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HOMOGENEOUS LIQUID-LIQUID EXTRACTION

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HOMOGENEOUS LIQUID-LIQUID EXTRACTION

by

Chia-Swee Hong

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

1980

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May 16, 1980
date

David C. Locke
Executive Officer

Evan T. Williams

David C. Locke

Supervisory Committee

The City University of New York

Abstract

Solvent or liquid-liquid extraction is based on the principle that a solute will distribute itself in a certain ratio between two immiscible solvents, one of which is usually water and the other an organic solvent such as benzene, carbon tetrachloride or chloroform. In certain cases the initially aqueous solute is quantitatively transferred to the organic phase. The technique can be used for purposes of preparation, purification, enrichment, separation and analysis, on all scales of working from microanalysis to production processes.

Some problems do, however, remain in solvent extraction, e.g., slow extraction rates and incomplete extractions. A new homogeneous liquid-liquid extraction method using propylene carbonate has been developed, which is characterized by immediate formation of the complex upon achieving a single homogeneous liquid phase at elevated temperature. Two distinct phases appear upon cooling to room temperature. This method was applied to the extraction of a number of metal ions such as Fe(III), Cu(II), Ni(II), Pb(II) and Zn(II) from aqueous solution into propylene carbonate. The extraction behavior of both monodentate and bidentate complexes were

investigated and compared with the usual liquid-liquid extractions. Butylene carbonate, an analogue of propylene carbonate, was also studied as an extractant. Atomic absorption was applied to the analyses of both organic and aqueous phases by direct comparison with the standards.

We have demonstrated some potentialities of homogeneous liquid-liquid extraction, and believe that this idea might be advantageously applied to problems in separation chemistry for which the conventional solvent extraction procedure is inadequate.

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It is the author's wish to dedicate this thesis to her husband.

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I. Introduction

Recent advances in analytical chemistry are characterized by great progress toward more powerful methods of separation, equaling in significance the great forward strides made in instrumental methods of determination. Problems of chemical analysis almost always involve two steps: separation of the desired constituent and measurement of the amount or concentration of this constituent. Much worthy research has been dedicated to the development of more discriminatory methods of estimation, such as spectrophotometric and polarographic methods, which minimize the need for separation steps preceding the measurement. However, with the rapid growth of chemical technology, the analytical chemist is called upon to deal with mixtures of increasing complexity. In recent years, many elements previously considered laboratory curiosities have assumed industrial significance. The use of titanium, tantalum, niobium, and zirconium, for example, either as pure metals or as important high-temperature alloy constituents, of germanium in the rapidly expanding transistor field, of uranium, thorium, the lanthanides, and actinides in the nuclear energy program has forced the analytical chemist to take cognizance of these and other elements in his analytical schemes. Despite the availability of the modern, more discriminating methods of measurement, successful solutions to many analytical problems depend heavily on separation processes. It can be further observed that many separation processes of vital interest to the analytical chemist have been successfully translated to plant-scale operations.

The liquid-liquid extraction method has been extensively applied to studies of chemical equilibria, the separation of different elements, and the synthesis of inorganic compounds. However, some problems do remain in solvent extraction, e.g., slow extraction rates and incomplete extractions. Murata et al. have devised a new homogeneous liquid-liquid extraction method and obtained satisfactory results in the extraction of molybdenum (VI) with a simple procedure.[18] This method is based on the high solubility of an organic solvent in water at higher temperature and is characterized by immediate formation of the complex upon attaining a state of homogeneous solution consisting of water and the organic solvent during the procedure. At elevated temperature there is a transition to a single homogeneous phase which separates into the 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 the 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 may affect extraction; such a condition is not satisfied in the conventional extraction method.

One of the most suitable organic solvents for the homogeneous liquid-liquid extraction is propylene carbonate, which has found recent use in solvent extractions[19,20], and in electrochemical studies.[21-23] It has a high dielectric constant (65 at 25 °C), low vapor pressure, and high boiling point.

Especially noteworthy is the characteristic property of infinite solubility in water at temperatures higher than 71 °C. This method is applied for extracting various metal complexes in this investigation; also the behavior of propylene carbonate in the extraction process in general is studied.

II. Theory and Review of Literature of Solvent Extractions

1. Principles of Solvent Extraction

Phase Rule

The classical phase rule of Gibbs applies for all phase distributions,

$$P + V = C + 2$$

where P is the number of phases, V the variance or degree of freedom, and C the number of components. There is a definite relation between the solute concentrations in each of the solvent phases, which is quantitatively described in the distribution law.

Distribution Law

The distribution law states that a solute will distribute between two phases in such a manner that, at equilibrium, the ratio of the activities of the solute in the two phases at a particular temperature will be a constant, provided the solute has the same molecular weight in each phase. To the extent that the activities can be substituted with the molar concentrations one can express the distribution law for a solute X distributing between solvents 1 and 2 as

$$X_1 \rightleftharpoons X_2$$

$$K_D = [X]_2/[X]_1 \quad ,$$

where K_D is the distribution coefficient, a constant independent of total solute concentration, and the brackets denote concentrations.

Thermodynamic Derivation of 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 each phase are equal. Thus

$$\phi_1 = \phi_2$$

where the subscripts 1 and 2 refer to the respective solvent phases. Substituting suitable expressions for ϕ, we have

$$\phi_1^o + RT \ln m_1 + RT \ln \gamma_1 = \phi_2^o + RT \ln m_2 + RT \ln \gamma_2$$

Where ϕ^o represents the chemical potential of solute in ideal 1 molal solution, m, the solute concentration in molality, and γ, the molal activity coefficient. From this we may obtain an expression for the molal distribution coefficient, K_D

$$K_D = \frac{a_2}{a_1} = e^{-(\phi_2^o - \phi_1^o)/RT}$$

For most of the systems of concern to us, the solute is not present in quantities large enough to alter significantly the relative magnitudes of the activity coefficients in the two solvents, so we may write the above equation as

$$K_D = \frac{m_2}{m_1}$$

Distribution Ratio

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

This is a stoichiometric ratio including all species of the same component in the respective phases. If we are aware of all the significant interactions of the distributing species, it is usually possible to properly evaluate them, so that we may arrive at an expression for D as a function of the experimental parameters. If only one form of complex is present, D would reduce to K_D.

Percentage Extraction

Percent extracted into the organic phase, %E, is related to the distribution ratio, D, by the following equation

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

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

Process of Extraction

In the process of extraction an uncharged complex is transferred from an aqueous phase to an immiscible organic phase, according to the following three steps.

a. Formation of an Uncharged Complex

This step involves reactions of the metal cation in the aqueous phase leading to the formation of neutral extractable species. Complex formation may be accomplished by coordination, including chelation as well as simple coordination, or by ion association.

b. Distribution of the Extractable Complex

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

Reactions involving the extractable complex in the organic phase, e.g., polymerization or dissociation of the complex; interaction with other components, such as the reagent in the organic phase, are included in this stage.

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 the factors governing their formation will be explored.

Coordination Complexes

Acid-Base Character of Coordination Complexes

The application of G. N. Lewis' electronic theory of acids and bases to the consideration of coordination compounds is very useful. A metal cation, being electron-pair deficient, may be 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. Indeed, the formation of complexes by a metal ion may be interpreted in terms of its tendency to fill up unoccupied orbitals and thereby achieve the stable electronic configuration. The coordination number also depends on the size of the metal ion, which determines its ability to accommodate groups around it. When a metal cation and a ligand approach each other, the attraction of the electron atmosphere of the latter by the metal cation induces a deformation or polarization in the ligand. Ion deformation is favored by highly charged metal cations, by large ligand, and by metal ions with a non-inert-gas atom electronic configuration.

The stability of a metal coordination complex will depend on (1) factors related to the "acidity" of the metal ion, (2) factors related to the "basicity" of the coordination ligand, and (3) special factors related to the configuration of the resultant complex.

Chelate Complexes

Chelating reagents play an important role in extraction of metal cations because they comprise an impressive body of useful extraction agents and also masking agents. Metal chelates represent a type of coordination compound in which a metal ion combines with a polyfunctional base capable of occupying two or more positions of the coordination sphere of the metal ion to form a cyclic compound. The functional groups of the base must be so situated in the molecule that they permit the formation of a stable ring, generally five- or six-membered.

Structural factors of reagents which determine their effectiveness as chelating agents include the basic strengths of the functional groups, the electronegativity of the bonding atoms, as well as the size and number of the chelate rings formed.

Ion Association Complexes

The forces of attraction in ion-pair formation are "physical" as contrasted to the "chemical" forces involved in the formation of coordination complexes. Hence, for two ions A^+ and B^- which associate to form (A^+,B^-) according to the equation

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

the equilibrium expression is

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

The existence and behavior of such complexes was predicted by N. Bjerrum[4], whose theory relates the value of the ion-pair formation constant K to the dielectric constant of the solvent ϵ, to the temperature, and to the size of the ions involved. Thus

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

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

where N is 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 representing the distance between charge centers of the paired ions when in contact.

3. Distribution of the Extractable Species

Solubility Characteristics of Chelates

Most chelating agents used as extraction agents belong to the type that contain one uncharged and one anionic basic functionality so that both the electrovalency and maximum coordination of the metal ion is satisfied in the chelate formed. The resulting metal chelates, being covalent compounds, are far less soluble in water than they are in organic solvents, which they resemble structurally.

Hildebrand's theory of regular solutions[5] defines a quantity δ, called the solubility parameter and compares the solubility parameters of solvent and solute. He defines δ as the square root of the heat of vaporization of the liquid per milliliter, which is a measure of cohesive energy density or "internal pressure". The solubility increases with increasing similarity of the solubility parameter values since the heat of mixing of the solute and solvent depends on the difference of their δ values.

Feigl's useful generalization that solubility in chloroform is a characteristic of metal chelates which have no free acid or basic groups can be understood on the basis of the principle that "like dissolves like".[6] Also, an increase in solubility of a chelate in organic solvents can be expected to result from a substitution of a hydrocarbon group in the chelate structure, since this substituted chelate would now more closely resemble the organic solvent. Thus, although the neodymium chelate of cupferron is not soluble in organic solvents, the corresponding chelate with neocupferron is.[7] Similarly, the nickel chelate of cycloheptanedionedioxime (heptoxime) is more soluble than that of dimethylglyoxime.[8]

Chelates of divalent metals having a coordination number of six can be singled out for special attention, since water often occupies two coordination positions with the result that the solubility of the chelate in organic solvents is extremely low. The failure of nickel(II) and cobalt(II) acetylacetonates to extract into organic solvents may be attributed to this fact. This effect is especially marked in the chelates of the more electropositive alkaline earth metals. For example, the 8-quinolinates of the alkaline earths are not extracted at any pH by a solution containing 1 g of 8-quinolinol per 100 ml of chloroform. In a recently developed modification of the usual procedure, a higher reagent concentration (~3%) and the addition of a quantity of monobutyl ether of ethylene glycol are employed for the successful extraction of magnesium and calcium.[9] In an even more revealing study, strontium was found to be extracted by more concentrated 8-quinolinol solutions in a form identified as $Sr(C_9H_6NO)_2 \cdot 2C_9H_6NOH$.[10] The success of extraction can be attributed to the displacement of water molecules by 8-quinolinol molecules in the coordination sphere of the metal ion to give a species that more closely resembles the solvent than does the hydrated chelate molecule.

Solubility Characteristics of Ion Association Compounds

Ion association compounds can be considered as polar molecules, i.e., those having dipole moments, whose solubility in organic solvents depends in large measure on their structual resemblance to those solvents. Thus, if the ions involved contain large organic groups, then solubility in organic solvents is a reasonable expectation.

Oxonium systems occupy a special place among ion association systems because of the participation of the solvent molecules in the formation of the extractable complex. Oxygen-containing organic liquids will serve effectively as solvents for a number of metal salts because the basic character of the oxygen atom enables the incorporation of the solvent molecule in the coordination sphere of the metal ion, giving rise to an ion association compound that bears a structural resemblance to the solvent.

The ability of oxonium solvents to successfully compete with water for the acidic metal ion depends on the basicity of the oxygen in the molecule. The basicity, in turn, will reflect the steric availability of the electrons at the oxygen atom as well as the electron density. Steric considerations are of particular importance in coordination with metal ions, which are, of course, much larger than protons. At the same time, the competitive strength of water may be reduced by the use of high concentration of salts and acids. A high electrolyte concentration helps extraction in three ways: (1) by the mass action effect-if the electrolyte possesses suitable coordinating anions, the high anion concentration makes the replacement of water by the anion easier; (2) by greatly reducing the water activity(salting-out); and (3) by lowering the dielectric constant, thus favoring ion-pair formation.

4. Chemical Interactions in the Organic Phase

Chemical interactions of the extractable species in the organic phase owe their importance to their effect on the concentration of the complex and, hence, on the extent of extraction.

One of the most important types of organic phase reactions is polymerization of ion association complexes. Virtually all ion-pair complexes, by their very nature, 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 more polar solvents such as β, β'-dichloroethyl ether. This reaction would result in increased extraction at very low metal concentrations.

Since extractable metal chelates are covalent compounds, their solution in neutral organic solvents are relatively free from chemical interaction. One noteworthy exception arises in the use of buffers that have extractable components.

5. Quantitative Treatment of Extraction Equilibria

Chelate Extraction Systems-Derivation of the General Equation

When a metal ion is extracted with some complexing agent into an organic solvent in which the metal complex is soluble, equilibrium is attained after sufficient time. The extent of the extraction of the metal is given by an equilibrium distribution ratio.

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

(i) ionization of the reagent to give the active chelating anion

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

(ii) stepwise formation of the chelate[11]

$$\begin{array}{llll} M^{n+} + R^- \rightleftharpoons MR^{(n-1)+} & & k_1 = \dfrac{[MR^{(n-1)+}]}{[M^{n+}][R^-]} & (2) \\ \vdots & & \vdots & \\ MR^+_{n-1} + R^- \rightleftharpoons MR_n & & k_n = \dfrac{[MR_n]}{[MR^+_{n-1}][R^-]} & \end{array}$$

The overall formation constant, K_f, may readily be seen to be $K_f = k_1 k_2 \ldots k_n$

(iii) competing reactions for the metal ion are, respectively, hydrolysis and metal anion coordination

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

(b) $M^{n+} + X^- \rightleftharpoons MX^{(n-1)+}$, etc. (4)

where X^- represents the anion present, e.g., Cl^-, NO_3^-, SO_4^{2-} etc.

(iv) distribution of the reagent

$$K_{DR} = \frac{[HR]_o}{[HR]} \tag{5}$$

(v) distribution of the chelate

$$K_{DX} = \frac{[MR_n]_o}{[MR_n]} \tag{6}$$

These equilibrium expressions may be used to derive an expression for D, the ratio of the stoichiometric metal concentrations in the two phases. If it is assumed that the only metal-bearing species in the organic phase is the fully formed chelate, MR_n, then

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

$$\frac{[MR_n]_o}{[M^{n+}]+[MR^{(n-1)+}]+\ldots+[MR_n] + \sum_i [M(OH)_i^{(n-i)+}] + \sum_j [MX_j^{(n-j)+}]} \tag{7}$$

Dividing both numerator and denominator by $[MR_n]$ and substituting appropriate values from eqs. (2) and (6) for the ratios obtained, we find

$$D = \frac{K_f K_{DX} [R^-]^n}{1 + k_1[R^-] + k_1 k_2 [R^-]^2 + \ldots + K_f [R^-]^n (1 + x)}$$

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

Further substitutions of eqs. (1) and (5) give

$$D = \frac{K_f K_{DX} K_i^{\,n}}{K_{DR}^{\,n}} \left[\left\{ \frac{[H^+]}{[HR]_o} \right\}^n + \frac{k_1 K_i}{K_{DR}} \left\{ \frac{[H^+]}{[HR]_o} \right\}^{n-1} + \ldots + \frac{k_1 \ldots k_{n-1} K_i^{\,n-1}}{K_{DR}^{\,n-1}} \frac{[H^+]}{[HR]_o} + \frac{K_f K_i^{\,n}}{K_{DR}^{\,n}} (1 + x) \right]^{-1} \qquad (9)$$

In many practical cases, the equation (9) can be simplified by making the following assumptions:

(a) hydrolysis and anion complexation are not appreciable in the aqueous phase $(x = 0)$

(b) the chelate concentration 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 concentrations of the intermediate chelate species are negligible. Thus eq. (9) simplifies to

$$D = \frac{K_f K_{DX} K_i^{\,n}}{K_{DR}^{\,n}} \left\{ \frac{[HR]_o}{[H^+]} \right\}^n = K^* \left\{ \frac{[HR]_o}{[H^+]} \right\}^n \qquad (10)$$

Equation (10) has been experimentally established for extraction in many cases.[12,13] The extractability of a metal depends inversely upon the hydrogen ion concentration in the aqueous phase and directly upon the reagent concentration in the organic phase.

Effect of Hydrolysis of the Metal Ion in the Aqueous Phase

According to eq. (7), if it is assumed that the average number of hydroxyl groups coordinated to the metal is i, the total metal ion concentration in the aqueous phase may be represented by $M(OH)_i^{(n-i)+}$. The distribution ratio becomes

$$D = \frac{[M]_o}{[M]} = \frac{[MR_n]_o}{[M(OH)_i^{(n-i)+}]} = \frac{K^*[HR]_o^n}{K_h[H^+]^{n-i}} \qquad (11)$$

where K_h is the hydrolysis constant.

Eq. (10) demonstrates the importance of chelate stability (K_f) and relative solubility of the chelate in the organic phase(K_{DX}) to metal extractability.

Effect of Changing the Solvent

The effect of changing the solvent on the extractability of a particular metal may be evaluated from eq. (10) in terms of the changes in the K_D values. Thus,

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

Although the effect of changing the solvent on the value of a distribution coefficient of a particular compound may not be known, such a change may well be similar for similar compounds, i.e., a reagent and its chelates, so that

$$\frac{K_{DX}}{K'_{DX}} \simeq \frac{K_{DR}}{K'_{DR}} \qquad (13)$$

By incorporating this reasonable assumption in eq. (12)

$$\frac{D}{D'} = \left[\frac{K'_{DR}}{K_{DR}}\right]^{n-1} \qquad (14)$$

From eq. (14) we may infer that a change to a solvent in which a reagent and its multivalent metal ($n > 1$) chelates are more soluble will result in a lower D value so that extractions will require higher pH values (or higher reagent concentrations).

When the metal chelate is relatively soluble in water (i.e., K_{DX} is small), eq. (10) must be modified.[59] Starting with eq. (7), we may write

$$D = \frac{[MR_n]_o}{[M^{n+}]+[MR_n]} = \frac{K_{DX}}{K_f[R^-]^n+1} = \frac{[K_{DX}-D]K_f K_i^n}{K_{DR}{}^n} \cdot \frac{[HR]_o^n}{[H^+]^n} \qquad (15)$$

Equation (15) indicates that D rises to a maximum value equal to K_{DX}. If competing reactions of the metal ion occur with anions such as chloride, sulfate, etc., then the course of the extraction will depend on the concentration of the anion. If the anion concentration is kept constant, then the fraction of metal combined will also be constant so that, at a given anion concentration, the extraction can be described according to eq. (11). The value of K* will vary with the competing anion concentration. Such a result was found by Sandell and Cumming[60] in their study of iron(III) cupferrate extraction from hydrochloric acid-sodium chloride solutions. The log K* values were found to decrease regularly with increasing Cl^- concentration.

It can be seen that, if the reagent concentration is maintained constant, the distribution of the metal is a function of pH alone. For this reason, a plot of distribution versus pH at constant reagent concentration is of great analytical significance. Eq. (10) may be written as

$$D = K^* \frac{[HR]_o^n}{[H^+]^n} = K^* \cdot [H^+]^{-n}$$

if $[HR]_o$ remains a constant.

Ion Association Extraction Systems

The problem of reducing the behavior of ion association extraction systems to analytical expressions that quantitatively describe the relation between the extent of extraction and the experimental parameters is far more difficult than it is for chelate extractions. This kind of extraction involves high concentration of acid or salt, and consequently there is great difference between concentration and activity. Another factor is the relatively large number of equilibria that are involved in the formation of the extractable ion association complex.

The extraction of iron(III) chloride from hydrochloric acid solution by ether will be considered as a general example.

The reactions involved in the iron chloride extraction process are:

(1). Formation of $FeCl_4^-$ Anion

$$\begin{array}{ccccccc}
\mathrm{Fe(H_2O)_6}^{3+} & + & \mathrm{Cl}^- & \overset{k_1}{\rightleftharpoons} & \mathrm{Fe(H_2O)_5Cl}^{2+} & + & \mathrm{H_2O}\\
\vdots & & \vdots & & \vdots & & \vdots\\
\mathrm{Fe(H_2O)_3Cl_3} & + & \mathrm{Cl}^- & \overset{k_4}{\rightleftharpoons} & \mathrm{Fe(H_2O)_2Cl_4}^- & + & \mathrm{H_2O}
\end{array}$$

The overall reaction is:

$$Fe(H_2O)_6^{3+} + 4\ Cl^- \underset{}{\overset{k_1k_2k_3k_4}{\rightleftharpoons}} Fe(H_2O)_2Cl_4^- + 4\ H_2O$$

$$K_1' = k_1k_2k_3k_4 = \frac{[Fe(H_2O)_2Cl_4^-][H_2O]^4}{[Fe(H_2O)_6^{3+}][Cl^-]^4}$$

At high chloride concentrations, the $FeCl_4^-$ is probably the major species in solution.

