Metal Complexation at the Liquid–Liquid Interface

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Most scientists interested in the chemistry of solvent extraction processes tended, until relatively recently, to overlook or minimize the role of the liquid–liquid (L–L) interface. Particularly when extraction of metal ions is concerned, involving substitution of hydrated water by a number of (usually) anionic organic ligands to form a neutral, extractable chelate, much of the chemistry has been viewed as occurring in the bulk aqueous phase.[1] The adequately organic soluble ligand or metal chelate was not thought to be adsorbed at the L–L interface. Moreover, even though procedures for phase mixing to reach equilibrium or for studying extraction kinetics[2] were conducted under conditions of energetic mixing or stirring, bound to create a substantial interfacial region, procedures for the subsequent examination of the systems called for quiescent phases so that the interface was of little or no influence.

A number of engineering scientists, with extensive experience in mass-transfer processes, tend to interpose chemical reaction influence on top of other more nonspecific effects, such as diffusion. In other words, those interested in mass-transfer kinetics in liquid–liquid distribution systems start by considering diffusion as the primary source of "resistance" and then include slow chemical reaction kinetics as added "resistances", usually without attempting to account quantitatively for the chemical reaction rate constants. These workers tend to favor experiments in which the interfacial area is well-known but relatively small. Fixed interfacial area designs[3-8] are rooted in the assumption that the reaction is either diffusion or interfacially controlled. Inasmuch as rate constraints of such reactions must be expressed in terms of unit interfacial area, fixed-interface experiments permit this measurement to be made. Until recently, this has not been considered to be possible with high-dispersion experiments because the interfacial contact area is unknown. Most fixed-interface experiments have been performed with either a series of single drops in a continuous phase or a Lewis cell. In the drop method, droplets of one phase are allowed to rise (or fall) through a column containing the second phase. This approach has been criticized for not overcoming diffusion effects in the droplet. The Lewis cell is designed so that both phases stand in contact with each other while each phase is stirred separately. Stirring supposedly overcomes diffusion problems by replenishing the interface with reactant from each bulk phase. Nevertheless, since the vigor of the stirring must be severely limited to avoid vortex formation, it is doubtful that diffusion effects are totally eliminated.

For the first 20 years of our own research into the kinetics and mechanisms of reactions of metal chelate formation and dissociation using solvent extraction techniques,[9] we did not believe that the liquid–liquid (L–L) interface played any significant role. At first, frankly, we simply did not give the matter too much thought. With high-speed stirring, which we believed would eliminate the need to consider mass-transfer steps as rate determining, our results led us to conclude

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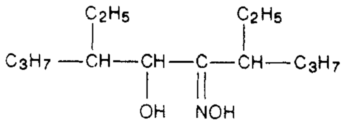
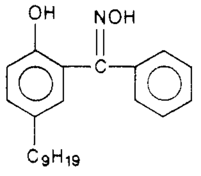
that the rate-determining step (rds) was the formation of an intermediate (usually a 1:1) metal chelate complex in the bulk aqueous phase.[1] This conclusion was greatly reinforced by the generally good agreement between the rate constants we calculated for such reactions with those in the literature obtained by a variety of experimental approaches. While the technique we developed is uniquely useful for systems involving highly insoluble metal chelates, it was especially gratifying to note that it gave results that were in good agreement with those obtained by stopped-flow and other methods in at least two systems, Ni(II)-1,10-phenanthroline[10] and Ni(II)-8-quinolinol.[11]

The introduction of higher molecular weight chelating extractants for large-scale, hydrometallurgical metal recoveries in the 1960s and the subsequent study of some of the fundamentals of the behavior of these interesting reagents served to focus attention on the interesting questions about the role of the interface in such extraction systems. For this reason, we conducted a detailed study of the kinetics of extraction of Cu(II) with aromatic (e.g., LIX 65N) and aliphatic (e.g., LIX 63) hydroxy oximes, which were introduced in the 1960s by General Mills for the large-scale extraction of copper.[12]



4,7-diethyl-5-hydroxy dodecan-6-one oxime (LIX 63)



2-hydroxy-5-nonyl benzophenone oxime (LIX 65 N)

Previous workers, pointing to the low aqueous solubility of the LIX reagents, almost intuitively discarded the possibility of chelate formation in the aqueous phase and proposed that interfacial reaction kinetics, rather than homogeneous chemically controlled rates, are dominant.[13-15] Thus, in a review of the kinetics and mechanisms of Cu(II) extraction by LIX reagents, Flett[16] took the extraordinary position that, because these reagents are "so hydrophobic", their aqueous-phase solubility could be totally ignored! Having adopted this view, when chemical parameters appeared in the extraction rate expressions, these investigators invoked an "interfacial reaction" as the rate-determining step.

