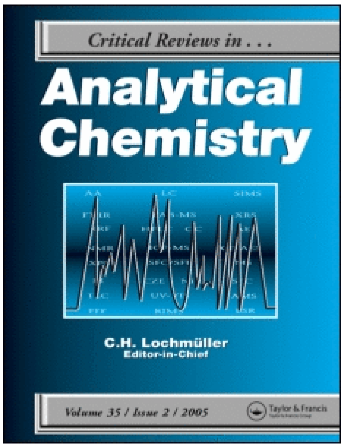

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SOME RECENT DEVELOPMENTS IN SOLVENT EXTRACTION

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INTRODUCTION

Almost a century has passed since Berthelot and Jungfleisch[1] first stated the law that forms the basis for equilibrium studies using solvent extraction. Further elaborated by Nernst,[2] the distribution law states that a solute will be distributed between two essentially immiscible solvents in such a manner that, at equilibrium, the ratio of the activities of the solute in the two liquid phases at a particular temperature will be a constant, K_D, called the distribution constant:

$$K_D = a_1/a_2 \tag{1}$$

where the subscripts $_1$ and $_2$ refer to the two solvents.

The essence of the use of solvent extraction or, indeed, any other distribution method (e.g., precipitation, ion exchange, or partition chromatography) in equilibrium studies lies in arranging experimental conditions so as to maintain an essentially constant activity of the species or component of interest in one of the phases while permitting various changes over the range of interest in the other. With the help of the distribution law, the activity of the species of interest in the phase where a great array of (reversible) reactions has occurred, is then readily accessible from the directly and simply measured activity in the other phase. The relatively 'inactive' phase provides a means of measuring activity without disturbing the equilibria, in close analogy to potentiometric measurements. From the distribution law and a knowledge of the stoichiometry of the system many or all of the equilibrium constants of the participating reactions can be reliably evaluated. The distribution of acetic acid (HOAc) between benzene and water provides a simple illustration of the method. At low pH values, the distribution of HOAc varies with total concentration only because the acid dimerizes in benzene, permitting a calculation of the dimerization constant from distribution data. At higher pH values, the dissociation of HOAc represents yet another reaction, this time in the aqueous phase. Distribution data obtained at various pH values provide a means of calculating the acid dissociation constant. It can be shown that the distribution ratio D_{HOAc}, the stoichiometric ratio of acetic acid concentrations in benzene and water, is given by

$$D_{HOAc} = \frac{[HOAc]_o + [(HOAc)_2]_o}{[HOAc] + [OAc^-]} = \frac{K_D\{1 + K_2[HOAc]_o\}}{1 + (K_a/[H^+])} \tag{2}$$

where the subscript $_o$ represents concentrations in benzene, and K_D, K_2, and K_a are the distribution, dimerization, and acid dissociation constants, respectively. For simplicity, the activity coefficients in equation (2) have been assumed to be unity but the more rigorous equations can be developed for evaluation of these thermodynamic parameters from distribution data as well.

Although solvent-extraction techniques for the separation of metal ions have been available for a long time (for example, removal of uranium as uranyl nitrate with ethyl ether by Peligot in 1842[3] and of iron as chloroferric acid with ether by Rothe in 1892[4]), the current high interest stems largely from the attention given, during World War II, to developing and understanding separation techniques for fissionable elements and fission products. A continuing high rate of publication in solvent extraction[5] and the frequency of symposia and conferences on an international scale testify to the vitality and interest of solvent extraction.

Because the nature of the metal-containing extractable complex so dominates the experimental conditions of its formation, and therefore the extraction conditions, it is logical and expedient to base classification schemes for metal extraction systems on this aspect. Such a scheme, proposed in 1964,[6] provides for the great majority of extraction systems.

The formation of an uncharged species that is extractable by the relatively non-polar organic solvent can involve

1. Simple (monodentate) coordination alone, as with $GeCl_4$,
2. Heteropoly acids, a class of coordination complexes in which the central ion is complex rather than monatomic, as with phosphomolybdic acid, $H_3PO_4 \cdot 12MoO_3$,
3. Chelation (polydentate coordination) alone, as with Al(8-quinolinolate)$_3$,
4. Ion-association alone, as with Cs^+,

$(C_6H_5)_4B^-$, or combinations of the above, such as

5. Simple coordination and ion-association —e.g., ("Onium")$^+$•$FeCl_4^-$, ["Onium" stands for one of the following cation types, hydrated hydronium ion, $(H_3O)_3O^+$, a rather labile cation requiring stabilization by solvation with an oxygen-containing solvent, a substituted ammonium ion, $R_nNH^+_{(4-n)}$, where R is an alkyl or aralkyl group and N may vary from 1 to 3, a substituted phosphonium ion R_4P^+, stibonium ion R_4Sb^+, sulfonium ion, and other ions of this sort, including the important category of cationic dyes such as Rhodamine B].

6. Chelation and ion-association with either positively or negatively charged metal chelates — e.g., Cu(2,9-dimethyl-1,10-phenanthroline)$_2^+$•ClO_4^- or $3(n\text{-}C_4H_9NH_3^+)$•Co(Nitroso R Salt)$_3^{-3}$ — and, finally,

7. Simple coordination and chelation — e.g., Zn(oxinate)$_2$•pyridine. This category is of significance for chelates that are coordinatively unsaturated — i.e., those with a monoprotic bidentate reagent in which the coordination number of the metal is greater than twice its valence.

An examination of the foregoing material and of Table 1 serves to underline the close relationship between inorganic and analytical chemistry employed in the principles and practice of metal extraction systems. A thorough understanding of analytical solvent extraction of metals requires a deep appreciation of many branches of coordination chemistry. Conversely, study of the equilibrium and kinetic aspects of solvent extraction chemistry results in substantial contributions to the chemistry of metal coordination complexes. In this review, such interrelations will be stressed.

EXPERIMENTAL METHODS

Three basic types of solvent extraction techniques are generally utilized: batch, continuous, and counter-current distribution methods.[7] When a single equilibration serves to quantitatively extract the component of interest and thus separate it from interferences, then a simple batch extraction, using a separatory funnel in one of its many modifications, will suffice. Continuous extractors are required to extract components whose *D*-values are so low that large volumes would have to be used if the batch technique were employed. Finally, in order to separate components whose *D*-values are too similar to permit the use of the simple batch technique, counter-current distribution (CCD) must be employed. Although the latter technique is usually thought to involve a rather elaborate apparatus, Peppard[8] has pointed out the value of a simple version of CCD employing as few as three separatory funnels. With this technique, called the "push-through" method, the sample is placed in the first separatory funnel which contains equal volumes of a light phase and a heavy phase. After equilibration, the heavy phase is transferred to the second funnel and a fresh (sample-free) sample of heavy phase is added to the first funnel. After a given number of similar equilibrations and transfers, a prearranged number (perhaps 5) of separate portions of the heavy phase will have been collected. The separation of the components between what remains in the funnels and what has been collected in the several fractions represents a substantial improvement over what would be obtained with a simple batch equilibration. For example, for an equimolar mixture of A and B whose *D*-values are 10 and 0.10, respectively, a single equilibration would give 90% A and 10% B in the organic phase, or a 9:1 separation, whereas with a 3-funnel-5-fraction "push-through" procedure, the funnels would contain 97.4% A and 0.01% B, or a 974:1 separation. Not only is the separation greatly enhanced but the yield of the component of interest is significantly improved. Another advantage of the "push-through" method lies in its adaptation to a kind of gradient elution in which a complex mixture can be separated into individual components by using, sequentially, several solvents selected so that the *D*-value of only one of the components is such to make it move readily through the system, while the others remain behind. As an example, Peppard describes the extraction into tributyl phosphate (TBP) of Th (IV), Pa (V), and U (VI) using in succession 4 portions of 5.0 *M* HCl, 5 portions that were 5.0 *M* in HCl and 0.5 *M* in HF, and 4 portions of 0.5 *M* HCl and 1.0 *M* HF. For each of the nuclides, better than 60% yield was found in a single fraction.

A recent development in extraction apparatus,

TABLE I

Metal Extraction Systems[6]

PRIMARY SYSTEMS

I. Simple (Monodentate) Coordination Systems
  1. Certain halide systems—e. g., $HgCl_2$, $GeCl_4$
  2. Certain nitrate systems—e. g., $(UO_2)(TBP)_2(NO_3)_3)_2$

II. Heteropoly Acid Systems—e. g., $H_3PO_4 \cdot 12MoO_3$

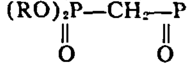
III. Chelate Systems	
A. Bidentate chelating agents	Reactive Grouping
a) 4-Membered ring systems	
1. Disubstituted dithiocarbamates—e. g., Na^+, $(C_2H_5)_2NCSS^-$ or $(C_6H_5CH_2)_2NCSS^-$	S=C—S$^-$
Xanthates—e. g., Na^+, $C_2H_5OCSS^-$	
2. Dithiophosphoric acids—e. g., diethyldithiophosphoric acid	S—P—S$^-$
3. Arsinic and arsonic acids—e. g., benzenearsonic acid	$^-$O—As—O$^-$
b) 5-Membered ring systems	
1. *N*-Acyl hydroxylamines—e. g., *N*-benzoylphenylhydroxylamine (BPHA) or benzohydroxamic acid	O=C—N—O$^-$
2. *N*-Nitroso-*N*-arylhydroxylamines—e. g., cupferron (*N*-nitrosophenylhydroxylamine) or neocupferron, (*N*-nitrosonaphthylhydroxylamine)	O=N—N—O$^-$
3. α-Dioximes—e. g., dimethylglyoxime, cyclohexanedionedioxime (Nioxime)	N=C—C=N$^-$
4. Diaryldithiocarbazones—e. g., dithizone (diphenyldithiocarbazone)	N—N=C—S$^-$
5. 8-Quinolinols—e. g., oxine (8-quinolinol), methyloxine, (2-methyl-8-quinolinol)	N=C—C—O$^-$
6. Quinoline-8-thiols, dithioxamides—e. g., thiooxine (quinoline-8-thiol) *N*,*N*′-didodecyldithiooxamide	N=C—C—S$^-$
7. Quinoline-8-selenol	N=C—C—Se$^-$
8. *o*-Dihydroxybenzenes—e. g., catechol, phenylfluorone, rhodizonic acid	$^-$O—C=C—O$^-$
9. *o*-Dimercaptobenzenes—e. g., toluene-3,4-dithiol	$^-$S—C=C—S$^-$
10. Thionalid (thioglycolic-β-aminophthalide)	O—C—C—S$^-$
c) 6-Membered ring systems	
1. β-Diketones—e. g., Acetylacetone, TTA (thenoyltrifluoroacetone) dibenzoylmethane, Morin, quercetin, quinalizarin	O=C—C=C—O$^-$
2. *o*-Nitrosophenols—e. g., 1-nitroso-2-naphthol	O=N—C=C—O$^-$
3. *o*-Hydroxyloximes—e. g., salicylaldoxime	N=C—C=C—O$^-$
d) Larger ring systems	
1. Mono or dialkyl-phosphoric or -phosphonic acids	O=P—OHO=P—O$^-$
B. Polydentate chelating systems	
1. Pyridylazonaphthol (PAN) and pyridylazoresorcinol (PAR)	N=C—N=N—C=C—O$^-$
2. *o*,*o*′-Dihydroxyazobenzenes—e. g., 2,2′-dihydroxy-5′-isopropyl-4′-methyl-4-nitroazobenzene	O—C=C—N=N—C=C—O$^-$
3. *N*, *N*′-(Disalicylidene)ethylenediimine (also S analog)	$^-$O—C=C—N=C—C=N—C=O—O$^-$
4. Glyoxal bis(2-hydroxyanil) (also S analog)	$^-$O—C=C—N=C—C=N—C=O—O$^-$

