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HOMOGENEOUS LIQUID - LIQUID EXTRACTION OF METAL CATIONS AT NEAR NEUTRAL PH

City University of New York

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Homogeneous Liquid - Liquid Extraction of Metal Cations at Near Neutral pH

by

Nandani Rajapakse

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

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Abstract

Homogeneous Liquid-Liquid Extraction of Metal Cations at Near Neutral pH

by

Nandani Rajapakse

Advisor: Professor H. L. Finston

Solvent extraction procedures are, for the most part, performed at low pH to prevent hydrolysis of the cations, the very condition which limits the concentration of the extracting ligand, an anion. At low pH the undissociated species is predominant and, therefore, the formation of extractable species is not favored. The cation of interest can be maintained in solution at near neutral pH by adding an auxiliary complexing agent to form a charged complex, and then the cation can be extracted into a non-polar solvent by equilibration with another complexing agent which forms a neutral complex. Thus, it is possible to maintain conditions of higher pH to favor the enolate ion form of chelating extractants, and the anionic form of the various monodentate complexing agents. This technique has been studied in conjunction with

homogeneous liquid-liquid solvent extraction into propylene carbonate, which forms a homogeneous solution with an aqueous phase when heated above 71°C. Thus, extraction is achieved with heating and cooling upon which the phases separate. Also, propylene carbonate yields a homogeneous phase with water and ethanol in the ratio, propylene carbonate/water/ethanol 2:2:1; thus permitting direct comparison by, e.g., absorption spectrophotometry of aqueous phase, organic phase and calibration standards.

Thenoyltrifluoroacetone chelates of Fe(III), Co(II) and Cu(II) have been extracted from an aqueous phase containing tartrate, at pH values from 6 to 8, into propylene carbonate by the homogeneous liquid-liquid extraction technique. The extractions were very rapid, and quantitative under optimum coditions. Iron(III) was also quantitatively and rapidly extracted with acetylacetone under these same conditions. Normal extraction technique into propylene carbonate and toluene also gave rapid and quantitative results for Fe(III)-TTA from this aqueous medium. These results, attributed to the significantly higher ratio of enolate ion, suggest an alternative mechanism for the synergic effect of various organic bases in TTA extractions. Acid-base reactions in the organic phase yield similar higher concentrations of enolate ion in the aqueous phase.

A method was developed to extract uranium from ores and fuel elements using homogeneous liquid-liquid solvent extraction.

Dedication

To my parents, for their support and encouragement throughout my studies.

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Chapter I

INTRODUCTION

An examination of the development of analytical chemistry during the past few decades reveals an increase in popularity of such fields of analysis as chromatography, ion exchange, electrodepositions and solvent extraction. This trend is easily explained when one considers the increasing need for methods of separating complex materials. Solvent extraction is a popular separation technique because of its elegance, simplicity, speed, and applicability to both tracer and macro amounts of metal ions. With apparatus as simple as a separatory funnel, extraction procedures can offer a complete separation of trace- or macroquantities in as little as a few minutes. Solvent extraction technique can be used for purposes of preparation, purification, enrichment, separation, and analysis over a very wide range of concentrations corresponding to microanalysis and even large scale production processes. A further advantage of the extraction method over the widely used precipitation method lies in the cleaner separations that can be achieved by the former.

The liquid-liquid extraction phenomenon is based upon the fact that a substance dissolved in a system of two immiscible or slightly miscible liquids will distribute between the two layers in a definite manner. The most important factor for separation is the relative concentration of the solute in both solvents and it is usually expressed as the distribution or partition coefficient, i.e., the ratio of the activity of the solute species in one phase to that in the other. Charged species of cations are more soluble in polar aqueous solutions whereas neutral species are more soluble in less polar organic medium. To achieve a good separation, the various components must have different distribution coefficients.

Solvent extraction procedures for cations are normally performed under very acidic conditions which is necessary in order to prevent precipitation of their respective hydrated oxides. It is possible, even under relatively acid conditions, to lose significant amounts of analyte by hydrolysis even when only trace concentrations are present. However, acidic conditions are not favorable for the formation of extractable (i.e., neutral) metal cation complexes with all the usual complexing agents. For example, the competing associations of H^+ with anions of typical extracting agents, such as CN^-, SCN^-, the carboxylates and the enolate ions of beta-diketones such as thenoyltrifluoroacetone, etc., to form the very weak undissociated acids (which are themselves extracted

into the organic solvents) are favored at low pH. The ligands are anions, and the ratio of anion to undissociated acid is a function of pH;

$$[\text{Anion}]/[\text{Acid}] = 10^{(\text{pH} - \text{pK})}$$

Thus for every unit increase in pH there is a ten-fold increase in the ratio [anion]/[acid].

It is possible to maintain the cation of interest in solution at near neutral pH by adding a complexing agent to form a charged complex and, then, to extract the cation into a non-polar solvent by equilibration with another complexing agent which forms a neutral complex. These conditions of higher pH favor the enolate ion form of chelating extractants and the anionic form of the various monodentate complexing agents. The criteria for an ideal auxiliary ligand are that it should form a stable charged complex soluble at near neutral pH (6-8) and yet not hinder the formation of an uncharged complex with the extracting chelate. Decomposition of complexing agents may occur at higher pH. For example, at pH 9, thenoyltrifluoroacetone(TTA) cleaves into trifluoroacetic acid and acetylthiophene faster than it enolizes(1).

A homogeneous liquid-liquid extraction method was devised by Murata et al. to extract molybdenum(VI)(2) and later Murata(3) and also Ting (nee Hong) et al.(4,5) used the same method to extract several other cations and obtained quantitative extractions in very short time.

The method is based on high solubility of the organic solvent in water at a high temperature and is characterized by immediate formation of the complex upon attaining a state of homogeneous solution. The single homogeneous phase separates into two phases again upon cooling. During these sequential procedures, the species in the aqueous phase transfers into the organic phase, i.e., the extraction is achieved. This method of equilibration, by achieving a homogeneous state, is different from the common mechanical shaking method. Molecules of organic solvent rather freely enter into the aqueous solution and, consequently, the water structure of the aqueous media and the environment of solute species will be altered remarkably by participation of the organic solvent molecules. This "unshielding" of the environment must affect extraction. Such a condition is not satisfied in the conventional extraction method.

Propylene carbonate, which has found recent use in solvent extraction and also in electrochemical studies(6-10), is a most suitable organic solvent for homogeneous liquid-liquid extractions. It has a high dielectric constant (65 at 25°C), low vapor pressure, high boiling point, high flash point, and the unusual property of being completely miscible with aqueous solutions above 71°C and it becomes immiscible again upon cooling(11,12). Another special property of propylene carbonate permits a direct comparison of analyte concentration in each phase with standard.

Propylene carbonate/aqueous/ethanol in the ratio 2:2:1 yields a single homogeneous phase. Thus, propylene carbonate and ethanol are added to the aqueous phase (and standard) and aqueous plus ethanol are added to the propylene carbonate phase enabling direct comparison and material balance(13).

The only disadvantage of propylene carbonate as an extractant is the relatively high solubility of propylene carbonate in water. Although propylene carbonate is soluble in water, the metal chelate complex remains in the organic phase. Large scale processing of aqueous media could result in significant losses of propylene carbonate. The possibility of recovering propylene carbonate from aqueous solutions was investigated.

It was anticipated that extractions at near neutral pH using homogeneous liquid-liquid extraction technique would afford more rapid equilibrations under all conditions and greater extraction efficiencies under optimum conditions.

Homogeneous liquid-liquid extraction of Fe(III), Co(II), Cu(II) and UO_2^{2+} would appear to have possible application to hydrometallurgy. Hydrometallurgy, in general, has advantages for application to complex ores, may offer considerable cost savings by direct treatment that eliminates crushing, grinding, and flotation treatments, and can eliminate the air pollution associated with smelters.

The systems studied include Cu(II), Co(II), Fe(III) complexed with tartaric acid as auxilliary ligand, and both TTA and acetylacetone in propylene carbonate as extractants. The advantage of TTA over acetylacetone does not exist at these higher pH's. TTA is a stronger acid than acetylacetone and consequently is more highly dissociated at low pH than is acetylacetone. However at pH > 6 the difference may not be significant. Also a method was developed to extract uranium from ores and spent fuel elements.

Chapter II

THEORY AND REVIEW OF LITERATURE OF SOLVENT EXTRACTION

2.1 Principles of Solvent Extraction

2.1.1 Phase Rule

Almost all the techniques of chemical separation involve the distribution of matter between two different phases, and for all phase distributions we can apply Gibbs Phase Rule.

$$F = C - P + 2$$

where P is the number of phases, F the variance or degrees of freedom, and C the number of components. For the case of solvent extraction we deal with two immiscible solvents and one solute distributed between them. Thus P = 2, C = 3 and F = 3. If we fix two of these parameters by holding temperature and pressure constant, which is

normal practice since we carry out extractions at room temperature and atmospheric pressure, then the only remaining variable is concentration in each phase. Thus, there is a definite relationship between the solute concentration in each of the solvent phases, which is quantitatively described by the distribution law.

2.1.2 Distribution Law

Only the relative concentration of solute in each of the phases is derived from the phase rule. However, the distribution law states further that the ratio of solute is invariant, i.e., it is independent of total concentration. The distribution law was first expressed by Berthelot and Jungfleisch(14) and further elaborated by Nernst(15) in 1891. For a solute X distributing between solvents 1 and 2,

$$X_1 \rightleftharpoons X_2$$

$$K_D = \frac{[X_2]}{[X_1]}$$

That is, a solute will distribute between two essentially immiscible solvents in such a manner that, at equilibrium, the ratio of concentra-

tions of the solute in the two phases, at a particular temperature and pressure, will be a constant provided that the solute has the same molecular weight in each phase.

2.1.3 Thermodynamic Derivation of the Distribution Law

A thermodynamic explanation of the conditions existing in each of the phases at equilibrium will be useful in understanding the nature of the approximations involved in the distribution law. Equilibrium is attained at constant temperature and pressure when the chemical potentials, ϕ (partial molal free energies), of the solute in the two phases are equal. Thus,

$$\phi_1 = \phi_2$$

where the subscripts 1 and 2 refer to the respective solvent phases. Expressing ϕ in terms of molality and activity coefficient, we have

$$\phi_1^{\circ} + RT \ln m_1 + RT \ln \gamma_1 = \phi^{\circ}_2 + RT \ln m_2 + RT \ln \gamma_2$$

where ϕ° represents the chemical potential of the solute in a hypothetical ideal 1 molal solution; m is the molal concentration of the solute and

γ, the molal activity coefficient of the solute. From this we obtain an expression for the molal distribution coefficient, K_D

$$K_D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-(\phi^o_2 - \phi_1^o)/RT}$$

As long as the presence of the solute does not significantly affect the mutual solubilities of the two solvents, and this is generally the case, ϕ^o_1 and ϕ^o_2 are constants. Thus,

$$K_D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} K'$$

where K' is a constant at constant temperature.

2.1.4 Distribution Ratio

Distribution ratio, denoted by D, is the concentration ratio of the solute including all species in the respective phases.

$$D = \frac{\text{Total solute concentration in the organic phase}}{\text{Total solute concentration in the aqueous phase}}$$

When we are aware of all the interactions that occur it is usually possible to evaluate them in order to obtain D as a function of the experimental parameters. When there are no interactions of the distributing species, then D and K_D are identical.

2.1.5 Percentage Extraction

Percent extracted, %E, is the term used to describe extraction efficiency for practical purposes, and it is related to the distribution ratio, D, by the following equation:

$$\%E = \frac{100\ D}{D + (V_w/V_0)}$$

where V_0 and V_w represent the volumes of the organic and aqueous phases respectively.

2.1.6 Process of Extraction

Although details of the specific nature of the interactions differ from system to system a helpful organizational pattern may be adopted which is based on three essential aspects common to every metal extraction system(16):

a. **Formation of an Uncharged Complex**

This step involves reactions of the metal ion in the aqueous phase leading to the formation of an extractable species. Complex formation may result from coordination, including chelation, or by ion association, or by a combination of coordination followed by ion association.

b. **Distribution of the Extractable Complex**

This is the second aspect and the simplest from a standpoint of the mathematics. The distribution of the extractable species between the two liquid phases follows the distribution law. However, factors affecting extractability are quite complex.

c. **Interactions of the Complex in the Organic Phase**

This includes polymerization of the complex, dissociation of the complex and interactions with the reagent, and also polymerization of unreacted ligand.

This type of organizational pattern for extraction processes applies just as well for extraction of organic compounds with the possible simplifying modification that many such compounds are directly extractable without the necessity for a complex forming reagent.

2.2 Formation of Metal Complexes

Since the formation of an extractable complex is a vital step in the extraction process, the nature of metal complexes and factors governing their formation will now be explored.

2.2.1 Coordination Complexes

Our understanding of the metal complexes which we term coordination compounds derives from Werner's conception of the coordination of ions or groups in a definite geometric arrangement about a central ion. This concept, in turn, is best explained in terms of Lewis acid-base theory which was expounded by both Sidgwick(17) and Lowry(18).

a. Acid-Base Character of Coordination Complexes

The application of the Lewis electronic theory of acids and bases in discussion of coordination compounds is very useful. According to the Lewis theory, acid-base reactions involve the formation of a coordinate

covalent bond between an acid, defined as an electron-pair acceptor, and a base, defined as an electron-pair donor. A metallic cation, being electron-pair deficient, is considered as a polybasic acid capable of reacting with several basic entities, the number of which is related to the coordination number of the metal ion.

The basic entities, characterized by possesing at least one pair of electrons, are usually either neutral or negative. The nature of the bonds vary from almost completely covalent to almost completely electrostatic. The transition between these extremes may be interpreted in terms of polarizabilities of the ions or groups involved(19). As a ligand approaches a cation, a deformity or polarization is induced in the ligand due to interaction with the highly charged metal cations, and with metal cations having a non-inert gas electronic configuration.

b. Factors Influencing Coordination

From consideration of the metal cation as a Lewis acid we can infer that the stability of a metal coordination complex will depend upon

1) factors related to "acidity" of the metal ion,
2) factors related to the "basicity" of the coordinating ligand, and
3) special factors related to configuration of the resultant complex.

c. Types of Coordination Complexes

Among the many metal complexes of interest in extraction, several types may be distinguished.

1) Simple coordination complexes - metal ions combine with monodentate ligands in a number equal to the coordination number.
2) Chelates - Metal ions combine with polydentate ligands which can occupy more than one position in the coordination sphere of the metal cation.
3) Heteropoly acids - These are distinguished by the presence of a central complex ion rather than a central monoatomic ion.

2.2.2 Chelate Complexes

Chelating reagents play an important role in extraction of metals because they comprise an impressive body of both useful extracting agents and also masking agents. Metal chelates represent a type of coordination compound in which a metal cation combines with a polyfunctional base capable of occupying two or more positions of the coordination sphere of the metal cation to form a cyclic compound. The latter should be a stable ring structure, five or six membered.

The structural factors of reagents which determine their effectiveness as chelating agents are the basic strengths of the functional groups, electronegativity of the bonding atoms, the size of the chelate ring and the number of chelate rings formed.

2.2.3 Ion Association Complexes

A major fraction of the extractable species other than neutral chelates exist in the organic solvent as ion association aggregates. Although ion-pair formation involves physical rather than chemical bonds, both types of complexes behave in accordance with the Mass Action Law. Hence, for two ions A^+ and B^- which associate to form (A^+,B^-)

$$A^+ + B^- \rightleftharpoons (A^+,B^-)$$

the equilibrium expression is

$$K = \frac{[(A^+,B^-)]}{[(A^+)][B^-]}$$

There are two types of ion association complexes:

a. Ion pairing with no chelation - (A^+,B^-).

b. Ion pairing and chelation - $\left[M(L)_n\right]^{+n} Y^{-n}$

Bjerrum(20) predicted such complexes and their behavior by relating the value of ion pair formation constant to the dielectric constant of the solvent, ε, to the temperature, and to the size of the ions involved.

Thus,

$$K = \frac{4\pi N}{1000} \frac{e^2}{\varepsilon kT} Q(b)$$

$$b = \frac{e^2}{a\varepsilon kT}$$

where N is the Avogadro's number, e is the unit of charge, k is the Boltzmann constant, T is the absolute temperature, Q(b) is a calculable function, and a is an empirical parameter which has been interpreted as the distance between charge centers of the paired ions when in contact.

2.3 Distribution of Extractable Species

2.3.1 Solubility and Distribution

The relationship between the ratio of solubilities in the two solvents and the distribution coefficient is not unequivocal. Two major factors responsible for the disparity are

a) The activity coefficients in each phase change as the total solute concentration changes.

b) The second cause is the effect of the presence of the second solvent on the solubility of solute in the first solvent. The solute may form a solvate with the second solvent which has different solubility in the first solvent than the original solute species.

2.3.2 Factors Affecting Solubility

The process of solvation which consists of solute molecules forcing themselves between solvent molecules may be classified by the type of bonds involved(21).

a) Electrostatic Bonds

These bonds involve forces between ion-ion, ion-dipole, and/or dipole-dipole and we may recall that lattice energies are a guide to solubility for electrolytes.

b) Hydrogen Bonds

Hydrogen bonds are essentially electrostatic but warrant special consideration because of their overriding importance. The solubility of a substance in water or alcohol is determined more by its ability to form hydrogen bonds than by its polarity as measured by dipole moment.

c) Chemical Bonds

These depend upon the specific system and are in general temperature dependent. We are particularly concerned with Lewis acid-base interactions; the solvent action of water, alcohol, ether, etc. reflect their basic characters.

2.3.3 Solubility Characteristics of Chelates

The chelating agents most frequently used for solvent extraction have one uncharged and one anionic basic group thus satisfying both the electron valency and maximum coordination of the cation. The chelates are essentially covalent in character and consequently are more soluble in organic solvents than in water.

The intermolecular forces which characterize solution of chelates in organic solvents are "weak physical forces." For such solutions we may apply Hildebrand's theory of regular solutions(22).

The solubility parameter, δ, of solute and solvent, defined as the square root of the heat of vaporization of the liquid per unit volume is a measure of the cohesive energy density, also called the "internal pressure." The solubility increases with increasing similarity of the respective solubility parameter values. Similarly, the heat of fusion of a solid and temperature will affect its solubility in all solvents; consequently the same considerations lead to the choice of best solvent.

2.3.4 Solubility Characteristics of Ion Association Compounds

The solubilities of these polar compounds in organic solvents depend upon, for the most part, their structural resemblance to the various organic solvents. When the complex contains large organic solvents the solubility in organic solvents is a reasonable expectation.

Oxonium systems in which the solvent molecules participate in the formation of the extractable complex warrant special consideration. The basic character of the oxygen atom may enable the incorporation of the solvent molecule in the coordination sphere of the metal cation giving rise to an ion association compound that strongly resembles the solvent.

The ability of oxonium solvents to compete with water for the metal ion depends upon the basicity of the oxygen in the solvent molecule, which in turn depends upon the steric availability of the electrons at the oxygen atom and upon the electron density.

The competitive strength of water may be reduced by the use of high concentrations of salts and acids. High electrolyte concentration favors extraction by the following three effects:

a. The mass action effect.

If the electrolyte has suitable coordination anions, the high concentration makes replacement of water molecules easier.

b. The activity of water is reduced.

c. The dielectric constant is lowered, thus favoring ion-pair formation.

Solvent Basicity

Relative basicity as determined by infra-red spectroscopic measurements of proton affinity yields the order alcohols > ethers > ketones(23). However, because ether oxygens are sometimes more subject to steric hindrance than carbonyl oxygen, the latter two sometimes reverse.