A key aspect of the extraction mechanism controversy lies in the nature of the experimental configuration used by various investigators. Under conditions of vigorous shaking[17,18] or high-speed stirring,[19,20] mass-transfer rates in metal chelate solvent extraction processes are much higher than chemical reaction rates. It is axiomatic that, in any multistep process, the overall kinetics of the process gives information about the slowest, i.e., the rate-determining, step. Our high-speed stirring apparatus is based on the classical Morton flask assembly[21] capable of speeds up to 20000 rpm. Our apparatus[19] is always operated at a stirring speed beyond the level at which the extraction rate achieves a plateau value that is independent of the stirring speed. The plateau is a consequence of the balance between dispersion and coalescence, i.e., where further stirring energy does not reduce drop size of the dispersed phase but simply contributes to overall convective movement in the reaction flask. The data we obtain are highly reproducible and almost always result in simple experimental rate expressions having very nearly integral reaction orders. Furthermore, the values of chelation rate constants derived from the data are generally in accord with those expected for the substitution rates of metal ions in aqueous media and, where available, in good agreement with published values from studies utilizing independent methods.

We studied various "LIX" systems of which LIX 65N-Cu(II) is typical. First, we determined the distribution equilibrium of LIX 65N between chloroform and water to be $10^{4.6\pm0.3}$,[20] which means that LIX 65N is significantly less hydrophobic than dithizone. The rate expression obtained from our kinetic data for the extraction of copper by LIX 65N can be quantitatively described by

$$-\frac{d[Cu^{2+}]}{dt} = k'\frac{[Cu^{2+}][HL]_o^{2.0}}{[H^+]^{1.0}} \tag{1}$$

where HL represents LIX 65N.

From the observed kinetics, a reasonable mechanism for this system identifies the rds as the reaction of CuL^+ with HL (eq 4)

$$HL(o) \overset{K_{DR}}{\rightleftharpoons} HL \qquad \text{fast} \tag{2}$$

$$Cu^{2+} + HL \overset{\beta_1 K_a}{\rightleftharpoons} CuL^+ + H^+ \qquad \text{fast} \tag{3}$$

$$CuL^+ + HL \xrightarrow{k_1} CuL_2 + H^+ \qquad \text{slow} \tag{4}$$

$$CuL_2 \overset{K_{DC}}{\rightleftharpoons} CuL_2(o) \qquad \text{fast} \tag{5}$$

where K_{DR} and K_{DC} represent the distribution constants of ligand and chelate, K_a the acid dissociation constant of LIX 65N, and β_1 the equilibrium formation constant of CuL^+ from Cu^{2+} and L^{-1}. The kinetic expression for the rds, eq 4, is

$$-\frac{d[Cu^{2+}]}{dt} = k_1[CuL^+][HL] \tag{6}$$

By substituting appropriately from eq 2 and 3 into eq 6, one obtains eq 7, with which the observed dependence on metal ion, ligand, and pH is consistent.

$$-\frac{d[Cu^{2+}]}{dt} = \frac{k_1\beta_1K_a[Cu^{2+}][HL]_o^2}{K_{DR}^2[H^+]} \tag{7}$$

The extraction of copper by LIX 65N is unusual in that the observed second-order dependence on ligand concentration contrasts sharply with the nearly universally observed first-order ligand dependencies.[22] This behavior is not unique, however, since for d^9 metal ions the rate constants for the 1:1 and 1:2 complexes are not as different as they are for most other transition-metal ions. The observed reaction rate constant, k', is given in eq 8:

$$k' = (k_1\beta_1K_a)/K_{DR}^2 \tag{8}$$

Together with a K_{DR} value of $10^{4.6}$ and a k' of 1.37, k_1 for LIX 65N is seen to be 2.2×10^7 M^{-1} s^{-1}, a value that is quite similar to rate constants for typical substitution reactions of Cu^{2+} (the corresponding rate constant for Cu and phenanthroline is only 3 times larger).[23]