(2). Solvate Formation

At high acid concentrations when the water activity decreases and the ether activity in the aqueous phase increases, solvent exchange in the complex probably occurs.

$$Fe(H_2O)_2Cl_4^- + 2R_2O \overset{k_5}{\rightleftharpoons} Fe(R_2O)_2Cl_4^- + 2H_2O$$

Also, hydronium ions may react as follows:[14]

$$H_3O^+ + R_2O \overset{k_6}{\rightleftharpoons} R_2OH^+ + H_2O$$

(3). Formation of Extractable Complex by Ion Pairing

$$H_3O^+ + Fe(H_2O)_2Cl_4^- \overset{k_7}{\rightleftharpoons} [(H_3O^+,Fe(H_2O)_2Cl_4^-)]$$

$$R_2OH^+ + Fe(R_2O)_2Cl_4^- \overset{k_8}{\rightleftharpoons} [(R_2OH^+,Fe(R_2O)_2Cl_4^-)]$$

or more generally

$$H(S)^+ + Fe(S)_2Cl_4^- \underset{}{\overset{k_9}{\rightleftharpoons}} [(HS^+, Fe(S)_2Cl_4^-)]$$

where S = H_2O or R_2O depending on relative activities.

(4). Distribution of Reagent and Extractable Complex

$$(HS^+, Cl^-)_a \overset{K_D}{\rightleftharpoons} (HS^+, Cl^-)_o$$

$$[(HS^+, Fe(S)_2Cl_4^-)]_a \overset{K'_D}{\rightleftharpoons} [(HS^+, Fe(S)_2Cl_4^-)]_o$$

(5). Polymerization of Ion Pair in Ether Phase

$$n[(HS^+, Fe(S)_2Cl_4^-)]_o \overset{k_{10}}{\rightleftharpoons} [(HS^+, FeS_2Cl_4^-)_n]_o$$

n varies from 2 to 4.[15]

(6). Dissociation of Extractable Complex and of Reagent in Ether Phase

$$(HS^+, Fe(S)_2Cl_4^-)_o \overset{k_{11}}{\rightleftharpoons} (HS^+)_o + (Fe(S)_2Cl_4^-)_o$$

$$(HS^+, Cl^-)_o \overset{k_{12}}{\rightleftharpoons} (HS^+)_o + (Cl^-)_o$$

The overall distribution ratio is

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

$$= \frac{[(HS^+, FeS_2Cl_4^-)]_o + [FeS_2Cl_4^-]_o + n[(HS^+, FeS_2Cl_4^-)_n]_o}{[FeS_2Cl_4^-] + [(HS^+, FeS_2Cl_4^-)]}$$

By suitable substitution of the previous equations we obtain

$$D = K'_D k_7[HS^+][1+k_{11}\{K_D k_7 k_{11}[HS^+][Fe] +k_{12}K_D[HS^+][Cl^-]\}^{-1/2} +nk_{10}(K_D k_7)^{n-1}[HS^+]^{n-1}[Fe]^{n-1}]$$

From the above equation it can be seen that D is a very complex function and depends mainly on iron concentration and hydrogen ion concentration.

6. Analytical Applications

The extraction of metal complexes plays a very important role in analytical chemistry because of its speed, versatility, simplicity, and selectivity. The amount of metal separated can be determined either by absorption spectrophotometry, emission spectrophotometry, trace techniques or other convenient analytical method. The element to be determined must be separated selectively and quantitatively. The latter condition is achieved by using an excess of the organic reagent and by choosing a suitable organic reagent, masking agent, and pH value.

A method of substoichiometry-radioisotope dilution analysis has been developed in which a smaller amount of the reagent is used than corresponds to the amount of metal to be determined. The main advantage of this method compared with all other analytical methods is that the element to be determined need not be isolated quantitatively, as its amount can be calculated from the activity isolated. Although this technique can be applied in precipitation, it is most easily applied in solvent extraction. The greatest importance of this method lies in the fields of trace metal analysis.

Solvent extraction is particularly well suited to the purification of many radioisotopes, since after several extractions of a substance, the final product is usually relatively free from extraneous impurities which may be present when coprecipitation or other separation procedures are employed. Also, if the isotope of interest has a short half life, a rapid separation is essential and extraction procedures have proved invaluable. Solvent extraction has been widely applied for the separation of fission products.

III. Experimental

1. Reagents

2-thenoyltrifluoroacetone (TTA) was Fisher Scientific Company reagent grade.

Acetylacetone, trifluoroacetylacetone, benzoylacetone, dibenzoylmethane, benzoyltrifluoroacetone, 8-quinolinol, cupferron, bathophenanthroline, diethyl carbonate and propylene carbonate were obtained from Eastman Kodak Company. Propylene carbonate was distilled under reduced pressure (b.p. 92 ^{o}C at 4.5 mm Hg) for purification.

The various salts were Baker Analyzed reagents of the purity indicated; ferric chloride(99.9%), copper chloride(99.5%), nickel perchlorate(99.7%), zinc chloride(99.8%), cadmium chloride(99.5%), lead nitrate(99.6%), calcium chloride(99.7%), barium chloride(99.7%) and magnesium chloride(99.8%) respectively.

1,2-butandiol was obtained from Aldrich Chemical Company. Ethanol was purified by distilling over a Mg-ether mixture.

All the other chemicals such as sodium tartrate, ammonium chloride, ammonium bromide etc. were of the highest purity grade available.

2. Apparatus

All the pH measurements were made with a Corning Model 12 B pH meter.

Metal cation concentrations were determined with a Perkin-Elmer 372 Atomic Absorption/Atomic Emission Spectrophotometer.

Samples were equilibrated using a Lab-Line Instruments, Inc. shaker bath with variable shaking speed.

The proton magnetic resonance measurements were made with a Varian T-60 Spectrometer operating at 60 M Hz.

A Beckman IR 18A and Cary 17 were also used for identification.

3. Procedures

The Solubility of Propylene Carbonate in Water

The phase diagram of the system propylene carbonate-water was investigated. Measurements were made using laboratory distilled water and propylene carbonate of purity $>$ 99%; the latter material was dried over molecular sieves.

Observations were made using the cloud-point method[16] at temperatures above 0 °C. Mixtures were prepared by weight in pyrex tubes of 5 mm internal diameter, which were sealed and immersed in a water bath at a higher temperature to give a single homogeneous phase; the bath was then cooled at about 0.5 °C/min until cloudiness was observed. The cloud point temperatures were measured with a mercury-in-glass thermometer. The temperatures recorded are the means of two observations on each mixture.

Cloud point temperatures below 0 °C were taken from cooling curves[17] measured on mixtures prepared by weight in 25 cc test tubes and cooled slowly by a dry ice-acetone bath. Temperatures were measured with a thallium amalgam thermometer.

Density of the Mixture of Water and Propylene Carbonate

The solubility of propylene carbonate in water and the solubility of water in propylene carbonate are given by the phase diagram of propylene carbonate-water system. Mixtures were prepared by weight in glass stoppered Erlenmeyer flasks and then transferred to pycnometers to the level above the mark. Pycnometers were immersed in a water bath at 25 °C for about 20 minutes and the level adjusted exactly to the mark. The outside of the pycnometer was dried, the pycnometer was weighed on an analytical balance, and the density calculated as follows.

$$d_4^{25} = \frac{W_m}{W_w} (0.99707-0.00119) + 0.00119$$

$$= \frac{W_m}{W_w} .0.99588 + 0.00119$$

where W_m is weight of the mixture in pycnometer, Ww is weight of the water in pycnometer. The density given for each mixture is the mean of two measurements.

Densities of the mixtures of propylene carbonate and ethanol was determined by the same method as above.

Phase Diagram for the Liquid System Ethanol-Water-Propylene Carbonate

The mixture of any two components was prepared by weight in a glass stoppered Erlenmeyer flask and titrated with the third component until the clear solution became cloudy or the cloudy solution became clear. The whole titration system was maintained at constant temperature (25 °C). The curve was constructed from the known compositions. The tie lines through the two-phase region joining the compositions of the two phases that are in equilibrium were constructed as follows. First, the points are chosen which are in the two-phase region and the corresponding mixture of ethanol-water-propylene carbonate is prepared by weight. The mixture was transferred to a separatory funnel and kept in the water bath at 25 ^{o}C and periodically agitated to reach equilibrium. The phases were weighed separately and the weight ratio of the two phases determined. This procedure was repeated until a smooth continuous line bordering the two-phase region was completed.

Atomic Absorption Analysis: Preparation of Calibration Curves for Aqueous and Organic Phases

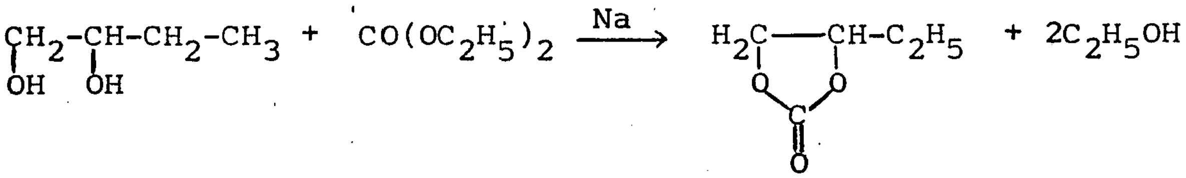
Standard stock solution was prepared by dissolving 1.000 g of iron wire in 50 ml of (1+1) HNO_3, and diluting to 1 liter with deionized water. Solutions of Fe(III) were prepared by dilution of the standard stock solution. Fe(III) calibration curves for the aqueous phase were prepared in the concentration range from 0 μg/ml to 10 μg/ml in deionized water saturated with propylene carbonate. Fe(III) calibration curves for the organic phase were prepared by the addition of 10 ml of Fe(III) standard solutions containing up to 25 μg/ml to a 25 ml volumetric flask, addition of 10 ml of 0.01 M TTA solution in propylene carbonate and dilution to the mark with ethyl alcohol which yields a single homogeneous phase.

Extraction Procedure

A series of extraction columns were used, each column containing 10.0 ml of an aqueous phase and 10.0 ml of an organic phase; the aqueous phase containing a known concentration of metal ion was adjusted to a desired pH value with either concentrated solutions of hydrochloric acid or sodium hydroxide; the organic phase was a propylene carbonate solution of extractant at a fixed concentration. Each column was shaken on the shaker bath maintained at 80 ^{o}C and the phases were then separated after being cooled to room temperature. The Perkin-Elmer 372 atomic absorption spectrophotometer was used to determine the percent extraction by analyses of both phases. The analyses of both phases are important in order to obtain a mass balance of the metal ion. This analysis was undertaken with the preparation of separate calibration curves for aqueous and organic phase respectively.

Synthesis of Butylene Carbonate

Butylene carbonate which is not commercially available was prepared by ester exchange between 1,2-butandiol and diethyl carbonate in the presence of a small amount of sodium. The reaction is as follows,



Technique: A piece of sodium (1-2 g) was dissolved in 100 g of 1,2-butandiol contained in a 250 ml reflux flask by heating slowly in an oil bath, and then 131 g of ethyl carbonate was added. The mixture was then maintained at a temperature between 110 -135 °C (oil bath temperature) to distill ethyl alcohol (~120 ml); after two hours of heating, the residue was cooled somewhat and the mixture refluxed for one hour. The residue was dissolved in benzene. This solution was washed twice with 2% HCl, and once with distilled water.

Butylene carbonate was purified by first drying over anhydrous sodium sulfate followed by distillation of benzene. Vacuum distillation of the product yielded 90 g of 1,2-butylene carbonate (b.p. 97 °C at 1-2 mm Hg).

IV. Results and Discussion

1. Phase Diagram of Propylene Carbonate-Water System

The miscibility of propylene carbonate and water at elevated temperature is the essential property for homogeneous liquid-liquid extraction. The phase diagram of the system was investigated at atmospheric pressure and the phase behavior is shown in Fig. 1. The heavy line on the diagram bounds the region in which two liquid phases appear. The line also gives the composition of the liquid layers as seen by the following; referring to Fig. 1, the initial addition of the second component, propylene carbonate, to a quantity of pure water at 25 °C forms a single phase, and this solubility persists upon further additions until the total composition of the system corresponds to point a. The limit of solubility of propylene carbonate in water is reached at this point and further addition produces a second layer of composition c. Thus a total composition corresponding to point b, at 25 °C, results in a two-phase system, the phases having compositions a and c. As the amount of the second component increases, the total composition approaches c, at which point all the water-rich layer has finally dissolved in the propylene carbonate-rich layer to give again a one-phase system. Given a total composition, the composition of each liquid phase can be determined from Fig. 1.

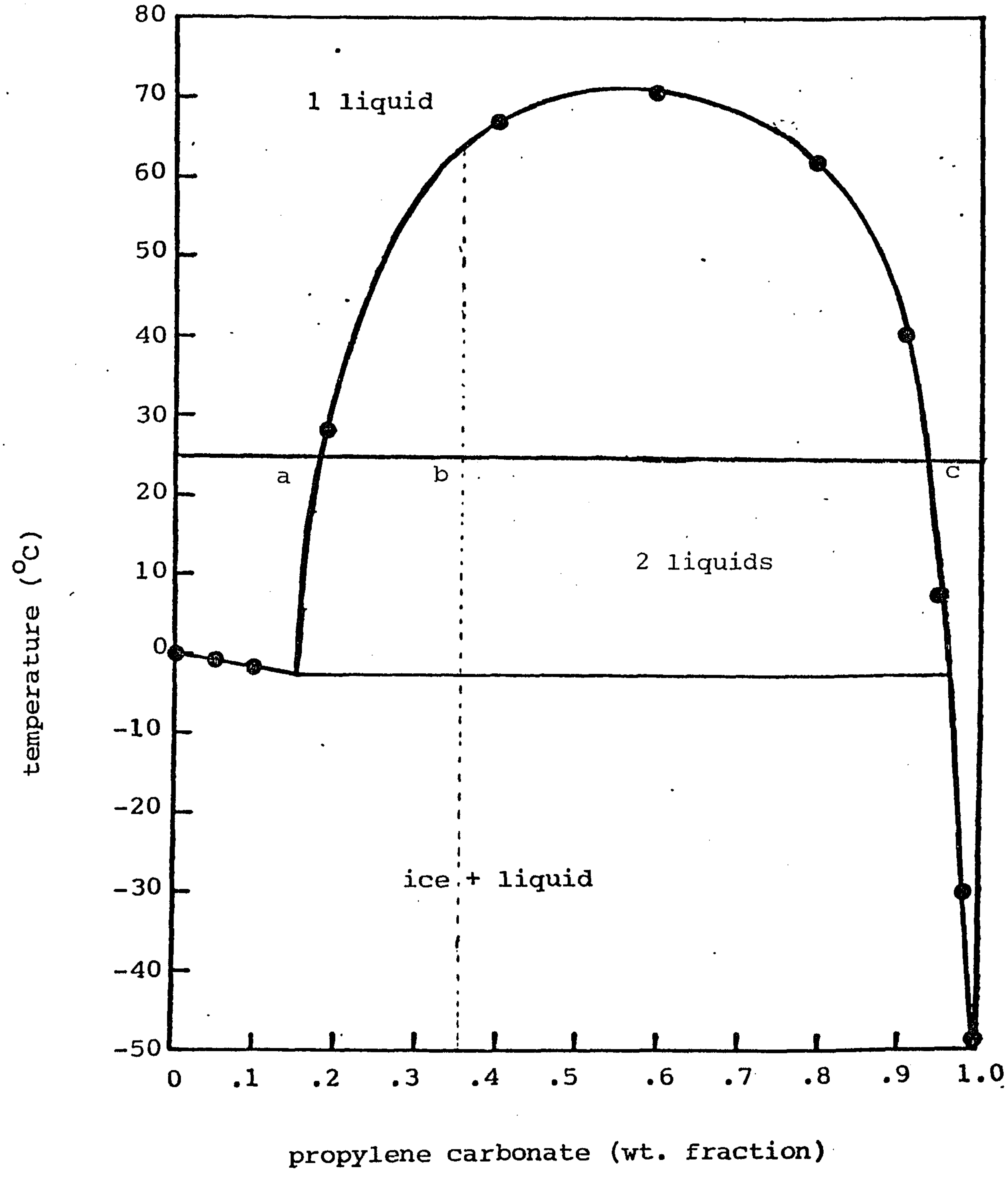


Fig. 1 Phase diagram of propylene carbonate-water system at 1 atm pressure

It is of interest to investigate the changes that occur when the temperature of a two-phase system is raised. If the temperature is increased for the system of total composition of b, the system moves up along the dashed line. The fraction of the system composed of the water-rich layer gradually increases until the two-phase boundary curve is reached, i.e., the solubility of propylene carbonate in the water layer increases to a greater extent than the solubility of water in the propylene carbonate layer. By contrast, if a composition equal to that of the curve maximum is picked, the two layers remain in about equal amounts until, at the two-phase boundary, their composition become identical and they form a one-phase system.

The phase separation temperatures of propylene carbonate-water system are listed in Table 1. As Fig. 1 shows, the solubility of propylene carbonate rises very sharply with temperature, and above 71 ^{o}C, 10 ml of propylene carbonate is completely miscible with 10 ml of water. The experimental procedure in the homogeneous liquid-liquid extraction was performed at 80 ^{o}C for convenience.

Table 1. Phase Separation Temperatures for Propylene Carbonate-Water at Atmospheric Pressure

Wt fraction propylene carbonate	t/ °C
0	0
0.0513	-0.9
0.1011	-1.8
0.2046	27.1
0.3941	67.2
0.5958	71.0
0.7976	62.6
0.8934	40.1
0.9494	7.5
0.9876	-28.1
1.0000	-50.2

2. Densities of Water-Propylene Carbonate Mixtures and Ethanol-Propylene Carbonate Mixtures

Densities of mixtures of water and propylene carbonate were determined in the mutually miscible range; the results are shown in Table 2 and Figures 2, 3, 4. The density is linearly proportional to weight fraction of propylene carbonate.

Ethanol and propylene carbonate are completely miscible in any proportion and Fig. 5 shows the density of propylene carbonate-ethanol (99%) over the whole concentration range. The density differences between propylene carbonate-ethanol (99%) and propylene carbonate-ethanol (99.4%) systems are shown in Fig. 6.

Table 2. Densities of Propylene Carbonate-Water Mixtures at Atmospheric Pressure and 25 °C

Wt fraction propylene carbonate	Density(g/ml)
0	0.9986
0.0147	1.0001
0.0297	1.0030
0.0449	1.0062
0.0593	1.0094
0.0731	1.0124
0.1039	1.0192
0.1323	1.0249
0.1466	1.0277
0.1761	1.0338
0.9288	1.1838
0.9475	1.1878
0.9579	1.1900
0.9687	1.1927
0.9792	1.1950
0.9897	1.1976
1.0000	1.2004

