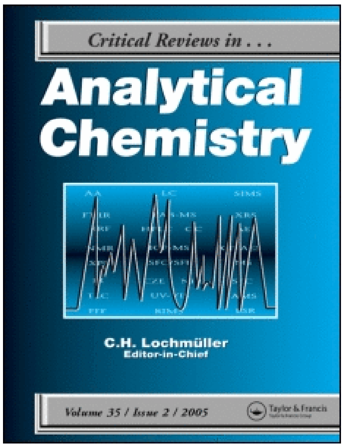

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# THE KINETICS OF METAL SOLVENT EXTRACTION

Authors: Pier Roberto Danesi
Renato Chiarizia
Physical Chemistry Laboratory
CNEN, CSN-Casaccia
Rome, Italy

Referee: Charles F. Coleman
Oak Ridge National Laboratory
Oak Ridge, Tennessee

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## FOREWORD

The solvent extraction of metals is a subject of wide technological, analytical, and fundamental interest which has been already systematized in a number of excellent textbooks. Nevertheless, none of the books or reviews dealing with the topic has until now covered the very important kinetic aspects in a sufficiently broad and general way. The reasons for this lack have been essentially the following

1. The relatively few works which had been performed on the kinetics of metal extraction
2. The interdisciplinary nature of the subject which deals with closely interwoven engineering and chemical concepts
3. The difficulty to find suitable homogenizing criteria for the existing data which range from engineering mass transfer studies to physico-chemical, reaction mechanisms-oriented, investigations.

It is the opinion of the authors that during the last few years the first reason has gradually ceased to exist, and consequently an attempt should be initiated to organize in a unique body the available data and relative interpretations, trying to overcome difficulties associated with the second and third reasons.

The following pages are the result of this attempt. The general criteria which have been followed to organize the matter obviously reflect the biases of the authors, who are inorganic chemists with a solution chemistry experience and background. Moreover, because of the difficulties mentioned in 2. and 3., probably not all the works pertaining to the subject have been reviewed. Sometimes it has also been necessary to make a selection, and, like all selections, the possibility exists that some representative contribution has not been properly quoted. Therefore, we apologize in advance for the omissions which have been inevitably made.

The Authors

# I. EXTRACTING REAGENTS

In the present review, dealing with the kinetics of solvent extraction of metal species, we will consider biphasic systems consisting of:

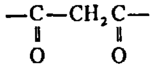
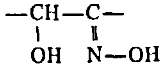
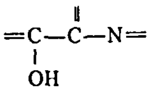
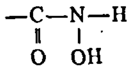
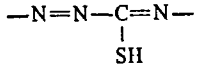
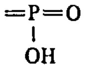
1. An aqueous electrolyte solution containing a metal cation which, according to the nature and composition of the electrolyte, can exist either as a free (hydrated) ion or as neutral, positively or negatively charged complex species
2. An organic phase which is a solution, in a water-immiscible organic diluent, of an organic molecule called extractant; only organic diluent not exhibiting appreciable extraction properties by themselves will be considered; the extractant will instead be a molecule capable of reacting with the aqueous metal species, transferring them into the organic phase; this reactivity is conferred to the extractant by the presence of a functional group which has binding properties with respect to the metal species; the only purpose of the diluent will then be that of dissolving the extractant and possibly to improve its physical properties

It is then clear from the above reported definitions that only organic phases which are binary systems (extractant + diluent) will be described. Therefore, solvent extraction systems implying the distribution of an aqueous electrolyte between water and pure organic solvents such as undiluted alcohols, ethers, ketones, esters, etc. will be not discussed.

The classification of extracting reagents (extractants) can be performed in quite a wide variety of ways considering both the extraction mechanism and the physico-chemical properties of the extractant. Consequently, various classifications have been proposed and they are described in very great detail in specialized textbooks dealing with the thermodynamics of solvent extraction.[1,2] Such classifications inevitably are arbitrary to a certain degree since they require a schematization of the extraction mechanism (solvation, chelation, ion-exchange, etc.) and of the properties of the extracting reagent (basic, acidic, ionic, inert, etc.). In fact, the macroscopic physico-chemical properties of extractants do vary continuously and often can be looked upon simultaneously from different points of view. Thus any newly chosen criterium of classification cannot be expected to further clarify the situation, even if the kinetic behavior, instead of the equilibrium properties, is considered. Therefore, in order not to add further confusion to the matter, we will adopt an already established classification scheme of the extractant reagents. This scheme is based on the property that the functional group has of releasing or accepting protons. According to this classification scheme, the extractant reagents will be divided into three classes: (A) — acidic extractants; (B) — basic extractants; and (C) — neutral extractants.

## A. Acidic Extractants

Acidic extractants are organic reagents characterized by the presence of a donor group having a dissociating proton such as, for example, the hydroxyl group $-OH$. The dissociation of this group forms a conjugate base by the release of a proton $H^+$ which can be replaced with a positively charged metal ion initially present in the aqueous phase. Of course a sufficient number of anionic species must combine with the metal cation to form uncharged species. In addition to the acidic group, acidic extractants may possess another donor group which does not contain a dissociating proton. These second types of donor groups can be, for example, $-C=O$, $-P=O$, etc. When the electron denating capacity of this group is sufficiently strong and its position in the reagent molecule is sterically favorable, a chelate compound can be formed with the metal cation. Acidic extractants which have been used to perform kinetics studies are the following,

| compound | functional group | chelating properties |
|---|---|---|
| β-diketones |  $-\underset{\underset{O}{\|}}{C}-CH_2\underset{\underset{O}{\|}}{C}-$ | strong |
| hydroxy-oximes |  $-\underset{\underset{OH}{\mid}}{CH}-\underset{\underset{N-OH}{\|}}{C}-$ | strong |
| 8-hydroxyquinolines<br>(oxines) |  $=\underset{\underset{OH}{\mid}}{C}-\overset{\|}{C}-N=$ | strong |
| hydroxamic acids |  $-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{\mid}}{N}-H$ | strong |
| thiocarbazones |  $-N=N-\underset{\underset{SH}{\mid}}{C}=N-$ | strong |
| alkyl-phosphoric acids |  $=\underset{\underset{OH}{\mid}}{P}=O$ | medium |
| sulfonic acids | $-SO_2-OH$ | none |

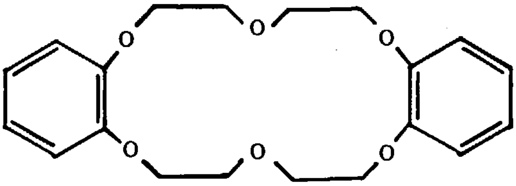
## B. Basic Extractants

Basic extractants are organic reagents which can easily form a salt when in contact with an aqueous acid solution. The only basic extractants which have been studied in some detail from the point of view of the kinetics of extraction are high molecular weight amines. Since the extraction of metals occurs with long-chain amines which have been previously converted into alkylammonium salts, the interactions between the extractable metals and the organic reagent are mainly electrostatic. This fact means that extraction can take place through the formation of an ion-pair and for this reason, these extractants have been also called "liquid anion exchangers". Similarly to anion exchange resins, metal ions can be extracted both as negatively charged complexes and neutral complexes. The neutral or negatively charged metal species are formed in the aqueous phase with water-soluble anions. Basic extractants, in the form of -onium salts, which have been used to perform kinetics studies, are of the following type,

| Name | Formula |
|---|---|
| tri-laurylammonium chloride | $(\text{lauryl})_3\text{NH Cl}$ |
| di-trimethylhexylammonium chloride | $(\text{trimethylhexyl})_2\text{NH}_2\text{ Cl}$ |

## C. Neutral Extractants

Neutral extractants are organic reagents that possess only donor groups that do not contain dissociating protons. Since no anionic or cationic groups are available in the reagent molecule, the metal species are extracted from the water phase as neutral complexes. The neutralizing ion is a water soluble negatively charged ligand. The extraction takes place by solvation in the organic phase of the neutral metal salt by means of the uncharged organic reagent. Water molecules coordinately bound to the cation can be substituted with the donor group of the extracting reagent. The extracted solvated metal species can then be regarded as a mixed complex since it is coordinated with two different types of ligands, i.e., a water-soluble anion and an organic-soluble electro-donating function. The donor group is usually an oxygen atom. Neutral extractants which have been used to perform kinetics studies are of the following types,

| | |
|---|---|
| tri-n-butylphosphate<br>(TBP) | $(\text{But—O})_3\text{—P=O}$ |
| tri-n-octylphosphine oxide<br>(TOPO) | $(\text{Octyl})_3\text{—P=O}$ |
| cyclic polyether<br>di-benzo-18-crown-6<br>(D B C) |  |

## II. GENERAL PRINCIPLES OF EXTRACTION KINETICS

The kinetics of solvent extraction of metal species from aqueous solutions, where they can exist either as simple hydrated cations or as complexed species, can be in the most general case a function of both the kinetics or the chemical reactions taking place in the system and the rates of diffusion (molecular and eddy) of the species present in the two phases. In fact, since the final products of the extraction processes are in a chemical state (or at least in a solvation state) different from that of the starting materials, it follows that rupture and formation of chemical bonds occurs during the extraction. As an example, we can consider the extraction of metal cations from an aqueous phase by chelating extractants. In the course of the extraction, water molecules have to be removed from the metal ion, and a new coordination compound, soluble in the organic phase, is formed with the chelating group. Moreover the extracting reagent or the extractant-metal complex can undergo aggregation-disaggregation processes.

It is obvious that all the reaction steps which characterize the overall reaction mechanism, either occurring in bulk phases (homogeneous reactions) or at the liquid-liquid interface (heterogeneous reactions), can in principle be slow enough to determine the rate of solvent extraction. In addition, since the chemical species are transferred from one phase to another, the transport of material from the bulk of the phases to and from the interface is another very important factor to be taken into consideration. This means that diffusion processes can be also rate determining. However, since in

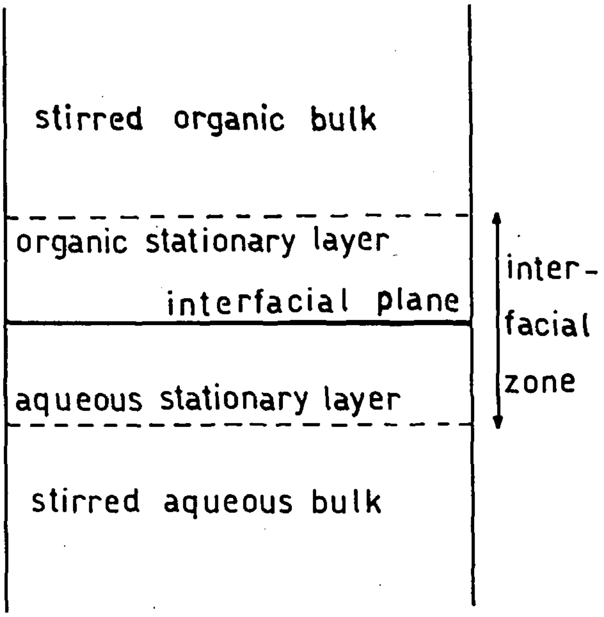


FIGURE 1. Schematic representation of the interfacial zone.

most of the extraction processes having some practical interest (either analytical or technological) the two phases are more or less efficiently agitated, the diffusion processes are generally limited to a zone located in the immediate proximity of the interface. It is therefore often assumed that the interface can be approximated by a three-dimensional zone where two stationary layers, one on the aqueous side and the other on the organic side, are in contact (see Figure 1).

The thickness of these two stationary layers, also called diffusion films, is of course a function of the hydrodynamic conditions occurring inside the apparatus where the extraction takes place. When the hydrodynamics is such that this thickness can be taken equal to zero, the diffusional contribution to the rate of extraction disappears.

The physico-chemical properties of this interfacial zone such as viscosity, dielectric constant, density, etc., can be rather different from those of the bulk phases and unfortunately are generally unknown. Nevertheless, some information on the interface can be obtained from interfacial viscosity, interfacial potential, and interfacial tension measurments. Interfacial tension studies are in this respect particularly important since they can provide useful information about the interfacial concentration of the extractant, namely the number of extractant molecules per unit interfacial area. In fact, it has to be pointed out that, as a general rule, extracting reagents are characterized by both a hydrophilic and hydrophobic nature.[3] The hydrophilic nature is due to the group which specifically interacts with the metal species while the hydrophobic part of the molecule assures enough solubility in the water-immiscible organic diluent. This means that the zone which the extracting reagents are going to prefer is generally the interface, where their free energy of solution is minimized. An adsorption equilibrium between the organic bulk and the interface, largely shifted in favor of the interface, can then easily promote the formation of an adsorption layer of extractant molecules at the interface.

As a consequence of their adsorption at the water-organic interface, extracting reagents often exhibit surface active properties. A result of this adsorption is that the interfacial concentration can be larger than that of the reagent in the organic bulk, and this fact can strongly favor the occurrence of interfacial reactions. When these are sufficiently slow, they show up as an interfacial resistance. We can then expect that the crossing of the interface by metal species will be largely affected by the specific nature of the interfacial zone, i.e., the physico-chemical properties of the diffusion films and the presence of an adsorbed layer of extractant molecules at the interface. However, if the chemical reactions which take place both in the bulk phases and at the interface are sufficiently fast, the extraction process is rate determined only by the diffusion processes occurring in the two diffusion films. In this case the system is said to be in a "diffusional regime", and the kinetics of solvent extraction can be treated in terms of diffusional theories. In this instance we are dealing with a "mass transfer with instantaneous chemical reaction", a topic which has been treated mainly in specialized engineering books, at least for the case of simple reaction mechanisms. On the other hand, when the diffusional processes can be considered practically instantaneous with respect to the chemical reactions, the extraction process is considered entirely chemically controlled and the system is said to be in a "kinetic regime".This situation can occur when either the thickness of the two diffusion films can be set equal to zero or when the diffusion coefficients of the transported species are very large. In this case, to entirely describe the system, information is needed about the rates at which the various chemical species react and the solvent extraction kinetics can be treated in terms of "chemical kinetics". This is the well-developed branch of physical chemistry dealing with the mechanism of chemical reactions and the rates at which they occur.

Unfortunately, as it will be reported in greater detail further on, in practical experimental work it is often difficult to draw a sharp line between these two limiting cases, i.e., pure diffusional regime and pure kinetic regime. In fact, although criteria that can be used to disinguish between kinetically controlled and diffusion-controlled processes have been reported,[4] they are not completely unambiguous when applied to experimental data. Moreover, a nonnegligible fraction of the literature work on solvent extraction kinetics seems to have been carried out in conditions where the presence of a mixed regime could not be completely excluded. In this case to fully describe the kinetics of extraction it is necessary to simultaneously solve the equations of diffusion and the equations of chemical kinetics.

A mixed regime can therefore be described as a case of mass transfer with slow chemical reactions where the rates of diffusion and of the chemical reactions can never be neglected with respect to each other. As will be described in the following sections, the unambiguous identification of an extraction rate regime (diffusional, kinetic, or mixed) introduces both experimental and theoretical difficulties. The former are mainly associated with the fact that a large set of different experimental information obtained in self-consistent conditions is needed. The latter are instead associated with the fact that, unless the introduction of simplifying assumptions is demonstrated as legitimate, the solution to differential equations having no analytical solutions and to which boundary conditions have to be determined by ad hoc experimental work is often required.

Finally it has to be mentioned that some confusion in obtaining a clear picture of solvent extraction kinetics has also occasionally been introduced by the personal biases due to the engineering or chemical backgrounds of the people who have performed the kinetics studies. Chemists have, in fact, generally shown a tendency towards explanations based only on kinetic regimes, looking for rate controlling steps as a function of the concentrations in order to identify a chemical extraction mechanism. Engineers, on the other hand, have generally shown a tendency towards explanations based only on diffusional regimes in terms of mass-transfer coefficients for a material flux driven by concentration gradients through resistances. Unfortunately, the kinetics of solvent extraction appear to be quite an interdisciplinary subject where a certain feeling about the influence that the hydrodynamics of the system has on the kinetics is strongly required even by the chemist whose only interest is to eliminate unwanted diffusional contributions in order to operate in a domain only chemically controlled.

## III. IDENTIFICATION OF THE EXTRACTION REGIME

The experimental identification of the regime that controls the extraction kinetics is, in general, a problem which cannot be solved by recurring to only one set of measurements. On the contrary, a definite clear-cut situation in some cases cannot be reached even when the rate of extraction is studied as a function of both hydrodynamic parameters and the concentration of chemical species involved in the extraction reaction. The reason for this difficulty lies in the fact that sometimes the rates may show the same dependence on hydrodynamic and concentration parameters even though the processes responsible for the rate of extraction are quite different, i.e., diffusion or chemical reaction. In this instance in order to formulate a correct hypothesis on the type of regime which controls the extraction kinetics, it is necessary to supplement the proper kinetics investigations with other information concerning the biphasic system. They may concern the interfacial tension, the solubility of the extractant in the aqueous phase, the composition of the species existing in the solutions, etc. It may therefore occur that only from the simultaneous convergence of many different experimental facts can a decision be made about the type of regime which controls the rate of an extraction process which is performed at given hydrodynamic conditions and chemical composition.

The most useful approach to identifying the extraction regime is the study of the extraction kinetics, using a constant interfacial area cell, i.e., an extraction apparatus which allows both a knowledge of the contact area between the two phases and at the same time a variance of the rate of stirring in a sufficiently broad range. These types of cells, also often called Lewis-type cells, from the name of the investigator who first made large use of them,[5,6,7] have been indeed employed by several authors in a number of different versions and will be described in the next section. When the initial rate of metal extraction, i.e., $V_o = -d\,C/dt$ at time approaching zero ($C$ = molar concentration of the extracted metal in the bulk aqueous phase), is measured in such cells as a function of the stirring speed of the aqueous phase, $n_w$, a plot of $V_o$ vs. $n_w$ is always characterized at the beginning by a straight-line behavior (the same situation of course holds when the initial rate of back extraction is plotted vs. $n_{org}$, i.e., stirring speed of the organic phase). The reason for this initial linear dependence has to be found in the fact that, even if a slow heterogeneous (interfacial) or homogeneous (aqueous bulk) chemical reaction occurs in the system, at low stirring rates the thickness of the stagnant interfacial films is always so large that the processes of diffusion, which precede the arrival of the metal species to the interface, are always the slowest ones. Since the relationship between the mass-transfer coefficients and the rate of stirring is linear, it follows that the relationship between $V_o$ and $n_w$ will also be linear. This linear dependence of the initial rate on the stirring speed in the case of transport- (diffusion) limited mass-transfer has been thoroughly demonstrated experimentally.[8-12] Therefore, a diffusion regime will always be characterized by a linear dependence of $V_o$ on $n_w$. A typical straight-line plot of $V_o$ vs. $n_w$ for the extraction of zinc by dithizone occurring in a diffusional regime is shown in Figure 2.

A further support to the fact that in the linear part of the $V_o$ vs. $n_w$ curve the rate of extraction is limited only by transport processes can be obtained by studying heat transfer in exactly the same hydrodynamic conditions, i.e., using the same apparatus and

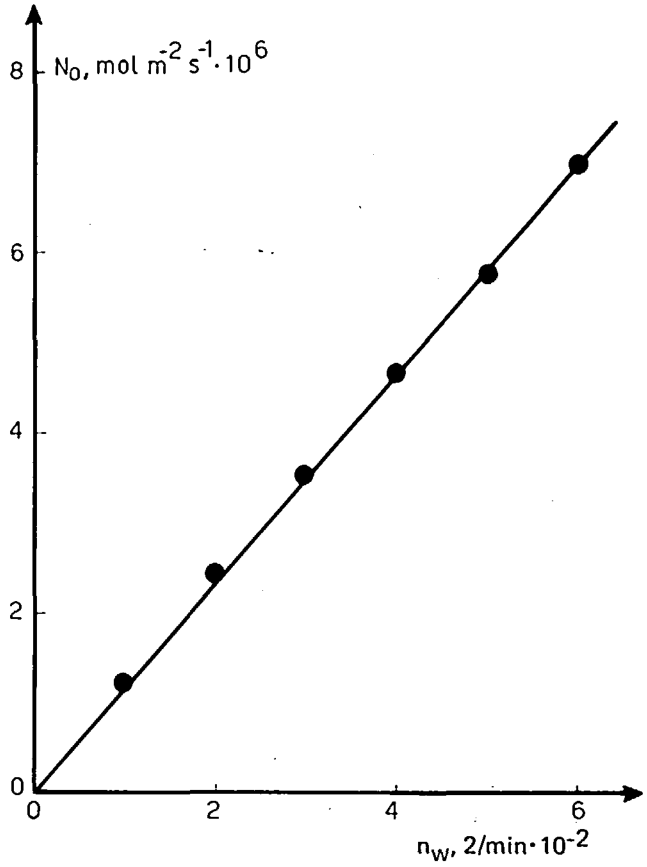


FIGURE 2. Influence of the stirring speed in the aqueous phase $n_w$ on the initial interfacial flux, $\vec{N}_0$, for the transfer of $Zn^{2+}$ from an aqueous phase into a dithizone solution in $CCl_4$. Results obtained with the constant interfacial area stirred cell of Figure 14. (From Nitsch, W. and Kruis, B., *J. Inorg. Nucl. Chem.*, 40, 857, 1978. With permission.)

the same fluids. Due to the strict analogies existing between the heat-transfer coefficient and the mass-transfer coefficient, when the rate of extraction is only controlled by diffusion, the same linear dependence of the heat-transfer coefficient (heat is transported through diffusion like processes) and the mass-transfer coefficient (proportional to $V_o$ when the concentration gradient is constant) on $n_w$ (or $n_{org}$) can be taken as a further demonstration that the extraction rate is only diffusion controlled.

However, the method of studying both the heat- and mass-transfer under the same conditions, (the principles of which can be found in References 4, 13, and 17), presents experimental difficulties and has been mainly used in engineering-oriented extraction kinetics studies.[14,15,16]

When a slow chemical reaction (heterogeneous or homogeneous) starts to become competitive with the diffusional processes in controlling the rate of extraction, the progressive increase of the stirring rate, which reduces the thickness of the stagnant films, will no longer cause proportional increases in $V_o$. In fact, as the diffusion processes become faster, the chemical reaction itself becomes rate determining up to a point where a further decrease of thickness of the stagnant films will have no influence at all on the overall velocity of the extraction process. For these conditions, $V_o$ will be

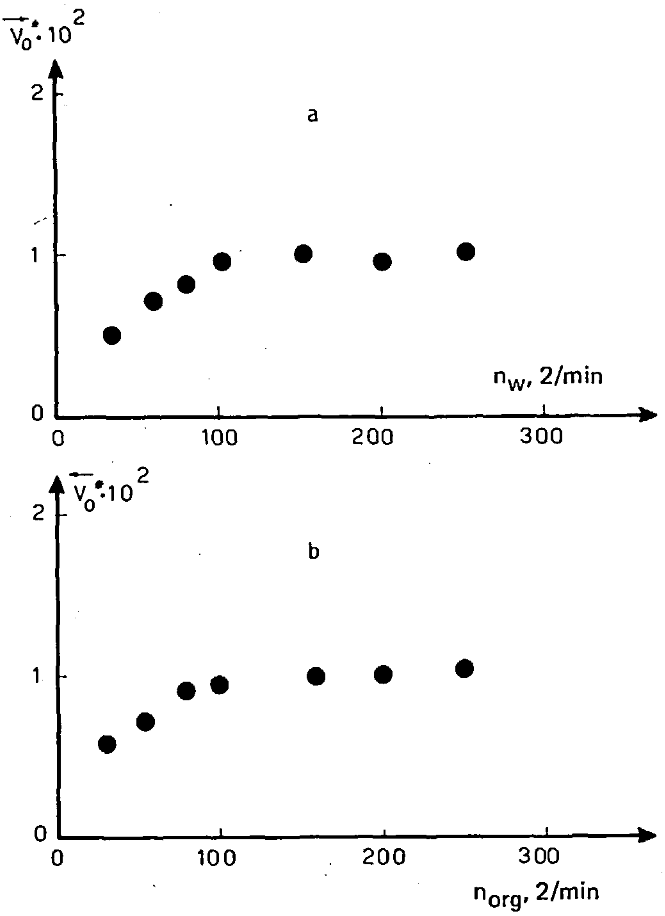


FIGURE 3. Influence of the stirring speed in the aqueous $n_w$ and organic $n_{org}$ phase on the initial forward $\vec{V}_0^*$ (a) and reverse $\overleftarrow{V}_0^*$ (b) normalized mass-transfer rates of iron(III) between aqueous HCl solutions and toluene solutions of trilaurylammonium chloride. Results obtained with the constant interfacial area stirred cell of Figure 17. (From Chiarizia, R. and Danesi, P. R., *J. Inorg. Nucl. Chem.*, 40, 1811, 1978. With permission.)

independent of the rate of stirring, and the plot of $V_o$ vs. $n_w$, after the previously described linear part, will show a plateau region. A typical experimental $V_o$ vs. $n_w$ plot, where a plateau is reached, is shown in Figure 3a. Figure 3b shows that the same situation occurs when the initial back-extraction rate is plotted against the organic stirring speed, $n_{org}$. In this specific case the plateau begins at approximately the same stirring speed of 100 r/min. This means that at this stirring value the diffusion processes in both the aqueous and the organic films have become so fast compared to the chemical reactions that they no longer influence the rate of extraction. Therefore, the presence of a plateau region in the $V_o$ vs. rate of stirring curves is an indication that in that zone the extraction rate is kinetically controlled.

Nevertheless, plateau regions can be also generated by other phenomena, and it is still possible that in spite of the experimentally determined independence of $V_o$ on the stirring speed, the rate of extraction is still diffusion controlled or, at least, not fully kinetically controlled. One example is when the biphasic system is characterized by very intensive interfacial instabilities of the Marangoni type. These instabilities produce a degree of local mixing, and hence transfer can occur also in total absence of bulk agitation. In this case, the curve $V_o$ vs. $n_w$ can be a flat valley extending from $n_w = 0$ to some moderate value of $n_w$ before a region of $V_o \propto n_w$ occurs. Another physical reason of independence of $V_o$ from the stirring speed can derive from the "slip effect",[17] i.e., from the fact that at high speeds the agitators can lose efficiency and the thickness of the stagnant diffusion films is unaffected by the increased rotation of the stirrers. A third reason is of chemical nature. This effect,[17] is caused by the presence of interfacial films formed by side-reaction products which are coordinatively unsaturated and then polymerize at the interface. These films, which present a high diffusional resistance, have been reported to exist when the extraction kinetics of heavy metals (Zr, Ti) by alkylphosphoric acids was studied.[18]

It is clear then that only when these plateau-simulating effects can be excluded, the plateau region can be reliably attributed to an extraction rate being controlled only by chemical reactions. A possible technique which allows the correct identification of the kinetic regime has been suggested by Russian workers.[16,18] The method, which has been defined as "the reference substance method", is based on the addition to the solution containing the species whose transfer rate is going to be investigated of another inert component whose rate of extraction is known to be controlled only by diffusion. As reference components organic molecules such as benzene, chloroform, and ethanol have been used. By following simultaneous transfer of the species of interest and of the reference component as a function of both the hydrodynamic conditions and the concentration of the extractable species, it is possible to distinguish between diffusional and kinetic regimes. Since the mass transfer rate can be generally described by the dimensionless Nusselt function,

$$Nu = \text{constant}\ R_e^{p} P_r^{q} \qquad (1)$$

(with Re = Reynolds number = $L^2 n/\nu$, Pr = Prandtl number of the limiting phase = $\nu$/thermal diffusivity, L = length (tip to tip) of stirrer blades, n = stirring speed, $\nu$ = kinematic viscosity, and p and q = coefficients of parametric sensitivity) with the following relationship existing between the mass-transfer coefficient $\beta$ and the stirring speed:

$$\log \beta = \text{constant} + p \log n, \qquad (2)$$

From the experimental dependence of $\beta$ on n, it is possible to evaluate p for the substance of interest ($p_s$) and for the reference component ($p_r$). In fact when the extraction regime is of kinetic type, it will be $p_s/p_r \simeq 0$ and when, on the other hand, it is of diffusional type, $p_s/p_r = 1$. An experimental plot of $p_s/p_r$ vs. the concentration of the extractable species will then allow distinguishing between the types of regimes. An exemplificative curve $p_s/p_r$ is shown in Figure 4, where the different regimes are indicated by Roman numbers.

The chemical reactions which control the rate of extraction in a kinetic regime can in turn occur either in the bulk phases or at the interface. The distinction between the two types of reactions can be performed by studying how the initial rate of extraction $V_o$ varies both with the interfacial area A and the volume of the phase from which the metal species is extracted. This volume is aqueous for water-to-organic extractions and organic for organic-to-water back extractions. If the slow chemical reactions occur in the bulk phases, the initial rate will be independent of both the volume and the interfacial area. In fact, the number of metal molecules which disappear per unit time will not be controlled by the interfacial area since the process associated with its crossing

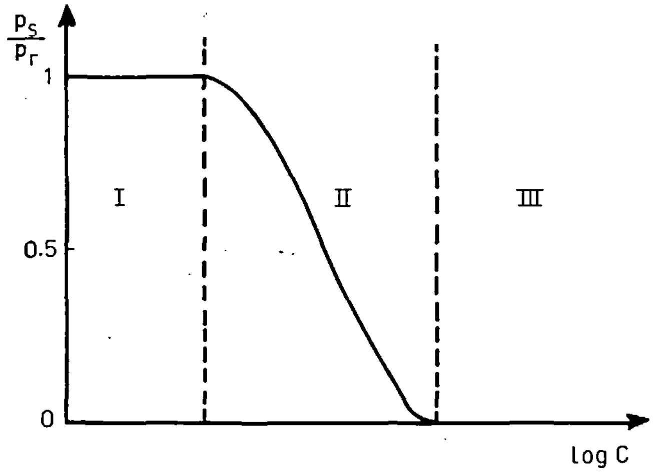


FIGURE 4. $P_s/P_r$ vs. log C (logarithm of the extractable species concentration) plot. $P_s$ and $P_r$ are defined in Section III: I = diffusional regime, II = mixed regime, III = kinetic regime.

is fast. Moreover, since the slow reaction is homogeneous, the rate will be independent of the volume of the phase where the reaction occurs. A reaction occurring at the interface will show instead a direct proportionality between the rate and the interfacial area. In fact, the overall decrease of concentration per unit time in the bulk phase $-dC/dt$ will be directly proportional to the number of molecules which cross the interfacial area per unit time. Similarly, $-dC/dt$ will be inversely proportional to the total volume of the bulk phase.

