

SOME INTERESTING ASPECTS OF THE EXTRACTION OF ZINC

HENRY FREISER

*Department of Chemistry,
The University of Arizona, Tucson, Arizona 85721.*

Realizing that, for a forty five minute talk, a title of "Solvent Extraction of Metal Chelates" is entirely too ambitious, I have chosen instead to speak about the experiences my students, associates and myself have encountered in the extraction of zinc, hoping that you will find this an appropriate illustration of the interesting variety of behaviour and information obtainable in the study of metal chelate extractions.

One interesting aspect of the solution chemistry of Zn(II) is the variation of coordination number observed in zinc complexes; *e.g.*, six, as in $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Zn}(\text{NH}_3)_6^{2+}$, $\text{Zn}(\text{CN})_6^{4-}$ and four, as in ZnCl_4^{2-} , and $\text{Zn}(\text{C}_2\text{O}_4)_2^{2-}$. The zinc complexes of such chelating extractants as acetylacetonone and 8-quinolinol occur as the hexacoordinated dihydrates, which upon heating, transform to the quadridentate anhydrous chelates. As a divalent metal ion of coordination number six, zinc chelates with bidentate mono-anionic reagents would not be as readily extractable with coordinated water as with other, more hydrophobic, "auxiliary" ligands.

Several years ago our attention was attracted by conflicting reports^{1,2} of the efficacy of 8-quinolinol as a zinc extractant. A study of the extraction equilibria of zinc with 8-quinolinol and its 2-methyl- and 4-methyl-analogues helped to resolve the conflict by revealing that the extracted species in the 8-quinolinol (HOx) extraction is $\text{ZnOx}_2 \cdot \text{HOx}$ [slope of $\log D$ versus pH was found to be 2; slope of $\log D$ versus $(\text{HOx})_0$ was 3]³. The extraction of such a complex, termed a self-adduct, calls for significantly higher 8-quinolinol concentrations than would be needed for the simple chelate; thus, the results directed attention to and explained the significance of the higher $(\text{HOx})_0$ used in the publication¹ reporting successful Zn extraction, resolving the apparent conflict.

The course of the extraction of zinc with 4-methyl-8-quinolinol (HL) was found to parallel that with 8-quinolinol, but that with 2-methyl-8-quinolinol (HQ) differed, as the extracted species was found to be a simple chelate ZnQ_2 , rather than a self-adduct.³ This difference probably arises from the steric hindrance to adduct formation presented by the substituent in the 2-position, which makes it likely that the adducting ligand coordinates through the quinoline nitrogen. Strengthening this hypothesis is the observation that the adduct formed by 4-methyl-8-quinolinol is more stable than that of the parent ligand, reflecting the increasing basicity of the nitrogen in the former ligand (*Table 1*).

Table 1. Equilibrium constants for zinc chelates of 8-quinolinol and substituted 8-quinolinols

Substituted 8-quinolinol	Log K_{AD}	Log K_{DC}	Log K_{DR}	$pK_{a1} + pK_{a2}$	Log K_f
<i>Parent Compound</i>	2.17	1.41	2.64	14.90	17.06
2-methyl-	...	2.99	3.22	15.90	15.68
4-methyl-	2.20	1.97	3.27	15.66	18.11
5-chloro-	1.95	2.40	3.32	13.00	15.58
5-bromo-	2.04	3.76	3.51	12.80	14.62
5-iodo-	...	4.00	3.75	11.90	14.86
5-nitro-	1.52	1.43	2.64	8.79	12.14

Although extraction equilibrium studies with other substituted 8-quinolinols also show an increase in adduct stability with increasing basicity of the quinoline nitrogen,⁴ this change is relatively small by comparison with the change in the primary chelate formation. This may be explained in terms of the effect ligands can have on the further coordination by the metal ion. It is reasonable to suppose that the Lewis acidity of a metal ion, *i.e.*, its ability to form complexes, is sensitive to the Lewis basicity of the ligands to which it is already coordinated. Thus, as the metal forms increasingly more stable chelates, these should have correspondingly less tendency to coordinate further, to form adducts. Similarly, for a given chelate, adduct forming tendency can be expected to increase with ligand basicity. Both of these effects must be considered in adduct extraction, and therefore, as seen in *Table 1*, nearly cancel one another.