IV. Simple Ion Association Systems
  A. Metal in cation
    1. Inorganic anions—e. g., Cs^+, I_3^-, or PF_6^-
    2. Tetraphenylberate anion
    3. Dipicrylamine anion
    4. Alkylphenolate anion
    5. Carboxylate and perfluorocarboxylate anions

MIXED SYSTEMS

V. Ion Association and Simple Coordination Systems
  A. Metal in cation
    1. Oxygen solvents—e. g., alcohols, ketones, esters, ethers
    2. Neutral phosphorus compounds, phosphates, phosphonates, phosphinates, phosphine oxides, and sulfides
  B. Metal in anion (paired with "onium" ion)
    1. Halides—e. g., $FeCl_4^-$
    2. Thiocyanates—e. g., $Co(CNS)_4^{2-}$
    3. Oxyanions—e. g., MnO_4^-

- VI. Ion Association and Chelation Systems
  - A. Cationic chelates
    - 1. Phenanthrolines and polypyridyls—e. g., Cu(I) (2,9-dimethylphenanthroline)$_2^+$
    - 2. Tetraalkyl methylenediphosphonates—e. g.,



$$\underset{\overset{\|}{O}}{(RO)_2P}\text{—}CH_2\text{—}\underset{\overset{\|}{O}}{P(OR)_2}$$

  - B. Anionic chelates
    - 1. Sulfonated chelating agents
      - a. 1-Nitroso-2-naphthol—e. g., Co (III) (nitroso R salt)$_3^{-3}$
      - b. 8-Quinolinol—e. g., Fe(III) (7-iodo-8-quinolinol-5-sulfonate)$_3^{-3}$
- VII. Chelation and Simple Coordination Systems—e. g., Th(TTA)$_4$·TBP, Ca(TTA)·(TOPO)$_2$

of particular interest for collection of extraction equilibrium data, is the AKUFVE equipment developed by Reinhardt and Rydberg.[9] The AKUFVE, which affords a great improvement both in speed and accuracy over the point-by-point accumulation of extraction equilibrium data, consists of a large mixing chamber from which samples are withdrawn for analysis after the two liquid phases have been separated absolutely by a specially constructed high-speed, small internal-volume centrifuge. Phase equilibrium in the present model is reached in about 40 sec which might well be reduced to 10 sec in subsequent models. Analysis can be carried out by scintillation counting, spectrophotometry, conductivity, or refractive-index measurements, depending on the properties of the species under study. A complete extraction curve (log *D* *vs.* pH, for example) with as many as 20-30 points may be obtained in about 30-40 min. The use of this ingenious apparatus, which costs between $10,000 and $20,000, should do much for solvent extraction research.

SOLVENT EXTRACTION EQUILIBRIA

The utter simplicity of experiments designed for the evaluation of equilibria of various reactions participating in the extraction makes this approach very attractive. Values of the distribution ratio *D* for the metal under study can be obtained by any of a wide variety of methods capable of handling the very low concentrations encountered with very high *D*-values (needed for evaluations of K_{DC} as discussed below). Radioisotope methods, especially those involving γ-emitting isotopes, atomic absorption, and other spectrometric techniques are widely used. It should be mentioned that special care, particularly when chelate formation is involved, must be taken to ensure that the system under study is really at equilibrium.

Methods of Calculating Equilibrium Constants

Chelate Systems

It is not too surprising that the earliest description of metal extraction equilibria involved a chelate system [zinc-dithizone by Kolthoff and Sandell[10]] since the high value of the chelate formation constant makes it possible for relatively low concentrations to be used. This in turn causes the behavior of the system to approach ideality and therefore permits the use of a simple equilibrium expression.

By combining the mass-action expressions for the contributing equilibria (a) distribution of the chelating agent, typically a monoprotic acid HL, (b) dissociation of the acid HL, and (c) formation of the metal chelate ML_n in the aqueous phase, and (d) distribution of the chelate, the following description of the overall extraction equilibrium may be derived:

$$D = \frac{\beta_n K_{D_C} K_a^n [HL]_o^n}{K_{D_R}^n [H^+]^n} \tag{3}$$

where K_{DR} and K_{DC} are the distribution constants of the chelating agent and the metal chelate, respectively, K_a is the acid dissociation constant of HL, β_n is the overall formation constant of ML_n,[11] and n is the charge of the hydrated metal ion M^{n+}.

It has been assumed in the derivation of equation (3) that there is only one metal-containing species in each of the two phases, the hydrated metal ion M^{n+}, and the simple chelate ML_n. Although this situation is approximated reasonably well in many chelate extractions, it is necessary, particularly in extraction equilibrium studies, to take into account other complexing reactions which may involve the metal ion (aqueous phase) or the chelate (organic phase). Hence, if we let μ be the fraction of total metal concentration in the aqueous phase that is present as M^{n+} and μ' be the fraction of the total metal concentration in the organic phase that is present as the simple chelate ML_n, then the distribution equation becomes

$$D = \frac{\beta_n K_{D_C} K_a^n}{K_{D_R}^n} \frac{\mu}{\mu'} \frac{[HL]_o^n}{[H^+]^n} \tag{4}$$

The fractions μ and μ' will be functions of the equilibrium constants of the pertinent reactions as well as of the concentrations of the complexing agents.

With the help of equation (4) it is possible to take into account (and therefore evaluate) the effect of stepwise chelate formation. If this occurs,

$$\mu = \left[1 + \sum_{i=1}^{n} \beta_i [L^-]^i\right]^{-1} \tag{5}$$

where β_i represents the cumulative stepwise chelation equilibrium constant in the aqueous phase, study of the metal extraction over a variety of experimental conditions of pH and $[HL]_o$ will then yield values of K_{D_C} as well as of all the β_i (including β_n). It will, of course, have been necessary to previously evaluate K_a and K_{D_R} of the chelating agent using an expression similar to equation (2).

When an auxiliary complexing agent, X (e.g., chloride, hydroxide, citrate, or EDTA) is present in the aqueous phase

$$\mu = \left[1 + \sum_{i=1}^{n} \beta_i [L^-]^i + \sum_{i=1}^{n} \beta'_i [X]^i\right]^{-1} \tag{5'}$$

where β'_i represent the cumulative stepwise equilibrium constants of the metal complexes formed by X. If X can combine with one or more protons (i.e., if it is a Brønsted base), then the values of μ will also be functions of the pH of the solution.
Thus

$$\mu = [1 + \sum_{i=1}^{n} \beta_i (\alpha_L C_L)^i + \sum_{i=1}^{n} \beta'_i (\alpha_X C_X)^i]^{-1} \tag{6}$$

where α_X, which is a function of the acid dissociation constants of H_yX as well as of the pH, represents the fraction of C_X (the total equilibrium concentration of X) which is not bound to metal. For HL, the distributing chelating agent, C_L represents its total concentration in both phases and

$$\alpha_L = K_a / \left[K_{D_R}[H^+] + K_a\right] \tag{7}$$

The parameter μ' in equation (4) is of particular interest when the metal chelate ML_n reacts with "adducting" ligands, B, in the organic phase to give $ML_n.B_m$. Then

$$\mu' = \left[1 + \sum_{i=1}^{m} \beta'[B]_o^i\right]^{-1}$$

In the interest of brevity, two points have not been considered in the expressions outlined above. Activity coefficients have been neglected. It has usually been assumed that, as long as the ionic strength of the aqueous phase is maintained constant, the constancy of all pertinent activity coefficients is assured so that the equilibrium "quotients" are significant. Nor have polynuclear complexes (those containing more than one metal atom) been included, but these can easily be studied within the framework outlined.

Ion-Association Systems

The major difference between expressions for chelate and non-chelate extraction arises from the presence of relatively high reagent concentrations made necessary by the relatively low complex-formation equilibrium constants. Inasmuch as the complexing agents are often parts of strong electrolytes, the equilibria to be considered often occur in media having high ionic strengths. Under such conditions large deviations from ideality are commonplace and activity-coefficient corrections can become as large as the equilibrium constants themselves. Unless suitably careful account is taken of such effects, "complexes" may be reported which do not exist.[12]

ADDUCT OR MIXED-LIGAND EXTRACTION SYSTEMS

A mixed-ligand chelate most frequently involves a metal ion whose charge is less than half its coordination number and a monoanionic bidentate chelating agent, because these form a neutral chelate in which the coordination capacity of the metal ion is not saturated. Generally, such "coordination-unsaturated"[13] chelates form hydrates which are not particularly soluble in organic hydrocarbon and halogenated hydrocarbon solvents and are therefore usually poorly extracted. By adding organic components which can act as ligands strong or concentrated enough to replace the coordinated water, the resulting adduct or mixed-ligand chelate is made much more hydrophobic and therefore significant and often dramatic increases in metal extractability occur. The term synergistic extraction has gained acceptance for systems exhibiting such enhancement.