In studying the dependence of $V_o$ on the interfacial area and the volume of the phases, these two parameters are often considered together in the so-called specific interfacial area a defined as the ratio of the total interfacial area to the volume of the phase of interest. In this case, when the slow chemical reactions occur at the interface, a linear dependence between $V_o$ and a must follow. An exemplificative dependence of this type is shown in Figure 5. When this type of dependences is experimentally studied, much care has to be taken in keeping the hydrodynamic conditions as constant as possible. To keep constant the stirring speed of the agitators is not, in fact, sufficient to assure constant hydrodynamic conditions if the cell geometry and/or the volumes inside the cells are varied too much. This means that in practice both the volume and the interfacial area cannot vary over too wide of a range. When the experimental techniques which are used to study the extraction kinetics do not allow the determination of the contact area between the phases, as in the case of highly stirred tanks, mixer-settlers, or the AKUFVE apparatus[29] or do not permit variations of the hydrodynamic conditions, as in the case of the single drop method (these techniques will be discussed in detail in Section IV), it is extremely difficult to draw definite conclusions about both the type of extraction regime and the location of the reaction zone.

A further criterion which has been sometimes reported to enable distinguishing between a diffusion-controlled and a kinetic regime is the experimental determination of the activation energy of the extraction process. In fact if the rate is controlled by a chemical reaction, the activation energy is generally higher than that expected for a diffusion-controlled process. However, this criterion does not seem to be very meaningful since many chemical reactions occurring in solvent extraction processes exhibit activation energies of only a few kcal/mol, i.e., have the same order of magnitude as those of diffusion processes. This situation occurs, for instance, when metals are extracted in their hydrated form by a ion-pair-forming extractants. Moreover, since the

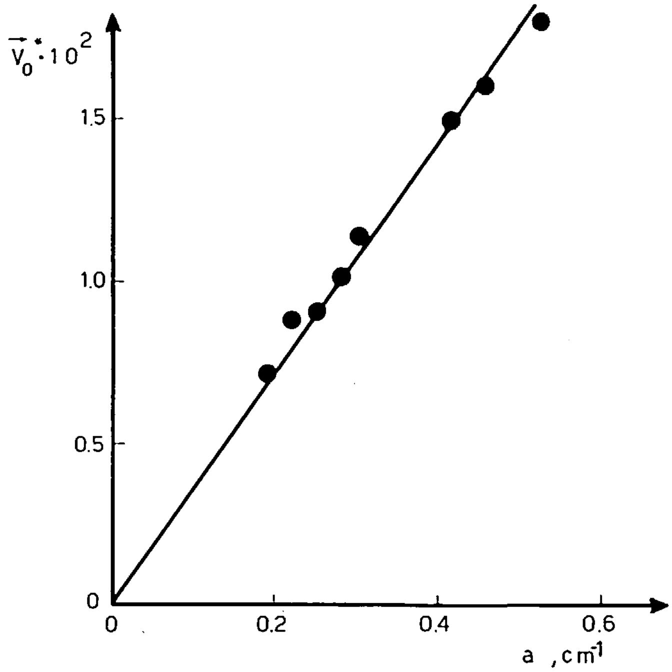


FIGURE 5. Influence of the specific interfacial area a on the normalized initial forward mass-transfer rate $\vec{V}_0^*$ of $Fe^{3+}$ from an aqueous HCl solution into a toluene solution of trilaurylammonum chloride. Results obtained with the constant interfacial area stirred cell of Figure 17. (From Chiarizia, R. and Danesi, P. R., *J. Inorg. Nucl. Chem.*,40, 1811, 1978. With permission.)

experimental activation energies are quite often obtained by studying the rate of extraction at different temperatures, the activation energies so determined are generally very uncertain due to the simultaneous temperature variation of both the chemical equilibriums and the diffusion rates. These uncertainties make very unrealistic the further possibility of distinguishing the different values of the activation energies between a chemical regime characterized by interfacial reactions and that characterized by bulk reactions.

This possibility, suggested in Reference 19, seems then of little practical application. Further support to the hypothesis that the reactions are taking place in the bulk or at the interface can be obtained by studying the mutual solubility of the reacting species, the interfacial tension of the biphasic system, and how these properties influence the rate of extraction. In fact, in order to have an extraction rate controlled by a chemical reaction occurring in the bulk phase, both reactants must exist in appreciable quantities in that phase. Since the low dielectric constant of most organic diluents does not allow the existence of ions in the organic phases, generally a slow homogeneous rate-controlling chemical reaction is associated with a partial solubility of the extracting reagent in in the aqueous phase. Consequently, the rate of extraction must show an increase when the water solubility of the organic reagent is increased. This increased solubility can be achieved either by reducing the length of the alkyl chains, which are often present in the organic reagent in order to improve its organic solubility, or by altering the composition of the aqueous phase. A change in the water solubility of the extractant can sometimes be obtained by varying the pH and/or the ionic strength of the aqueous phase. If, for example, the organic reagent is a weak acid, the dissociated form being partly soluble in water, an increase in pH must be reflected in an increased reaction rate any time that the acid anion is the kinetically important species. However, when evaluating these effects, great attention must be paid to also take into proper account the influence that the hydrogen ion concentration alone has on the extraction rate.

Interfacial tension studies are extremely useful to establish if an extracting reagent is capable of forming a high concentration region in the interfacial zone. A general review regarding the surface activity of solvent extraction reagents has been published by Cox and Flett.[3] As these authors have shown and we have already mentioned in Section II, it has to be expected that most solvent extraction reagents will exhibit interfacial activity at an oil-water interface. In fact, the simultaneous hydrophobic-hydrophilic nature of an extracting reagent, necessary to maintaining a high solubility in low dielectric constant diluents and a high complexing power with respect to inorganic metal species, has the resulting effect of maximizing the affinity of the reagent for the interfacial zone, where both the hydrophobic and the hydrophilic part of the molecule can minimize their free energy of solution. Consequently, most solvent extraction reagents are interfacially adsorbed and produce a lowering of the aqueous-organic diluent interfacial tension. The extent of this adsorption is a function of the nature of the hydrophilic groups of the extractant, its geometry, its bulk concentration, and the physico-chemical nature of the diluent dissolving it. Moreover, the interfacial concentration of the extractant can often largely exceed its bulk concentration and even moderately strong surfactants can form an interface saturated with extractant molecules when their bulk concentration is less than $10^{-3}M$. As a consequence, when the extracting reagent shows surface activity and low solubility in the aqueous phase, the interfacial zone is a region where a high probability exists that the reaction between the metal species and the extracting reagent can take place. This is the reason why a strong surface activity can lend support to extraction kinetic regimes explained in terms of heterogeneous (interfacial) chemical reactions.

When the reactions occur at the interface, it is very important, in order to derive the rate equations in terms of measurable quantities, i.e., bulk concentrations, to know how the extractant interfacial concentration depends on the chemical composition of the system. Interfacial concentrations can be in principle calculated from the Gibbs equation,

$$d\,\pi/d\ln C = n_i\,KT \qquad (3)$$

where $\pi$ is the interfacial pressure of the aqueous-organic system, C is the bulk organic concentration of the extracting reagent, and $n_i$ is the number of adsorbed molecules at the interface per unit area. By plotting $\pi$ vs. ln C, $n_i$ therefore can be evaluated from the slopes of the curves. However, some care has to be taken when evaluating interfacial concentrations from the slopes of the $\pi$ vs. ln C curves. In fact, Equation 3 is an ideal law, and some systems do not conform to this ideal behavior even when the solutions are diluted. The proportionality constant between $d\pi/d\ln C$ and $n_i$ is, in these cases, different from KT. Nevertheless, Equation 3 can still be used to derive information on the bulk organic concentration necessary to achieve an interface completely saturated with extractant molecules, i.e., a constant interfacial concentration.

According to Equation 3, the occurrence of a constant interfacial concentration is, in fact, indicated by a constant slope in a $\pi$ vs. ln C plot. Figures 6-12 show typical $\pi$ vs. ln C plots for some acidic, neutral, and basic extractants. It can be noticed that most extractants exhibit a constant interfacial concentration at bulk organic concentrations far below the practical concentrations which are generally used to perform extraction kinetics studies. This means that when developing a rate law derived from an

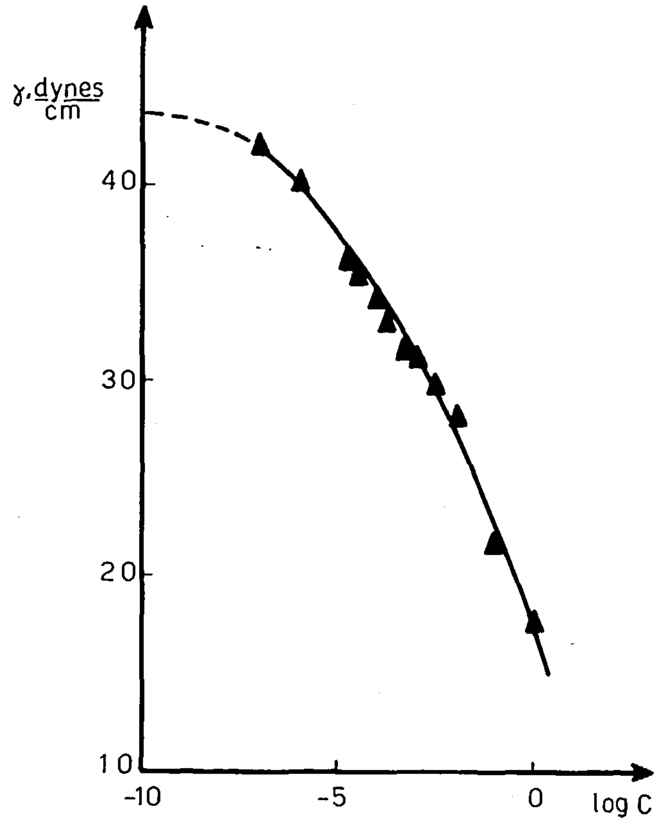


FIGURE 6. Interfacial tension γ vs. logarithm of bulk organic concentration of di (2-ethylhexyl) phosphoric acid, log C, in n-dodecane. Aqueous phase: $HNO_3$ 0.001 *M*. (From Vandegrift, G. F. and Horwitz, E. P., *J. Inorg. Nucl. Chem.*, 39, 1425, 977. With permission.)

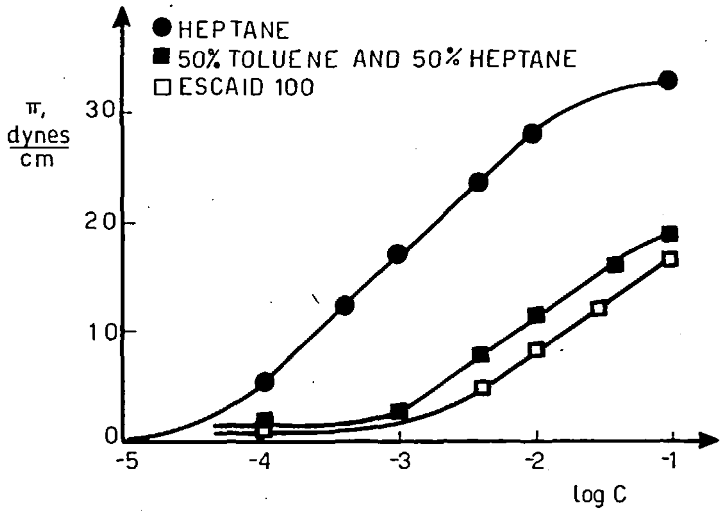


FIGURE 7. Interfacial pressure π vs. logarithm of bulk organic concentration of hydroxyoxime LIX 65 N, log C. ● heptane, ■ 50% toluene — 50% heptane, □ escaid 100. Aqueous phase: $Na_2SO_4$ 1*M*. (From Flett, D. S., *Acc. Chem. Res.*, 10, 99, 1977. With permission.)

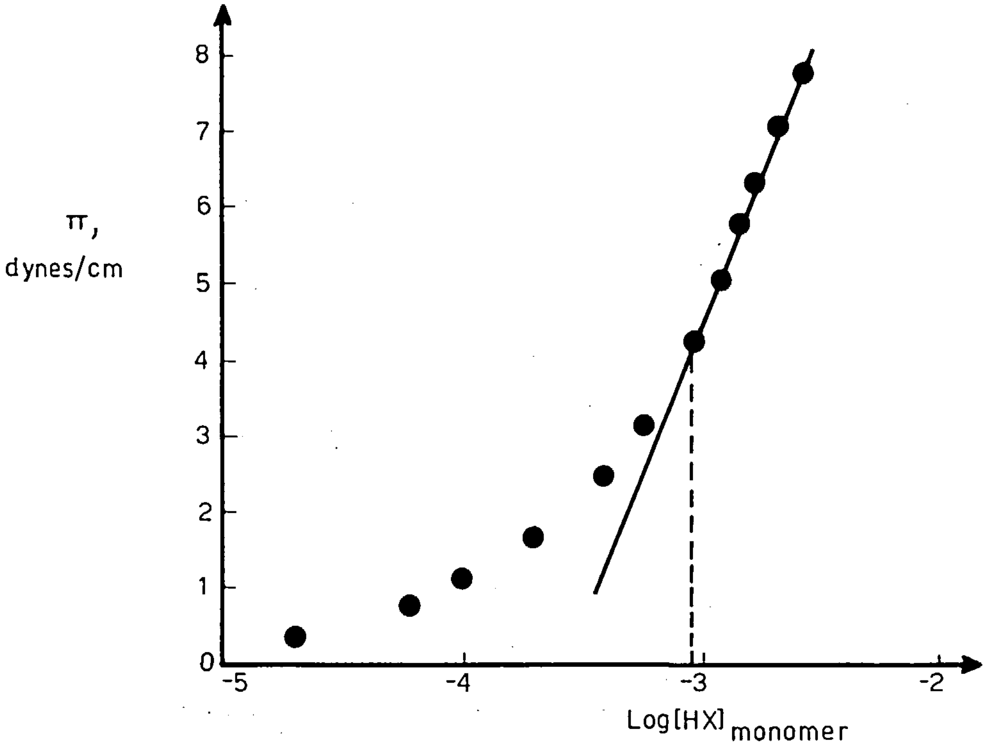


FIGURE 8. Interfacial pressure π vs. logarithm of bulk organic monomer concentration of tri-n-butylacetohydroxamic acid, log $HX_{monomer}$, in toluene. The occurrence of a straight line indicates interface saturation. Aqueous phase: $HNO_3$ 1*M*, LiNO3 1*M*. (From Chiarizia, R., Danesi, P. R., and Fornarini, S., *J. Inorg. Nucl. Chem.*, 41, 1465, 1979. With permission.)

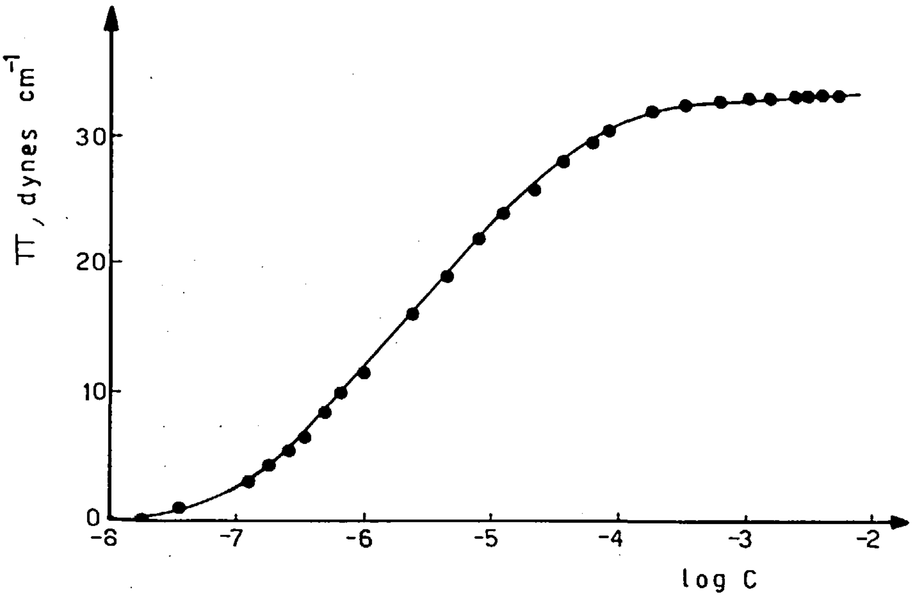


FIGURE 9. Interfacial pressure π vs. logarithm of bulk organic concentration of dinonylnaphthalene sulfonic acid, log C, in toluene. The occurrence of a straight line indicates interface saturation. Aqueous phase: $HClO_4$ 0.1*M*. (From Chiarizia, R., Danesi, P. R., D'Alessendro, G., and Scuppa. B., *J. Inorg. Nucl. Chem.*, 38, 1367, 1976. With permission.)

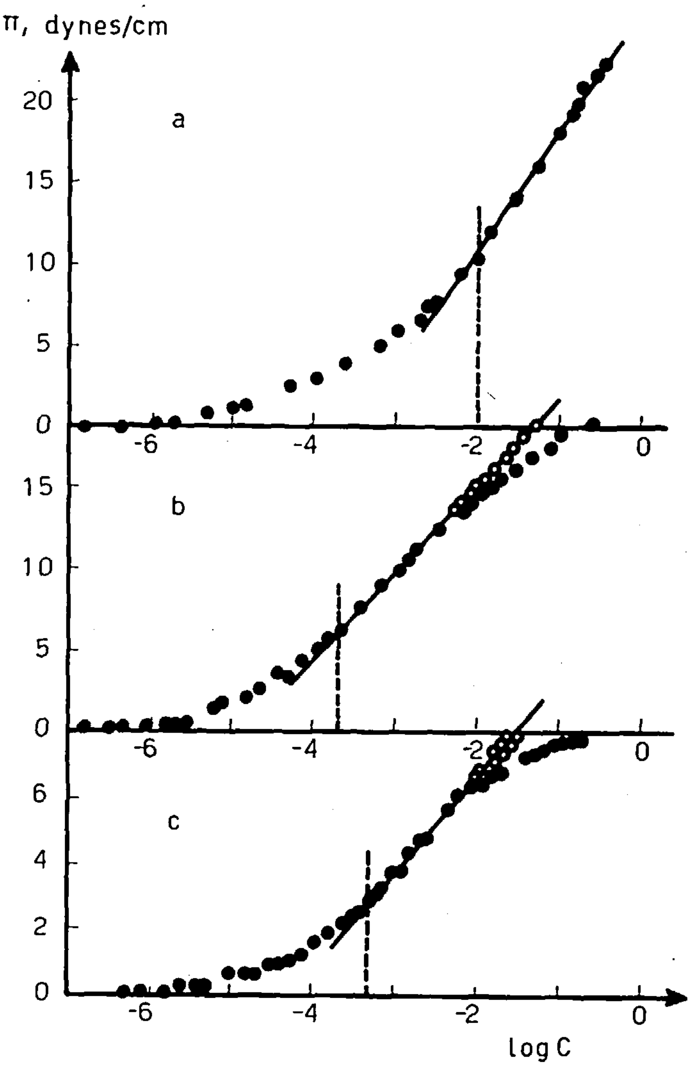


FIGURE 10. Interfacial pressure π vs. logarithm of bulk organic concentration log C for the following extracting agents: (1) trilaurylamine in toluene; aqueous phase: NaCl 1*M*, (2) trilaurylammonium chloride in toluene; aqueous phase: HCl 1*M*, and (3) trilaurylammonium nitrate in *o*-xylene; aqueous phase: $HNO_3$ 4*M*. The occurrence of a straight line indicates interface saturation. ● total concentration and O monomer concentration. (From Pizzichini, M., Chiarizia, R., and Danesi, P. R., *J. Inorg. Nucl. Chem.*, 40, 669, 1978. With permission.)

extraction mechanism based on interfacial chemical reactions, the interfacial concentrations can often be incorporated into the rate constants, and therefore they do not constitute a variable parameter of the rate law.

It is interesting to note that alkylammonium salts,[20] alkylarylsulfonic acids,[21] hydroxyoximes,[22] alkylphosphoric acids,[23] alkylhydroxamic acids,[24] as well as neutral extractants such as crown ethers[25] and tributylphosphate[3] all form a saturated water-organic interface when the organic bulk concentration is larger than $10^{-3}M$. As will be shown, the extraction rate with all these extractants, in suitable hydrodynamic conditions, has been explained in terms of interfacial chemical reactions.

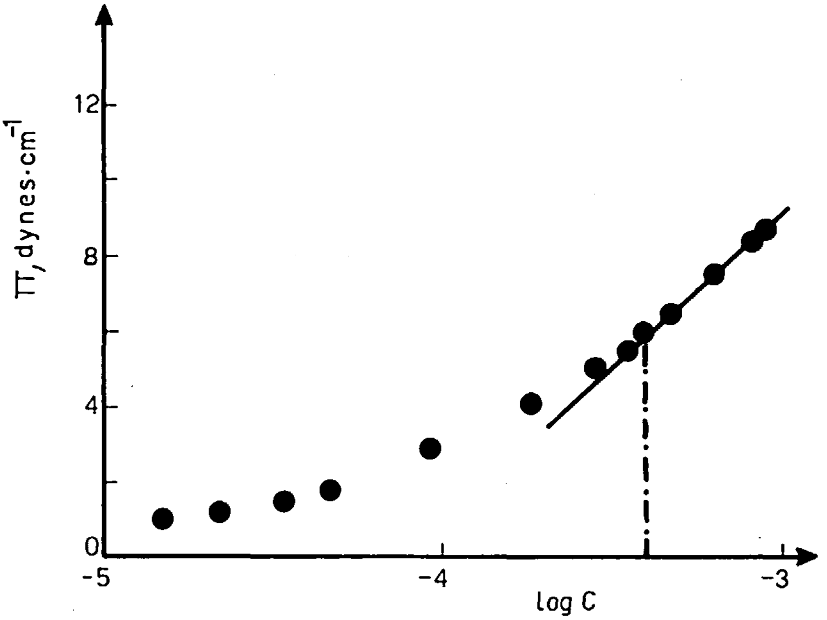


FIGURE 11. Interfacial pressure π vs. logarithm of bulk organic concentration of dibeno-18-crown 6 in benzene, log C. The occurrence of a straight line indicates interface saturation. Aqueous phase: KCl 0.017*M*. (From Danesi, P. R., Chiarizia, R., Pizzichini, M., and Saltelli, A., *J. Inorg. Nucl. Chem.*, 40, 1119, 1978. With permission.)

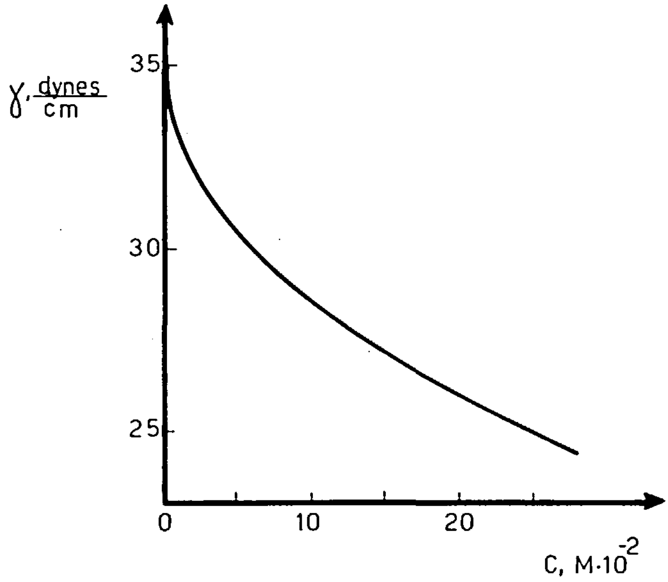


FIGURE 12. Interfacial tension γ vs. concentration of tributylphosphate in benzene, C. Aqueous phase: water. (From Cox, M. and Flett, D. S., paper 5A in Proc. Int. Solv. Extr. Conf., ISEC 77, Toronto, 1977. With permission.)

A further support to a kinetic regime controlled by heterogeneous chemical reactions can finally be found in studying the types of dependence that the initial rates show on the concentration of the extractants. In fact, as will be more quantitatively demonstrated in Section V, interfacial chemical reactions occurring at an interface saturated with extractant molecules are characterized by rate vs. extractant concentrations plots which reach a plateau region. This means that the apparent reaction order with respect to the extractant generally varies from an integer number to zero as long as the concentration of the extracting reagent is increased.

In conclusion, it appears then that by studying the influence that the stirring speed of the phases and the specific interfacial area have on the rate of extraction, it is possible to indicate the type of regime which controls the extraction kinetics as well as to find the location of the rate-determining chemical reactions. This indication must be supported, however, by other nonkinetic information such as the interfacial properties of the two-phase system and the water solubility of the extractant. Unfortunately, accurate measurements of the low water solubilities of the extractants are quite difficult to perform, and sometimes erroneously high values have been reported in the literature. This fact has been discussed in References 129 and 157. Further, it has to be strongly emphasized that both the hydrodynamics (stirring rate, geometry of extractor and stirrer, distance of the stirrer blades from the interface, etc.) and concentrations of the species involved in the extraction reaction simultaneously determine whether the extraction regime is of kinetic, diffusional, or diffusional-kinetic mixed type. This, of course, implies that when a practical solvent extraction process is carried out in given experimental conditions, and providing that the chemical reactions which occur are not too fast, these specific conditions determine the type of extraction regime together, of course, with the chemical nature of the system involved. As will be shown, the same metal-species-extracting reagent system in different hydrodynamic and concentration conditions can in fact be characterized by completely different extraction regimes. Furthermore, as will be shown in Section VII, the hydrodynamic and concentration parameters are not independent variables in determining the extraction regime. This interdependence introduces further difficulties when one tries to identify the regime from experimental data. In fact, the influence of the stirring speed on the extraction rate should be studied in a wide range of concentrations in order to determine the limits of existence of each regime.

In spite of all these difficulties, some general qualitative criteria which can be used to obtain a rough indication of the type of rate-determining process of the extraction kinetics can still be drawn. They are schematically reported in Table 1.

## IV. EXPERIMENTAL TECHNIQUES

Several experimental techniques to study the kinetics of metal extraction have been reported in the literature. Most of these techniques can be conveniently grouped into four categories,

1. Highly stirred tanks — this category groups all those techniques where the two phases are so highly agitated that droplets of one phase are dispersed in a continuum of the second phase (the dispersing phase).
2. Constant interfacial area stirred cells — this category groups those techniques where the two phases can be agitated to a varied extent while a known and constant interfacial area is kept throughout.
3. Moving drops — the technique is based on measuring the extraction which takes place during the time when a single droplet of one phase travels along a vertical tube filled with the second phase.
4. Short-time-phase-contacting method — in this technique the two phases are not agitated, and the contact time between them is very short.

Table 1
QUALITATIVE CRITERIA TO IDENTIFY THE PROBABLE PROCESSES WHICH CONTROL THE EXTRACTION KINETICS ON THE BASIS OF THE DEGREE OF MIXING, THE SURFACE ACTIVITY OF THE EXTRACTANT AND THE CONCENTRATION OF THE METAL TO BE EXTRACTED

| Extractant surface activity | Aqueous metal species concentration | Degree of mixing (Reynolds number) | Rate determining process |
|---|---|---|---|
| Strong | Low | High | Interfacial chemical reaction |
| Strong | High | High | Transport processes |
| Weak | Low | High | Interfacial or aqueous chemical reactions |
| Weak | High | High | Transport processes |
| Strong or weak | Low or high | Low | Transport processes |

### A. Highly Stirred Tanks

When the two phases are so highly agitated that one phase is dispersed into the other in the form of minute droplets, it is generally difficult to control the interfacial area through which the mass transfer takes place. Although the rate of extraction is in this case under experimental conditions rather similar to those which can be met in practical technological or analytical extractions, the difficulty to control the specific interfacial area may constitute a drawback to the use of this technique to derive unequivocal information on the extraction regime. In fact, although the drop diameter of the dispersed phase is generally a decreasing function of the stirring rate of the phases, to establish a quantitative correlation between the two is, in most cases, rather difficult. Moreover, when the stirring rate is increased beyond a critical value, which depends on the cell and stirrer geometry as well as on the physical properties of the two fluids, the proportionality existing between the drop diameter and the stirring speed often changes. Beyond this critical value, because of a slip effect, an increase in agitation gives progressively smaller increases in interfacial area. Another difficulty met while studying the extraction kinetics in highly stirred systems is due to the fact that the efficiency of the stirring inside the droplets of the dispersed phase can sometimes be quite reduced because of insufficient internal drop circulation. Consequently, in spite of the high agitation, the transport inside the droplets in the dispersed phase can be little influenced by the increased speed of stirring of the biphasic system. Further, even if the stirring speed is increased, the coalescence of the droplets can in some instances compensate for the decrease of the drop diameters. As a result, the area available for the mass transfer can become independent of the stirring speed. From all these facts, it appears then that when the rate of extraction is studied as a function of the increased stirring of the phases, a plateau in the curves describing the rate of extraction as a function of the stirring speed can be misleading since it can be originated by physical phenomena which have nothing to do with the occurrence of a kinetic regime.

To overcome these difficulties, some methods have been proposed which allow the evaluation of the interfacial area. These methods, which are mainly based on optical measurements, are, however, experimentally quite complicated and can be found in References 26, 27, and 28.

Another disadvantage which is met when this technique is used to study the extraction kinetics derives from the experimental difficulty of taking really significant samplings to measure how the concentrations vary with time. In fact, the extraction process can still proceed while the biphasic sample, taken at each time, is centrifuged and then mechanically separated, unless a phase-selective filter is used as reported in References 4 and 102. The use of techniques which allow a continuous monitoring of the concentration, such as conductometric measurements, is of limited applicability. Nevertheless, when all these drawbacks can be overcome, the technique can be very useful in studying very slow heterogeneous processes. In fact, the very high values of the interfacial area which the technique yields, makes possible the convenient study of very slow solvent extraction kinetics.

Highly stirred tanks have been used in kinetic studies in different versions. The differences mainly reflect the features of the various devices used to obtain equilibrium information on solvent extraction systems. The characteristic common to all versions is that samples are removed from the extraction apparatus at different times while the phases are stirred in order to reach thermodynamic equilibrium as rapidly as possible. Simple laboratory extraction procedures, such as shaken separatory funnels or test tubes and bottles stirred by suitable mechanical devices, or more sophisticated stirring equipment useful for chemical engineering solvent studies, such as mixed tanks, mixer-settlers, or the AKUFVE apparatus,[29] have been used. Since most of the authors who have used these techniques have claimed that a high turbulent regime was established in their experimental conditions, and consequently the hydrodynamic conditions were such to give prominence to kinetic regimes (at least at the highest stirring speeds), highly agitated extraction tanks have been mainly used to derive information on the reaction orders and in some cases also on the mechanisms of the chemical reactions which characterize the extraction of metal species by organic-extracting reagents.