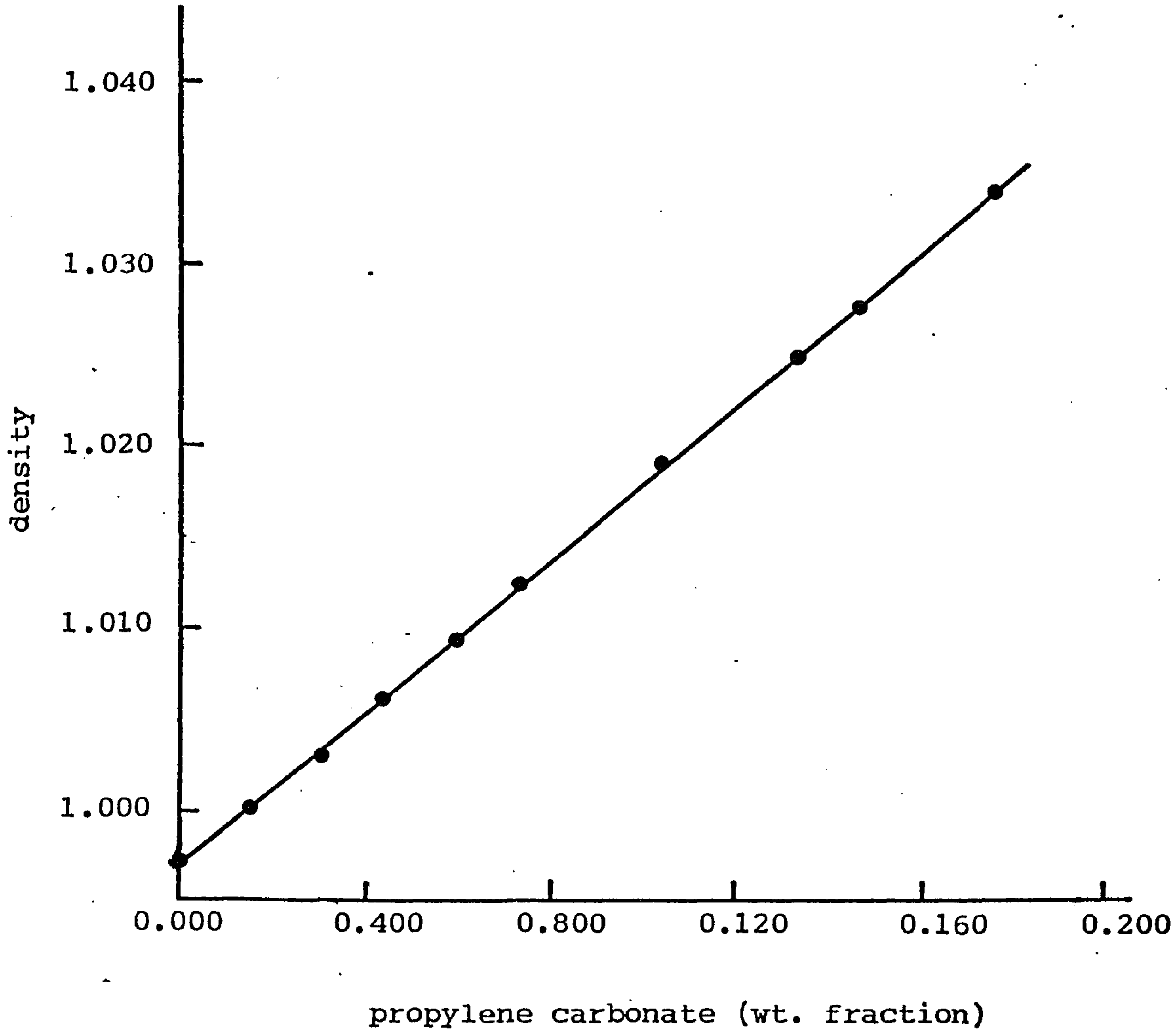


Fig. 2 Density of propylene carbonate-water system at 25 ^{o}C

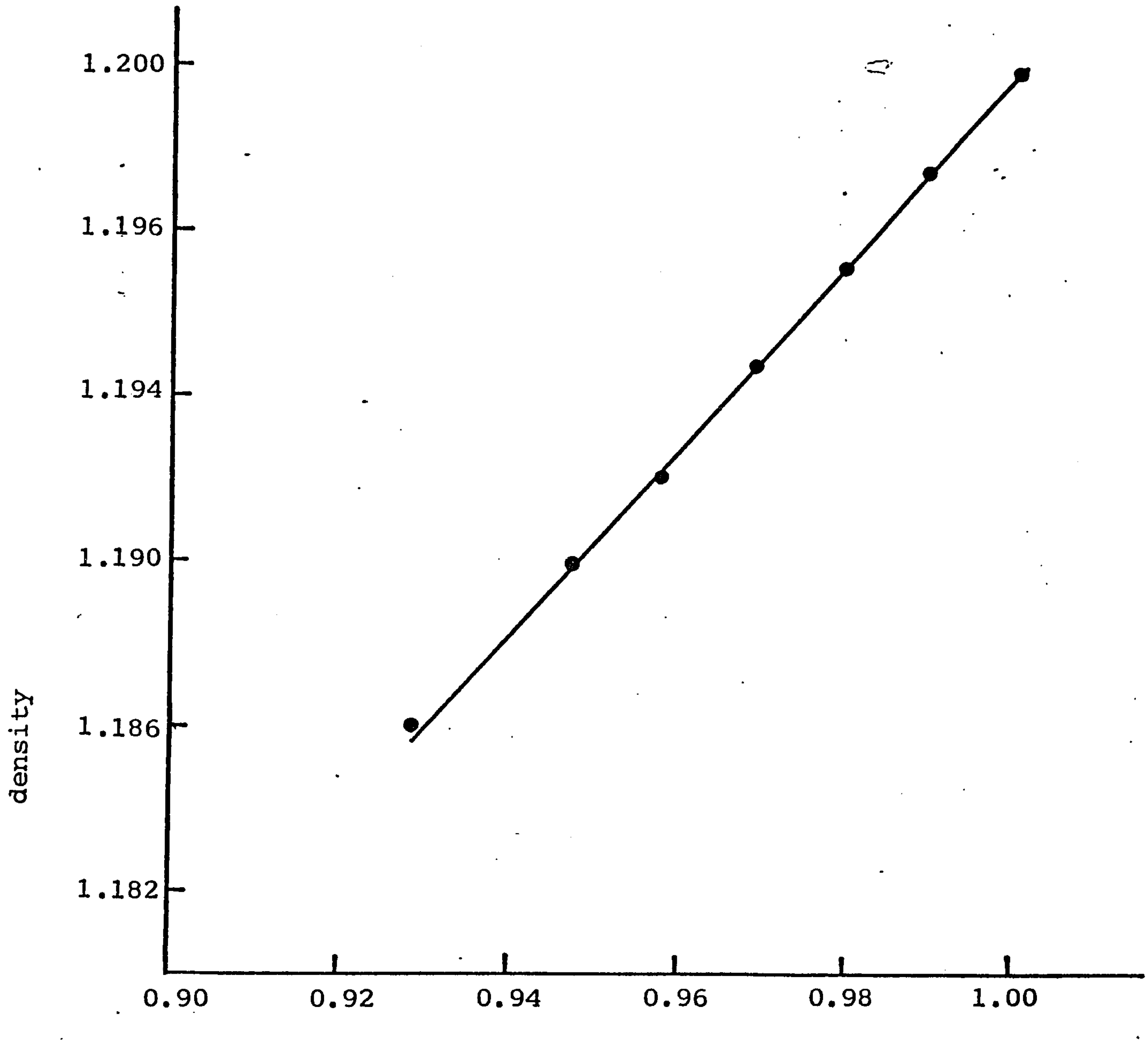


Fig. 3 Density of propylene carbonate-water system at 25 °C

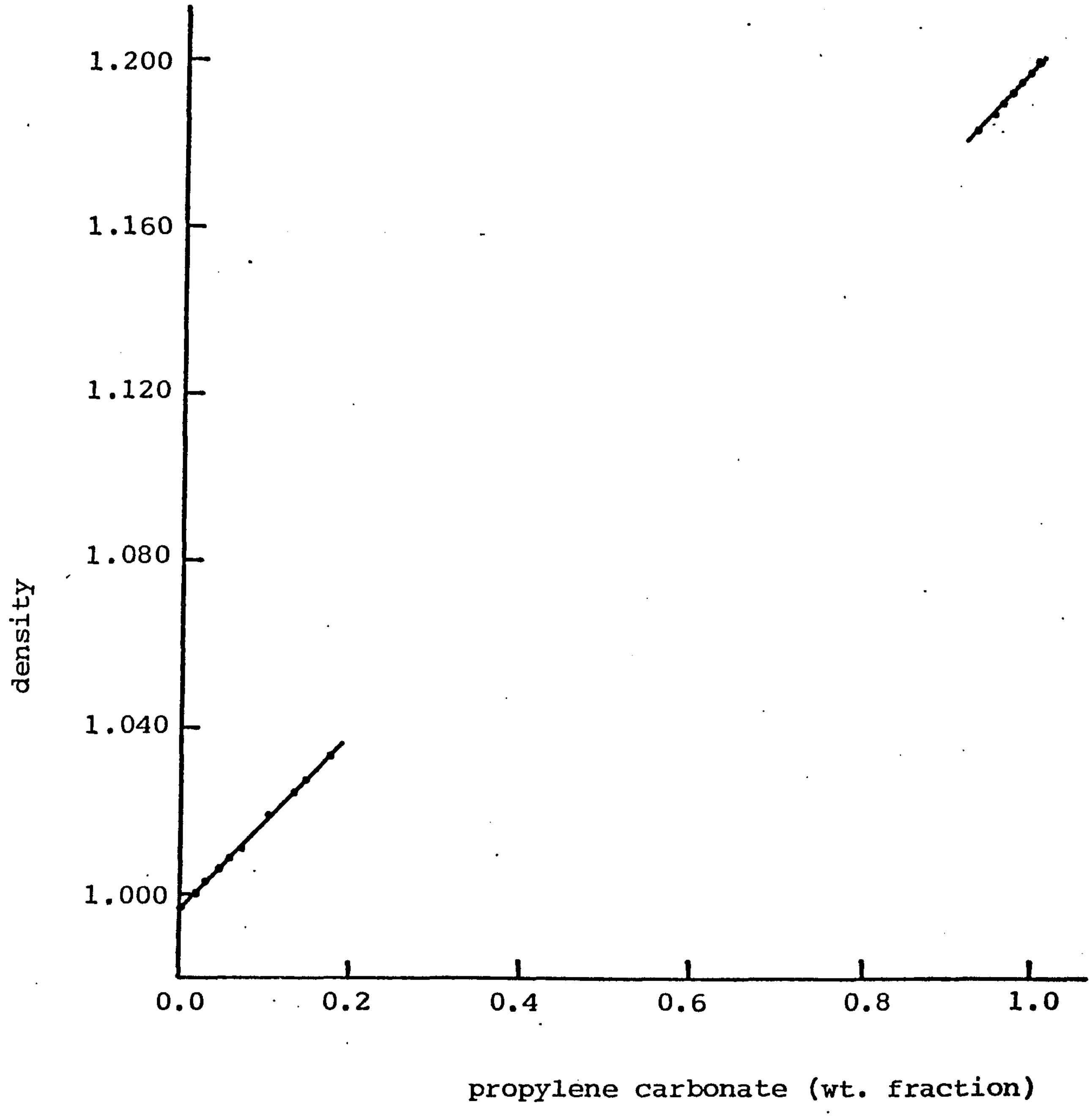


Fig. 4 Density of propylene carbonate-water system in the range of miscibility at 25 °C

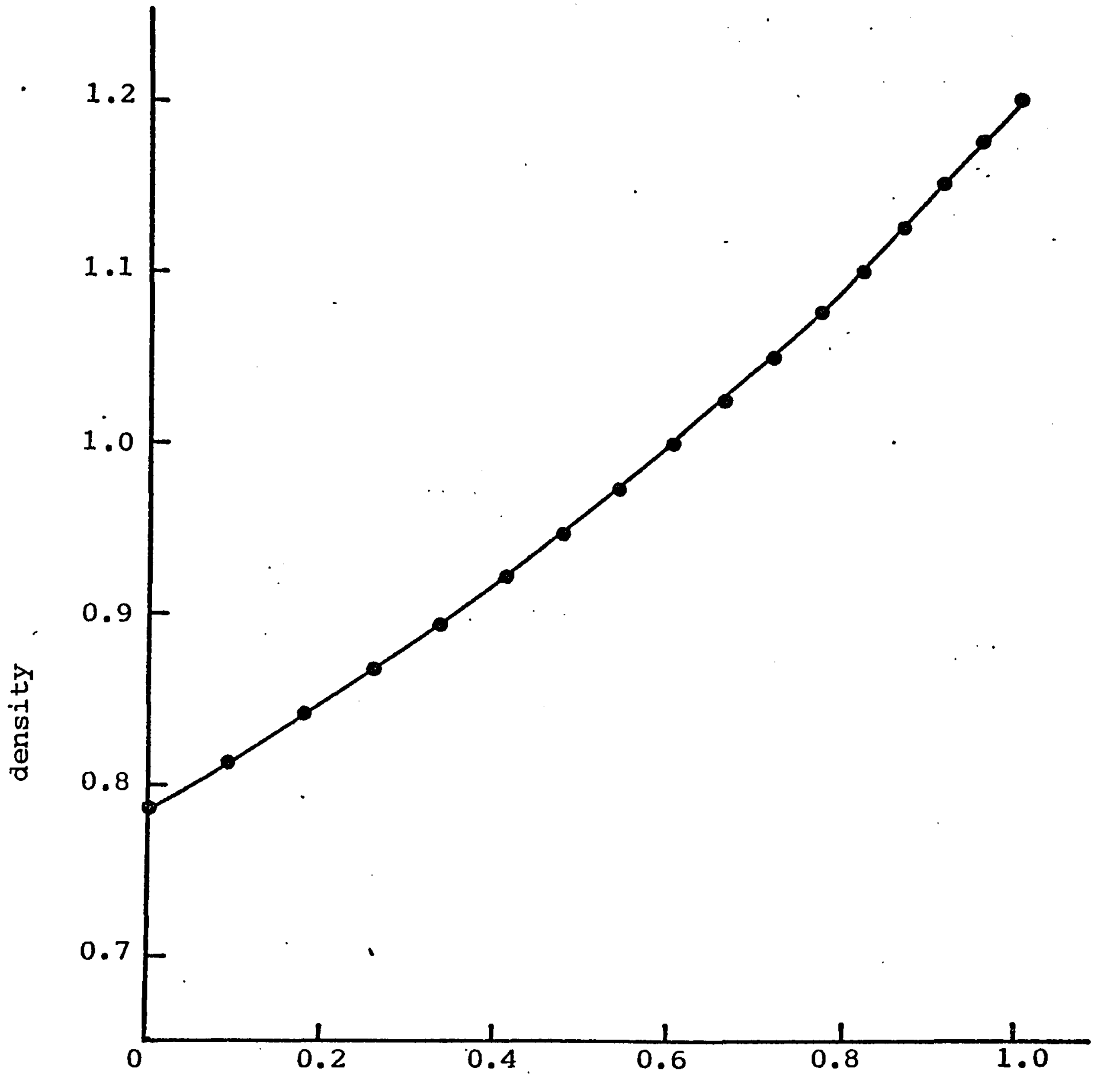


Fig. 5 Density of propylene carbonate-ethanol (99%) system at 25 ^{o}C

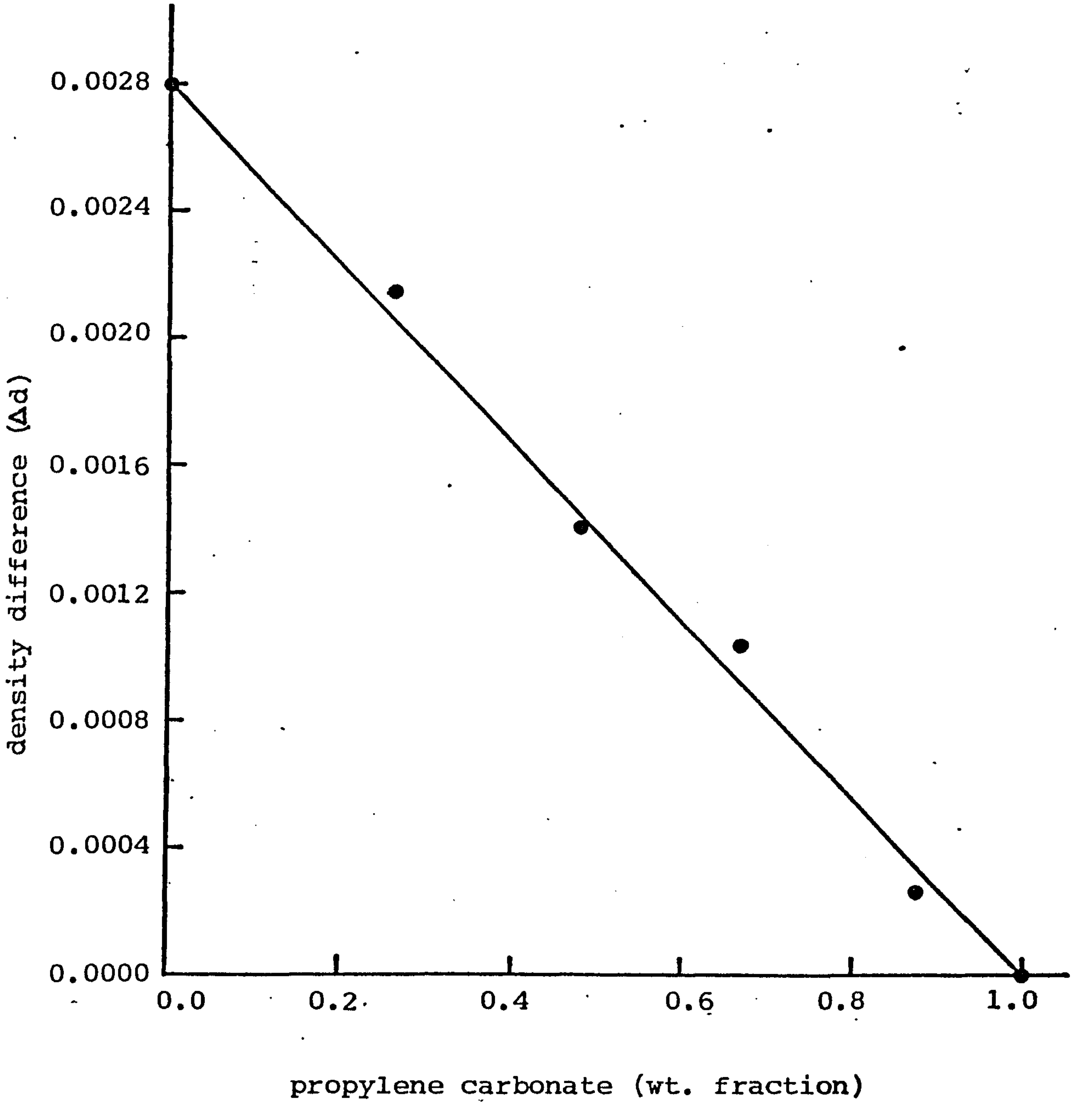


Fig. 6 Density difference between propylene carbonate-ethanol (99%) and propylene carbonate-ethanol(99.4%) system at 25 °C

Table 3. Densities of ethanol (99%)-Propylene Carbonate Mixtures at Atmospheric Pressure and 25 ^{O}C

Wt fraction Propylene Carbonate	Density(g/ml)
0	0.7893
0.0925	0.8154
0.1792	0.8420
0.2608	0.8691
0.3343	0.8940
0.4083	0.9205
0.4774	0.9467
0.5421	0.9720
0.6044	0.9983
0.6609	1.0233
0.7169	1.0491
0.7701	1.0749
0.8199	1.0993
0.8689	1.1252
0.9136	1.1498
0.9579	1.1754
1.0000	1.2004

Table 4. Densities of ethanol (99.4%)-Propylene Carbonate Mixtures at Atmospheric Pressure and 25 °C

Wt fraction propylene carbonate	Density(g/ml)
0	0.7865
0.2628	0.8677
0.4811	0.9463
0.6631	1.0234
0.8676	1.1241
1.0000	1.2004

3. Phase Diagram for the System Ethanol-Propylene Carbonate-water

To depict the phase behavior of a three-component system on a two-dimentional 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 relative amounts of the three components, usually presented as percent by weight, can be shown on a triangular plot, as indicated in Fig. 7. The corners of the triangle labeled A, B, and C correspond to the pure components ethanol, propylene carbonate, and water. The side of the triangle opposite the corner labeled A, for example, corresponds to the absence of A. Thus the horizontal lines across the triangle show increasing percentages of A from zero at the base to 100 percent at the apex. In a similar way the percentages of B and C are given by the distances from the other two sides to the respective apices. The composition corresponding to any point can be read off from the three composition scales of the diagram.

The simplest three-component systems are those in which a liquid system breaks down into two phases. The system ethanol-propylene carbonate-water (Fig. 7) is such a system, showing, at 25 °C, a two-phase region when the amount of ethanol is quite small. A necessary part of the diagrams are the tie lines through

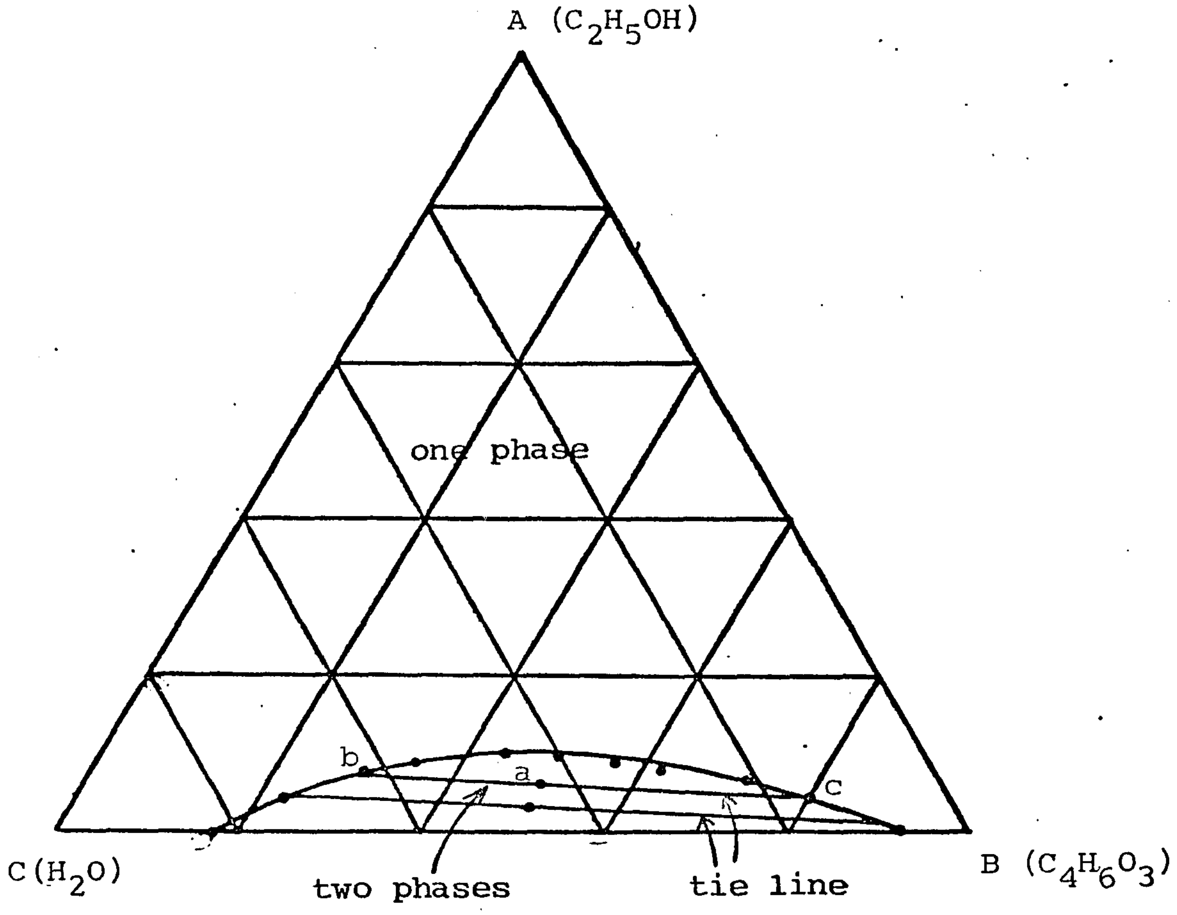


Fig. 7 Phase diagram of the liquid system ethanol-water-propylene carbonate at 1 atm pressure and 25 °C

the two-phase region joining the compositions of the two phases that are in equilibrium. Thus a total composition corresponding to point a in the two-phase region gives two phases, one of composition b and the other of composition c.

