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Role of the Interface in the Kinetics and Mechanisms of Extraction of Nickel by 8-Quinolinols

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Role of the Interface in the Kinetics and Mechanisms of Extraction of Nickel by 8-Quinolinols

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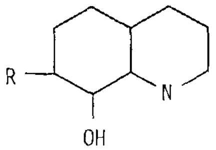
ABSTRACT

The measurement of individual rate constants, as well as the quantitative determination of the contribution of the liquid-liquid interface to the overall extraction kinetics in a well known extraction system, nickel extraction by oxine and its high molecular weight analog (KELEX 100), has revealed that a three path extraction mechanism is operative. The results indicate that the interfacial region provides a more conducive reaction medium in comparison to the bulk aqueous phase. The finding of concurrent bulk and interfacial mechanisms not only reveals the complexity that can be involved in this extraction system, but also enables one to design more efficient separation techniques based on these differences in mechanisms.

INTRODUCTION

Solvent extraction processes such as those involving metals and chelating extractants, in addition to being of high interest to such diverse groups as analytical chemists and hydrometallurgists, provide unique opportunities to evaluate the role of liquid-liquid interface in complex mass transfer processes. In fact, over the last twenty years, lively controversy has developed over this role. Two extreme positions based on extraction kinetics studies have received most of the attention: (1) The rate of extraction of a metal ion in the aqueous phase by a "hydrophobic" chelating extractant in the organic phase reflects the formation of a metal chelate species entirely in the interface [1]; (2) The bulk, aqueous phase is the site of the rate-determining chelate formation reaction [2]. A significant barrier to resolution of this issue lies in the difficulties of the experimental techniques used by both factions. The concern of those championing the interfacial mechanism for conducting experiments under conditions of fixed, well-defined interfacial area led them to use Lewis cell and falling (or rising) drop methods in which relative movement of two phases is slow enough to make them subject to diffusion control. On the other hand, use of high speed stirring by those who believe in the bulk aqueous phase mechanism, while effectively eliminating diffusion, did not until recently permit the interfacial area to be measured, and hence the role of the interface could not be fully assessed. With the recent development in this Laboratory of a high speed stirring apparatus incorporating a microporous Teflon filter element [3], it became possible to observe interfacial adsorption of extractants [4] under steady-state conditions and to apply properly such findings to extraction kinetics [5]. More recently, by combining extraction experiments with interfacial tension measurements, and applying Gibbs' adsorption isotherm, we can reliably measure and control the interfacial area [6] and thus study its effect on the overall extraction kinetics in a wide variety of extraction systems.

We have been particularly interested in the kinetics and mechanism of metal chelate extraction systems. Previous studies [7, 8] have demonstrated that nickel extraction by 8-quinolinol (oxine) (A) occurs via two reaction pathways: (1) reaction between nickel and neutral oxine and (2) reaction of metal with ligand anion. In each case, it has been postulated that these rate determining reactions occur in the bulk aqueous phase. Recent work in this laboratory [4,5] 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 [9] 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 analog, KELEX 100, are taking place in the bulk aqueous phase or in the interfacial region, this system has been studied with the new apparatus. The nickel/oxine system affords one the opportunity to test the applicability of the apparatus as a diagnostic tool in determining reaction mechanisms in typical solvent extraction systems.



(A) R = H
(B) R = dodecenyl

EXPERIMENTAL

8-Quinolinol (oxine) (Eastman Kodak) was purified by recrystallization from ethanol. 7-Dodecenyl-8-quinolinol (KELEX 100) was obtained from Sherex Chemicals and was purified by washing 100 mL of undiluted KELEX 100 with about 20 L of 1 M sulfuric acid. The yellow aqueous phase containing the major impurity (oxine) was discarded and the washing continued until the aqueous phase was colorless. The solution was washed with water and the light brown organic phase evaporated on a rotary evaporator until only the purified KELEX 100 remained. All other chemicals were of analytical grade. Phosphate and THAM buffers, sodium perchlorate and sodium hydroxide solutions were washed with solutions of KELEX 100 in chloroform to remove metal impurities. Chloroform was washed with water twice before use. Nickel solutions were prepared from nickel perchlorate and standardized by complexometric titration with EDTA at pH 10 with murexide as the indicator.