Although all of our work to this point convinced us of the primary importance of the bulk aqueous phase as the site of the rds, the chemical reaction of metal complex formation, we did not mean to imply that an interfacial influence on extraction kinetics conducted under high-speed stirring conditions would never occur. Indeed, we set about to search for systems in which these effects could occur by preparing and studying a series of symmetrically dialkylated dithizones, from methyl (HMeDz) to hexyl (HHxDz). An automated solvent extraction apparatus was developed,[24] of which a microporous Teflon phase separator (MTPS) is a key element. With the MTPS, the bulk organic phase is cleanly separated from a fine dispersion of the two phases in the flask, circulated through a spectrophotometric flow cell, and returned. It seemed appropriate to start our search with derivatives of dithizone, the extractant having the highest K_{DR} of all of the extractants studied to date. With use of the automated extraction apparatus, at high pH values, a drop in the alkylated dithizone concentration in chloroform was observed; this decrement increased with stirring speed up to a plateau region. The extent of the decrease in concentration varied with pH at stirring speeds in the plateau region in a manner parallel to the nonstirring experiment. The stirring vs nostirring difference in $pH_{1/2}$ values (pH at which 50% of the ligand remains in the organic phase), $\Delta pH_{1/2}$, increased from 0.16 to 0.66, 3.0, and 5.0 as the alkyl group varied from methyl to ethyl, butyl, and hexyl. No observable change was obtained with dithizone itself.

Measurements of interfacial tension, γ_1, were carried out with aqueous phases at two pH values, 3.5 and 12.0, and the following organic phases: HDz in $CHCl_3$, HBuDz in CCl_4, and HBuDz in $CHCl_3$. In the acidic systems, there was no change in the γ_i value that could be attributed to the presence of the solute. In the alkaline systems, however, a decrease in γ_i was observed which became linear with an increase of the logarithm of the solute concentration. By means of the Gibbs adsorption isotherm

$$\Gamma = -(RT)^{-1}(\delta\gamma_i/\delta \ln C)_T \tag{9}$$

one obtains a surface excess, Γ, in mol/cm^2, from which we estimated the surface area occupied by one molecule, a_m (Å^2/molecule): 90 for HDz in $CHCl_3$, 70 for HBuDz in CCl_4, and 150 for HBuDz in $CHCl_3$. The minimum solute concentration required for interfacial saturation, C_m, can also be estimated from the γ_1–ln C data; the values for log C_m were −2.2 for HDz in $CHCl_3$, −3.7 for HBuDz in CCl_4, and −2.8 for HBuDz in $CHCl_3$. As might be expected, the greater effect is observed in the poorer solvent. The decrease in interfacial tension under alkaline but not acid conditions suggests that it is the reagent anion rather than the nonionized reagent that is surface active.

The reversible concentration change in the organic phase caused by stirring can be equated with the amount of the extractant adsorbed in the interface.[25] Thus

$$\log D/D' \equiv \log (10^{\Delta pH_{1/2}} - 1)$$

(where D' and D are the observed extractant distribution ratios with and without stirring) was shown to increase in a linear manner with the number of carbons in the alkyl substituent in the dithizones with a slope of 1.12, permitting a reliable estimate of the directly unobservable log D/D' for dithizone of −1.57. From values of log D/D', the interfacial component can be calculated as 2.6% for dithizone. It then rises rather rapidly: 26% in HMeDz, 82% in HEtDz, 99.9% in HBuDz, and all but 7×10^{-4}% in HHxDz. These changes are indicative of the dramatic change in the heterogeneous acid–base equilibrium constant (up to a factor of 10^5) that occurs because the anionic alkyldithizonate (but not the neutral ligand) is surface active and is adsorbed into the interfacial region.[25]

The extraction kinetics of nickel and zinc with the alkyldithizonates[25] closely resembled those with dithizone and its analogues studied earlier,[26] in that the rate was first order each in metal and ligand and inverse first order in hydrogen ion. If one were to assume that the mechanism remained the same, however, i.e., that the rds is the formation of the 1:1 complex from metal and ligand anion in the aqueous phase, the resulting second-order reaction rate constants increase with the size of alkyl group until, with the hexyldithizone, the values for both Ni and Zn would far exceed the diffusion-limited rate constant for bimolecular reaction!