### B. Constant Interfacial Area Stirred Cells

As we have already mentioned, the best possible way to establish the nature of an extraction regime lies in the determination of the initial rate of extraction as a function of the stirring speed of the phases at constant interfacial area. Further, to distinguish between a kinetic regime controlled by interfacial or by bulk chemical reactions, it is necessary to evaluate how the rate varies with the interfacial area while the hydrodynamic conditions are kept constant. These conditions can be most easily achieved in those extraction cells where the two phases are permanently separated by a constant interfacial contact area. The interfacial area, which coincides with the geometrical horizontal section of the cell where the contact between the two phases is established (if the curvature of the liquids at the cell walls can be neglected), is always kept constant when the degree of stirring of the two phases is varied over the widest possible range. Several different versions of extraction cells of this type have been reported in the literature, which also refers to them as Lewis cells. The main differences between the various cells lies in the presence or absence of internal baffles, which modify the internal forced convection, and in the shape and dimensions of the stirrers, which drive the forced convection. Some versions allow the changing of the revolution number of the stirrers in the two phases independently. In this way, the different influence of the density and viscosity of the two phases can be taken into account, and the liquids can be agitated at the same Reynolds numbers. Moreover a continuous monitoring of the concentrations as a function of time has often been used, mainly by radiometric, electrochemical, and optical techniques. In this way, besides the greater experimental convenience in obtaining concentration vs. time data, the difficulties associated with the volume variations caused by volume samplings are eliminated. These cells also can be hydrodynamically calibrated by studying the rate of distribution of an inert substance, having a known diffusivity, between the aqueous phase and the pure organic diluent (no extractant). In this way, it is possible to have information on the thickness of the stagnant interfacial films at the various stirring speeds. The specific interfacial area can also be varied by inserting inside the cells rings or baffles which reduce the contact area between the two phases. These devices must be, however, used rather carefully in order not to vary the hydrodynamic conditions too much. The specific interfacial area can also be varied by keeping the interfacial area constant and varying the bulk volumes.

The range of variation of the stirring speed of the phases can be made quite wide by inserting suitable grids around the stirrers which prevent the rippling of the interface. These grids limit the maximum size of the eddies and transform most of the translational kinetic energy of the liquids into turbulent energy. In some cases, the further introduction of metallic nets close to the interface allows operation at very high Reynolds numbers without disturbing the interfacial area. By using constant interfacial area cells, it is therefore possible to obtain rate vs. stirring speed curves at different chemical compositions which allow recognition when the rate of extraction is diffusionally or kinetically controlled. When a plateau which can be univocally attributed to a kinetic regime is obtained, the possibility also exists to identify the reaction mechanism by studying the dependence of the rate of extraction on the chemical composition.

The main inconvenience connected with the use of constant interfacial area cells is that they are not very suitable for studying very slow extraction processes since the area available for the extraction is always quite limited. Some examples of constant interfacial area cells are reported below to show the different technical solutions which have been proposed. Figure 13 shows a Lewis type cell which has been used in Reference 30 for studying the mass transfer in the systems water-ethylacetate and water-isobutanol. Such a cell could also be easily employed for studying the extraction kinetics of metal species. It is interesting to notice that the cell of Figure 13 is a modification of the classical Lewis cell since the stirrers are impellers with 45° inclined blades surrounded by two cylindrical grids. This modification has been introduced to improve the forced convection. Figures 14 a and b show another constant interfacial area cell which has been used[8,14] to study the extraction of zinc by dithizone in $CCl_4$ and $CHCl_3$. Figure 14 c shows the direction of the forced convection inside this cell. The main difference from the cell of Figure 13 is the presence of curved baffles placed in the anulus between a cylindrical insert and the cell wall and of interfacial nets. The baffles produce a lifting of the fluids and together with the interfacial nets help stabilize the interfacial surface. Moreover, the interfacial area is much larger here since no central interfacial baffle is present. A common drawback of both the cells of Figures 13 and 14 is that volume samples of the liquids had to be taken at various times and then analyzed to obtain concentration vs. time curves. A continuous monitoring of the concentrations has been realized in other investigations instead.

Figure 15 shows the constant interfacial area cell used[31] to study the extraction kinetics of Fe (III) by bis(2-ethyl-hexyl) phosphoric acid in n-octane. Here the continuous monitoring of the concentration was obtained through radioactivity and pH measurements. The radioactivity measurements have been carried out by a continuous flow sampling followed by automatic counting and printout at fixed-time intervals. Figures 16 and 17 show the constant interfacial area cells used in References 25 and 32. The concentration variations with time have been followed here by potentiometric[25] ($K^+$ glass electrode) and amperometric[32] (Platinum rotating electrode) methods. In the cells shown in Figures 15 and 17, the interfacial area was varied by introducing interfacial teflon rings of different diameters which reduced the contact area between the two phases. In the case of Reference 25, the interfacial area was varied by using different cells having the same volume but different interfacial area. Finally, Figure 18 shows the cell used in Reference 33 to study the extraction of uranium by TBP in n-dodecane.

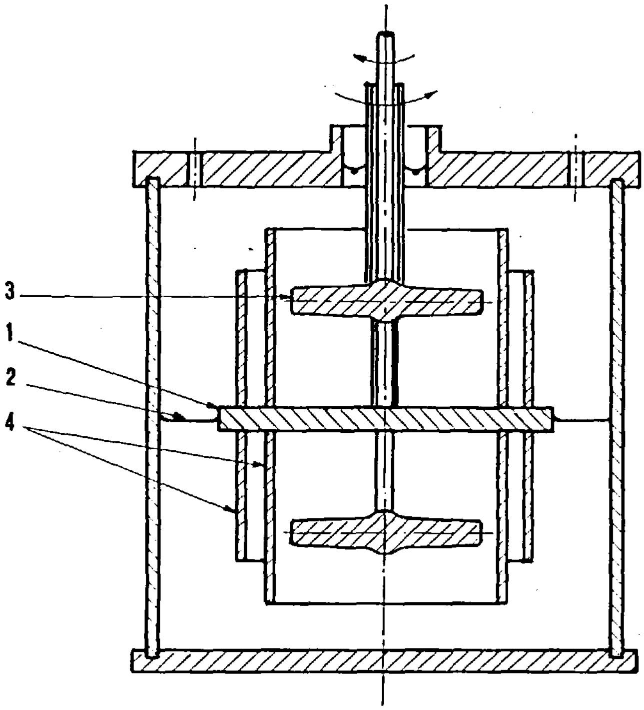


FIGURE 13. Constant interfacial area stirred cell used in Reference 30. (1) Horizontal baffle which limits the interfacial area, (2) Interface formed between the baffle and the cell wall, (3) Impellers having 45° inclined blades, (4) Cylindrical grids.

In this cell a very small interfacial contact area was obtained even though the stirring speed was as high as 3000 r/min. The uranium concentration was monitored by counting the alpha particles which penetrated the mylar window. It is obvious that such a miniaturized apparatus did not allow a variation of the interfacial area.

### C. Moving Drops

The principle of the moving drops technique consists in producing a drop of the organic or aqueous phase at the end of a vertical column which is filled with the other phase; the drop then travels along the tube and during the time of travelling metal extraction takes place across the drop surface. By measuring the time of travelling, the drop size, and analyzing a known volume of the collected drops, it is then possible to evaluate the rate of extraction and the interfacial flux. The technique can be applied both to drops which move upwards (rising drops) and downwards (falling drops), the choice depending on the higher or lower density of the unloaded drops with respect to the continuum liquid which fills the column. The interfacial area is generally calculated by assuming the drops are perfect spheres. A detailed description of the various apparatus which have been used can be found in References 34 through 39. Figure 19 shows the experimental apparatus of Reference 36 in the two different modifications for falling and rising drops. As in the case of Lewis cells, some modifications of this basic scheme have been proposed in the literature. They concern the substitution of the glass capillary where the drop is formed with a stainless steel jet,[38] the modification of the collection head with a tubing of constant diameter to maintain the level of the interface,[37] and in the elimination of the stagnant pool of the dispersed phase.[39] Although the technique allows the control of both the drop size and the interfacial area, there

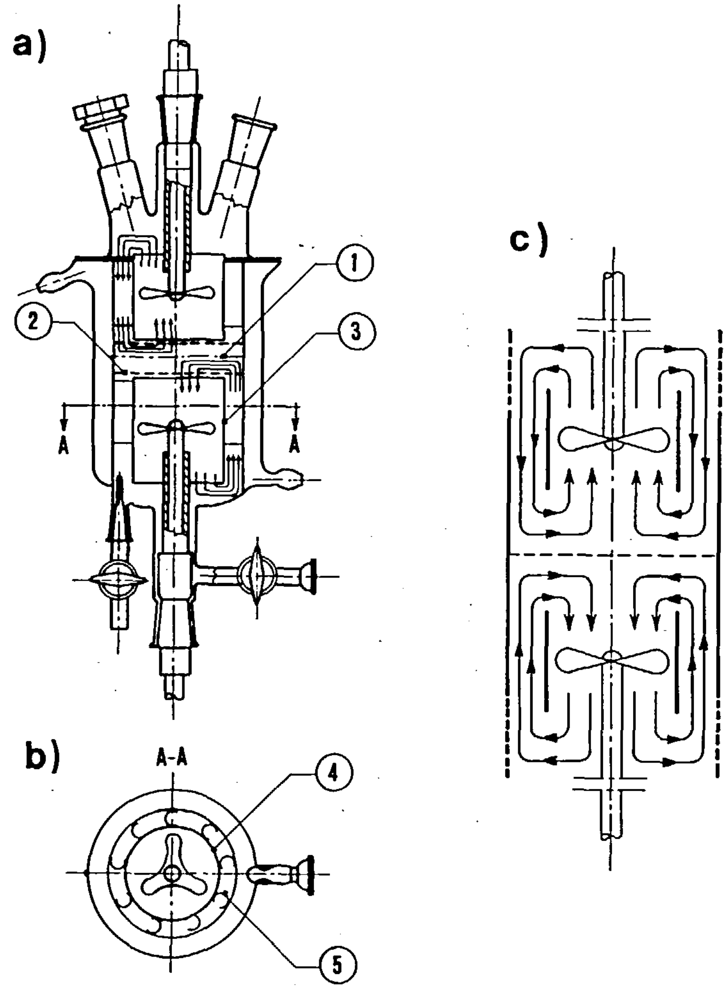


FIGURE 14. Constant interfacial area stirred cell used in References 8 and 14. (a) Vertical section: 1 Interface, 2 Interfacial net, 3 Cylindrical insert, (b) Horizontal section: 4 Cylindrical insert, 5 Curved baffles, (c) Schematic illustration of forced convection.

are some disadvantages which impose the use of great care both in the treatment of the experimental data and in the planning of the apparatus. When the extraction kinetics is very rapid, much of the extraction can take place during drop formation. Further extraction can also take place in the stagnant pool where the drops are collected. The data have to be properly corrected as described in References 8, 38, and 40. On the other hand, when the extraction kinetics is very slow, very long columns are required to assure long enough drop residence times. Finally, the hydrodynamic control of the single drops can be very difficult because of a lack of internal circulation and the presence of drop oscillations and wakes.[36]

Figure 20 shows a schematic representation of the flow regime for a falling drop. As described in References 39, and 41 through 43, the hydrodynamics of the drops can be rather complex and variable according to the experimental conditions which are used. In general, since the drops are not rigid, a transfer of momentum can take place through the interface, and an internal drop circulation should be promoted. However, when the drops are very small or the extractant is a surfactant which adsorbs

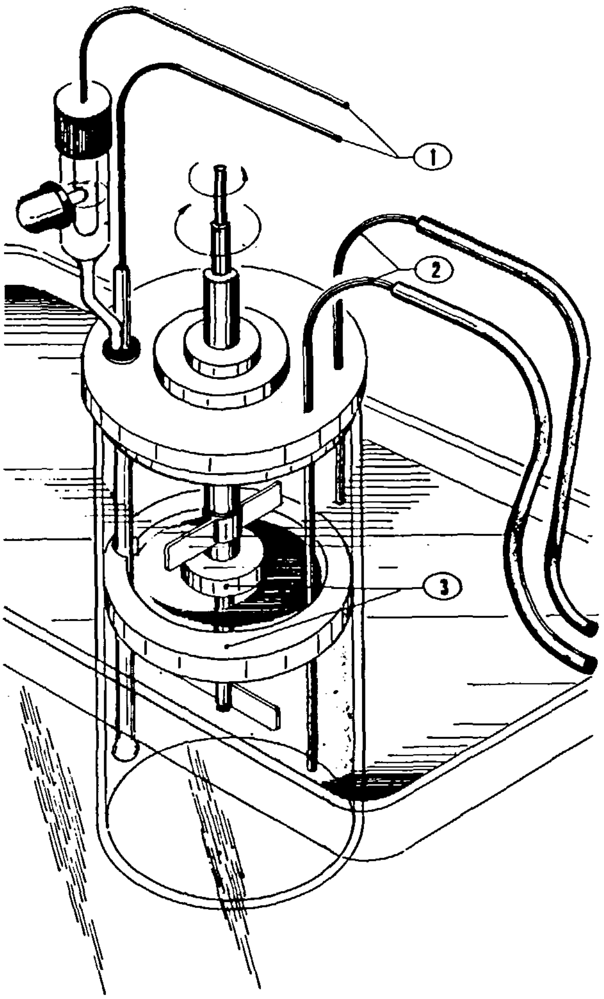


FIGURE 15. Constant interfacial area stirred cell used in Reference 31. 1 Glass electrode, 2 sampling probes for continuous withdrawing of small volumes of the phases which are automatically assayed by a scintillation spectrometer, 3 interface limiting rings.

on the drop surface, this internal circulation can be absent. As a consequence, the extraction kinetics can become extremely slow. It is then very difficult to establish whether the degree of turbulence of the two phases which is obtained with the moving drop method can ever be high enough to ensure the measurement of the transfer rate in a kinetic regime or, on the opposite side, is so low that the mass-transfer rate is always occurring in a diffusional regime (providing extremely slow chemical reactions do not take place). This uncertainty in establishing the type of extraction regime which occurs when the single moving drop method is used to study the extraction kinetics has often introduced difficulties in the interpretation of the data. As an example of this difficulty, it is worth quoting that, according to the opinion reported in Reference 44, the single drop technique provides the least turbulent conditions compared to those which can be achieved in an AKUFVE apparatus or in a Lewis cell. On the contrary, according to what was reported in Reference 14, the hydrodynamic conditions which occur in the falling drops produce an interfacial turbulence which is higher than that achieved in the constant interfacial area cell of Figure 14 when the stirring speed was 1000 r/min.

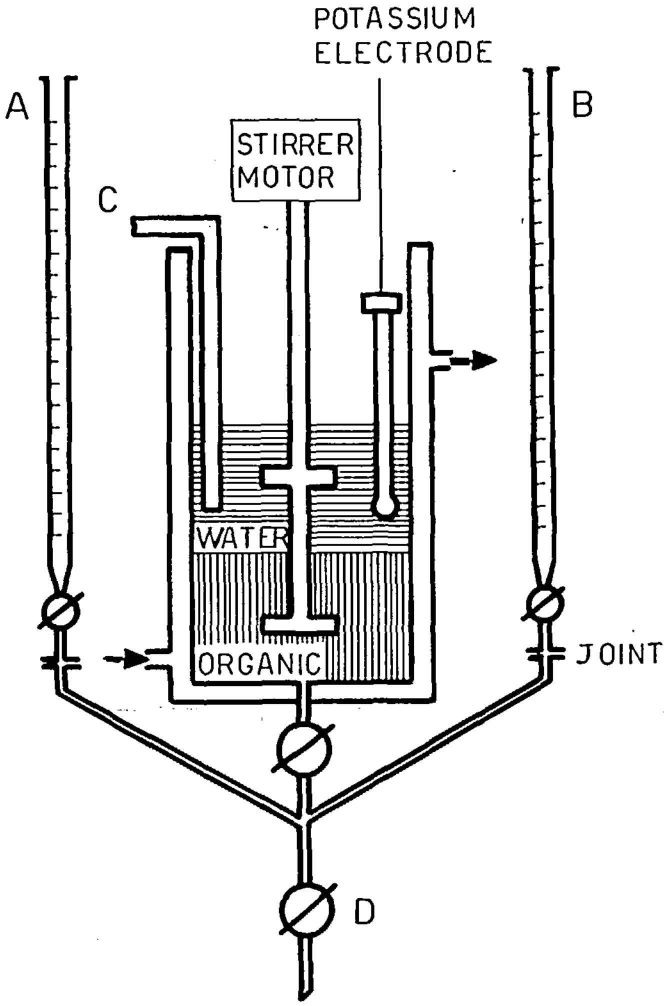


FIGURE 16. Constant interfacial area stirred cell used in Reference 25 to study the transfer rate of $K^+$ by continuous monitoring of the $K^+$ concentration in the aqueous phase through potentiometry by $K^+$ glass electrode. (A) Burette for adding aqueous phase, (B) burette for adding organic phase, (C) salt bridge to reference electrode, and (D) stopcock for emptying the cell.

### D. Short-Time-Phase-Contacting Method

The theoretical foundations of this method are reported in Section VII where the mixed diffusional-kinetic regime is described. The theory shows that for a nonsteady-state diffusion into a nonstirred system the mass transfer at contact times close to zero is limited only by chemical reactions. The primary aim of the technique therefore is to obtain concentration vs. time data concerning the first few seconds during which the extraction occurs. These data allow the obtaining of information on both the chemical reactions and the diffusional processes which control the rate of extraction. The experimental technique is made easier by the fact that it is not necessary to stir the system. In the experimental devices which have been used, the two phases are initially kept separate inside the thermostated extraction cell and then instantaneously contacted through a known contact area. At this moment, the concentration variation in one

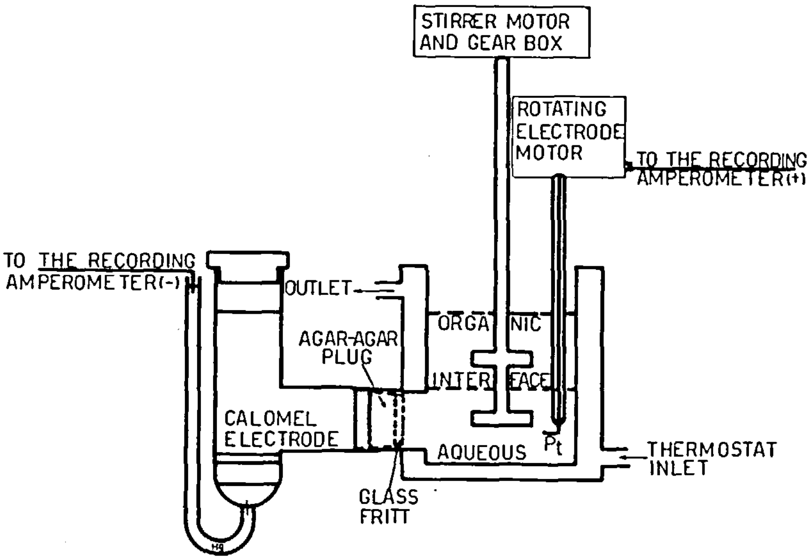


FIGURE 17. Constant interfacial area stirred cell used in Reference 32 to study the transfer rate of Fe(III) by continuous amperometric monitoring of the $Fe^{3+}$ aqueous concentration.

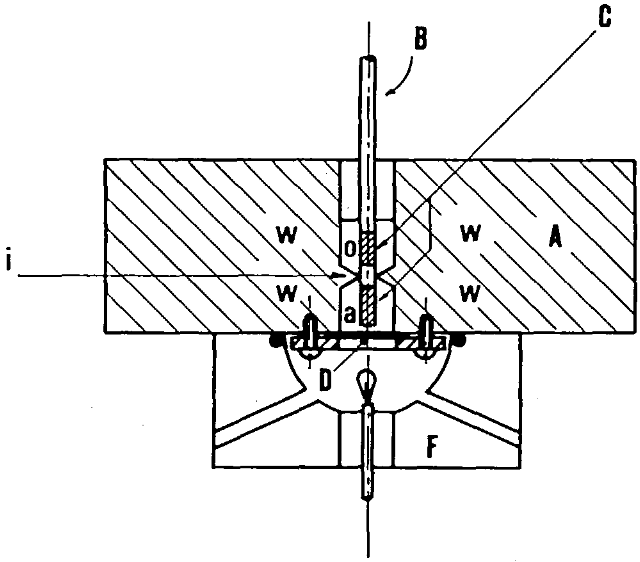


FIGURE 18. Constant interfacial area stirred cell used in Reference 33 to study the transfer rate of $UO_2(NO_3)_2$ by $\alpha$ paricle monitoring. (A) Teflon block, (B) Stirring rod, (C) Flats on stirring rod, (D) Aluminized mylar window, and (F) Counter chamber. a; aqueous phase (1.2 m*l*), o; organic phase (1.2 m*l*), i; anular interface (0.4 $cm^2$), and w; water circulating from thermostatic bath.

phase is recorded as a function of time, generally through conductometric measurements.

The technique was initially developed for studying the kinetics of mass transfer of mineral acids,[45,46] with separators originally made using strips of paper or porous discs

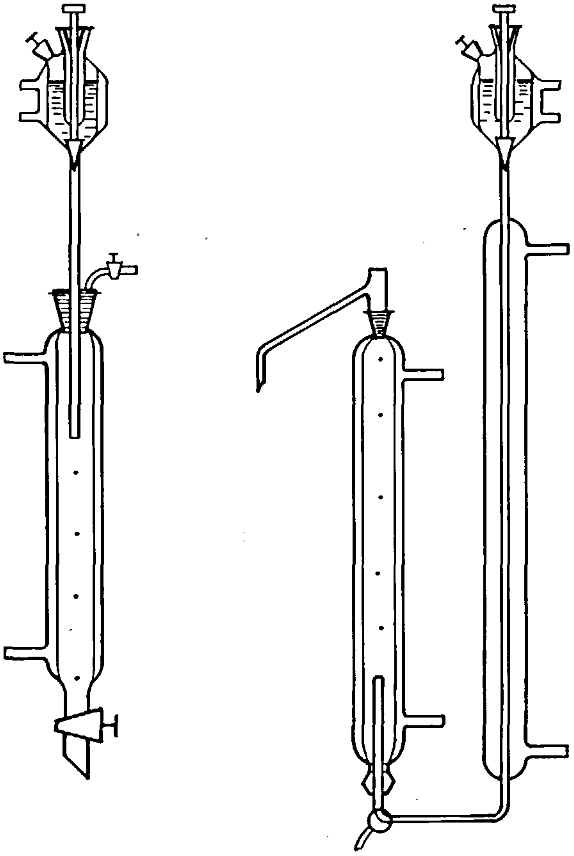


FIGURE 19. Experimental apparatus used in Reference 36 to study the extraction kinetics by the moving drop technique. Left side: falling drop. Right side: rising drop.

to support one of the phases. The use of these supports has introduced some difficulties due to uncertainties in knowing the contact area and the diffusion coefficients in the porous materials. To overcome these difficulties, a later version of the technique has been proposed[47] where the support has been abolished and one of the phases was contained in a very small metal capillary. The capillary, constructed of Au - Ni, has a depth equal to its diameter (1.5 to 2.8 mm) and is filled with about 10 $\mu\ell$ of aqueous phase. The capillary itself, together with an auxiliary wire, works as an electrode which can measure conductivity variations in the aqueous phase when it is pushed into the lower part of the cell which contains the organic phase. In this case, the contact area between the two phases is a flat, stable, and constant surface. A schematic representation of the apparatus is shown in Figure 21. This apparatus has been used in Reference 47 to study the extraction kinetics of $UO_2(NO_3)_2$ by toluene solutions of trioctylphosphine oxide (TOPO).

The advantages of this technique mainly consist in the possibility of getting information on the slow chemical reactions which can be rate limiting, even when the quantity of exchanged material is still very low since their influence shows up at very short times. Moreover, very small volumes of the reactants can be used.

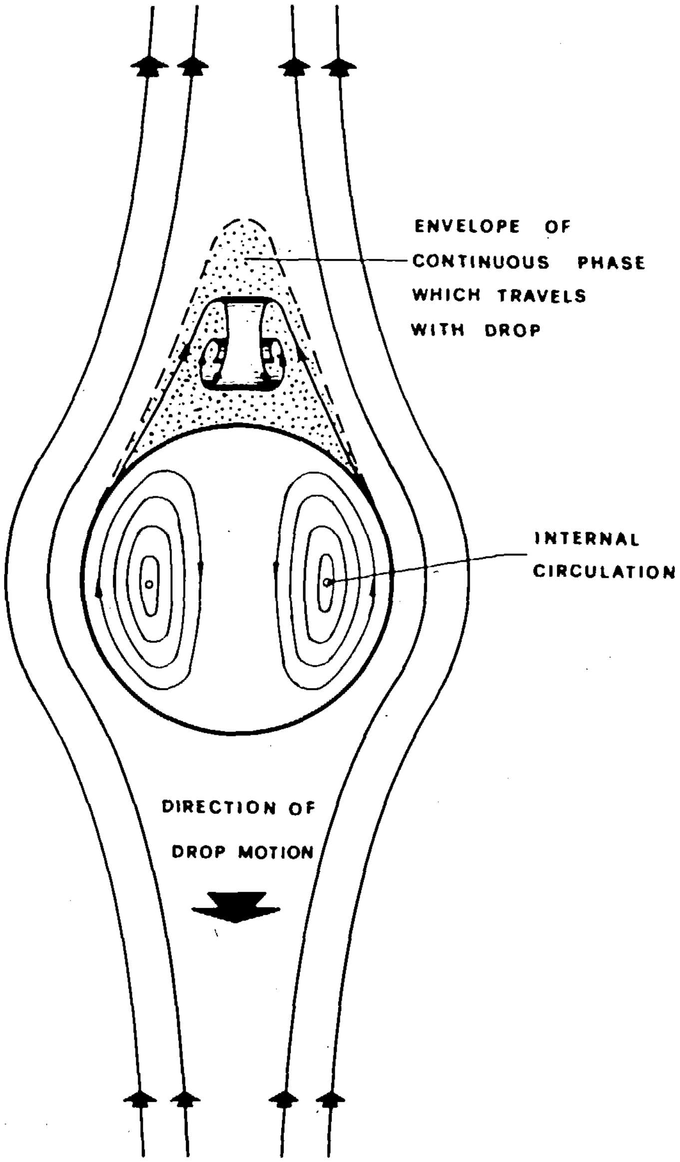


FIGURE 20. Flow regime for a falling drop. Copyright by American Society for Metals and the Metallurgical Society of AIME 1975. (From Atwood, R. L., Thatcher, D. N., and Miller, J. D., *Metall. Trans.*, 6B, 465, 1975. With permission.)

# V. KINETIC REGIME

As previously mentioned, an extraction of metal species is considered to proceed in a kinetic regime when the transport of material to or from the interface is very fast compared to the rate of the chemical reactions which take place in the system. This situation occurs when slow chemical reactions are present and, at the same time, the thickness of the two diffusion films adjacent to the interface is practically zero and/ or the diffusion of the reacting species through these films is a very fast process. These

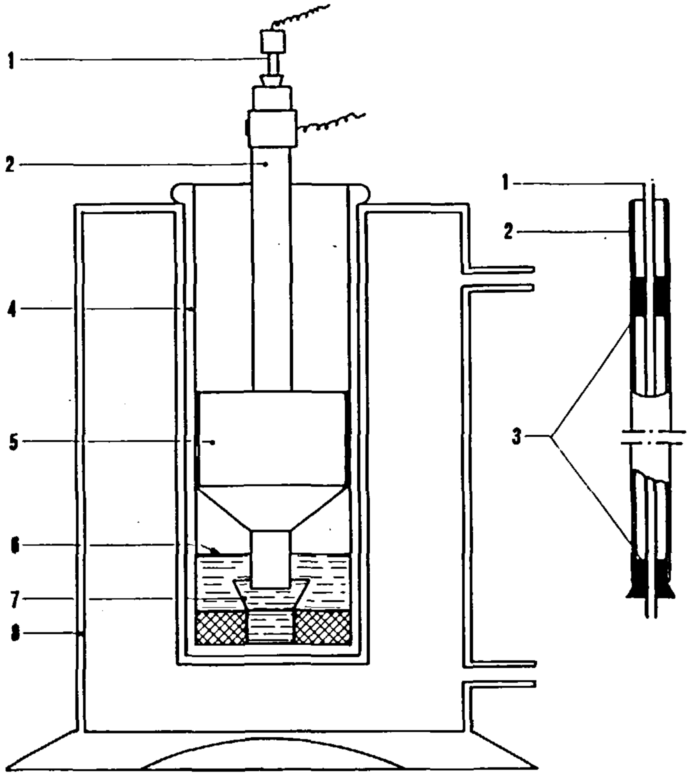


FIGURE 21. Short time phase contacting apparatus used to study extraction kinetics in Reference 47. (1) Central electrode, (2) wall electrode and capillary, (3) nonconducting plugs, (4) central vessel, (5) plastic positioner of the capillary, (6) organic phase, (7) polyethylene tube, and (8) thermostated jacket.

two latter conditions are associated with a very efficient degree of stirring of the two phases and with large values of the diffusion coefficients. In these circumstances, the laws and theories of chemical kinetics apply, and the reader has to refer to many specialized textbooks existing on the subject for a detailed and comprehensive treatment. References 48 through 51 are reported as examples.

Figures 22, 23, and 24 report in a schematic way the main equilibriums which are important from a thermodynamic point of view in the case of metal extraction by acidic, neutral, and basic extractants. The equilibriums shown in the figures, or their more refined formulation, are quite important to evaluate the free energy variations involved in the extraction and to forecast how the equilibriums are shifted when the concentrations of the various components present in the system are varied.