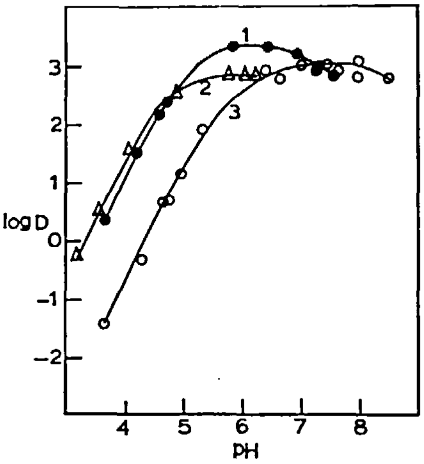
In a very real sense, mixed-ligand extractions have been employed for quite some time. As Alimarin and Zolotov[13] pointed out, the extraction of coordinated-unsaturated chelates is greatly improved by the use of polar oxygen-containing solvents which probably participate directly in the formation of the extractable complex. For example, the TTA complexes of neptunium (V), cobalt (II), and uranium (VI) and the 8-quinolinolates of thallium (I) and barium (II) are better extracted by alcohols, ketones, and esters but are less well extracted by ethers, hydrocarbons, and halogenated hydrocarbons. In contrast, coordination-saturated chelates such as the TTA complexes of cerium (III), iron (III), and thorium (IV) as well as the 8-quinolinolates of lanthanum (III), thallium (III), and tungsten (VI) are extracted almost equally well by oxygen-containing and less polar solvents.

The use of mixed solvents became fairly commonplace in the 1950s. Magnesium 8-quinolinolate is normally not extractable in chloroform, but was found to be extracted efficiently upon using the monobutyl ether of ethylene glycol[14] or butylamine[15] as auxiliary solvent components. Substantial enhancement of extraction of lanthanides from aqueous nitrate media by using a mixture of TTA and TBP in a hydrocarbon diluent, rather than either extractant alone, was reported by Cuninghame et al.[16] at Harwell. Oak Ridge investigators[17] reported enhancement of the extraction of uranium by the use of mixtures of acidic and neutral organophosphorus extractants. The use of neutral organophosphorus compounds as adducting ligands in conjunction with dialkylphosphoric acids or TTA as chelating agents for the extraction of various metals [such as the alkaline earths, lanthanides, actinides, thorium (IV), and uranium (VI)] has been studied extensively by Healy,[18-21] Irving and Edgington,[22] and Dyrssen.[23 24]

Similarly, chelating extractants can also function as monodentate or chelating adducts. Several years ago our attention was attracted by conflicting reports[25 26] of the efficacy of 8-quinolinol as a zinc extractant. Accordingly, we initiated extraction-equilibrium studies of zinc with a series of 8-quinolinols chosen to permit examining both the steric and electronic effects of substituents on the course of extraction.[27 28]

In general, the extraction of a simple chelate can be described by a plot of log D *vs.* pH, at constant reagent concentration in the organic phase, which consists essentially of two linear portions. Starting at a low pH, the value of log D increases over a region in which the slope of the plot is equal to n, the number of protons released on chelate formation, and then eventually reaches a constant and pH-independent value determined by the distribution coefficient K_{D_C} of the chelate. At a higher value of the reagent concentration the entire curve shifts to the left (i.e., toward lower pH values) without alteration of either the slope or the maximum value of log D, which remains equal to log K_{D_C}. When the extractable complex is an adduct rather than a simple chelate, the entire extraction curve will be affected by the concentration of the adduct reagent. In the event that the chelating agent is

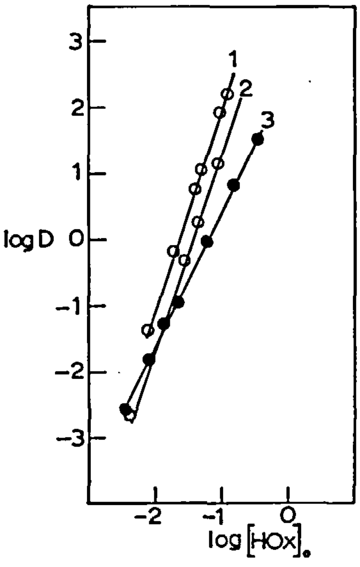
FIGURE 1



Distribution of zinc (II) chelates of 8-quinolinols between chloroform and water.[27]

1. 4-Methyl-8-quinolinol. $[\mathrm{HOx}]_o = 0.12M$
2. 8-Quinolinol. $[\mathrm{HOx}]_o = 0.17M$
3. 2-Methyl-8-quinolinol. $[\mathrm{HOx}]_o = 0.36M$

FIGURE 2



Distribution of zinc (II) chelates of 8-quinolinols between chloroform and water.[27]

1. 4-Methyl-8-quinolinol at pH 4.63
2. 8-Quinolinol at pH 4.56
3. 2-Methyl-8-quinolinol at pH 4.60

also involved in adduct formation, an increase in its concentration will shift the plateau portion of the extraction curve toward a higher value of log *D*, and will shift the initial linear portion of the curve toward lower pH values but will not change its slope. In Figure 1 there are shown the extraction curves (log *D* *vs.* pH) for the three reagents in the lower pH range. For each curve the slope at low pH-values is equal to 2, which shows that in each of these extractions two protons are released on the formation of the extractable complex.

The slopes of similar plots of log *D* against the logarithm of the reagent concentration will show the number of reagent molecules incorporated in the extractable complex. Such plots were constructed for the extraction of zinc(II) with the 8-quinolinols as shown in Figure 2. The behavior of the plot for the extraction with 2-methyl-8-quinolinol indicates that the extractable complex is the simple chelate, since two reagent molecules per zinc ion are involved in the extraction. With the other two 8-quinolinols, where no adverse steric hindrance is involved, the extractable complexes are the adducts, $\mathrm{ZnOx_2 \cdot HOx}$.

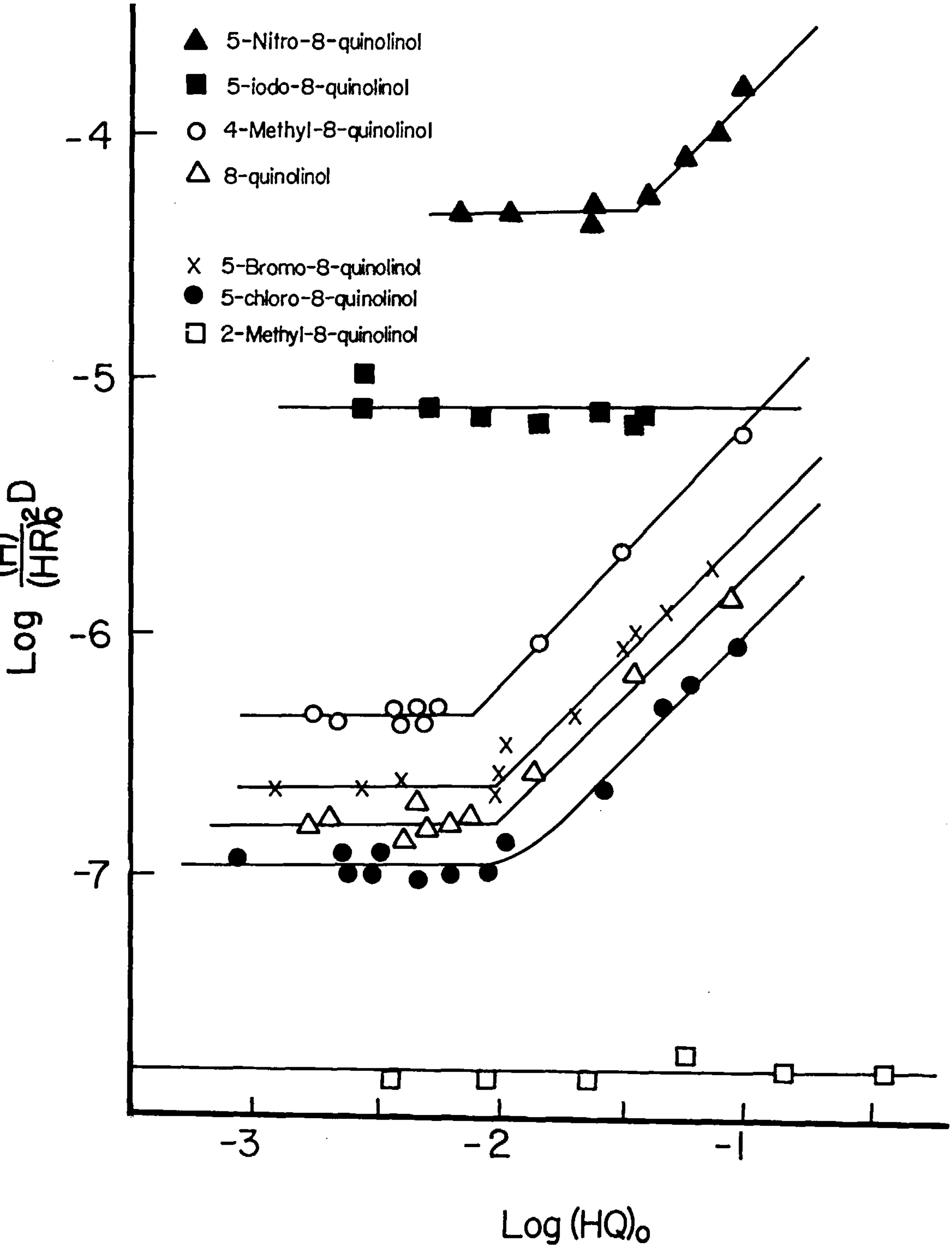
As mentioned in an earlier section, adduct formation equilibria can be accounted for in the general extraction expression in terms of μ', the fraction of the metal concentration in the organic phase that is present as the simple chelate. In the case of self-adduct formation in zinc-8-quinolinol systems $\mu' = [1 + K_{\mathrm{AD}}\,[\mathrm{B}]_o^a]^{-1}$ and equation (4) may be written as

$$D = K_{\mathrm{ex}} \frac{[\mathrm{HOx}]_o^2}{[\mathrm{H^+}]^2} [1 + K_{\mathrm{AD}}\,[\mathrm{HOx}]_o^a]$$

where $K_{\mathrm{ex}} = \beta_2\, K_{\mathrm{D_C}}\, K_a{}^2 \,/\, K_{\mathrm{D_R}}{}^2$ and K_{AD} is the equilibrium constant for the reaction, in the organic phase, of the simple 2:1 chelate with **a** moles of an adducting base, which in these cases is the particular 8-quinolinol itself. A plot of log $(D[\mathrm{H^+}]^2/[\mathrm{HQ}]_o^2)$ *vs.* log $[\mathrm{HQ}]_o$ gives a curve with two linear portions, from which K_{ex}, **a**, and K_{AD} can be evaluated (Figure 3). Extraction data at lower values of *D* can then be used to evaluate the component parts of K_{ex} as shown in Table 2.