This unrealistic conclusion is avoided by accounting for the adsorption of the ligand anion in the interface, which is the probable locus for the formation of the 1:1 complex. Calculating the correct value of the ligand anion concentration in the interface from the observed differences in $pH_{1/2}$ values (vide supra) and assuming that since the metal ion is not surface active, its concentration in the interface is the same as it is in the bulk aqueous phase, we obtained values for rate constants that were eminently reasonable, i.e., essentially constant values for all the alkylated dithizones. Log k_1 for Ni and Zn is 5.13 and 8.80, respectively, somewhat higher than the rates for the corresponding parent complexes as might be expected from the electron-release character of the p-alkyl substituents. These are consistent with those obtained from these metals in a broad cross section of ligand-substitution reactions. Essentially, the entire cause of the unusual kinetic behavior, as well as of the unusual extraction equilibrium behavior, is the adsorption of the ligand anion into the interfacial region, whose area is greatly enlarged by high-speed stirring.

From interfacial tension measurements, together with the use of MTPS, we were now able to interpret the variation of rates of extraction with stirring speed. We wished particularly to understand why, when the ligand anion was adsorbed into the interface, the rates reached maximum values at stirring speeds above 5000–6000 rpm. Combining the interfacial tension measurement of a particular system with the decrements in absorbance, ΔA, observed under stirring conditions yields the expression[27]

$$\Gamma a_i = \frac{\Delta A}{\epsilon} V_o \left(1 + \frac{1}{K_D}\right) \sim \frac{\Delta A}{\epsilon} V_o \tag{10}$$

in which Γ is the surface excess in mol/cm^2 (see eq 9, a_i the interfacial area, ΔA the absorbance decrement obtained with stirring, ϵ and K_D the molar absorbance and distribution constant of the extractant, and V_o the volume of the organic phase. Since every other parameter in eq 10 is experimentally determined, this now serves to evaluate a_i, the interfacial area.

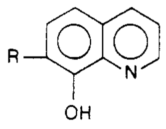
To summarize the results of a study of the variation of interfacial area (recalculated as average drop size) with stirring speed for aqueous–$CHCl_3$ systems containing the extractant bis(*p*-(*n*-butyl)phenyl)thiocarbazone (HBuDz), seen previously to function as an anionic surfactant, a neutral surfactant (either Triton X-45 (TX-45) or Triton X-100 (TX-100)), or a cationic surfactant (cetylpyridinium chloride (CPC)): the average drop size (d) decreases with increasing stirring rate (ω), reaching a minimum at rates of about 80–100 rps, reflecting a balance between breakup and coalescence. It is interesting to note that while the minimum average drop size observed for the butyldithizone and the two Triton X systems was about the same, namely, 210 ± 10 μm, the average drop size observed for CPC, a more active surfactant, is distinctly smaller, 160 μm.

An interesting question arises about the fate of the adsorbed species when the droplets of organic phase pass through the MTPS. As the organic drops hit and penetrate the MTPS membrane, does the adsorbed species, which is relatively hydrophobic, accompany the organic phase, or is it desorbed and returned to be equilibrated with the two-phase mixture in the flask? Our standard procedure cannot serve to decide this question because such a small fraction of the droplets of organic phase and their accompanying adsorbed material is removed at any point in time; therefore, the fate of this adsorbate cannot be deduced from this experiment. If, instead of the separated organic phase being returned to the reaction flask as before, the return stream goes to waste, however, the organic phase volume will be continuously reduced, and the question can be resolved.

If the first of the two possibilities described above occurs, the observed absorbance should remain constant throughout the experiment. Alternatively, if the adsorbed species were stripped from the interface and returned to the reaction flask as the total organic phase volume and total interfacial area decreased, the absorbance should rise during the course of the experiment.

From such experiments conducted on three systems (LIX 65N in heptane/water, 7-dodecenyl-8-quinolinol (KELEX 100) in xylene/water, and 4,7-diphenyl-1,10-phenanthroline in $CHCl_3$/water) it was evident that the species adsorbed on the interface during the initial phase of the experiment, i.e., before any filtered organic phase is removed, is essentially all retained in the reaction flask.[28] This would be consistent with the positioning of the polar end of the adsorbed species in the aqueous side of the interface and the nonpolar end in the organic side. As the phases separate on the MTPS, the adsorbed species are retained in the aqueous interfacial region. This probably can be attributed to an energetically more unfavorable dehydration of the polar portion of the molecule than to desolvation of the nonpolar portion required when the species leaves the organic interfacial region.