Salting-Out Agents

The term salting-out agents is applied here to those electrolytes whose addition enhances extractability, and are most important in oxonium systems. The functions of salting out agents are as follows.

a. To provide higher concentration of complexing anion.

b. To bind water making water less available as a free solvent.

c. To influence activity coefficients of participating ions.

d. To decrease the dielectric constant of the aqueous phase, thus favoring formation of ion association complexes(24).

2.4 Chemical Interactions in the Organic Phase

Chemical interactions of the extractable species in the organic phase can have important effects on the concentration of the complex and, hence, on the extent of extraction.

One of the most important types of organic phase reaction is polymerization of ion association complexes. By their very nature, virtually all ion-pair complexes tend to form higher aggregates as the concentration increases. Naturally, as polymerization tends to reduce the activity of the extractable species in the organic phase, the overall extraction equilibrium is shifted in favor of higher distribution ratios.

Dissociation of ion association complexes may also occur in very dilute solutions, particularly in the polar solvents(25,26). This reaction would result in increased extraction at very low metal concentrations(27).

Since extractable metal chelates are essentially covalent compounds, their solutions in neutral organic solvents are relatively free from chemical interaction. One noteworthy exception arises in the use of buffers that have extractable components. The use of an acetic acid-acetate buffer to adjust the pH of the aqueous medium could easily result in extraction of acetic acid into the organic phase. The acetic acid might react with either the chelating reagent or the chelate itself, and thereby affect the course of the extraction. For example, when 8-Quinolinol is used as the chelating agent, it reacts with acetic acid. The acetate ion could also react with the metal ion, keeping it in the aqueous phase. This depends upon the competition with the extracting ligand.

2.5 Quantitative Treatment of Extraction Equilibria

2.5.1 Chelate Extraction Systems

Let us take the case in which the metal ion M^{n+} is extracted by an organic solution of a weakly acidic chelating agent (HR) like HTTA from an aqueous phase containing some complexing anion. The interactions that have to be taken in account are the following:

1) Ionization of HR to give the active chelating anion.

$$HR \rightleftharpoons H^+ + R^- \qquad K_i = \frac{[H^+][R^-]}{[HR]} \qquad (1)$$

2) Formation of the chelate which has been shown to be stepwise(28).

$$M^{n+} + R^- \rightleftharpoons MR^{n-1} \qquad k_1 = \frac{[MR^{n-1}]}{[M^{n+}][R^-]} \qquad (2)$$

$$\vdots \qquad \vdots \qquad \vdots \qquad \vdots$$

$$MR^+_{n-1} + R^- \rightleftharpoons MR_n \qquad k_n = \frac{[MR_n]}{[MR^+_{n-1}][R^-]}$$

The overall formation constant $K_f = k_1 . k_2 . k_3 \ldots . k_n$

$$K_f = \frac{[MR_n]}{[M^{n+}][R^-]^n}$$

3) Competing reactions in the aqueous phase; hydrolysis and coordination of the metal ion with anions other than the chelating agent, e.g.,

$$a)\quad M^{n+} + OH^- \rightleftharpoons M(OH)^{n-1}, \quad \text{etc.} \tag{3}$$

$$b)\quad M^{n+} + X^- \rightleftharpoons MX^{n-1}, \quad \text{etc.}$$

where X^- represents the anion present, e.g. Cl^-, NO_3^- etc.

4) Distribution of the chelating agent between the two phases.

$$K_{DR} = \frac{[HR]_o}{[HR]} \tag{4}$$

where subscript o refers the organic phase.

5) Distribution of the chelate between the phases.

$$K_{DX} = \frac{[MR_n]_o}{[MR_n]} \tag{5}$$

All these interactions are taken into account when writing the distribution ratio of the metal between the phases. Assuming that the only metal-bearing species in the organic phase is the neutral chelate MR_n, then

$$D = \frac{[M]_o}{[M]} =$$

$$\frac{[MR_n]_o}{[M^{n+}]+[MR^{(n-1)+}]+\ldots+[MR_n] \quad +\sum_i [M(OH)_i^{(n-i)+}]+\sum_j [MX_j^{(n-j)+}]} \quad (6)$$

Dividing both numerator and denominator by $[MR_n]$ and substituting appropriate values from eqs.(2) and (5) for the ratios obtained, we find

$$D = \frac{K_f K_{DX} [R^-]^n}{1 + k_1[R^-] + k_1k_2[R^-]\ldots + K_f[R^-]^n(1+x)} \quad (7)$$

where

$$x = \frac{\left\{\sum_i [M(OH)_i^{n-i}] + \sum_j [MX_j^{n-j}]\right\}}{[MR_n]}$$

Introducing the expression for the ionization constant of the chelating agents and its distribution constant (equations 1 and 4)

$$D = \frac{K_f K_{DX} K_i^n}{K_{DR}^n} \left[\left\{ \frac{[H^+]}{[HR]_o} \right\}^n + \frac{k_1 K_i}{K_{DR}} \left\{ \frac{[H^+]}{[HR]_o} \right\}^{n-1} + \cdots + \right.$$

$$\left. \frac{k_1 \cdots k_{n-1} K_i^{n-1}}{K_{DR}^{n-1}} \frac{[H^+]}{[HR]_o} + \frac{K_f K_i^n}{K_{DR}^n}(1 + x) \right]^{-1} \quad (8)$$

Simplification of the general equation:

This is a general expression for the stoichiometric distribution of the metal between the phases when only the metal chelate is extractable. In many practical cases, the above equation can be simplified by making a number of assumptions.

a) Hydrolysis and anion complexation are not appreciable in the aqueous phase, $x = 0$.

b) The concentration of the metal chelate in the aqueous phase is negligible.

$$[MR_n] \longrightarrow 0 \quad \text{or} \quad \left\{ \frac{[H^+]}{[HR]_o} \right\}^n \gg \frac{K_f K_i^n}{K_{DR}^n}$$

c) The concentration of all intermediate chelate species is negligible. Then equation (8) reduces to

$$D = \frac{K_f K_{DX} K_i^{\,n}}{K_{DR}^{\,n}} \left\{ \frac{[HR]_o}{[H^+]} \right\}^n = K^* \left\{ \frac{[HR]_o}{[H^+]} \right\}^n \qquad (9)$$

This equation has been verified for many cases and accordingly the extractability of a metal ion depends on both the chelate concentration and the hydrogen ion concentration to the same extent. This equation is often used to determine n, the number of chelate molecules per metal ion. A plot of log D vs. log [HR] at constant hydrogen ion activity yields a straight line with a slope of n, in accord with this simple picture. Similarly, varying the hydrogen ion activity, a plot of log D vs. pH, at constant large chelate activity, should also yield a straight line with slope = n. Any deviation from linearity of these log-log curves means that this simple picture is not applicable to the case in study and that the equilibrium of extraction is more complex.

Effect of Hydrolysis and Anion Complexation

When hydrolysis of the metal takes place in the aqueous phase, D is given by

$$D = \frac{[M]_o}{[M]} = \frac{[MR_n]_o}{[M(OH)_i^{(n-i)+}]} = \frac{K^*[HR]_o^n}{K_h[H^+]^{n-i}} \qquad (10)$$

where i is the average number of hydroxyl groups coordinated to the metal ion and K_h represents the appropriate hydrolysis constant(s).

When the metal cation forms complexes with anions existing in the aqueous phase, the distribution ratio will decrease with increasing anion concentration. However, at constant anion concentration, equation (10) might still apply, but K will be different.

The Effect of Chelate Solubility in Aqueous Phase

When the neutral chelate is soluble in the aqueous phase (i.e., K_{DX} is small)

$$D = \frac{[MR_n]_o}{[M^{n+}]+[MR_n]} = \frac{K_{DX}}{K_f[R^-]^n+1} = \frac{[K_{DX}-D]K_f K_i^n}{K_{DR}^n} \cdot \frac{[HR]_o^n}{[H^+]^n} \quad (11)$$

Equation (11) indicates that D rises to a maximum value equal to K_{DX}.

When intermediate chelates are also soluble in water, it can cause the extraction to have an unusually small dependence on pH.

Effect of Changing the Solvent

The dependence of the distribution ratio on the organic solvent used, for otherwise similar systems, is given by,

$$\frac{D}{D'} = \frac{K_{DX}/K_{DR}^n}{K'_{DX}/K'^n_{DR}} = \frac{K_{DX}/K'_{DX}}{[K_{DR}/K'_{DR}]^n} \quad (12)$$

If one can assume that the change of the distribution coefficients will be the same for the chelating agent and its chelate

$$\frac{K_{DX}}{K'_{DX}} = \frac{K_{DR}}{K'_{DR}} \quad (13)$$

and therefore

$$\frac{D}{D'} = \left[\frac{K'_{DR}}{K_{DR}}\right] \qquad (14)$$

From equation (14) it is evident that a change to a solvent in which the chelating agent and the multivalent metal chelate are more soluble will result in lower D.

2.5.2 Ion Association Extraction Systems

Ion association extraction systems generally involve high electrolyte concentrations and consequently there are great differences between concentrations and activities. Another complication, that usually does not come into consideration when dealing with chelate compounds, is the interactions of the ion association complex in the organic phase. In addition, the number of interactions in the aqueous phase that have to be taken into account is very large. When a metal ion is in the aqueous phase, its coordination sphere is fully occupied by anions, hydroxyl groups, water molecules, or as is usually the case, by a combination of these. When this metal complex ion forms an ion association complex with an anion or cation, and is extracted into the organic phase, the coordinated water can be exchanged by the solvent, the complex ion can form a dimer, trimer or any other polymer, or it can even dissociate, and each ion can be solvated by the organic solvent.

Quantitative Treatment of Ion Association Systems

The extraction of uranyl nitrate by oxonium solvent can be considered as a general example.

The reactions involved in the distribution of uranyl nitrate between an oxonium solvent and water may be described as follows:

1. Formation of the complex

$$UO_2(H_2O)_6^{2+} + 2NO_3^- \rightleftharpoons (UO_2(H_2O)_6^{2+}, 2NO_3^-) \quad (15)$$

or, if the water activity is low

$$UO_2(H_2O)_6^{2+} + 2NO_3^- \rightleftharpoons (UO_2(H_2O)_4(NO_3)_2 + 2H_2O \quad (16)$$

2. Distribution of the complex

$$(UO_2(H_2O)_6^{2+}, 2NO_3^-) \rightleftharpoons (UO_2(H_2O)_6^{2+}, 2NO_3^-)_o \quad (17)$$

$$(UO_2(H_2O)_4(NO_3)_2) \rightleftharpoons (UO_2(H_2O)_4(NO_3)_2)_o \quad (18)$$

3. Reactions in the organic phase

$$(UO_2(H_2O)_6^{2+}, 2NO_3^-)_o + nS \rightleftharpoons UO_2S_n(H_2O)_{4-n}(NO_3)_2 + (n+2)H_2O \quad (19)$$

or,

$$UO_2(H_2O)_4(NO_3)_2 + nS \rightleftharpoons UO_2(H_2O)_{4-n}S_n(NO_3)_2 + nH_2O \quad (20)$$

If S represents a strongly basic solvent such as butanol, then

$$(UO_2)(H_2O)_4(NO_3)_2 + 6S \rightleftharpoons ((UO_2)S_6^{2+}, 2NO_3^-) + 4H_2O \quad (21)$$

In addition polymerization reactions will occur at higher concentrations of uranyl nitrate where equation (21) is valid.

When ether is used as the extraction solvent, the distribution ratio can be given by(16)

$$D = \frac{[U]_o}{[U]} =$$

$$\frac{\left[UO_2(H_2O)_6^{2+},\ 2NO_3^-\right]_o + \sum_{n=0}^{n=4}\left[UO_2S_n(H_2O)_{4-n}(NO_3)_2\right]}{\left[UO_2(H_2O)_6^{2+}\right] + \left[(UO_2(H_2O)_6^{2+},\ 2NO_3^-)\right] + \left[UO_2(H_2O)_4(NO_3)_2\right]}$$

In solutions of low to moderate ionic strengths, the reactions represented by equations (19) and (20) proceed to a sufficiently small extent so that |U| simplifies to just $[(UO_2)(H_2O)_6^{2+}]$(29).

Thus,

$$D = [NO_3^-]^2 \gamma_t^3 K_f K_D (1+K_s/a_w^{n+2})\gamma_o + K'_f K'_D (1+K'_s/a_w^{n})\gamma'_o \quad (23)$$

where K's represent thermodynamic constants, concentrations are expressed in molality, γ_o and γ_o' are the molal activity coefficients of the complex in the ether phase, γ_t is the mean activity coefficient of the uranyl nitrate, and a_w is the activity of water.

At relatively low uranyl concentrations γ_o and γ_o' may be considered unity. So that

$$D = K^*[NO_3^-]^2 \gamma_\pm^3 \quad (24)$$

Equation (24) predicts that the addition of other nitrates as salting out agents will improve the extraction.

Effect of Changing the Solvent in an Ion Association System

Taube(30) compared the influence of solvent polarity on the extraction of plutonium by chelating and other complexing reagents including ion association complex formers. He used a mixture of two solvents, one of which was more polar, and plotted the distribution ratio of the metal as a function of solvent composition. The distribution ratio decreased with solvent polarity for TTA, TBP and DB. However, the

curve had a maximum for the ion association extraction system with tetra-n-butyl ammonium nitrate (TBAN). For an ion association complex, an increase of D with solvent polarity would be expected if only the dissociation and solvation are taken into account. However, this experiment showed that for a low concentration of a nonpolar solvent, D was higher than for the pure solvent; in this region the ion association complex behaved like a chelate.

2.5.3 Mathematical Treatment of Systems Involving Both Chelates and Ion Association Complexes

In most of the experiments investigating the existence and cause of synergism, the extraction systems included both chelating agents and ion association formers. This mixed system is of course even more complicated than the two described previously, but since, in many cases, the experiments are not performed in a very wide range of metal concentrations, reagent concentrations and pH values, it is usual practice to view only the most important interactions. For example, Irving et al.(31) investigated the extraction of uranyl ion by TTA in cyclohexane from 0.01M HNO_3 and varying concentrations of tributyl phosphate (TBP) or tri-n-butylphospine oxide (TBPO). These are complicated

system. TBP also extracts UO_2^{2+} from HNO_3 solutions to some extent, but this reaction was neglected and the process was described as the simple chelate extraction followed by the organic phase reaction:

$$[UO_2(TTA)_2]_o + [TBP]_o \rightleftharpoons [UO_2(TTA)_2TBP]_o$$

If all the simplifing assumptions for chelate extraction are made as before, the process can be described by the mixed phase equilibrium:

$$UO_2^{2+} + 2\ HTTA + xS \rightleftharpoons UO_2(TTA)_2S_x + 2H^+$$

S = TBP or TBPO

for which the equilibrium constant is

$$K = \frac{[UO_2(TTA)_2S_x][H^+]^2}{[UO_2^{2+}][HTTA]^2[S]^x}$$

or

$$D \propto \frac{[HTTA]^2[S]^x}{[H^+]^2}$$

The equation was verified by changing one of these variables while keeping the others constant, and plotting log D vs. log [HTTA] or log [S].

2.6 Synergism

The word "synergism" was first coined by Blake et al.(32) in 1958 to describe their discovery of a definite enhancement of the extraction of uranium (called synergic effect) from aqueous solution by a mixture of an acidic dialkyl phosphate and certain neutral organophosphorus esters, the resulting mixture giving a better extraction of uranium than either the acid or neutral phosphate alone. This phenomenon of greatly enhanced extraction, or synergism, due to a mixture of extractants has attracted considerable attention in recent years.

2.7 Mechanisms Proposed to Explain Synergism

2.7.1 Substitution of Coordinated Water by a Neutral Ligand

Irving et al.(31) were the first to investigate the synergic effect on the extraction of uranium with a combination of TTA and TBP. As previously stated, they worked in nitrate media. From the change of log D with log [HTTA] and log [TBP] or log [TBPO], they concluded that the mixed complexes $UO_2(TTA)_2TBP$, $UO_2(TTA)NO_3$ TBP, $UO_2(TTA)_2(TBPO)_3$ and $UO_2(TTA)_2$ TBPO were present in the organic phase, and that these mixed ligand complexes were responsible for the enhanced extraction. The additional ligands were considered to be coor-

dinated directly to the metal, thus increasing the coordination number of uranium. It seemed to them that this coordination number, 7, was possible for uranium, and that there was also strong indication that this was the real coordination number of uranium in the TTA chelate, the additional ligand being one water molecule. Accordingly, the synergic reaction was represented by

$$[UO_2(TTA)_2H_2O]_o + TBP \rightleftharpoons [UO_2(TTA)_2TBP]_o + H_2O$$

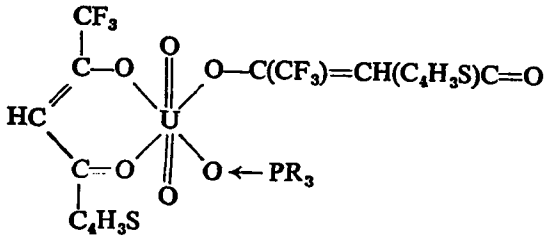
In this way the TTA complex is made less hydrophilic and more extractable into the organic solvent. Irving originally proposed this as a possible general explanation for all synergic extractions, and on this basis predicted that this effect on the extraction would be observed only for chelates in which the coordination sphere of the metal is not saturated by chelating agent.

Subsequent experiments with trivalent(33) and tetravalent(34) actinides did not confirm this prediction.

2.7.2 Formation of Mixed Ligand Complexes, Resulting in an Open Chelate Ring

Healy(35), repeated Irving's experiments in a rather extensive study but in a different aqueous medium. He used HCl media, and claimed the extraction of a mixed ligand complex of thorium with TTA and TBP, of the type $Th(TTA)_4$ TBP. For uranium and the trivalent actinides he found the same mixed complexes as Irving did, but he investigated many other phosphate esters, phosphonic oxides and phosphonates, and also the trivalent rare earths. Healy's initial evidence for the synergic extractions was based on tracer experiments, in low reagent concentrations and constant aqueous activity, which was subsequently verified by a spectrophotometric method using much higher metal concentrations(36). He successfully isolated the mixed solid complexes, determined their melting points, showed that they contained no water and studied their infrared absorption spectra(37). Healy found that the synergic effect in the extraction of TTA chelates was not confined to organo-phosporus compounds, but could be produced by alcohols, ketones, amines and even inert solvents such as cyclohexane. His discovery by ultraviolet spectroscopy that there is some interaction between HTTA and TBP in a concentration range in which the synergic effect is observed, led him to conclude that the TTA becomes monodentate and that there could also be direct coordination between TBP and

metal ion. He confirmed this by infrared spectrometry of the isolated solid complexes. Thus the synergic species was considered to have the oxygen of the P-O bond of the organic phosphate bound to the metal, and for each such bond one TTA chelate ring was opened, making the TTA monodentate. Thus the uranyl complex was pictured as follows:



2.7.3 Adduct Formation without a Direct Bond of Neutral Ligand to Metal

Newman and Klotz(38) investigated the synergic effect of tri-n-octyl amine (TNOA) on the extraction of thorium by TTA. They found in preliminary work(39) that the amine was extracted from HCl solutions as R_3NHCl, and by tracer work they found that in the presence of the amine the thorium chelate was extracted with one amine molecule per thorium chelate. This result, although essentially the same as Healy's, was explained by Newman et al. in a different way.

They found(40) that amine hydrochloride itself could form an addition compound with HTTA upon extraction from HCl, corresponding to the formula $R_3NHClHTTA$, and therefore concluded that in the presence of thorium the amine must be bound to the TTA and not directly to the metal ion. This was confirmed by the fact that although R_3NHCl, R_3NHTTA and $R_3NHClHTTA$ were shown to be present in solution, only one of them, the R_3NHCl, seemed to affect the thorium chelate extraction synergically. Later Newman calculated "synergic constants", (K_s)(41), for some mixed complexes that Healy found to cause synergic extractions and found that K_s did not depend on the nature of, or the valency of, the metal ion. This was very strong indication for the validity of his theory, that in the mixed complexes the neutral reagent was not bound directly to the metal, but to the TTA chelate ring.

