Role of the Interface in the Extraction Kinetics of Zinc and Nickel Ions with Alkyl-Substituted Dithizones

Hitoshi Watarai[†] and Henry Freiser*

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721.
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Abstract: Extraction rates of zinc and nickel with ethyldithizone, butyldithizone, or hexyldithizone in chloroform were found to be proportional to the first order of the ligand and metal concentrations and to the inverse first order of hydrogen ion concentration. In contrast to the behavior with dithizone, where the rate-determining step is the formation of the 1:1 chelates in the bulk aqueous phase, results in this study could only be explained by chelate formation in an interface region.

Introduction

Kinetic studies on the liquid–liquid extraction of metal ions by chelating extractants have led some workers to propose that the rate-determining step was the formation of the 1:1 metal chelate in the aqueous phase,[1] while others strongly suggested an interfacial site for this reaction.[2] Early work done in our laboratory strongly indicated that the rate-determining step in the extraction of Zn^{2+} by diphenylthiocarbazone (dithizone) was the 1:1 complex formation in aqueous phase.[2] Vinokurova and Kletenik reported the contribution of interfacial reaction in the same systems based on the dependence of metal extraction rate on the interfacial area.[3] Unfortunately, insufficient detail was given in their report to assess their results quantitatively.

Recently, we observed a reversible change of concentration in the distribution of a series of alkyl-substituted dithizones, which was caused by stirring of two phases.[4] This was interpreted to arise from adsorption of the ligand in the interface. A key point in assessing the kinetic mechanism of the chelate extraction of metal ions would be whether the ligand adsorbs at an interface. Using ligands that have a tendency to adsorb on the interface, and stirring vigorously so interfacial area would be extensive, we might have a chance to observe an interfacial reaction.

Experimental Section

Materials. Di(*p*-alkylphenyl)thiocarbazones (alkyldithizones), including ethyldithizone (EtDz), butyldithizone (BuDz), and hexyldithizone (HexDz) used as extractants, were prepared as reported previously.[4] All other chemicals used in this work were analytical grade. Stock solutions of zinc and nickel ions were prepared by dissolving a weighted amount of high-purity metal in perchloric acid.

Apparatus. The high-speed extraction kinetics apparatus previously described[5] was used.

Extraction Kinetics. The procedure was essentially similar to that described previously except that the stirrer blades were made of Teflon and the stainless steel shaft was covered with polyolefin tubing. One hundred milliliters of an aqueous solution containing 10^{-5} M Zn^{2+} or 3×10^{-5} M Ni^{2+} and an equal volume of reagent solution were poured into the reaction flask, and the reaction was begun by starting a high-speed stirring motor. Experiments were carried out in the "plateau" region where an increase in agitation gave no effect on the rate of extraction. At regular intervals, samples containing equal volumes of each phase were taken by purging the reaction flask with nitrogen and then immediately centrifuging them. the Zn^{2+} or Ni^{2+} ion concentration in the aqueous phase was determined by a Varian AA-6 atomic absorption spectrophotometer at 213.9 or 232.0 nm, respectively, with an air-acetylene flame.

All experiments were carried out at 25 °C. The forward extraction rate constants, k (s^{-1}), were calculated according to the equation

$$\ln (A_0/A_t) = kt \tag{1}$$

where A_0 and A_t correspond to the absorbance of metal ion at reaction time zero and at time t.

Table I. Kinetic Data in Extraction of Zn^{2+} and Ni^{2+} with Alkyl-Substituted Dithizones in $CHCl_3$ at 25 °C

			Zn^{2+}		Ni^{2+}	
compd	$\log \frac{K_{DR}}{K_a}$	$\log K_L' \frac{Ad}{V}$ [a]	$\log k'$	$\log k' \frac{K_{DR}}{K_a}$	$\log k'$	$\log k' \frac{K_{DR}}{K_a}$
Dz	10.17[b] 10.21[c]	0	−3.33[b]	6.84[b]	−6.42[c]	3.78[c]
MeDz	11.89[b]	0.16	−3.05[b]	8.84[b]	−7.51[b]	4.38[b]
EtDz	12.80	0.67	−4.00 ±0.04[f]	8.81 ±0.04	−6.93 ±0.02	5.87 ±0.02
BuDz	15.50[d]	3.00	−4.51 ±0.02	10.99 ±0.02	−7.45 ±0.04	8.05 ±0.04
HexDz	17.80[e]	5.02	−4.50 ±0.09	13.20 ±0.09	−7.51 ±0.12	10.30 ±0.11

[a] Decrease in apparent distribution ratio under high-speed stirring. [b] Reference 6. [c] Reference 7. [d] Reference 11. [e] Reference 12. [f] Standard deviation for at least 3 replicates.