In the series of 8-quinolinols examined, adducts with one mole of the neutral 8-quinolinol were formed with all the reagents except for the 2-methyl- and 5-iodo- substituted 8-quinolinols. With the 5-iodo-8-quinolinol, the limited solubility of the reagent precluded the extension of

FIGURE 3



Distribution of zinc chelates of 8-quinolinol and substituted 8-quinolinols between chloroform and water.

the work to concentrations high enough that adduct formation might have occurred. In the case of the 2-methyl derivative, however, the failure to form an adduct was clearly shown; it probably reflects adverse steric influence of the methyl group.

The formation of an adduct served to resolve the conflicting reports about the efficacy of 8-quinolinol as a zinc extractant. The successful procedure[25] employed a significantly higher 8-quinolinol concentration, and thereby met the requirements imposed by the higher reagent dependence in self-adduct formation.

It is likely that the adducting ligand is bonded to the metal ion through nitrogen. Strengthening this hypothesis is the observation that the adduct formed by 4-methyl-8-quinolinol is more stable than that formed by the parent ligand, reflecting the increased basicity of the nitrogen in the former reagent.

Although extraction-equilibrium studies with other substituted 8-quinolinols also show an increase in adduct stability with increasing basicity of the quinoline nitrogen,[28] this change is much smaller than 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; as may be seen from Table 2, they 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 ligands.[28] Quantitative evaluation of the equilibrium data of the pyridine-enhanced extractions, summarized in Table 3, confirmed our hypothesis. That adduct stability increased as the stability of the metal-ligand complex increased is seen from the fact that the values of log K_{AD} are 0.4 unit higher with 4-methylpyridine than they are with pyridine for the chelates with either 8-quinolinol or its 4-methyl derivative; there is a smaller but significant increase with 2-methyl-8-quinolinol chelates.

Second, that increasingly stable chelates form weaker adducts is shown by the fact that the value of log K_{AD} is 0.5 unit smaller for the 4-methyl-8-quinolinol chelate, which is more stable that that of 8-quinolinol.

Finally, the decrease of adduct stability expected to result from steric hindrance is illustrated by the following order of adduct stabilities: pyridine > 2-methyl-pyridine > 2,4,6-trimethylpyridine. The 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 1:1 stoichiometry was observed in all of the cases of self-adduct and other adduct complexes. This accounts for

TABLE 2

Equilibrium Constants for Zinc Chelates of 8-Quinolinol and Substituted 8-Quinolinols[28]

Substituted 8-quinolinol	log K_{AD}	log K_{DC}	log K_{DR}	$pK_{a1} + pK_{a2}$	log $K_x \beta_2$
Parent compound	2.17	1.41	2.64	14.9	17.06
2-Methyl-	—	2.99	3.22	15.9	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

only five coordination positions. In the sterically unhindered complexes, it is likely that 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, pentacoordination would seem more reasonable.

TABLE 3

Logarithmic Values of Adduct-Formation Constants for Various Pyridine Adducts of the Zinc 8-Quinolinolates in Chloroform at 25°C[28]

Chelating agent	Adducting base Pyridine	2-Methyl-pyridine	4-Methyl-pyridine	2,4,6-Tri-methyl-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

TABLE 4

Summary of Extraction Constants[30]

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
$Zn(phen)_2Ox^+ \cdot ClO_4^-$	$\log K_{ex2}$	6.8 ± 0.6	8.7 ± 1.1
$Zn(phen)_3^{2+} \cdot 2ClO_4^-$	$\log K_{ex3}$	13.7 ± 0.4	18.5 ± 1.5
$Zn(phen)(OAc)_2$	$\log K_{ex4}$	4.3 ± 0.2	5.5 ± 0.2

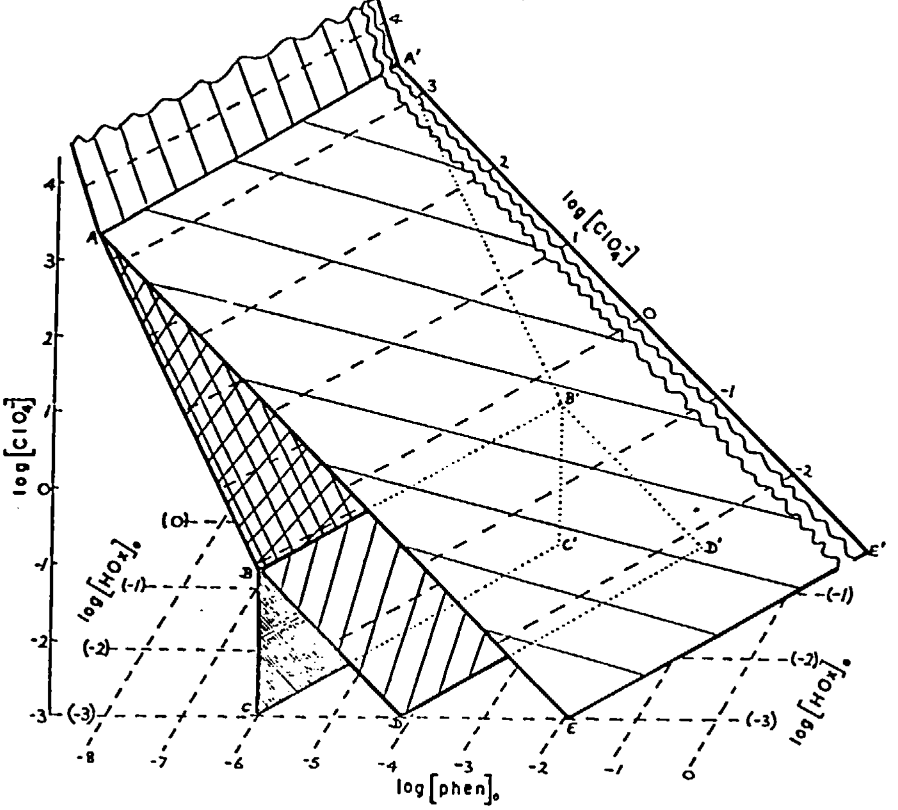
Because chelating agents such as 8-quinolinol and its 4-methyl derivative behaved as monodentate ligands in adduct formation, whereas the sterically hindered 2-methyl-8-quinolinol did not, we were curious to see how 1,10-phenanthroline (phen) would behave under similar circumstances. If phen behaved as a monodentate adducting ligand at the 1-nitrogen, would the other pyridine nucleus sterically hinder complex formation?[29,30] 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 a *mixed ligand chelate than an adduct*, for the value of log K_{AD}, though it was not measured, is undoubtedly high enough to classify the phen as a bidentate ligand in this complex, $ZnOx_2phen$.[30]

The extraction system Zn-HOx-phen is as *interesting as it is complex. Not too surprisingly,* $Zn(phen)_3^{2+}$ forms an extractable ion-association complex with ClO_4^-, as does $Fe(phen)_3^{2+}$.[29] In addition to the ion-association complex and the self-adduct, $ZnOx_2 \cdot HOx$, there are two other extractable species, $Zn(phen)_2Ox^+ \cdot ClO_4^-$ and $ZnOx_2 \cdot phen$, whose contributions could be sufficiently sorted out to permit the calculation of the various extraction constants (Table 4). The extraction-equilibrium data were used to construct a three-dimensional (oxine-phenanthroline-perchlorate) "phase" diagram that described the natures of the predominating extracted species under various conditions. Such a diagram is extremely helpful in designing experiments for optimizing total extraction and for isolating particular intermediate complexes, as well as in improving understanding of the overall extraction system. A projection of this diagram is shown in Figure 4. 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 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 which comes with increasing ligand basicity is effectively counterbalanced by the corresponding increase in the acid dissociation constant of the ligand (i.e., the proton displacement constant of chelation does not increase), in the case of the reaction of phenanthrolines with zinc, the extraction constant does not involve K_a for the ligand. Hence, the increase of K_a with alkyl substitution is fully effective.

Toluene-3,4-dithiol (H_2T,dithiol) has frequently been used in solvent-extraction methods

FIGURE 4



Projection of species distribution diagram for Zn-8-quinolinol-phenanthroline system at pH 4.85[30]

for a number of the higher valent metal ions such as molybdenum, tungsten, and rhenium[31-33] because the doubly charged dithiolate anion (T^{2-}) forms neutral chelate species with these metal ions that are "coordination-saturated." Although dithiol has enjoyed some use as a qualitative reagent because it forms colored complexes with many metal ions,[34] it has not been employed in extraction procedures for metals of lower valences because of the difficulty of forming a suitable complex. With zinc, for example, the 2:1 complex, ZnT_2^{-2}, is charged and therefore water-soluble. Although the 1:1 ZnT complex is neutral, it is not extractable because zinc is 4-coordinate and gives an organic-insoluble dihydrate, $ZnT \cdot 2H_2O$. If it is desired to incorporate such complexes into extraction processes, two courses are open. If conditions are adjusted to favor the formation of the anionic chelate ZnT_2^{2-}, then the addition of a suitable cation such as a quaternary ammonium ion might be expected to result in an extractable ion-association complex. Alternatively, replacement of the water of hydration from the neutral ZnT complex by neutral bases (adducting agents) might also be effective in producing an extractable species. In order to explore the feasibility of these two approaches to enlarging the scope of dithiol as an analytical extraction agent, we decided to study quantitatively the effects of tetrahexylammonium iodide (THAI) in promoting the extraction of an ion-association complex and of phenanthroline (phen) in effecting the formation of an extractable mixed ligand complex, using zinc as a typical divalent metal ion.[35]

The distribution of zinc between chloroform and aqueous buffer solutions in the presence of H_2T and THAI is given by

$$D_{Zn} = \frac{[2\ THA^{+} \cdot ZnT_2^{2-}]_o}{C_{Zn}}$$

where C_{Zn}, the total concentration of zinc in the aqueous phase, can be expressed as $[Zn^{2+}]/\mu$, where μ is the fraction of zinc in the aqueous phase present as uncomplexed Zn^{2+}. A quantitative description of the extraction of zinc as the complex ($2\,THA^+ \cdot ZnT_2^{2-}$) requires consideration of the two ion-association reactions

$$2\,THA^+ + ZnT_2^{2-} \overset{K_{IPC}}{\rightleftharpoons} 2\,THA^+ \cdot ZnT_2^{2-}$$

$$THA^+ + X^- \overset{K_{IPQX}}{\rightleftharpoons} THA^+ \cdot X^-$$

the following distribution equilibria

$$K_{DRT} = \frac{[H_2T]_o}{[H_2T]}$$

$$K_{DRQX} = \frac{[THAX]_o}{[THAX]}$$

$$K_{DC} = \frac{[2\,THA^+ \cdot ZnT_2^{2-}]_o}{[2\,THA^+ \cdot ZnT_2^{2-}]}$$

and the chelate-formation equilibrium in the aqueous phase.