Since the formation of a mixed ligand complex was believed to be responsible for the synergic effect in solvent extraction, many investigators(42-45) studied the TTA chelates of metals in the presence of TBP, TBPO, TOPO and 4-methyl pyridine. In most of the systems, a synergic effect on the chelate extraction was observed, and evidence was found for a mixed ligand complex.

2.7.4 Kinetic mechanism

A completely different approach to the synergic solvent extraction was reported by Finston and Inoue(46). They investigated the effect of thiocyanate on the extraction of Fe(III) ion by TTA. They emphasize the kinetic factor in some extraction systems, especially the TTA system. It is well known that the extraction of many metal ions by TTA is very slow, and equilibrium is attained only after contacting for some hours. In the system Fe(III)-TTA, the extraction into benzene is slow and is considered to proceed through the following steps.

a) Distribution of TTA into the aqueous phase.

b) Ionization of TTA.

c) Reaction of Fe(III) with TTA enolate ion.

d) Distribution of the chelate into benzene.

Taft and Cook(47) reported that the rate determining step is the reaction of Fe(III) with TTA enolate ion. Finston and Inoue(46) examined the effect of thiocyanate ion on the above extraction system, and found a pronounced effect on the rate of extraction. The increased rate of extraction upon the addition of thiocyanate is attributed to the replacement of the slowest step in the TTA extraction, i.e., the direct formation of extractable species, by another fast process. The absorption spectra of Fe(III)-TTA/benzene extracted from aqueous phases with

and without thiocyanate were identical at any pH for all thiocyanate concentrations. Furthermore, identical spectra were observed for the aqueous thiocyanate phases before and after extraction. These observations, plus the fact that the effect does not increase with increasing thiocyanate concentrations, negates a mixed-ligand complex. The mechanism proposed by Finston and Inoue for the enhanced extraction rate is a series of fast reactions:

a) Formation of Fe(III)-SCN complex in the aqueous phase.

b) Extraction of Fe(III)-SCN into the organic phase by forming the ion-pair.

c) Replacement of SCN^- with TTA in the organic phase.

A later study by the same authors(48) on the same system, showed a large synergic effect of thiocyanate on the extraction of Fe(III)-TTA chelate when they used mixtures of hexone and benzene. The difference between this new solvent system and the former is that Fe(III)-SCN complex can be extracted into hexone, whereas it was extracted only to a very small extent by benzene. Later Finston and Gnizi(49) verified the proposed mechanism using the Zr-TTA-SCN system with benzene and benzene-hexone solvents.

Thus, there were four different opinions about the mechanisms of the synergic effect in solvent extraction.

a. Formation of a mixed complex, by opening of one chelate ring per molecule of neutral ligand.

b. Formation of an adduct without opening any chelate ring, which could be the result of substitution of coordinated water, or simply increasing the coordination number. The resulting adduct is thought to be less hydrophilic and thus more soluble in organic solvent.

c. Formation of an addition compound, with the adduct molecule bound to the chelate and not directly to the metal ion.

d. Kinetic mechanism- elimination of the slow step in the metal chelate extraction with the addition of SCN^- ion to the aqueous phase.

Chapter III

EXPERIMENTAL

3.1 Reagents

Uranyl nitrate (certified A.C.S), ammonium nitrate, calcium nitrate and sodium tartrate were obtained from Fisher Scientific Company.

Thorium nitrate and iron wire, 99.95%, and methyl iso-butyl ketone were Baker analyzed reagent grade.

2-Thenoyltrifluoroacetone(TTA), Lancaster Synthesis, Ltd., was used without further purification.

Propylene carbonate, MCB reagents, 98% by GC, was distilled under reduced pressure (b.p. 92°C at 4.5 mm Hg) for purification.

Copper metal was obtained from J.T.Baker Chemical Company.

All the other chemicals such as sodium hydroxide, perchloric acid, ethanol, ammonium hydroxide, etc., were the highest purity grade available.

3.2 Apparatus

Metal cation concentrations were determined with a Perkin Elmer Lambda 3B UV/Visible spectrophotometer connected to the PE 3600 data station.

A Burrel wrist action shaker was used for solvent extraction.

pH measurements were made with a Corning model 12 pH meter, using glass and calomel electrodes.

3.3 Procedures

3.3.1 Extraction of Fe(III), Co(II) and Cu(II)

Cation solutions were prepared by dissolving the metals in a minimum amount of perchloric acid followed by evaporation to incipient dryness. The residues were dissolved in tartrate solution and the pH was adjusted to the desired value with NaOH solution and diluted with distilled water to the correct volume. Homogeneous extraction into propylene carbonate was performed by heating and stirring equal volumes of the aqueous cation solutions and the propylene carbonate solution of the chelating agent in a 125 ml erlenmeyer flask. A "cold-finger" condensor placed in the neck of the flask minimized any loss of solution by evaporation. When a single homogeneous phase was achieved, the mixture was cooled to room temperature and cation concentrations in both phases were determined by absorption spectrophotometry as follows.

A calibration curve was obtained for each cation by mixing 2/2/1 ratios of propylene carbonate solution of the chelating agent/aqueous concentration standard/ethanol to yield a single homogeneous phase. Propylene carbonate and ethanol were added to the aqueous phase; aqueous plus ethanol was added to the propylene carbonate phase, and the same calibration curve was used to determined the metal ion concentration in both phases.

Conventional liquid-liquid extractions into propylene carbonate and toluene were performed by shaking equal volumes of the aqueous cation solutions and the propylene carbonate solution of the chelate in a separatory funnel with a wrist-action shaker. In propylene carbonate extraction, the cation concentration in each phase was determined using the above procedures. In toluene extraction, the iron concentration in the aqueous phase was determined using the 1,10-phenanthroline colorimetric method(50).

3.3.2 Extraction of Uranium

Uranyl ion was extracted into propylene carbonate from uranyl nitrate solution saturated with a suitable salting out reagent by heating (to 99°C) and stirring equal volumes of the aqueous and propylene carbonate phases.

The uranium extracted from nitrate solution into propylene carbonate was stripped from the organic phase with carbonate solutions of varying pH values. The carbonate solutions were equilibrated with propylene carbonate before stripping to minimize the loss of propylene carbonate phase.

A final separation step consisted of extraction of uranyl ion into propylene carbonate containing dibenzoyl methane. The carbonate complex was first destroyed by heating the aqueous phase with nitric acid, and the pH was adjusted from 6 to 8 before the extraction.

In each step, extraction was performed by heating and stirring the mixture at temperature higher than 71°C until a homogeneous phase was achieved. After the mixture was cooled to room temperature, the uranium concentrations in both phases were determined by absorption spectrophotometry using dibenzoyl methane(51).

3.3.3 Phase diagram for the liquid system Water + Propylene carbonate + Methyl iso-butyl ketone

The three component liquid-liquid phase diagrams at 25°C and 50°C were obtained by titrating homogeneous mixtures of MIBK + propylene carbonate of different compositions with water and water with homogeneous mixtures of MIBK + propylene carbonate. The whole titration system was maintained at constant temperature during the titration. The end point of the titration was the cloud point(52).

The densities of methyl isobutyl ketone, propylene carbonate, and their mixtures, and also water, were obtained using pyconometers. Pyconometers were filled to a level above the calibration mark, and immersed in a water bath of constant temperature for about 20 minutes, and the level adjusted exactly to the mark. The pyconometer was weighed, and density was calculated from the formula;

$$d(t) = \frac{W_m}{W_w} (d_w - d_a) + d_a,$$

where d(t) is the density of the mixture at a given temperature; W_m is the weight of the mixture in the pyconometer; W_w is the weight of the water in the pyconometer; d_a is the density of the air; and d_w is the density of the water at the given temperature.

The tie lines were obtained as follows. A mixture of water, methyl isobutyl ketone and propylene carbonate of known composition was added to a separatory funnel, then which was kept in a constant temperature water bath, and periodically agitated to reach equilibrium. After separation the two phases were weighed and the weight ratio of the two phases were determined. With the help of the lever rule, the slopes of the tie lines were determined.

Chapter IV

RESULTS AND DISCUSSION

4.1 Homogeneous Liquid-Liquid extraction of the TTA Complexes of Fe(III), Cu(II) and Co(II)

Extraction of iron is of particular interest in hydrometallurgical processing since it is both ubiquitous and frequently an interference. Solvent extraction procedures of copper are still of great current interest as evidenced by the large number of papers on copper ore processing at the International Solvent Extraction Congress, Liege, 1980.

The beta-diketones are a class of chelating agents of particular interest for study because they form readily strong complexes with a wide variety of cations. Furthermore, a number of homologues into which various substituents have been introduced have been widely studied. For example, the $-CF_3$ group in thenoyltrifluoroacetone reduces the base strength of the ligand and permits extraction from more acid medium. In general, the effectiveness of the beta-diketones is a conse-

quence of the ease with which they enolize, and because the conjugated double bonds in the enol structure results in stabilization of the six membered chelate formed. Also, many of the chelating agents are chromogenic.

Fe(III)-TTA extraction by the conventional liquid-liquid extraction method at room temperature is known to be slow. For example, 12 hours is required to establish equilibrium during the extraction of Fe(III)-TTA from hydrochloric acid solutions with 0.2 M solution of the reagent in benzene(53). Akaza et al.(54) also reported that rather long shaking times are required in colorimetric determinations with TTA. Finston et al.(46) reported 1 hour shaking time for the complete extraction of Fe(III) with 0.5 M TTA in benzene in the presence of SCN^-. Murata et al.(3) and Ting et al.(4) achieved complete and rapid (5 minutes) extraction of Fe(III)-TTA into propylene carbonate, using the homogeneous method. These extractions were performed at low pH, about 3, to avoid the formation of hydrolysis products at higher pH.

The effects of higher pH (6 to 8) and TTA concentration on the extractability of Fe(III)-, Co(II)- and Cu(II)-TTA into propylene carbonate are shown in Fig. 1, 2 and 3. The extraction of Fe(III)-TTA decreases with increasing pH; extraction of Co(II)-TTA increases with increasing pH; there is no effect of pH on the extraction of

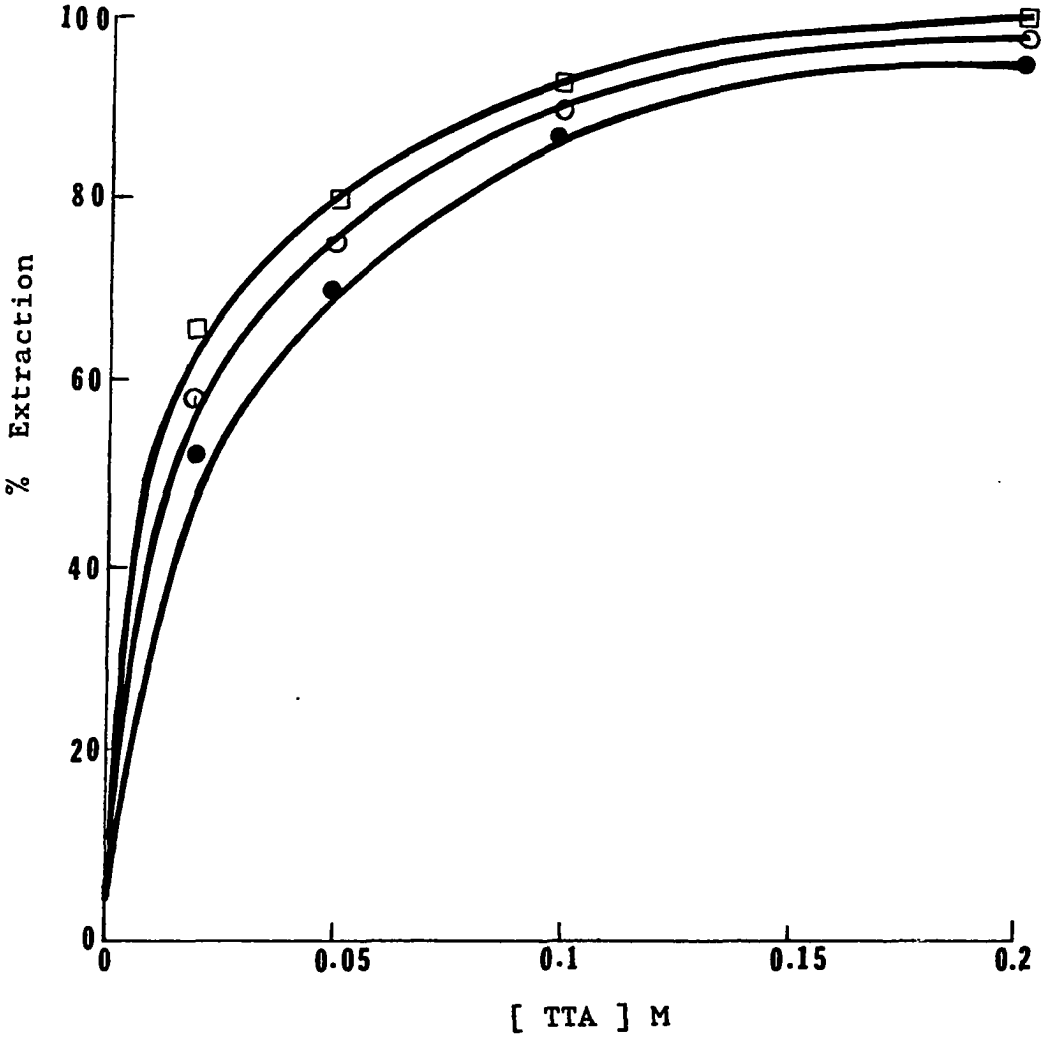


Fig. 1 Effect of TTA concentration on the homogeneous extraction of Fe(III)-thenoyltrifluoroacetonate into propylene carbonate, at different initial aqueous pH values
$[Fe^{+3}] = 5.0 \times 10^{-3}$ M [tartrate] = 0.1 M

□ pH = 6 ○ pH = 7 ● pH = 8

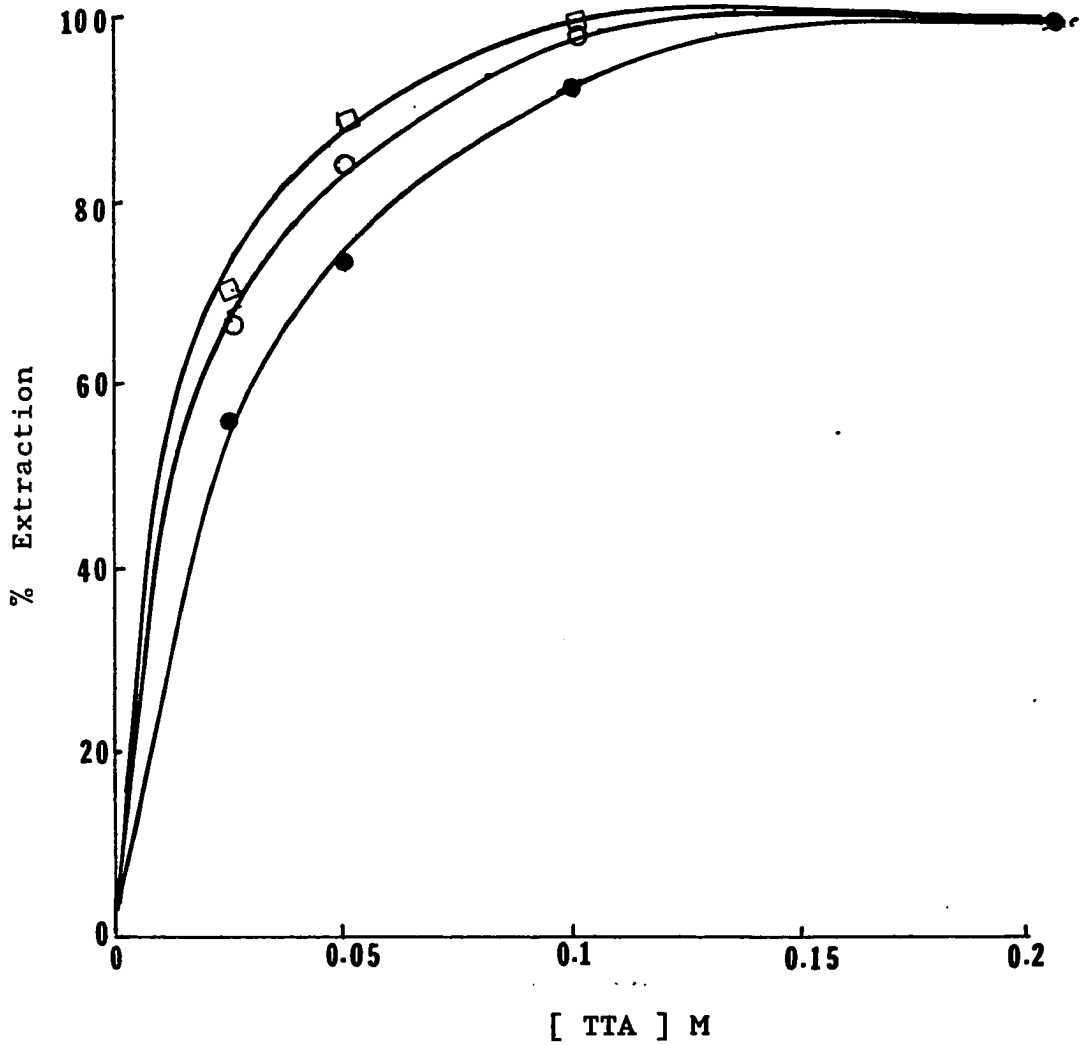


Fig. 2 Effect of TTA concentration on the homogeneous extraction of Co(II)-thenoyltrifluoroacetonate into propylene carbonate, at different initial aqueous pH values.
$[Co^{+2}] = 5.0 \times 10^{-3}$ M [tartrate] = 0.1 M

● pH = 6 ○ pH = 7 □ pH = 8

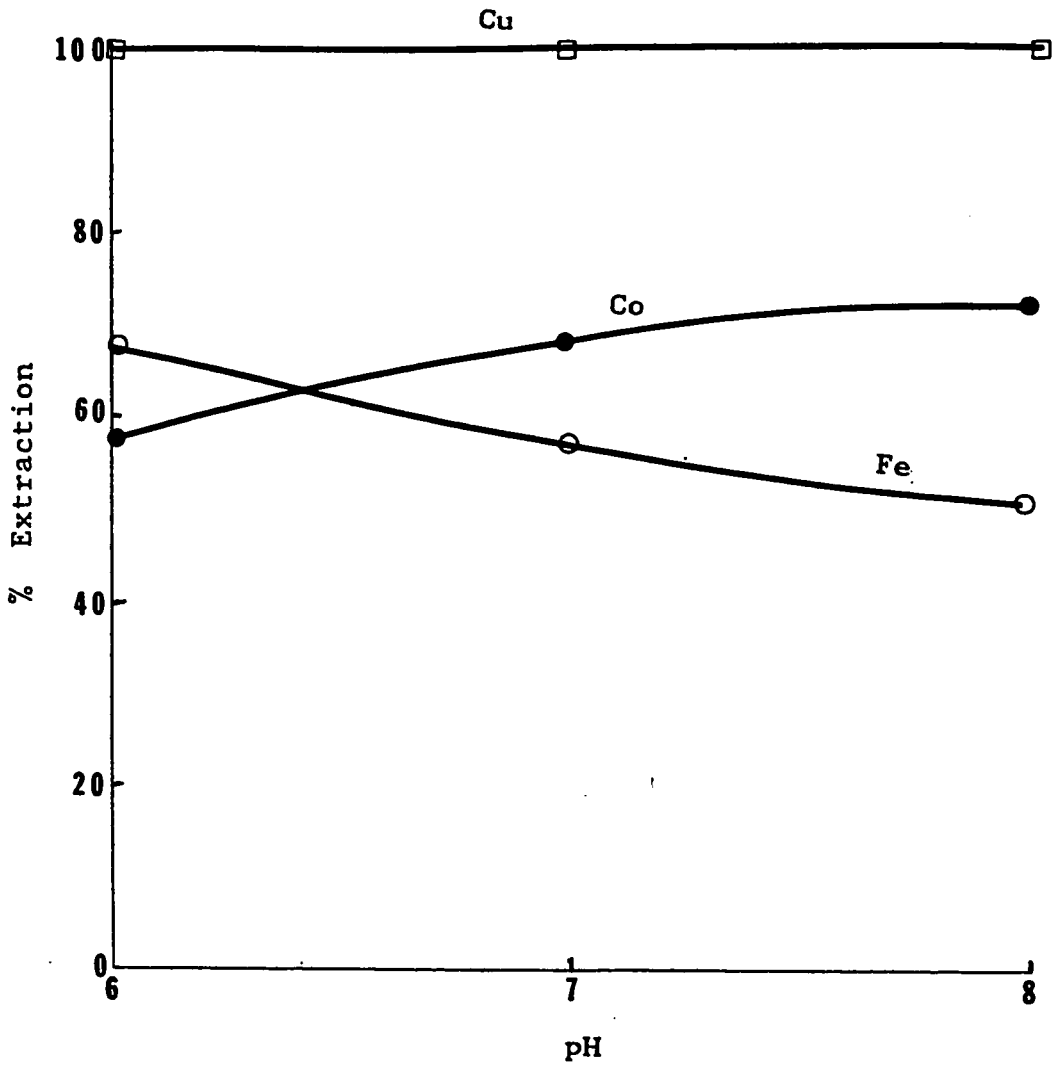


Fig. 3 Effect of initial aqueous pH on the homogeneous extraction of metal-TTA complexes into propylene carbonate.