Obviously, the equilibriums reported in Figures 22, 23, and 24 do not provide information about the chemical steps which can be kinetically important and do not necessarily represent reaction mechanisms. In particular, these equilibriums do not emphasize a peculiarity of many solvent extraction systems, i.e., the presence of an interface where the extractant molecules can be preferentially adsorbed because of their simultaneous hydrophilic-hydrophobic character. This interfacial adsorption, causing a high interfacial concentration of the extractant, can, in fact, lead to kinetic regimes where the rate determining reactions occur at the interface. Moreover, it is worth noticing that since the equilibriums of Figures 22, 23, and 24 do not necessarily represent reac-

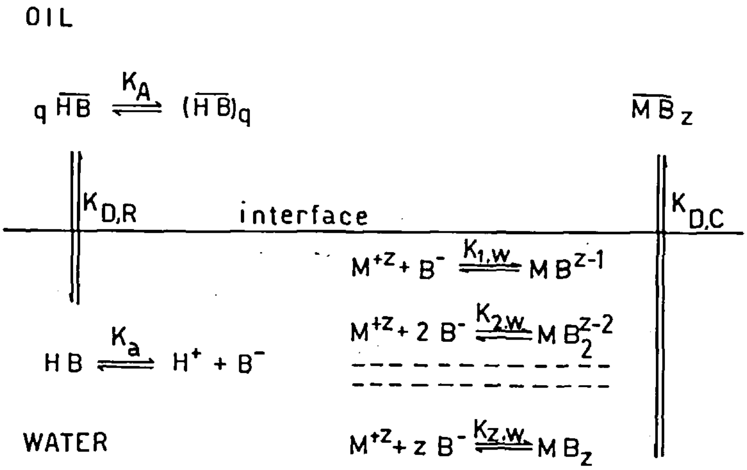


FIGURE 22. Schematic diagram of the main equilibriums for a weak acid chelating extractant with significant aqueous solubility, HB — organic diluent — metal cation, M⁺ᶻ — water, system.

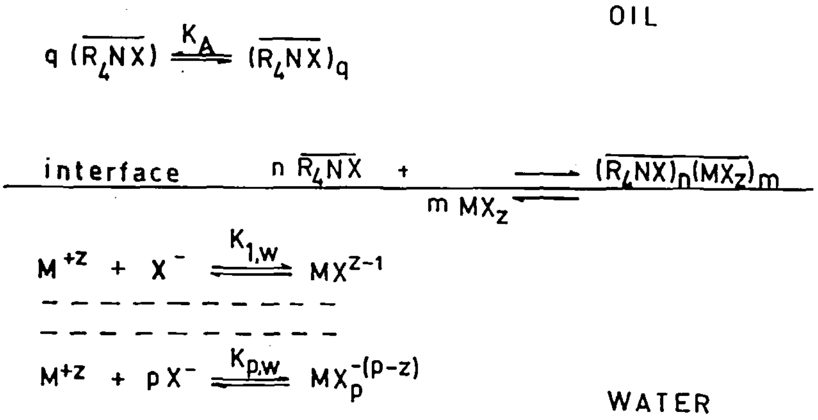


FIGURE 23. Schematic diagram of the main equilibriums for an alkylammonium salt basic extractant $R_4X$, — organic diluent — metal cation, $M^{+z}$, inorganic anion $X^-$, — water system.

tion mechanisms, as a rule integer values cannot be expected corresponding to the stoichiometric coefficients of any of the above-mentioned reactions when the orders of reaction are evaluated. In fact, as will be shown later, even very simple reaction mechanisms, implying a steady state interfacial reaction step, may lead to noninteger and variable reaction orders. Unfortunately this point has often been neglected in the literature, and sometimes no integer variable reaction orders have been attributed without any further evidence to a contribution of mass transfer to the rate of extraction. To this purpose, it is worth recalling that unlike the molecularity of a reaction, which represents the number of molecules involved in a simple collisional process, the order of reaction is an empirical quantity which can be occasionally fractional as well as negative, depending on the complexity of the reaction mechanism. Moreover, the order-of-reaction concept can be strictly applied only to those rate expressions which, in a full range of experimental conditions, can be formulated in the form of a product of powers of concentrations, i.e.,

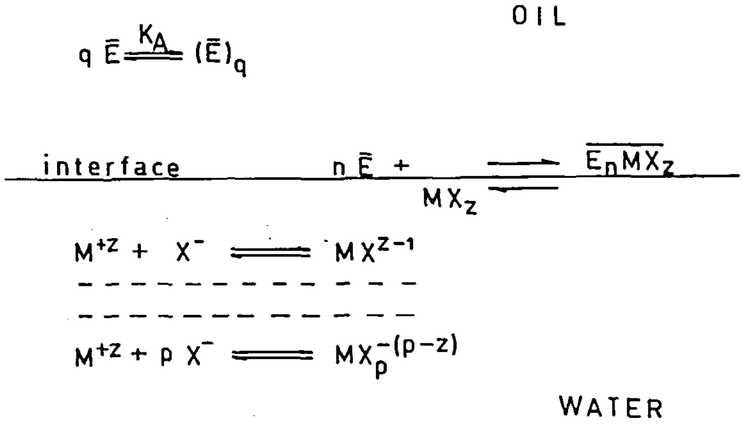


FIGURE 24. Schematic diagram of the main equilibria for a neutral metal extractant E, — organic diluent — metal cation, $M^{+z}$, inorganic anion, $X^-$, — water, system.

$$-d[A]/dt = K[A]^a [B]^b [C]^c$$

with n = a + b + c = total order of reaction and a, b, c, = orders with respect to components A, B, C.

Before describing in detail some reaction mechanisms which can be met in metal solvent extraction, it is worth mentioning also that, in kinetic studies concerning solvent extraction, the risk always exists that more than one reaction mechanism can lead to the same rate law. This risk is particularly present when only the concentrations of the reactants or their products are measured as functions of time. Concerning the best methods which can be followed to arrive at a reaction mechanism from kinetic data, those reported in Reference 52 can be quoted,

1. The fundamental-intuitive method which works best for simple systems, consists in developing a path from the reactants to the products by selecting reaction paths which are likely to be important.
2. The experimental method whereby mechanisms that have been proved successful in the past are used unchanged or extended to include new reaction paths.
3. The extensive method whereby all the reactions which can be found in the literature as plausible are put into the mechanism and a computer program is used to calculate the most probable reaction route.

## A. Extraction Mechanism and Rate Laws

Although the extraction mechanisms and the corresponding rate laws are characteristic of each system and have to be determined by specific experiments, the experience accumulated until now has indicated that when the extraction of metal species takes place in a kinetic regime, the kinetic data give rise to rate laws that can be generally explained in terms of simple and recurring reaction mechanisms. The slow steps of these reaction mechanisms are generally the following,

1. Chelation and water substitution reactions occurring in the aqueous phase
2. Complexation reactions occurring at the interface
3. Adsorption-desorption processes as the interface

These slow steps can be present either separately or in various combinations, according to the properties of both the aqueous phase containing the extractable metal and the organic phase containing the extracting reagent. In particular, Step 1. is often characteristic of metal extractions carried out from weakly complexing aqueous phases by acidic extractants having chelating properties and exhibiting some solubility in the aqueous phase. Steps 2. and 3. are met instead when the extracting reagent is a strong surfactant and are very dependent on the interfacial concentrations.

Following are a few examples of reaction mechanisms which can be generated by various combinations of the three above-mentioned slow steps. The corresponding rate laws will be also derived. These mechanisms and their rate laws have been occasionally presented as plausible explanations in the literature on solvent extraction kinetics, and it can be expected that, as long as many other systems will be studied in detail in kinetic regimes, they will find an increasing extension of applicability.

Some general criteria which can be followed to identify the locale (homogeneous phase or interface) of the reaction have been already given. As we have already seen, they are based on the determination of the dependence that the rate of extraction has on the interfacial area and the volume of the phases, on the surface activity of the extracting reagent, and on its solubility in the aqueous phase. However, it has to be recalled that no unique criterion exists which can be used to draw unambiguous conclusions.

For the sake of simplicity the treatment will be limited only to the case of metal ions with oxidation states of +3 ($M^{3+}$) and with coordination number 6. The extension of these exemplificative cases to metal cations having different oxidation states is indeed rather straightforward.

### *1. Acidic Extractants*

The nature of the acidic extractant will be assumed to be rather simple. We will in fact limit our treatment to a general monoprotic extractant HB which may also possess the properties of a bidentate ligand. Although the acidic extractants are generally rather weak acids, no special restriction will be imposed on the value of the acid dissociation constant. The exemplifying cases which will be described in some detail below will be mainly concerned with acidic extractants which react with the metal cation in their undissociated form, HB. This formulation finds its validity when the extractions are performed in quite acidic media, where the acidic extractants are practically undissociated. Furthermore, this condition is particularly verified when the extractant reacts at the interface since the lower dielectric constant existing at the interface, as compared to the bulk aqueous phase, reduces the extent of dissociation of the weak acid. However, if the reaction steps occur in aqueous solutions having such a pH to allow for the presence of nonnegligible amounts of the dissociated reagent $B^-$, the rate laws which will follow can be easily modified by taking into account either the reduced concentration of HB or the fact that $B^-$ instead of HB is reacting with the metal cation. The bar over the symbols will represent species existing in the organic phase, the subscript "ad" will indicate interfacially adsorbed species, while aqueous species will be only indicated by their symbols. Both equilibrium and rate constants will be represented with K, and a subscript, "e" (or "eq") will differentiate, only when necessary, equilibrium from kinetic parameters. The rates at time zero will be indicated as $V_o$, and an arrow above $V_o$ will be used to distinguish between direct and reverse reactions only if necessary. Square brackets will indicate molar concentrations. Ideal behavior of all species in both phases will also be assumed.

### a. One Slow Step in the Aqueous Phase

The slow step is the reaction between the metal cation and the acidic reagent which is rapidly solubilized in water. If the extractant is initially present in the organic phase, the following equations will describe the system:

$$\overline{HB} \rightleftharpoons HB \quad \text{fast} \quad ; \quad K_{D,R} = [\overline{HB}] \,/\, [HB] \tag{4}$$

$$M^{3+} + HB \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} MB^{2+} + H^+ \;\text{slow} \tag{5}$$

$$MB^{2+} + 2HB \rightleftharpoons MB_3 + 2H^+ \;\text{fast} \,;\, K_{e,w} = \frac{[MB_3][H^+]^2}{[MB^{2+}][HB]^2} \tag{6}$$

$$MB_3 \rightleftharpoons \overline{MB_3} \quad \text{fast} \quad ; \quad K_{D,C} = [\overline{MB_3}] \,/\, [MB_3] \tag{7}$$

Therefore the following rate laws will describe extraction kinetics:

$$\overrightarrow{V}_0 = \frac{K_1}{K_{D,R}} [M^{3+}][\overline{HB}] \tag{8a}$$

$$\overleftarrow{V}_0 = \frac{K_{-1} K^2_{D,R}}{K_{e,w} K_{D,C}} [\overline{MB_3}][H^+]^3[\overline{HB}]^{-2} \tag{8b}$$

with

$$K_{eq} = \frac{K_1 K_{D,C} K_{e,w}}{K_{-1} K^3_{D,R}} = \frac{[\overline{MB_3}][H^+]^3}{[M^{3+}][\overline{HB}]^3} \tag{9}$$

If the hydrolyzed metal ion is the reacting species, i.e.,

$$M(OH)^{2+} + HB \underset{K^*_{-1}}{\overset{K^*_1}{\rightleftharpoons}} MB^{2+} + H_2O \quad \text{slow;} \tag{10}$$

it follows

$$\overrightarrow{V}_0 = \frac{K^*_1 K_h}{K_{D,R}} [M^{3+}][\overline{HB}][H^+]^{-1} \tag{11a}$$

$$\overleftarrow{V}_0 = \frac{K^*_{-1} K^2_{D,R}}{K_{D,C} K_{e,w}} [\overline{MB_3}][H^+]^2[\overline{HB}]^{-2} \tag{11b}$$

where $K_h$ represents the first hydrolysis constant of the metal cation. If Equations 5 and 10 occur in parallel the equations for the initial rates become

$$\overrightarrow{V}_0 = \frac{(K_1 + K_1^{\ne} K_h [H^+]^{-1})}{K_{D,R}} [M^{+3}][\overline{HB}] \qquad (12a)$$

$$\overleftarrow{V}_0 = \frac{(K_{-1}[H^+] + K_{-1}^{\ne}) K^2{}_{D,R}}{K_{D,C} K_{e,w}} [\overline{MB_3}][H^+][\overline{HB}]^{-2} \qquad (12b)$$

If the metal cation instead of reacting with the undissociated extractant HB reacts with its dissociated form $B^-$, i.e.,

$$M^{3+} + B^- \rightleftharpoons MB^{2+} \quad \text{slow} \qquad (13)$$

the rate equations will be the same as Equation 11a with $K_a = [B^-][H^+]/[HB]$, acid dissociation constant, replacing $K_h$. Similarly if both the undissociated and dissociated forms of the extracting reagent react with $M^{3+}$ in parallel, the rate law will be equal to the rate (Equation 12a) with $K_a$ replacing $K_h$. These equal rate laws and the impossibility to make a decision about the reacting species simply on the form of the rate law is often referred in the literature as the "proton ambiguity".[53-58] When the rate laws (Equations 8 and 11) hold, by plotting in logarithmic form $\overrightarrow{V}_0$ and $\overleftarrow{V}_0$ vs. the concentrations of the various species, straight lines with integer slope values will be obtained. In the case of Equation 12 two straight lines connected by a transition region will be obtained when the abscissa is log $[H^+]$. Since no slow steps involving the crossing of the interface are implied, the presence of only one slow step occurring in the aqueous phase will be characterized by an independence of $V_0$ from both the interfacial area A and the volume of the aqueous phase $V_w$ in contact with the organic phase. These rate laws are likely to be met when the extracting reagent exhibits some solubility in the aqueous phase and its adsorption at the interface is quite negligible. It has to be mentioned that the slow step (Equation 5) can be regarded as a water substitution reaction. This fact will reflect on the rate constant which will be specific for the cation involved in the extraction reaction and must have the same value of the water substitution rate constants.

### *b. One Interfacial and One Aqueous Phase Slow Steps*

The interfacial step is the slow partition of the acidic extractant between the two phases. This step is followed by the slow reaction of the metal cation with the reagent. For the sake of simplicity we will restrict the treatment only to pseudo-first order reactions. This condition occurs when the concentration of the aqueous metal largely exceeds the concentration of the solubilized extractant and only $V_0$ is considered. Further, the contribution of the reverse reaction taking place in the aqueous phase will be neglected. Since the extracting reagent is initially present in the organic phase, it follows:

$$\overline{HB} \underset{K_{-1}^{\ne}}{\overset{K_1^{\ne}}{\rightleftharpoons}} HB \quad \text{slow} \qquad (14)$$

The rate of this heterogeneous distribution reaction will be proportional to the interfacial area A and to the inverse of the volume of the phases, i.e., to $1/V_{org}$ for the $\overline{HB} \rightarrow HB$ process and to $1/V_w$ for the opposite reaction.

$$HB + M^{3+} \xrightarrow{K_2^{\ne}} MB^{2+} + H^+ \quad \text{slow} \qquad (15)$$

The rate of this homogeneous reaction will be instead independent of both the interfacial area and the volume.

When HB is very reactive and present at very small concentrations, we can introduce the steady-state approximation at time equal to zero. We have then

$$\frac{d[HB]}{dt} = 0 = K_1[\overline{HB}] - (K_{-1} + K_2)[HB] \qquad (16)$$

$$\frac{d[MB^{2+}]}{dt} = K_1K_2/(K_{-1} + K_2)[\overline{HB}] \qquad (17)$$

with $K_1 = K_1^{*} A/V_{org}$, $K_{-1} = K_{-1}^{*} A/V_w$ and $K_2 = K_2^{*}[M^{3+}]$.
When $V_{org} = V_w$ and $K_{-1} \gg K_2$,

$$\frac{d[MB^{2+}]}{dt} = \frac{K_1}{K_{-1}} K_2[\overline{HB}]$$

In this case the rate at time zero is independent of $A/V_w$, and the situation is exactly the same as that reported in Section V.A.1.a., as the comparison between Equations 17 and 8a clearly shows when it is set

$$K_1/K_{-1} = K_1^{*}/K_{-1}^{*} = 1/K_{D,R}$$

Different results are instead obtained when the organic reagent, once present in the water phase, exhibits a much higher probability to react with the metal cation than to return into the organic phase. In this case $K_2 \gg K_{-1}$ and it follows

$$\frac{d[MB^{2+}]}{dt} = K_1^{*} \frac{A}{V_{org}} [\overline{HB}] \qquad (18)$$

i.e., the rate will be controlled essentially by the rate of partition of the extractant, and then it is proprotional to the interfacial area even though the complex formation reaction does not occur at the interface.

### *c. The Slow Steps Occur at the Interface*

We will consider here those reaction mechanisms where the reaction between the metal species and the extraction reagent occurs at the interface. Slow interfacial reactions can often be found when the extractant exhibits low solubility in the aqueous phase and at the same time is a surfactant. As will be shown, the degree of surface activity of the extraction reagents will reflect on the rate law since the interfacial concentration will appear in it. Strong surfactants will in fact give a constant interfacial concentration even at very low bulk concentrations, while less strong ones will yield interfacial concentrations which are proportional to the bulk concentration.

In general we will assume that the extraction reagent is adsorbed at the liquid-liquid interface according to a Langmuir law, which for the case of an acidic extractant HB can be written as

$$[HB]_{ad} = \frac{\alpha_2[\overline{HB}]/\gamma}{1 + [\overline{HB}]/\gamma} \qquad (19)$$

where $\alpha_2$ and $\gamma$ are Langmuir adsorption constants with values characteristic for each system. We will then distinguish two regions of adsorption, one defined as ideal where $1 \gg [HB]/\gamma$ with

$$[HB]_{ad} = \frac{\alpha_2}{\gamma}\,[\overline{HB}] = \alpha_1\,[\overline{HB}] \tag{20}$$

and one of complete saturation where $1 \ll [HB]/\gamma$ with

$$[HB]_{ad} = \alpha_2 \tag{21}$$

With strong surfactants, Equation 21 holds in all the concentration ranges of extractant which are of practical interest in kinetics studies. In fact, the interface becomes saturated with the extractant molecules when its bulk organic concentration is as low as $10^{-4}$ to $10^{-5}$ *M*. We will first describe the case of monoprotic bidentate acidic reagents HB which extract trivalent metal cations, $M^{3+}$, from an aqueous phase containing no other metal complexing agents. The acidic reagents will be considered completely undissociated at the interface, and the existence of charged species will be assumed possible only in the aqueous bulk phase and on the interface. The volume of both the aqueous and the organic phases will be considered equal, i.e., $V_w = V_{org} = V$, and we will often unify the interfacial area A and the volume, V in one single parameter a = A/V, i.e., the specific interfacial area. The mechanisms reported in the following will be characterized by the following features:

1. The reaction between the metal cation and the reagent is a slow step occurring at the interface; this leads to the formation of an interfacial complex which is always present at very low concentrations; as a consequence, the steady state approximation can be applied to it; further, the interfacial concentration of the extractant will not be affected by the formation of the interfacial complex.
2. The driving force for the transfer of this interfacial complex into the organic phase is the stronger surface activity of the reagent which replaces the less surface active metal complex at the interface.

The following four reactions will be therefore considered:

$$\text{I)}\quad M^{3+} + (HB)_{ad} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} (MB^{2+})_{ad} + H^+ \tag{22}$$

$$\text{II)}\quad (MB^{2+})_{ad} + (HB)_{ad} \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} (MB_2^+)_{ad} + H^+ \tag{23}$$

$$\text{III)}\quad (MB_2^+)_{ad} + (HB)_{ad} \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} (MB_3)_{ad} + H^+ \tag{24}$$

$$\text{IV)}\quad (MB_3)_{ad} + 3\,\overline{HB} \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} \overline{MB_3} + 3(HB)_{ad} \tag{25}$$

Equation 25 describes the adsorption-desorption process at the interface. Charges will be omitted in order to simplify the notation.

### *i. (I) slow; (II), (III), (IV) fast*

This case is characterized by a fast adsorption-desorption equilibrium of the interfacial complex as well as by the fast introduction of the second and third ligand molecules. We have then

$$V_I = K_1 a[M][HB]_{ad} - K_{-1} a[MB]_{ad}[H]$$

$$K_{2,e} = \frac{[MB_2]_{ad}[H]}{[MB]_{ad}[HB]_{ad}} ; K_{3,e} = \frac{[MB_3]_{ad}[H]}{[MB_2]_{ad}[HB]_{ad}} ; K_{4,e} = \frac{[\overline{MB_3}][HB]^3_{ad}}{[MB_3]_{ad}[\overline{HB}]^3} \quad (26)$$

We can therefore substitute the concentration of the interfacial complex with

$$[MB]_{ad} = \frac{[\overline{MB_3}][HB]_{ad}[H]^2}{K_{2,e}K_{3,e}K_{4,e}[\overline{HB}]^3} \quad (27)$$

We obtain then for the forward and reverse initial rates of extraction

$$\overrightarrow{V}_0 = -d[M]/dt = aK_1 [M][HB]_{ad} \quad (28)$$

and

$$\overleftarrow{V}_0 = +d[M]/dt = \frac{aK_{-1}}{K_{2,e} K_{3,e} K_{4,e}} \frac{[\overline{MB_3}][H]^3[HB]_{ad}}{[\overline{HB}]^3} \quad (29)$$

Replacing the interfacial extractant concentration with the bulk concentrations, Equations 28 and 29 become

$$\overrightarrow{V}_0 = aK_1\alpha_1 [M][\overline{HB}] \quad (30)$$

and

$$\overleftarrow{V}_0 = \frac{K_{-1} a\alpha_1}{K_{2,e} K_{3,e} K_{4,e}} \frac{[\overline{MB_3}][H]^3}{[\overline{HB}]^2} \quad (31)$$

for an ideal adsorption, and

$$\overrightarrow{V}_0 = aK_1\alpha_2 [M] \quad (32)$$

and

$$\overleftarrow{V}_0 = \frac{K_{-1} a\alpha_2}{K_{2,e} K_{3,e} K_{4,e}} \frac{[\overline{MB_3}][H]^3}{[\overline{HB}]^3} \quad (33)$$

for a saturated interface.

At equilibrium, by setting $\overrightarrow{V}_0 = \overleftarrow{V}_0$, we get

$$K_{eq} = \frac{K_1}{K_{-1}} K_{2,e} K_{3,e} K_{4,e} \quad (34)$$

If Reaction (I) occurs between the hydrolyzed metal cation and the extracting reagent, i.e.,

$$MOH + (HB)_{ad} \underset{K^*_{-1}}{\overset{K^*_1}{\rightleftharpoons}} (MB)_{ad} + H_2O \quad (35)$$

the rate laws will be the following

$$\vec{V}_0 = K_1^* K_h a \alpha_1 [M][H]^{-1}[\overline{HB}] \quad (36)$$

and

$$\overleftarrow{V}_0 = \frac{K_{-1}^* a \alpha_1}{K_{2,e} K_{3,e} K_{4,e}} [\overline{MB_3}][\overline{HB}]^{-2}[H]^2 \quad (37)$$

for an ideal adsorption, and

$$\vec{V}_0 = K_1^* K_h a \alpha_2 [M][H]^{-1} \quad (38)$$

and

$$\overleftarrow{V}_0 = \frac{K_{-1}^* a \alpha_2}{K_{2,e} K_{3,e} K_{4,e}} [\overline{MB_3}][\overline{HB}]^{-3}[H]^2 \quad (39)$$

for a saturated interface.

The dependence of $\vec{V}_0$ and $\overleftarrow{V}_0$ on [M], [H], $[\overline{HB}]$ and $[MB_3]$ is exactly the same in Equations 8a and 8b and Equations 30 and 31 (referring to the unhydrolyzed metal) and in Equations 11a and 11b and Equations 36 and 37 (referring to the hydrolyzed metal). This fact clearly indicates that unless the dependence of the initial rate on the specific interfacial area a is evaluated, the two cases cannot be distinguished. It is in fact impossible to identify the localization of the slow step simply by studying how the rate varies with the composition of the system. Figure 25 shows in a schematic way some of the reaction orders which will be expected in these cases.

### *ii. (I) and (II) slow; (III) and (IV) fast*

This mechanism is also characterized by a fast adsorption-desorption equilibrium of the interfacial complex. However, the introduction of the second ligand molecule at the interface is considered as a slow step. It follows then

$$V_I = K_1 a[M][HB]_{ad} - K_{-1} a[MB]_{ad}[H] \quad (40)$$

$$V_{II} = K_2 a[MB]_{ad}[HB]_{ad} - K_{-2} a[MB_2]_{ad}[H] \quad (41)$$

By applying the stationary state condition at $[MB]_{ad}$, i.e., $V_I = V_{II}$, we obtain

$$[MB]_{ad} = \frac{K_1[M][HB]_{ad} + K_{-2}[MB_2]_{ad}[H]}{K_{-1}[H] + K_2[HB]_{ad}} \quad (42)$$

$[MB_2]_{ad}$ in Equation 42 can be expressed in terms of equilibrium constants, $[HB]_{ad}$, and bulk concentrations. The following rate laws are then derived:

$$\vec{V}_0 = \frac{K_2 a K_1 [M][HB]_{ad}^2}{K_{-1}[H] + K_2[HB]_{ad}} \quad (43)$$

and

$$\overleftarrow{V}_0 = \frac{\frac{K_{-1} K_{-2}}{K_{3,e} K_{4,e}} a[\overline{MB_3}][H]^3[\overline{HB}]^{-3}[HB]_{ad}^2}{K_{-1}[H] + K_2[HB]_{ad}} \quad (44)$$

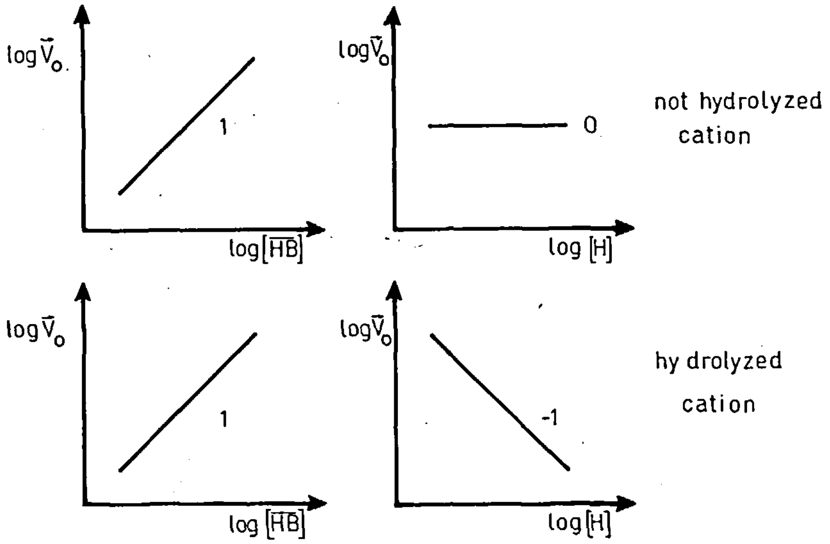


FIGURE 25. Reaction orders expected for cases: (Section V.A.1.a.) one slow step in the aqueous phase. Equations 8a and 11a; and (Section V.A.1.c.i.) one slow step at the interface with ideal adsorption. The slow step is the reaction between the metal cation and the acidic reagent. Equations 30 and 36.

Equations 43 and 44 become

$$\vec{V}_0 = \frac{K_1\ K_2 a\,\alpha_1\,[M][\overline{HB}]^2}{K_{-1}[H] + K_2\alpha_1[\overline{HB}]} \tag{45}$$

and

$$\overleftarrow{V}_0 = \frac{\dfrac{K_{-1}K_{-2}}{K_{3,e}\,K_{4,e}}\ a\alpha_1^2\ [\overline{MB_3}][H]^3}{K_{-1}[H][\overline{HB}] + K_2\alpha_1[\overline{HB}]^2} \tag{46}$$

for an ideal adsorption, and

$$\vec{V}_0 = \frac{K_1K_2a\alpha_2[M]}{K_1[H] + K_2\alpha_2} \tag{47}$$

and

$$\overleftarrow{V}_0 = \frac{\dfrac{K_{-1}\ K_{-2}}{K_{3,e}\,K_{4,e}}\ a\,\alpha_2^2[\overline{MB_3}][H]^3}{[\overline{HB}]^3(K_{-1}[H] + K_2\alpha_2)} \tag{48}$$

for a saturated interface. Figure 26 shows the logarithmic plots of Equations 45 and 46. The plots clearly indicate that variable orders of reaction are obtained in different ranges of the abscissa values. It is worth noticing that when such a mechanism holds a linear dependence of the rates on the specific interfacial area, a, must be experimentally found.

*iii. (I) and (IV) slow; (II) and (III) fast*

This mechanism is characterized by the slow reaction of the metal cation with the acidic extractant HB at the interface. While the reaction of the second- and third-

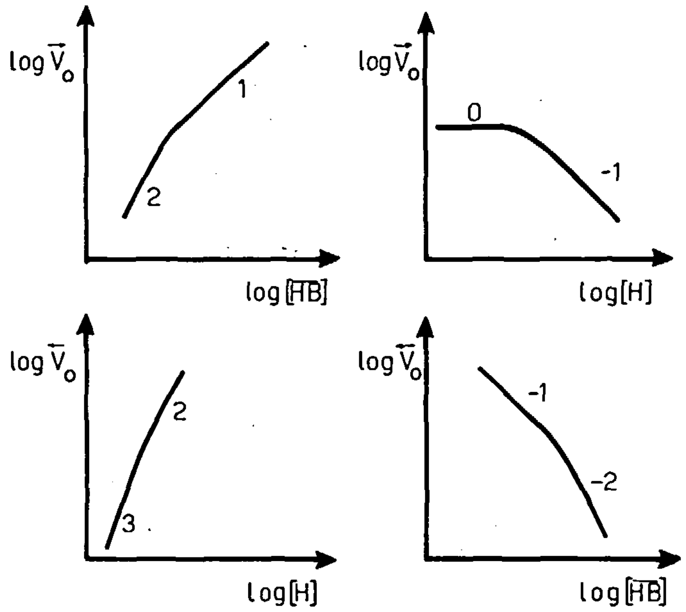


FIGURE 26. Logarithmic plot of functions (Equations 45 and 46). The rate laws refer to case (Section V.A.1.c.ii) where the slow steps are the interfacial reactions of the metal cation with the first and second molecules of the acidic extracting reagent, HB. An ideal adsorption of the extracting reagent is considered.

reagent molecules are considered as fast steps, the adsorption-desorption processes of the interfacial complex and the extracting reagent from and to the interface are also slow steps. This mechanism has been hypothesized in the metal extraction from acidic solutions by extracting reagents which are strong surfactants (such as the long chain sulfonic acids).