$$\beta_2 = \frac{[ZnT_2^{2-}]}{[Zn^{2+}][T^{2-}]^2}$$

From these equilibria the overall extraction expression is found to be

$$D_{Zn} = \frac{\beta_2 K_{a_1}^2 K_{a_2}^2 (K_{IPC} K_{DC}) [H_2T]_o^2 [THAX]_o^2}{K_{DR_T}^2 (K_{DR_{QX}}^2 K_{IP_{QX}}^2)} \mu \tag{8}$$

The validity of this expression in describing the extraction of zinc with H_2T and THAI is evident from the following distribution studies. As shown in Figure 5, a plot of log D_{Zn} *vs.* pH shows that log D increases with increasing pH over a region in which the slope is 4, a value which is in accord with the predicted release of four protons upon formation of the ZnT_2^{2-} complex. Further, logarithmic plots of extraction data obtained at constant pH against $[H_2T]_o$ and $[THAI]_o$ show slopes of 2.0 and 1.9, respectively, in agreement with equation (8). These data are presented in Table 5.

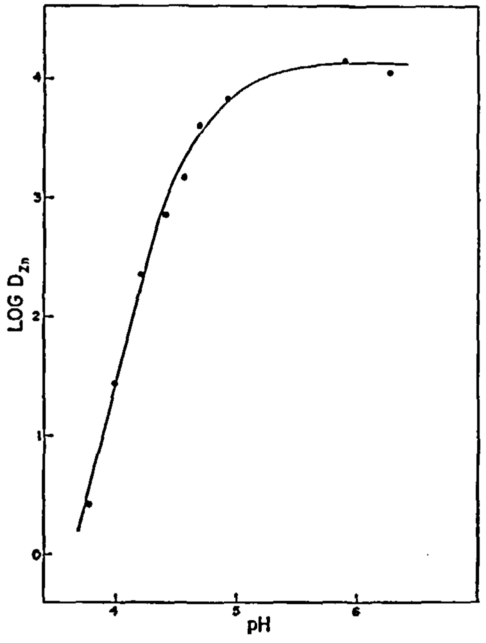
A fourth extraction variable, included in equation (8) and denoted as [X], results from the competition of anions in the aqueous phase for the quaternary ammonium ion. It was shown that the effect of ClO_4^-, a readily extractable anion, is quantitatively in accord with what would be predicted from equation (8).

TABLE 5

Extraction of Zinc with
Toluene-3,4-Dithiol in the Presence of
Tetra-*n*-Hexylammonium Iodide,
pH = 4.50, T = 25°C, u = 0.10,
$[OAc^-] = 2.55 \times 10^{-3} M$[35]

A. Variation of log *D* with −Log $[H_2T]_o$ at [THAI] = $8.21 \times 10^{-3} M$		B. Variation of log *D* with −Log [THAI] at $[H_2T]_o$ = $3.28 \times 10^{-3} M$	
−Log $[H_2T]_o$	Log *D*	−Log $[THAI]_o$	Log *D*
3.74	−0.19	3.33	−0.02
3.44	0.44	3.03	0.40
3.15	1.00	2.57	1.23
2.98	1.34	2.35	1.53
2.86	1.56	2.19	1.89
2.77	1.73	2.07	2.14
$D \alpha [H_2T]_o^{2.0 \pm 0.1}$		$D \alpha\ [THAI]^{1.9 \pm 1.0}$	

FIGURE 5



Extraction of zinc as $2R_4N^+ \cdot ZnT_2^{2-}$ in $CHCl_3$ at 25°C and $\mu = 0.10\ M$[35]
$[THAI]_o = 8.30 \times 10^{-4} M$, $[H_2T]_o = 3.08 \times 10^{-4} M$.

For the extraction of zinc as the complex

ZnT·phen, the distribution is given as

$$D = \frac{[\mathrm{ZnT \cdot phen}]_o}{C_{Zn}}$$

The following expression describing the extraction of ZnT·phen may then be written

$$D = \frac{\beta_N K_{DC} K_{a_1} K_{a_2}}{K_{DR_T} K_{DR_P}} \frac{[\mathrm{H_2T}]_o[\mathrm{phen}]_o}{[\mathrm{H^+}]^2} \mu \qquad (9)$$

where β_N is the formation constant of ZnT·phen, K_{a_1} and K_{a_2} are the dissociation constants of H_2T, K_{DC} is the distribution constant of the mixed ligand complex, and K_{DR_T} and K_{DR_P} are the distribution ratios of the ligands H_2T and phen, respectively.

Extraction studies were carried out over the pH range 3.75 to 8.92. The results of these investigations are shown in Figure 6, where it should be noted that as the pH increases, the values of log D_{Zn} first increase, with a slope of 2.0 ± 0.1, in the low pH range, then pass through a maximum or plateau and finally decrease, with a slope of -1.8 ± 0.1, in the higher pH range.

Each of these regions of the extraction curve may be quantitatively attributed to changes in the value of μ as various zinc-containing species predominate under different conditions. Thus, in the low pH region the predominant zinc species is the hydrated ion so that $\mu = 1$, and the plot of log D_{Zn} *vs.* pH is expected to have a slope of 2.

In this range, an interesting effect is observed when the concentration of phenanthroline is increased. At first the extraction is improved, as might be expected, but a further increase causes the extraction curve to shift to the right. This effect arises from the formation of higher zinc-phen complexes [such as $\mathrm{Zn(phen)_2^{2+}}$ and $\mathrm{Zn(phen)_3^{2+}}$]. When the presence of these higher complexes is quantitatively accounted for in the calculation by means of the known stability constants, the various portions of the lower pH region of the extraction curves coalesce to give a single linear portion whose slope is equal to 2. In the region in which ZnT(phen) predominates, it can be shown that

$$\mu \simeq \frac{K_{DRP} \cdot K_{DRT}[\mathrm{H^+}]^2}{\beta_N[\mathrm{phen}]_o[\mathrm{H_2T}]_o}$$

which, when combined with equation (9), predicts that the slope of the plot of log D *vs.* pH will be zero in this region, where $D = K_{DC}$. Finally, at higher pH values, the predominant species in the aqueous phase is $\mathrm{ZnT_2^{2-}}$, and it can be seen that

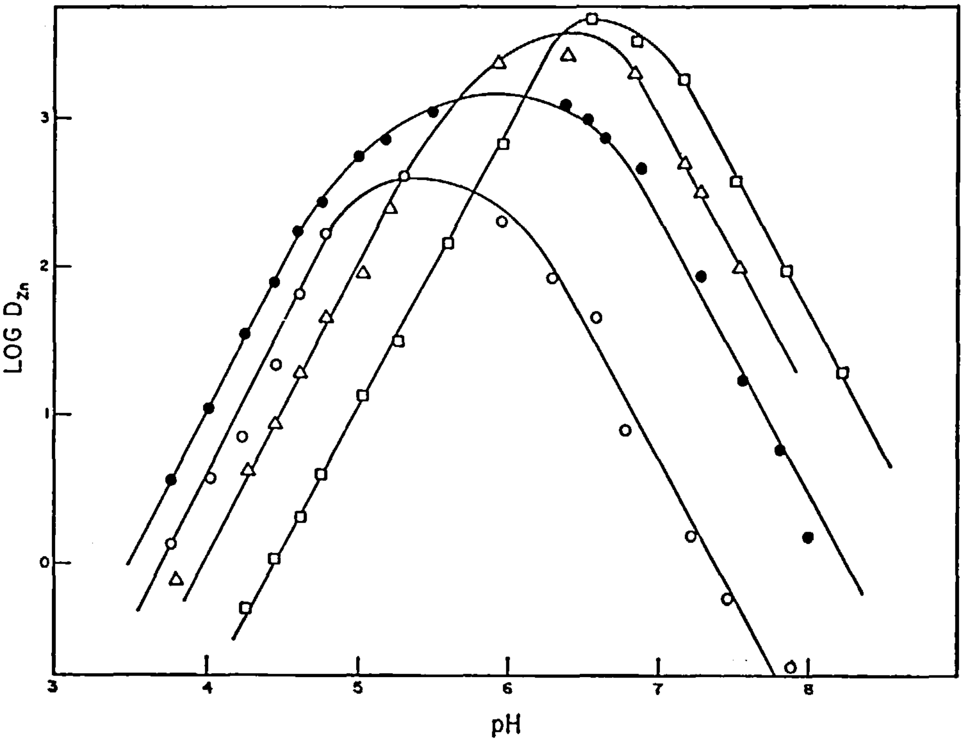
$$\mu \simeq \frac{K^2_{DRT}[\mathrm{H^+}]^4}{\beta_N[\mathrm{H_2T}]_o^2}$$

Upon substituting this into equation (9), one finds that in this high pH range the slope of the extraction curve will be -2. A decrease in log D with increasing log $[\mathrm{H_2T}]_o$ in this region should occur with a slope of -1 as was observed.

Extraction studies which parallel those just discussed were conducted with H_2T together with 4,7-dimethylphenanthroline and 3,4,7,8-tetramethylphenanthroline abbreviated as DMP and TMP, respectively, as ligands. Extraction data obtained as functions of pH and of ligand concentration for these two systems provided verification that the extracted species are ZnT·DMP and ZnT·TMP.

With the help of equations (8) and (9), it is possible to evaluate various component equilibrium constants using the extraction data. In Table 6 there are listed the formation and distribution constants for the mixed ligand chelates formed by toluenedithiol and either phen or one of its methyl derivatives. It is interesting to note that although the values of the formation constants (log β_N) increase about as rapidly as those of the acid dissociation constants of the phenanthrolines decrease (i.e., as the values of pK_a increase), the extraction constant shows only the beneficial effect of the increasing value of log β_N. This results from the fact that the value of log K_{DR} is high, so that the bulk of the phenanthroline is retained in the $\mathrm{CHCl_3}$ phase even at pH-values significantly smaller than pK_a, and consequently the concentration of phenanthroline in the aqueous phase is almost pH-independent. An additional advantage in using the methylated phenanthrolines arises from the increase in K_{DC}, so that higher values of D_{Zn} are achieved at the maxima. The increase in K_{DC} is matched by the increase in K_{DR}, so that this factor does not have any appreciable effect on the extraction constant.