Armed with this technique, enabling us to measure and control reliably the interfacial area, we are now in the process of studying the effect of the interface on the overall extraction kinetics in a variety of chelate extraction systems. To begin with, we selected the system Ni(II)–7-dodecenyl-8-quinolinol (KELEX 100) (B)[29] and Ni(II)–8-quinolinol (A), because previous studies[30,31] have demonstrated that nickel extraction by 8-quinolinol (oxine) (A) occurs via two reaction pathways: (1) reaction between nickel and neutral oxime and (2) reaction of metal with ligand anion. In each case, it has been postulated in earlier studies that these rate-determining reactions occur in the bulk aqueous phase. Recent work in this laboratory[22,25] has revealed that, in cases where the ligand anion is a surface active species, the extraction may, at least partially, proceed through a reaction path involving the interfacial region. Haraguchi and Freiser[32] have found that for KELEX 100 (B) the pH value is affected by high-speed stirring, indicating that the distribution of the ligand anion is sensitive to changes in interfacial area. To help answer the question of whether the rate-determining steps for the extraction of nickel by oxine and its higher molecular weight analogue, KELEX 100, are taking place in the bulk aqueous phase or in the interfacial region, this system has been studied with the MTPS apparatus.



A, R=H
B, R=dodecenyl

The rates of extraction of nickel with oxine and KELEX 100 were found to be dependent on hydrogen ion concentration raised to a fractional power,[30,31] indicating two concurrent pathways, whose rate-determining steps involve either neutral or anionic forms of the ligand. These two paths had been previously presumed to occur strictly in the bulk aqueous phase. Finding that an increase in interfacial area can cause a drop in absorbance of the neutral reagent in the bulk organic phase under alkaline conditions suggests that the ligand anion is surface active.[25] This leads to the possibility that the reaction of nickel with ligand anion may, at least in part, involve an interfacial reaction mechanism.

It was determined from the drop in absorbance of the species in the organic phase upon stirring that, at pH 11.3, the oxine anion exhibited an interfacial excess of 3×10^{-12} mol/cm^2, while for KELEX 100 the excess was 6×10^{-12} mol/cm^2, twice that of oxine. Even in the case of KELEX 100, the value of Γ is equivalent to each molecule occupying about 2800 Å^2 of interface, a value much larger than that expected for an interface saturated with a monolayer of the molecules. The rather small Γ values indicate that these species are only weakly surface active, yet even this leads to the kinetic effects observed.

In order to evaluate the role of the interface in the extraction kinetics of nickel with 8-quinolinols, the rates of reaction were measured as a function of specific interfacial area (interfacial area per unit volume of the organic phase). The results are illustrated in Figure 1 for KELEX 100. The experiments were run over a range of pH values to see how the ratio of neutral to ligand anion would affect the balance between the two possible pathways (bulk and interfacial). The results, which indicate that the pH of extraction is very important in determining what combinations of mecha-

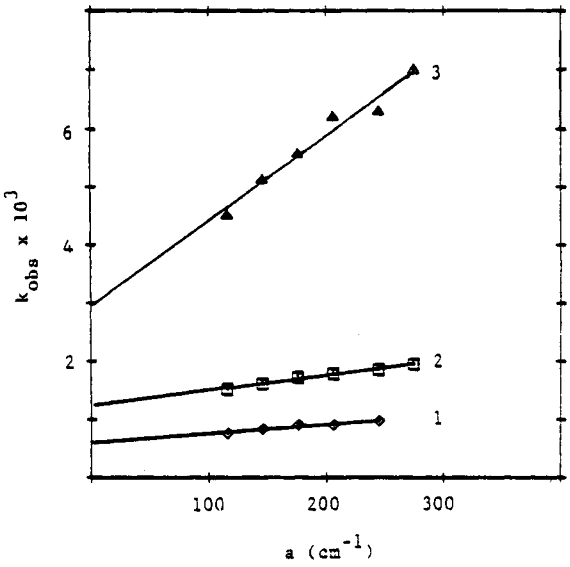


Figure 1.