Application of the phase rule to a system corresponding to a point in the two-phase region gives

$$\begin{aligned} \phi &= C - P + 2 \\ &= 3 - 2 + 2 = 3 \end{aligned}$$

The 3 degrees of freedom can be accounted for by the pressure, the temperature, and one composition variable. Thus the composition of both phases cannot be arbitrarily fixed. If one is fixed, the tie line from that composition fixes the composition of the second phase.

4. A Comparison of Atomic Absorption Technique with Other Analytical Methods

The most commonly used method for determining the distribution coefficient in the solvent extraction of metal chelates is the radiochemical tracer technique. Measurement of the activity of the tracers in both the aqueous and organic phases are easily made. Another method of analysis[57] is required to confirm mass balance for the metal cation. In addition, rather long counting times, often longer than ten minutes per sample, are required to achieve maximum precision.

Colorimetric methods have also been widely used for the determination of the distribution coefficient. However, sample preparation is quite involved, especially if the presence of the extracting ligand interferes with the colorimetric reagent employed in the analysis step. A second problem arises if there is no direct colorimetric method for the determination of the metal cation in the organic phase. Then, a time consuming, wet-ashing procedure is required before the colorimetric analysis, or a "stripping" procedure must be developed.

The technique of atomic absorption spectroscopy might be especially applicable in the study of solvent extraction equilibria considering the rapidity of the technique and minimal sample preparation required. The analysis of the aqueous phase is straightforward and presents no problem, but it may be difficult to prepare an adequate calibration curve for the organic phase, which probably accounts for the very minimal application of atomic absorption in the study of extraction equilibria. The preparation of suitable calibration curves has been described in the experimental part. The calibration curves for Fe(III) in both the aqueous and organic phases(to which was added water and ethanol) are illustrated in Fig. 8. There is a linear relationship between absorbance and concentration up to 6 μg/ml in both phases; the sensitivity was greater in the organic phase. The problem of preparing a calibration curve for analysis of the organic phase is thus solved and the metal content of the organic phase can be directly determined by atomic absorption using the same method used to prepare the standards for the organic phase calibration curve.

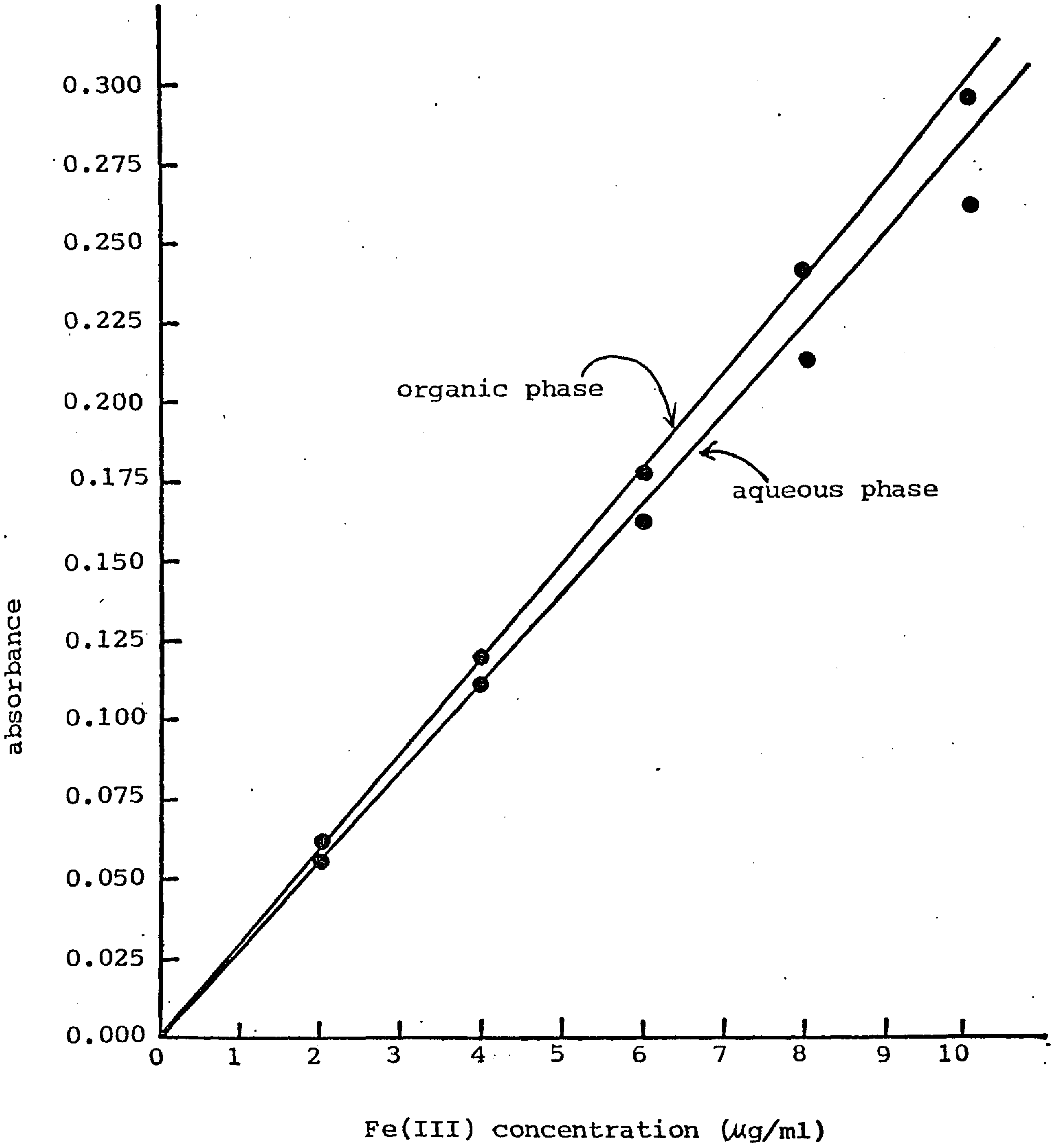


Fig. 8 Calibration curves for the determination of Fe(III) in the aqueous and organic phases

5. Iron(III)-Thenoyltrifluoroacetonate(TTA) Extraction

Usual Liquid-Liquid Extraction Method-Influence of Temperature and Shaking Time on the Extraction of Fe(III)TTA

In order to obtain some information about the extraction behavior of Fe(III)-TTA complex, it was desirable to investigate it by the usual liquid-liquid extraction method. As seen in the previous work[24], the higher the concentration of TTA and the longer the shaking time, the greater the percent extraction of Fe(III). The complete extraction of Fe(III) was achieved after shaking for 1 hour with 0.5 M TTA in benzene.[24] However, this is not favorable for a routine analysis. The rate of chemical reactions in general increases with an increase in temperature. However, the temperature effect was not investigated in that extraction system. The influence of temperature and shaking time on the extraction of Fe(III) with 0.05 M TTA in propylene carbonate is shown in Fig. 9. The temperature dependence is more remarkable than the dependence on shaking time. Thus an increase in temperature considerably promotes the extraction rate of Fe(III)-TTA with 0.05 M TTA in propylene carbonate. At 40 °C, the extraction equilibrium is achieved within 5 minutes; however, complete extraction is not attained. On the other hand, with 0.05 M TTA in benzene solutions, the extraction equilibrium is not achieved within 1 hr, even at 60 °C, as shown in Fig. 10. A comparison of Fig. 9 and Fig. 10

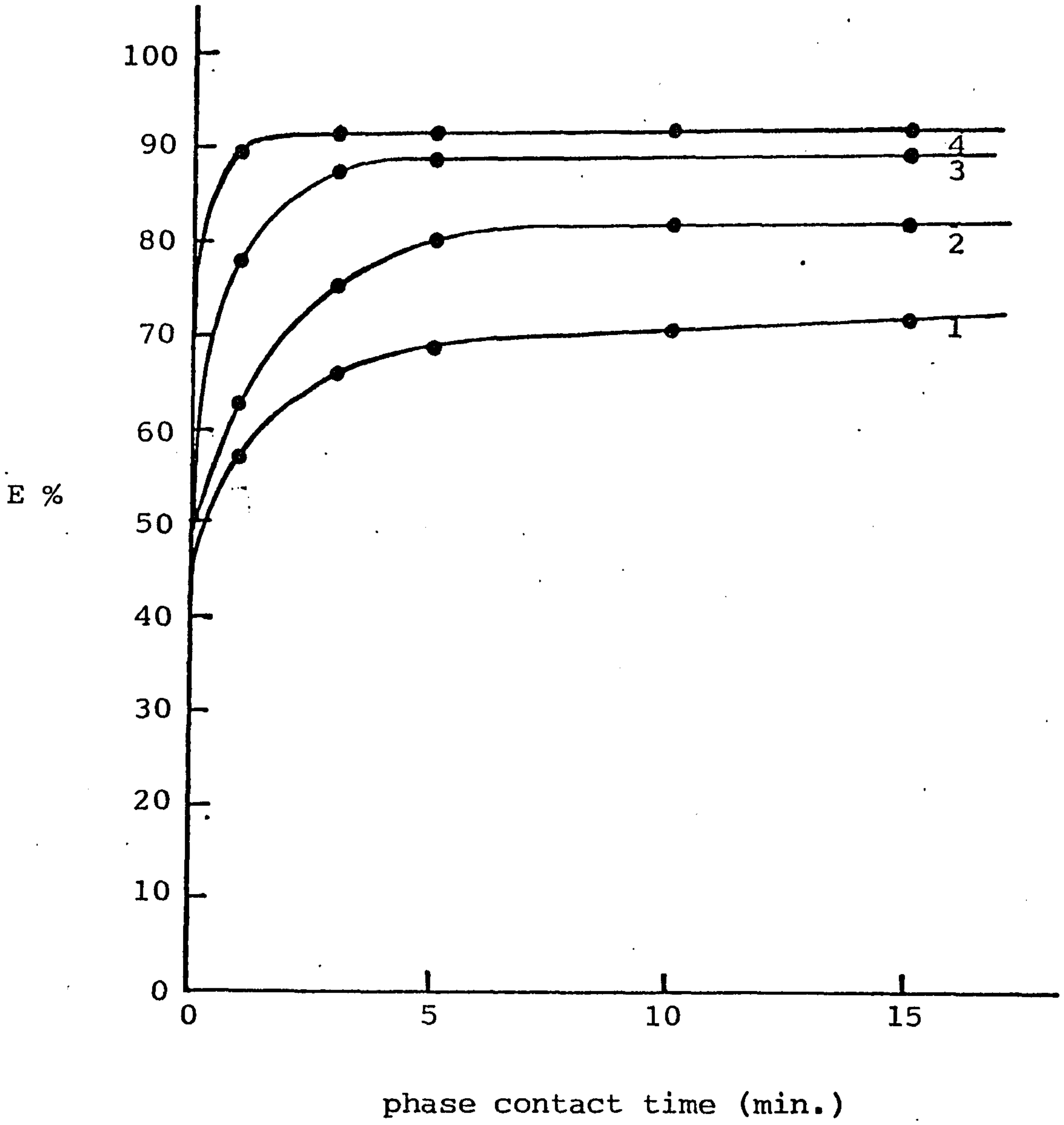


Fig. 9 Extraction of Fe(III) with 5 x 10^{-2} M TTA of propylene carbonate solution at various temperatures [Fe(III)] = 5 x 10^{-3} M
(1) 20 °C, (2) 30 °C, (3) 40 °C, (4) 50 °C

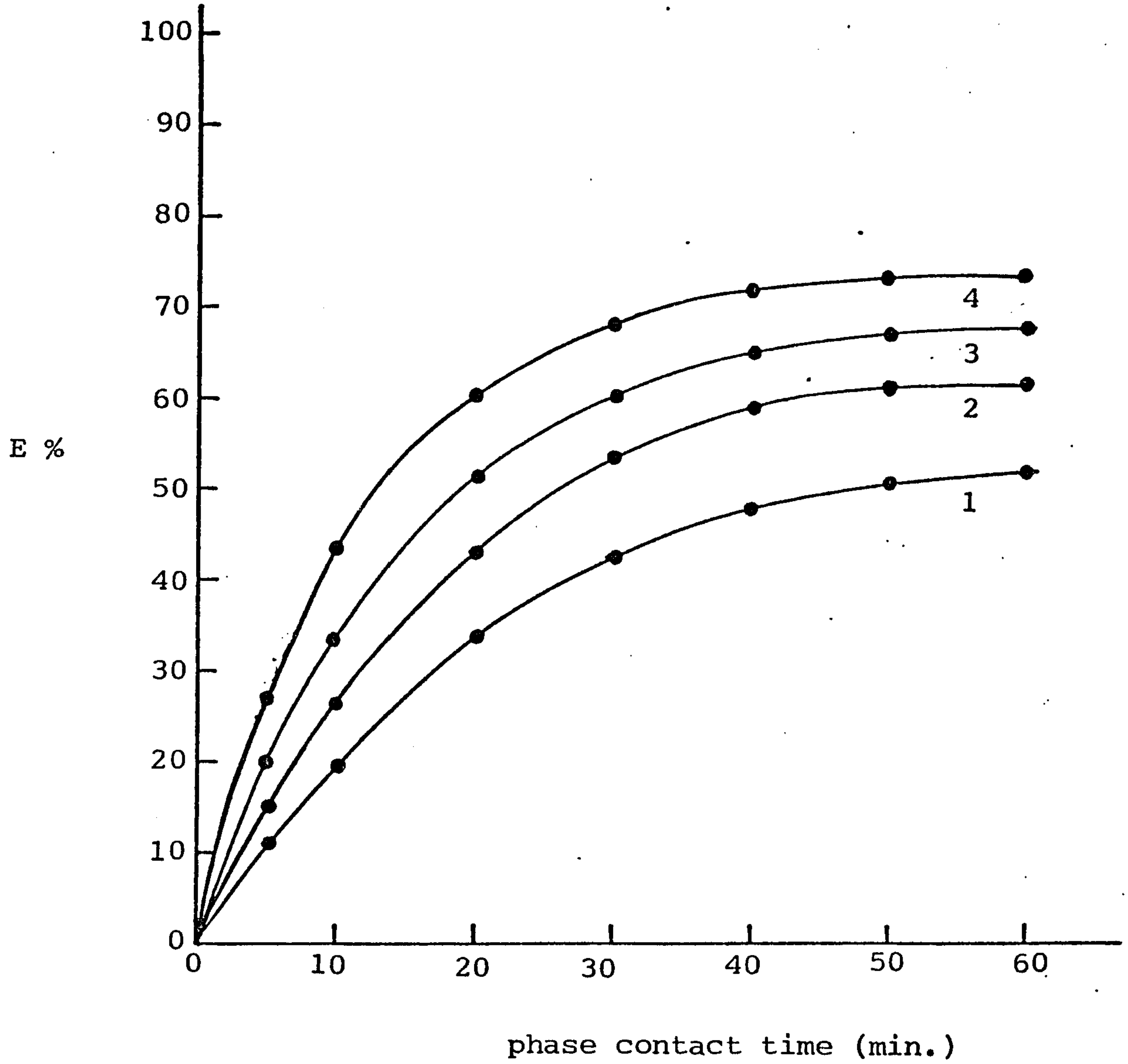


Fig. 10 Extraction of Fe(III) with 5 x 10^{-2} M TTA of benzene solution at various temperatures
[Fe(III)] = 5 x 10^{-3} M
(1) 30 °C, (2) 40 °C, (3) 50 °C, (4) 60 °C

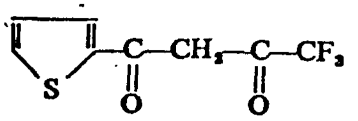
makes it obvious that propylene carbonate solvent is also superior to benzene in the ordinary batch extraction of Fe(III)-TTA even at room temperature.

Homogeneous Liquid-Liquid Extraction of Fe(III)-TTA by Propylene Carbonate

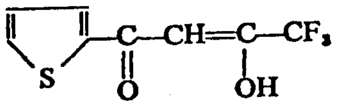
Fe(III)-TTA is rapidly and completely extracted by the homogeneous liquid-liquid extraction method, in as little as a 5 minute equilibration time in the homogeneous state at 80 °C. It has been pointed out by some authors[24-26] that certain metal cation complexes with TTA are extracted very slowly. For example, 12 hours are required to establish equilibrium during extraction of Fe(III)-TTA from hydrochloric acid solutions with a 0.2 M solution of the reagent in benzene.[25] Akaza et al. also reported rather long shaking times in colorimetric determinations with TTA.[26] Finston and Inoue showed the dependence of phase contact time on the concentraction of TTA (0.010 M-0.50 M) and succeeded in enhancing the extraction rate by addition of thiocyanate.[24] The homogeneous liquid-liquid extraction method gives rapid and complete extraction of Fe(III)-TTA complex. The effectiveness of this method might result from higher reaction temperature and the disturbance of the water structure in the medium (the decrease of water activity), in which the aqueous species is caught by intrusion of propylene carbonate molecules. Another characteristic is that the formation and the distribution of the extractable species are achieved in the single phase of the mixed solvent composed of water and propylene carbonate, which enables the extraction of Fe(III) from the aqueous phase very rapidly upon separation of the mixed solvent into two immiscible phases.

Chemical State of TTA in Water, Benzene, and Propylene Carbonate

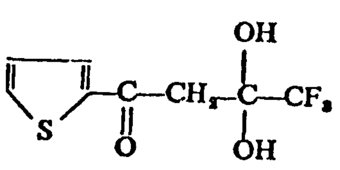
As mentioned previously, a great difference was seen between the extraction by benzene solution and by propylene carbonate solution of TTA. This led to a study of the chemical state of TTA in these solvents. TTA is a 1,3-diketone and exists in the following three forms:[20]



(keto)

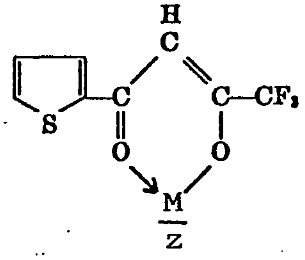


(enol)



(keto hydrate)

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



where z is the charge on the uncomplexed metal ion. In the benzene phase, TTA is about 11 percent in the keto hydrate form, the remainder is in the enol form.[28] In dilute acid about 1.6 percent of the TTA is in the enol form, the remainder in the keto hydrate form.[58] Fig. 11 shows the UV absorption spectra of TTA in water, in benzene, and in propylene carbonate. The spectrum in water corresponds to keto hydrate form, and that in benzene to the enol form. In propylene carbonate the spectrum of TTA is different from those in benzene and water. The same UV absorption spectrum of TTA in tributylphosphate, corresponding to the enol form (probably by hydrogen bonding onto the enolic form), was observed by Healy et al.[29] Thus, this spectrum is considered to be the enol form.

