,s}/[P]_{o,s}{}^*) \qquad (4)$$

Three different kinds of limiting currents are seen in the polarograms in Figure 1, i.e. i_1, the diffusion-controlled limiting current for the transfer of PH^+ in the absence of any metal ion in the aqueous phase, i_2, the kinetically controlled limiting current for the transfer of complex ion in the presence of metal ion M^{n+} in the aqueous phase, and i_3, the diffusion-controlled limiting current for PH^+ in the presence of M^{n+} in the aqueous phase. Over the potential region where the limiting currents i_1 and i_3 are obtained, the total limiting currents, i.e. i_1 in curve 1 and $(i_2 + i_3)$ in curve 2, are controlled by the mass transfer of phen diffusing from the bulk organic phase to the interface. The diffusion-controlled limiting current, i_1, can be related to the diffusion-controlled flux of phen (or identically, PH^+), J, across the electrode interface, i.e.

$$i_1 = FAJ \qquad (5)$$

where A is the surface area of the electrode.

Assuming that the transferable complex ion, $MP_a{}^{n+}$ is formed in the aqueous phase and that the successive addition of phen occurs in the organic phase forming $MP_{a+b}{}^{n+}$, the limiting currents i_2 and i_3 are given by

$$i_2 = nFAX/a \qquad (6)$$

$$i_3 = FA(J - X - Y) \qquad (7)$$

where X and Y are the fluxes of phen consumed by complex formation in the aqueous and organic phases, respectively. These phen fluxes *are* related by

$$Y/X = b/a \qquad (8)$$

Equation 4 can be rewritten with eq 5 and 8 as

$$\begin{aligned}\Delta(\Delta_o^a\phi_{1/2,PH^+}) &= (RT/F) \ln [J/(J - Y)] \\ &= (RT/F) \ln [i_1/[i_3 + (a/n)i_2]] \qquad (9)\end{aligned}$$

It is evident from curve 2 in Figure 1 that, in the presence of Co^{2+} ion, $\Delta_o^a\phi_{1/2,PH^+}$ shiftsa more positively. The shifts of $\Delta_o^a\phi_{1/2,PH^+}$ under different experimental conditions are cited in Table I. Although there are differences between the observed values and those calculated from eq 9 that cannot be quantitatively explained, they are linearly related and represent further evidence of the reaction of MP^{n+} with additional phen in the organic phase. These differences, from 10–30 mV, equivalent to a 1.5- to 3-fold decrease in $[P]_{o,s}{}^*$ (eq 4), probably arise from the oversimplified assumption of a linear gradient included in the concept of the flux Y in eq 9. Because MP^{n+} reacts rapidly with phen in the organic phase where its concentration is relatively high, a greater phen depletion occurs in the immediate vicinity of the interface, increasing Y in this region.

From the relationships in eq 5–8, the composition of the overall reaction product, i.e. $MP_{a+b}{}^{n+}$, can also be predicted by the following simple formulation:

$$(a + b)/n = (i_1 - i_3)/i_2 \qquad (10)$$

The results of $(a + b)/n$ determined from the polarograms under different conditions are listed in Table I. A value of 1.5 of $(a + b)/n$ corresponds to the formation of the generally accepted $MP_3{}^{2+}$ complex ion.

Evaluation of the Rate of the Aqueous Complex Formation Reaction. The overall reaction is as follows:

$$M^{n+} + P \underset{k_b}{\overset{k_f}{\rightleftharpoons}} MP^{n+}$$

As a first approximation, it is presumed that the rate-determining step is the aqueous complex formation process producing the transferable complex ion (MP^{n+}) that will be followed by the successive organic reaction, $MP^{n+} + 2P \rightleftharpoons MP_3$. The reaction steps for the second and the third reactions that occur in the organic phase are much faster than the first one in the aqueous phase by virtue of the mass action effect of the much higher phen concentration in the organic phase.

It is evident that the kinetic current is determined by the number of electrochemically active ions, in this case MP^{n+}, formed within the aqueous reaction layer in unit time. In the reaction, $M^{n+} + P \rightleftharpoons MP^{n+}$, the rate of the dissociation of the complex, k_b, may be neglected, since the complex ion formed in the reaction layer must be, under the given experimental conditions, instantaneously removed by rapid electrolytic transfer into the organic phase.