[TTA] = 2.5 x 10^{-3} M; $[Me^{n+}]$ = 5.0 x 10^{-3} M;

[tartrate] = 0.1 M

Cu(II)-TTA. As shown in Figures 1, 2 and 3, under the same conditions, the extraction of Cu(II)-TTA > Co(II)-TTA > Fe(III)-TTA. These results can be qualitatively explained by considering the stability constants of both the respective metal-TTA complexes, and the metal-tartrate complexes, and the solubility product constants of the respective metal hydroxides (Table I). The stability constants of Cu(II)-TTA and Co(II)-TTA complexes are higher than the stability constants of the respective metal tartrates. Therefore, there is no interference from tartrate complexes in the extraction of Cu(II)- and Co(II)-TTA complexes. However, the stability constant of the Fe(III)-tartrate complex is higher than the stability constant of the Fe(III)-TTA complex; the solubility product constants of the respective hydroxides are in the order $Fe(OH)_3$ < $Cu(OH)_2$ < $Co(OH)_2$; and the formation constants are in the order Cu(II)-TTA > Co(II)-TTA > Fe(III)-TTA. Therefore there should be greater extraction of the Cu(II)-TTA complex. The lower extractability of iron as compared with copper and cobalt may be due to the competition of tartrate, TTA and hydroxide ions. Although the formation constant of the Fe(III)-tartrate complex is significantly greater than the formation constant of Fe(III)-TTA complex, the latter is extracted into the organic phase. Thus, the

$$[\text{Fe(III)-tartrate}]^{+1} \rightleftharpoons \text{Fe(III)} + [\text{tartrate}]^{2-}$$

Table I. Stability constants of the metal-tartrates(55,56), metal-TTA(57) complexes and the solubility product constants of metal hydroxides(58).

Metal	log K (tartrate)	log K (TTA)	pK_{sp} (hydroxides)
Fe(III)	18.6?	6.9	38.6
Co(II)	2.1	7.81	14.2
Cu(II)	3.2	8.23	18.6

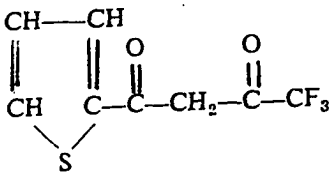
equilibrium is shifted to the right by equilibration with TTA in propylene carbonate. Another possible reason for the lower extractability of Fe(III) may be due to the higher charge on the Fe^{3+} ion; three molecules of chelating agents are needed to form a neutral complex. For the metal ions from Mn^{2+} to Zn^{2+} the following Irving-Williams order(59), or natural order, of stability of complexes is known.

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$$

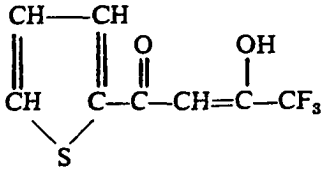
This order can also be well explained in terms of the heat of formation of the complexes(60). Therefore, we get better extraction in the case of copper.

As seen both in previous work(46), and the results obtained here, the higher the concentration of TTA, the greater is the extraction of metals. Hong et al.(5) reported only ca. 80% extraction of Cu(II)-TTA at low pH, even with 0.2 M TTA and for Fe(III)-TTA only ca. 90% was extracted after 30 minutes shaking time. The results we obtained at higher pH with 0.2 M TTA show quantitative extraction of Fe(III), Co(II) and Cu(II) within a few minutes. Complete extraction of Cu(II) is possible even with 0.025 M TTA. At higher concentrations of TTA the metal-TTA extractions are independent of pH in the range 6 to 8 as shown in Figs. 1, 2 and 3.

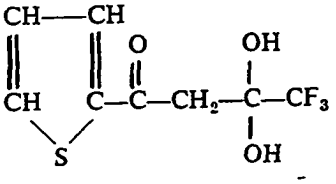
TTA is a 1,3-diketone and exists in the following three forms(53):



keto form

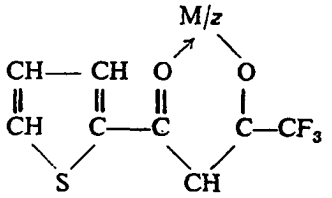


enol form



keto hydrate form

The TTA enolate ion forms highly extractable metal chelates of the form



where z is the charge of the uncomplexed metal ion. In dilute acid only about 1.6% of the TTA is in enol form, the remainder is in the keto hydrate form(61). TTA in the benzene phase consists of about 11%

keto hydrate form, the remainder is in the enol form(62). TTA in propylene carbonate is in the keto mother form(3) (enol form of TTA with intermolecular hydrogen bond formed with the solvent). Figure 4 shows the UV absorption spectra of TTA in 2/2/1 ratio of propylene carbonate, aqueous and ethanol medium at pH 2 and 7. The spectrum at pH 7 is identical to the spectrum of TTA that Healy et al.(63) observed in dry tributylphosphate, and the spectrum at pH 2 is identical to the TTA spectrum in wet tributylphosphate. Thus, the spectrum at pH 7 is considered to correspond to that of the enolate form and at pH 2 to that of the ketohydrate form. We can conclude from this evidence that at higher pH (6 to 8) there is more enolate ion form of the TTA in solution, resulting in better extraction at higher pH.

The UV-visible spectra of the respective Fe(III)-TTA, Cu(II)-TTA and Co(II)-TTA complexes extracted into propylene carbonate and made homogeneous with aqueous and ethanol are shown in Fig. 5, 6 and 7. The UV-Visible spectrum of the Fe(III)-TTA complex is the same as that of the UV-visible spectra of Fe(III)-TTA in benzene at pH 2, as observed by Khopkar et al.(64) and that of the Cu(II)-TTA complex is the same as that of the UV-visible spectrum of Cu(II)-TTA in methanol, as observed by Walker et al.(65). Therefore, it can be concluded that the same metal-TTA complexes are formed at higher pH.

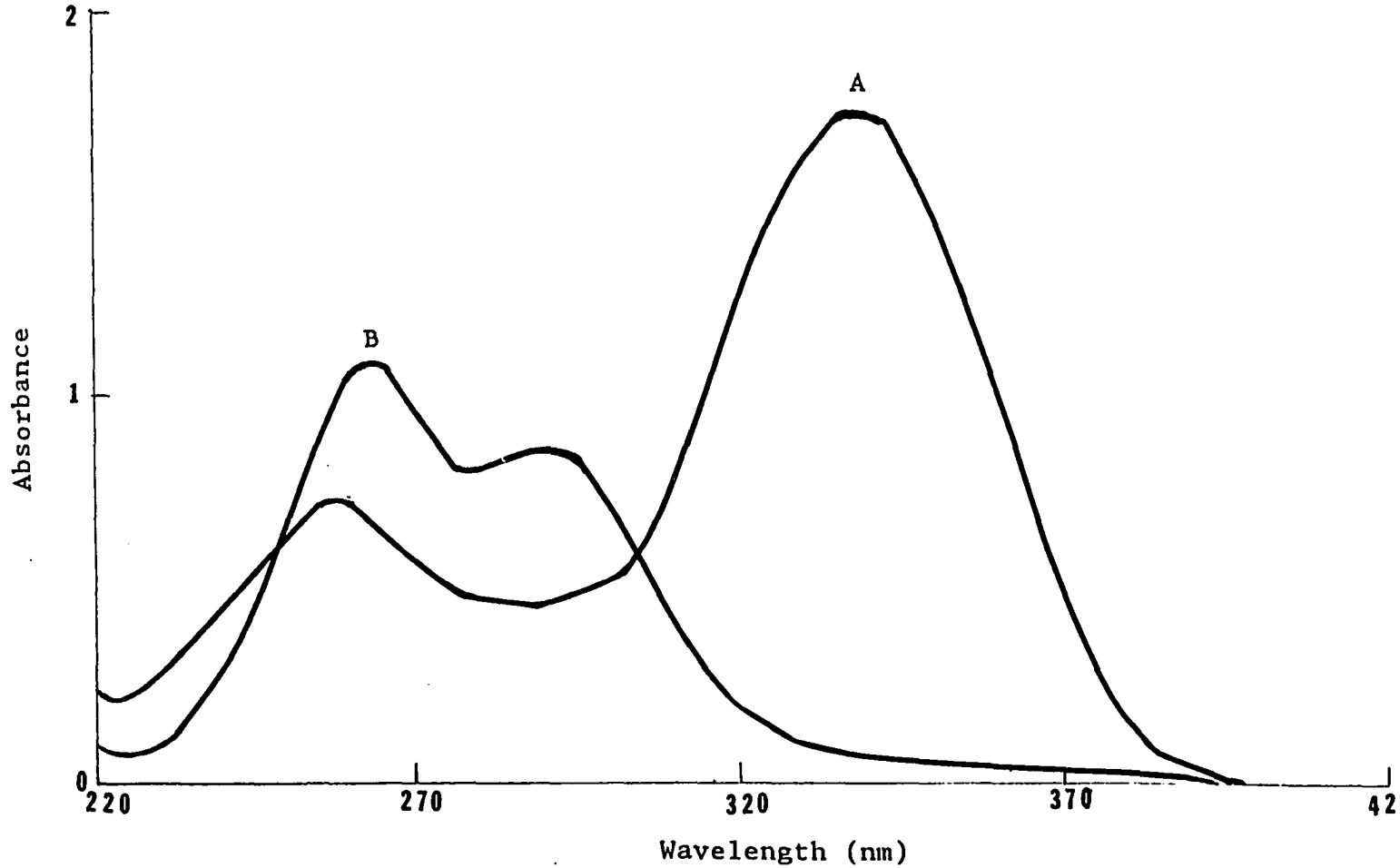


Fig. 4 Absorption spectra for 1 x 10^{-4}M TTA.
medium: 2:2:1 ratio of propylene carbonate/aqueous/ethanol
A. pH 7 B. pH 2

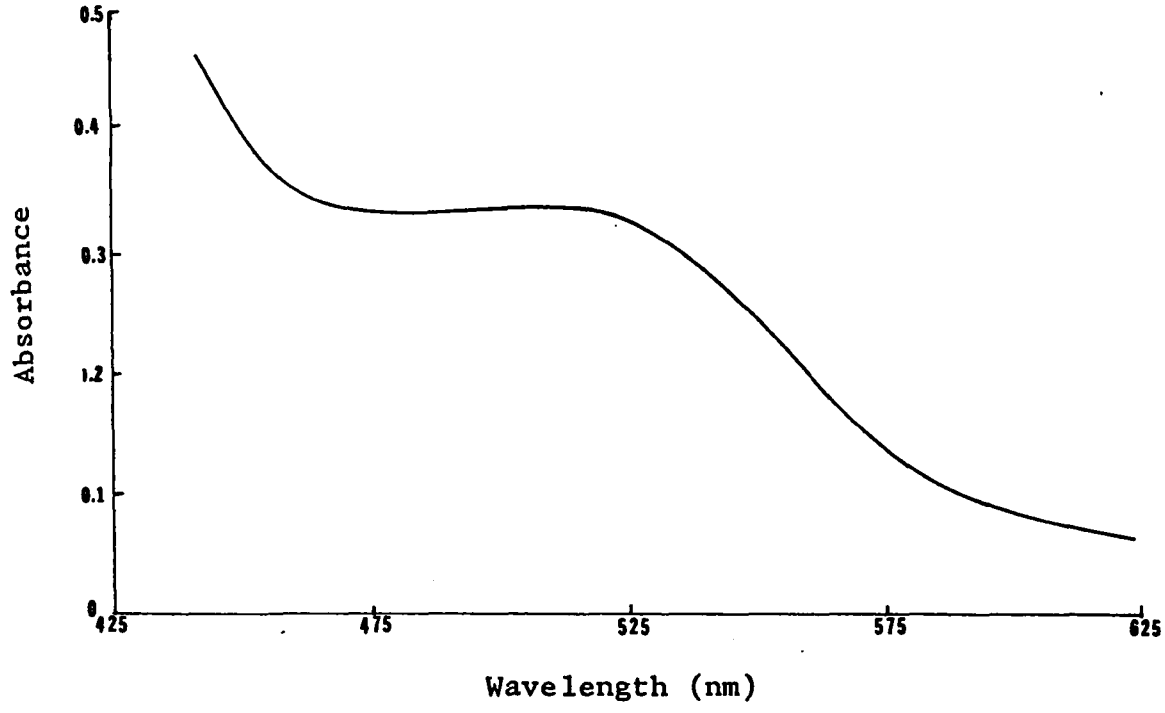


Fig.5 Absorption spectra of the Fe(III)-TTA complex in 2:2:1 ratio of PC/aqueous/ethanol at pH 7.

$[Fe^{+3}] = 8.0 \times 10^{-5}$ M [TTA] = 4.0×10^{-3} M [tartrate] = 2.0×10^{-2} M

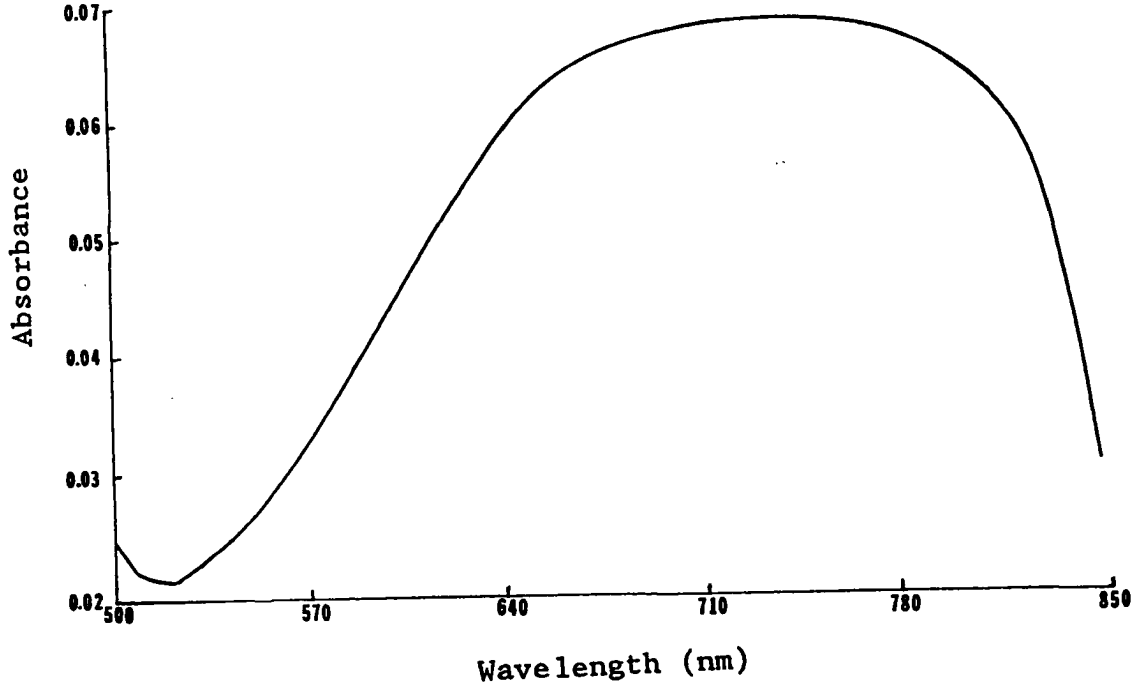


Fig. 6 Absorption spectra of the Cu(II)-TTA complex in 2:2:1 ratio of PC/aqueous/ethanol at pH 7.

$[Cu^{+2}] = 8.0 \times 10^{-5}$ M $[TTA] = 4.0 \times 10^{-3}$ M [tartrate] = 4.0×10^{-2} M

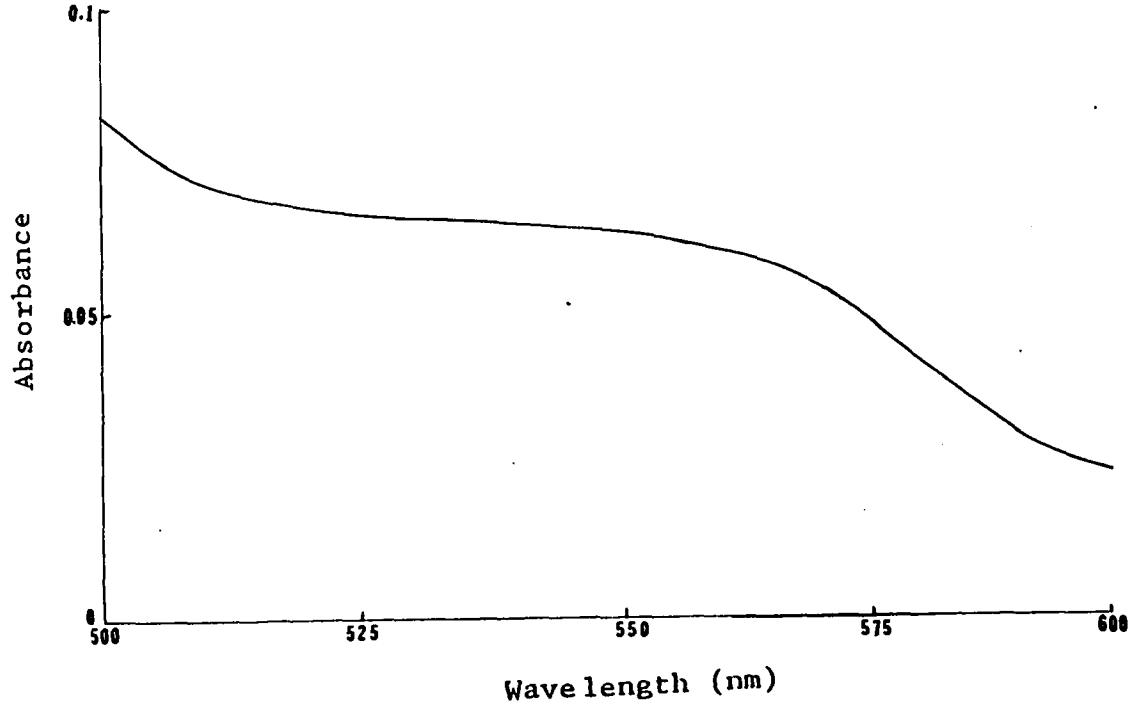


Fig.7 Absorption spectra of the Co(II)-TTA complex in 2:2:1 ratio of PC/aqueous/ethanol at pH 8.