FIGURE 6



Extraction of Zn(Phen)(T) into $CHCl_3$ at 25°C; = 0.10
$[H_2T]_0 = 1.0 \times 10^{-4} M$.[35]
$[Phen]_0$
○ = $1.0 \times 10^{-4} M$
● = $1.0 \times 10^{-3} M$
△ = $1.0 \times 10^{-2} M$
□ = $5.0 \times 10^{-2} M$

TABLE 6

Dissociation and Distribution Constants of Some 1,10-Phenanthrolines and Formation Constants of Their Zn(Phen)T Complexes between $CHCl_3$ and Aqueous Media at 25°C and Ionic Strength 0.10 M[35]

	pK_a	log β_N	log K_{DR}	log K_{DC}
1,10-Phenanthroline	5.05 ± 0.10	20.3	3.05 ± 0.15	3.60 ± 0.20
4,7-Dimethyl-1,10-phenanthroline	6.04 ± 0.14	21.9	3.70 ± 0.15	3.95 ± 0.20
3,4,7,8-Tetramethyl-1,10-phenanthroline	6.42 ± 0.11	22.3	4.76 ± 0.23	4.50 ± 0.30

As was mentioned earlier, ZnT_2^{2-} becomes the predominant Zn species in the aqueous phase at higher pH-values, and this makes it possible to use the H_2T-phen extraction data to evaluate the formation constant β_2 of this complex. Values of log β_2 of 25.9, 25.7, and 25.4 were obtained by using the data from the phen, dimethylphen, and tetramethylphen systems, respectively. This complex is among the most stable zinc complexes known [log β_2 is 17.1[36] for Zn(oxinate)$_2$; it is 16.4[37] for ZnEDTA; for ZnL_2 it is 18.2 when L is cysteine and 12.80 when β-mercaptopropionic acid[38]].

With the help of the values of log β_2 for ZnT_2^{2-} obtained from the ZnT·phen data together with the acid dissociation and distribution constants of H_2T, it is possible to evaluate the other equilibrium constants that appear in equation (8). Using a value of 8.04[39] for log $(K_{IP}K_{DR})_{QX}$ for THA•ClO_4, the value of the combined ion-association and distribution constants of the complex $2R_4N^+ \cdot ZnT_2^{2-}$ may be calculated to be 19.2. This is a very high value indeed, considering that simple divalent anions such as sulfate cannot be extracted by $CHCl_3$ to any significant extent using tetrahexylammonium cations with which to pair.

Although the maximum coordination number of zinc ion is four when a sulfur-containing ligand is involved, this is not necessarily true for nickel(II). Analytically interesting examples of this are seen with the nickel chelates of such sulfur-containing reagents as dithizone and 8-mercaptoquinoline,[40] which exhibit unusual spectra. The spectrum of nickel dithizonate differs from that of most of the other metal dithizonates. Whereas most of the other metal dithizonates (Hg, Pb, Zn, etc.) and the dithizonate anion have a single absorption band in the entire visible region (at about 500-530 nm with $\varepsilon_{mol} \sim 40 \times 10^3$), the spectrum of nickel dithizonate has four characteristic absorption bands (λ_{max} = 340, 475, 565, and 675 nm with ε_{mol} = 20.0, 27.0, 23.6, and 19.9 x 10^3, respectively). The spectrum of nickel dithizonate undergoes a profound change upon the addition of pyridine or other N-bases, collapsing to a single absorption band in the visible range between 520 and 535 nm and having ε_{mol} = 48-50 x 10^{+3} (Figure 7), thus resembling closely the spectra of the other dithizonates. The spectral behaviors of the nickel chelates of di-*p*-tolylthiocarbazone and di-2-naphthylthiocarbazone are closely analogous to that of the nickel dithizonate system.

Similarly, the spectrum of the nickel chelate with 8-mercaptoquinoline, has several absorption bands in the visible region (λ_{max} = 332, 390 and 538 nm with ε_{mol} = 11.6, 6.4 and 5.1 x 10^3, respectively) in contrast to most of the other metal 8-mercaptoquinolinates (e.g., those of mercury, lead, and zinc) and the reagent anion (8 MQ^-), which have only a single absorption band in the visible region, at 410-440 nm with $\varepsilon_{mol} \sim 7000$. As with the dithizones, on the addition of pyridine or other N-bases to nickel 8-mercaptoquinolinate the spectrum simplifies to a single band in the range of 420-435 nm with $\varepsilon_{mol} \sim 8000$.

From the behaviors of the sulfur-containing ligands studied here it would appear that, although adduct formation of the nickel chelate results in the appearance of an absorption band which is significantly stronger than that of the original chelate, the most strongly absorbing adduct band is obtained with the ligand having the strongest absorption.

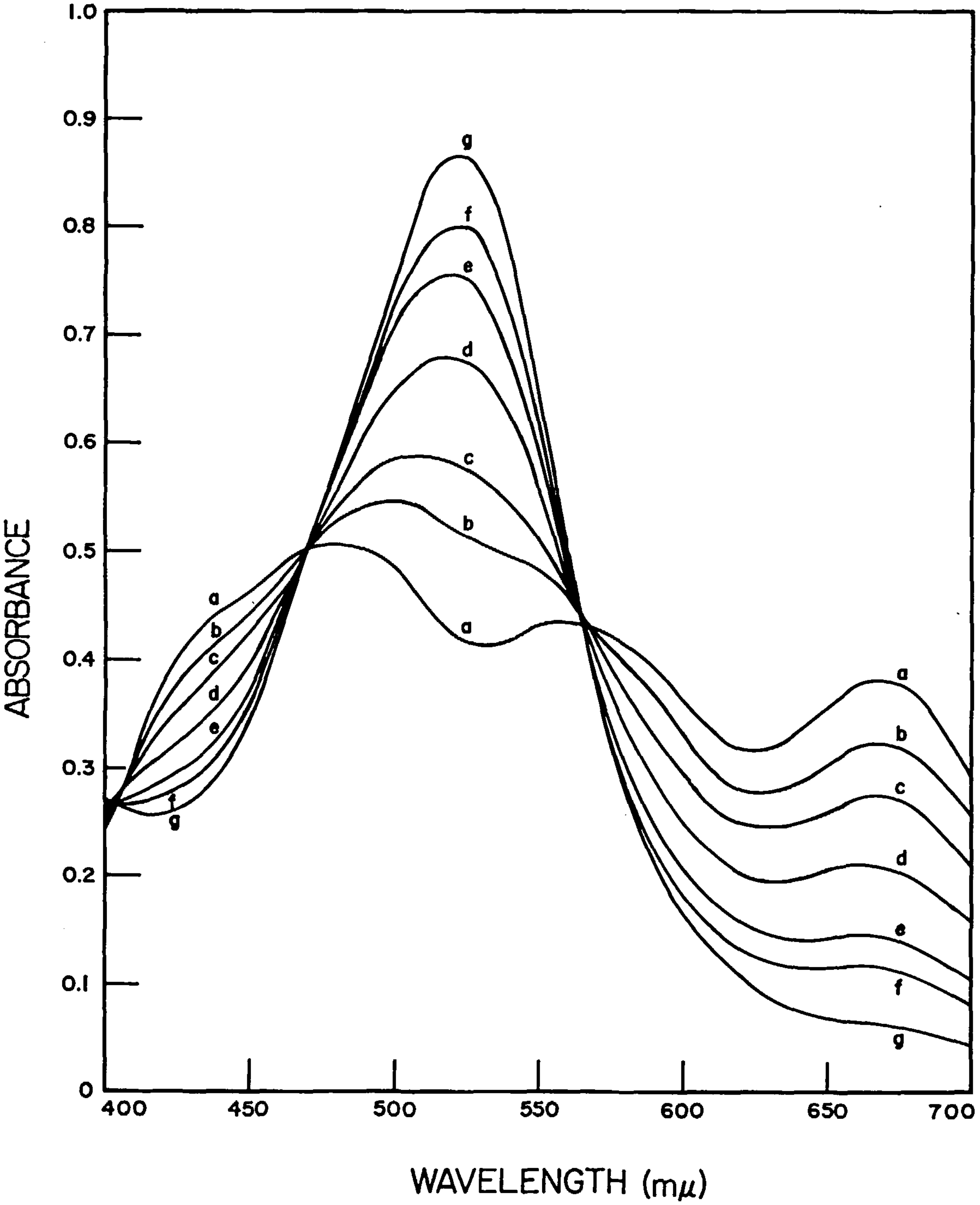
The change in the spectra of the nickel com-

TABLE 7

Adduct Formation Equilibrium Constants[40]

BASE	log K_{AD}				
	Nickel in $CHCl_3$	Dithizonate in CCl_4	Ni 8-mercapto-quinolinate in $CHCl_3$	Ni di-*p*-tolyl-thiocarbazonate in $CHCl_3$	Ni di-2-naphthylthiocarbazonate
Pyridine	1.08	1.46	−0.54	0.88	1.29
2-Picoline	−0.42	0.01	very weak	−0.53	0.04
3-Picoline	1.32	—	−0.44	0.94	1.59
4-Picoline	1.45	1.92	−0.16	1.22	1.72
2,6-Lutidine	−0.60		very weak	−0.82	—
α, α′-Dipyridyl	4.63		2.35	3.80	4.45
1,10-Phenanthroline	5.96		3.97	5.16	5.49
5-Nitro-1,10-phenanthroline	4.65		—	—	—
Ethylenediamine	3.86		3.38	3.74	—

FIGURE 7



Absorption spectra of NiDz$_2$–5-nitrophenanthroline mixtures in chloroform. $[\mathrm{NiDz_2}]_0$ = 1.88×10^{-5} *M*. $[\mathrm{5NO_2\text{-}phen}]_0$ = (a) 0.0, (b) 8.0, (c) 16.0, (d) 32.0, (e) 56.0, (f) 80.0, and (g) 160.0×10^{-6} *M*.

plexes (NiL_2) under investigation that accompanies the addition of pyridine or other bases can be used to determine the equilibrium constant of adduct formation (Table 7). The values of these formation constants exhibit the expected increase with adducting ligand basicity. In the cases of pyridine, 3-picoline, and 4-picoline the values of log K_{AD} increase linearly with the values of pK_a for these ligands. For 2-picoline and 2,6-lutidine, however, steric hindrance results in weaker adducts. In all of these cases, the adducts contain only one mole of base, accounting for only five coordination sites around the nickel. Five-coordinate nickel has been observed in 1:1 adducts of N bases with nickel chelates of other sulfur-containing ligands.[41] Yet ligands such as dipyridyl, phenanthroline, and ethylenediamine are bidentate, as indicated by the substantial increase in log K_{AD} so that in these complexes, nickel would appear to be six-coordinated.