A separation of these effects can be achieved by studying the equilibrium extraction behavior of zinc with 8-quinolinols in the presence of pyridines as possible adducting ligands⁴. Quantitative evaluation of the equilibrium data of the pyridine-enhanced extractions, summarized in *Table 2*, confirmed

Table 2. Logarithmic values of adduct formation constants for various pyridine adducts of the zinc 8-quinolinolates in chloroform at 25°

<i>Chelating agent</i>	<i>Adducting base</i>			
	Pyridine	2-Methyl-pyridine	4-Methyl-pyridine	2,4,6-Trimethyl-pyridine
8-quinolinol	3.05	2.10	3.40	1.50
2-methyl-8-quinolinol	1.60	1.00	1.75	0.20
4-methyl-8-quinolinol	2.47	2.00	2.87	1.50

our hypothesis. That adduct stability increased with increasing ligand stability is seen from the increase of 0.4 units in 4-methyl pyridine log K_{AD} values over those of pyridine in both 8-quinolinol and the 4-methyl analogue chelates, and a smaller, but significant, increase with 2-methyl-8-quinolinol chelates.

SOME INTERESTING ASPECTS OF THE EXTRACTION OF ZINC

Second, that increasingly stable chelates formed weaker adducts is seen in the 0.5 unit drop in $\log K_{AD}$ value for the 4-methyl-8-quinolinol chelate which is more stable than that of 8-quinolinol.

Finally, that decrease in adduct stability would be observed whenever steric hindrance occurs is reflected by the order: pyridine > 2-methyl pyridine > 2,4,6-trimethylpyridine in adduct stability. Adverse steric effects of methyl substituted pyridines are even more important with the 2-methyl-8-quinolinol zinc chelate.

It is interesting to note that in all of the cases of self- and other adduct complexes, 1:1 stoichiometry was observed, accounting therefore, for only five coordination positions. It is likely that, in the sterically unhindered complexes, water is coordinated in the sixth position, since a solid pyridine- $ZnOx_2$ adduct isolated from the mixture of anhydrous $ZnOx_2$ and pyridine was a di-adduct. With sterically hindered adduct complexes, however, penta-coordination would seem more reasonable.

Because chelating agents such as 8-quinolinol and its 4-methyl analogue behaved as monodentate ligands in adduct formation, whereas the sterically hindered 2-methyl-8-quinolinol did not, we were curious to see how 1,10-phenanthroline (phen) would behave under similar circumstances. If phen behaved as a monodentate adducting ligand at the 1-nitrogen, would the other pyridine nucleus sterically hinder complex formation?^{5,6} The extraction of zinc in the presence of low concentrations of both 8-quinolinol and phen proceeded through the formation of a complex more properly called mixed ligand chelate than adduct since $\log K_{AD}$ (not quantitatively evaluated) is undoubtedly high enough to classify the phen as a bidentate ligand in this complex, $ZnOx_2$ phen⁶.

The extraction system of $Zn-HOx$ -phen is as interesting as it is complex. Not too surprisingly, $Znphen_3^{2+}$ forms an extractable ion association complex with ClO_4^- , as does $Fephen_3^{2+}$ ⁵. In addition to the ion-association complex and the self-adduct, $ZnOx_2 \cdot HOx$, there are two other extractable species, $Znphen_2Ox^+$, ClO_4^- and $ZnOx_2 \cdot phen$, whose contributions could be sufficiently separated to permit calculation of the various extraction constants (Table 3). The extraction equilibrium data were used to construct

Table 3. Summary of extraction constants

Extracted species		phen	4,7-DMP
$ZnOx_2 \cdot HOx$	$\log K_{ex0}$	-5.2 ± 0.4	-5.2 ± 0.4
$ZnOx_2 \cdot phen$	$\log K_{ex1}$	-2.2 ± 0.3	-1.4 ± 0.7
$Znphen_2Ox^+ ClO_4^-$	$\log K_{ex2}$	6.8 ± 0.6	8.7 ± 1.1
$Znphen_3^{2+} \cdot 2ClO_4^-$	$\log K_{ex3}$	13.7 ± 0.4	18.5 ± 1.5
$Znphen(OAc)_2$	$\log K_{ex4}$	4.3 ± 0.2	5.5 ± 0.2

a three-dimensional (oxine-phenanthroline-perchlorate) "phase" diagram to describe the nature of the predominating extracted species under given conditions. Such a diagram is extremely helpful in designing experiments for optimizing total extraction, for isolating particular intermediate com-

plexes as well as improving understanding of the overall extraction system. A projection of this diagram is shown in *Figure 1*. A striking feature of the phase diagram is the important role played by perchlorate in determining the number of mixed complexes of significance. One of the ways in which