The equations which describe the system are the following,

$$V_I = K_1\, a[M][HB]_{ad} - K_{-1}\, a[MB]_{ad}[H] \tag{49}$$

$$V_{IV} = K_4\, a[MB_3]_{ad}[\overline{HB}]^3 - K_{-4}\, a[\overline{MB_3}][HB]^3_{ad} \tag{50}$$

The concentration of $[MB]_{ad}$ can be expressed through the equilibrium constants of the two fast steps and the concentration of the neutral complex $[MB_3]_{ad}$, i.e.,

$$[MB_3]_{ad} = \frac{K_1[M][HB]_{ad} + K_{-4}[\overline{MB_3}][HB]^3_{ad}}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}}\,\dfrac{[H]^3}{[HB]^2_{ad}} + K_4[\overline{HB}]^3} \tag{51}$$

Once the concentration of the interfacial complex has been evaluated the following rate laws are easily obtained

$$\vec{V}_0 = \frac{K_1K_4\, a[M][\overline{HB}]^3[HB]^3_{ad}}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}}\,\dfrac{[H]^3}{[HB]^2_{ad}} + K_4[\overline{HB}]^3} \tag{52}$$

and

$$\overleftarrow{V}_0 = \frac{\dfrac{K_{-1}K_{-4}a}{K_{2,e}K_{3,e}}[\overline{MB_3}][H]^3[HB]_{ad}}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}}\dfrac{[H]^3}{[HB]^2_{ad}} + K_4[\overline{HB}]^3} \qquad (53)$$

In the case of a saturated interface, Equations 52 and 53 become

$$\overrightarrow{V}_0 = \frac{K_1K_4a\,\alpha_2[M][\overline{HB}]^3}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}\alpha_2^2}[H]^3 + K_4[\overline{HB}]^3} \qquad (54)$$

and

$$\overleftarrow{V}_0 = \frac{\dfrac{K_{-1}K_{-4}a\,\alpha_2}{K_{2,e}K_{3,e}}[\overline{MB_3}][H]^3}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}\alpha_2^2}[H]^3 + K_4[\overline{HB}]^3} \qquad (55)$$

Also in this case, the interfacial location of the reactions is indicated by the direct proportionality existing between the initial rates and the specific interfacial area a. A graphic representation of Equations 54 and 55 is reported in Figures 27 and 28. Figure 28 clearly indicates that the order of reaction, obtained through the slopes of the logarithmic plots, can be fractional and variable according to the concentration ranges which are considered.

If Reaction (I) occurs with the hydrolyzed metal cation. In this case Equation 22 has to be written in the form

$$MOH^{2+} + (HB)_{ad} \underset{K^*_{-1}}{\overset{K^*_1}{\rightleftharpoons}} (MB^{2+})_{ad} + H_2O \qquad (56)$$

Following a procedure very similar to that of the previous case, the following rate equations are derived for a saturated interface:

$$\overrightarrow{V}_0 = \frac{K^*_1K_4a\,\alpha_2K_h[M][H]^{-1}[\overline{HB}]^3}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}\alpha_2^2}[H]^2 + K_4[\overline{HB}]^3} \qquad (57)$$

and

$$\overleftarrow{V}_0 = \frac{\dfrac{K^*_{-1}K_{-4}a\,\alpha_2}{K_{2,e}K_{3,e}}[\overline{MB_3}][H]^2}{\dfrac{K_{-1}}{K_{2,e}K_{3,e}\alpha_2^2}[H]^2 + K_4[\overline{HB}]^3} \qquad (58)$$

where $K_h$ represents the first hydrolysis constant of the metal cation, i.e., $K_h = [MOH][H][M]^{-1}$.

A graphic representation of Equation 57 is reported in Figure 29. Although the general trend of Equations 57 and 58 is similar to that of Equations 54 and 55, the two cases can be easily distinguished by studying the curves $\overrightarrow{V}_o/[M]$ vs. $[\overline{HB}]$ at different constant acidities. In fact when Equation 54 holds, the plateau values of the curves $\overrightarrow{V}_o/[M]$ will be the same at all the acidities. When, on the other hand, Equation 57 holds, different plateau values will be obtained.

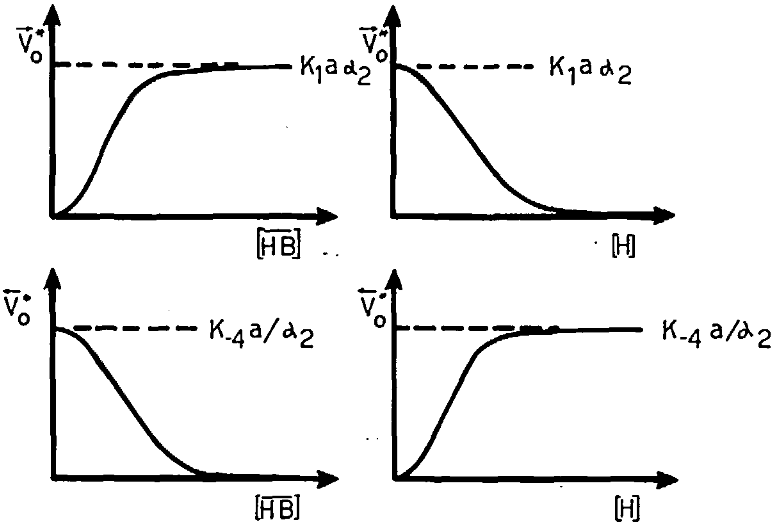


FIGURE 27. Linear plot of functions Equations 54 and 55. The rate laws refer to case (Section V.A.1.c.iii) where the two slow steps are the interfacial reaction of the metal cation with one molecule of the acidic reagent and the adsorption-desorption of the extracting reagent and the interfacial complex at the interface A saturated interface is considered. Normalized rates, $\vec{V}_o/[M] = \vec{V}_o^*$ and $\overleftarrow{V}_o/[\overline{M}] = \overleftarrow{V}_o^*$

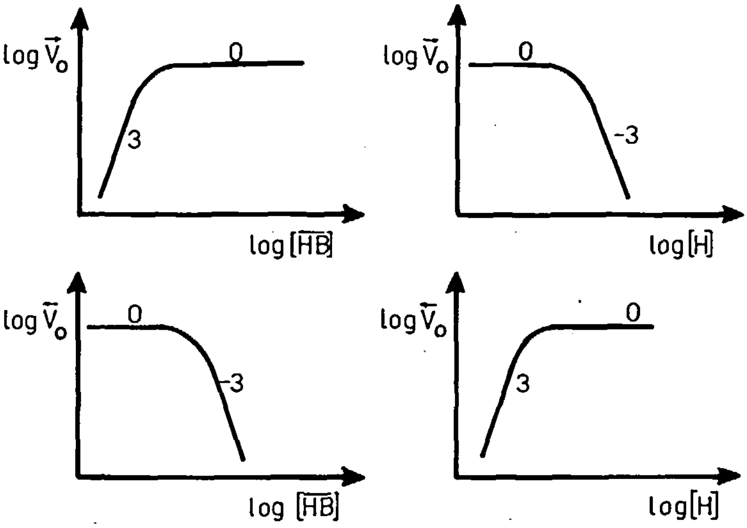


FIGURE 28. Logarithmic plot of functions Equations 54 and 55. Same case as in Figure 27.

#### *iv. (I) and (IV) slow; (II) and (III) fast with slow steps also in the aqueous phase*

A slow reaction step also occurs in the aqueous phase with the reagent solubilized in water. Both the unhydrolyzed and the hydrolyzed cations react simultaneously. This case is a combination of case A.1.a and cases A.1.c.iii. When the extracting reagent is partially solubilized in water and adsorbed at the liquid-liquid interface and the metal cation is present also in its hydrolyzed form, the following five slow steps will be simultaneously operative.

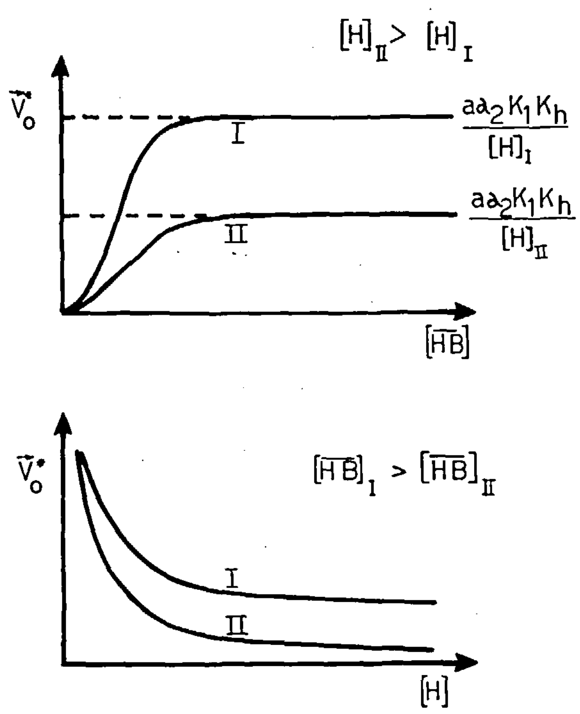


FIGURE 29. Linear plots of function Equation 57. The rate law refers to case (Section V.A.1.c.iii). Case similar to that described in Figure 27 except that the reacting species is the hydrolyzed cation MOH²⁺.

$$\left.\begin{array}{ll} M^{3+} + HB \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} MB^{2+} + H^+ & (59) \\ M(OH)^{2+} + HB \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} MB^{2+} + H_2O & (60) \end{array}\right\} \text{homogeneous parallel reactions}$$

$$\left.\begin{array}{ll} M^{3+} + (HB)_{ad} \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} (MB^{2+})_{ad} + H^+ & (61) \\ M(OH)^{2+} + (HB)_{ad} \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} (MB^{2+})_{ad} + H_2O & (62) \end{array}\right\} \text{interfacial parallel reactions}$$

$$(MB_3)_{ad} + 3\overline{HB} \underset{K_{-5}}{\overset{K_5}{\rightleftharpoons}} \overline{MB_3} + 3(HB)_{ad} \tag{63}$$

Equation 63 refers to the slow adsorption-desorption reaction occurring at the interface. In order to derive the rate laws the same way of reasoning previously described can be followed. To this purpose we have to introduce the equilibrium parameters of the four fast steps:

$$K_{D,R} = \frac{[\overline{HB}]}{[HB]},\ K_h = [MOH][H][M]^{-1},\ K_{e,1} = \frac{[MB_3]_{ad}[H]^2}{[MB][HB]^2_{ad}}$$

$$K_{e,2} = \frac{[MB_3]_{ad}[H]^2}{[MB]_{ad}[HB]_{ad}^2}$$

The interfacial concentration of the complex $[MB_3]_{ad}$ can be similarly derived from the steady state condition, i.e.,

$$[MB_3]_{ad} = \frac{[M]f_I + K_{-5}\,a\,\alpha_2^3[\overline{MB_3}]}{f_{II} + K_5 a[\overline{HB}]^3} \tag{64}$$

where

$$f_I = [HB]\left(\frac{K_1}{K_{D,R}} + \frac{K_2 K_h}{K_{D,R}}[H]^{-1}\right) + (K_3\,\alpha_2 a + K_4 a\,\alpha_2 K_h[H]^{-1}) \tag{65}$$

$$f_{II} = \left(\frac{K_{-4}a}{K_{e,2}} + \frac{K_{-2}}{K_{e,1}}\right)[H]^2 + \left(\frac{K_{-3}a}{K_{e,2}} + \frac{K_{-1}}{K_{e,1}}\right)[H]^3 \tag{66}$$

and then used to calculate the forward and reverse initial rates of reaction when the interface is completely saturated with the extractant molecules. The two rate equations are then obtained

$$\overrightarrow{V}_0 = \frac{f_I K_5 a[\overline{HB}]^3[M]}{f_{II} + K_5 a[\overline{HB}]^3} \tag{67}$$

and

$$\overleftarrow{V}_0 = \frac{f_{II} K_{-5} a[\overline{MB_3}]}{f_{II} + K_5 a[\overline{HB}]^3} \tag{68}$$

Equations 67 and 68 cannot be made equal at equilibrium to get a relationship between the rate constants and the equilibrium constant. This procedure would in fact lead to paradoxical results. The principle of microscopic reversibility must instead be applied.[49] This means that at equilibrium the reaction rates of hydrolyzed and nonhydrolyzed metal (Equations 61 and 62) have to be set equal to the rate of the adsorption-desorption process (Equation 63) separately. In this way, consistent relationships between the rate constants and the equilibrium constant of the overall extraction process can be obtained. A detailed description of this case can be found in Reference 24. Figure 30 shows a linear plot of Equations 67 and 68. The trend of the functions is similar to that reported in Figure 29. However the $\overrightarrow{V}_0$ vs. $[\overline{HB}]$ function never reaches a plateau value since at high $\overline{HB}$ concentrations the influence of the aqueous phase reaction shows up as a linear dependence of $\overrightarrow{V}_0$ on $[\overline{HB}]$. Obviously the actual shape of the curves of Figure 30, as well as those of Figures 27 to 29, will depend on the specific values of the rate and equilibrium constants which appear in the rate law. The actual value of the specific interfacial area a and the adsorption Langmuir constant $\alpha_2$ will also influence the actual shape of the rate vs. concentrations curves.

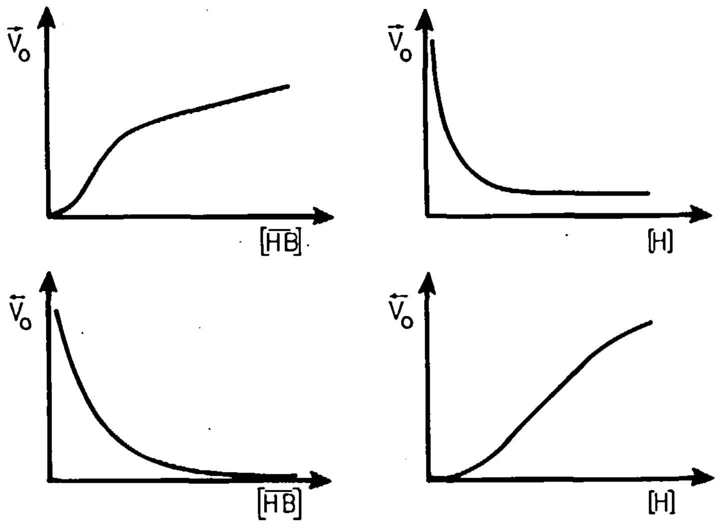


FIGURE 30. Linear plot of functions Equations 67 and 68. The rate laws refer to case (Section V.A.1.c.iv) where five slow steps are simultaneously operative. Two slow steps occur in the aqueous phase. They are the reaction of the metal cation and its hydrolyzed form with the water solubilized extractant. Three slow steps occur at the interface. They are the reaction of the metal cation and its hydrolyzed form with the interfacially adsorbed extracting reagent molecules. The fifth slow step is the desorption-adsorption reaction of the interfacial complex and the extractant at the interface. A saturated interface is considered.

Finally, it has to be considered that the concentration of the extracting reagent $[\overline{HB}]$ which appears in all the rate laws derived up to this point refers to the monomer concentration and not to the analytical (total) one. Therefore, since in low dielectric constant diluents the extracting reagents can undergo association equilibriums (generally rather fast), these always have to be taken into consideration when the rate laws are used to interpret experimental rate vs. concentrations data. Similarly, whenever the extracted metal complex and the aqueous species do not behave ideally, the quantities inside the square brackets have to be replaced with activities.

### 2. *Basic Extractants*

Basic extractants, such as alkylammonium salts, are generally very strong surfactants and when the alkyl chains are sufficiently long, they exhibit very low solubilities in the aqueous phases. They extract metal species when these are present in the aqueous solutions in the form of complexes. We will consider below only one simplified case which occurs when all the slow steps take place at the interface. The extracting reagent will be assumed to be in its $X^-$ salt form, i.e., BX, where $X^-$ is the same anion which forms complexes with the metal cation in the aqueous phase. Only the case of a completely saturated interface will be reported. The concentration of $X^-$ in the aqueous phase will be considered constant, and only one extractable complex $MX_3$ will be assumed. The two slow steps will then be the following;

$$MX_3 + (BX)_{ad} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} (BX\,MX_3)_{ad} \qquad (69)$$

and

$$[(BX)_3MX_3]_{ad} + 3\overline{BX} \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} \overline{B_3MX_6} + 3(BX)_{ad} \tag{70}$$

Equation 69 describes the slow formation of an interfacial complex between the aqueous metal complex and the interfacially adsorbed extractant. The additions of the fifth and sixth coordinating ligand $X^-$ supplied by BX, occurring at the interface, are then considered as fast steps. Equation 70 represents the desorption of the interfacial complex from the interface and the replacement of the interfacial vacancies by the extractant molecules. By considering a steady-state situation instantaneously established at the interface for the interfacial complex, $(BXMX_3)_{ad}$, and by following the same procedure described in the other sections, the following rate laws are derived:

$$\overrightarrow{V}_0 = \frac{K_1 K_4 a \alpha_2 [MX_3][\overline{BX}]^3}{\frac{K_{-1}}{K_e \alpha_2^2} + K_4 [\overline{BX}]^3} \tag{71}$$

and

$$\overleftarrow{V}_0 = \frac{\frac{K_{-1}K_{-4}}{K_e} \alpha_2 [\overline{B_3MX_6}]}{\frac{K_{-1}}{K_e} + K_4 [\overline{BX}]^3} \tag{72}$$

where $K_e$ represents the equilibrium constant of the fast reaction

$$(BXMX_3)_{ad} + 2(BX)_{ad} \rightleftharpoons [(BX)_3MX_3]_{ad}$$

A plot of Equations 71 and 72 against $[\overline{BX}]$ will give rise to curves essentially similar to those shown in Figure 27. This case can be further complicated by considering that many basic extractants can form dimers, trimers, and higher polymers in low dielectric constant diluents. In addition to the monomer BX, these species can in fact contribute to the kinetics of transfer of the interfacial complex into the bulk organic phase. In this instance, several parallel reactions, similar to Equation 70, will occur simultaneously. Consequently, their contribution will show up in the rate laws.

### 3. *Neutral Extractants*

Neutral extractants are generally less strong surfactants than basic ones. Nevertheless, they can be equally adsorbed at the interface. When the two slow steps are the formation of an interfacial complex followed by the transfer of this into the bulk organic phase and the aqueous solution contains a constant concentration of a ligand $X^-$, the rate equations which are derived are very similar to Equations 71 and 72. In this case the X of BX will be the donor group of the neutral extractant and will be different from the aqueous complexing agent of the metal, $X^-$. The power to which the monomer extractant concentration will be raised (three in Equations 71 and 72) will again depend on the number of donor groups of the extractant which are required to saturate the coordination bonds of the metal cation. However, also in this case, the presence of an interfacial slow step will give rise to $\overrightarrow{V}_o$ and $\overleftarrow{V}_o$ vs. extractant concentration plots similar to those of Figure 27.

## VI. DIFFUSIONAL REGIME

When the chemical reactions which occur in the solvent extraction process are very fast compared to the diffusion processes to and from the interface, the rate of extraction is controlled by the diffusional rate. In this case the extraction kinetics are said to proceed in a diffusional regime. As previously reported, when the fast chemical reactions responsible for the extraction process take place at the interface, or more generally near the interface, the problem describing the extraction kinetics can also be termed as a mass transfer with instantaneous chemical reaction. In order to better understand the meaning of the correlations existing between the rate of extraction, the mass-transfer coefficients, the rate constants, and the concentrations of the reagents, we will first briefly discuss the correlations holding in absence of chemical reactions.

## A. Mass-Transfer Rate Without Chemical Reaction

One way to face the problem is to consider that in the process of transfer from one phase to the other, the transferring species will encounter a general resistance R which is the sum of three separate resistances. Two of these resistances are of diffusional nature and depend on the fact that diffusion through the stagnant interfacial films can be a slow process. These resistances will be indicated as $R_w$ and $R_{org}$, where $R_w$ includes all the diffusional contributions on the water side of the interface, assumed to occur entirely through a stagnant film of thickness $\delta_w$, and $R_{org}$ includes the corresponding contributions on the organic side where the thickness of the stagnant film is $\delta_{org}$. The resistance associated to the crossing of the interface will be indicated as $R_i$. As a consequence, the total transfer resistance R will be

$$R = R_w + R_i + R_{org} \tag{73}$$

Equation 73 holds for the stationary state.

In a diffusional regime and in the absence of surfactants, $R_i$ is generally negligible with respect to both $R_w$ and $R_{org}$. Figure 31 shows the localization of the three resistances. The possible presence of interfacially adsorbed molecules of a surfactant is also shown. The thickness of the stagnant films, also called diffusion films, will depend on the extent of stirring of the two phases through the Reynolds number which for a Lewis type cell is correlated to the length of the stirrer blades L, the number of revolutions of the stirrer in the unit time n, and the kinematic viscosity $\nu$, according to the relationship $Re = L^2n/\nu$.

The diffusional resistances $R_w$ and $R_{org}$ are the inverse of the mass-transfer coefficients $\beta_w$ and $\beta_{org}$. These can be simply defined by the Whitman two-films theory,[59,60] which considers the system always in a stationary state, i.e., with concentration profiles independent of time through the diffusion films. Within this approximation, the simple differential equation for the transfer across a plane interface is

$$\frac{dm}{dt} = A\beta\,\Delta C \tag{74}$$

where A = interfacial area, m = moles of metal species crossing the interface, $\Delta C$ = concentration difference of the distributing species between the bulk phase and the interface, and $\beta$ = proportionality constant, i.e., mass-transfer coefficient, also called the permeability coefficient.

When Equation 74 is applied to a solute which distributes between two liquid immiscible phases, it becomes

$$N = \frac{dm}{dt}\,\frac{1}{A} = \beta_w(C_w - C_{w,i}) = \beta_{org}(C_{org,i} - C_{org}) \tag{75}$$

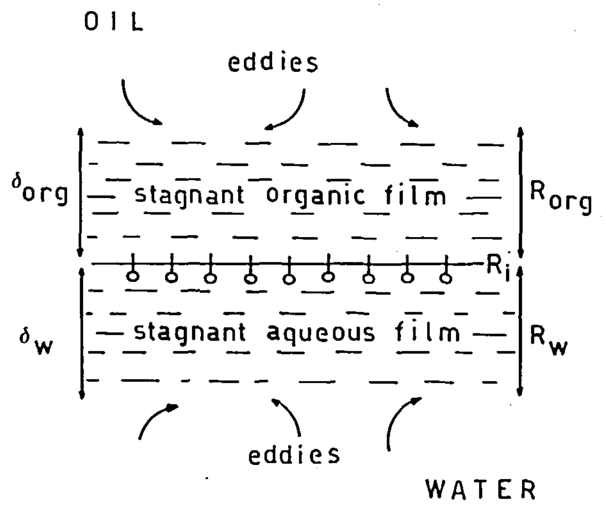


FIGURE 31. Total resistance of the interfacial zone $R = R_w + R_i + R_{org}$, and thickness of the diffusion films $\delta_w$, $\delta_{org}$. The interfacially adsorbed extractant molecules are also shown.

where N = flux through the interface, $\beta_w$ = aqueous mass-transfer coefficient, $\beta_{org}$ = organic mass-transfer coefficient, $C_w$ and $C_{org}$ = aqueous and organic phase bulk concentrations of the distributing species, $C_{w,i}$ and $C_{org,i}$ = aqueous and organic side interfacial concentrations of the distributing species. These concentrations should not be confused with those of the substances adsorbed on the interface (indicated by the subscript "ad"), they are instead the concentrations present at a plane parallel and immediately adjacent to the interface, where the diffusion films end. The situation is schematically reported in Figure 32.

An equation formally similar to Equation 75 can be formulated by substituting the unknown interfacial concentrations with fictitious equilibrium concentrations $C_{w,f}$ and $C_{org,f}$. These *fictitious equilibrium concentrations* can be defined as the aqueous and organic concentrations that would be at equilibrium with the actual concentrations present at each time in each phase, i.e., $C_{w,f} = C_{org}/K_D$ and $C_{org,f} = K_D C_w$, where $K_D$ is the organic/water partition coefficient of the distributing substance. In this case the proportionality constant between the flux N and the concentration gradients $(C_w - C_{w,f})$ and $(C_{org,f} - C_{org})$ is defined as the overall mass-transfer coefficient $\bar{\beta}$. Equation 75 together with the new flux equations

$$N = \bar{\beta}_w(C_w - C_{w,f}) = \bar{\beta}_{org}(C_{org,f} - C_{org}) \tag{76}$$

and the *equilibrium distribution ratio*

$$K_D = C_{org,eq}/C_{w,eq} \tag{77}$$

can then be solved to obtain the following relationships between the mass-transfer coefficients:

$$\frac{1}{\bar{\beta}_w} = \frac{1}{\beta_w} + \frac{1}{K_D \beta_{org}} \tag{78}$$

and

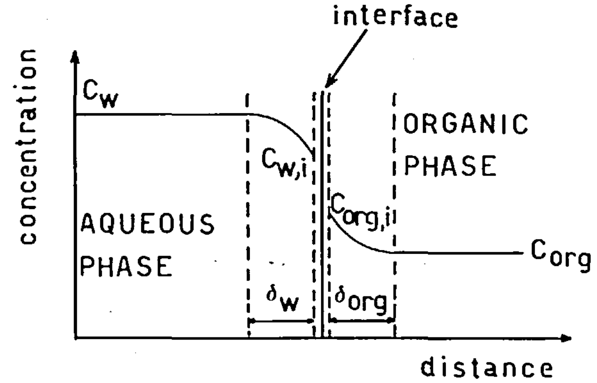


FIGURE 32. Concentration profiles for a solute which distributes between two immiscible liquid phases.

$$\frac{1}{\beta_{org}} = \frac{1}{\beta_{org}} + \frac{K_D}{\beta_w} \qquad (78a)$$

Equations 78 and 78a can be also formulated in terms of resistances, i.e.,

$$R = R_w + R_{org}/K_D \qquad (79)$$

$$R = R_{org} + K_D R_w \qquad (79a)$$

Equations 79 and 79a show that when the distribution ratio $K_D$ is very high, the total resistance to the mass transfer lies in the aqueous phase. The opposite, of course, occurs when $K_D$ is very low. If an interfacial resistance is also present, due, for example, to the presence of interfacially adsorbed surfactants,this has to be added to the two right-side terms of equations 79 and 79a.

When the concentration of the diffusing components is very low compared to that of the solvents, and the two-films theory is assumed to hold, the following approximations can be introduced:

$$\beta_w = \frac{D_w}{\delta_w} \qquad (80)$$

and

$$\beta_{org} = \frac{D_{org}}{\delta_{org}} \qquad (81)$$

where $D_w$ and $D_{org}$ are the diffusivities of the metal-containing species. This simple two-films theory has been subsequently modified by Dankwerts[61] into the so-called penetration theory. According to this theory, an interfacial unsteady-state situation is postulated, with eddies of the fluid resting only for some time at the interface, being then replaced by other eddies coming from the bulk of the solvent. Therefore, this theory implies that an unsteady interfacial mass transfer occurs during the period when the eddies rest at the interface. In this case the relationship between the mass-transfer coefficients and the diffusitivies are the following,

$$\beta_w = \sqrt{s_w D_w} \tag{82}$$

and

$$\beta_{org} = \sqrt{s_{org} D_{org}} \tag{83}$$

where $s_w$ and $s_{org}$ represent the average velocity of renewal of the eddies at the interface. Therefore, the main difference between the two treatments is that the mass-transfer coefficient is simply proportional to the diffusivity in the two-films theory, while, according to the penetration theory, the proportionality is established with the square root of the diffusivity. During the last few years the penetration theory has been shown to be in better agreement with experimental mass-transfer data of inert species[62] than the older two-films theory. However, the available evidence has not yet definitely indicated which picture is closer to the truth.

### B. Mass-Transfer Rate with Fast Chemical Reaction

When a chemical reaction accompanies the transfer of a chemical species from one phase into another, and the reaction is so much faster than the diffusion processes that it can be considered instantaneous, both the two previously mentioned theories can still be applied providing suitable modifications are introduced. In general, the mathematical treatment of mass transfer in the presence of a chemical reaction can be quite complicated even when the reactions are rather simple. For this reason, all of the reported models have been developed by introducing simplifying assumptions. Therefore, reference has to be made to specialized chemical engineering textbooks for a comprehensive treatment of all the cases which have been developed in detail. References 17 and 63 through 65 are reported as example of books dealing with the problem. In the following section, we will briefly discuss only some exemplificative cases in order to show how the problem can be faced and the type of functional dependences of the rates on the concentrations and other physico-chemical parameters characterizing the mass transfer which can be expected. Also in this instance, as for the kinetic regime, we can distinguish between two cases according to the possible localization of the reaction. On the basis of chemical considerations, the possibility of a reaction zone localized into the organic phase is very unlikely and will not be taken into consideration. Two possible reaction zones will instead then be considered, i.e.,

1. The reaction zone is in the aqueous phase, adjacent to the interface.
2. The reaction takes place on the interface.

#### *1. The Reaction Zone is in the Aqueous Phase*

The mathematical treatment associated with this case, with the further restriction that the reaction zone is limited to a surface, was developed long ago by chemical engineers[63] for very simple irreversible reactions by applying both the two-films and the penetration theories.

By considering a fast irreversible reaction of the type

$$M + B \longrightarrow MB \tag{84}$$

occurring on a plane parallel to the interface in the aqueous phase, where M is the aqueous metal and B is the organic extracting reagent which has been slightly solubilized at the aqueous side of the interface, the two-films theory leads to the following equation for the flux:

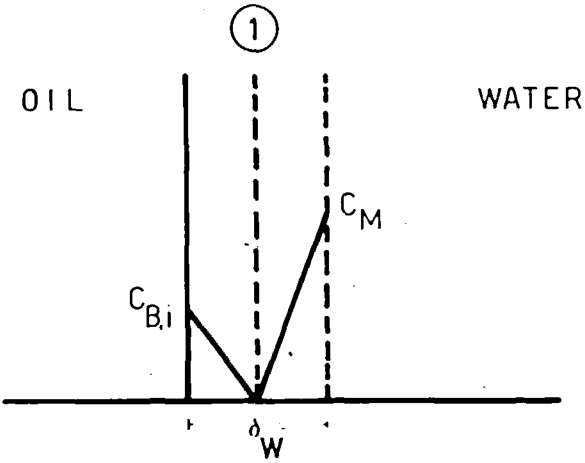


FIGURE 33. Concentration profile for a fast irreversible reaction occurring on a reaction plane① localized on the aqueous side of the interface. $\delta_w$ is the aqueous film thickness.

$$N = \frac{D_b C_{B,i}}{\delta_w} \left(1 + \frac{D_m C_M}{D_b C_{B,i}}\right) \tag{85}$$

where $D_b$ and $D_m$ are the diffusitivies of B and M in the aqueous film of thickness $\delta_w$, $C_M$ is the metal concentration in the bulk and $C_{B,i}$ is the concentration at the interface of the extracting reagent. The situation is schematically represented in Figure 33.