Results and Discussion

The rates of extraction of the metal ions by the alkyl-substituted dithizones in chloroform were found to follow pseudo-first-order kinetics. Variation of the observed rate constant as a function of pH and ligand concentration led to the expression

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

where M^{2+} is Zn^{2+} or Ni^{2+} and $[HL]_0$ is the ligand concentration in the organic phase. The values of k' obtained experimentally are listed in Table I along with those for dithizone (Dz) and methyldithizone (MeDz) systems reported previously.[6,7] As in earlier studies, eq 2 suggests that the rate-determining step of the extraction is formation of the 1:1 chelate, ML^+. Finding that the extraction equilibria of the alkyldithizonates are affected by the interface,[4] however, raises some fundamental questions about the site of the rate-determining step.

If, as traditionally considered, the rate-determining reaction proceeds in the aqueous phase, k' is represented by a combination of the three constants; K_a, the acid dissociation constant of ligand, K_{DR}, the distribution constant of ligand, and k_1, the rate constant for the 1:1 chelate formation, i.e.

$$k_1 = k'\frac{K_{DR}}{K_a} \tag{3}$$

According to eq 3, k_1 was calculated for each system and the results are shown in Table I. The calculated k_1 values from eq

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[†] Department of Chemistry, Faculty of Education, Akita University, Tegata-gakuencho, Akita, 010 Japan.

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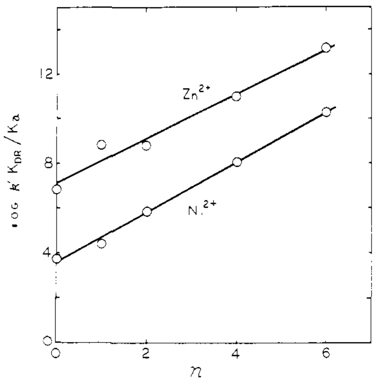
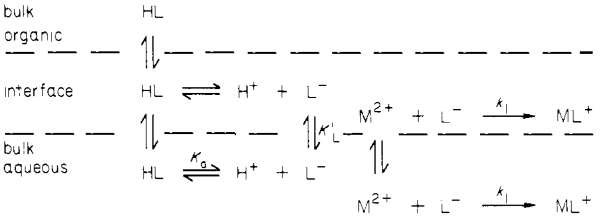


Figure 1. Variation of apparent reaction rate constant with size of alkyl group; n = number of carbons in alkyl group.

Scheme I



3 depend remarkably on the length of alkyl chain attached to the para position of the phenyl group of dithizone. As illustrated in Figure 1, log $k'K_{\mathrm{DR}}/K_{\mathrm{a}}$ values increase markedly with the increase of the number of carbon atoms in the alkyl group. This trend seems difficult to explain, because usually increasing the size of the alkyl group beyond ethyl does not result in any further change in an ionic reaction, in keeping with the Taft σ value for alkyl groups.[8]

An even more distressing anomaly in k_1 calculated from eq 3 is the unexpectedly large values, especially in the Zn^{2+}–HexDz system, where the extraordinary value of 10^{13} $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$, larger than the diffusion controlled rate, was calculated.

These results force us to reconsider the meaning of eq 2. Our recent finding of the enhanced level of alkyldithizonate anions in an interfacial region when a liquid–liquid reaction mixture is subject to vigorous, high-speed stirring[4] suggests that the metal chelate formation in these systems may also occur in the interfacial region. That is, a modified reaction scheme (Scheme I) involving concurrent formation of the 1:1 chelate in both the bulk aqueous and interfacial phases should be considered. With this scheme, k' of eq 1 becomes

$$k' = \frac{K_{\mathrm{a}}}{K_{\mathrm{DR}}}\left(k_1 + k_i K_{\mathrm{M}}' K_{\mathrm{L}}' \frac{Ad}{V}\right) \tag{4}$$

where K_{M}' is the distribution constant of metal ion between interface and bulk aqueous phase defined by $[\mathrm{M}^{2+}]_i/[\mathrm{M}^{2+}]$, K_{M}' is the distribution constant of dithizonate ion defined by $[\mathrm{L}^-]_i/[\mathrm{L}^-]$, A is the total interfacial area in the extraction system, d is the thickness of the interfacial layer, and V is the volume of aqueous phase. The second term in eq 4 shows the contribution of the interfacial component of the reaction.

