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Interfacial Role in the Kinetics of Extraction of Nickel(II) and Zinc(II) with Halogenated Dithizones in Aqueous Chloroform Systems

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The kinetics of solvent extraction of Ni(II) and Zn(II) by halogen-substituted dithizones studied at temperatures from 0 to 25 °C by using a high-speed stirring apparatus at stirring speeds of 2000–5000 rpm has been shown to be in the "kinetic regime", i.e., that diffusion barriers are not rate-determining. In all cases, the formation of the 1:1 metal dithizonate is rate-determining. The reaction mechanisms differ in that the site of the dithizone reaction with Ni(II) at pH = 6.0 is essentially all interfacial while that with Zn(II) at pH = 4.0 involves both the interface and the bulk aqueous phase as reaction sites. Thus, the extent of the interfacial adsorption of the ligand anion is not the only influence on the relative importance of interfacial and bulk aqueous phases as reaction sites of the rate-determining step (rds) in metal chelate extraction mechanisms. Additional mechanistic information was obtained from activation parameters obtained for the bulk-phase and interfacial reactions.

Introduction

The nature and the location of the rate-determining step (rds) have been the subject of much study in solvent extraction of metals. There is a general agreement that except when the phases are intentionally poorly mixed, the rate-determining step (rds) in metal chelate extraction kinetics involves a chemical rather than a mass-transfer process; i.e., it involves the formation of a metal complex. The location of this reaction has been debated energetically, some holding the view[1] that the interface is the site of the reaction and others, ourselves included, who argue that the reaction occurs exclusively in the bulk aqueous phase. More recently, however, Watarai and Freiser[2] have shown that the extraction mechanism of metal chelates of *p*-alkyl-substituted dithizones does have an interfacial component. With increasing alkyl chain length (n in C_nH_{2n+1}) in the substituted dithizone their interfacial activity increased; i.e., the interfacial adsorption became increasingly important. When the alkyl group had $n \geq 4$, almost all the ligand anions in the system existed in the interfacial region under conditions of high-speed stirring (5000 rpm). It was also shown that the interfacial region, as well as the bulk aqueous phase, provides a site of the rds in the nickel–8-quinolinol system, despite the barely observable interfacial activity of the 8-quinolinolate anion.[3]

The question of the exact distribution between the bulk pathway and of the interfacial pathway in the metal extraction kinetics with dithizone and substituted dithizones still remains an interesting one. A recent kinetics study,[4] utilizing a microporous Teflon phase separator (MTPS), of the reactions of Zn^{2+} and Ni^{2+} with both dithizone and bis(4-*n*-butylphenyl)thiocarbazone (HBuDz) added to the puzzle by revealing that while the Ni dithizone reaction is observed to depend entirely on an rds that is interfacial in character, the corresponding Zn reaction has two concurrent pathways, with reaction sites in both the bulk aqueous phase and in the interface. In this paper, this question is addressed by examining para-halogenated dithizones (hereafter called dithizones) from chloro to bromo to iodo substitution. Will the observations made in the earlier studies find parallels in the reactions of these substituted dithizones? How will the size and hydrophobicity increase affect the importance of the interfacial path?

Experimental Section

Materials. Bis(*p*-chlorophenyl)thiocarbazone (HClDz), bis(*p*-bromophenyl)thiocarbazone (HBrDz), and bis(*p*-iodophenyl)thiocarbazone (HIDz) were synthesized in our laboratory as reported previously.[5] Diphenylthiocarbazone (HDz) was used after purification.[6] Analytical reagent grade chloroform was washed three times with deionized water just before use. Acetate and phosphate buffer solutions (0.01 M, pH = 4.0 and pH = 6.5, respectively), were prepared from AR grade reagents and were washed three times with the same dithizonate/chloroform solutions to remove any metal impurities. Deionized water was used throughout the experiment. Triton X-100 (TX-100) was obtained from Sigma Chemical Co. (St. Louis, MO) and was used as received. All of the glassware was carefully cleaned with saturated KOH/2-propanol prior to use to eliminate all surface active impurities.

Apparatus. The apparatus has been described in detail elsewhere.[7] Kinetics studies were performed by introducing 50 mL of the organic phase, a $CHCl_3$ solution of the dithizone in the concentration region of 10^{-5} M, into a 250-mL Morton flask containing 45 mL of an aqueous phase at the appropriate pH and ionic strength and starting the peristaltic pump. The organic phase passes through the MTPS into the flow cell in the Cary 219 spectrophotometer and returns to the flask. The aqueous phase (50 mL) contains a buffer and $NaClO_4$ to maintain the ionic strength at 0.1 M. To initiate the reaction, a 5.0-mL aliquot of the given metal ion solution was injected into the reaction mixture, which was already stirring at a selected speed.