It is interesting to note that in carbon tetrachloride, which is a poorer solvent for $NnDz_2$ than chloroform, the values of log K_{AD} are uniformly greater than they are in chloroform, a fact which may reflect some (weak) interaction between $NiDz_2$ and chloroform.

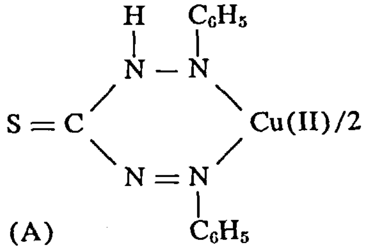
The reactions of pyridine, dipyridyl, phenanthroline, and ethylenediamine with the nickel complexes under investigation serve not only to give complexes that are more useful analytically (i.e., more stable, more soluble, and more highly colored), but also to effect changes in their properties that help to improve our understanding of the structures of the low-spin nickel chelates studied here. The behavior of these complexes is indicative of the square planar configuration of nickel. The multiple absorption bands observed in the spectra of the simple nickel chelates might be reasonably attributed to charge-transfer transitions. Gray and Ballhausen's[42] analysis of the spectra of a series of symmetrical square planar nickel complexes with ligands having π-orbital systems predicted the existence of two types of charge-transfer transitions: (a) ligand→metal, which should give two bands 10,000 cm^{-1} apart and (b) metal→ligand, which will have three closely spaced bands. Although the nickel chelates studied here have, at best, $\mathbf{D}_{2h}$ symmetry, the close resemblance of their spectra to those of the nickel, platinum, and palladium cyanides strongly indicates that, as in the cyanide cases, metal→ligand transitions are involved here.

The molecular orbital of particular importance in square planar metal complexes is one consisting of a $4p_z$ metal (nickel) orbital with four ligand "ring" π orbitals giving rise to a stable π-bonding orbital.[42] Because the strongly coordinating nitrogen bases can form axial bonds with nickel, they remove the $4p_z$ orbital from the ring π systems and eliminate the charge-transfer bands. Hence, the multiple absorption bands disappear in the presence of adduct-forming bases.

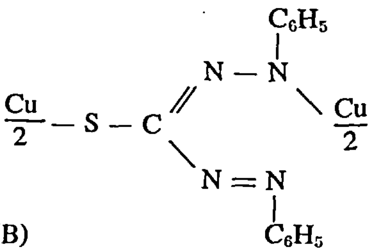
The "ring" π-orbital stability can be considered to rise as stability constants of the complexes increase. The latter are in order nickel dithizonate > nickel di-*p*-tolylthiocarbazonate > nickel 8-mercaptoquinolinate. In this case one would expect the corresponding values of K_{AD} to be in the reverse order, as was observed (Table 7). The plot of K_{AD}-values of nickel dithizone adducts against complex stability constants for the nickel di-*p*-tolylthiocarbazonate and nickel 8-mercaptoquinolinate systems gave two parallel straight lines, which indicates that factors influencing adduct formation in all cases are similar in nature.

NATURE OF "ENOL" DITHIZONATE COMPLEXES

Dithizone (diphenylthiocarbazone), characterized by Sandell as "the general heavy-metal reagent par excellence,"[26] and its chelates have quite properly received much attention since this reagent was introduced in 1925 by H. Fischer.[43] Fischer noted that some metal ions (principally those of copper, mercury, and silver) formed, in addition to the normal, or "keto" chelate (A), a second complex of lesser dithizone content referred to as an "enol" (B) complex, and formulated these two complexes as follows:



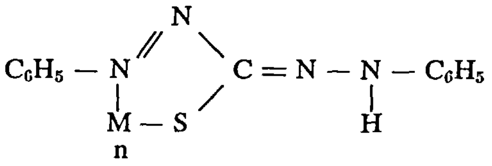
(A)



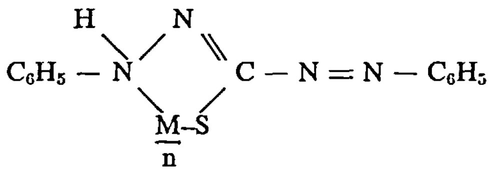
(B)

The first of these, the "keto" form, could be prepared in acidic solution with an excess of dithizone but the formation of the "enol" form was favored by the use of higher pH and excess metal.

Fischer's formulation of the analytically more significant "keto" forms went unchallenged until 1954, when Irving[44] conclusively proved that these involved bonding with sulfur:



or



The structures of the "enol" or "secondary" chelates have remained an insoluble puzzle down to the present. In these, because of the observed stoichiometry, dithizone has been thought to behave as a diprotic acid, which lost the remaining N-attached proton when the "enol" complex was formed. This seemed highly unlikely because dithizone itself was shown not to lose a second proton at least up to pH 14,[45] despite the low value of its first acid dissociation constant (pK_{a_1} = 4.7). Although acid-strengthening influences on organic liquids by metal chelation are frequently large, to invoke this effect in the case of copper(II) "enol" dithizonate, observed to form at a pH under 2,[45] would require a change of more than 10^{12} in effective acidity, almost 10^5 times larger than any other observed.

The case of copper(II) "enol" chelate provides a useful means of examining an alternate hypothesis to the formation of these complexes.[46] If the reaction with Cu(II) involves a dianionic dithizone species

$$Cu^{2+} + L^{=} \rightleftharpoons Cu\,L$$

the resulting complex should be paramagnetic, as are all copper(II) complexes. If, however, the species Cu L results from the interaction of the customary singly charged dithizonate anion L^- with copper(I), the chelate should be diamagnetic. Solutions of approximately 5 x 10^{-4} *M* "keto" and "enol" copper dithizonate in chloroform were prepared by extracting the copper(II) contained in a weakly acidic solution and from an ammoniacal ammonium chloride buffer of pH 10, respectively, with a chloroform solution of dithizone. The purple "keto" solution exhibited a normal copper(II) ESR spectrum (a quartet with $g = 2.059$), but the brown "enol" gave no signal indicating that it was diamagnetic and therefore was a copper(I) chelate.

The spectrum of the normal or "keto" copper(I) dithizonate in chloroform, which was prepared by dithizone extraction from a weakly acidic copper solution containing hydroxylamine, consisted of a single broad absorption band with a maximum at 478 nm. The spectrum of the "enol" chelate was quite similar but its band maximum was displaced to 446 nm. Inasmuch as the oxidation state of the copper in the "enol" complex is unity, it becomes likely that its chloroform solution should contain a stoichiometrically related quantity of diphenylthiocarbadiazone (DTD), the oxidation product of dithizone, according to the reaction

$$2\,Cu^{2+} + 3\,HDz \rightarrow 2\,Cu\,Dz + DTD$$

A difference spectrum calculated from the spectra of Cu(I)Dz and the Cu(II) "enol" complex was found to resemble closely that of DTD (λ_{max} = 425 nm). Equilibrating the $CHCl_3$ solution of the Cu(II) "enol" complex with aqueous hydroxylamine at pH 4-5, which might be expected to reduce DTD or other oxidation products to dithizone, resulted in the formation of some normal purple Cu(II) dithizonate. Similarly, the addition of dithizone to a solution of Cu(I) dithizonate resulted in the formation of some purple Cu(II) chelate, proving that the so-called "keto-enol" equilibrium[45] for Cu(II) dithizonate is really a Cu(II)-Cu(I) redox equilibrium.

Because of the unusual coordination number of copper that would be required to explain a 1:1 dithizone complex, it was decided to measure the molecular weights of both the Cu(II) "enol" and Cu(I) "keto" complexes. Vapor-pressure osmometry of solutions of these compounds gave values of 6300 ± 300 for the "enol" and 3100 ± 200 for the Cu(I) primary complex. Thus, through intermolecular bonding copper may achieve a coordination number of four. Although the possibility exists that the diamagnetism observed with the Cu(II) "enol" results from metal-metal bonding with consequent electron-pairing, it would seem to be improbable because of the need for dithizone to lose a second proton to form an uncharged, chloroform-soluble species.

Other "enol" dithizone complex may be formed by mechanisms different from the redox scheme involved in the case of copper. Thus it was recently reported that normal mercury(II) dithizonate reacted with $HgCl_2$ to form a mixed ligand complex, ClHgDz.[47] Inasmuch as similar complexes formed in which nitrate or bromide replaced chloride, it is likely that under conditions favoring "enol" formation, namely when Hg(II) is in excess, mixed-ligand chelates form. We found that a solution of the pink Hg(II) "enol" dithizonate in chloroform changed to yellow upon equilibration with dilute NH_3. That the resulting mercury complex was not the primary or "keto" form (also yellow) was seen from the failure of either KI or $Na_2S_2O_3$ solutions to decompose it, although such treatment readily transformed the "keto" complex into the green free dithizone in $CHCl_3$. The complex, which may well be N_2NHgDz, is thus more stable in the presence of the masking agents and may provide the basis for novel analytical applications.

To attribute the formation of the "enol" or "secondary" series of metal dithizonates to the formation of a doubly charged dithizonate anion, therefore, is no longer possible.