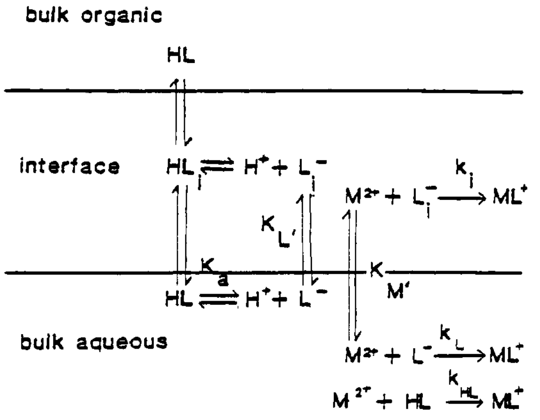


Figure 2.

nisms is operative, can be rationalized by the reaction scheme illustrated in Figure 2.

This scheme allows for three distinct concurrent reaction pathways: path 1, reaction between metal and neutral ligand in the bulk aqueous phase; path 2, reaction of metal with ligand anion in the bulk aqueous phase; path 3, reaction of metal and ligand anion in the interface.

Evidence in support of this reaction scheme is seen in Figure 1. In the low pH range, the rate constants are relatively independent of specific interfacial area. In this range the neutral form of the ligand predominates, and its reaction with nickel ion occurs in the bulk (path 1). The fact that the neutral ligand shows no observable surface activity lends support to the likelihood of a purely bulk phase reaction.

With increasing pH, increases in both slopes and intercepts are observed, indicating the dual anion mechanisms (paths 2 and 3). The significance of the increasing intercept is that, in the limit of zero interfacial area, the rate increases with pH, as required by a bulk-phase reaction of the ligand anion.

The increase of the observed rate with interfacial area is heightened with increasing pH, demonstrating that the ligand anion participates in a rate-determining step at the interface (path 3).

TABLE I. Summary of Rate Constants for Nickel Extraction with Oxine and Its Analogues

extractant	log k_{HL}, M^{-1} s^{-1}	log k_L, M^{-1} s^{-1}	log k_i, M^{-1} s^{-1}
oxine[a]	2.97	5.46	6.7 ± 0.2
oxine[b]	3.55	5.73	
thiooxine[c]	3.45	5.45	
KELEX 100[a]	4.4	6.8	6.7 ± 1.0
KELEX 100[d]	3.74		6.92

[a] Present work. [b] Reference 34. [c] Reference 38. [d] Reference 35.

These findings can be represented quantitatively by the following derived relations:

$$-\frac{d[\mathrm{Ni}]}{dt} = k_{\mathrm{obsd}}[\mathrm{Ni}] \tag{11}$$

$$-\frac{d[\mathrm{Ni}]}{dt} = \left(k_{\mathrm{HL}} + k_{\mathrm{L}}\frac{K_{\mathrm{a}}}{[\mathrm{H}^+]}\right)\frac{[\mathrm{HL}]_{\mathrm{o}}[\mathrm{Ni}]}{K_{\mathrm{D}}} + k_i K_{\mathrm{M}} K_{\mathrm{L}} a d \frac{K_{\mathrm{a}}}{[\mathrm{H}^+]}\frac{[\mathrm{Ni}][\mathrm{HL}]_{\mathrm{o}}}{K_{\mathrm{D}}} \tag{12}$$

$$k_{\mathrm{obsd}} = \left(k_{\mathrm{HL}} + k_{\mathrm{L}}\frac{K_{\mathrm{a}}}{[\mathrm{H}^+]}\frac{[\mathrm{HL}]_{\mathrm{o}}}{K_{\mathrm{D}}} + k_i K_{\mathrm{M}} K_{\mathrm{L}} a d \frac{K_{\mathrm{a}}}{[\mathrm{H}^+]}\frac{[\mathrm{HL}]_{\mathrm{o}}}{K_{\mathrm{D}}}\right) \tag{13}$$

where k_{obsd} is the observed pseudo-first-order rate constant, k_{HL} is the second-order rate constant of metal plus neutral ligand in the bulk aqueous phase, k_{L} is the second-order rate constant for metal plus ligand anion in the bulk aqueous phase, k_i is the interfacial rate constant, K_{a} is the acid dissociation constant (pK_{a} of 9.90 and 10.40 for oxine and KELEX 100, respectively[32]), K_{D} is the distribution constant of the neutral ligand ($10^{2.6}$ and $10^{5.52}$ for oxine and KELEX, respectively[33]), K_{M} is the distribution constant of the metal between the interface and bulk aqueous phase, K_{L} is the distribution constant of the ligand anion between the interface and the bulk aqueous phase, d is the thickness of the interface, and a is the specific interfacial area. A plot of k_{obsd} vs a (Figure 1) permits the evaluation of all the rate constants, provided the other values are known. The excellent linearity seen in the plots confirms the applicability of eq 13.