Determination of the Instrument Response Time. Chloroform (45 mL) was introduced into the 250-mL Morton flask containing 50 mL of aqueous phase at 0.1 M ionic strength with the peristaltic pump in operation. The stirrer was then started at a predetermined stirring speed. The bulk organic phase passes readily through the MTPS and circulates through the flow cell of the Cary 219 spectrophotometer and back to the reaction flask. When the absorbance reading reached a constant value, it was adjusted to 0 at 605 nm, and 5.00 mL of 2.5×10^{-5} M dithizone in $CHCl_3$ was injected. The instrument response time (the time required for the absorbance increase to reach a steady value) was found to be independent of the stirring speed over the entire range of speeds used. A time of 23 s was needed to attain 90% of the steady absorbance value. About 18 s of this represents the transit time of the dithizone solution from the MTPS to the flow-through cell. Hence, the 5 (±1) s required to achieve at least 90% of the steady-state value can be attributed to the homogeneous mixing time.

Determination of the "Kinetic Regime". Since proton-transfer reactions are generally essentially instantaneous, the two-phase reaction between NaOH and the weak acid dithizone dissolved in chloroform was studied in order to see how rapidly the dithizonate anion appeared in the aqueous phase as a function of stirring speed. It took almost 23 s to attain 90% of the equilibration absorbance for all stirring speeds, a value identical with the instrument response time. This demonstrated that the mass-transfer rate is so rapid that it is not a factor in this heterogeneous reaction. Hence, the system may be considered to be in the "kinetic regime" in the stirring speed range of 2000–5000 rpm.

Calculation of Interfacial Area. In an earlier study,[8] we developed a convenient and reliable method of determining total interfacial area in a rapidly stirring two-ligand-phase mixture by equating the absorbance decrease, $A_u - A_s$, resulting from the selective removal of adsorbed ligand from the bulk organic phase by means of the MTPS.

Use of the MTPS, which selectively removes bulk organic phase from the stirred two-phase mixture, allows us to obtain the amount of ligand species adsorbed at the L–L interface. This is the product of the decrease in organic phase concentration, $(A_u - A_s)/\epsilon$, where A_u and A_s are the

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Table I. Interfacial Area and Specific Interfacial Area as a Function of Stirring Speed[a]

stirring speed, rpm	ΔA at 280 nm	interfacial area, cm^2	specific interfacial area, cm^2
5000	0.0142	8.9×10^3	1.8×10^2
4000	0.0117	7.3×10^3	1.5×10^2
3000	0.0088	5.5×10^3	1.1×10^2
2000	0.0043	2.7×10^3	5.3×10

[a] Interfacial excess of TX-100 = 4.7×10^{-11} mol cm^{-1}. Concentration of TX-100 = 5×10^{-4} M.

unstirred and stirred absorbance and ϵ is the molar absorbance of the analyte, and the organic phase volume is V_o (L). Thus

$$\text{amount adsorbed (mol)} = \frac{A_u - A_s}{\epsilon} V_o \qquad (1)$$

An independent examination of the interfacial tension of the same liquid-phase pair, using the drop weight method for a series of analyte concentrations and applying the Gibbs adsorption isotherm, allows us to obtain the surface excess, Γ, in mol/cm^2. The amount adsorbed from this approach is $\Gamma\alpha$, where α is the interfacial area in cm^2.

By equating this with that obtained above, we can now evaluate α. An equivolume (50.0 mL) mixture of 5.0×10^{-4} M Triton X-100 in $CHCl_3$ and an aqueous phase at pH = 4.0 containing an acetate buffer and 0.1 M $NaClO_4$ were used, and spectrophotometric measurements were taken at 280 nm for this calibration. The interfacial areas calculated from runs at various stirring speeds (Table I) were used in all of the systems studied. The validity of obtaining values of interfacial areas in this manner is based on the observation that the rates of the nickel dithizone reaction are not affected by the presence of Triton X-100 at any of the stirring speeds utilized.