The possible structures in the enol form of TTA[30] are:

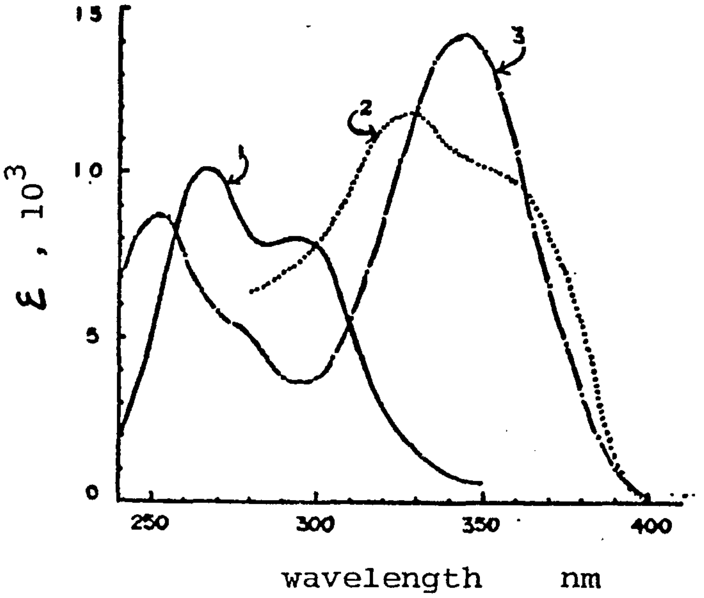


Fig. 11 Ultraviolet absorption spectra of TTA in some solvents
(1)TTA in water,(2)TTA in benzene,(3)TTA in propylene carbonate

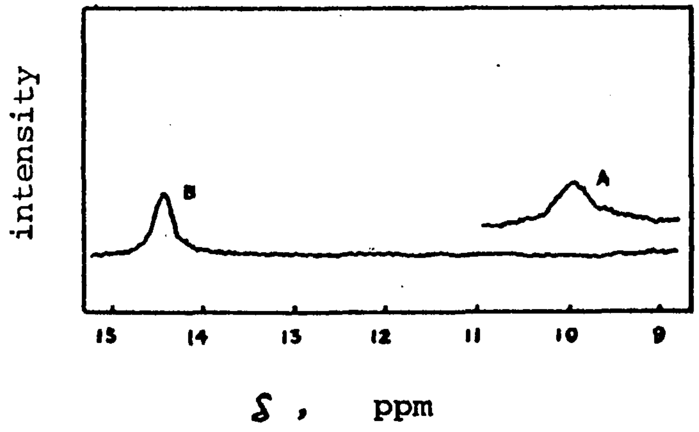
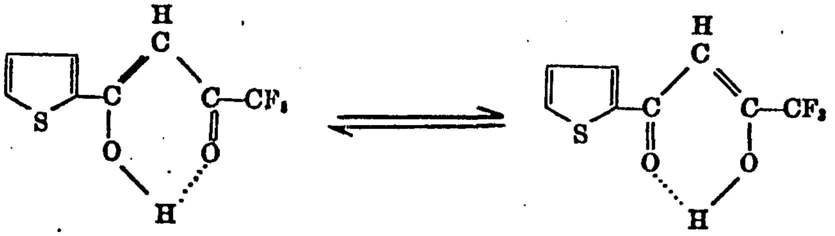
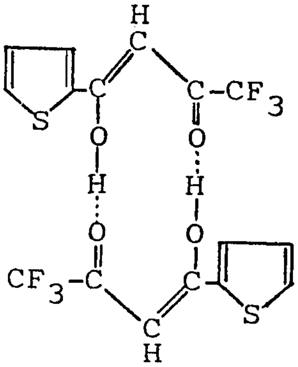


Fig.12 PMR lines of OH proton in TTA
(A) 0.5 M TTA in propylene carbonate
(B) 0.5 M TTA in benzene

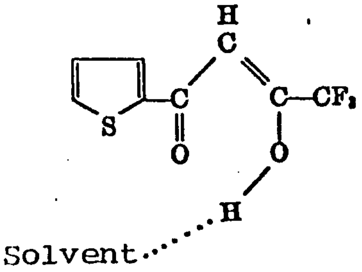
Intramolecular hydrogen-bonded TTA:



The dimer of TTA:



The keto mother of TTA (of which the intramolecular hydrogen bond breaks, and the intermolecular hydrogen bond forms with the solvent):



When the chemical shift of the OH proton is considered in these three kinds of enol form TTA, the resonance lines of OH proton in TTA(intra) and TTA(dimer) are observed at a lower magnetic field owing to the intramolecular hydrogen bond, and that of TTA keto mother is shifted to higher field owing to breaking of the intramolecular hydrogen bond. In polar solvent, the solvation is considered to stabilize TTA keto mother form. Indeed, as seen in Fig. 12, 0.5 M TTA in propylene carbonate solution shows the upfield shift of OH proton, as compared with benzene solution, which indicates solvation by propylene carbonate. Therefore in benzene the enol form of TTA is expected to be TTA(intra) or TTA(dimer), whereas in propylene carbonate the enol form is expected to be TTA(keto mother), provided that ionization of TTA is required before the reaction between Fe(III) and TTA enolate ion. TTA keto mother type is considered to be more favorable for extraction than TTA(intra) or TTA(dimer). From this point of view, TTA in propylene carbonate should be superior to TTA in benzene in the extraction.

Mechanism of Fe(III)-TTA Extraction

The extraction in general proceeds through the following steps: (a) distribution of organic reagent (in this case, TTA) into aqueous phase, (b) ionization of TTA, (c) reaction of Fe(III) with TTA enolate ion, and (d) distribution of the chelate into organic phase. Taft and Cook[32] carried out kinetic and equilibrium studies of Fe(III)-TTA by spectrophotometry. They reported that the rate determining step was not the ionization of TTA, but was the reaction of Fe(III) with TTA enolate ion. An explanation for a synergic mechanism was presented in 1967 by Finston and Inoue,[24,33] who investigated the effect of thiocyanate ion on the extraction of Fe(III)-TTA. They also emphasize the kinetic factor in some extraction systems, especially the TTA system. A kinetic study of the extraction of plutonium(IV) with TTA [34] showed that the rate determining step in the extraction was the formation of the chelate in the aqueous phase. The conclusion of the study was that the value of the distribution ratio at equilibrium should affect the rate of extraction, and the rate of extraction should depend on reagent conditions and pH. Finston and Inoue showed this to be true for the Fe(III) case and also showed that the distribution ratio was not a true equilibrium value. Murata et al.[31] reported that the rate determining step in the slow extraction with benzene solution is the transfer process of extracted species, and in the case of the extraction with TTA propylene carbonate solution the rate determining step is the formation of the complex in the aqueous solution. They studied the extraction behavior with benzene and propylene carbonate by equilibrating these solvents with aqueous solutions of the "first" complex (Fe(III) in excess). Propylene carbonate immediately extracts this complex; benzene does not extract it rapidly. In other words, propylene carbonate can extract iron(III)-TTA complex after the step corresponding to the formation of the first charged complex, but benzene can not extract until the fully substituted subsequent chelate is formed. The very slow rate in the benzene extraction is attributed to the long time required in the stepwise substitution of ferric aquocomplex by TTA. On the other hand, the extraction rate of Fe(III) is greater in propylene carbonate, because Fe(III) can be extracted before the substitution reaction is completed (as the first complex of Fe(III)-TTA chelate). Stephens and Suddeth[19],who studied the extractability of "ion association-chelate" systems into propylene carbonate,reported that the $Fe(phen)_3^{2+}$ and $Fe(TPTZ)_2^{2+}$ complexes are completely extracted in the presence of perchlorate. This requires participation of perchlorate ion to form the neutral complex. Thus, in our extraction system from hydrochloric acid medium, it is reasonable to consider that the first complex of Fe(III)-TTA chelate, associated with chloride ion, is extracted into propylene carbonate as the "ion association-chelate".

6. Extraction of Other Metal TTA Complexes

The extraction behavior of Fe(III), Cu(II), Ni(II), and Zn(II), respectively, as a function of aqueous pH and TTA concentration are shown in Fig. 13 and Fig. 14. The percent extracted increases with increasing pH and TTA concentration. The extraction of Fe(III) at higher pH range can not be determined due to the precipitation of the hydrolysis product. In general, at higher pH values, TTA is converted to the enolate ion to a greater extent, increasing the metal cation extraction from the aqueous phase.

Under the conditions specified in the figure legends of Figures 13 and 14, Fe(III), Cu(II) and Ni(II) are extracted to a varying extent even in the absence of TTA. A number of other cations, tested under comparable experimental conditions (pH ~3.2, [M(II)] ~1x 10^{-3} M), were also extracted by propylene carbonate alone; Ca(II) and Mg(II) extract to the extent of 18%, and Ba(II) to as much as 33%. Their extraction was not affected by the presence of 0.2 M TTA in the propylene carbonate phase. On the other hand, under similar conditions, Zn(II), Cd(II), and Pb(II) are not extracted by propylene carbonate alone. However, in the presence of 0.2 M TTA, Zn(II) is extracted to the extent of about 30% (Fig. 13); Cd(II) and Pb(II) were extracted to about 20% and 13%, respectively. The extractability of all these metal cations as a function of aqueous pH and TTA concentration were investigated. It was found that extractions of Fe(III), Ni(II), Cu(II), Zn(II), and Pb(II) depend on both pH and TTA concentration. However, extractions of Ca(II), Ba(II), and Mg(II) are independent of pH and TTA concentration. Therefore, the species extracted in these cases are other than TTA complexes. Because propylene carbonate is an oxygenated organic solvent, the basic character of the oxygen atom enables the incorporation of the solvent molecule in the coordination sphere of the metal ion, giving rise to an ion association compound that bears a structural resemblance to the solvent.

We may conclude that Fe(III), Ni(II), and Cu(II) with unfilled d orbitals are able to accept electrons from TTA enolate to form coordination compounds. The other cations with filled d orbitals can not accept electrons from TTA enolate, thus they are not able to form TTA complexes. This is consistent with the results; Fe(III), Cu(II), and Ni(II) are extracted to a greater extent, the others to a lesser extent. Hydrolysis, chelate stability, chelate solubility etc. will also effect the extent of extraction.

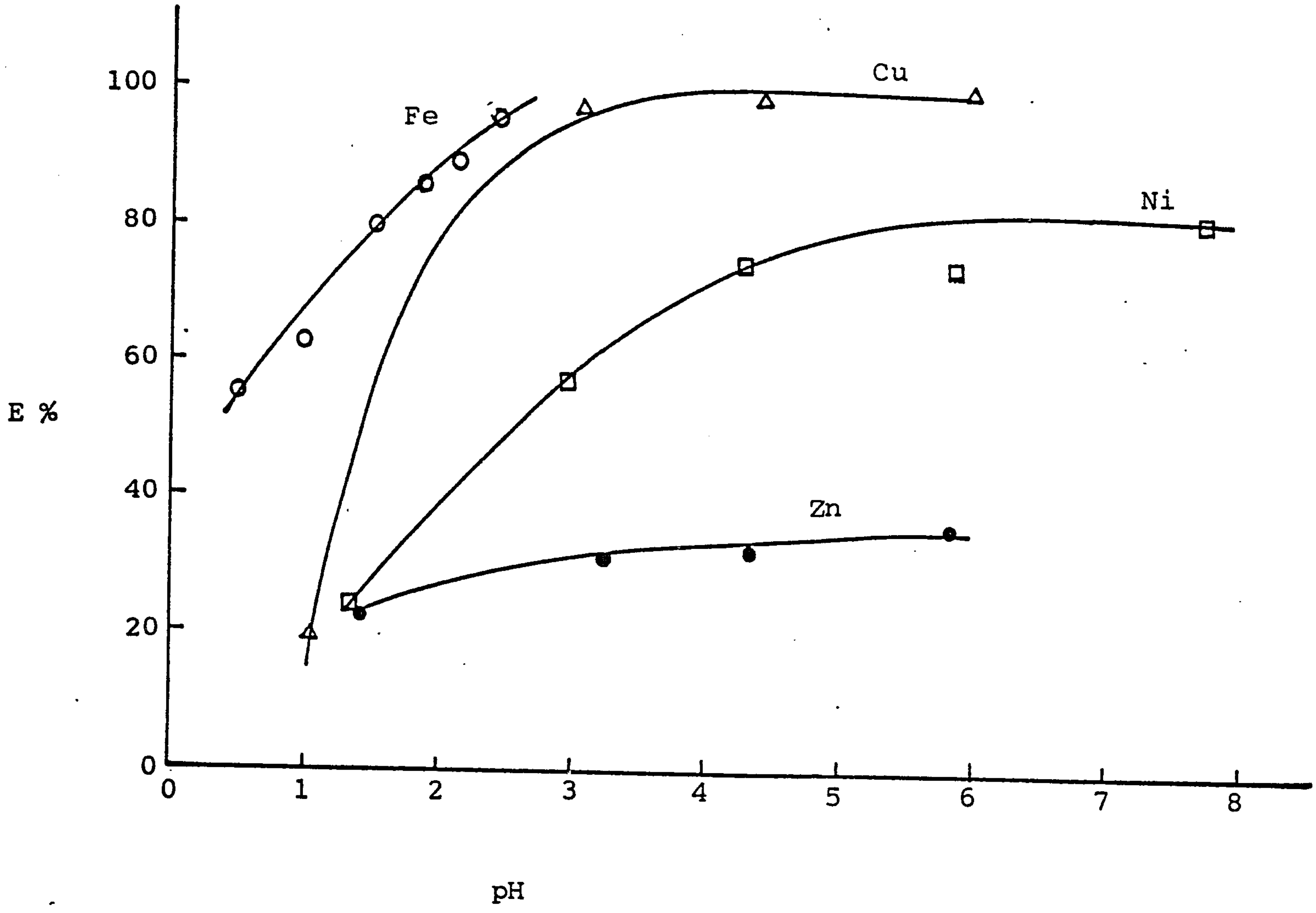


Fig. 13 Effect of aqueous pH on the extractability of metal-thenoyltrifluoroacetonates into propylene carbonate, 80 °C.
Conditions: [TTA] = 0.2 M; $[Me^{n+}]$ = 0.02-0.001 M; contact time=30 min.

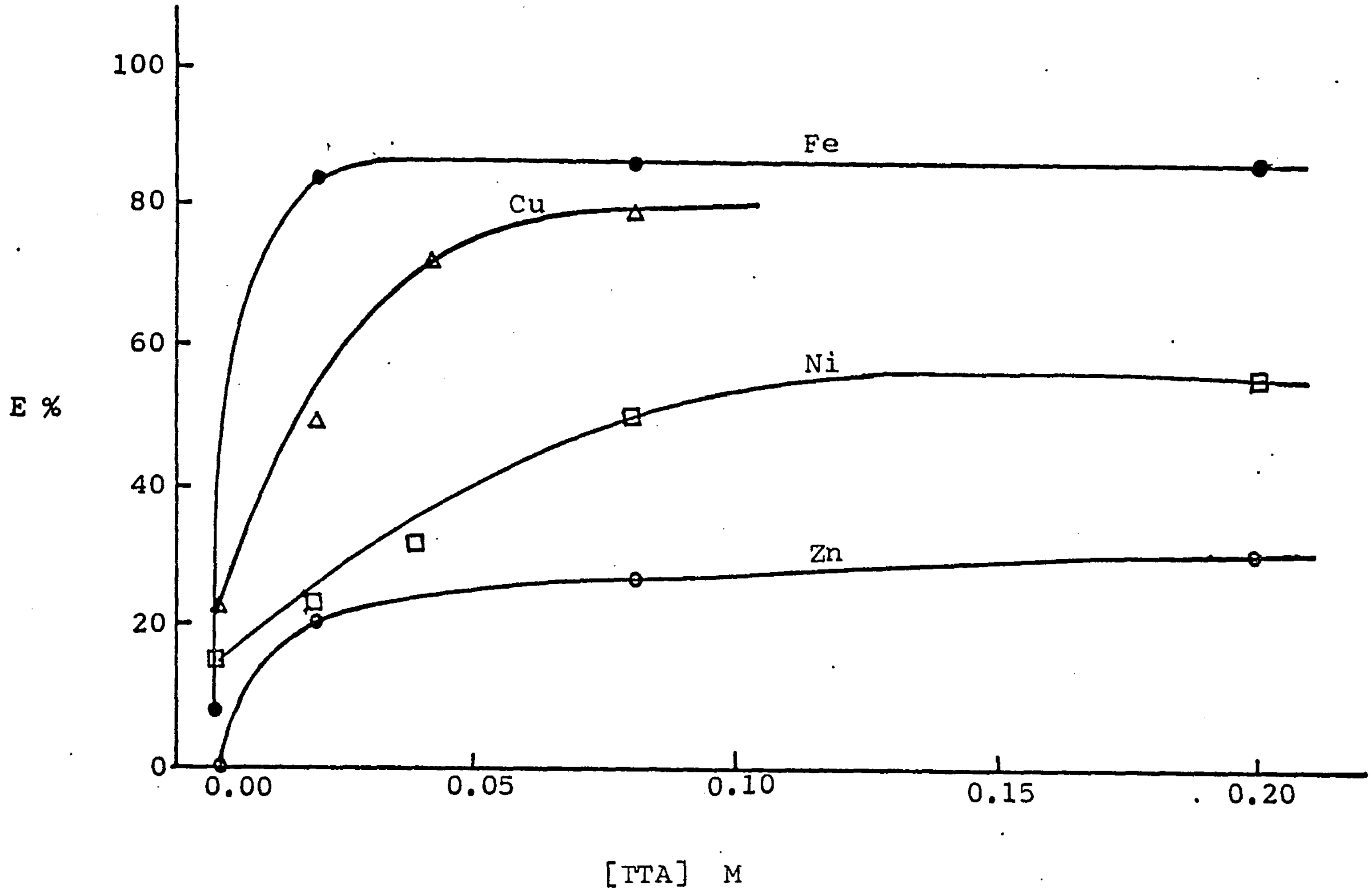


Fig. 14 Effect of TTA concentration on the extractability of metal-thenoyltrifluoroacetonates into propylene carbonate, 80 °C. Conditions : pH for $Me^{n+} \sim 3.1$, for $Fe^{3+} = 1.9$; $[Me^{n+}] = 0.02 - 0.001$ M; contact time=30 min.

7. Extraction of Fe(III) into Propylene Carbonate by Some Other Complexing Agents

An extensive study of the extraction of Fe(III) with a number of other complexing agents into propylene carbonate by the homogeneous liquid-liquid extraction technique has been performed.

a. Monodentate Systems

There are a large number of uncharged compounds formed by the association of oppositely charged ions in pairs or clusters of higher order. Extraction by such an interaction is considered to be an extraction of ion-associates. The parameters controlling the extraction of metal ions are those affecting the formation of such extractable species in the aqueous phase, such as the aqueous ligand concentration, concentration of other complexants that may compete for the metal ion, presence of other anions that compete for the cation, the hydrogen ion concentration, the concentration of the metal ion itself and such physical parameters as temperature. A simple aqueous system is expected to conform to equations derived from the mass-action law, and if no complication arises from the state of solute in the organic phase, the overall extraction equilibrium conforms also to simple mass-action equations. However, in the majority of the actual extraction systems, simple mass-action equations fail to describe the underlying reaction of extraction. This is due mainly to the fact that the state of the solute in the organic phase satisfies only exceptionally the requirements of ideal behavior. Lack of proper understanding of the non-ideal nature of the solute in the organic solvent, and even more, the non-quantitative presentation, renders even the most elaborate set of mass-action equations of little use for a more general application.

The responsibility for the specificity of the process has been placed on factors such as the degree of electrostatic interaction in ion-pairing, degree of hydration of the ions, their polarizability,etc. Empirically, the trend of selectivity of the extraction process was successfully correlated with the degree of hydration of the anion, which is in turn a function on its size.

Five examples of such systems which were studied are described in the following.

Thiocyanate

The use of alkali thiocyanates as complexing reagents for the colorimetric estimation of a number of metals is well known. Thus, the red color of $FeSCN^{+2}$ has long been employed for the colorimetric estimation of Fe(III) and it was found in this study that, in the presence of excess of thiocyanate, Fe(III) can be extracted as a stable red complex into propylene carbonate. The extraction of Fe(III) thiocyanates into propylene carbonate in the concentration range 0-1 M has been studied and the results are shown in Fig. 15; the extraction of Fe(III) reaches a maximum at 0.5-0.8 M and drops off slightly at higher thiocyanate concentrations.

Advantage has been taken of thiocyanate complexing as a method of chemical separation; for example, several of the rare earth elements have been separated, based on the slightly different solubilities of their thiocyanates in butanol.[35] The complete extraction of Fe(III) thiocyanate complexes by propylene carbonate as a solvent can be used for the removal of iron in the analysis of steel. The advantages of this solvent include non-volatility, non-flammability, and rapid extraction. It is possible to effect various separations among different elements by the proper choice of acid concentration, thiocyanate concentration, valence state of metal,etc.