APPARATUS

The extraction kinetics apparatus described previously [3] was used with some minor changes, such as the introduction of a computer controlled data acquisition unit. The absorbance readings from the Cary 219 were sent at chosen intervals (usually 1 Hz) to an Apple II Plus computer. A Pascal software program was written to collect and store the data on floppy disks. Stirrer rotation rates were measured with an analog tachometer (precision of ± 2%).

PROCEDURE

The spectrophotometer was first zeroed at the desired wavelength by pumping clean chloroform through the flow cell. The Morton flask was immersed in a water bath being held at 22° C, and the phase separator and stirrer were incorporated into the system. To the reaction vessel was added 100 mL of chloroform which was 10^{-3} M in ligand concentration. Next, 90 mL of aqueous buffer (10^{-3} M buffer and 0.1 M $NaClO_4$) was added and, following thermal equilibration, the peristaltic pump was started to circulate the organic phase through the flow cell. The stirrer was set to the desired stir rate and the mixture was allowed to equilibrate for 5 minutes.

The kinetics of extraction was started by the rapid (<1 sec) injection of 10 mL of 10^{-3} nickel solution. The reaction process was monitored at the respective wavelength maxima: 390 nm for $Ni(Ox)_2$ and 487 nm for $Ni\ (KELEX)_2$. These two wavelengths correspond to different electronic transitions.

The experiments were carried out under pseudo-first order conditions with ligand in the organic phase in large excess over nickel ion in the aqueous phase. The pseudo first order rate constants, k_{obs}, were determined from

$$\ln \frac{A_e - A_o}{A_e - A_t} = k_{obs}$$

where A_e is the absorbance at equilibrium, A_o is the absorbance at time zero, and A_t is the absorbance at time t.

Interfacial tension was determined by the drop-volume method using a Gilmont micro buret and polyethylene tip.

RESULTS AND DISCUSSION

In a previous study [6], it was demonstrated that the amount of interfacial area, or average droplet size, a liquid-liquid dispersion can be measured as a function of stirring rate. This allows the measurement of extraction rate under varying interfacial area, and thus, the evaluation of the role of the interfacial area in solvent extraction kinetics. It has been assumed that since the chloroform and aqueous phases in the pH range used in this study were found to have identical interfacial tension (32.5 dyn/cm) to the system used previously (butyldithizone), the relation between specific interfacial area (interfacial area divided by volume) and stirring rate, are essentially the same [6] (see Table 1). It should be pointed out that, while subject to small absolute errors in interfacial area, our method [6] for determining this clearly demonstrates a good linear relationship between stirring speed and interfacial area in the range of 2000-4000 r.p.m. for the chloroform-aqueous phase pairs used. This results in a high degree of internal consistency on which are based the major conclusions concerning the respective roles of bulk aqueous and interfacial pathways.

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 [7, 9], indicating two concurrent pathways whose rate determining steps involve either neutral and anionic forms of the ligand. These two paths have 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 [5]. This leads to the possibility that the reaction of nickel with ligand anion may, in part, utilize an interfacial reaction mechanism.

Table 1
Interfacial Area Dependence of Stir Rates

Stir Rate (RPM)	Interfacial Area (cm^2)	Specific Int. Area (cm^{-1})
2000	11,600	116
2500	14,600	146
3000	17,600	176
3500	20,600	206
4000	24,500	245
6000	27,500	275

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 x 10^{-12} mol/cm^2, while for KELEX 100 the excess by 6 x 10^{-12} mol/cm^2, twice that of oxine. Even in the case of KELEX 100, the value of y 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 quite small Γ values indicate that these species are only weakly surface active, yet still sufficiently so to produce 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. The results are illustrated in Figure 1 for oxine and Figure 2 for KELEX 100. The experiments were run over a range of pH values to see how the ratio of