Since in absence of chemical reaction, it is

$$N = \frac{D_b}{\delta_w} (C_{B,i} - 0) \tag{86}$$

by comparing Equations 85 and 86 it follows

$$\frac{\text{mass transfer coefficient with chemical reaction}}{\text{mass transfer coefficient without chemical reaction}} = 1 + \frac{D_m C_M}{D_b C_{B,i}} \tag{87}$$

i.e., the presence of a fast irreversible chemical reaction increases the mass-transfer coefficient.

When instead the penetration theory is used, it has been shown[63] that the left term of Equation 87 becomes equal to

$$1 + \sqrt{\frac{D_m}{D_b}} \cdot \frac{C_M}{C_{B,i}}$$

This means that when the diffusitivies of M and B are equal, the penetration and the two-films theories give the same results. Therefore, the simpler two-films theory can be used with good reliability.

A different approach to solvent extraction of metal species in the presence of a fast chemical reaction has been proposed in Reference 66 by assuming that the reaction zone consists of a small volume adjacent to the interface. Starting with a general model developed by Astarita,[64] based on the two-films theory, which leads to the following expression for the interfacial flux

$$N = \sqrt{2D\int_{\text{bulk}}^{i} r(B)\,d\,B} \tag{88}$$

where bulk and i refer to the bulk aqueous phase and to the interface and r(B) is the rate of reaction with respect to B, the treatment has been extended to an extraction reaction of the type

$$M^{n+} + n\,HB \underset{K_2}{\overset{K_1}{\rightleftharpoons}} M\,B_n + n\,H^+ \tag{89}$$

which is assumed to proceed with the following rate, r,

$$r = K_1[M^{n+}][HB]^n - K_2[MB_n][H^+]^n \tag{90}$$

Since the reaction takes place through the whole aqueous reaction zone, Equation 90 must be integrated and then inserted into Equation 88. By considering that according to the two-films theory the system is in the stationary state and by introducing a suitable approximation based on the low aqueous bulk concentration of both HB and $MB_n$, the following two equations have been derived for the direct and reverse fluxes at time zero, $\vec{N}_0$ and $\overleftarrow{N}_0$, when the valence of the extracted metal ion is two:

$$\vec{N}_0 = -\left(\frac{[\overline{HB}]}{K_{D,HB}}\right)^{3/2}\sqrt{\frac{1}{6}D_{HB}K_1[M^{2+}]} \tag{91}$$

$$\overleftarrow{N}_0 = \frac{[\overline{MB_2}][H^+]}{K_{D,MB_2}}\sqrt{D_{MB_2}K_2} \tag{92}$$

where $K_{D,HB}$ and $K_{D,MB_2}$ are the organic/aqueous partition coefficients of the extracting reagent and the metal complex, respectively, and $D_{HB}$ and $D_{MB_2}$ represent the diffusitivies in the reaction zone.

Equations 91 and 92 have the advantage over Equation 85 in containing only measurable quantities (no interfacial concentrations are present). Their validity can be therefore tested by comparing their predictions with experimental data. In this way, it has been shown that the developed model is not always very representative of extraction kinetics data. In fact, some experimental evidence has indicated that the reaction orders with respect to $[M^{2+}]$ and $[H^+]$ are in contradiction with equation 91.

### 2. *The Reaction Takes Place at the Interface*

When the fast chemical reaction occurs at the interface, the metal species, the extracting reagent, as well as the reaction products will be in equilibrium there. It follows then that for an extraction of the type

$$M^{2+} + 2\overline{HB} \rightleftharpoons \overline{MB_2} + 2H^+ \tag{93}$$

the equilibrium law at the interface

$$K_{eq} = \frac{[MB_2]_i[H^+]_i^2}{[M^{2+}]_i[HB]_i^2} \tag{94}$$

has to be always respected. If a steady-state condition is assumed, the rates of mass transport of each species to and from the interface must be equal. This means that

$$N = \beta_{H^+}([H^+]_i - [H^+]) = 2\beta_{M^{2+}}([M^{2+}] - [M^{2+}]_i)$$
$$= \beta_{HB}([\overline{HB}] - [HB]_i) = 2\beta_{MB_2}([MB_2]_i - [\overline{MB_2}]) \tag{95}$$

The interfacial concentrations appearing in Equation 94 could then be expressed, by using Equation 95 as function of the flux N, the mass-transfer coefficients

$$\beta_{H^+}, \beta_{M^{2+}}, \beta_{HB}, \beta_{MB_2}$$

and the bulk concentrations of the species. However the resulting equation is not easily analytically solvable. In fact the flux will appear in it raised to the third power and the mass-transfer coefficients of the individual species are generally unknown. Nevertheless with the assumption that the mass-transfer coefficients for all species are equal, and by taking advantage of the fact that the experimental conditions to which the equation refers often allow neglecting the contribution of one or more species, the resulting equation for the mass transfer can be made explicit in terms of measurable quantities. For example in Reference 67 it has been shown that for the initial extraction of $Cu^{2+}$ by hydroxyoximes, when the hydrodynamic conditions are so chosen that the rate is controlled only by diffusion, and with the further simplification of considering linear concentration gradients through the two stagnant interfacial films i.e., $\beta = D/\delta$, the implicit equation becomes

$$N_0 = \frac{D_{HB}}{2\,\delta_{org}}[\overline{HB}] \tag{96}$$

In this case the rate is proportional to the extractant concentration and depends only on the degree of stirring of the organic phase. On the other hand as reaction (93) proceeds, $[H^+]$ cannot be neglected and the rate of extraction becomes smaller. In this case the rate law becomes

$$N_0 = \frac{2K_{eq}D_{MB_2}[M^{2+}][\overline{HB}]^2}{\delta_{org}[H^+]^2} \tag{97}$$

and the rate is now dependent also on the concentrations of $M^{2+}$ and $H^+$. Both Equations 96 and 97 have been found in agreement with the experimental data in Reference 67.

It is interesting to notice that when the metal concentration is very low compared to those of $\overline{HB}$ and $H^+$, the rate equation becomes

$$N_0 = \frac{2K_{eq}\,D_{M^{2+}}\,D_{MB_2}[M^{2+}][\overline{HB}]^2}{D_{M^{2+}}\,\delta_{org}[H^+]^2 + K_{eq}\,D_{MB_2}\,\delta_w[\overline{HB}]^2} \tag{98}$$

This equation is formally identical to Equation 54, derived in a kinetic regime at a saturated interface for a metal of valence 2, when only the dependence on the concentrations is considered. In this case the possibility of distinguishing between the two controlling regimes obviously lies in the fact that Equation 98 must show a dependence on the stirring speed of the aqueous and organic phases. In fact, both $\delta_{org}$ and $\delta_w$ vary with the Reynolds numbers of the two fluids.

An equation similar to Equation 96 has also been found to hold for the extraction of zinc at a high concentration by dithizone.[14] In this case the term $D_{HB}/\delta_{org}$ was replaced by the mass-transfer coefficient. The authors have also shown that the mass-transfer coefficient was varying as expected, in a linear way with the stirring speed of the phases in their constant interfacial area cell. The proportionality is shown in Figure 2. As a concluding remark, it is possible to state that when the extraction kinetics are controlled by mass transport and the chemical reaction between the metal species and the extractant is fast and occurs at the interface, the solution of the equation which correlates the flux through the interface with the mass-transfer coefficients and the concentrations of the reagents in the bulk is strictly dependent on the possibility of introducing simplifying assumptions. These simplifications are specific for each case, and consequently general simplifying criteria cannot be given. Fortunately in most of the experimental works, legitimate simplifications can be introduced, and representative equations for the extraction kinetics have often been derived.

Obviously, as for the case of a fast reaction in an aqueous zone adjacent to the interface, the overall effect of the fast interfacial reaction is to accelerate the kinetics of extraction compared to that expected for a simple distribution process between the aqueous phase and a pure diluent. This effect is somehow equivalent to a decrease in the thickness of the diffusion films which are responsible for the mass-transfer resistances in agitated extractors. This fact can be alternatively formulated by saying that the presence of a fast chemical reaction causes a reduction of the overall mass-transfer resistance.

## VII. DIFFUSIONAL-KINETIC MIXED REGIME

As we have already mentioned in Sections II and III, in a solvent extraction biphasic system which is progressively stirred at higher stirring speeds, the transition from a pure diffusional regime (which is predominant at low stirring rates) to a pure kinetic one (which can be predominant at high stirring rates) occurs in a continuous way. The two previously described regimes are then limiting cases and an intermediate region can exist where both the process of diffusion of the species through the diffusion films and the slowness of the chemical reaction have comparable effects on the overall rate of solvent extraction.

Since the diffusion process can be accelerated by stirring and through the reduction of the thickness of the diffusion films $\delta_w$ and $\delta_{org}$, and the velocity of the chemical reaction can be altered by varying the concentrations of the reactants and their products, the range of experimental conditions which determine the nature of the extraction regime will be specific for each chemical system and will depend on the hydrodynamic conditions occurring in the vessel where the extraction takes place. The analytical description of the extraction kinetics of a system where the rate of extraction occurs in a mixed regime is in general rather complicated. In fact, all of the difficulties associated with both the kinetics and diffusional regimes previously reported are simultaneously met. To fully describe the kinetics, it is in fact necessary to simultaneously solve the equations of diffusion and those of chemical kinetics. Further, the chemical reaction can be of two types, namely: homogeneous, where the chemical changes occur in the entire volume of a phase, and heterogeneous, where the chemical changes take place at the interface. The description of a diffusion regime coupled to a homogeneous chemical reaction is particularly complicated since the rate of matter production has to appear as a source term in the diffusional differential equation obtained from a shell mass balance which must then be integrated. However, we will not describe this type of coupling since in practical solvent extraction systems the bulk volumes are always sufficiently agitated. Therefore, only the contribution of slow bulk chemical reactions, when they are present, can be left to control the extraction rate in addition to interfacial diffusion processes.

On the other hand, when the slow chemical reactions are heterogeneous, i.e., interfacial, the rate of the chemical reactions will only appear in the boundary conditions of the differential diffusion equations. This type of situation is more likely to be met in solvent extraction kinetics where a slow interfacial chemical reaction appears as a boundary condition to the slow diffusion of the reacting species and their products through the interfacial stationary films. Although this case is mathematically less complex than the homogeneous one, the solution of the problem always requires that detailed information is available on the boundary conditions, i.e., on the rates at which the chemical species appear and disappear at the interface. This means that the chemical kinetics at the interface should be known in detail from separate experiments carried out in a pure kinetic regime. In fact, although the problem has some similarities with that of a slow mass transfer associated with a fast chemical reaction as previously described, where the equilibrium law was set up as an interfacial boundary condition of the diffusion of the species, here the further complication exists that the interfacial chemical rate laws cannot be *a priori* known. This difficulty has sometimes been bypassed either by assuming that the interfacial rate laws could be inferred from the reaction stoichiometry or by trying to derive information on the interfacial reaction rate through the fit of analytical solutions of equations, based on models taking into account both diffusion and chemical reactions to experimental data obtained in a mixed regime. However, both of these procedures can be dangerous and can easily lead to erroneous interpretations. In fact, very rarely can the rate laws be correctly derived from equilibrium stoichiometric considerations and when too many variables, i.e., rate constants and diffusional parameters, are simultaneously adjusted to fit the experimental data, very many alternative models can lead to the same explanation. This means that it can be quite difficult to differentiate between the contribution of the diffusional component and that of the chemical reaction to the total mass-transfer resistance. It is therefore of primary importance that the boundary conditions of the diffusion equations, i.e., the interfacial rate laws, are derived by separate, suitable experiments.

The influence on the extraction kinetics of both diffusion and a slow chemical reaction has been analyzed theoretically in Reference 68 for diffusion in two semiinfinite media with no stationary conditions when the mechanism of the interfacial reaction is the following,

$$M + z\bar{B} \rightleftharpoons \overline{MB_z} \qquad (99)$$

where M represents the metal species, insoluble in the organic phase, B and $MB_z$ are the organic reagent and the metal-reagent complex, respectively, both insoluble in the aqueous phase, and K and $K_{eq}$ are the forward rate constant and the biphasic equilibrium constant of the reaction. However, the solution of the diffusion equations in only one dimension (x axis) for the following boundary conditions

$$x = 0 \quad \text{(interface)}$$

$$D_M \frac{dC_M}{d\,x} = -z\, D_B \frac{dC_B}{d\,x} = D_{MB_z} \frac{dC_{MB_z}}{d\,x}$$

$$= K(C_M C_B^z - C_{MB_z}/K_{eq}) \qquad (100)$$

and the initial conditions ($t = 0$)

$$\left.\begin{array}{ll} x > 0 \text{ (aqueous phase)}, & C_M = C_{M,0} \\ x < 0 \text{ (organic phase)}, & C_B = C_{B,0}, C_{MB_z} = 0 \end{array}\right\} \qquad (101)$$

has not been analytically obtained by the authors because of the nonlinear boundary conditions. The authors instead report the analytical solution which can be derived with the assumption that the concentration of the metal is always negligible with respect to that of the extractant. Since in this case the interfacial reaction is pseudo first order, the solution for the interfacial flux is

$$N = K\,\eta\, C_{M,0}\, C_{B,0}^z \qquad \text{(102}$$

with

$$\eta = \exp(\tau^2)\,\mathrm{erfc}\,(\tau);\ \tau = K\, C_{B,0}^z \sqrt{t/D};\ \frac{1}{\sqrt{D}} = \frac{1}{\sqrt{D_M}} + \frac{1}{K_{eq}\, C_{B,0}^z \sqrt{D_{MB_z}}}$$

The dependence of $\eta$ on t indicates that the equation also holds for nonstationary states. The average flux during time t is given by

$$N_{av} = K\eta_{av}\, C_{M,0}\, C_{B,0}^z \qquad (103)$$

with

$$\eta_{av} = \frac{1}{\tau^2} \int_0^{\tau} 2\,\tau' \exp(\tau'^2)\,\mathrm{erfc}(\tau')\,d\,\tau' \qquad (104)$$

The relationship between $\eta_{av}$ and $\tau$ is reported in Figure 34.

The mixed regime can be identified with the region where $0.1 < \tau < 10$, while for $\tau < 0.1$ and $\tau > 10$ the extraction proceeds in kinetic and diffusion controlled regimes, respectively. In the region where the regime can be considered only kinetic or only diffusional Equation 102 can be integrated to obtain the number of moles of M extracted per unit area as a function of time, m:

$$m = K\, C_{M,0}\, C_{B,0}^z\, t \qquad \text{for } \tau < 0.1 \qquad (105)$$

$$m = 2C_{M,0} \sqrt{Dt/\pi} \qquad \text{for } \tau > 10 \qquad (106)$$

Therefore Equations 105 and 106 allow differentiation between the two regimes from the different dependence of m on t.

The authors also report a numerical solution to the diffusion equation for a second order interfacial reaction with the assumptions

$$z = 1, C_{M,0} = C_{B,0}, D_M = D_B = D_{MB_z} = 10^{-5}\,\mathrm{cm}^2/\mathrm{sec}, K_{eq}\, C_{B,0} = 1$$

and show that the results are not very different from those obtained for the pseudo first order reaction.

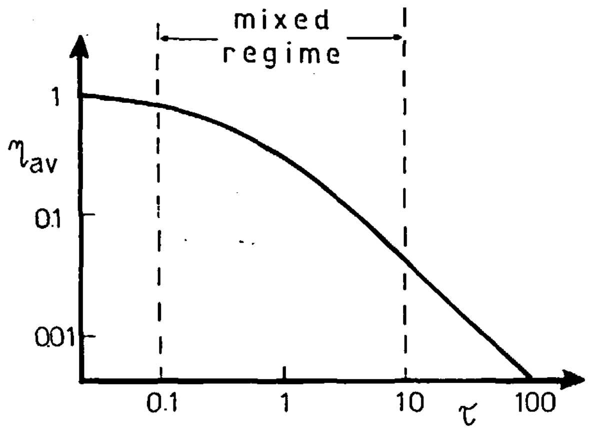


FIGURE 34. Relationship between $\eta_{av}$ and $\tau$. (From Nakashio, F., Tsuneyuki, T., Inoue, K., and Sakai, W.,Vol. 2, Proc. Int. Solv. Extr. Conf., ISEC 71, Society Chemical Industry, 1971, 78. With permission.)

The same authors later reported a somewhat different approach[69] where reactions in the aqueous phase and diffusion processes have been coupled. By studying the extraction of $Cu^{2+}$ with benzoylacetone in a Lewis-type cell, they arrived at the conclusion that the rate law

$$V_0 = \frac{K_1 K_a}{K_{D,R}} \frac{[Cu^{+2}][\overline{HB}]}{[H^+]} \tag{107}$$

which they expected to hold in the case of metal ion extraction by acidic chelating extractants with a slow substitution step in the aqueous phase (see Section V, Equation 11a) could not explain their experimental data. These were in fact characterized by:

1. A reaction order with respect to $[H^+]$ equal to $-1/2$ at low pH and 0 at high pH
2. A reaction order with respect to $[Cu^{2+}]$ equal to ½ at low pH and 1 at high pH.

The authors then inferred that their data were not obtained in a kinetic regime and that diffusion had to be properly considered. To take into account the diffusion processes accompanied by the reaction between $Cu^{2+}$ and the anion of benzoylacetone (HB) in the aqueous phase, they have applied the one-dimensional diffusion equation for a nonstationary state in the diffusion aqueous film of thickness $\delta_w$, obtaining the following basic equations:

$$D_{HB}\left(\frac{d^2[\overline{HB}]}{dx^2}\right) - \frac{K_1 K_a}{[H^+]}[Cu^{2+}][HB] = 0 \tag{108}$$

$$D_{Cu^{2+}}\left(\frac{d^2[Cu^{2+}]}{dx^2}\right) - \frac{K_1 K_a}{[H^+]}[Cu^{2+}][HB] = 0 \tag{109}$$

with the following boundary conditions

$$x = 0, [HB] = [HB]_i, d[Cu^{2+}]/dx = 0$$

$$x = \delta_w, [HB] = 0, [Cu^{2+}] = [Cu^{2+}]_0 \tag{110}$$

Since an analytical solution of these differential equations was not available, the authors have taken from the literature an approximate solution from which they could obtain, under suitable conditions, the two following equations for the initial rate:

$$V_0 = [HB]_i \sqrt{\frac{D_{HB} K_1 K_a [Cu^{2+}]_0}{[H^+]}} \tag{111}$$

$$V_0 = \bar{\beta}\, 2 \frac{D_{Cu^{+2}}}{D_{HB}} [Cu^{2+}]_0 \tag{112}$$

Equation 111 obtained for a pseudo first order reaction, could then explain the data at low pH, while Equation 112 referring to a situation where the rate was diffusion controlled, explained the data at high pH.

Another approach to the study of nonsteady-state diffusion accompanied by slow chemical reaction has been developed in References 45 and 70 and mainly applied to explain the kinetics of mass transfer of mineral acids between water and organic solvents.[45,70-72] However, the approach seems to be sufficiently general to be applied also to the extraction kinetics of metal species. The method is based on the principle that the one-dimensional diffusion equation for a nonstationary state

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \tag{113}$$

could be analytically solved also in the presence of interfacial slow chemical reactions. By analytically solving Equation 113 using Laplace transforms and assuming boundary conditions which depend on the postulated slow reaction mechanism, an equation has been obtained which correlates the number of moles of the extracted species m to time. In the case of a slow interfacial irreversible chemical reaction of the first order with rate constant K, the boundary condition is

$$D \frac{dC}{dx} = KC \tag{114}$$

for x = 0, where C is the concentration of the extractable species and D is diffusivity. The following solution of the differential equation is then derived:

$$m = 2C_0 A D^{1/2} \pi^{-1/2} t^{1/2} + C_0 A \frac{D}{K} [\exp(K^2 t/D) \mathrm{erfc}(K t^{1/2}/D^{1/2}) - 1] \tag{115}$$

where $C_0$ is the bulk concentration of the species to be extracted, A is the interfacial area, and K is the rate constant of the irreversible reaction

$$A \longrightarrow B$$

When the rate constant has a high value, that is the reaction is quite fast, it follows

$$m = 2C_0 A D^{1/2} \pi^{-1/2} t^{1/2} \tag{116}$$

and the kinetics of transfer are controlled only by diffusion. Equation (116) has the same form as equation 106 previously reported for a diffusional regime. When, on the other hand, the rate constant is small, that is the reaction is slow, the analysis of Equation 115 indicates that the extraction is retarded by the reaction and is characterized by a transition with time from a kinetic to a diffusional regime, with an intermediate region where the transfer kinetics proceeds in a mixed regime. In fact, the second term of Equation 115 becomes time independent only for large t values. In this case, for small K and high t, Equation 115 becomes

$$m = 2C_0\,A\,D^{1/2}\,\pi^{-1/2}\,t^{1/2} - \frac{C_0\,A\,D}{K} \qquad (117)$$

This means that when m is plotted against $\sqrt{t}$, the plot is linear only for high t, showing an intercept on the $\sqrt{t}$ axis equal to $t_*^{1/2}$; this intercept can allow the calculation of the rate constant, i.e.,

$$K = D^{1/2}\,\pi^{1/2}/2\,t_*^{1/2} \qquad (118)$$

The situation is graphically exemplified in Figure 35, which shows that when the transfer kinetics are only diffusion controlled a straight line is obtained. When, on the other hand, there is an initial chemical controlled region followed by a diffusional controlled one, the straight line does not pass through the origin, and it is possible to evaluate the rate constant. A very similar line of reasoning has also been followed by the authors for the case of reactions which are reversible and occur with more complex mechanisms.[70] However, the derived equations, which are more complicated, lead to similar analytical solutions, and all of the experimental results obtained up to this point have been sufficiently well explained only with first-order reversible and irreversible reactions. This method has been successfully applied to experimental data obtained with the "short-time-phase-contacting method", described in Section IV, which allows the experimental determination of the mass transfer during the first few seconds of the extraction process.

The approach to the mixed regime up to this point refers to a nonstationary situation, that is for conditions where the fluxes through the interface are time dependent. When, on the other hand, a steady-state situation is assumed, the overall mathematical description of the extraction kinetics becomes simpler, and cases involving more complicated interfacial slow chemical reactions have been treated. One way of facing the problem of a steady-state mass transfer associated with a slow interfacial chemical reaction can be in terms of mass-transfer resistances.[73] This means that the overall mass-transfer resistance R can be considered as the sum of the two diffusional resistances (previously defined) $R_w$ and $R_{org}$ and the interfacial resistance arising from the slow chemical reaction, $R_{ch}$, i.e.,

$$R = R_{org} + R_w + R_{ch} \qquad (119)$$

In general, in order to simplify the problem, the theoretical treatments have been applied to experimental conditions where either $R_{org}$ or $R_w$ in Equation 119 are negligible. In References 8 and 14, the steady-state mixed regime has been treated with reference to the specific case of the extraction of zinc by chloroform and carbon tetrachloride solutions of dithizone, HDz. The authors have shown how $R_{ch}$ can be made explicit in terms of concentrations and rate constant of the slow interfacial reaction

$$Zn^{2+} + Dz^- \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ZnDz^+ \qquad (120)$$

The two other interfacial reactions, i.e., dissociation of HDz and formation of the final complex are assumed as fast instead. The overall rate equation describing the mixed regime, where both transport processes and interfacial reactions contribute to the extraction kinetics, is derived by considering that the transport equations

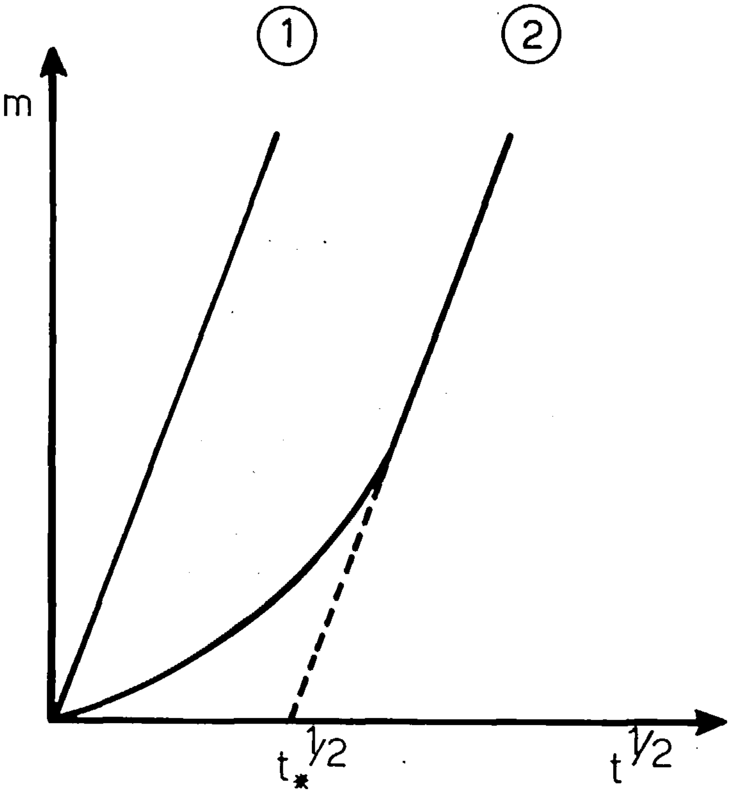


FIGURE 35. Number of moles of an extractable species m transferred into an extracting organic phase as function of the square root of time, $t^{1/2}$. ① represents a process always controlled by diffusion, ② represents a process first controlled by a slow chemical reaction and then diffusion controlled. From the intercept, $t_*^{1/2}$, it is possible to evaluate the rate constant of the reaction. The region of curvature is the mixed regime zone.

$$\vec{N} = \frac{d[\mathrm{Zn\,Dz_2}]}{dt}\,\frac{V}{A} = \tfrac{1}{2}\beta_{\mathrm{HDz}}([\overline{\mathrm{HDz}}]-[\mathrm{HDz}]_i) =$$

$$\beta_{\mathrm{Zn}}([\mathrm{Zn}]-[\mathrm{Zn}]_i) = \beta_{\mathrm{ZnDz_2}}([\mathrm{ZnDz_2}]_i - [\overline{\mathrm{ZnDz_2}}]) \qquad (121)$$

(where the gradient of the [H⁺] is neglected) and the interfacial rate expression

$$\vec{N} = K_1\,\frac{[\mathrm{Zn}]_i[\mathrm{HDz}]_i}{[\mathrm{H^+}]_i} - K_{-1}\,\frac{[\mathrm{ZnDz_2}]_i[\mathrm{H^+}]_i}{[\mathrm{HDz}]_i} \qquad (122)$$

must simultaneously hold. $\vec{N}$ represents the interfacial flux of zinc, $\beta$ the mass-transfer coefficients, A the interfacial area, and V the volume of the aqueous or organic phase (they are equal).

The resulting equation is then simplified by assuming that all the mass-transfer coefficients of the species have the same value $\beta$, and by considering only initial rates ($t = 0$). The following final rate equation is then obtained:

$$\vec{N}_0 = \frac{[\overline{HD_z}]}{\frac{2}{\beta} + \frac{[H^+]}{K_1[Zn^{2+}]_i}} \qquad (123)$$

The correlation with the resistances is then obtained by using the further relationship

$$\vec{N}_0 = \tfrac{1}{2}\bar{\beta}[\overline{HDz}] \qquad (124)$$

derived for a pure diffusional regime and which also holds when both the mass transport and the chemical reaction are rate limiting. $\bar{\beta}$ represents the overall mass-transfer coefficient. Making the right hand terms of Equations 123 and 124 equal and introducing the linear relationship between the transport coefficient $\beta$ and the stirring speed $n_w$ inside the constant interfacial area cell,

$$\beta = \text{const} \cdot n_W \qquad (125)$$

the following correlation is obtained

$$\frac{1}{\bar{\beta}} = \frac{1}{\text{const} \cdot n_W} + \frac{[H^+]}{2K_1[Zn^{2+}]_i} \qquad (126)$$

which can be alternatively written as

$$R = R_W + R_{ch} \qquad (127)$$

by setting

$$R = 1/\bar{\beta},\ R_W = 1/\beta,\ R_{ch} = [H^+]/2K_1[Zn^{2+}]_i$$

When the experimental R values are plotted against $1/n_w$, straight lines are obtained with an intercept on the ordinate axis which equals $R_{ch}$. This chemical resistance increases by decreasing the metal concentration. An example of such a plot is shown in Figure 36. This treatment nicely explains the experimental fact that by increasing the metal concentration, i.e., $[Zn^{2+}]_i$ in Equation 126 the extraction kinetics becomes diffusion controlled. In fact, at high metal concentrations the second right-hand term of Equation 126 tends to zero. It is worth noticing that according to this model the mixed diffusional-kinetic regime can be identified with those conditions where $R_w$ and $R_{ch}$ are never negligible with respect to each other. These conditions have been shown to depend both on the concentration of the metal to be extracted and the stirring efficiency of the biphasic system.

Another approach to the mixed regime based on the steady-state assumption has been developed in Reference 44 for the specific case of an interfacial reaction between $Cu^{2+}$ and an acidic reagent of the hydroxyoxime family, HB. In this approach, the following forward rate law

$$N_0 = K\frac{[Cu^{2+}]_i^l[HB]_i^m}{[H^+]_i^n} \qquad (128)$$

has been assumed to describe the kinetics at the interface.