Chloride

The extraction of Fe(III) from HCl solutions into ethyl ether has been in the past the most studied of the extraction systems involving inorganic substances. As early as 1892, Rothe[36]

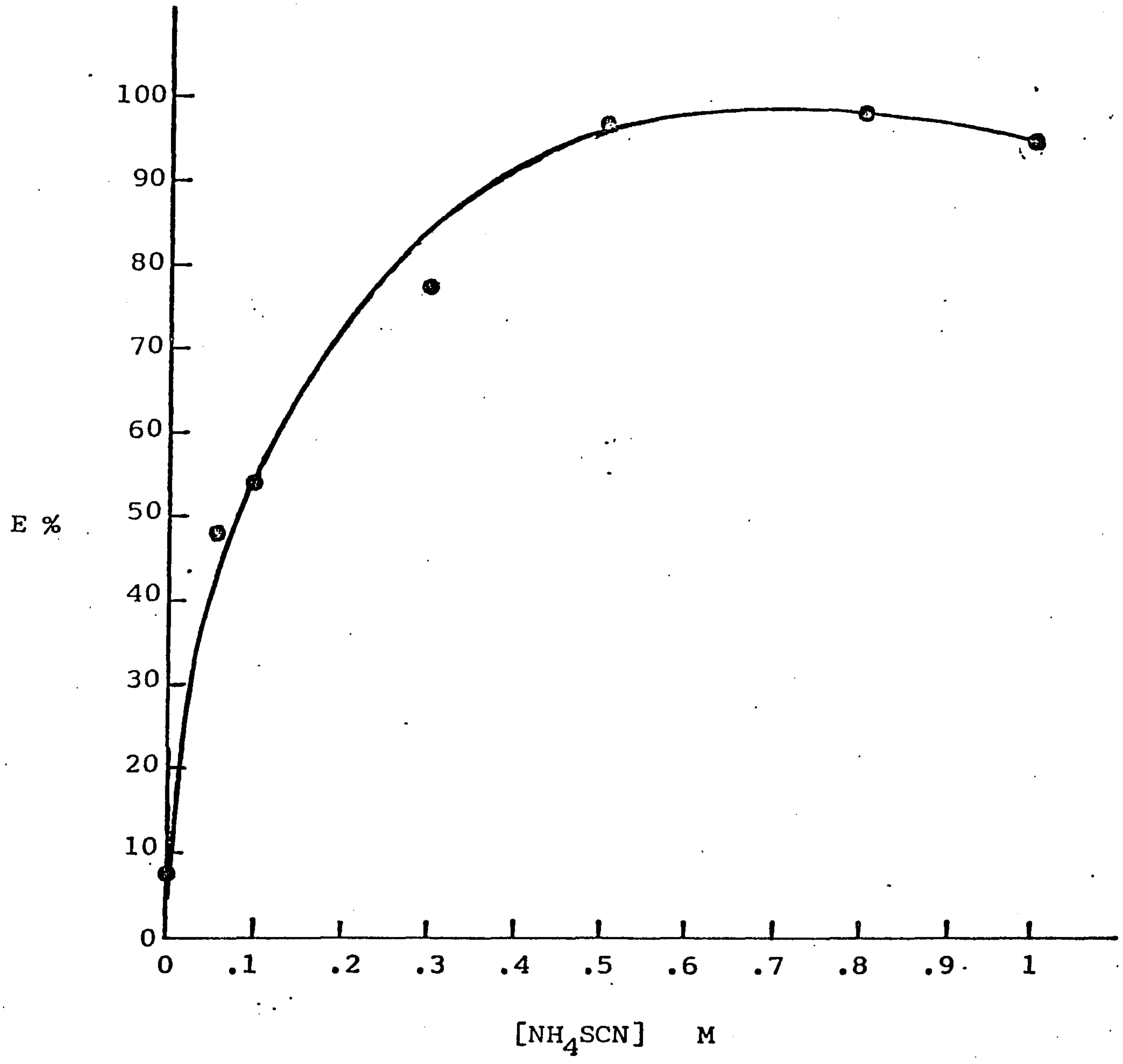


Fig. 15 Effect of NH_4SCN concentration on the extractability of Fe(III) into propylene carbonate, 80 °C.
[Fe(III)] = 1.8×10^{-3} M
contact time=10 min.

recognized the possibilities of this process, and the work of Speller[37], Langmuir[38], and Kern[39] led to the first procedures for the separation of this metal ion from many others. The study of the extraction of Fe(III) from HCl solutions into propylene carbonate was limited because of the miscibility of propylene carbonate with HCl at HCl concentrations higher than 3 M. The effect of variation of HCl concentration in range 0-3 M of the aqueous phase on the extraction of Fe(III) is shown in Fig. 16. The extraction increases with increasing HCl concentration, reaching 87% at 3 M HCl. The use of ammonium chloride as complexing reagent for the extraction of Fe(III) shows a similar result, but the addition of 1.5 M HCl to the NH_4Cl solution greatly increases extraction of Fe(III), as shown in Fig. 17; at a total chloride concentration of 5 molar, complete extraction is obtained.

Bromide

Bock[40] had conducted a systematic investigation into the extraction of metallic bromides. He had chosen ether as a solvent. Isolated cases do occur in the literature in which other solvents have been used in extraction and separation studies, but it is only feasible as yet to make comparisons between systems involving the use of ether as an extractant. Consequently, investigations with other solvents are desirable.

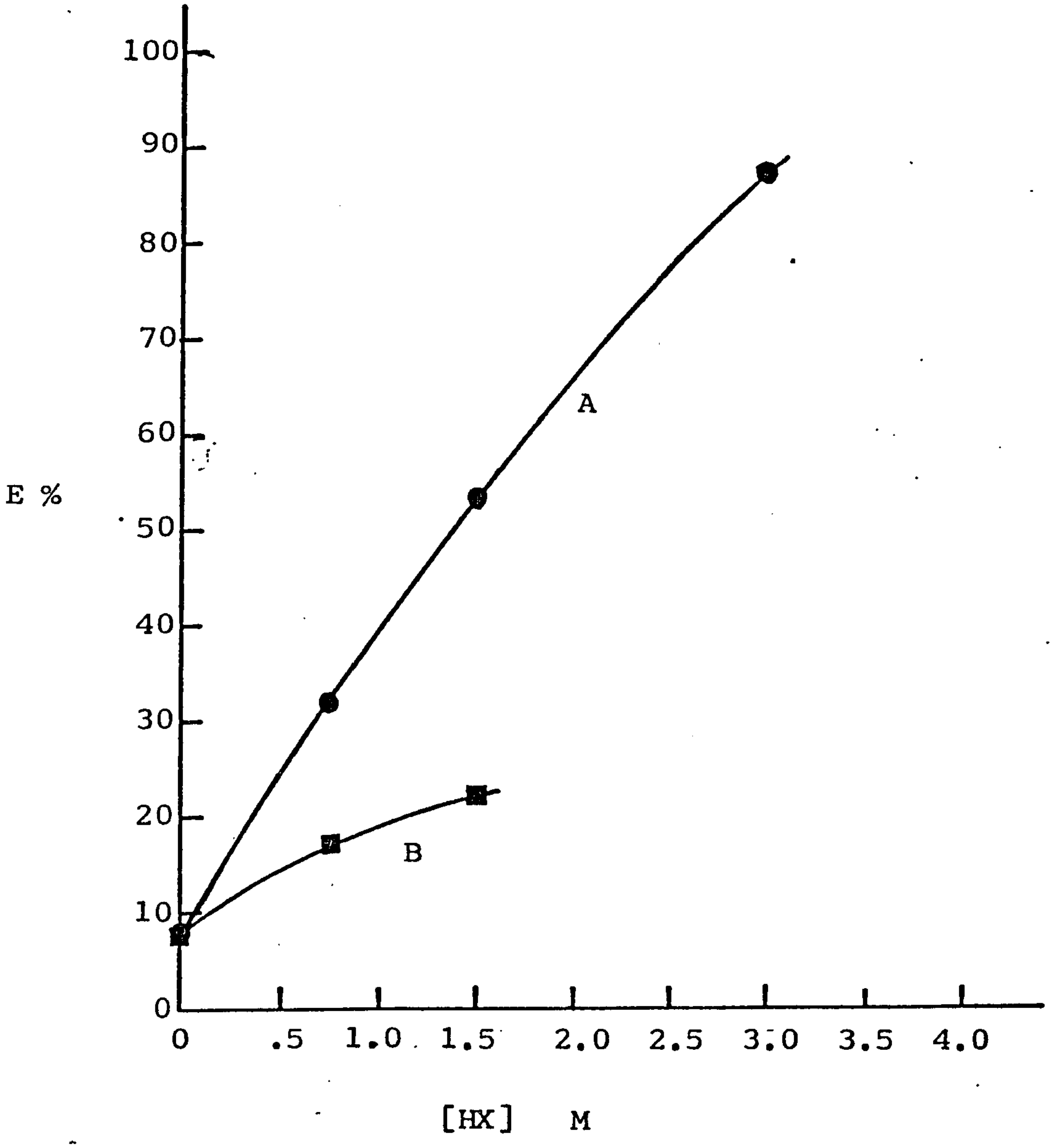


Fig.16 Effect of HX concentration on the extractability of Fe(III) into propylene carbonate, 80 °C.
[Fe(III)] = 3.6×10^{-3} M, contact time=10 min.
(A) ● : HCl (B) ■ : HBr

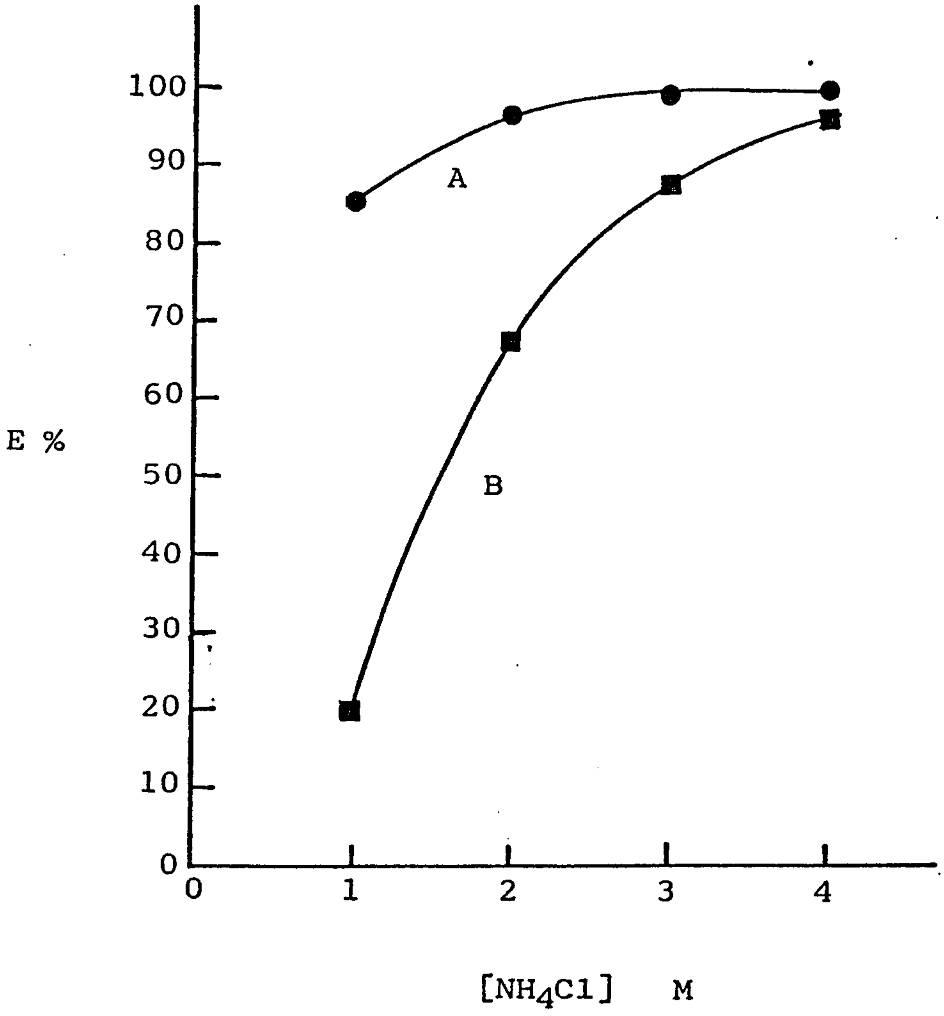


Fig. 17 Effect of NH_4Cl concentration on the extractability of Fe(III) into propylene carbonate, 80 °C, contact time=10 min.
[Fe(III)] = 1.8×10^{-3} M
(A) ●: 1.5 M HCl present (B) ■: without HCl

An investigation of the solvent extraction of Fe(III) bromides has been conducted using propylene carbonate as solvent. The extraction of Fe(III) from HBr solutions to propylene carbonate is also strictly limited in scope by the solubility of propylene carbonate in HBr solutions at HBr concentration higher than 1.5 M. However, the free acid can be replaced by NH_4Br or LiBr. The results in Fig. 16 show that at 1.5 M HBr, Fe(III) is extracted only to the extent of 20%. The effect of adding NH_4Br, as shown in Fig. 18, is that the extraction of Fe(III) increases up to 85% with an increase of NH_4Br concentration to 4 M in the presence of 1.5 M HBr. There is no effective extraction of Fe(III) by NH_4Br only as shown by curve c. The effect of LiBr only in the concentration range 1-6 M of the aqueous phase on the extraction of Fe(III) is also shown in Fig. 18. The extraction increases with increasing LiBr concentration, reaching 95% at 6 M LiBr.

Benzoate

Solutions of carboxylic acids in organic solvents have been found effective for extracting several metal cations into propylene carbonate from alkaline aqueous solutions. Fe(III) benzoate was extracted following the procedure of Johnson[41], who reported that the extraction of Fe(III) into ethyl acetate is best made from a

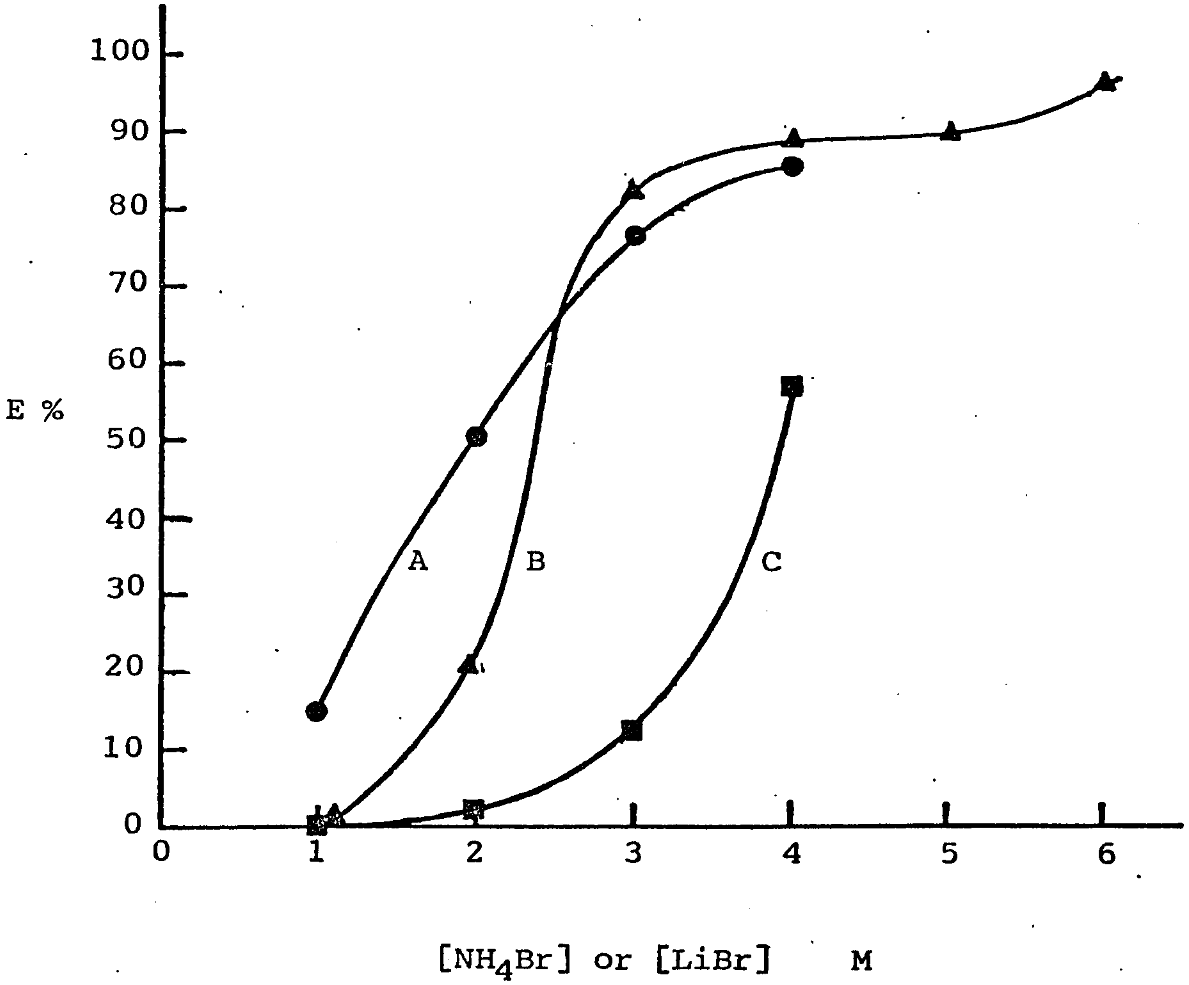


Fig. 18 Effect of bromide concentration on the extractability of Fe(III) into propylene carbonate, 80 °C, contact time=10 min.
[Fe(III)] = 1.8 X 10^{-3} M
(A) ● : NH$_4$Br with 1.5 M HBr (B) ▲ : LiBr
(C) ■ : NH$_4$Br

neutral or very slightly acid medium. Ammonium acetate was conveniently used to buffer the solution to a pH of approximately 7. Fig. 19 shows the effect of benzoate concentration on the extraction of Fe(III) into propylene carbonate. Because the ion association compound of Fe(III) benzoate bears a structural resemblance to the solvent, it is expected that the extraction efficiency will be good, and in fact it reachs 95% at even relatively low benzoate concentration and drops off slightly at higher concentration.

4,7-Diphenylphenanthroline (Bathophenanthroline)

This reagent is specific for iron, forming a tris type molecular complex with ferrous iron. Ferric iron can be reduced to ferrous by reaction with 10% hydroxylamine prior to reaction with the reagent. In this experiment, the quantity of iron extracted was about 10 μg, the pH was adjusted to a high value with 10% sodium acetate, and 0.001 M bathophenanthroline in propylene carbonate was used as extractant. The effect of pH on the percent extracted is shown in Fig. 20; increasing extraction is observed with increasing pH, reaching 90% at pH 5. It has been reported[17] that the most important application of bathophenanthroline is for the determination of iron at extremely low concentrations ranging from 0.001 to 0.01 ppm.

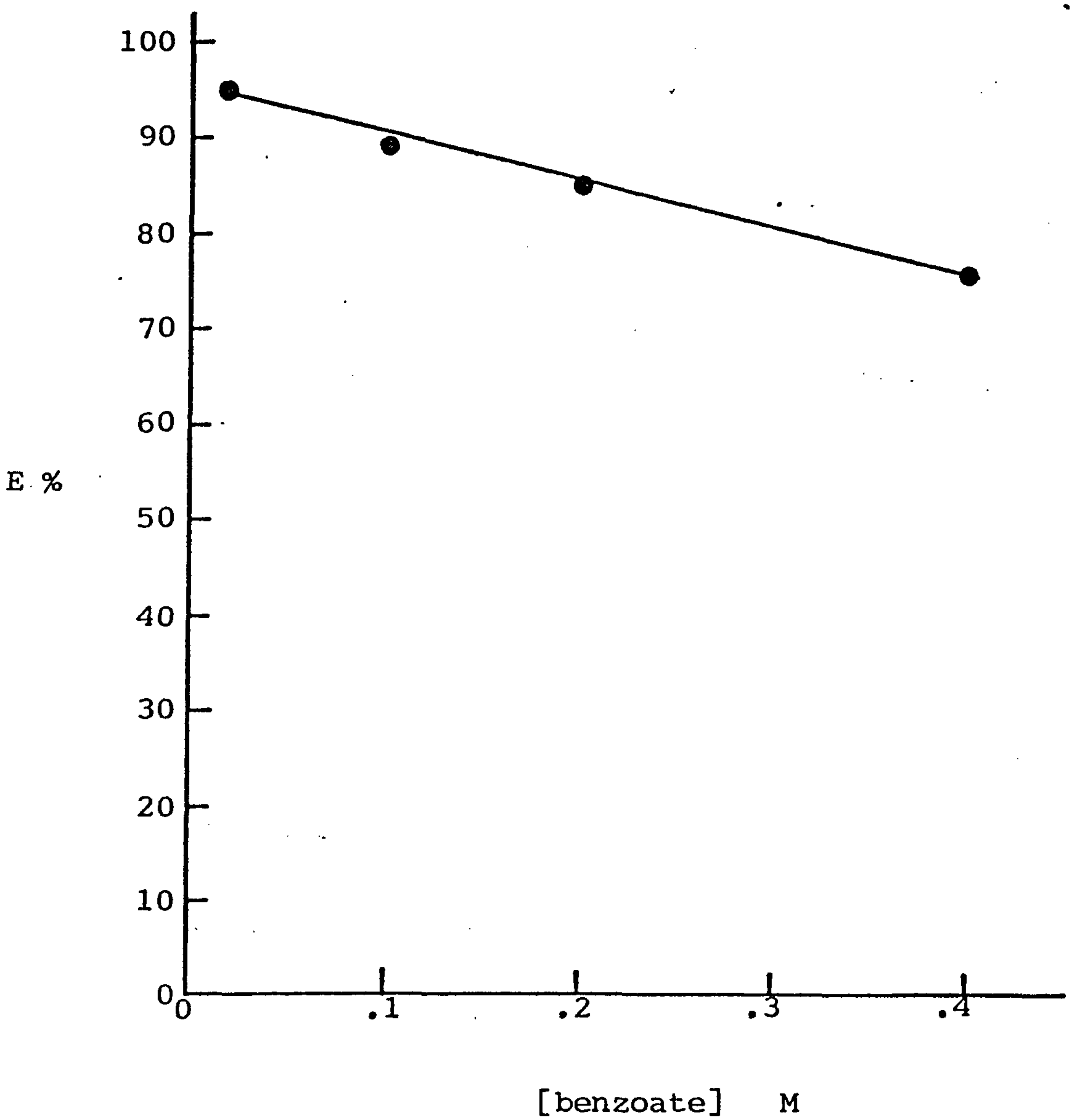


Fig. 19 Effect of benzoate concentration on the extractability of Fe(III) into propylene carbonate, 80 °C, contact time=10 min.
[Fe(III)] = 9×10^{-4} M