The simple but approximate method by Brdicka and Wiesner[7,8] developed for polarography at the dropping mercury

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electrode on the basis of the concept of the reaction layer can be employed to interpret the kinetic current in this study.

With the thickness of the aqueous reaction layer denoted by d and the volume of the reaction layer by Ad (A is the surface area of the reaction layer, i.e., the surface area of the electrode), then the limiting kinetic current, i_2, can be given by

$$i_2 = nFAdk_f[\mathrm{M}^{n+}]_s[\mathrm{P}]_s \tag{11}$$

When $[\mathrm{M}^{n+}]_s >> [\mathrm{P}]_s$, the concentration of M^{n+} in the reaction layer corresponds practically to that in the bulk solution and, moreover, remains constant during the electrolysis, i.e.

$$[\mathrm{M}^{n+}]_s = [\mathrm{M}^{n+}] \tag{12}$$

It may be assumed that the distribution of phen between two phases is rapid enough to attain equilibrium instantly. Therefore

$$[\mathrm{P}]_s = K_{\mathrm{DR}}{}^{-1}[\mathrm{P}]_{o,s}{}^* \tag{13}$$

The concentration $[\mathrm{P}]_{o,s}{}^*$ depends on the rate of the complex formation reaction in the aqueous phase, decreasing as this reaction increases, and in the limiting case, becomes zero. Under these conditions the current will be determined by the diffusion of phen from the bulk solution, i.e., that it will attain the value of the diffusion-controlled current $i_{2,\mathrm{d}}$, whose value is given from eq 5–8 with $i_3 = 0$ as

$$i_{2,\mathrm{d}} = nFAj/(a + b) = ni_1/(a + b) \tag{14}$$

If $a = 1$, $b = 2$, and $n = 2$, then $i_{2,\mathrm{d}}$ equals to $^2/_3 i_1$ for the PH^+ transfer. This condition was observed qualitatively in the case of the Cd^{2+}–phen wave.

The modified Ilkovič equation (see Appendix, eq A-3) assumes the form

$$i_1 = \alpha C \tag{15}$$

where $\alpha = (4.02 \times 10^5)nD^{1/2}m^{2/3}t^{1/6}$, since the second term in eq A-3 is negligible when the radius of the AWE is much bigger than that of the Teflon capillary, and $C = [\mathrm{P}]_o$. According to the treatment by Brdicka and Weisner,[7,8] which includes the assumption that the concentration gradient of phen is constant within the organic reaction layer, the concentration $[\mathrm{P}]_{o,s}{}^*$ can approximately be correlated to the currents under diffusion-controlled and kinetic-controlled conditions by

$$[\mathrm{P}]_{o,s}{}^* = (a + b)(i_{2,\mathrm{d}} - i_2)/n\alpha \tag{16}$$

because the ratio $i_{2,\mathrm{d}}$ to i_i is proportional to the ratio $[\mathrm{P}]_o$ to $([\mathrm{P}]_o - [\mathrm{P}]_{o,s})$. Combining eq 11–13 and 16 yields

$$i_2 = \beta k_f(i_{2,\mathrm{d}} - i_2) \tag{17}$$

where $\beta = (a + b)FAd[\mathrm{M}^{n+}]K_{\mathrm{DR}}{}^{-1}\alpha_{-1}$. Therefore

$$i_{2,\mathrm{d}}/i_2 = (1 + \beta k_f)/\beta k_f \tag{18}$$

The effective reaction layer whose thickness is d was defined as the average free path length that can be traversed by an electrochemically active particle in its lifetime. The mean lifetime of the particle is inversely proportional to the rate of the reaction leading to the disappearance of the particle; therefore, d was given by $d = (D/k_b)^{1/2}$. This classical treatment employed for an analysis of the kinetically controlled polarographic wave at the dropping mercury electrode[9,10] is applicable to the hypothetical system in which the nonelectroactive species (in this case both phen and M^{n+}) are present in the bulk aqueous phase. In this hypothetical system, the thickness of the aqueous reaction layer, where slow complex formation occurs, increases with the increase of the diffusion coefficient of the complex ion formed and decreases with the increase of the rate of the dissociation reaction of the complex ion.