pH Dependence of the Extraction of the Dithizones. The two-phase mixture was added together in the 250-mL flask and equilibrated as mentioned above. Dropwise addition of 0.1 M NaOH was used to adjust the pH of the aqueous phase to the desired value. The absorbance difference ΔA [$=(A_s - A_u)$] was used to calculate D and D' as defined by

$$D = \frac{A_o}{A_i - A_o}$$

$$D' = \frac{A_o - \Delta A}{\Delta A}$$

where D = distribution ratio without stirring, D' = distribution ratio with high speed stirring, A_i = the initial absorbance of the organic phase before the equilibration with the aqueous phase, A_o = the absorbance of the organic phase after the equilibration with the aqueous phase, and ΔA = the absorbance difference caused by stirring.[9]

Kinetic Studies. Fifty milliliters of 1.0×10^{-5} M HDz in chloroform and 45 mL of the aqueous phase consisting of 10.0 mL of 0.5 M $NaClO_4$, 10.0 mL of the buffer, and 25.0 mL of deionized water were introduced into a 250-mL Morton flask fitted with a high-speed stirrer. The mixture was mechanically and thermally preequilibrated by stirring at a designated stirring speed and circulating the organic phase through the MTPS to the spectrophotometer flow-through cell. Metal ion solution (5.0 mL) was then injected, initiating the kinetics run. The absorbance of the organic phase was used to monitor the reaction kinetics at 605 nm (λ_{max} of HDz). Rate constants were calculated by first order treatment of absorbance vs time data for at least 3 half lives.

Results and Discussion

The $pH_{1/2}$ of a distribution plot (log D vs pH) is defined as the pH corresponding to half of the total analyte concentration in the organic phase (i.e. when D = 1). Similarly, under rapid stirring, i.e., in the presence of large interfacial area, $pH'_{1/2}$ can be defined as the pH corresponding to half of the analyte in the organic phase:

$$pH_{1/2} = \log \frac{K_{DR}}{K_a}$$

$$pH'_{1/2} = \log \frac{K_{DR}/K_a}{K'_L Ad/V + 1}$$

A plot of log (D/D') vs pH serves to identify $\Delta pH_{1/2}$:

$$\Delta pH_{1/2} = pH_{1/2} - pH'_{1/2}$$

Table II. Percentage of Adsorbed Dithizonate (from Eq 3)

reagent	$\Delta pH_{1/2}$	log ($K'_L Ad/V$)	% Dz^-_{int}
Dz[7]		−1.57	2.6
MeDz[7]	0.16	−0.45	26.2
EtDz[7]	0.67	0.67	82.4
BuDz[7]	3.00	2.91	99.9
HeDz[7]	5.02	5.02	99.9
PClDz	0.22	−0.18	39.8
PBrDz	0.50	0.33	68.1
PIDz	1.00	0.95	89.9

The extent of interfacial adsorption of the dithizones can be described in terms of K'_L:

$$K'_L = [L^-]_i/[L^-]$$

$$\log (D/D' - 1) = \log (10^{\Delta pH_{1/2}} - 1) = \log (K'_L Ad/V) \qquad (2)$$

A_i = interfacial area $\qquad d$ = thickness of interface

Plots of both log D and log D' vs pH are linear for p-iododithizone and p-bromodithizone. The observed increase in $\Delta pH_{1/2}$ and hence $K'_L Ad/V$ indicates that interfacial activity increases in this order (Table II). The parameter $K'_L Ad/V$ can be used as a measure of interfacial activity. Thus, the percentage of interfacially active ligand anion species may be calculated as

$$\% \, Dz^-_{int} = \frac{K'_L d/V}{(K'_L Ad/V) + 1} \times 100\% \qquad (3)$$

The results, ranging from 40% to 90%, indicate that the interfacial activities of the p-halodithizonates lie between that of p-methyl dithizonate and p-butyl dithizonate (Table II). The results shown in Table II along with those of previously studied alkylated dithizones[9] for comparison indicate that the effect of Cl is somewhat greater than that of CH_3, that of Br somewhat less than that of C_2H_5, and that of I much less than that of C_4H_9 and probably about equal to that of C_3H_7. It is interesting to note that the plot of log ($10^{\Delta pH} - 1$) vs length of alkyl group for p-alkyl-substituted dithizones exhibits a nonzero intercept in the curve, indicating a small interfacial activity (ca. 2.6%) even for the parent dithizone anion.[10]