The only unknown values in eq 13 are K_{M}, K_{L}, and d. Since it is assumed that the metal is not surface active, K_{M} is taken as unity. The values of the product of K_{L} and ad can be obtained by measurement of $\Delta\mathrm{pH}_{1/2}$. This relation[25] is

$$10^{\Delta\mathrm{pH}_{1/2}} - 1 = K_{\mathrm{L}}(ad) \tag{14}$$

The $\Delta\mathrm{pH}_{1/2}$ value for oxine was 0.03 ± 0.01 and for KELEX 100 was 0.8 ± 0.6, yielding $K_{\mathrm{L}}ad$ of values from eq 14 of $10^{-3.6\pm0.2}$ for oxine and $10^{-1.7\pm1.0}$ for KELEX 100.

The values of the slopes and intercepts of the lines of Figure 1 can be used to evaluate all three rate constants, as well as the degrees of contribution of the three pathways. Results are tabulated in Table I along with values from other studies. A similar ligand, 8-mercaptoquinoline, is included for comparative purposes.

These results are in fairly good agreement with those of Yamada et al.[30] for the Ni(II) system, despite the different assumptions about the reaction mechanism.

The 10-fold higher interfacial rate constant we reported[29] might be accounted for in terms of the different environment in the bulk and interfacial phases. For example, if the dielectric constant at the interface were somewhere between that of the bulk solvents, and hence lower than that of bulk water, the interfacial region would be a more conducive environment for the reaction involving charge neutralization, as was found in this case. Also, the number of degrees of freedom for the adsorbed ligand should be lower at the interface than for the free anion in bulk water, resulting in a more positive entropy change. In addition, the geometric orientation of the weakly surface active chelating agent may be affected by the different environment that the interface provides. The polar chelating group is expected to be pointing toward the aqueous phase, which will also enhance the chances of reaction. These factors would all lead to the observed larger interfacial rate constant found for oxine.

Although the more hydrophobic KELEX 100 anion is more highly adsorbed into the interfacial region than is the 8-quinolinolate (i.e., K_L' is higher) and thus a greater proportion of the reaction of the anion with Ni^{2+} takes place in that region, it is interesting to note that the corresponding rate constants, k_L and k_i, are not significantly different. Thus, the interfacial region would seem to have an essentially aqueous character. Further investigation is necessary to obtain a general answer to the question of how the interfacial and bulk rate constants compare to one another.

The finding is this study of a three-path reaction mechanism for the extraction of a well-known, simple chelating system and a high molecular weight analogue indicates the complexity that may be involved. Here, as in other systems we have studied, the ligand anion exhibits interfacial activity resulting in a concentration enrichment and consequent enhancement in chelate formation rate. This, and not any dramatic increase in "interfacial rate constants", most logically explains these results. A number of provocative and significant questions remain. Why, for example, is the relative proportion of interfacial vs bulk aqueous pathway not much different for KELEX 100, itself interfacially active, than for 8-quinolinol? In studies of the dithizone system and its analogues with Ni(II) and Zn(II),[34] why does the reaction with Ni(II) and the ligand anion appear to proceed by the interfacial pathway only, whereas that with Zn(II) involves two concurrent mechanisms, bulk aqueous and interfacial? Recently, Watarai[35] has shown that several cationic metal chelates can be adsorbed at a L–L interface, and we have observed that some but not all neutral chelates of 8-quinolinol also have this characteristic.[36] It is highly likely that both partially and fully formed extractable chelates must play an important role in the overall effect of L–L interfaces in solvent extraction chemistry, but this is part of an as yet unexplored exciting future.

The usefulness of the new extraction kinetics apparatus as a diagnostic tool for evaluating the role of the liquid–liquid interface in solvent extraction systems has been demonstrated. The ability to differentiate between bulk phase and interfacial reactions can be very important in the design of improved extractants, as well as in the understanding of the fundamental chemical properties of the liquid–liquid interface.

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