$[Co^{+2}]$ = 8.0×10^{-4} M [TTA] = 4.0×10^{-3} M [tartrate] = 4.0×10^{-2} M

4.2 Conventional Liquid-Liquid Extraction of Fe(III)-TTA Complex

In order to compare the effectiveness of the homogeneous liquid-liquid extraction method with the conventional liquid-liquid extraction methods at near neutral pH it was necessary to perform the extractions by the conventional liquid-liquid extraction method. As seen in previous work(46), the higher the concentration of TTA and the longer the shaking time, the greater is the percent extraction of Fe(III). It has been pointed out by some authors(53,54,46,66) that certain metal cation complexes with TTA are extracted very slowly. The effect of aqueous pH (6 to 8) and TTA concentration on the extractability of 1.0×10^{-3} M Fe(III) with TTA into propylene carbonate and toluene are shown in Figs. 8 and 9. The influence of the shaking time on the extractability of Fe(III)-TTA into propylene carbonate and toluene are shown in Figs. 10 and 11. In both solvents the higher the TTA concentration and the longer the shaking time, the greater is the extraction. About 4% extraction into propylene carbonate was observed in the absence of TTA. As pH increases, the extraction of Fe(III)-TTA decreases; this may be due to hydroxide formation. The effect of shaking time and pH on the extractability of 5.0×10^{-3} M Fe(III) with 0.025 M TTA into propylene carbonate is shown in Figure 12; the values obtained for percent extracted are 62%, 52% and 45% at pH 6, 7 and 8, respectively, with 30 minutes shaking. The homogeneous extraction of Fe(III)-TTA

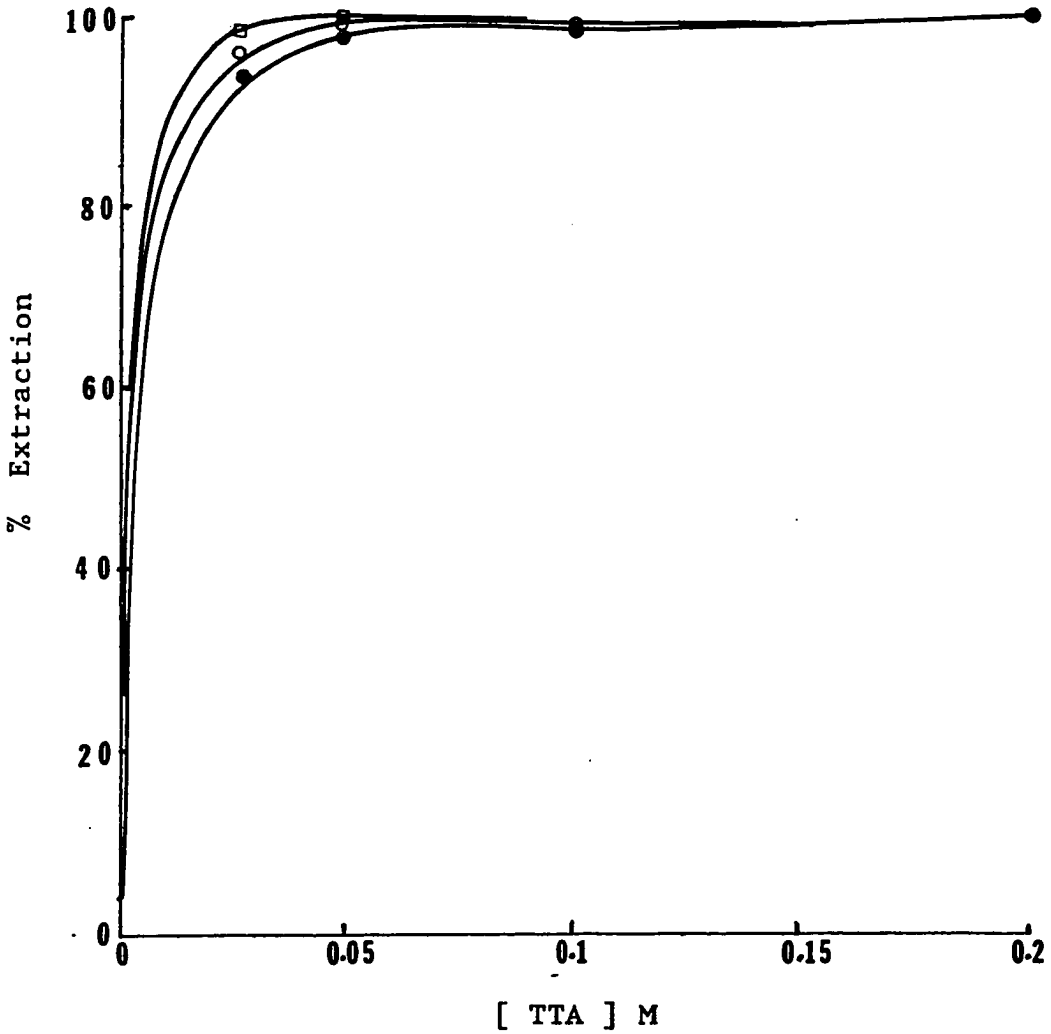


Fig. 8 Effect of TTA concentration on the conventional extraction of Fe(III)-thenoyltrifluoroacetonate into propylene carbonate, at 30°C, at different initial aqueous pH values.

contact time = 2 min. $[Fe^{+3}] = 1.0 \times 10^{-3}$ M
[tartrate] = 0.05 M

□ pH = 6 o pH = 7 ● pH = 8

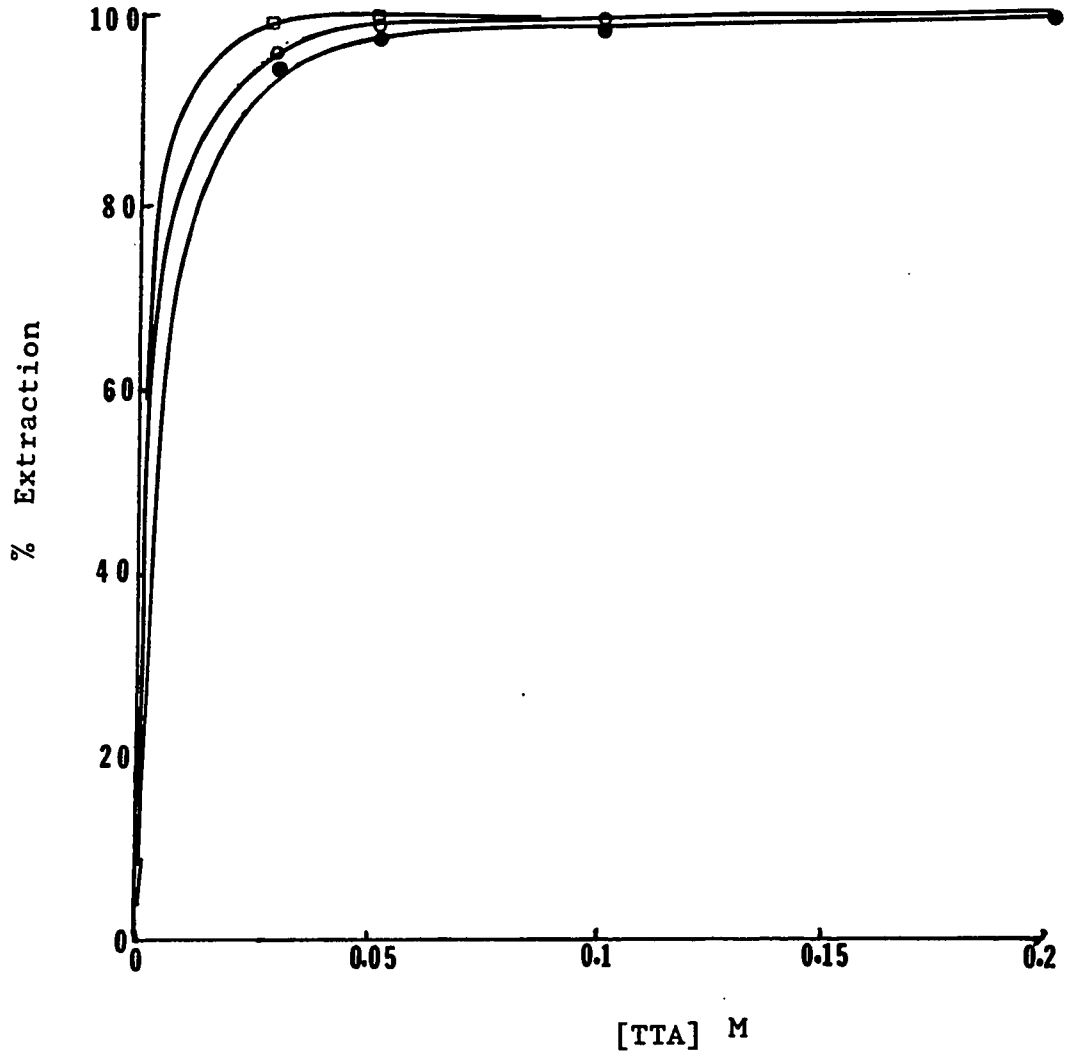


Fig. 9 Effect of TTA concentration on the conventional extraction of Fe(III)-thenoyltrifluoroacetonate into toluene, at 30°C, at different initial aqueous pH values.

contact time = 2 min. $[Fe^{+3}] = 1.0 \times 10^{-3}$ M
[tartrate] = 0.05 M

□ pH = 6 o pH = 7 ● pH = 8

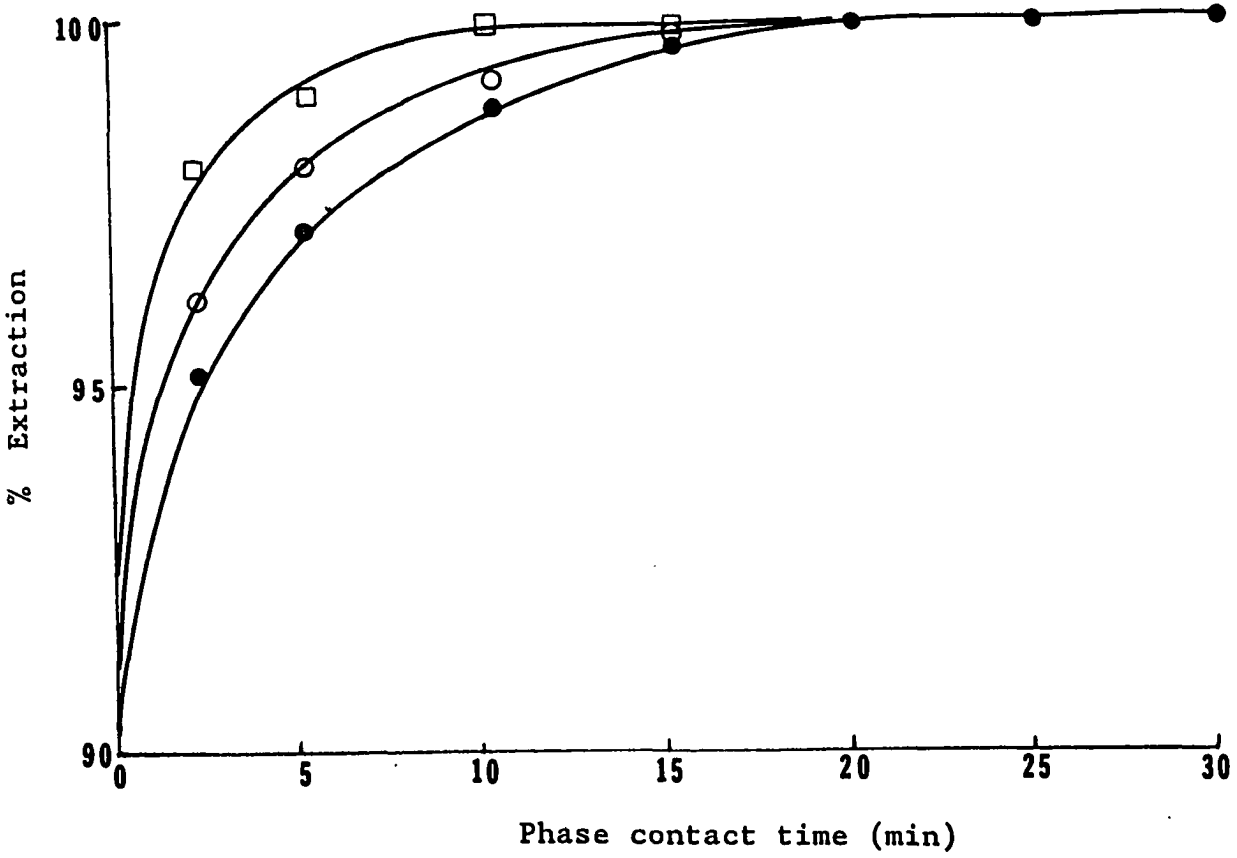


Fig. 10 Conventional extraction of Fe(III) with 2.5×10^{-3} M TTA of propylene carbonate solutions at various initial aqueous pH values, at 30°C.

$[Fe^{+3}] = 1.0 \times 10^{-3}$ M [tartrate] = 0.05 M

□ pH = 6 ○ pH = 7 ● pH = 8

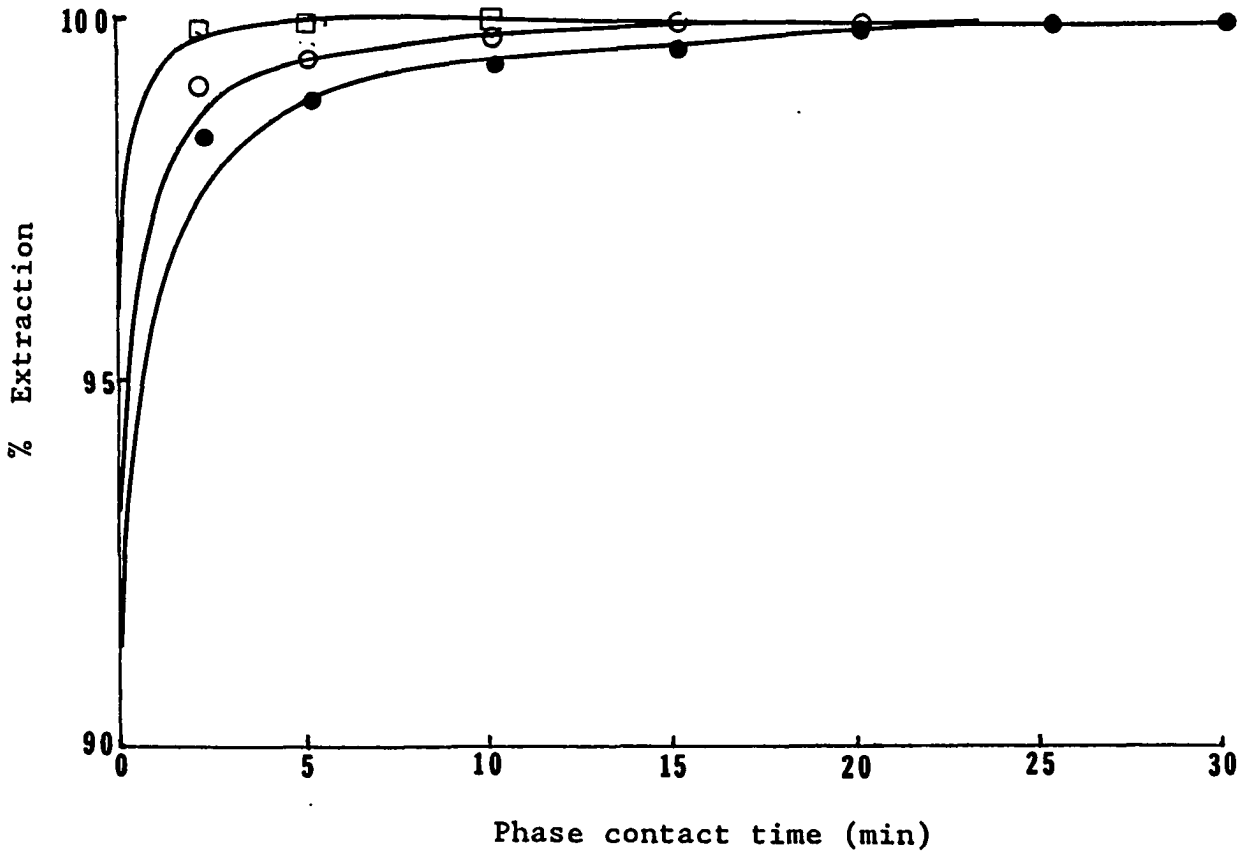


Fig. 11 Conventional extraction of Fe(III) with 2.5×10^{-3} M TTA of toluene solutions at various initial aqueous pH, at 30°C.

$[Fe^{3+}] = 1.0 \times 10^{-3}$ M [tartrate] = 0.05 M

□ pH = 6 ○ pH = 7 ● pH = 8

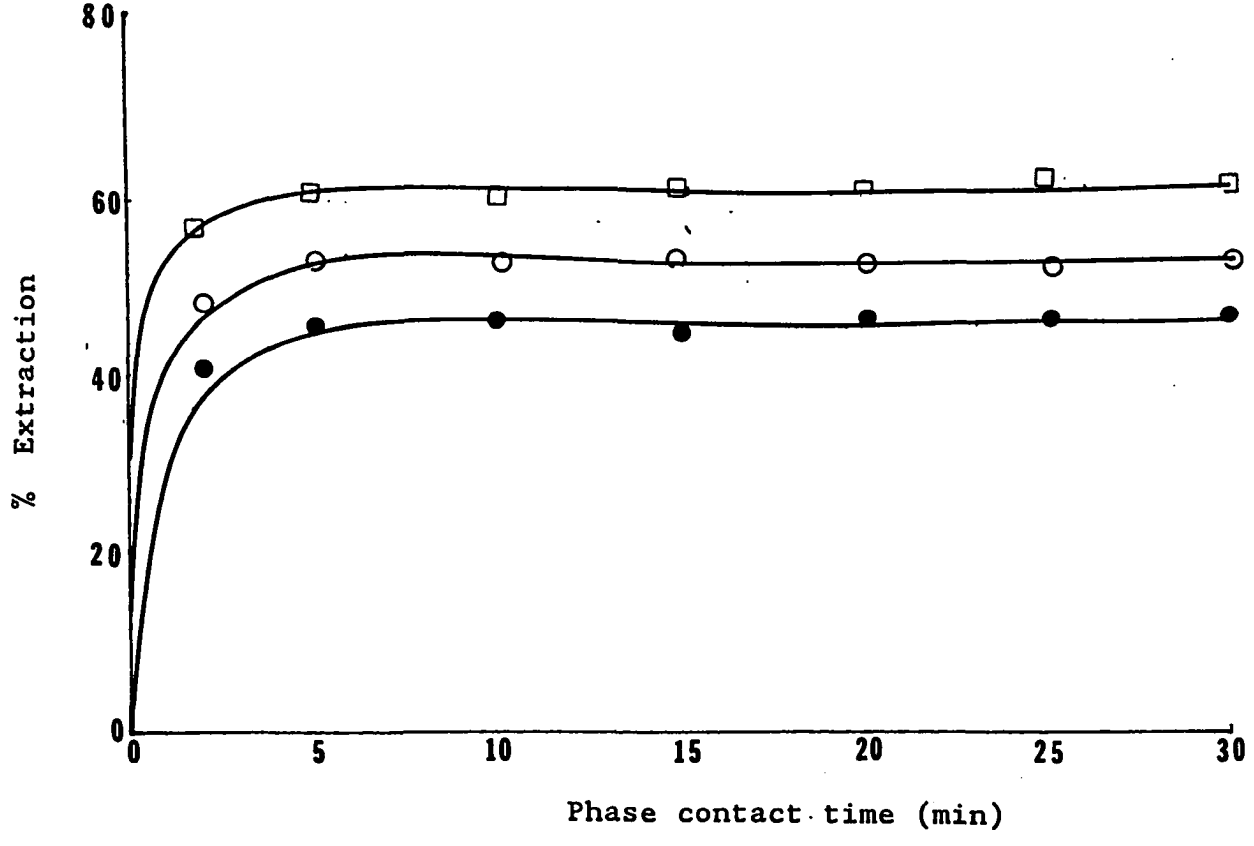


Fig. 12 Conventional extraction of Fe(III) with 2.5×10^{-3} M TTA of propylene carbonate solutions at various initial aqueous pH values, at 30°C.