Under the experimental conditions employed here, however, the nonelectroactive phen is fed from the organic phase across the electrode interface. In such a system it is reasonable to postulate alternatively that the thickness of the aqueous reaction layer, in which phen molecules can exist, increases with the increase of rate of the dissociation of the metal–phen complex as well as with the increase of the diffusion coefficient of phen. Therefore

$$d = (Dk_b)^{1/2} \tag{19}$$

Walden's rule[11] gives the relation between the diffusion coefficients in two media, 1 and 2, namely $D_1\eta_1 = D_2\eta_2$, where η denotes the viscosity of the media; therefore

$$D = 0.8D_0 \tag{20}$$

from viscosity values 0.8 and 1.00 cP of the DCE solution and the aqueous solution, respectively. The equilibrium constant of the first complex formation reaction in the aqueous phase is

$$K = k_f/k_b \tag{21}$$

From eq 19–21, eq 18 is rewritten as

$$i_{2,\mathrm{d}}/i_2 = (1 + \mu k_f{}^{3/2})/\mu k_f{}^{3/2} \tag{22}$$

where

$$\mu = 0.213(a + b)n^{-1}A[\mathrm{M}^{n+}]K^{-1/2}K_{\mathrm{DR}}{}^{-1}m^{-2/3}t^{-1/6}$$

The values of k_f that were calculated from eq 22 by substituting the experimental results are listed in Table I. The K_{DR} for phen distributing between aqueous and DCE phases is $10^{1.82}$.[1] The stability constants of CoP^{2+} and ZnP^{2+} are $10^{7.25}$ and $10^{6.4}$, respectively.[12] All values of stability constants for acetic acid, citric acid, cobalt(II) acetate, and zinc(II) citrate employed for the calculation are given in ref 12.

When rate constants for the formation of MP^{2+} in media containing relatively high concentrations of auxiliary ligands such as acetate and citrate are calculated, the question of whether the hydrated metal ion or its complex with the auxiliary ligand reacts with phen must be considered. It has been shown that some monodentate ligands such as acetate or thiocyanate give metal complexes that react more rapidly than do the free, or hydrated, ion.[13] When such auxiliary ligands are polydentate, however, it is more likely that the free metal ions react more rapidly. Thus, for the calculation of k_f of CoP^{2+}, the total aqueous Co^{2+} concentration was used for M^{n+} in eq 22 and the resulting value, $(5.0 \pm 1.6) \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, is in reasonable agreement with rates of Co^{2+} substitution reactions reported earlier.[5] When the free Co^{2+}, calculated from the CoOAc^+ formation equilibrium expression, was used, the resulting rate constant not only was abnormally high, $\sim 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, but varied with the acetate concentration. For k_f of ZnP^{2+}, on the other hand, a rational, though imprecise, value was obtained only when the concentration of free Zn^{2+}, cal-

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culated from the equilibrium constant for the zinc citrate complex, was used in eq 22.

These results indicate that solvent extraction of metals using phenanthroline and related neutral chelating agents involve, first, the formation of a 1:1 complex in the aqueous phase. The location of further complex formation must depend on a balance between the equilibrium extractability of the 1:1 complex (which, in turn, depends on the lipophilicity of the ligand as well as the suitability of the counterion:e.g., CNS^-, ClO_4^-, NO_3^-, and I^- give more extractable ion pairs than do Cl^- of SO_4^{2-}) and the rates of formation of the higher complexes in the aqueous phase. Although the higher metal–phen complexes are unarguably more extractable than the 1:1 complex, the most dramatic increase in facilitating metal ion transfer occurs during the formation of the latter. It is not unreasonable to suppose that even with those chelating extractants yielding neutral chelates, β-diketones, 8-quinolinols, dithizones, etc., the cationic intermediate complexes can form an extractable ion pair when a suitable counterion is present. In such instances, suitable anions may enhance the rate of extraction.[14]

This work demonstrates the usefulness of current scan polarography at the ascending water electrode in characterizing transfer processes of interest in solvent extraction systems. Further work with other metal extraction systems is under way in our laboratory.