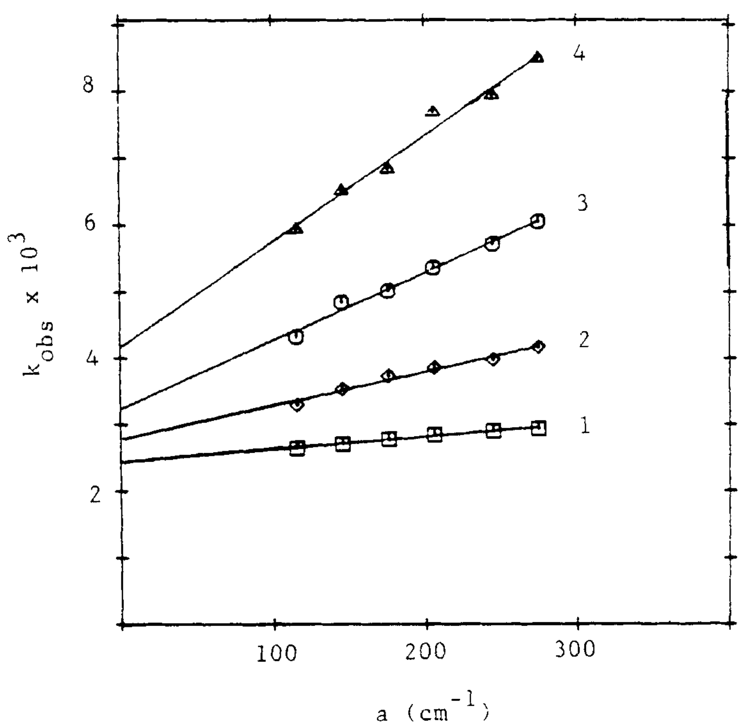


Figure 1. Specific Interfacial Area Dependency of Nickel Extraction by Oxine. (1) pH 6.54; (2) pH 6.77; (3) pH 7.03; (4) pH 7.15.
Conditions: (Oxine) = 1 x 10^{-3} M; ($NaClO_4$) = 0.1 M; (Ni) = 1 x 10^{-4} M.

neutral to ligand anion would affect the balance between the two possible pathways (bulk and interfacial). The results, which indicate that the extraction pH is very important in determining what combination of mechanisms is operative, can be rationalized by the reaction scheme illustrated in Figure 3.

This scheme (Figure 3) 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.

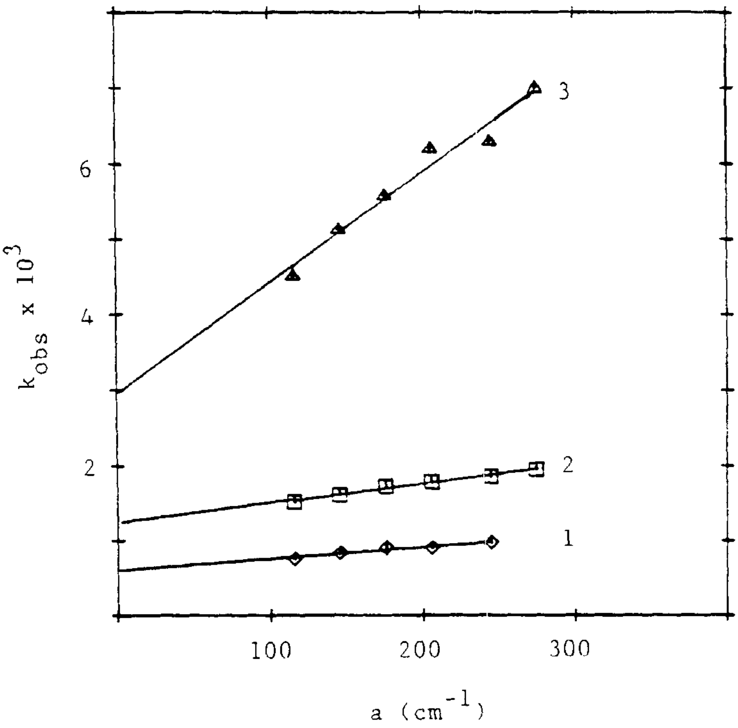


Figure 2. Specific Interfacial Area Dependency of Nickel Extraction by KELEX 100. (1) pH 7.27; (2) pH 7.7; (3) pH 8.45. Conditions: (KELEX) = 1×10^{-2} M; ($NaClO_4$) = 0.1 M; (Ni) = 1×10^{-4} M.

Evidence in support of this reaction scheme is seen in Figure 1 and 2. In the low pH range, the reactions are practically 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 neutral ligand shows unobservably low surface active tendencies lends support to the likelihood of a strictly bulk phase reaction.

With increasing pH, increases in both slopes and intercepts in both figures is observed, indicating the dual anion mechanisms. 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).