The rates of extraction of Ni(II) and Zn(II) by dithizones were found to follow pseudo-first-order kinetics with respect to [M^{2+}] in accord with earlier work.[4] The following expression can be written:

$$-\frac{d}{dt}[HL] = \frac{k'[M^{2+}][HL]}{[H^+]} \qquad (4)$$

where k' = observed rate constant, K_{DR} = $[HL]_o/[HL]$ [M^{2+}] is [Zn^{2+}] or [Ni^{2+}], and K_a = acid dissociation constant. $[HL]_o$ and [HL] are the concentrations of the ligand in the organic and the aqueous phases respectively. The observed rate constant, k', can be expressed in terms of the sum of contributions from the concurrent pathways of bulk aqueous phase and the interfacial reaction. Thus

$$k = k'K_{DR}/K_a = k_1 + k_i K'_M K'_L Ad/V \qquad (5)$$

where k_i = interfacial rate constant, k_1 = bulk rate constant, d = thickness of the interfacial layer, V = volume of the aqueous phase, and K_M = $[M]_i/[M]$ = 1 (based on the reasonable assumption that the hydrated metal ion is not surface active).

When the rate constant (k') was plotted against the specific interfacial area, A/V, for the bulk-phase volume reaction of Ni(II) with dithizone, the plot of k' vs specific interfacial area is linear and goes through the origin (Tables III and IV), signifying this reaction is purely interfacial. For the reaction of Zn(II) with dithizone, however, a nonzero intercept for the plot of k' vs specific interfacial area was obtained, indicating a significant bulk-phase pathway in addition to the interfacial reaction. With PIDz, both metal ions exhibited bulk and interfacial reactions. Both reaction

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Table III. Observed Reaction Rate Constants, k', as a Function of Specific Interfacial Area and Temperature

specific area, cm^2	k'					
	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C
Ni(II) + Dz						
178	1.74×10^{-7}	1.21×10^{-7}	8.10×10^{-8}	6.40×10^{-8}		
147	1.45×10^{-7}	9.99×10^{-8}	6.48×10^{-8}	5.19×10^{-8}		
110	1.12×10^{-7}	7.05×10^{-8}	4.46×10^{-8}	3.83×10^{-8}		
53.4	5.34×10^{-8}	3.23×10^{-8}	2.06×10^{-8}	1.83×10^{-8}		
Zn(II) + Dz						
178	5.63×10^{-4}	4.84×10^{-4}	4.27×10^{-4}	3.51×10^{-4}	2.28×10^{-4}	
147	4.84×10^{-4}	4.30×10^{-4}	3.83×10^{-4}	3.16×10^{-4}	1.99×10^{-4}	
110	4.11×10^{-4}	3.57×10^{-4}	3.10×10^{-4}	2.47×10^{-4}	1.71×10^{-4}	
53.4	3.00×10^{-4}	2.55×10^{-4}	2.21×10^{-4}	1.77×10^{-4}	1.23×10^{-4}	
Ni(II) + PIDz						
178	4.92×10^{-7}	3.63×10^{-7}	2.16×10^{-7}	1.33×10^{-7}	8.55×10^{-8}	
147	4.64×10^{-7}	3.31×10^{-7}	1.96×10^{-7}	1.16×10^{-7}	7.10×10^{-8}	
110	3.96×10^{-7}	2.84×10^{-7}	1.89×10^{-7}	1.07×10^{-7}	6.46×10^{-8}	
53.4	3.38×10^{-7}	2.42×10^{-7}	1.62×10^{-7}	9.62×10^{-8}	6.22×10^{-8}	
Zn(II) + PIDz						
178		7.80×10^{-4}	6.01×10^{-4}	4.51×10^{-4}	3.25×10^{-4}	2.27×10^{-4}
147		6.95×10^{-4}	5.28×10^{-4}	3.87×10^{-4}	2.91×10^{-4}	2.10×10^{-4}
110		6.01×10^{-4}	4.47×10^{-4}	3.36×10^{-4}	2.24×10^{-4}	1.57×10^{-4}
53.4		4.55×10^{-4}	3.36×10^{-4}	2.59×10^{-4}	1.99×10^{-4}	1.35×10^{-4}