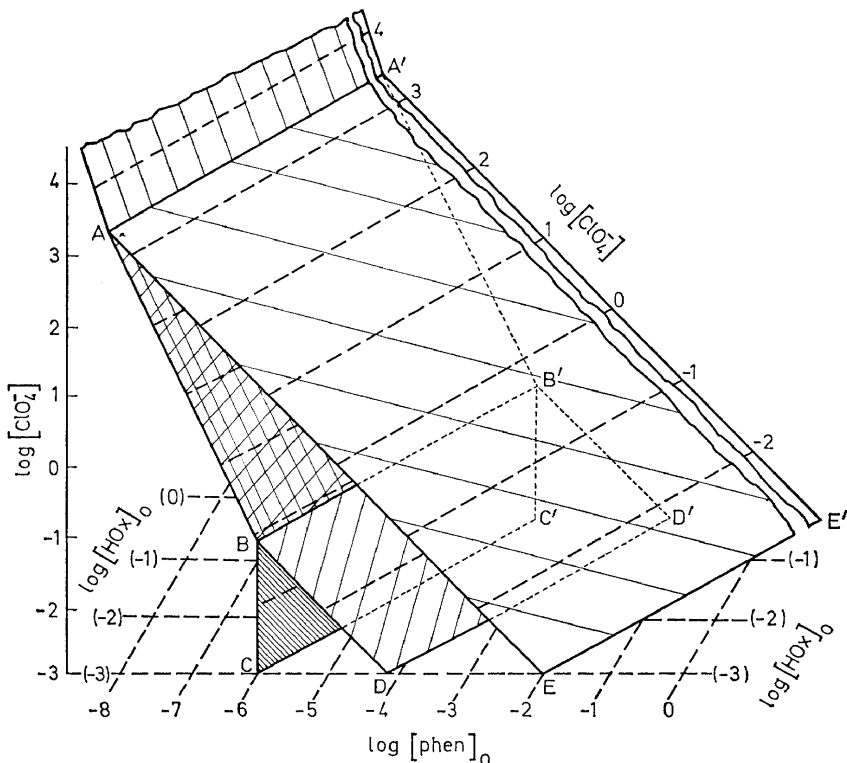


Figure 1. A projection of the three-dimensional (oxine-phenanthroline-perchlorate) "phase" diagram.

this diagram has proved useful is in examination of sections through it made at constant D values.

A parallel study using 4,7-dimethylphen revealed that use of the alkylated phen results in a significantly improved extraction system. Although in many families of chelating agents the increase in stability with increasing ligand basicity is effectively counter-balanced by the corresponding increase in the acid dissociation constant of the ligand (*i.e.* the proton displacement constant⁷ of chelation does not increase), in the case of the reaction of phenanthrolines with zinc, the extraction constant does not involve K_f for this ligand. Hence, the increase of K_f with alkyl substitution is fully effective.

SOME INTERESTING ASPECTS OF THE EXTRACTION OF ZINC

Phenanthroline is also a very effective ligand to use in conjunction with chelating agents of the type H_2L , such as toluene-3,4-dithiol, which can form two chelates with divalent metal ions such as zinc, ZnL and ZnL_2^{2-} , which are not extractable in $CHCl_3$. The 1:1 chelate ZnL , although neutral, is not extractable probably because two molecules of water of coordination may well be present in the complex. With a $CHCl_3$ solution containing both toluene dithiol and phenanthroline, zinc is readily extracted as a mixed ligand complex $ZnL \cdot phen$.^{8†} The extraction equilibrium parameters are shown in *Table 4*. It is of interest to note that no evidence was obtained for

Table 4. Equilibrium formation constants of the mixed ligand zinc chelates involving toluenedithiol and phenanthrolines

<i>Phenanthroline ligands</i>	pK_a	$\text{Log } K_f$	$\text{Log } K_{DR}$	$\text{Log } K_{DC}$
<i>Parent</i>	5.05	20.3	3.05	3.60
4,7-dimethyl	6.04	21.9	3.70	3.95
3,4,7,8-tetramethyl	6.42	22.3	4.46	4.60

the formation of $ZnL \cdot phen_2$, a species which would require Zn to have coordination number of six. This is in accord with expectations—based on earlier work⁹ in which the extraction of zinc with a variety of sulphur-containing ligands (dithizone, 8-mercaptoquinoline) showed no increase in the presence of various nitrogen-containing ligands (such as pyridine and 4-methylpyridine)—that zinc displays a coordination number of four if sulphur is at least one of the bonding atoms in its coordination sphere.

In the preceding review of equilibrium studies, evidence for and the effects of changes in the coordination number of zinc have been discussed. The kinetic behavior of zinc chelate formation observed via a solvent extraction technique developed in our laboratory,^{10,11} also indicates the role of changing coordination number for zinc. The rate of change of zinc from its hexacoordinated aquo ion to the tetracoordinated extractable dithizone complex was found to be limited by the formation of the 1:1 $ZnDz^+$ complex. This probably reflects the tetracoordinate character of this intermediate complex with the slow rate of the reaction (second order rate constant $10^{6.6}M^{-1}sec^{-1}$) in which the number of water-zinc bonds that are broken (four) is greater than the number of zinc-ligand bonds formed (two). In a study of the kinetics of chelate formation by zinc and a series of substituted dithizones¹², the course of the reaction was analogous to that of the parent compound, *i.e.*, the formation of the 1:1 complex is rate-determining, and the rate constants were all larger than that found for the parent compound, regardless of whether the substituents were electron-releasing or -withdrawing. This peculiar behaviour has been observed in other systems and we hope to pursue the reasons for this in our future studies.