$[Fe^{3+}] = 5.0 \times 10^{-3}$ M [tartrate] = 0.1 M

□ pH = 6 ○ pH = 7 ● pH = 8

into propylene carbonate under the same conditions gave 67%, 58% and 53% extraction at pH 6, 7 and 8, respectively. At higher (TTA)/(metal) ratio there is no significant difference between conventional and homogeneous extraction methods. There was 100% extraction of Fe(III) at the higher pH by both techniques. The homogeneous method gave better extraction at low (TTA)/(metal) ratios. The effectiveness of homogeneous liquid-liquid extraction is attributed to the higher reaction temperature which brings about a disturbance of the water structure in the medium (decreases the water activity) in which the aqueous species is caught by intrusion of propylene carbonate molecules, the easier mass transfer, increased rate of reaction, the interaction between iron(III) and TTA in the single phase, and the completion of the successive chelation of iron(III) with TTA. Murata et al.(3) reported ca. 85% extraction of Fe(III)-TTA into propylene carbonate at 30°C with 2 x 10^{-2} M TTA at pH 2. The lower extraction efficiency of Fe(III)-TTA at near neutral pH with low (TTA)/(metal) ratio may be due to the higher formation constant of Fe(III)-tartrate and the competition between TTA and hydroxide ions. Therefore, it may be better to use malonate (log stability constant of Fe(III)-malonate = 7.46)(67) or succinate (log stability constant of Fe(III)-succinate = 7.49)(67) instead of tartrate at low (TTA)/(metal) ratios.

The absorption spectra of Fe(III)-TTA complex extracted into toluene from pH 7 aqueous medium is shown in Fig. 13. Khopkar et al.(64) and Satake et al.(68) also reported the same spectra for the Fe(III)-TTA complex extracted at low pH. Thus, it can be inferred that the same complex is formed at both the high and low pH.

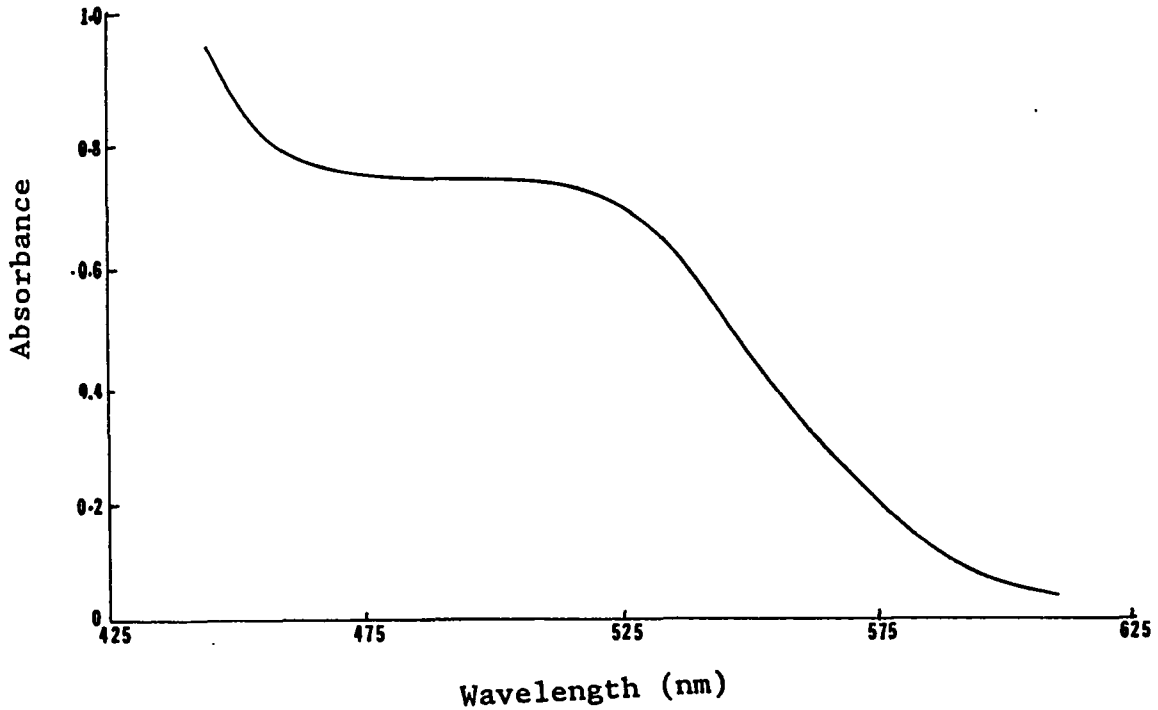


Fig. 13 Absorption spectra of the Fe(III)-TTA complex in toluene at pH 7.

$[Fe^{+3}] = 1.6 \times 10^{-4}$ M [TTA] = 1.6×10^{-2} M [tartrate] = 2.0×10^{-2} M

4.3 Homogeneous Liquid-Liquid Extraction of Fe(III)-Acetylacetonate

Acetylacetone reacts with over 60 metals to give chelates of sufficient stability(69) that formation occurs even at low metal ion concentrations. The solubility of acetylacetonates in organic solvents is of a much higher order of magnitude than most analytically used chelates; acetylacetonates have solubilities expressed in grams per liter rather than in milligrams per liter. Thus, with acetylacetone both micro and macro separations are feasible. Acetylacetone is readily available and is a cheaper reagent than TTA. Acetylacetone can also serve the dual purpose of chelating agent and extracting solvent(69). The effect of initial aqueous pH and acetylacetone concentration on the extractability of Fe(III)-acetylacetonate into propylene carbonate using homogeneous method is shown in Fig. 14. The extraction of Fe(III)-acetylacetonate decreases with increasing pH, similar to Fe(III)-TTA. This may be due to the competition of tartrate, acetylacetonate and hydroxide ions at higher pH values. Quantitative extraction of Fe(III) is achieved at pH 6 and 7 with 0.2 M acetylacetone. The effect of TTA and acetylacetone concentration on the homogeneous extraction of Fe(III) at initial aqueous pH 6 is shown in Fig. 15. In the case of TTA, quantitative extraction of Fe(III) is possible even with 0.025 M TTA and in the case of acetylacetone quantitative extraction is possible only with 0.2 M acetylacetone. Better extraction is achieved with TTA because it enolizes faster than acetylacetone.

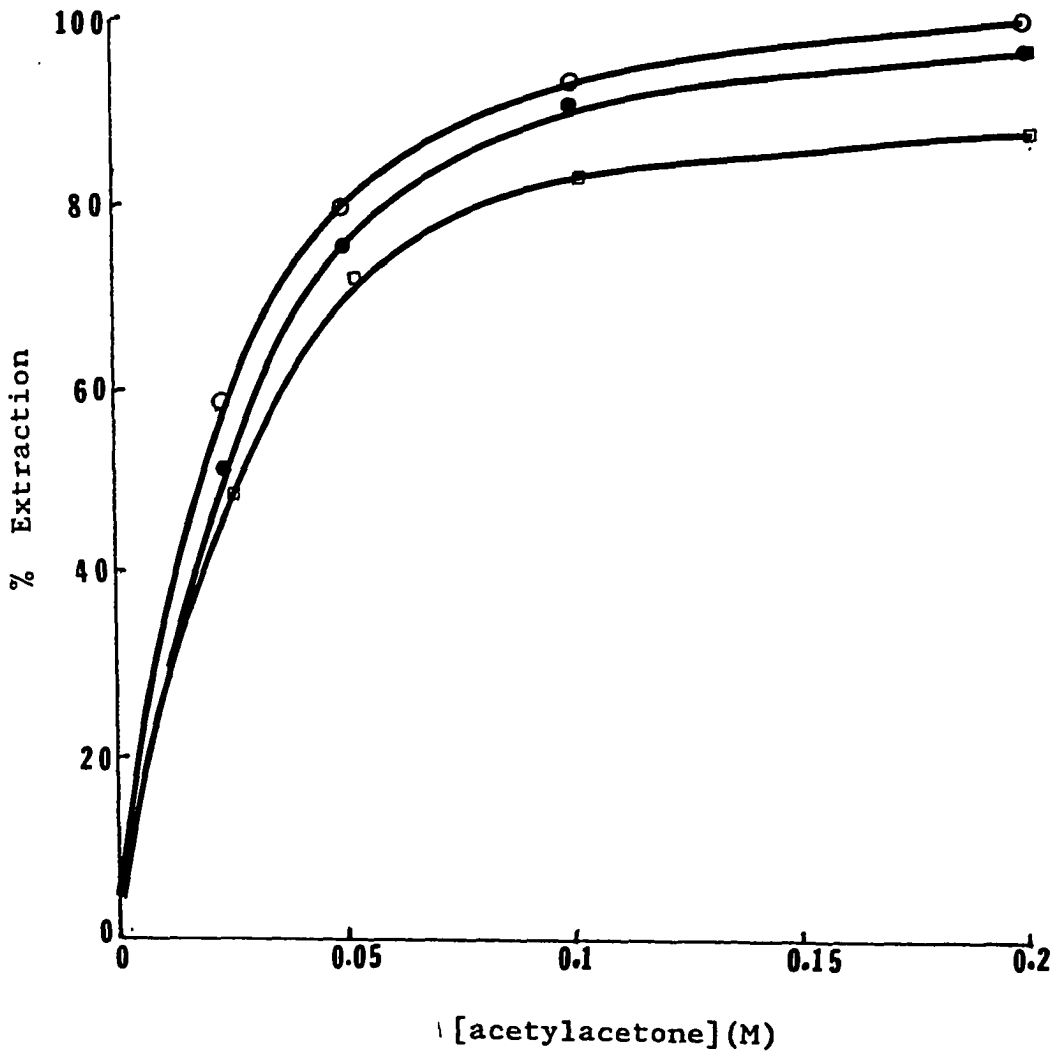


Fig. 14 Effect of acetylacetone concentration on the homogeneous extraction of Fe(III)-acetylacetonate into propylene carbonate, at different initial aqueous pH values.
$[Fe^{3+}] = 1.0 \times 10^{-3}$ M [tartrate] = 0.05 M

o pH = 6 ● pH = 7 □ pH = 8

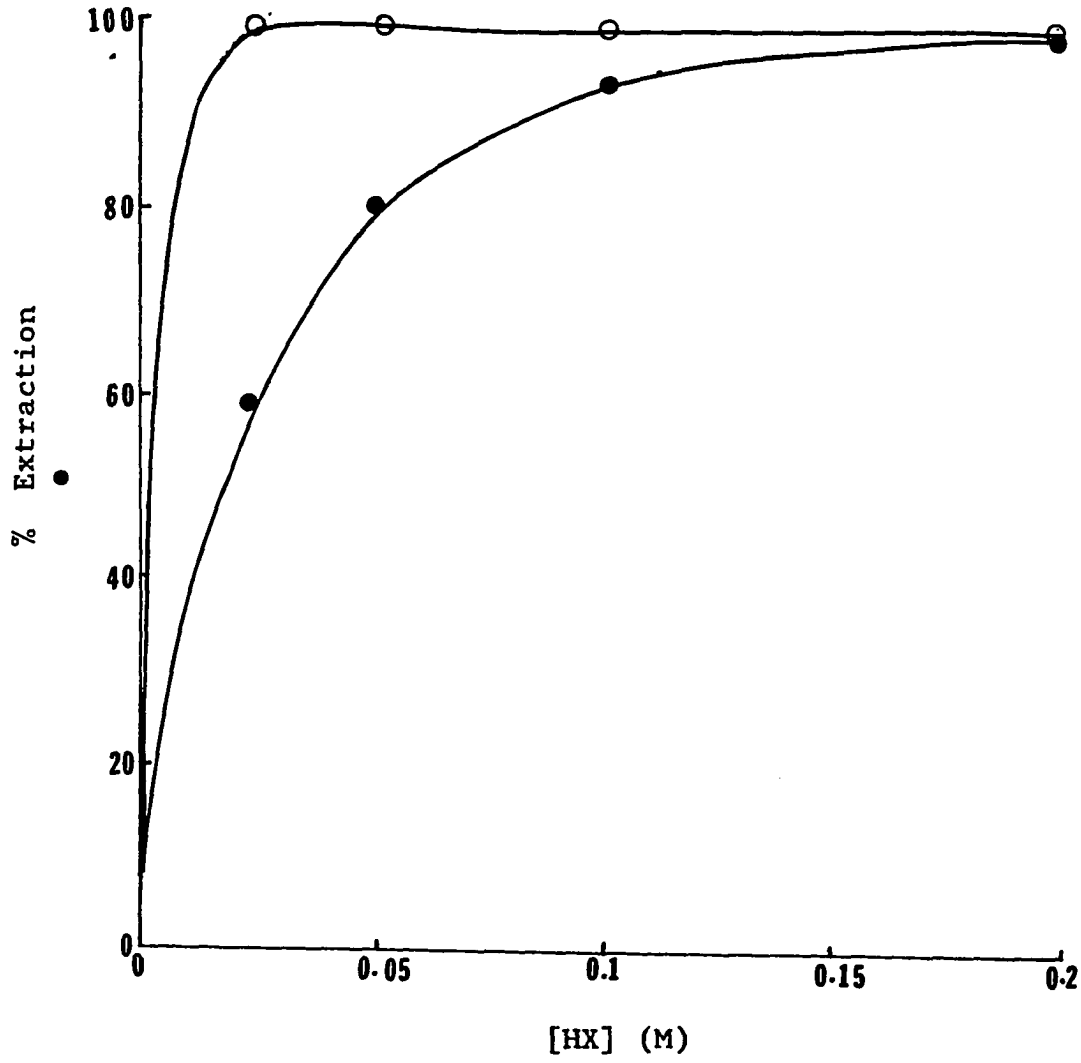
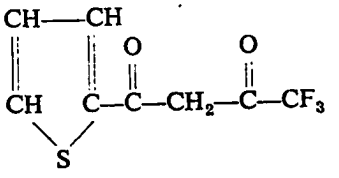


Fig. 15 Effect of chelating agent concentration on the homogeneous extraction of Fe(III) into propylene carbonate, at initial aqueous pH 6.

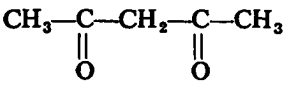
$[Fe^{3+}] = 1.0 \times 10^{-3}$ M [tartrate] = 0.05 M

O TTA ● acetylacetone

Keto forms of TTA and acetylacetone:



TTA



acetylacetone

The electronwithdrawing group $-CF_3$ gives rise to more enolate ion in TTA than does the $-CH_3$ group in acetylacetone. However, quantitative extraction of Fe(III) can be achieved at near neutral pH using homogeneous method with the cheaper reagent, acetylacetone. At pH 1.0 Fe(III) has also been quantitatively extracted with pure acetylacetone(70-72).

4.4 The mechanism of the metal-chelate extraction

The mechanism of the metal-chelate extraction can be described by the following steps:

1. Distribution of chelating agent into the aqueous phase.
2. Ionization of the chelating agent.
3. Reaction of metal cation with enolate ion.
4. Distribution of the chelate into the organic phase.

Taft and Cook(47) carried out kinetic and equilibrium studies of iron(III) thenoyltrifluoroacetonate by spectrophotometric means and reported that the rate determining step was the reaction of iron(III) with the enolate ion. Extractions at higher pH favors formation of the enolate ion, thus increasing the rate of the slow step in chelate extraction. Homogeneous extraction also circumvents this limiting step because at higher temperatures the reaction rates increases, there is easier mass transfer, there is a disturbance of the water structure and the interaction between the metal and chelating agent is in a single homogeneous phase. Thus, the homogeneous extraction of Fe(III), Co(II) and Cu(II) chelates at near neutral pH gives rapid and quantitative extraction.

4.5 Alternative Mechanism for Synergic Solvent Extraction

Synergism in solvent extraction was observed when neutral organophosphorus esters or amines present in the organic phase or addition of thiocyanate ion to the aqueous phase. The mechanisms proposed for synergic solvent extractions are as follows:

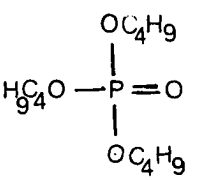
a. Formation of a mixed complex, by opening of one chelate ring per molecule of neutral ligand(25).
b. Formation of an adduct without opening any chelate ring, which could be the result of substitution of coordinated water, or simply increasing the coordination number. The resulting adduct is thought to be less hydrophilic and thus more soluble in organic solvent(22).
c. Formation of an addition compound, with the adduct molecule bound to the chelate and not directly to the metal ion(28).
d. Kinetic mechanism- elimination of the slow step in the metal chelate extraction with the addition of SCN^- ion to the aqueous phase(46).

Fig. 4 shows the absorption spectra of TTA in 2:2:1 ratio of propylene carbonate/aqueous/ethanol at pH 2 and 7. The spectrum at pH 7 is identical to the enolate form of TTA and at pH 2 the spectrum is identical to the ketohydrate form, observed by Healy et al.(49). There-

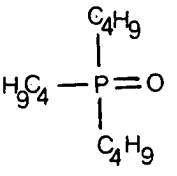
fore, it appears that the metal chelate extractions were rapid and quantitative due to the formation of the enolate ion of the chelating agent at higher pH. This implies that the synergic effect may be due to the formation of the enolate ion of the chelating agent in the organic phase in the presence of neutral organophosphorus esters or amines. A series of absorption spectra of TTA were obtained in the presence of tributylphosphine oxide (TBPO), tributylphosphate (TBP), tri-n-octylamine (TNOA) and tri-n-octylphosphine oxide (TNOPO) respectively, and are shown in Fig. 16.

In benzene solution 11% of TTA is in the ketohydrate form and the remainder is in the enol form(48). In the presence of TBP, TOPO and TNOPO the peak corresponding to the enol form of TTA was increased and in the presence of TNOA the peak corresponding to the enolate form of TTA was obtained. The peak corresponding to the enol form of TTA increases in the order

TNOPO > TBPO > TBP.