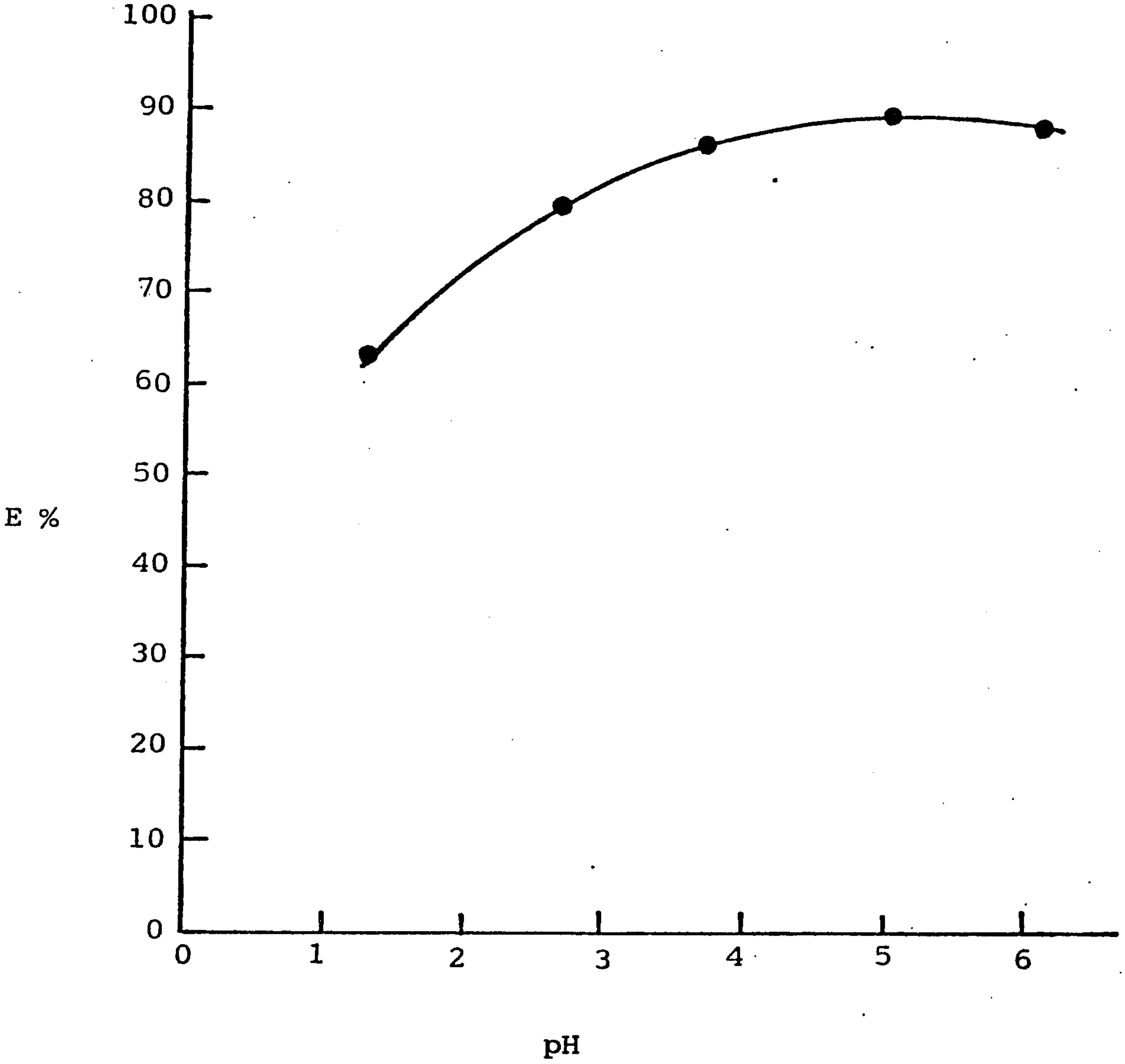


Fig.20 Effect of aqueous pH on the extractability of Fe(III)-bathophenanthrolines into propylene carbonate, contact time=10 min, 80 °C.
[Fe(III)] = 1.8 x 10^{-4} M, [bathophenanthroline] = 1 x 10^{-3} M

b. Bidentate Systems

Many organic reagents which precipitate metal cations from aqueous solutions form chelates which are frequently extractable into an organic solvent. In chelate extraction systems, the organic chelating agent acts as a weak acid and contains a donor group so as to form a bidentate complex with the metal cation. The metal cation complex in the organic phase must contain a number of chelating molecules equal to the actual charge on the metal ion, in order to yield an electrically neutral species.

Since metal-chelate extraction is usually achieved from aqueous solutions of low electrolyte concentration, there are no complicating thermodynamic factors affecting the activity coefficient of the solutes in the aqueous phase. Under such conditions, metal complexing in the aqueous phase can readily be accounted for if the equilibrium constants of the aqueous metal-bearing species are known, which is usually the case. For a given series of closely related chelating extractants there is a relationship between the dissociation constant of the acid and the stability constants of the complexes formed with any given metal.

(1). Extraction Characteristics of Chelate Systems

Aqueous Phase Parameters

Although almost all the chelating agents which form extractable metal complexes react with a large number of metals, the reaction may be rendered selective, or even specific for certain metals, by a proper adjustment of the initial aqueous solution. Since all the extracting reagents are weak acids, the formation of extractable complexes will greatly depend on the pH of the aqueous solution. Thus the simplest way to achieve separation is to affect equilibrium by adjustment of the aqueous pH. This procedure is useful for separation of metal cations by solvent extraction whenever the equilibrium constants are sufficiently different. The effect of pH will obviously be different for metal cations with different charge.

Organic Phase Parameters

Chelating agents which form uncharged and extractable chelates have at least two functional groups entering into reaction with the metal ion. One of these groups of the chelating molecule is an OH group, the other is a basic functional group capable of coordinating to the metal by its donor properties. The hydrogen of the OH is replaced by an equivalent of metal cation, and a stable ring, usually five- or six-membered, is formed. The stability of the chelate will depend on the basic nature of the coordination site and the acidity of the OH group, and also the acidic nature, coordination number and coordination ability of the metal. Structural factors affect both the acidity of the OH group and the basic strength of the donor atom.

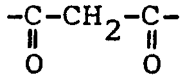
Two different aspects have to be considered with regard to the effect of acidity of the chelating agent on its ability to extract. A more basic chelating agent will form a more stable metal chelate. On the other hand, and this is the second aspect, a more acidic chelating agent with a lower pK value, will be more useful for the extraction of metal cations from acidic aqueous solutions.

The extent of extraction is much affected by solubility characteristics of chelates in organic solvents. Solubility is based on the principle that "like dissolves like".

(2). Chelating Agents and Metal Chelates

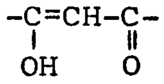
β-diketones

The β-diketones are characterized by the grouping



$-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-$

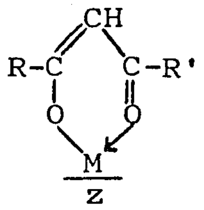
(I)



$-\underset{\underset{OH}{|}}{C}=CH-\underset{\underset{O}{\|}}{C}-$

(II)

In form (II) the enol hydrogen atom is replaceable by a metal cation, and the ketonic oxygen can complete a chelate ring as follows,



The β-diketones are versatile reagents because of the ease with which they enolize, and because the conjugated double bonds in the enol structure result in stabilization of the six-membered chelates formed.

(i). Acetylacetone, Trifluoroacetylacetone, and Benzoylacetone

The $-CF_3$ group in trifluoroacetylacetone reduces the basic strength of the ligand and thus permits extractions from more acid media; the aromatic ring substituent in benzoylacetone gives a more stable chelate than does an aliphatic group because of the conjugated system. These are the reasons why both trifluoroacetylacetone and benzoylacetone give a greater degree of extraction of Fe(III) than does acetylacetone; both reagents, at concentrations of 0.1 M completely extract Fe(III) at a pH of 2.65. The effect of pH on the extraction of Fe(III) by these reagents into propylene carbonate is shown in Fig. 21.

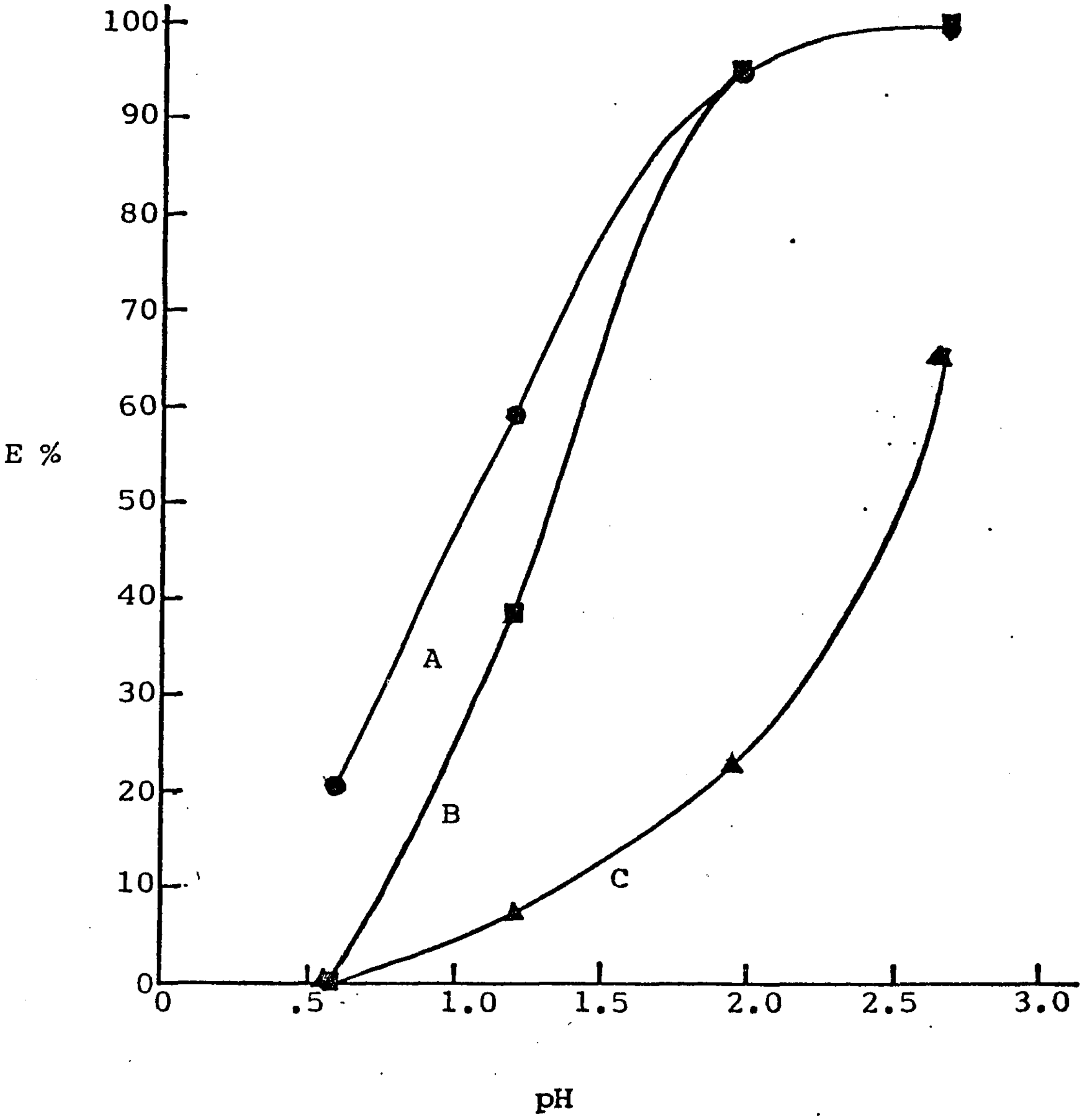


Fig.21 Effect of aqueous pH on the extractability of Fe(III)-complexes into propylene carbonate, 80°C , contact time=10 min.
[Fe(III)] = 3.6 x 10^{-3} M, [chelating agent] = 0.1 M
(A) ● : benzoylacetone, (B) ■ : trifluoroacetylacetone
(C) ▲ : acetylacetone

(ii). Benzoyltrifluoroacetone, Thenoyltrifluoroacetone, and Dibenzoylmethane

The presence of the $-CF_3$ group in benzoyltrifluoroacetone and thenoyltrifluoroacetone, as previously explained, permits extractions from more acid media, and the presence also in each of these three reagents of conjugated substituents stabilizes the chelates by a resonance effect. The effect of the two substituents present in each of these three reagents is greater than the effect of the only one substituent in trifluoroacetylacetone and benzoylacetone, hence there is a higher percent extraction. The percent extracted as a function of pH is shown in Fig. 22; dibenzoylmethane has an unusual extraction curve which passes through a maximum at a pH about 2, the other two reagents show similar results up to pH 2, but the percent extracted remains constant at least to pH 2.65. A comparison of the extraction behavior of all six β-diketone reagents is shown in Fig. 23.

8-Quinolinol (Oxine)

Oxine is a widely used precipitating agent in analytical chemistry. Its solubility in water depends sharply on the pH of the aqueous solutions; in the pH range 5.5-8.5, the reagent is difficultly soluble, and the steep increase in the solubility

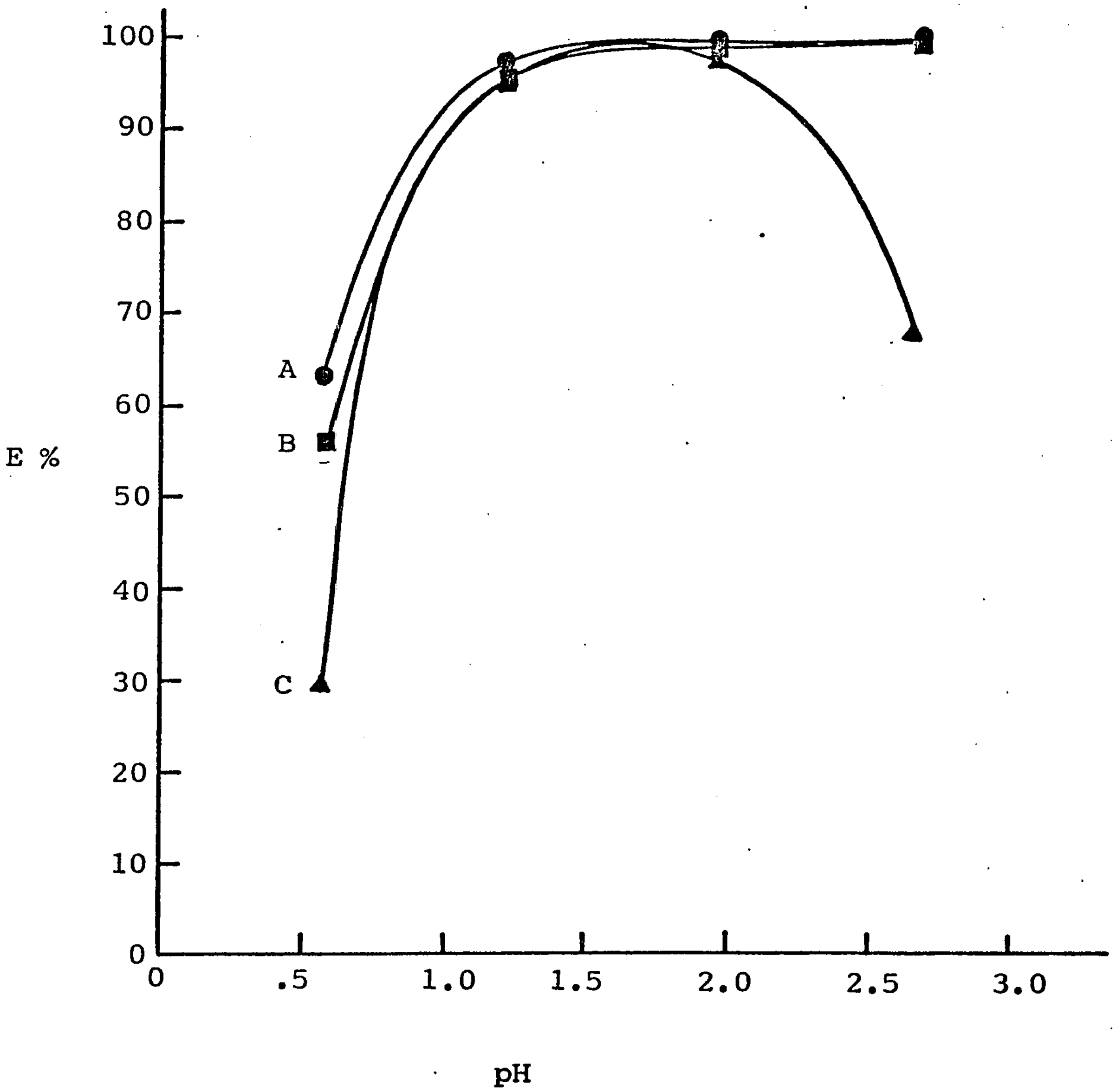


Fig. 22 Effect of aqueous pH on the extractability of Fe(III)-complexes into propylene carbonate, 80 °C, contact time=10 min.
[Fe(III)] = 3.6 x 10^{-3} M, [chelating agent] = 0.1 M
(A) ● : benzoyltrifluoroacetone
(B) ■ : thenoyltrifluoroacetone
(C) ▲ : dibenzoylmethane

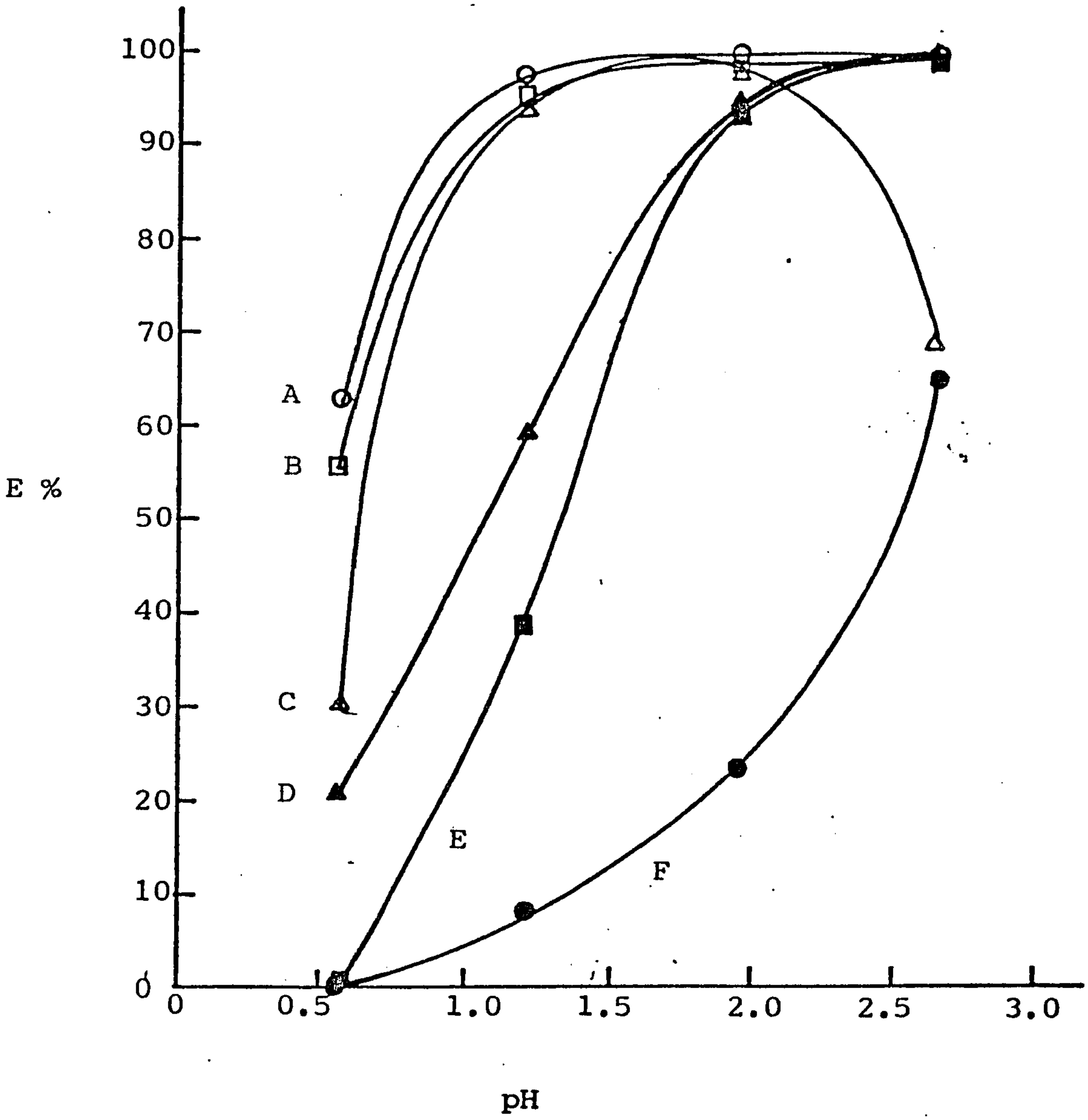


Fig. 23 Effect of aqueous pH on the extractability of Fe(III)-complexes into propylene carbonate, 80 °C, contact time=10 min.
[Fe(III)] = 3.6×10^{-3} M, [chelating agent] = 0.1 M
(A) ○ : benzoyltrifluoroacetone
(B) □ : thenoyltrifluoroacetone
(C) △ : dibenzoylmethane
(D) ▲ : benzoylacetone
(E) ■ : trifluoroacetylacetone
(F) ● : acetylacetone

both in acid and alkali ranges is due to the amphoteric character of the reagent. The reactivity of oxine with a large number of metals is due to the formation of stable five-membered chelates through the replacement of the hydrogen from the acidic phenolic group and coordination to the nitrogen,

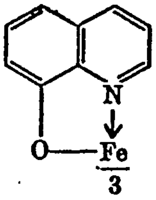


Fig. 24 shows the effect of pH on the extraction of Fe(III) into propylene carbonate with 0.1 M and 0.5 M reagent. The percent extracted reaches 98% and is almost independent of pH in the pH range 1.1-13. There was no difference at the two different concentrations of reagent.

In this experiment, 5% tartrate was added to the aqueous solution to prevent precipitation of the hydrous oxides, which would otherwise occur. The complete extraction over wide pH range has great value for the separation of iron from other heavy metals. Propylene carbonate extraction of 8-hydroxyquinolinates should have many applications as a means of separation of trace impurities and as a method of reagent purification.