In Equation 128 K is the rate constant and l, m, and n are the reaction orders. The aim of this treatment is to try to show how the coupled influence of mass transfer and chemical reaction generates apparent reaction orders which vary both with the different hydrodynamic conditions which are specific for a given extraction apparatus and

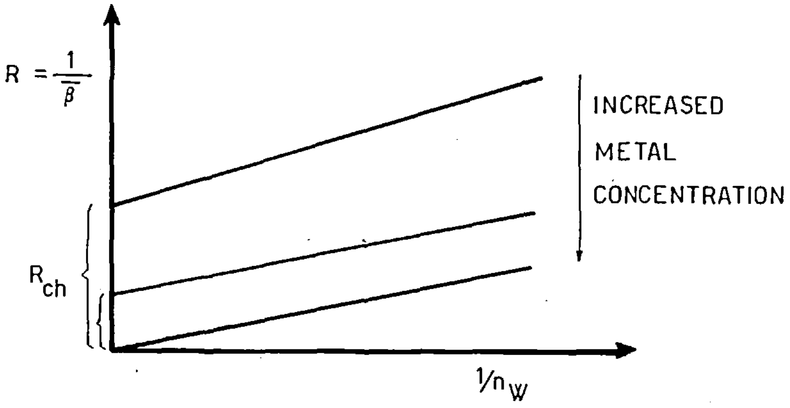


FIGURE 36. Linear relationship between the total mass-transfer coefficient $\bar{\beta}$ and the stirring speed of the phases. At very high $n_w$ values $1/n_w \cong 0$ and $R = R_{ch}$ independent of the stirring speed of the phases. (From Nitsch, W. and Kruis, B., *J. Inorg. Nucl. Chem.*, 40, 857, 1978. With permission.)

the composition of the system. With the usual assumption that the concentration gradients are all confined in the two stagnant interfacial films and that $Cu^{2+}$ and $H^+$ ions can only exist in the water phase, the transport equations

$$N_0 = \beta_{Cu}([Cu]-[Cu]_i) = -\tfrac{1}{2}\beta_H([H]-[H]_i) = \tfrac{1}{2}\beta_{HB}([\overline{HB}]-[HB]_i) = -\beta_{CuB_2}([\overline{Cu\,B_2}]-[Cu\,B_2]_i) \qquad (129)$$

and the interfacial rate Equation 128 have been solved with respect to $N_0$. To overcome the difficulty of finding an explicit solution for $N_0$, the equation obtaind by combining Equations 128 and 129, i.e.,

$$N_0 = K\,\frac{[Cu]^l\,[\overline{HB}]^m}{[H^+]^n}\cdot F \qquad (130)$$

where

$$F = \frac{\left(1-\frac{N_0}{\beta_{Cu}[Cu]}\right)^l\left(1-\frac{2N_0}{\beta_{HB}[\overline{HB}]}\right)^m}{\left(1+\frac{2N_0}{\beta_H[H^+]}\right)^n} \qquad (131)$$

has been simplified by assuming that the mass-transfer coefficients of all species have the same value, $\beta$, and $l = m = n = 1$.

Also in this case, from the qualitative analysis of Equation 131, it appears that F is a function of the hydrodynamic conditions of the system, through the variation of the mass-transfer coefficient $\beta$, the concentrations of the reactants, as well as the value of the initial flux $N_0$. Therefore, the authors explain in this way the different apparent and variable reaction orders with respect to $[Cu^{2+}]$, $[\overline{HB}]$, and $[H^+]$ which have been found in the literature for the extraction of copper by hydroxyoximes. In order to make the treatment quantitative, Equation 130 has been rearranged to a second degree equation in the variable $y = N_0/[Cu] = ([Cu] - [Cu]_i)/[Cu]$:

$$\frac{\frac{K}{\beta}(1 - y)(x_1 - 2y)}{y(x_2 - 2y)} = 1 \qquad (132)$$

with $x_1 = [\overline{HB}]/[Cu]$ and $x_2 = [H^+]/[Cu]$.

The variable y, proportional to the rate of extraction, has then been expressed as a function of the normalized concentrations $x_1$ and $x_2$ for different values of $K/\beta$ to demonstrate that different and variable apparent reaction orders, i.e., the slopes of the curves log y vs. log $x_1$, log y vs. log $x_2$, and log y vs. log[Cu], can be obtained providing $x_1$, $x_2$, [Cu] and $K/\beta$ are varied. In particular, in order to associate the values of $K/\beta$ with the different hydrodynamic conditions present in the various experimental works, the authors have assumed that $K/\beta = 0.1$ when the falling drop technique was used, $K/\beta = 0.01$ when the constant interfacial area Lewis-type cell was used, and $K/\beta = 0.001$ when highly agitated extraction tanks were used to study the solvent extraction kinetics. An example of the curves calculated by Equation 132 is reported in Figure 37. The apparent reaction order with respect to $[H^+]$ is here seen to become equal to $-1$ (that expected for a pure kinetic regime) only at the highest acidities, when the phases are vigorously stirred ($K/\beta = 0.001$) and at low values of extractant concentration (Figure 37a). The rate of extraction instead becomes independent of $[H^+]$ when the extractant concentration is high and the system is slowly stirred ($K/\beta = 0.1$) (Figure 37b). These results as well as the other predictions derived from Equation 132 have been found to explain, at least qualitatively, the different and often variable reaction orders reported by various authors who have studied the kinetics of copper extraction by hydroxyoximes in different concentration ranges and using experimental techniques characterized by different hydrodynamic features. According to this type of treatment, the mixed regime is then characterized by that set of hydrodynamic and concentration conditions which generate apparent reaction orders which are intermediate between those expected for a purely kinetic regime (F = 1 in Equation 130) and a purely diffusional regime. With reference to the exemplary Figures 37a and 37b, the region of curvature of lines represents the mixed regime. The region where the curves have slopes equal to $-1$ and 0 are represent instead pure kinetic and diffusional regimes, respectively.

The mixed regime produced by the simultaneous presence of slow interfacial chemical reactions of the type described in Section V.A.1.c and slow diffusion has been discussed in References 74 through 76 considering the influence of both the forward and reverse reactions. The flux equation has also then been integrated in order to obtain a concentration vs. time equation which could cover the whole duration of the extraction reaction. The treatment has been developed for the specific case of the extraction of trivalent metal cations by the acidic reagent dinonylnaphthalenesulfonic acid, which is a strong surfactant and is strongly polymerized in low dielectric constant organic diluents. The mechanism of the extraction reaction and the rate law have been first determined in hydrodynamic conditions where the extraction kinetics could be assumed to proceed in a kinetic regime. The following set of interfacial chemical reactions

$$M^{3+} + 3(HB)_{ad} \underset{K_3}{\overset{K_1'}{\rightleftharpoons}} (MB_3)_{ad} + 3H^+ \qquad (133)$$

$$(MB_3)_{ad} + (\overline{HB})_q \underset{K_1'}{\overset{K_2}{\rightleftharpoons}} \overline{MH_{q-3}B_q} + 3(HB)_{ad} \qquad (134)$$

leading to the following rate equation

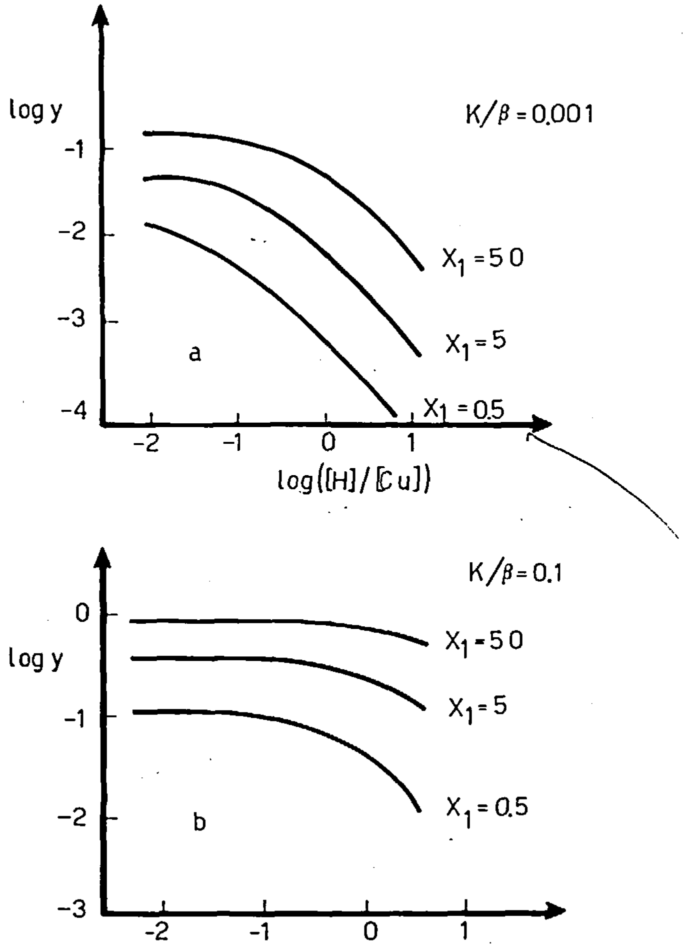


FIGURE 37. Logarithmic plot of the rate of extraction y vs. normalized hydrogen concentration [H]/[Cu] at different extractant concentrations. $X_1 = [\overline{BH}]/[Cu]$. (From Perez de Ortiz, E. S., Cox, M., and Flett, D. S., Paper 4c in Proc. Int. Solv. Extr. Conf., ISEC 77, Toronto, 1977. With permission.)

$$N\frac{A}{V} = \frac{K_1[M^{3+}][\overline{(HB)_q}] - \bar{K}_1 K_R[H^+]^3[\bar{M}]}{[\overline{(HB)_q}] + K_R[H^+]^3} \qquad (135)$$

where $K_1 = K_1'[HB]_{ad}$, $\bar{K}_1 = \bar{K}_1'[HB]_{ad}$ (the concentration of HB adsorbed on the interface is constant), $[\bar{M}] = [\overline{MH_{q-3}B_q}]$, q = extractant polymerization number, and $K_R = K_3/K_2q$, have been so identified. When the hydrodynamic conditions were such that the rate of the transfer process was controlled also by the diffusion to and from the interface of reagents and products, Equation 135 assumed this time valid only at the interface, had to be written as

$$N\frac{A}{V} = \frac{K_1[M^{3+}]_i[(HB)_q]_i - \bar{K}_1 K_R[H^+]_i^3[\bar{M}]_i}{[(HB)_q]_i + K_R[H^+]_i^3} \qquad (136)$$

and solved together with the mass-transfer equations

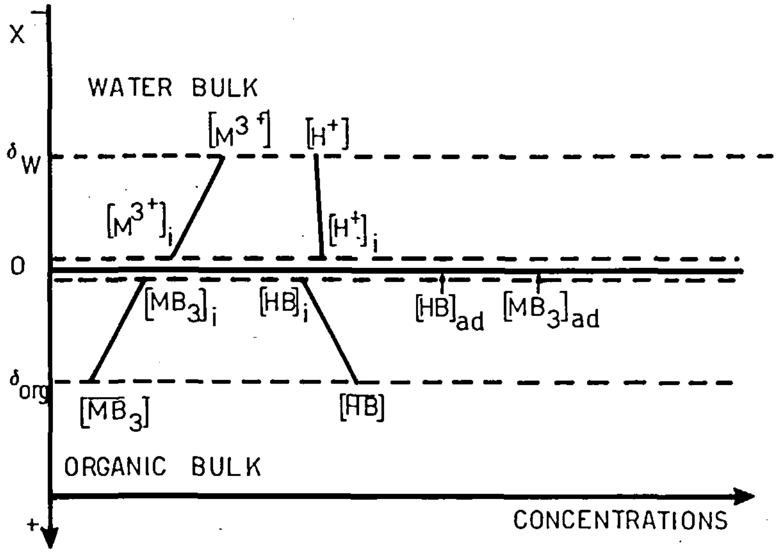


FIGURE 38. Schematic representation of the linear concentration profiles in References 74 to 76. The interface is localized at x = 0, where the slow chemical reactions occur.

$$N = \beta_{M^{3+}}([M^{3+}]-[M^{3+}]_i) = -\frac{1}{3}\beta_{H^+}([H^+]-[H^+]_i) = \beta_{(HB)_q}([\overline{HB})_q]-[(HB)_q]_i) = -\beta_{\overline{M}}([\overline{M}]-[\overline{M}]_i) \qquad (137)$$

to obtain an equation for the interfacial flux of the metal in terms of bulk concentrations, rate constants, and mass-transfer coefficients. By considering a linear concentration gradient through the aqueous and organic stagnant films, as shown in Figure 38, that is by setting

$$\beta_{M^{3+}} = \frac{D_M}{\delta_w}, \beta_{H^+} = \frac{D_H}{\delta_w}, \beta_{(HB)_q} = \frac{D_{(HB)_q}}{\delta_{org}}, \beta_{\overline{M}} = \frac{D_{\overline{M}}}{\delta_{org}}$$

and since the experimental conditions allowed the neglecting of the contribution of the hydrogen ion gradient, the following equation has been obtained for the flux N from Equations 136 and 137.

$$N\frac{A}{V} = \frac{K_1\left([M^{3+}] - \frac{N\delta_w}{D_M}\right)\left([(\overline{HB})_q] - \frac{N\delta_{org}}{D_{(HB)_q}}\right) - K_R\overline{K}_1[H^+]^3\left([\overline{M}] - \frac{N\delta_{org}}{D_{\overline{M}}}\right)}{\left([(\overline{HB})_q] - \frac{N\delta_{org}}{D_{(HB)_q}}\right) + K_R[H^+]^3} \qquad (138)$$

It has to be noticed that in this case the determination of the mechanism of the interfacial reaction by "ad hoc" experiments has led to a rate equation which is different from that which could be hypothesized from the simple extraction stoichiometry.

Equation 138 when only the forward reaction is present, i.e., at time zero, can in this case also be easily rearranged into a second degree equation:

$$aN^2 + bN + c = 0 \qquad (139)$$

where a, b, and c are numerical coefficients, the values of which depend on both the hydrodynamics and the chemical composition of the system in the following way:

$$a = \frac{\delta_{org}}{D_{(HB)_q}}\left(\frac{K_1\delta_w}{D_M} + \frac{A}{V}\right) \tag{140}$$

$$-b = \frac{A}{V}([\overline{HB})_q] + K_R[H^+]^3) + K_1\left(\frac{\delta_{org}[M^{3+}]}{D_{(HB)_q}} + \frac{\delta_w[(\overline{HB})_q]}{D_M}\right) \tag{141}$$

$$c = K_1[M^{3+}][(\overline{HB})_q] \tag{142}$$

The presence of the interfacial area to volume ratio of the phase (A/V) in Equations 140 and 141 compensates for the fact that the rate constants have been evaluated from $-dM/dt$ data rather than from interfacial fluxes. By further assuming that $\delta_{org} = \delta_w$ and that the diffusivities of all species are equal ($D = 3.10^{-4}cm^2min^{-1}$), Equation 139 has been used to evaluate the progressive influence of mass transport in slowing down the extraction rate. This evaluation has been performed in terms of a progressive increase in the thickness of the stagnant interfacial films when the rate of stirring of the two phases is decreased from that required to operate in a kinetic regime.

The curves calculated using Equation 139 and reported in Figure 39 show how the rate of extraction is influenced by the stirring rate of the phases at constant specific interfacial area. In this case, the presence of the mixed regime is shown by the lowering of the rate curves. The shape of the curves obtained in the mixed regime is in fact not different from that obtained in a pure kinetic regime. The predictions derived from this treatment have been found to be in good agreement with the experimental results. Moreover, from the comparison of calculated curves and experimental rate data and from a numerical estimation of the diffusivity D, an indication has been also obtained of the correlation existing between $\delta$ and the stirring speed of the two phases (r/min) in the Lewis-type extraction cell used to perform the extraction kinetics experiments. This correlation is reported in Figure 40. Similar to the treatments previously described in References 14 and 44, Equations 138 to 142 also indicate that the mixed regime is a function of both the hydrodynamics and the concentrations of the species. The different influence that the stirring rate inside the Lewis-type cell has on the attainement of the kinetic regime, when different concentrations of the metal to be extracted are used, is exemplified in Figure 41. The curves clearly indicate that the plateau region, where the extraction proceeds in a pure kinetic regime, is progressively obtained at lower stirring speeds when the metal concentration is decreased. Further, the typical linear relationship between the mass-transfer rate and the stirring speed which characterizes the mass-transport region of the extraction is shown in Figure 42. Here the curve referring to the highest metal concentration has been plotted on logarithmic axes. The transition from a pure diffusion controlled regime to the mixed one is evidenced by the bending of the straight line which starts when log (const·r/min) approaches four. Equation 138 has also been integrated when the experimental conditions were such to allow to consider $[H^+]$ and $[(\overline{HB})_q]$ as time independent (very low metal concentrations). In such circumstances, by recalling that $[M]_{tot} = [M^{3+}] + [\overline{M}]$ and $NA/V = d[M^{3+}]/dt$, the following integral

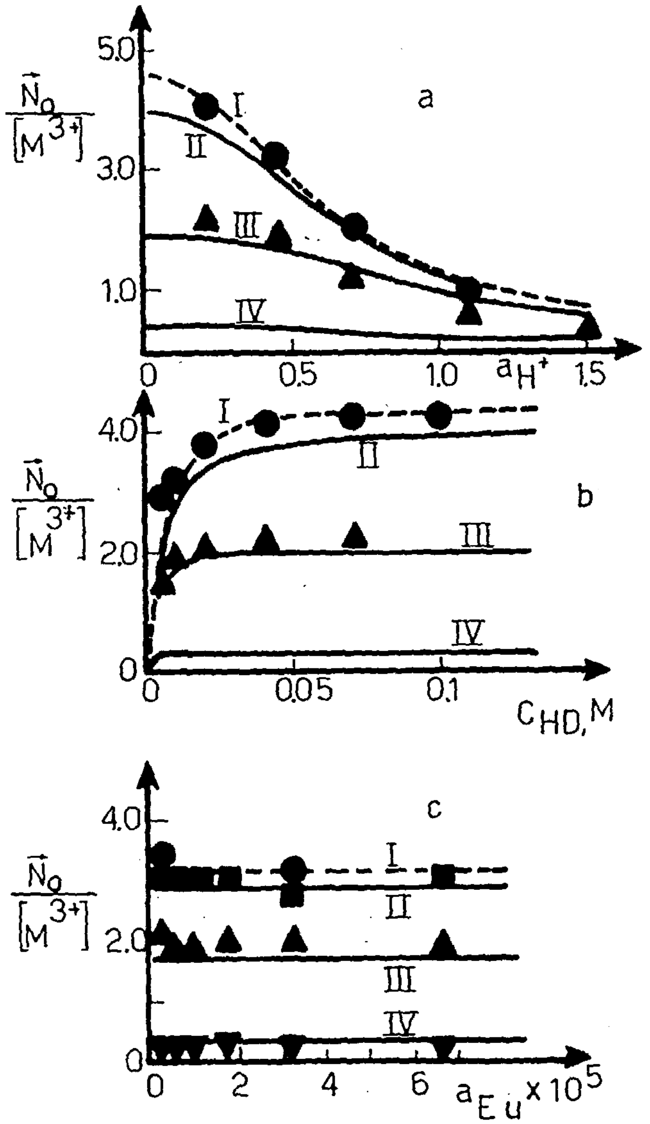


FIGURE 39. Normalized interfacial flux $\overline{N}_0/[M^{3+}]$, vs. activity (or concentration) plots. The experimental points have been obtained with the constant interfacial area stirred cell of Reference 74 at the following stirring speeds: ● 280 r/min, ■ 150 r/min, ▲ 100 r/min, ▼ 10 r/min. *Dashed line* I calculated through Equation 137 with rate constants of References 74-76. Solid lines calculated through Equations 138 and 139 with (*II*) $\delta = 10^{-3}$ cm, (*III*) $\delta = 10^{-2}$ cm, (IV) $\delta = 10^{-1}$ cm. (From Danesi, P. R., Chiarizia, R., and Sanad, W. A. A, *J. Inorg. Nucl. Chem.*, 39, 519, 1977. with permission.)

$$-\int_{[M]_{total}}^{[M^{3+}]} \frac{2\alpha \frac{V}{A} d[M^{3+}]}{-(\beta + \gamma [M^{3+}]) - \sqrt{(\beta + \gamma [M^{3+}])^2 - 4\alpha(\vartheta[M^{3+}] + \epsilon)}} = t \qquad (143)$$

with

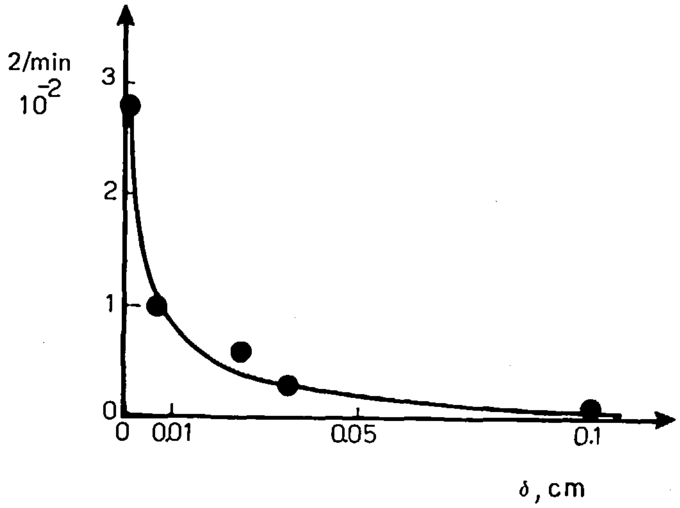


FIGURE 40. Stirring rate (r/min) vs. thickness of the diffusion films for the constant interfacial area stirred cell of References 74 to 76.

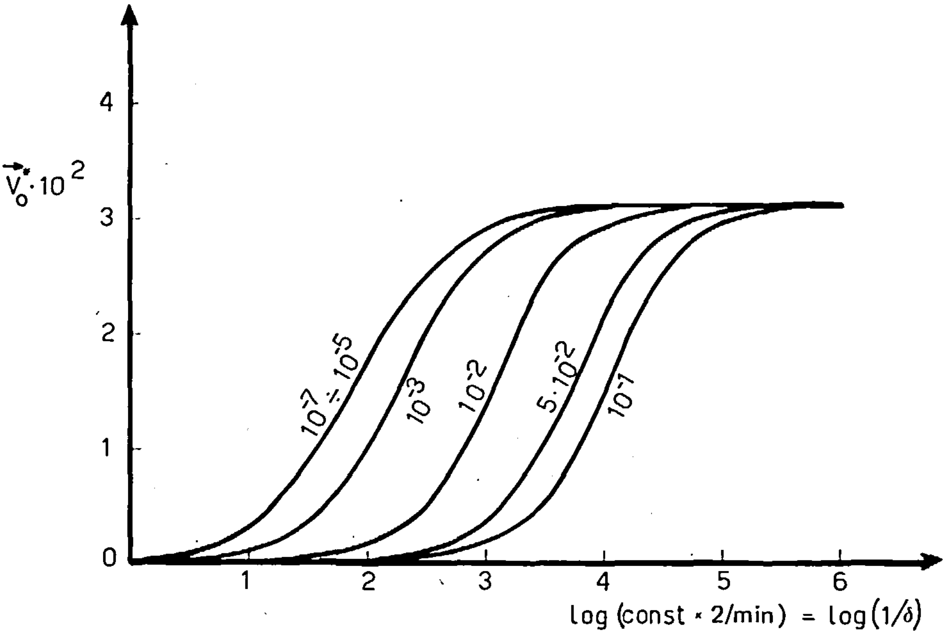


FIGURE 41. Influence of the stirring speed (thickness of the stagnant films) on the rate of europium extraction, $\vec{V}_0^* = \vec{V}_0/[M]$, by toluene solutions of dinonylnaphthalene sulfonic acid HD at different metal activities (indicated on each curve). The attainement of the kinetic regime corresponds with the plateau of the curves. The curves have been calculated through Equation 138 with rate constants and cell parameters of Reference 74.

$$\alpha = \frac{\delta_{org}}{D_{(HB)_q}} \left( K_1 \frac{\delta_w}{D_M} + \frac{A}{V} \right)$$

$$-\beta = \frac{A}{V} ([\overline{HB})_q] + K_R [H^+]^3) + K_1 [(\overline{HB})_q] \frac{\delta_w}{D_M} + \overline{K}_1 K_R [H^+]^3 \frac{\delta_{org}}{D_{\overline{M}}}$$

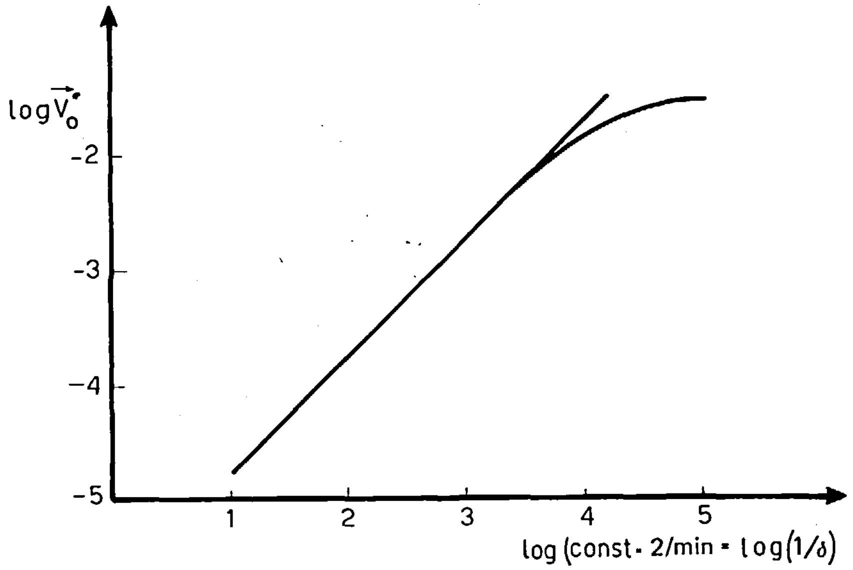


FIGURE 42. Influence of the stirring speed (thickness of the stagant films) on the rate of europium extraction at high $Eu^{3+}$ concentrations. Curve calculated as in Figure 41 with $[Eu^{3+}] = 0.3$ M, $[\overline{HD}] = 0.01$ M, $a_{H^+} = 0.435$ M. The straight line indicates a diffusional regime.

$$\gamma = K_1 \frac{\delta_{org}}{D_{(HB)_q}}$$

$$\vartheta = K_1 [(\overline{HB})_q] + \overline{K}_1 K_R [H^+]^3$$

$$-\epsilon = \overline{K}_1 K_R [H^+]^3 [M]_{total}$$

has been numerically evaluated. To perform the numerical integration the same simplifications concerning the diffusivities and the thickness of the stagnant films, already introduced to calculate the flux curves, have been made. Figure 43 shows the good agreement between the calculated concentration vs. time curves, obtained through Equation (143), and experimental data of concentration vs. time. The figures refer to mixed regimes where the relative importance of the interfacial chemical reactions and of the diffusion processes are varied by changing the stirring speed of the biphasic system. The rate constants used for the calculations have been taken from Reference 75. The values of δ and the corresponding stirring speeds are also indicated. The δ values which have been found to fit the concentration vs. time curves coincide with those derived from the initial rate vs. concentration data. These results seem to indicate that the mechanism of the interfacial reaction does not change as long as the extraction reaction proceeds and that the hypothesis of the diffusion processes occurring all of the time in a stationary state is a good approximation in describing this mixed kinetic-diffusional regime.

We can conclude this section by saying that concerning the approximations which have to be introduced to derive analytical solutions of the flux equations, most of the final comments formulated in Section VII with regard to the diffusional regime (i.e., mass transport with fast chemical reaction) also hold when the chemical reactions are

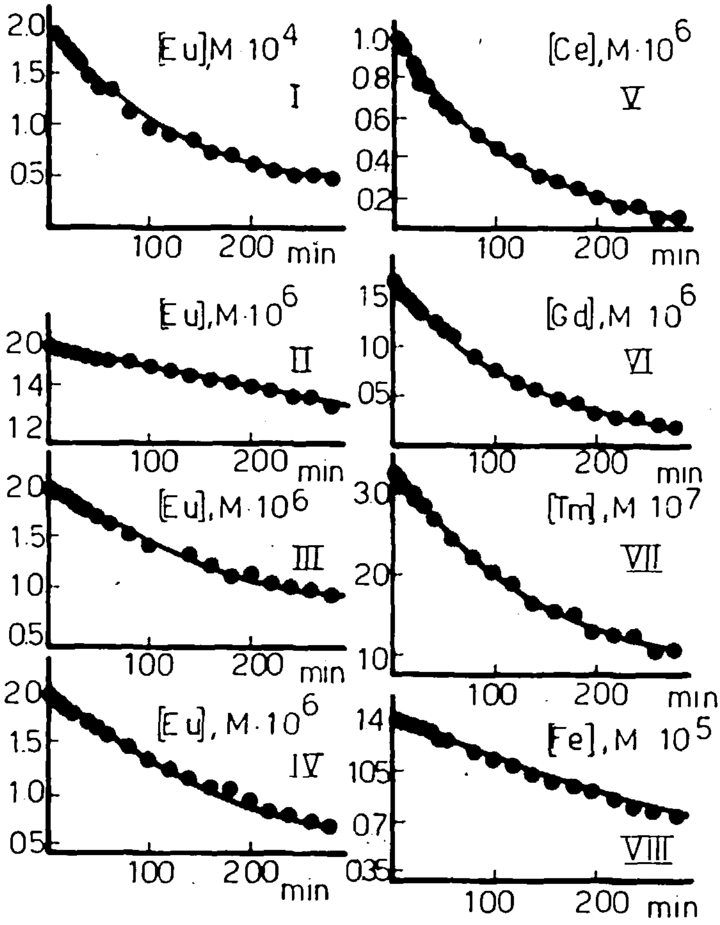


FIGURE 43. Concentration (molarity) vs. time (minutes) data (full points) for some $M^{3+}$ extractions by toluene solutions of dinonylnaphthalene sulfonic acid, HD, 0.01*M*. Solid lines calculated through Equation 143. $D = 3 \cdot 10^{-4}$ $cm^2\ min^{-1}$. I. $C_{Eu\ total} = 1.98 \cdot 10^{-4} M$, $[HClO_4] = 0.500M$, r/min = 110, δ/D = 17 min/cm. II. $C_{Eu\ total} = 2.00 \cdot 10^{-6} M$, $[HClO_4] = 0.118$, r/min = 10, δ/D = 333 min/cm. III. $C_{Eu\ total} = 1.98 \cdot 10^{-6} M$, $[HClO_4] = 0.118M$, r/min = 30, δ/D = 117 min/cm. IV. $C_{Eu\ total} = 1.94 \cdot 10^{-6} M$, $[HClO_4] = 0.118M$, r/min = 60, δ/D = 83 min/cm. V. $C_{Ce\ total} = 1.0 \cdot 10^{-6} M$, $[HClO_4] = 0.118M$, r/min = 100, δ/D = 30 min/cm. VI. $C_{Gd\ total} = 1.62 \cdot 10^{-6} M$, $[HClO_4] = 0.118M$, r/min = 100, δ/D = 30 min/cm. VII. $C_{Tm\ total} = 3.31 \cdot 10^{-7} M$, $[HClO_4] = 0.500M$, r/min = 100, δ/D = 23 min/cm. VIII. $C_{Fe\ total} = 1.40 \cdot 10^{-5} M$, $[HClO_4] = 0.118M$, r/min = 30, δ/D = 150 min/cm.

slow. The difference between the two cases mainly lies in the obvious fact that the presence of a slow chemical reaction has the effect of making the extraction kinetics slower. In fact, if a hypothetical extraction system with a fixed distribution coefficient in identical hydrodynamic conditions is assumed, while the presence of an interfacial fast chemical reaction has the overall effect of accelerating the rate of extraction with respect to a simple phase distribution process, the same is not any longer true when the interfacial reaction is slow. In terms of mass-transfer resistance, this effect can be attributed to an increase in the interfacial resistance. However, in the case of a simple distribution process, the occurrence of an interfacial resistance is physically explained by the presence of surfactant molecules at the interface which do not participate in the extraction, but only retard the process by forming a barrier which has to be crossed. On the contrary, when a slow interfacial chemical reaction occurs, the new interfacial resistance is of chemical nature. In this case, the retardation of the extraction process has to be attributed to the fact that the metal molecules arriving at the interface cannot be transferred into the other phase until they have been slowly transformed (at the interface) into the new chemical species which are soluble in the other solvent.