The increase in log $k'K_{\mathrm{DR}}/K_{\mathrm{a}}$ with increase in the size of the alkyl group (Figure 1) is essentially due to the increase of K_{L}', as the proportionality of log K_{L}' with n (number of carbons in alkyl group) has been noted.[4] The factor of Ad/V can be considered to be constant so long as the same solvent system, apparatus, and stirring speed are used.

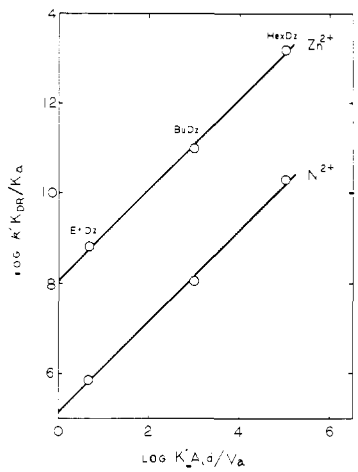


Figure 2. Variation of apparent reaction rate constant with interfacial distribution of ligand anion (eq 6).

Inasmuch as, for dithizone itself, no change in distribution equilibria with high-speed stirring was observed, the results obtained with both Ni^{2+} and Zn^{2+} can be properly interpreted with eq 3, yielding k_1 values of $10^{3.78}$ $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $10^{6.84}$ $\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ for Ni^{2+} and Zn^{2+}, respectively. For the remainder of the systems, eq 4 must be used.

Although an absolute sorting out of the contributions of k_1 and k_i to k' is not possible, it is reasonable to assume that the change in k_1 with increasing n becomes negligible beyond $n = 1$, i.e., with MeDz. Nevertheless, the values of k' continue to increase rapidly with n, until the second term in eq 4 is the only one that need be considered, i.e.

$$k' \simeq \frac{K_{\mathrm{a}}}{K_{\mathrm{DR}}} k_i K_{\mathrm{M}}' K_{\mathrm{L}}' \frac{Ad}{V} \tag{5}$$

or

$$\log \frac{k' K_{\mathrm{DR}}}{K_{\mathrm{a}}} = \log k_i K_{\mathrm{M}}' + \log K_{\mathrm{L}}' \frac{Ad}{V} \tag{6}$$

where $K_{\mathrm{L}}'Ad/V$ has been shown[4] to be equal to D/D' (equilibrium distribution ratios for the ligand without and with high-speed stirring, respectively). When log $k'K_{\mathrm{DR}}/K_{\mathrm{a}}$ is plotted against log D/D' ($\equiv K_{\mathrm{L}}'A_i d/Va$, Figure 2), good straight-line relationships for Ni^{2+} and Zn^{2+} (corr. coeff. 0.998 and 0.999) with unit slopes as required by eq 6 are obtained. The intercepts 5.13 and 8.08 can be taken as log $k_{\mathrm{L}}'K_{\mathrm{M}}'$ for Ni^{2+} and Zn^{2+}, respectively. These values are considerably larger than the k_1 values observed with dithizone but have a ratio, $10^{2.95}$, that is quite close to that for the former, $10^{3.09}$, signifying that K_{M}', whatever its value, is essentially the same for both Ni^{2+} and Zn^{2+}. If the distribution of the metal ions between the bulk aqueous and the essentially aqueous interfacial phases were characterized by a K_{M}' value of unity, the increase of k_i for the alkyldithizones over k_1, namely $10^{1.3}$, obtained is about what one would expect from the rate-enhancing influence of the alkyl group. Thus, the interfacial rate constant is not substantially different from the rate in the bulk aqueous phase. Essentially the entire cause of the unusual kinetic behavior, as well as of the extraction equilibrium behavior, may be attributed solely to the excess concentration of the ligand anion in the interfacial region, greatly expanded by the high-speed stirring.

This study suggests that in a highly hydrophobic, surface-active extractant system, the stirring speed employed plays an unusually large role since generation of an interfacial region serves to enhance the extraction kinetics. Further exploration of the role of the interface in other interesting extraction systems is currently underway in this laboratory.

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Registry No. Zn, 7440-66-6; Ni, 7440-02-0; EtDz, 83454-27-7; BuDz, 65388-10-5; HexDz, 70857-97-5.

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