TBP



TBPO

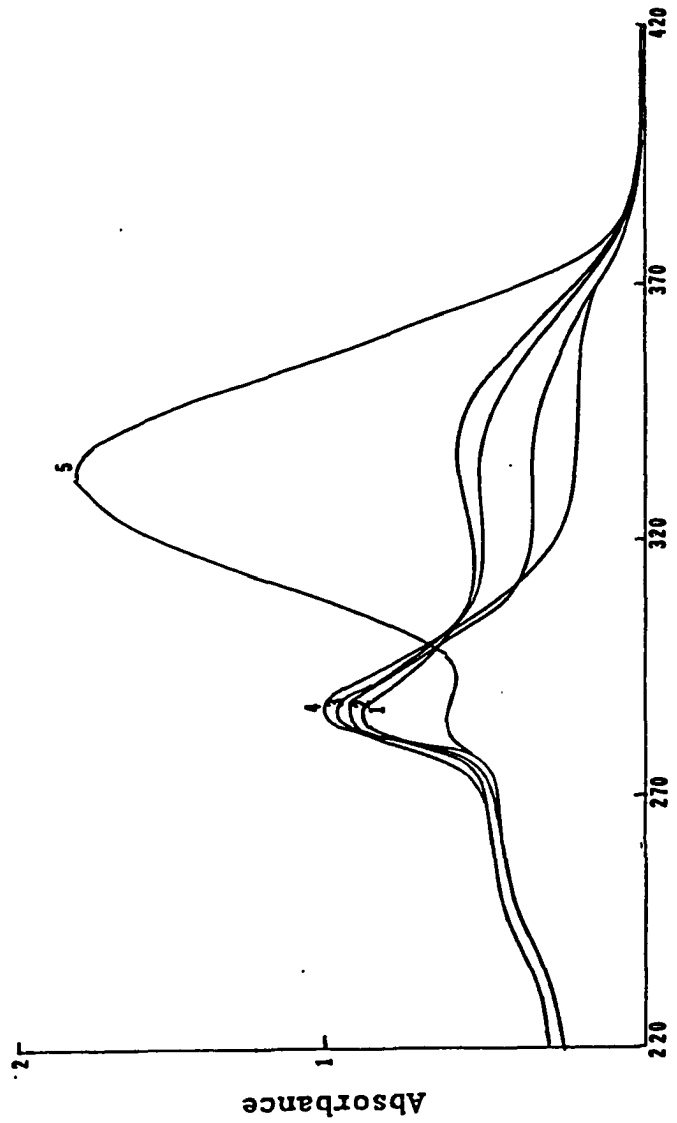
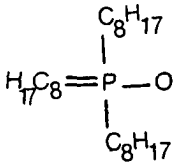
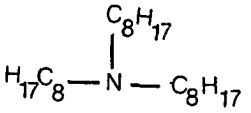


Fig.16 Absorption spectra of 1×10^{-4} M TTA in benzene in the presence of 3.3×10^{-2} M organic base.

1. TTA 2. TTA + TBP 3. TTA + TBPO
4. TTA + TNOPO 5. TTA + TNOA



TNOPO



TNOA

The basic strength of the bases increases in the order TNOA > TNOPO > TBPO > TBP.

It is known that the synergic effect increases with the increasing basicity of the esters or amines(35,36). Newman and Klotz(39) observed the TTA spectrum in the presence of TNOA. They obtained a peak at ca. 340 nm which corresponds to the enolate form of TTA observed by Healy et al.(63). The peak increased with increasing amounts of base. They attributed this peak to the association product of TTA and amine. However, obtain the same peak of TTA at pH 7, in 2:2:1 ratio of propylene carbonate/aqueous/ethanol medium in the absence of amine Therefore, we suggest an alternative mechanism for the synergic effect of various organic bases in TTA extractions. Acid base reactions between the chelating agent and the various bases in the organic phase yield higher concentrations of enol and enolate ions in the aqueous phase. Thus, there is a significant increase in the rate of the slowest step in metal-TTA extractions which results in more rapid achievement of extraction equilibria.

4.6 Extraction of Uranium

Homogeneous extraction of Fe(III), Co(II) and Cu(II)-chelates gave rapid and quantitative extraction efficiencies at near neutral pH (6 to 8). Therefore, our interest in both extractions at higher pH, and extractions by the homogeneous suggested an application to the extraction of uranium from ores and spent fuel elements.

A recent "Special Report" by Fathi Habashi(73) points out that a major breakthrough in hydrometallurgy was the introduction in the 1940's of the leaching process for uranium ore and solvent extraction for recovering the uranium. This article also describes the current application of an "in situ" leaching process in which sodium carbonate is pumped directly into the deposit to remove uranium, thus obviating ore transport.

Habashi also points out that the presence of uranium in phosphate rock (ca.200 ppm) used for fertilizer can possibly introduce uranium into our foodstuffs. This is a matter of current concern and methods are being developed for removing uranium.

Uranium(VI) can be extracted into propylene carbonate from nitrate medium and the uranium(VI) in the organic phase can be stripped into aqueous phase using aqueous carbonate solutions. The final separation

of uranium(VI) can be achieved by extracting uranium(VI) into dibenzoylmethane in propylene carbonate. The possibility of a preliminary extraction of uranyl nitrate into propylene carbonate suggests application to processing spent fuel elements.

Ever since Peligot(74) found that uranium(VI) in nitric acid is extractable into diethyl ether, this extraction of uranyl nitrate and extraction with many other solvents has been studied by numerous investigators(75,76). Although diethyl ether has been used for a very long time by many investigators, this solvent in nitrate systems has the following disadvantages. It is of comparatively low extractibility; complete recovery of uranium(VI) in nitric acid is obtained only after four or more successive extractions; it has a high solubility in water; there is coextraction of a large amount of nitric acid; and ether has a low flash point.

The results of the extraction of uranyl nitrate into propylene carbonate at 99°C using various salting out reagents, which heretofore has not been studied, are shown in Table (II). When the aqueous solution was saturated with nitrate salts, a homogeneous mixture was not obtained even by heating the aqueous solution with propylene carbonate to 99°C. According to the results in Table II the extraction of uranyl nitrate into propylene carbonate is not effective without a salting out

Table II. Extraction of uranyl nitrate into propylene carbonate at 99°C.

UO_2^{2+} concentration (moles/L)	Salting out reagent	% Extracted
10^{-4}	1 M HNO_3	16%
10^{-4}	0.2 g/ml NH_4NO_3	22%
10^{-4}	2 g/ml NH_4NO_3	65%
10^{-4}	2 g/ml NH_4NO_3 + 1 M HNO_3	97%
10^{-2}	2 g/ml NH_4NO_3 + 1 M HNO_3	97%
10^{-4}	$LiNO_3$	Solubility of PC in water increases
10^{-4}	$Al(NO_3)_3$	Interferes with DBM determination
10^{-4}	2 g/ml NH_4NO_3 + 1 M HNO_3 30 min shaking (without heating)	77%

agent; 97% was extracted under optimum conditions. Ordinary batch extraction (with 30 minutes shaking) even with a salting out agent yields only 77% recovery at room temperature. Uranyl nitrate can be quantitatively extracted into many ketones(77-79), esters of carboxylic acids(80,81), neutral organophosphorus compounds(77,82,83) and also into some other solvents(74,75) using varying amounts of salting out reagents and nitric acid. For example uranyl nitrate was quantitatively extracted into MIBK with 2.3 to 2.7 M aluminum nitrate or 1 M ammonium nitrate at pH 0 to 3(84,85); It has also been extracted into 0.1 M trioctylphophine oxide in cyclohexane with 1 to 7 M nitric acid(77,86,87). The advantage of using propylene carbonate as the solvent is that both organic and aqueous phases can be analyzed for material balance. It was found that higher temperatures and increasing amounts of salting out agents favor the uranyl nitrate extraction into propylene carbonate. Dizdar(88) and Shevchenko(89, had reported that increasing temperature decreases the uranyl extraction into toluene, and Evers(90) also found the same effect in ether and hexone.

A salting out agent which is highly hydrated, e.g., $Al(NO_3)_3$ facilitates extraction of uranium by reducing the water activity. But it interferes with the subsequent determination of uranium. When $LiNO_3$ is used as salting out reagent the solubility of propylene carbonate in water increases with increasing temperatures.

The addition of nitric acid to the aqueous phase favors the extraction of uranium by preventing or decreasing the hydrolysis of uranyl ion and by increasing the nitrate ion concentration(91). However, large concentrations of nitric acid are generally not desirable; the formation of $HNO_3.S_n$ complexes reduces the amount of free solvent; the extraction of other elements is enhanced; and the danger of an explosive reaction between solvent and acid is increased(92). The optimum matrix for uranyl nitrate extraction into propylene carbonate was 2 g/ml NH_4NO_3-1 M HNO_3.

The extraction of uranium in propylene carbonate by sodium carbonate solution as a function of pH is shown in Fig. 17. The advantage of using carbonate solution for stripping rather than water or acidic solutions is the insolubility of many cations (e.g., transition metals) in a solution with a moderate to high carbonate content, thus reducing the number of interferences. Extraction is incomplete both at low pH and at high pH. At low pH this may be due to the low concentration of carbonate ion, insufficient to form the complex. Although one would expect a higher percent extraction at higher pH, the extraction decreases with increasing pH above 7.6, which may be due to the competition with hydroxide formation. Also, dissociation of ligand can occur which can allow for anionic complexes which remain in aqueous phase. The success of the carbonate stripping is a result of the large overall formation

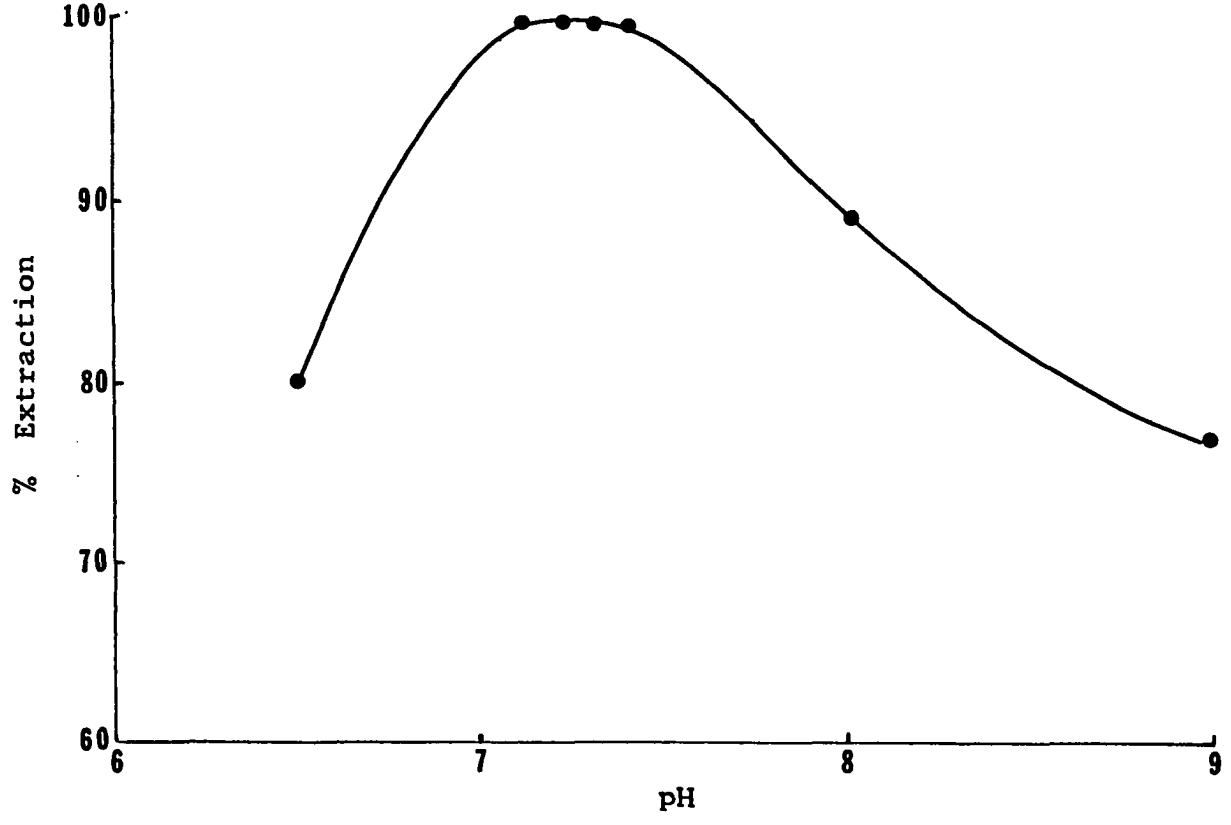


Fig.17 Effect of initial aqueous pH on the homogeneous extraction of uranium(VI) in propylene carbonate into aqueous carbonate solution.

$[CO_3^{-3}]$ = 0.1 M $[UO_2^{2+}]$ = 4.4 x 10^{-4} M

constant for uranyl-carbonate complexes(93).

$$UO_2^{2+} + 3CO_3^{2-} \quad [UO_2(CO_3)_3]^{4-} \qquad \beta_3 = 2 \times 10^{18}$$

$$UO_2^{2+} + 2CO_3^{2-} \quad [UO_2(CO_3)_2\ 2H_2O]^{2-} \qquad \beta_2 = 4 \times 10^{14}$$

Unfortunately, the stability of the complexes limits the possibility of a quantitative reaction between uranium and any known colorimetric reagent(94). Thus it is necessary to free the uranium from the carbonate complex by adding nitric acid and boiling to eliminate the CO_2. The uranium liberated from the carbonate complex reacts with the colorimetric reagent quantitatively.

The results of the final separation step of the extraction of uranyl ion into propylene carbonate containing dibenzoyl methane is given in Figure 18. As the pH of the aqueous solution increases above 7, the percent extraction decreases. This result agrees with Stary(95). It is anticipated that the initial extraction of uranyl nitrate into propylene carbonate and subsequent stripping with carbonate solution will reduce the activity from a fuel element sample so that the possibility of destroying the organic chelating agent is decreased. It is known(96) that the dibenzoyl methane exists in the enolic form, $C_6H_5COCH{=}COHC_6H_5$ and the structure of the yellow complex is given

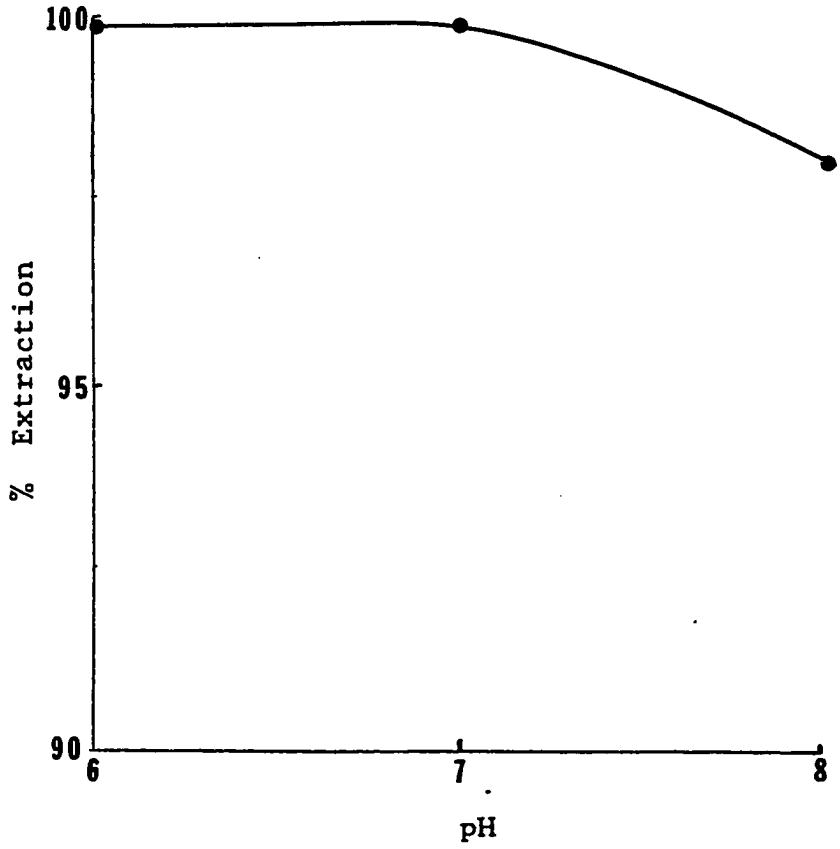
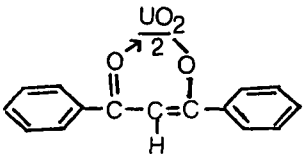


Fig.18 Effect of initial aqueous pH on the homogeneous extraction of uranyl-dibenzoylmethane into propylene carbonate.

[DBM] = 0.1 M $\quad [UO_2^{2+}] = 4.4 \times 10^{-4}$ M

as(51)



in alcohol water medium. Figure 19 shows the maximum in the absorption spectrum of uranium dibenzoyl methane to be 395 nm, as measured against a reagent blank. The medium is a 2/2/1 ratio of propylene carbonate phase, aqueous phase and ethanol, at pH 7. Yoe et al.(51) also reported the same spectrum in ethanol-aqueous medium at pH 7.

The effect of some diverse ions on the extraction of uranyl ion were investigated. The effect of Th(IV), Fe(III) and Ca(II) were studied here because these are some of the constituents in uranium ores. The optimum matrix for uranyl nitrate extraction into propylene carbonate was 2 g/ml NH_4NO_3+1 M HNO_3. The effect of Th(IV), Fe(III) and Ca(II) on the extraction of uranyl ion under the same conditions is shown in Table III. The percent of U(VI) extracted in the presence of Th(IV), Ca(II) and Fe(III) are 95%, 87% and 93% respectively. The homogeneous extraction of uranium(VI) in propylene carbonate by aqueous carbonate is quantitative with 0.1 M carbonate at pH 7.2 to 7.6 in the absence of diverse ions. The effect of Th(VI), Fe(III) and Ca(II)

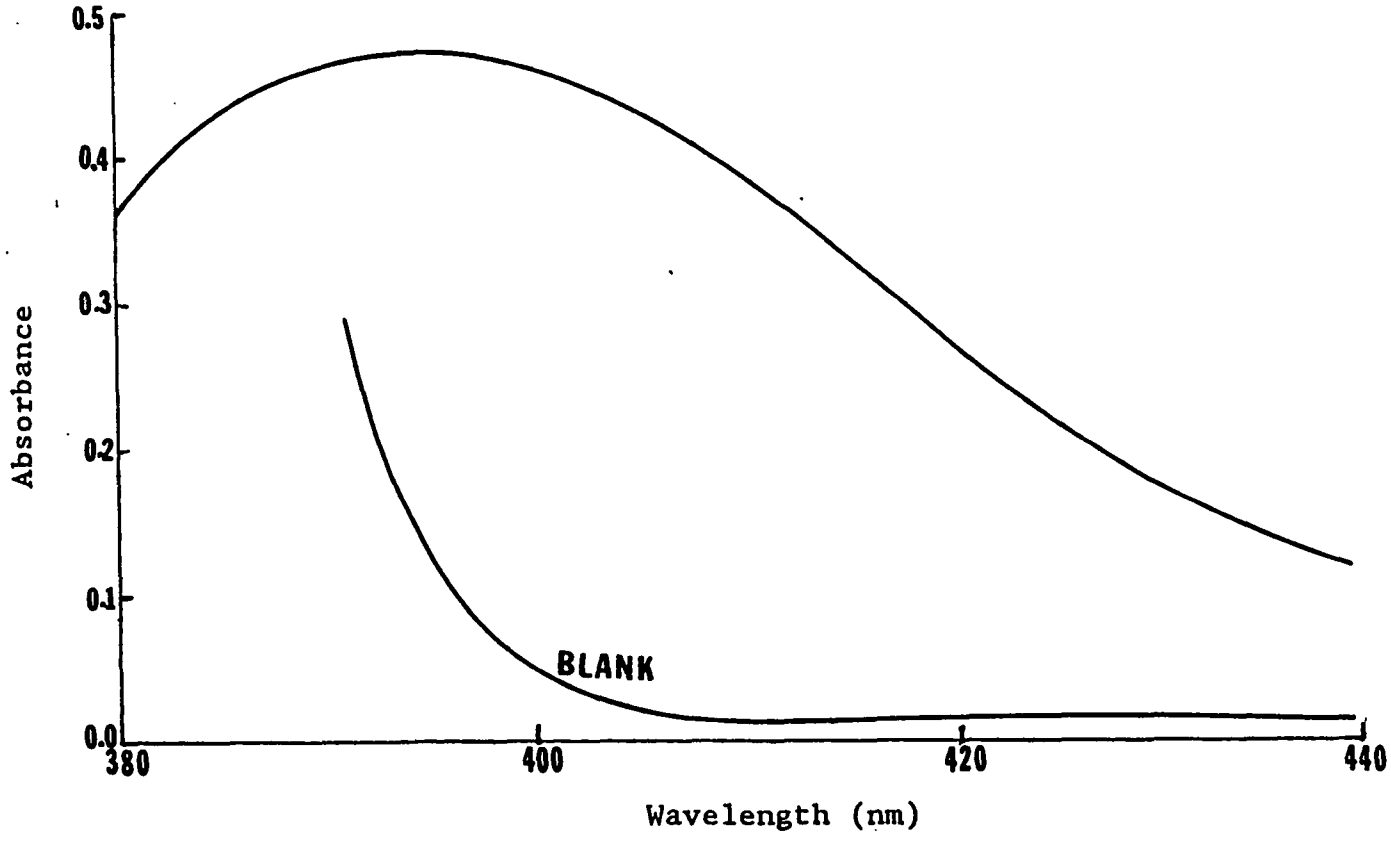


Fig.19 Absorption spectra of uranium-dibenzoylmethane in 2:2:1 ratio of PC/aqueous/ethanol at initial aqueous pH 7.