INFLUENCE OF SOLUBILITY PARAMETER ON EXTRACTION EQUILIBRIA

One would not a priori expect the theory of regular solutions[48] to apply to a pair of liquids that only are not immiscible but include a highly associated liquid, water. Nevertheless, there have been several interesting studies of the application of the solubility-parameter concept to solvent extraction. Irving and Lewis[49] used an expression involving the basicity and the dielectric constant as well as the solubility parameter of a diluent to account for the effect of diluent on the value of *D* for indium between aqueous hydrochloric acid and a mixture of methylisobutylketone with any of a variety of diluents. Siekierski and Olszer[50] were able to correlate the *D*-values for $GeCl_4$ in 18 organic solvent–aqueous system pairs with the solubility parameter, using the following expression based on the theory of regular solutions:

$$2.3\,RT\log K_{\mathrm{D}} = V_{\mathrm{C}}[\delta_{\mathrm{C}} - \delta_{\mathrm{W}})^2 - (\delta_{\mathrm{C}} - \delta_{\mathrm{O}})^2]$$

where K_D represents the distribution coefficient expressed as a ratio of mole fractions, δ_C and V_C represent the solubility parameter and molar volume of the distributing species, respectively, and δ_W and δ_O represent the solubility parameters of the aqueous and organic solvent phases, respectively. One can ignore the awkwardness of considering the applicability of regular solution theory to water, provided that the behavior of water can be considered to remain essentially constant where various organic solvents are employed. On this reasonable assumption, Siekierski and Olszer, adopting one organic solvent (subscript S) as a comparison standard, modified the above equation to

$$\frac{2.3\,RT}{\delta_O - \delta_S}\log\frac{K_D}{K_{D_S}} = -V_C(\delta_O + \delta_S) + 2V_C\delta_C$$

which, on plotting the left-hand side against $(\delta_O + \delta_S)$ for the distribution data for a series of solvents, will give a line of slope — V_C and intercept $2V_C\delta_C$. By means of this expression, values of δ_C and V_C for the germanium halides were obtained that were in good agreement with values obtained from the heats of vaporization and molar volumes of the halides.

Suzuki and coworkers[51] successfully employed a modified version of the Siekierski and Olszer approach in relating the variation of the distribution of several β-diketones and their scandium chelates to the solubility parameter of the organic phase. Fairly good correlation was also obtained in studies of some 8-quinolinols and their copper chelates.[52]

The relevance of the solubility parameter has also been demonstrated in ion-association extraction equilibria.[53] On a purely electrostatic basis, one would surely predict positive free energy changes for reactions such as

$$Q^+ + X^- \rightleftharpoons (Q^+ \cdot X^-)_{org}$$

because of the work required to transfer the pair of dissociated ions from water ($\varepsilon \sim 80$) to an organic solvent of low polarity ($\varepsilon < 10$), even when this is corrected for the energy involved in ion pairing. On this basis, as well as on the lack of correlation between the values for the extraction constant of trilaurylammonium perrhenate into a series of solvents and the dielectric constants of these solvents, Diamond[54] suggested that short-range "chemical" interactions existed between the extracted ion pair and the organic solvent. A plot of log K_{ex} against the solubility parameter was very nearly linear, however, indicating that the postulation of "chemical" interaction is unnecessary.

Higuchi et al.[55] found that the extent of extraction of protonated dextromorphan paired with various anions into cyclohexane increased as the concentration of chloroform in the organic phase was increased, and attributed to the formation of a tetra- or penta-solvate with chloroform on the basis of the slope of the plot of log D versus log $[CHCl_3]$. They overextended this generally useful technique of using extraction-equilibrium data to determine the stoichiometry of an extracted complex by ignoring the significant change in the solvent that resulted from the high $CHCl_3$ content (up to 10 M in $CHCl_3$). A plot of their values of log D against the solubility parameter of the cyclohexane — $CHCl_3$ mixed solvent exhibited good linearity.[53] It may be seen, therefore, that the role of the solubility parameter merits greater consideration in a variety of solvent-extraction systems than it has generally been accorded.

A further extension of this approach to evaluating ion-association extraction equilibria would be to calculate a value of the K_D of the ion pair to permit the separation of the extraction constant into the component factors K_D and K_{IP}, the aqueous ion-pair formation constant. Preliminary studies of the extraction equilibria of a series of tetraalkylammonium halides in a series of organic-aqueous solvent pairs appear very promising.[56]

KINETIC FACTORS IN SOLVENT EXTRACTION

The rates at which extractions take place involve both mass transfer and homogeneous chemical reactions taking place in either or both phases. Mass-transfer rates are sufficiently rapid that, using the conventional means of contacting the phases in analytical extraction processes, the overall extraction equilibration would occur within a minute or two except when one or more of the chemical reactions are sluggish. In this regard, coordination (particularly, chelation) complexes form and dissociate much more slowly than do ion association complexes, so that extractions involving the former are more likely to require longer shaking periods.

Increasing attention is being given to the kinetic aspects of extraction processes, not only to describe more completely the conditions necessary for optimal extraction separations, but also because of the information concerning homogeneous reaction-rate mechanisms provided thereby. In 1962, Honaker and Freiser[57] found that the rate-determining factor in the extraction of zinc(II) by dithizone in chloroform was the formation of the 1:1 zinc dithizonate chelate in the aqueous phase and that this was characterized by a second-order rate constant of $10^{6.6}$ M^{-1} sec^{-1}. The possibility of evaluating such large rate constants by solvent-extraction techniques can be seen to arise from the ability to provide very low, controlled concentrations of one of the reactants. This work was extended by McClellan and Freiser[58] and Oh and Freiser,[59] to the extractions of a series of metal ions and substituted dithizones, all of which were found to be kinetically controlled by the aqueous formation of the 1:1 metal dithizonate. The importance of the role of coordinated water in the rate of metal chelation could be seen from the parallel changes observed in the rates of water loss of the metal ions as reported by Eigen[60] and the rates of 1:1 dithizonate formation ($Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$). It is open to question whether this reflects greater water loss in the first chelation step due to a drop in the metal-ion coordination number (Zn^{2+} ?) or a generally greater resistance to the loss of the first water molecule, but it is highly likely that a kinetic order of complex formation for metal ions analogous to the equilibrium stability order for metals, which is almost independent of the nature of the ligand involved, will govern chelate extractions. One could exploit such rate differences in bringing about separations that, under equilibrium conditions, would be impossible. Thus, Irving et al.[61] could extract mercury in the presence of copper using dithizone in chloroform, McKaveney and Freiser[62] could separate many metals from chromium(III) using acetylacetone, and McClellan and Sabel[63] could extract zinc in the presence of nickel with dithizone by using short shaking time.

When some of the water coordinated to zinc ion is replaced by another ligand, such as acetate or thiocyanate, the rate of the reaction of the resulting complex with dithizone increases, despite the decrease in electrical charge.[64] A plot of the logarithm of the apparent second-order rate constant against the logarithm of the auxiliary ligand concentration serves for the determination of the equilibrium formation constant of the complex as well as for that of its reaction rate constant. From the kinetic behavior, it would appear that a mixed ligand complex, such as ZnOAcDz, is an intermediate in the formation of the extractable chelate. Because the $ZnOAc^+$ reacts some twenty-five times as rapidly as the hydrated zinc ion, whereas acetate does not affect the rate of extraction of $NiDz_2$, the presence of acetate further increases the difference in the rates of extraction of zinc and nickel, making a kinetically-based separation feasible.

ION-SELECTIVE LIQUID — LIQUID MEMBRANE ELECTRODES

The application of solvent-extraction chemistry to the development of suitable organic-phase components of ion-selective electrodes presents an exciting prospect for greater understanding of extraction processes as well as for new and improved electrochemical sensing devices. Ion-selective liquid membrane electrodes (LME) operate in a manner analogous to the glass pH electrode. Both types develop a potential across a thin conducting "membrane" which is glass in the pH electrode and a thin layer of an organic phase of a suitable extraction system in the LME. In the first LME introduced, a calcium-selective electrode, the organic phase contained the calcium chelate of dioctylphosphoric acid.[65] An internal aqueous "filling" solution containing calcium and chloride ions contacts the inside surface of the organic phase which is separated from the external or test solution by a thin, relatively inert, polymeric membrane. The chloride ion in the internal solution provides a stable potential between the Ag-AgCl internal reference electrode and this solution. Changes in electrode potential are due only to changes in the calcium-ion activity in the test solution. Nernstian responses are observed in the range of calcium-ion concentrations from $10^{-1}M$ to $10^{-4}M$. Since 1967, Ross and his associates[66] have applied a number of extraction systems of both chelate and ion-association types to the development of ion-selective electrodes for copper, divalent metal ions, chloride, fluoborate, perchlorate, and nitrate ions which can be used in the 10^{-1} to 10^{-5} M range.

At the University of Arizona, a number of different extraction systems have been employed

TABLE 8

Summary of Behaviors of Anion-Responsive Electrodes at 25 °C[68]

Ion	Slope (mV/log *a*)	Concentration range for linear response, *M*	Useful concentration range, *M*
Perchlorate	59.2	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Chloride	56.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Bromide	59.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Iodide	59.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Nitrate	57.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Sulfate	36.0	10^{-2} - 10^{-4}	10^{-1} - 10^{-5}
Thiocyanate	58.0	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Oxalate	40.0*	10^{-2} - 10^{-4}	10^{-1} - 10^{-5}
Formate	53.0*	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Acetate	53.0*	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Propionate	57.5*	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}
Benzoate	58.6*	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
Salicylate	56.0*	10^{-1} - 10^{-3}	10^{-1} - 10^{-3}
m-Toluate	58.0*	10^{-1} - 10^{-3}	10^{-1} - 10^{-4}
p-Toluate	57.0*	10^{-1} - 10^{-3}	10^{-1} - 10^{-5}

*mV against log C taken

in developing ion-selective electrodes. For example, a solution of a metal 8-quinolinolate in either pentanol or decanol can be used to make serviceable copper- and nickel-responsive electrodes,[67] but chelates of acetylacetone, thenoyltrifluoroacetone (TTA), or dithizone would not function. The further evaluation of a variety of chelate systems in this fashion would be of great importance. A series of ion-selective electrodes was prepared using ion-association extraction systems in which salts of methyl tricaprylyl ammonium ion (Aliquat 336) dissolved in decanol were used as "liquid membrane" components[68] (Table 8). These are stable electrodes which provide rapid and reliable means for determining the activities of both organic and inorganic anions in the range of concentrations from 0.1 *M* to 10^{-4} or 10^{-5} *M*. The interference of a particular anion was generally higher as the extractability of the corresponding quaternary ammonium salt increased. From the pH dependencies of the electrode responses for anions having proton affinity such as acetate and benzoate, it was found that the electrodes discriminated between the anion and the neutral acid. Thus, it would be possible to determine the activity of acetate in the presence of acetic acid. In a parallel study using tetraphenylborate salts of tetraalkylammonium ions dissolved in decanol, cation-responsive electrodes were prepared for tetramethyl-, -ethyl-, and -propylammonium ions.[69] More recently, liquid membrane electrodes responsive to anions of various amino acids including leucine, isoleucine, glutamic acid, and tryptophane have been prepared.[70] This approach offers great analytical promise for a wide range of organic and biochemical substances.

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