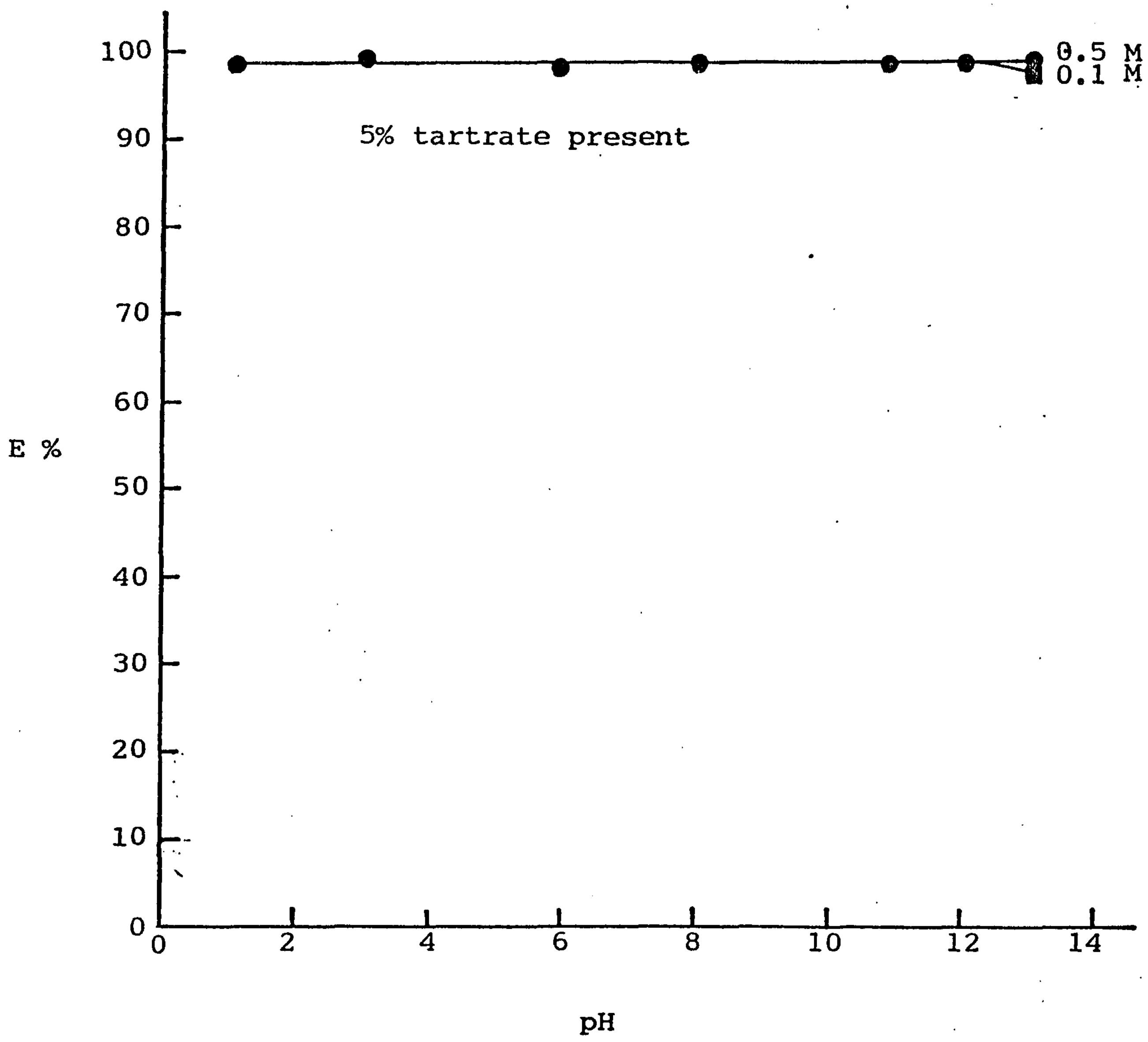


Fig. 24 Effect of aqueous pH on the extractability of Fe(III)-8-quinolinate into propylene carbonate, 80 °C, contact time= 10 min.
[Fe(III)] = 3.6 x 10^{-3} M, [8-quinolinol] = 0.1 M, 0.5 M

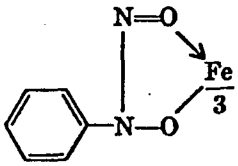
Cupferron

Cupferron which was first introduced by Baudisch[43] in 1909 as a specific precipitant for copper and iron, forms chelates with several metal cations which are soluble in various organic solvents. The reagent is now widely used in solvent extraction schemes.

Cupferron is generally used in aqueous solution, and since both the reagent and its chelates decompose upon heating to form nitrosobenzene, for best results cupferron solutions are refrigerated and extractions carried out in the cold. Decomposition of the reagent solution may be detected by a cloudy appearance.

One of the earliest applications of cupferron to the extraction of metals was performed by Meunier[44], who quantitatively extracted Fe(III), Ti(II), and Cu(II) from a 1.2 M HCl solution into chloroform, using an excess of cupferron. Furman et al.[13] showed in their systematic studies that cupferron is potentially more important as an extracting agent than as a precipitant in inorganic analysis.

Cupferron behaves as a weak acid in aqueous solution, the hydrogen can be replaced by an equivalent of metal cation to form a five-membered ring. Thus the metal coordinates through the oxygen to form a stable ring, as follows,



ferric cupferrate

These extractions performed at room temperature are not "homogeneous liquid-liquid extractions" but do show the efficacy of propylene carbonate as an extracting medium in general.

The effect of pH and reagent concentration on the extraction of Fe(III) is shown in Fig. 25. Extraction is complete with 0.5 M cupferron leaving not even a spectrographic trace of iron, and is independent of pH in the range 0.57-2.65; with 0.1 M cupferron, the extraction is also complete except at very low pH at which a small amount of Fe(III) remains in the aqueous phase. Extraction of cupferrates into propylene carbonate has proved to be a very effective procedure for removing iron prior to the estimation of other cations. The procedure is effective for the collection of microgram to milligram quantities of iron.

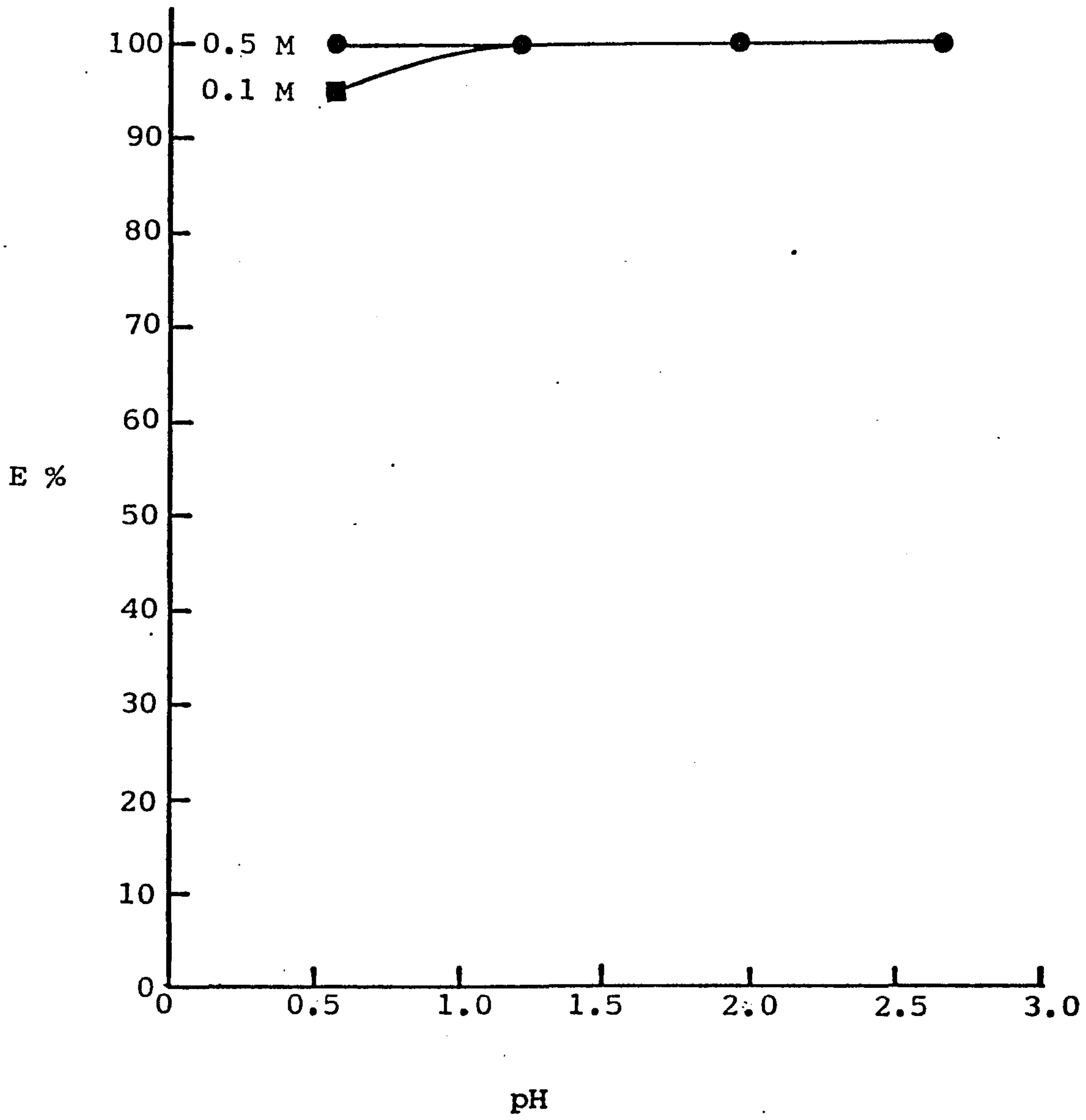


Fig. 25 Effect of aqueous pH on the extractability of Fe(III)-cupferrate into propylene carbonate, 25 °C, contact time=10 min.
[Fe(III)] = 3.6×10^{-3} M, [cupferron] = 0.1 M, 0.5 M

8. Analogues of Propylene Carbonate as Organic Solvent

1,2-butylene carbonate is not miscible with water at any temperature even up to 100 °C. However, the addition of ethanol to the water-butylene carbonate mixture yields a single homogeneous phase at room temperature. We have developed an alternative technique for homogeneous liquid-liquid solvent extraction by adding sufficient ethanol to the heterogeneous mixture of water and butylene carbonate solution of the extracting agent to yield a single homogeneous phase. The complex appears to form immediately, and ethanol can be evaporated which restores the two immiscible phase, i.e., an aqueous phase and a butylene carbonate phase containing the extracted complex. Fe(III) concentrations of both phases can be determined by atomic absorption. The effect of pH on the extraction of Fe(III)-TTA into butylene carbonate by this method compared with propylene carbonate is shown in Fig. 26. The result is that the extraction behavior is very similar to the extraction behavior of propylene carbonate. Thus, butylene carbonate is shown to be an appropriate solvent for homogeneous liquid-liquid solvent extraction by using the expedient of adding ethanol to achieve a single homogeneous phase.

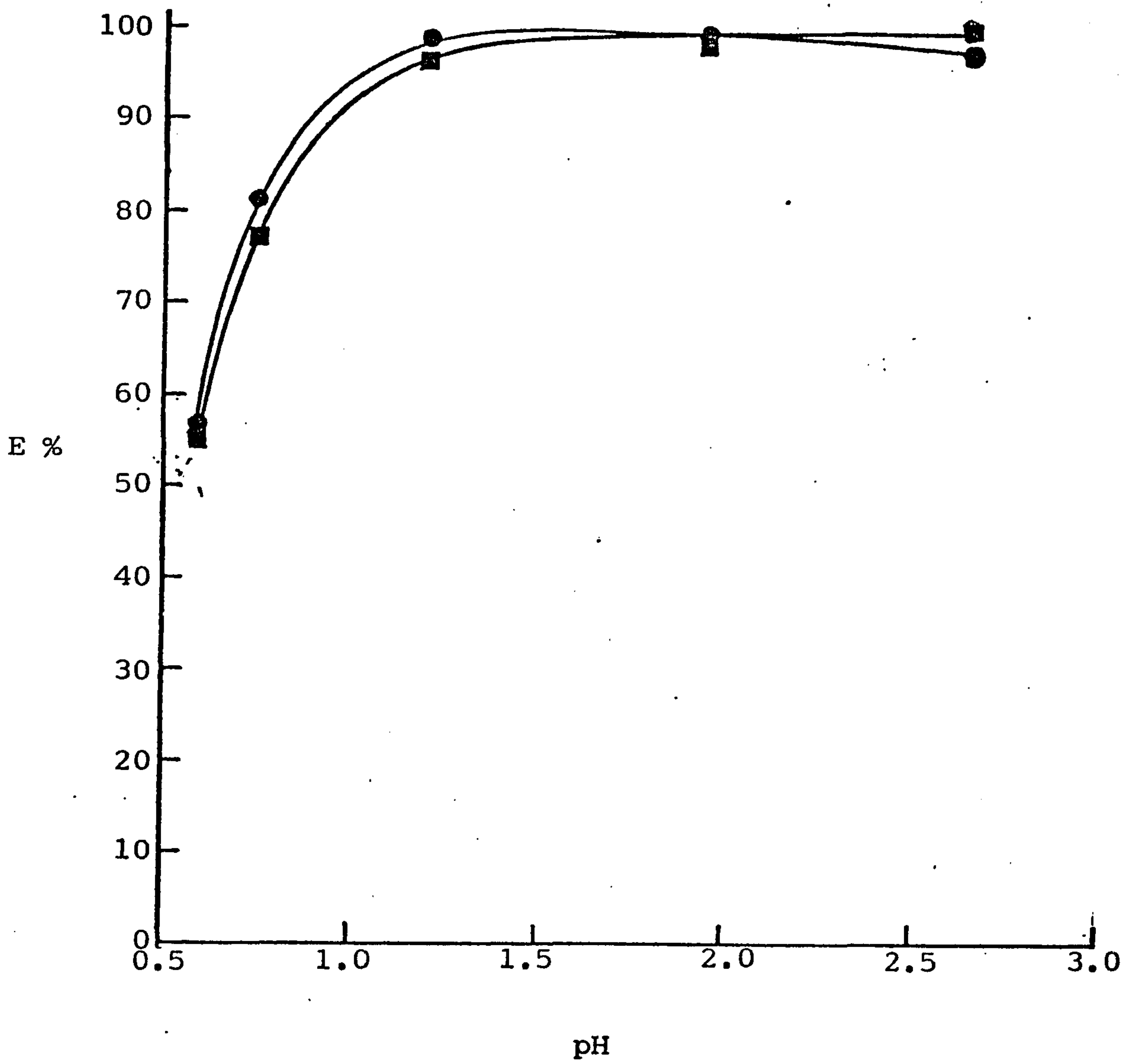
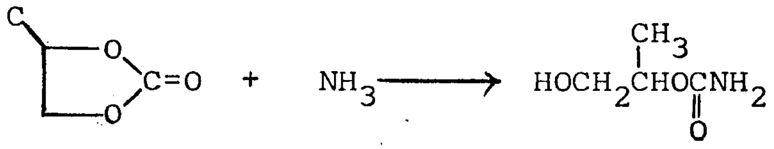


Fig. 26 Effect of aqueous pH on the extractability of Fe(III)-thenoyltrifluoroacetonate into propylene carbonate(■) and butylene carbonate(●), 80 °C, contact time=10 min.
[Fe(III)] = 3.6×10^{-3} M, [TTA] = 0.1 M

9. Solubility of Ammonia in Propylene Carbonate

Propylene carbonate has been shown[45] to react readily with anhydrous ammonia under pressure or in methanol solution at temperatures from 30 to 50 °C to form the carbamate as follows,



The possible application to nitrogen isotope enrichment encouraged a study of the solubility of ammonia in propylene carbonate by introducing anhydrous ammonia at pressures less than atmospheric and at room temperature. The study was performed in a vacuum system; the initial pressure was 0.45 atm and the final pressure was 0.31 atm and the volume of propylene carbonate was 20 ml. The IR, Raman, and NMR spectra are all very similar to the respective spectra for pure propylene carbonate, indicating that a 2.2 mole percent solution of ammonia in propylene carbonate was formed.

10. The Effect of Pressure on Water-Propylene Carbonate Mixtures

A suggestion was made that pressure may have the same effect on water-propylene carbonate mixtures that raising the temperature has, i.e., it may also bring about a single homogeneous phase. A stainless steel system containing a cell with a viewing port was designed and constructed which could accommodate pressures up to 20 atm. The junction of the two liquid phases could be viewed through the sight glasses and if a single homogeneous phase resulted from increased pressure this junction would disappear. Fig. 27 is a diagram of the apparatus.

Pressures up to 53 lbs per sq. in. could be obtained directly from the tank of nitrogen gas and up to this pressure no effect was observed. A higher pressure of 218 lbs per sq. in. was obtained by first freezing nitrogen gas into a reservoir (a copper coil), cooled to liquid nitrogen temperature, which is connected to the system. Certain anomalies were observed in the behavior of the two phases, but we did not observe a transition from two phases to a single homogeneous phase.

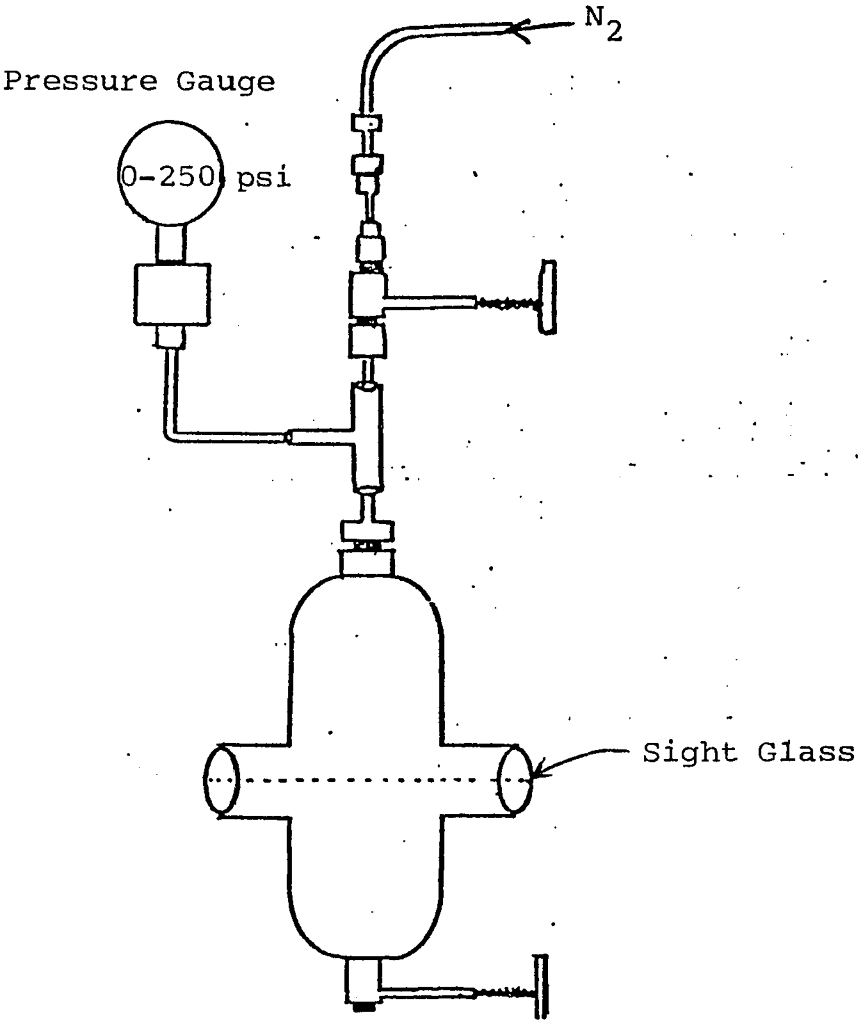


Fig. 27 Pressure apparatus

V. Conclusion

Homogeneous liquid-liquid extraction has been applied to the extraction of TTA complexes of many metal cations and a variety of chelate and ion association complexes of iron. The extraction rate was, in all cases, very rapid (less than 5 minutes) compared to the slow rate of conventional extraction methods.

The efficiency arises from both inherent characteristics of propylene carbonate, e.g., formation of a single homogeneous phase at temperatures above 71 ^{o}C, and in the case of TTA the higher percentage in the enolate form, and also from the fact that the extraction occurs at higher temperature with its concommitant more rapid mass transfer. The low vapor pressure of propylene carbonate makes it feasible to perform these extractions at high temperatures, and the formation of the single homogeneous phase eliminates the slow step in conventional chelate extractions. It is also noteworthy that in this uniform medium consisting of water and organic solvent, the activity of water is lowered, therefore the hydration sphere of the metal cation is affected (becoming smaller or broken) and the substitution reaction of the metal ion-aquocomplex with complexing agent is consequently expedited.

Phase diagrams were determined for the system water-propylene carbonate and also for the system water-ethanol-propylene carbonate which give the compositions of the respective phases as a function of temperature.

A convenient technique for atomic absorption analysis of the respective phases has been developed based on the fact that water-ethanol-propylene carbonate forms a single homogeneous phase at room temperature. This enables direct comparison of aqueous and organic phases with an aqueous standard that has been diluted with ethanol and propylene carbonate.

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