$[UO_2^{+2}]$ = 5 ppm

Table III. Effect of Fe(III), Ca(II) and Th(IV) on the extraction of uranyl nitrate from an aqueous medium 2 g/ml NH_4NO_3-HNO_3, into propylene carbonate at 99°C.

Metal	Metal added (mg)	Uranium added (mg)	Uranium recovered (mg)
Th	4.26	5.24	4.98
Ca	5.26	5.24	4.56
Fe	5.42	5.24	4.87
-	-	5.24	5.08

on the extraction of uranium(VI) in propylene carbonate into aqueous carbonate solution of pH 7.3 is shown in Table IV. The percent of U(VI) extracted in the presence of Th(IV), Ca(II) and Fe(III) are 98%, 88% and 95% respectively. The homogeneous extraction of uranium(VI) in aqueous carbonate solution with 0.1 M dibenzoylmethane in propylene carbonate is quantitative at pH 6 to 7 in the absence of diverse ions. The effect of Th(IV), Ca(II) and Fe(III) in the overall procedure indicates no loss of U(VI) in the extraction 0.1 M dibenzoylmethane in propylene carbonate at pH 7, as shown in Table V. In this step almost quantitative extractions were achieved in the presence of diverse ions, perhaps because of the removal of diverse ions in the first two separation steps.

Table IV. Effect of Fe(III), Ca(II) and Th(IV) on the extraction of uranium into 0.1 M aqueous carbonate solution at pH 7.3.

Metal	Metal added (mg)	Uranium added (mg)	Uranium recovered (mg)
Th	4.26	4.98	4.88
Ca	5.26	4.56	4.47
Fe	5.42	4.87	4.63
-	-	5.08	5.06

Table V. Effect of Fe(III), Ca(II) and Th(IV) on the extraction of uranium into 0.1 M DBM in propylene carbonate, at pH 7.

Metal	Metal added (mg)	Uranium added (mg)	Uranium recovered (mg)
Th	4.26	4.88	4.80
Ca	5.26	4.47	4.40
Fe	5.42	4.63	4.59
-	-	5.06	5.05

4.7 Liquid-liquid Phase Equilibria in the Propylene Carbonate + Methyl Iso-Butyl Ketone + Water System

The recovery of the solvent used in extraction is nearly always necessary, not only to make the solvent available for reuse, but also to provide solvent-free products. In many instances, the solvent recovery operation is the most costly part of the entire separation scheme, and consequently, it must be given special attention. Distillation, evaporation, crystallization, chemical reaction and liquid-liquid extraction are examples of some of the solvent recovery methods.

To depict the phase behavior of a three component system on a two-dimensional diagram, it is necessary to consider both the pressure and the temperature as fixed. The phases of the system can then be shown as a function of the composition. The overall composition of a ternary system can always be indicated by a point in an equilateral triangle. The apices of the triangle represent the pure components. The sum of the length of the perpendiculars from any point within the triangle to the three sides, equals the altitude(97). The length of the altitude is then allowed to represent 100 percent composition, and the length of the perpendiculars from any point represents the percentages of the three components. Any point on the side of the triangle represents a binary mixture of the two components at the two ends of that side.

The densities of the propylene carbonate + methyl iso-butyl ketone system at 30°C and 50°C are shown in Tables VI and VII. The solubility data and the liquid-liquid phase diagrams for the propylene carbonate + methyl iso-butyl ketone + water system, at 30°C and 50°C, are shown in Tables VIII, IX and Figs. 20 and 21, respectively. The phase diagrams we obtained belong to the type which forms two pairs of partially miscible liquids. According to the phase diagrams at 30°C and 50°C, both liquid pairs, propylene carbonate-water and water-methyl iso-butyl ketone are partially miscible, and methyl iso-butyl ketone dissolves in any proportion with propylene carbonate. When the temperature increases, the miscibility of the liquid phase increases. However, the solubility increase with temperature is very small and obviously high temperatures would be required to achieve complete miscibility. Because of the relatively difficult analysis of the two equilibrium liquid mixtures we used the lever rule technique(98) to obtain the tie lines. The compositions of the two equilibrium phases obtained by this technique at 30°C and 50°C are shown in Tables X and XI.

If a quantity of solvent (MIBK) is gradually added to a mixture of water and propylene carbonate (shown in Fig. 18 as point F), the overall composition of the ternary system moves along line FB. If equal parts of MIBK and mixture F have been taken, the overall composition of the resulting ternary system is represented by M, so situated that

Table VI Densities of the propylene carbonate + methyl iso-butyl ketone system at 30°C.

PC wt%	density g cm^{-3}
100.0	1.200
89.6	1.140
77.2	1.080
50.2	0.961
24.2	0.868
10.2	0.824
0.0	0.793

Table VII Densities of the propylene carbonate + methyl iso-butyl ketone system at 50°C.

PC wt%	density g cm^{-3}
100.0	1.170
90.0	1.120
74.8	1.050
49.3	0.937
28.0	0.861
11.6	0.807
0.0	0.774

Table VIII. Solubility data for the propylene carbonate + methyl iso-butyl ketone + water system, at 30°C.

Propylene carbonate phase			Aqueous phase		
PC wt%	MIBK wt%	water wt%	PC wt%	MIBK wt%	water wt%
0.00	97.00	3.00	0.00	1.60	98.40
9.81	86.90	3.29	0.21	1.69	98.10
23.20	73.20	3.60	0.69	1.71	97.60
48.00	47.50	4.50	1.73	1.77	96.50
72.00	21.20	6.80	5.22	1.77	93.01
82.90	9.68	7.42	12.52	1.38	86.10
91.60	0.00	8.40	21.90	0.00	78.10

Table IX. Solubility data for the propylene carbonate + methyl iso-butyl ketone + water system at 50°C.

Propylene carbonate phase			Aqueous phase		
PC wt%	MIBK wt%	water wt%	PC wt%	MIBK wt%	water wt%
0.00	95.60	4.40	0.00	1.70	98.30
11.00	84.20	4.80	0.23	1.77	98.00
26.60	68.50	4.90	0.66	1.84	97.50
46.40	47.70	5.90	1.75	1.85	96.40
68.40	23.00	8.60	5.47	1.83	92.70
80.20	8.80	11.00	13.32	1.48	85.20
86.60	0.00	13.40	26.30	0.00	73.70

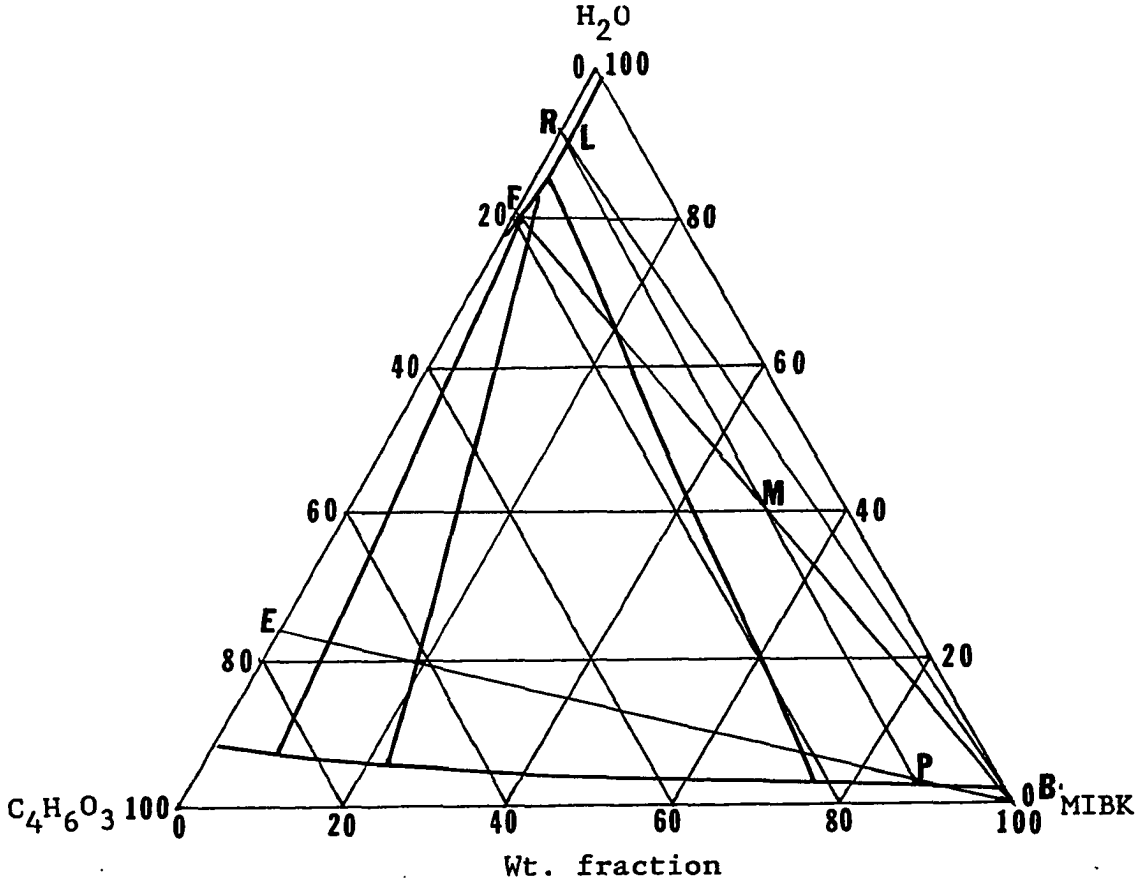


Fig. 20 Liquid-liquid phase diagrams of the propylene carbonate + water + methyl iso-butyl ketone system at 30°C.

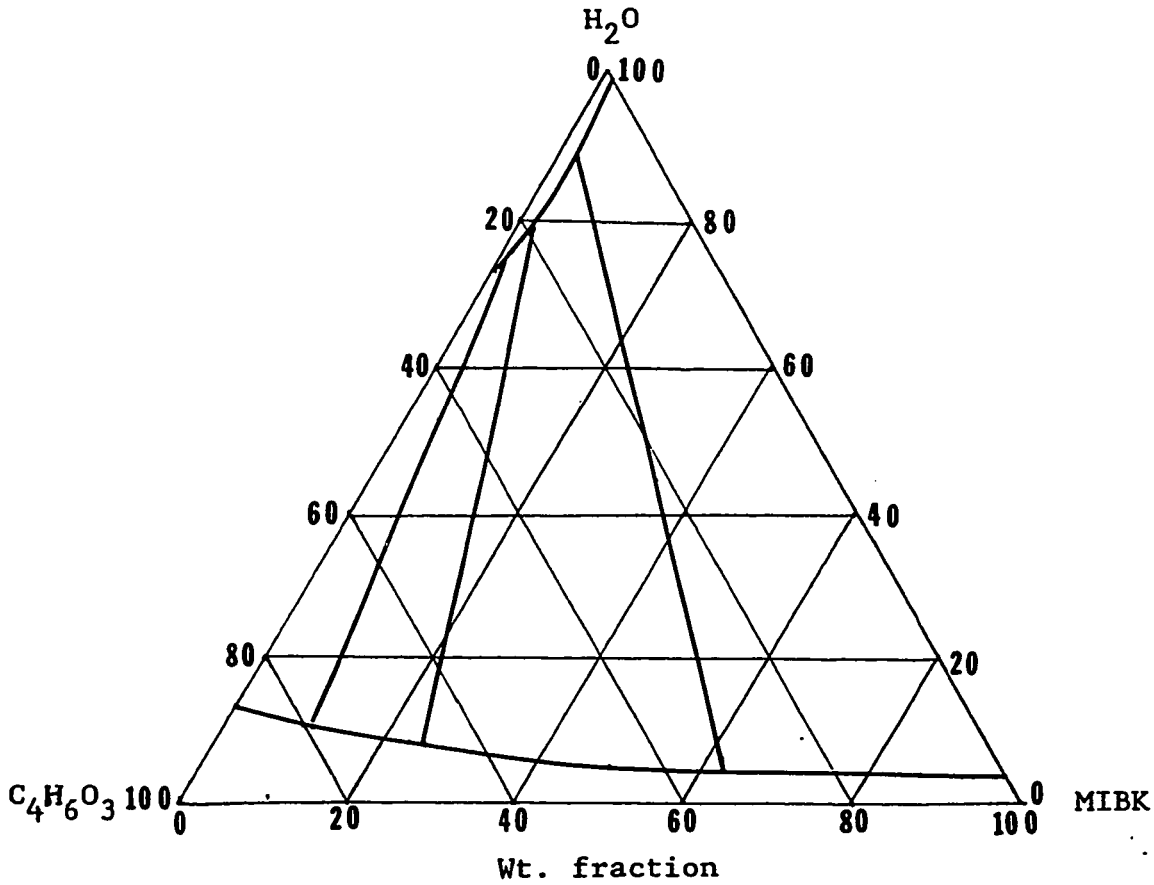


Fig. 21 Liquid-liquid phase diagrams of the propylene carbonate + water + methyl iso-butyl ketone system at 50°C.

Table X Composition of the two equilibrium phases for the MIBK + Water + PC system at 30°C.

water phase			MIBK phase		
water wt%	PC wt%	MIBK wt%	water wt%	PC wt%	MIBK wt%
85.5	13.0	1.5	3.0	22.5	74.5
84.7	14.0	1.3	6.0	71.0	23.0
83.8	15.0	1.2	7.0	84.0	9.0

Table XI Composition of the two equilibrium phases for the MIBK + water + PC system at 50°C.

Water phase			MIBK phase		
water wt%	PC wt%	MIBK wt%	water wt%	PC wt%	MIBK wt%
89.5	8.5	2.0	5.0	34.0	61.0
80.0	18.5	1.5	8.0	67.0	25.0
75.0	24.5	0.5	10.5	78.5	11.0

MB = FM. M is heterogeneous; it will therefore separate into two phases, whose compositions are given by P and L. Phase P has high content of MIBK and L has a low content of MIBK. By removing MIBK from phase P a MIBK-free extract is obtained, whose composition is represented by point E. In the same way, raffinate R is obtained from the raffinate phase L. Hence, by extraction followed by phase separation and solvent removal from the phases, the original mixture F is separated into the mixtures E and R. As compared with the original mixture F (83% H_2O and 17% PC), E has higher content of propylene carbonate (75%), and R contains less of propylene carbonate (9%). So that extraction has effected a partial separation between the components of the mixture of propylene carbonate and water. Therefore, according to the phase diagrams, complete recovery of propylene carbonate from aqueous medium using methyl iso-butyl ketone is not realized and this method is wasteful of methyl iso-butyl ketone.

Chapter V

CONCLUSION

Homogeneous liquid-liquid extractions of thenoyltrifluoroacetone chelates of Fe(III), Co(II) and Cu(II) and the acetylacetone chelates chelate of Fe(III) have been performed at near neutral pH (6 to 8) with the addition of tartrate as auxiliary ligand to maintain the cations in solution. The extraction of Fe(III)-TTA and Fe(III)-acetylacetonate decreases with increasing pH in this pH range; the extraction of Co(II)-TTA increases with increasing pH while extraction of Cu(II)-TTA was not a function of pH under the conditions studied. At higher (TTA)/(metal) ratio the extractions of Fe(III)-, Co(II)- and Cu(II)-TTA were quantitative at pH 6, 7 and 8. Extraction of Fe(III)-acetylacetonate was less efficient than the extraction of Fe(III)-TTA under the same conditions. However, rapid quantitative extractions were obtained with 0.2 M acetylacetone at pH 6 and 7. Thus, it is possible to extract Fe(III) quantitatively using a cheaper reagent than TTA e.g., acetylacetone, at near neutral pH (6 to 7).

Conventional extractions of Fe(III)-TTA into propylene carbonate and toluene have also been performed at near neutral pH. At low (TTA)/(metal) ratios the homogeneous method gave better extraction efficiency. At higher (metal)/(TTA) ratio the conventional method also gave quantitative extraction. At near neutral pH both conventional and homogeneous extractions were rapid and equilibrium was attained within a few minutes. Extractions at higher pH favors formation of the enolate ion, thus increasing the rate of the otherwise slow step in chelate extraction. Homogeneous extraction also circumvents this limiting step.

The higher pH results which show significantly higher ratio of enolate ion, suggest an alternative mechanism for the synergic effect of various organic bases in TTA extractions. It is proposed that acid-base reactions between the chelating agent and the various bases in the organic phase yield higher concentrations of both enol and enolate ions in the aqueous phase. Thus, there is a significant increase in the rate of the slowest step in the metal-TTA extractions which results in more rapid achievement of extraction equilibria.

Uranium(VI) was quantitatively extracted into propylene carbonate from an aqueous medium 2 g/ml NH_4NO_3 and 1 M HNO_3 at 99°C. The uranium(VI) in the organic phase was quantitatively stripped from the organic phase with 0.1 M sodium carbonate at pH 7.2 to 7.6 using the

homogeneous extraction technique. Final separation of uranium(VI) was obtained by extracting uranium(VI) into 0.1 M dibenzoylmethane in propylene carbonate using the homogeneous technique at pH 7. The effect of Th(IV), Fe(III) and Ca(II) on the extraction of uranium(VI) were investigated. There was no effect of these diverse ions on the extraction of uranium(VI) with dibenzoylmethane in propylene carbonate. Therefore, in the presence of these diverse ions, uranium(VI) can be extracted into propylene carbonate and quantitatively determined using this technique. This method can be used to extract uranium(VI) from ores and spent fuel elements.

The possibility of recovering propylene carbonate from aqueous solutions using methyl iso-butyl ketone as an extractive solvent was studied. From the data collected in this study we can conclude that methyl iso-butyl ketone is not an effective solvent for the extraction of propylene carbonate from an aqueous solutions.

The solvent extraction procedures outlined here can either be directed to remove the interferences, or the elements of interest may be extracted as a group. The extracted cations can be stripped from the organic phase under varying conditions of pH and in the presence of various complexing agents to achieve selective separations. This is viewed as an advantage for the separation of iron from commercial ores.

Present hydrometallurgical procedures involve an initial separation of iron(III) into the organic phase at low pH followed by extraction of desired cation at higher pH. Extraction of all the cations of interest along with iron into the organic phase followed by selective stripping of the former appears to offer a great advantage in cost since there is only one extraction in this case.

In general, it is expected that the homogeneous solvent extraction at near neutral pH will result in more effective solvent extraction, more rapid extractions, and will enable the design of commercial solvent extraction processes to be performed at higher pH with a concomitant improvement in corrosion resistance.

The uranium(VI) extraction method can be applied to separate uranium from ores, sea water and fuel elements. It is anticipated that the initial extraction of uranyl nitrate into propylene carbonate and subsequent stripping with aqueous carbonate solution will reduce the activity from a fuel element sample so that possibility of destroying the organic chelating agent is decreased. Behavior of typical high yield fission products will have to be studied before this separation scheme can be applied.

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