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

$$-\frac{d(\mathrm{Ni})}{dt} = k_{obs}\,(\mathrm{Ni}) \tag{1}$$

$$-\frac{d(\mathrm{Ni})}{dt} = \left(k_{HL} + k_{L}\frac{K_a}{[H^+]}\right)\frac{[HL]_o[Ni]}{K_D} + k_iK_{M},K_{L},$$

$$\mathrm{ad}\ \frac{K_a}{[H+]}\ \frac{[Ni][HL]_o}{K_D} \tag{2}$$

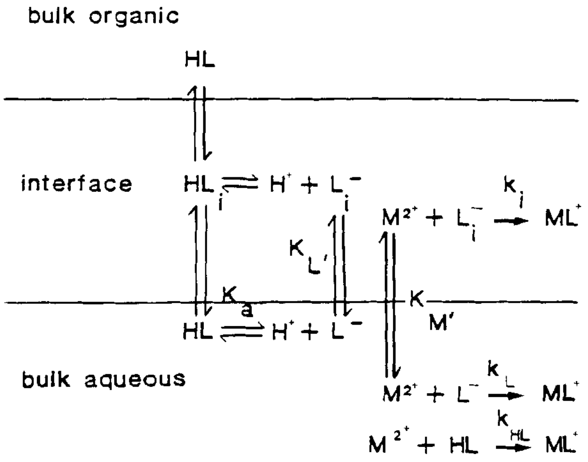


Figure 3. Reaction Scheme for 8-Quinolinols

$$k_{obs} = (k_{HL} + k_L \frac{K_a}{[H^+]} \frac{[HL]_o}{K_D} + k_i K_{M'} K_{L'} ad \frac{K_a}{[H^+]} \frac{[HL]_o}{K_D} \qquad (3)$$

where k_{obs} 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 9.90 and 10.40 for oxine and KELEX 100, respectively [10]), K_D is the distribution constant of the neutral ligand ($10^{2.6}$ and $10^{5.52}$ for oxine and KELEX, respectively [10]), 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_{obs} vs. a (Figures 1 and 2) 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 Equation 3.

The only unknown values in Equation 3 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 ($K_{L'}$ d) can be obtained by measurement of $\Delta pH_{1/2}$, the change in $pH_{1/2}$ to a lower value upon generation of a large interfacial area, $pH_{1/2}$ being the pH at which 50% of the ligand has left the organic phase and transfers to the interfacial and bulk aqueous phases. This relation has been previously derived by Watarai and Freiser [5]

$$10^{\Delta pH_{1/2}} - 1 = K_{L'} ad \qquad (4)$$

The observed shift in $pH_{1/2}$ for oxine was 0.03 ± 0.01 and that for KELEX 100 was 0.8 ± 0.6, yielding the values from Equation 4 of ($K_{L'}$d) as $10^{-3.6 \pm 0.2}$ for oxine and $10^{-1.7 \pm 1.0}$ for KELEX 100.

The values of the slopes and intercepts of the lines in Figures 1 and 2 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 2 along with values from other studies. A similar ligand, 8-mercaptoquinoline, is included for comparative purposes.

There is fairly good agreement with Yamada et al. [2] in the case of oxine kinetics. It must be pointed out that this study was done at a slightly lower temperature (22° C) than that of Yamada (25° C). Nevertheless, one must realize that their study was done under the assumption of a completely bulk phase reaction mechanism as opposed to this study's finding of a combination of bulk and interfacial reactions of the ligand anion. The 10 times higher interfacial rate constant can be understood in terms of the differences in many physical properties between the bulk and interfacial phases. It is possible that the dielectric constant at the interface is somewhere between that of the bulk solvents, yielding a much lower dielectric constant than that of bulk water. This would be expected to be a more conducive environment for the reaction between two oppositely charged ions, as is the case here. In addition, the geometric orientation of the weakly surface active chelating agent may be affected by the different environment that the interface provides. The number of degrees of freedom for the ligand anion should be lower at the interface, than in bulk water, due to the

Table 2
Summary of Rate Constants for Nickel Extraction
With Oxine and Its Analogs

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 7 [c]Reference 11 [d]Reference 9

presence of dispersive forces which tend to orient the species in such a way as to reduce its free energy. The polar chelating group is expected to be pointing towards 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.

The observation of a consistent difference between bulk rate constants for the neutral and anionic species of both oxine and KELEX 100, $10^{2.4}$ times greater for the respective anions, lends support to the validity of these rate constants. This difference reflects the greater facility for substitution that the anion possesses over the neutral ligand.

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 rate constants, k_L and k_i, are not 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 in this study of a three path reaction mechanism for the extraction of a well known, simple, chelating system indicates the complexity that may be involved. 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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