Table IV. Calculation of Bulk Phase and Interfacial Contributions to Reaction Rate Constants

temp, °C	intercept	slope	k'	
			bulk[a]	interfacial[b]
Ni(II) + Dz				
25	(3.78 ± 2.9)E−9[a]	(9.62 ± 0.22)E−10	0	2.01E5
20	(−5.31 ± 7.2)E−9	(6.86 ± 0.55)E−10	0	1.43E5
15	(−6.37 ± 2.9)E−9	(4.85 ± 0.22)E−10	0	1.01E5
10	(−1.99 ± 4.8)E−9	(3.83 ± 0.36)E−10	0	8.01E4
Zn(II) + Dz				
25	(1.85 ± 0.11)E−4	(2.08 ± 0.09)E−6	5.85E6	4.35E8
20	(1.57 ± 0.03)E−4	(1.84 ± 0.03)E−6	4.96E6	3.85E8
15	(1.30 ± 0.08)E−4	(1.68 ± 0.06)E−6	4.11E6	3.51E8
10	(9.85 ± 1.21)E−5	(1.43 ± 0.09)E−6	3.11E6	2.99E8
5	(7.88 ± 0.25)E−5	(8.31 ± 0.19)E−7	2.49E6	1.74E8
Ni(II) + PIDz				
25	(2.67 ± 0.15)E−7	(1.28 ± 0.12)E−9	1.25E4	1.19E3
20	(1.85 ± 0.11)E−7	(9.80 ± 0.83)E−10	8.65E3	9.13E2
15	(1.41 ± 0.07)E−7	(4.10 ± 0.48)E−10	6.60E3	3.82E2
10	(7.89 ± 0.69)E−8	(2.80 ± 0.53)E−10	3.69E3	2.61E2
5	(5.17 ± 1.10)E−8	(1.57 ± 0.82)E−10	2.42E3	1.46E2
Zn(II) + PIDz				
20	(2.97 ± 0.41)E−4	(2.66 ± 0.31)E−6	1.39E7	2.48E6
15	(2.20 ± 0.09)E−4	(2.11 ± 0.66)E−6	1.03E7	1.97E6
10	(1.75 ± 0.14)E−4	(1.50 ± 0.10)E−6	8.19E6	1.40E6
5	(1.32 ± 0.27)E−4	(1.04 ± 0.27)E−6	6.17E6	9.69E5
0	(8.70 ± 1.90)E−5	(7.80 ± 1.50)E−7	4.07E6	7.27E5

[a] Bulk = intercept/(K_a/K_{DR}). [b] Interfacial = slope/$((K_a/K_{DR})K'_L d)$. [c] In this notation (3.78 ± 2.9)E−9 = (3.78 ± 2.9) × 10^{-9}, etc.

Table V. Activation Parameters

	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	$\Delta G^{\ddagger}$(25 °C), kcal mol^{-1}
Bulk Reaction			
Ni + Dz			
Zn + Dz	6.61 ± 0.33	−5.36 ± 1.15	8.21
Ni + PIDz	13.08 ± 0.82	4.16 ± 2.86	11.84
Zn + PIDz	8.90 ± 0.50	4.56 ± 1.77	7.54
Interfacial Reaction			
Ni + Dz	9.83 ± 0.75	−1.34 ± 2.57	10.23
Zn + Dz	6.35 ± 1.59	2.47 ± 5.53	5.61
Ni + PIDz	17.39 ± 1.50	13.99 ± 5.22	10.07
Zn + PIDz	9.51 ± 0.37	3.26 ± 1.30	8.54

pathways were also observed for the reaction of *p*-butyldithizone/chloroform (% Dz^{-}_{int} = 99%) with Zn(II) and Co(II) at pH = 4.99 and 6.91, respectively.[4]

Since additional illumination on fundamental factors determining mechanistic details of such reactions might be furnished by determining their activation parameters, the kinetics of Ni(II) and Zn(II) with HDz and PIDz at different temperatures and stirring speeds were conducted (Table V). Inasmuch as so few systems involving concurrent bulk-phase and interfacial pathways have been studied, it is dangerous to read too much into our results at this time. Nevertheless, we can make some useful remarks that, at the very least, can guide further research in this field. Of course, the activation enthalpies for the Ni(II) reactions are uniformly higher than those of Zn(II). It is interesting to note that activation enthalpies of all of the corresponding bulk and interfacial reactions are about the same. The activation entropies, however, are somewhat higher for the interfacial than for the bulk pathways. This suggests that "anchoring" the dithizonate anion in the organic side of the interface with the more polar chelating functional group on the aqueous side results in restricting somewhat its degrees of freedom, favoring chelate formation with the metal ion also on the aqueous side.

While it would be tempting to try to read into our results possible changes of mechanism from associative to dissociative, this must await further work.

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Registry No. HClDz, 1643-05-6; HIDz, 2059-71-4; HBrDz, 1643-06-7; Dz, 60-10-6; Ni, 7440-02-0; Zn, 7440-66-6.