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Appendix

If the limiting current of the current scan polarogram is completely determined by the mass-transfer process of the diffusing species from the bulk liquid phase to the electrode interface, the diffusion-controlled limiting current, i, can be formulated in the manner of the classical Ilkovič equation used for the analysis of polarograms at the dropping mercury electrode. The volume (V, cm^3) of one drop of the AWE is expressed in terms of the mean flow rate of the aqueous solution and the drop time as

$$V = mt = 4\pi r_o^3/3 \tag{A-1}$$

Assuming that the AWE is an ideal sphere at any time, the surface area, A, of the AWE can be given as

$$A = 4\pi r_o^2 - A_s = 4\pi(3mt/4\pi)^{3/2} - \pi r^2 \tag{A-2}$$

where A_s is the area shielded by the appreciably large inner diamter of the Teflon capillary and r_o and r are the radii of the AWE and the inner radius of the capillary, respectively. With use of the Cottrell relation as $i_\alpha = nFAD^{1/2}C/\pi^{1/2}t^{1/2}$, the diffusion current at the AWE can be expressed by

$$(3/7)^{1/2}i = nFD^{1/2}C\pi^{-1/2}t^{-1/2}\{4\pi(3mt/4\pi)^{2/3} - \pi r^2\} = (2.64 \times 10^5)nD^{1/2}Ct^{1/6}m^{2/3} - (1.71 \times 10^5)nD^{1/2}Ct^{-1/2}r^2 \tag{A-3}$$

which includes the correction term for the stretching effect of the AWE, i.e. $^7/_3$. The first term on the right hand side of eq A-3 has the conventional form, which is identical with the classical Ilkovič equation, and the second term is negligible if r is much smaller than r_o. From this equation, the diffusion coefficient of phen in the DCE phase can be calculated to be 9.6×10^{-6} cm^2 s^{-1} as shown from the diffusion-controlled current in Figure 1, curve 1.

Registry No. Cd, 7440-43-9; Zn, 7440-66-6; Co, 7440-48-4; Ni, 7440-02-0; phen, 66-71-7.

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Electrochemical Behavior of $Ru(trpy)(bpy)(OH_2)^{3+}$ in Aqueous Solution and When Incorporated in Nafion Coatings

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The rate at which the Ru(III) complex is electrooxidized is controlled by the kinetics of a chemical step that precedes the electrode reaction. Three candidate reactions for the chemical step were examined. Both disproportionation and deprotonation of the Ru(III) complex could be ruled out as the limiting reactions. Instead, it is proposed that the oxidation rate is limited by the rate of pH-dependent ligand-exchange reactions in which a ruthenium–nitrogen bond is broken. Graphite electrodes coated with Nafion incorporate the Ru(II) complex and exhibit high catalytic activity toward the electrooxidation of benzyl alcohol. Unfortunately the incorporated catalyst is converted into an inactive form after about 150 turnovers.

Meyer and co-workers have demonstrated in recent studies that polypyridyl complexes of ruthenium that contain at least one aquo ligand can be oxidized to the corresponding oxo complexes of Ru(IV).[1,2] These oxo complexes were shown to oxidize a variety of normally unreactive organic substrates, and under some conditions the reaction could be made catalytic.[3-5] Attempts to employ the ruthenium complexes as catalysts for the electrooxidation of organic substrates have also been reported.[4,6] The electrochemical oxidation of the ruthenium(II) complexes proceeds in two one-electron steps, the first of which is simple and fully reversible.[1] However, the second oxidation step, in which the Ru(III) complex is oxidized to the Ru(IV)–oxo complex, yields notably smaller currents than the step that precedes it.[1] This phenomenon has been attributed to a slow disproportionation of the Ru(III) complex that was presumed to be the nonelectrochemical mechanism by which the Ru(IV) complex was formed.[1]

We became interested in these complexes as possible candidates for incorporation in Nafion coatings on electrode surfaces where they could serve as redox catalysts for elec-

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