†The anionic complex ZnL_2^{2-} may also be extracted when an ion association complex is formed by having a quaternary ammonium ion present.⁸

When some of the water coordinated to the zinc ion is replaced by another ligand, such as acetate or thiocyanate, the rate of reaction of the resulting complex with dithizone increases, despite the decrease in electrical charge.¹³ A plot of the logarithm of the apparent second order rate constant against the logarithm of the auxiliary ligand concentration serves to determine the equilibrium formation constant of the complex as well as its reaction rate constant (Figure 2). From the kinetic behaviour, it would appear that a

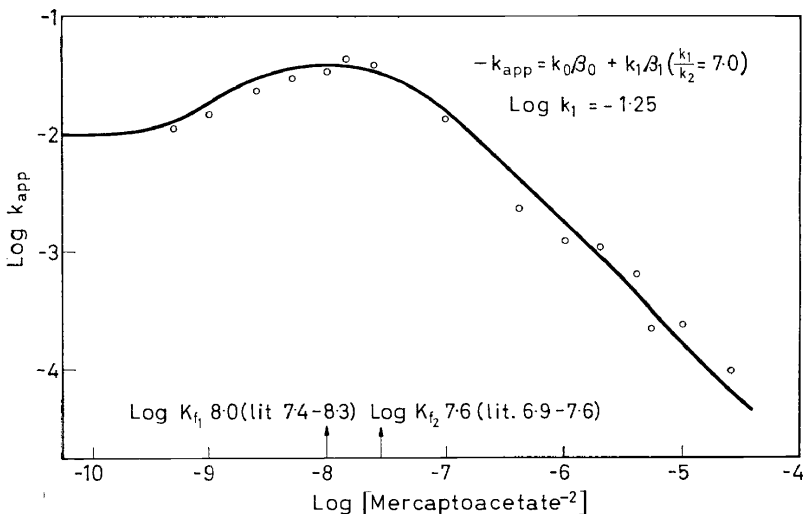


Figure 2. Effect of mercaptoacetate on rate of extraction of zinc dithizonate

mixed ligand complex, *e.g.*, ZnOAcDz, is an intermediate in the formation of the extractable chelate. Because the ZnOAc⁺ reacts some twenty-five times more rapidly than does the hydrated zinc ion, whereas acetate does not affect the rate of extraction of NiDz₂, the presence of acetate further increases the difference in the rates of extraction of Zn and Ni, making a kinetically-based separation feasible.

I would like to gratefully acknowledge the help of my co-workers in this research, Drs. Fa-chun Chou, Hobart Hamilton, Carl Honaker, Bobby McClellan, Joon S. Oh, P. R. Subbaraman, W. Van Willis, and Colin Woodward.

I would also like to gratefully acknowledge the financial support of both the United States Atomic Energy Commission and the National Science Foundation.

References

- 1 W. L. Medlund. *Anal. Chem.*, **32**, 632 (1960).
- 2 E. B. Sandell. *Colorimetric Determination of Traces of Metals*, Interscience, New York (1950).
- 3 F. Chou, Q. Fernando and H. Freiser. *Anal. Chem.*, **37**, 361 (1965).
- 4 F. Chou and H. Freiser. *Anal. Chem.*, **40**, 34 (1968).
- 5 F. Chou and H. Freiser. *Anal. Chem.*, **38**, 1925 (1966).
- 6 C. Woodward and H. Freiser. *Anal. Chem.*, **40**, 345 (1968).
- 7 P. J. Sun, Q. Fernando and H. Freiser. *Anal. Chem.*, **36**, 2485 (1964).
- 8 H. Hamilton and H. Freiser. *Anal. Chem.*, **41**, (1969) August (in press).

SOME INTERESTING ASPECTS OF THE EXTRACTION OF ZINC

- ⁹ W. Van Willis and H. Freiser. unpublished observations, University of Arizona 1967.
¹⁰ C. B. Honaker and H. Freiser. *J. Phys. Chem.*, **66**, 127 (1962).
¹¹ B. E. McClellan and H. Freiser. *J. Chem. Ed.*, **42**, 35 (1965).
¹² Joon S. Oh and Henry Freiser. *Anal. Chem.*, **39**, 295 (1967).
¹³ P. R. Subbaraman and H. Freiser. in press.