## VIII. EXTRACTION MECHANISMS AND RATE LAWS WITH ACIDIC, BASIC, AND NEUTRAL EXTRACTANTS

In this section, the works published on the extraction kinetics of metal species by acidic, basic, and neutral extractants will be reviewed. The main attempt of this section will be that of classifying the reaction mechanisms and the rate laws which characterize the extraction kinetics by the various types of extracting reagents when the extractions occur in a kinetic regime. These mechanisms and rates should be in fact rather specific for the chemically reacting groups and therefore dependent on the chemical nature of the metal species and extracting reagents which take part in the extraction, at least when the remaining chemical environment is not changed. Moreover, the knowledge of the mechanisms and rate laws which occur in kinetic extraction regimes may have practical importance. In fact, practical extraction processes, performed for either analytical or technological purposes, are generally carried out in conditions where the two phases are very vigrously mixed, in order to shorten the extraction time as much as possible. The hydrodynamic conditions are thus those of very high turbulence, and kinetic regimes are often established. Although diffusional contributions cannot be excluded in practical extraction processes and have to be taken into proper account to evaluate the extraction kinetics, they are generally rather unspecific with respect to the chemical nature of the metal species and extractant molecules involved. On the other hand, they are very much dependent on the concentration levels involved in the extraction processes, the density and viscosity of the diluents, as well as the general hydrodynamic conditions occurring inside the specific extraction apparatus used. It follows then that to completely foresee the kinetics of an extraction process performed in practical extractors for a given metal species-extracting reagent system, the knowledge of the rate laws in the kinetic regime as well as the chemical composition are required. Obviously, the hydrodynamic conditions and the interfacial area available for the transfer process have to be known also. The problem concerning the evaluation of the hydrodynamic conditions which are occurring inside practical solvent extraction tanks goes beyond the goals of this review and will not be treated here.

Concerning the chemical composition and the specific interfacial area, it is worth saying that while the former can always be easily determined, the same is unfortunately not always true for the latter. In fact, direct measurements of the specific interfacial area are rather difficult and in some cases even impossible. Nevertheless, by knowing the geometrical characteristics of the extraction apparatus, the power input of the stirrers, the density and viscosity of the fluids, and the interfacial tension and the settling time, estimates of the specific interfacial area can often be obtained using published engineering correlations. As an example References 99 through 102 can be consulted. In conclusion, it appears then that if the extraction hydrodynamics is such that a kinetic regime can be assumed, it is possible to make an estimation of the extraction kinetics once the mechanisms and the rate laws holding in a kinetic regime are known. However, as it will appear in the following discussion, not all of the investigations have been performed with such hydrodynamic conditions that allow unequivocal conclusions to be drawn on the reaction mechanisms and rate laws which are characteristic of a given metal species-extracting reagent system. In these cases, the reaction mechanisms and rate laws can be only roughly estimated through analogies with similar systems. Reference will be made in the following discussion, whenever necessary, to Sections I through VII where the general aspects of the extraction kinetics have been discussed in detail. The various works will be grouped according to the nature of the functional group present in the extractant molecule which interacts with the metal species.

## A. Acidic Extractants

### *1. β-Diketones*

The compound of this family most studied is 2-thenoyltrifluoroacetone (HTTA), an extracting reagent which has found wide analytical applications.[77-78] Unfortunately all of the kinetic studies performed with this extractant have been carried out by shaking the two phases in hydrodynamically uncontrolled conditions, i.e., using test tubes or bottles stirred in mechanical shakers. This means that the influence of the rate of stirring and the interfacial area of the extraction rate has never been quantitatively studied. Therefore, for the reasons reported in Section III, the conclusions drawn in these works about the type of regime controlling the extractions and the localization of the chemical reactions should not be considered as very definite. As we will see, in most of the studies it has been hypothesized that the rate of extraction was occurring in a kinetic regime, controlled by aqueous phase (homogeneous) chemical reactions. In some cases, this hypothesis has been supported by the experimental evidence that the rate of extraction was independent of the rate of shaking of the extraction vessel. Although this independence is not very conclusive, the nonnegligible solubility of HTTA in water, its probable low interfacial activity, and the type of rate laws experimentally found, all contribute to make this hypothesis rather sound.

The extraction kinetics of Fe(III) and Zr(IV) from perchloric aqueous phases by benzene solutions of HTTA in the presence of aqueous complexing agents ($Cl^-$ or $SCN^-$) and of a second organic extractant (TBP or TOPO) has been studied in References 79 through 83 in order to obtain information about synergistic extraction effects. The authors have assumed that the slow kinetics of extraction which is met when metal cations are extracted by organic solutions of HTTA had to be attributed to the slow reaction occurring in the aqueous phase between the metal cation and the water-solubilized enolic form of HTTA. This slowness has been indeed demonstrated in Reference 84 where the reaction was studied in a homogeneous aqueous phase. The following extraction mechanism has been therefore proposed:

$$\begin{array}{ll} \overline{\mathrm{HTTA}} \longrightarrow \mathrm{HTTA} \longrightarrow \mathrm{TTA}^- + \mathrm{H}^+ & \text{fast} \\ \mathrm{TTA}^- + \mathrm{M}^{3+} \longrightarrow \mathrm{MTTA}^{2+} & \text{slow} \\ 2\mathrm{TTA}^- + \mathrm{MTTA}^{2+} \longrightarrow \mathrm{M(TTA)}_3 & \text{fast} \\ \mathrm{M(TTA)}_3 \longrightarrow \overline{\mathrm{M(TTA)}_3} & \text{fast} \end{array}$$

where $TTA^-$ is the enolate anion reacting in water, and the bar as usual indicates organic species. From the experimental evidence showing that the presence of SCN and Cl anions in the aqueous phase greatly accelerated the rate of extraction, the authors have also concluded that the slow reaction between the metal cation and the enolate of HTTA was replaced by the faster aqueous complexation with $SCN^-$ (or $Cl^-$) and the faster organic extraction and complexation with HTTA of the inorganic metal complex, when complexing anions were added to the aqueous phase. This hypothesis has been experimentally supported by the further acceleration of the reaction which has been measured when methylisobutylketone (MIBK),[80] TOPO,[81] and TBP[80] were added to the organic phase to increase the organic solubility of the inorganic metal complex or ion-pair. The authors therefore concluded that in the presence of an aqueous inorganic complexing agent $X^-$, and of a second neutral organic extractant, E, the extraction reaction became faster because all of the following reaction steps

$$\left.\begin{aligned} &M(H_2O)_6^{3+} + 3X^- \longrightarrow \overline{M(H_2O)_3X_3};\ \overline{M(H_2O)_3X_3} + 2\overline{E} \longrightarrow \overline{ME_2X_3H_2O}; \\ &\overline{ME_2X_3H_2O} + \overline{3HTTA} \longrightarrow \overline{M(TTA)_3} + 2\overline{E} + 3H^+ + 3X^- + H_2O \quad . \end{aligned}\right\} \qquad (144)$$

were faster than the previous slow steps. The very slow extraction of $Cr^{3+}$ by HTTA in benzene has been attributed in Reference 85 to the same slow aqueous reaction between the water solubilized HTTA and the metal cation. The authors have here shown that the addition of fluoride anions in the aqueous phase highly enhanced the extraction rate, providing the aqueous solution was not allowed to stand for too long a time. This fact has been explained by the formation of chromium fluoride complexes, which in turn quickly react with the aqueous HTTA, at the expenses of the kinetically very inert hexaaquo-chromium (III) complex. The slow reaction with HTTA has been then attributed to the very slow kinetics of water substitution of the hydrated metal species. The authors have also noticed that once $Cr^{3+}$ had been extracted by HTTA it could not be stripped back by aqueous solutions of mineral acids, indicating again the very inert character of the Cr(III) complexes. It has also been reported that the behavior of Cr(III) was shared, at least partially, by a series of transition metal cations of groups VI to VIII. The influence of the stirring speed on the rate of extraction has not been considered at all in the studies[79-83,85] referred to up to this point. However, this functional dependence has been taken into consideration in Reference 88 where the rate of extraction of $Fe^{3+}$ by HTTA in benzene has been studied with phases so highly stirred that a further increase in the stirring no longer affected the extraction rate. Also, in Reference 88, it is mentioned that chloride ions accelerated the extraction rate. By first studying the reaction in the aqueous homogeneous phase and then determining the influence that the addition of $Cl^-$ ions had on the reaction rate, the authors have concluded that the rate determining steps of the extraction reaction were the aqueous phase reactions,

$$Fe^{3+} + (HTTA)_{enol} \xrightarrow{K_{ind}} FeTTA^{2+} + H^+ \qquad (145)$$

and

$$Fe(OH)^{2+} + (HTTA)_{enol} \xrightarrow{K_{dep}} FeTTA^{2+} + H_2O \qquad (146a)$$

As a consequence of Reactions 145 and 146a the rate expression showed a range of both pH dependence and pH independence. The following constants were reported:

$$K_{ind} = 0.5M^{-1}\,sec^{-1} \quad \text{and} \quad K_{dep} = 4.4.10^2M^{-1}\,sec^{-1}$$

The alternative path to Reaction 146a, i.e.,

$$Fe^{3+} + TTA^- \longrightarrow FeTTA^{2+} \qquad (146b)$$

leading to the same acid dependence (proton ambiguity) has been excluded on considerations based on the rate results obtained in the presence of chloride ions. As will be shown later, the identification of Reaction 146a as a cause of pH-dependent reaction rates is quite usual with strongly hydrated metal cations which can form hydrolyzed species able to exist at low pH. The enhancement of the extraction rate when $Cl^-$ ions were added to the aqueous phase has been attributed to the faster formation of the iron-β-diketone aqueous complex when iron-chloride complexes were preformed in the aqueous phase.

The extraction kinetics of $Be^{2+}$, $Fe^{3+}$, and $Ga^{3+}$ by HTTA has also been studied in References 89 through 92. The two phases were also shaken in this case in test tubes at such a speed that no further increase in the extraction rate was observed. The reaction orders with respect to all components have been determined in Reference 89 for the extraction of $Be^{2+}$ from aqueous solutions containing $Cl^-$, $NO_3^-$, and $ClO_4^-$ anions by HTTA solutions in $CCl_4$ or MIBK. A rate expression of the type

$$-\frac{d[Be^{2+}]}{dt} = K[Be^{2+}]^a[\overline{HTTA}]^b[H^+]^c[ClO_4^-]^d \qquad (147)$$

has been assumed by the authors. On the basis of the experimental results, the following rate laws have been then proposed:

$$-\frac{d[Be^{2+}]}{dt} = K[Be^{2+}][\overline{HTTA}][H^+]^{-1} \qquad (148)$$

for $CCl_4$, and

$$-\frac{d[Be^{2+}]}{dt} = K[Be^{2+}][\overline{HTTA}][H^+]^{-1}(1 + K_1[ClO_4^-] + K_2[ClO_4^-]^2) \qquad (149)$$

for MIBK. The rate Equations 148 and 149, which are of the type described in Section V.A.1.a, have been deduced from the reaction orders with respect to the concentrations, a, b, c, and d, evaluated from the slope values of logarithmic plots. The authors have explained Equation 148 as arising from the slow rate determining reaction, occurring in the aqueous phase, between $Be^{2+}$ and the anion of the extractant $TTA^-$. The rate constant value, taking into consideration the dissociation and distribution constants at 25°C of HTTA, has been reported to be $2 \cdot 10^4 M^{-1}$ min$^{-1}$ at $4M$ $NaClO_4$. Equation 149 has been explained by assuming the formation of aqueous ion-pairs, such as $Be(NO_3, ClO_4)$, $Be(Cl,ClO_4)$, and $Be(ClO_4)_2$, which could be rapidly extracted in MIBK. These ion-pairs were then considered to react rapidly in the organic phase with the extracting reagent. This explanation agrees with that reported in References 79 through 80. The rate constants of Equation 149, corrected for the dissociation and distribution of HTTA, have the following values: $K = 2.5 \cdot 10^4 M^{-1}$ min$^{-1}$, $K \cdot K_1 = 5 \cdot 10^5 M^{-2}$ min$^{-1}$ and $K \cdot K_2 = 1.6 \cdot 10^5 M^{-3}$ min$^{-1}$. An alternative explanation which has not been reported by the authors is that the rate determining step is the aqueous phase reaction between the undissociated extractant, HTTA, and the hydrolyzed cation $Be(OH)^+$. In fact for $Be^{2+}$, the rate of water substitution has been demonstrated to be much slower than that of hydrolysis.[94] In this case, the formation of a rather labile hydroxocomplex should catalyze the exchange of a water molecule. The authors have also reported that the rate of extraction of $Be^{2+}$ was the same whether or not the two phases were preequilibrated and found this independence rather unexplicable. This effect, however, can be easily attributed to the fact that, although the rate of distribution of HTTA between organic diluents and aqueous phases has been recognized as a slow process,[95] the very high interfacial area available in an extraction process performed with vigorously shaken vessels greatly enhances all slow interfacial processes making them negligible with respect to the other slow aqueous reactions. An alternative explanation, however, could be found assuming that the reaction takes place at the interface. In this case, providing the process of interfacial adsorption is a fast one, the extraction rate would be independent of the slow rate of water solubilization of HTTA. Furthermore, the mechanism of interfacial reactions, giving rise to rate laws as those reported in Section V.A.1.c.iii, could easily explain the deviations from +1 and −1 of the reaction orders with respect to $H^+$ and $\overline{HTTA}$ concentrations, respectively, which have been observed in Figures 2a and 3a of Reference 89. To this purpose, it is worth mentioning that the procedure of assuming that the extraction rate can be expressed as a product of concentrations (each one elevated to an integer coefficient) and then to evaluate the reaction orders from logarithmic plots can be very misleading. In fact, all of the deviations from straight-line behavior, which can be an indication of more complicated reaction mechanisms, are in this case erroneously attributed to systematic experimental errors.

The rate of extraction of $Fe^{3+}$ from aqueous solutions containing $ClO_4^-$ and $Cl^-$ ions has also been studied in Reference 90 using the same experimental procedure and deriving the rate law in the same way as in Reference 89. Only here $CCl_4$ has been used as the diluent of HTTA. The following rate equation,

$$-\frac{d[Fe^{3+}]}{dt} = K[Fe^{3+}][\overline{HTTA}](1 + K_H[H^+]^{-1}) \qquad (150)$$

has been reported. Surprisingly enough, the authors attributed this equation to the following two slow aqueous steps:

$$Fe^{3+} + HTTA \longrightarrow FeTTA^{2+} + H^+ \qquad (151)$$

$$Fe^{3+} + TTA^- \longrightarrow FeTTA^{2+} \qquad (152)$$

with $K = 3.71 M^{-1}\ min^{-1}$ (corrected for HTTA distribution) and $K \cdot K_H = 6.9 \cdot 10^6 M^{-1}$ $min^{-1}$ (corrected for HTTA distribution and dissociation in the aqueous phase). The contribution to the reaction rate of the hydrolyzed $Fe(OH)^{2+}$ species has instead been considered not significant on the basis of experiments carried out in the presence of chloride ions which accelerated the extraction rate in the same way in all of the acidity ranges studied. The same authors have also extended this study to other organic diluents, i.e., $CHCl_3$ and MIBK.[92] The enhanced extraction rate observed has also been in this instance attributed to the faster extraction of aqueous ion-pairs in the more polar organic diluents of HTTA. In this study, the reaction order with respect to $ClO_4^-$ concentration has been seen to increase, tending to the limiting value +3.

The extraction rate of $Ga^{3+}$ from perchloric acid solutions by HTTA solutions in $CHCl_3$, performed in the same experimental conditions, has instead been explained in Reference 91 by considering the contribution to the reaction rate of hydrolyzed species. In this investigation, where both the forward and reverse extraction rates have been measured, the following rate equations have been derived:

$$-\frac{d[Ga^{3+}]}{dt} = K_1[Ga^{3+}][\overline{HTTA}][H^+]^{-2} \qquad (153)$$

with $K_1 = 6.3 \cdot 10^{-5} M min^{-1}$, and

$$-\frac{d[Ga^{3+}]}{dt} = K_{-1}[\overline{Ga(TTA)_3}][H^+][\overline{HTTA}]^{-2} \qquad (154)$$

with $K_{-1} = 2.5 \cdot 10^{-4} M\,\mathrm{min}^{-1}$. Equations 153 and 154 have been explained by assuming the rate determining step to the aqueous phase reaction,

$$\mathrm{Ga(OH)^{2+} + TTA^- \longrightarrow Ga(TTA)^{2+} + OH^-} \qquad (155)$$

It is worth recalling that also in this case the alternative mechanism,

$$\mathrm{Ga(OH)_2^+ + HTTA \longrightarrow Ga(TTA)^{2+} + H_2O + OH^-} \qquad (156)$$

giving rise to the same equations, could have been proposed. However, the proton ambiguity between Reactions 155 and 156 could not have been solved simply on the basis of kinetic measurements. Nevertheless, it seems that the reaction of the undissociated extractant, HTTA, with the hydrolyzed metal cation is the most probable rate determining step of the acid dependent rate of $Ga^{3+}$ extraction by this reagent.

The validity of equations 153 and 154 has also been proven by the good agreement between the equilibrium constant of the extraction reaction

$$\mathrm{Ga^{3+}} + 3\overline{\mathrm{HTTA}} \overset{K_{eq}}{\rightleftharpoons} \overline{\mathrm{Ga(TTA)_3}} + 3\mathrm{H^+}$$

and the equilibrium constant derived by making Equations 153 and 154 equal, i.e., $K_{eq} = K_1/K_{-1}$. It has to be reported also that in this investigation sensible deviations from the straight-line behavior have been observed in the logarithmic plots used to evaluate the reaction orders (Figures 1b and 2a and b of Reference 91). Therefore, the criticism previously formulated in connection with Reference 89 applies also to this case.

The extraction kinetics of metal cations by other β-diketones has been also reported.[86,93,96] In Reference 86, the extraction kinetics of $Zn^{2+}$ from perchloric solutions by $CHCl_3$ solutions of acetylacetone, benzoylacetone, and dibenzoylmethane has been investigated. By operating with vigorously shaken test tubes, the authors have concluded that the rate determining step of the extraction reaction was the crossing of the interface of the neutral complex rapidly formed in the aqueous phase between the metal cation and the water-solubilized β-diketone. The authors reported that this mechanism seemed to change when strong complexing agents were added to the aqueous phase. This effect was demonstrated by extracting Co(III) from oxalate solutions with $CHCl_3$ solutions of acetylacetone.[96] The authors have in fact reported that in this case the rate determining steps of the extraction reaction were the rupture of the oxalic-cobalt complex bond at high pH values and the formation of the acetylacetone-cobalt complex at low pHs. The different behavior of Co(III) with respect to $Zn^{2+}$ was explained considering the rather inert behavior of many cobalt complexes,[87] implying rather slow substitution rates. However, due to the complete absence of hydrodynamic characterization of the extraction apparatus and since most of the information has been derived from few experimental data, reported as logarithm of zinc concentration vs. time plots, the conclusions drawn in References 86 and 96 have to be considered only as tentative explanations.

The extraction rate of $Fe^{3+}$ from perchloric aqueous solutions by $CCl_4$ solutions of acetylacetone, trifluoroacetylacetone, benzoyltrifluoroacetone, hexafluoroacetone, as well as HTTA has been studied in Reference 93. The authors have reported that for all of these β-diketones Equation 150 was holding. However, in this case, in addition to Reaction 151, Reaction 146a, involving the hydrolyzed cation, or Reaction 152 were also operative. The proton ambiguity between Reactions 146a and 152 has here been solved by comparing the rate constants relative to the two different paths. In fact, while Reaction 152 was leading to rate constants falling in the range of $10^5$ to $10^8 M^{-1}$

$sec^{-1}$, Reaction 146a allowed the calculation of rate constants having values equal to $10^3$ to $10^4 M^{-1}$ $sec^{-1}$. These lower rate constants appeared indeed more realistic considering that the following orders of magnitude have been reported in the literature[97] for the reaction of iron species with a ligand: 1 to $10^2 M^{-1}$ $sec^{-1}$ for $Fe^{3+}$ ions and $10^2$ to $10^5 M^{-1}$ $sec^{-1}$ for $Fe(OH)^{2+}$ ions.

Finally, a kinetic study of the extraction of $Fe^{3+}$ from perchloric acid solutions using $\beta$-isopropyltropolone (HIPT) in $CHCl_3$ as the extracting phase has to be mentioned.[98] Although HIPT is not a $\beta$-diketone, its functional groups are such to make this reagent very similar to these compounds. The work, which has been performed in experimental conditions basically equal to those of Reference 89, has again shown that the rate of extraction could be expressed by Equation 150. The authors attributed this rate to the two slow aqueous Reactions 145 and 146a with HIPT and $IPt^-$ replacing the $\beta$-diketone species. For Reaction 146a, a rate constant equal to $2.5 \cdot 10^8 M^{-1}$ $sec^{-1}$ was reported. However, following the same considerations just formulated concerning the order of magnitude expected for the rate constants, this high value seems to indicate that the rate determining step operative at low acidities must have been

$$FeOH^{2+} + HIPT \longrightarrow Fe(IPT)^{2+} + H_2O$$

In fact, when the first hydrolysis constant of $Fe^{+3}$ is considered (taken from Reference 53), the following value of the rate constant is obtained: $K = 5 \cdot 10^3 M^{-1}$ $sec^{-1}$.

We can then conclude this section concerning the kinetics of extraction of metal cations by $\beta$-diketones and HIPT by summarizing the results as follows:

1. When the organic diluent has a low polarity and the aqueous phase does not contain strong complexing agents acting on the cations, the extraction takes place rather slowly. The extraction mechanism and the rate laws can be described by the equations reported in Section V.A.1.a and in Figure 25. At high acidity, the slow step is the reaction of the metal cation with the water-solubilized acidic extractant. When, on the other hand, the acidity is not very high, the reaction takes place between the hydrolyzed metal cation and the undissociated reagent, at least with the cations characterized by a rate of hydrolysis higher than the rate of water substitution.
2. When diluents having a higher dielectric constant and anions forming aqueous complexes or ion-pairs with the metal cation are involved instead, the extraction reaction becomes faster. This enhancement of the extraction rate is caused by a change in the reaction mechanism, which now consists of the formation of an aqueous complex or ion-pair, its extraction in the organic phase, and the organic phase substitution reaction with extractant molecules.

A support to the hypothesis that the rates follow the description reported in Section V.A.1.a can be found in the rather high solubility of the extractants in the water phase. The saturation concentration of HTTA in water at pH = 1 is in fact about $0.04M$.[88] A further but weaker support could be found in the low surface activity of the extractants. Unfortunately, as far as we know, this has never been qantitatively evaluated. However, since the rate laws of Section V.A.1.a, arising from a slow step in the aqueous phase, are the same as those reported in Section V.A.1.c.i, which imply interfacial reactions, a definite exclusion of interfacial slow steps cannot be made. In fact, measurements concerning the dependence of the extraction rate on the specific interfacial area have not been performed in any of the quoted works. A further reason for uncertainty lies in the hydrodynamic conditions which have been used to perform the extraction rate experiments. They in fact do not necessarily imply (see Section IV) that the extraction rates were always measured in kinetic regimes.

### 2. *Hydroxy-Oximes*

Hydroxy-oximes have been used as analytical extractants since long ago.[77] More recently the practical importance of hydroxyoximes has been discovered since they can be used as selective extractants of copper from diluted acidic leach liquors. Solvent-extraction industrial plants using these reagents are indeed operative in the U.S., Great Britain, and Zambia. As a consequence, in addition to the studies concerning their extraction capacity and selectivity, investigations on the rate of extraction have been also performed. The most widely studied compound of this family is a commercial product denominated LIX 64 N. This product is basically a mixture of two compounds in a kerosene-type diluent, i.e., a $\beta$-hydroxybenzophenone oxime, LIX 65 N (whose anit-isomer has extracting properties), and an aliphatic $\alpha$-hydroxyoxime, LIX 63, which presence in small amounts is required to accelerate the extraction process. Table 2 summarizes the formulae and molecular weights of some of the most frequently used hydroxyoximes. The rate of extraction of $Cu^{2+}$ from aqueous solutions by toluene solutions of LIX extractants had first been studied in Reference 103 by using the AKUFVE apparatus, where the two phases were very highly stirred. Radiochemical monitoring of the copper concentration has been used to determine the transfer rate in the system, which was kept very close to equilibrium. Since the two phases were stirred at 650 r/min, a speed such that no more increase in the extraction rate occurred by further increase the authors have assumed that the extraction was occurring in a kinetic regime. The concentration vs. time data have been analyzed by assuming a first order reversible reaction for the copper transfer, i.e.,

$$Cu^{2+} \underset{K_r}{\overset{K_f}{\rightleftharpoons}} \overline{Cu} \qquad (157)$$

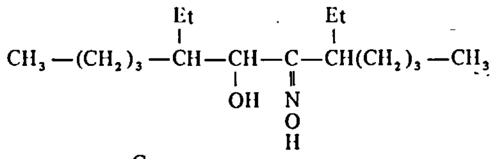
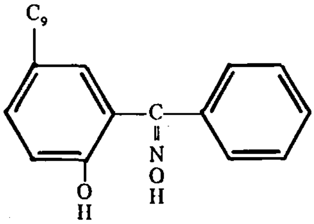
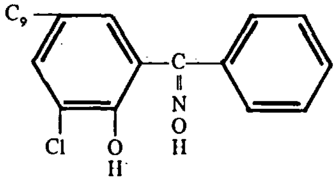
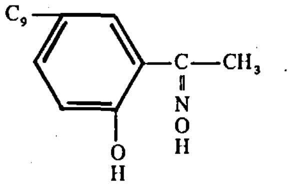
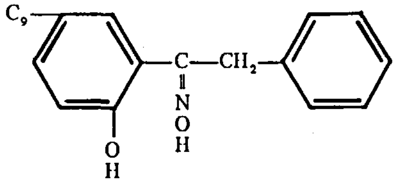
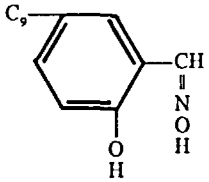
which led to the integrated kinetic equation

$$\frac{[Cu]_0-[Cu]_{eq}}{[Cu]_0} \ln \frac{[Cu]_0-[Cu]_{eq}}{[Cu]_t-[Cu]_{eq}} = K_f t \qquad (158)$$

By plotting the left member of equation (158) as a function of time, straight lines have been obtained which allowed the evaluation of $K_f$ as function of both the LIX and $H^+$ concentrations. As a result of these measurements the following reaction orders have been obtained: with respect to $[H^+]$: −1.22($Na_2SO_4$ 0.1r), −0.85($Na_2SO_4$1M), with respect to [LIX 65 N]: 1.27 ($Na_2SO_4$0.1M), 1.01 ($Na_2SO_4$1M). When LIX 63 was added to LIX 65 N a reaction order equal to 0.5, with respect to LIX 63 concentration, has been determined, while the other reaction orders were only slightly different from those already reported. A catalytic role has been attributed to LIX 63 on the experimental evidence of its absence in the final product of the extraction reaction and on the decreased value of the extraction activation energy (from ~6 to ~3 kcal/mole) caused by its presence in the extraction system. The fractional reaction order with respect to LIX 63, the low water solubility of the LIX compounds, and their $pK_a$ values have suggested to the authors the following reaction mechanisms based on interfacial steps (RH and BH represent LIX 65 N and LIX 63 respectively):

$$\overline{RH} \rightleftharpoons (RH)_{ad}; \qquad \overline{BH} \rightleftharpoons (BH)_{ad} \qquad \text{fast} \qquad (159)$$

## Table 2
## OXIMES USED IN THE HYDROMETALLURGICAL PROCESSES OF COPPER RECOVERY

| Reagent | Name | Molecular weight |
|---|---|---|
|  $CH_3{-}(CH_2)_3{-}\overset{Et}{CH}{-}\underset{OH}{CH}{-}\underset{\underset{\underset{H}{O}}{N}}{C}{-}\overset{Et}{C}H(CH_2)_3{-}CH_3$ | LIX 63[a] | 282 |
|  | LIX 65N[a] | 339 |
| LIX 65N + LIX 63 | LIX 64N[a] | |
|  | LIX 70[a] | 373.5 |
|  | SME 529[b] | 277 |
|  | P 17[c] | 353 |
|  | P 50[c] | 263 |

[a] General Mills Inc. - U.S.A.

[b] Shell Chemicals Ltd., U.K.

[c] Acorda Ltd., U.K.

$$Cu^{2+} + (RH)_{ad} \rightleftharpoons CuR^{+} + H^{+} \qquad \text{fast} \qquad (160)$$

$$CuR^{+} + (BH)_{ad} \rightleftharpoons (CuR\,B)_{ad} + H^{+} \qquad \text{slow} \qquad (161)$$

$$(CuR\,B)_{ad} \rightleftharpoons \overline{Cu\,R\,B} \qquad \text{fast} \qquad (162)$$

$$\overline{Cu\,R\,B} + \overline{RH} \rightleftharpoons \overline{Cu\,R_2} + \overline{BH} \qquad \text{fast} \qquad (163)$$

for a mixture of LIX compounds, and

$$\overline{RH} \rightleftharpoons (RH)_{ad} \qquad \text{fast} \qquad (164)$$

$$Cu^{2+} + (RH)_{ad} \rightleftharpoons Cu\,R^{+} + H^{+} \qquad \text{fast} \qquad (165)$$

$$Cu\,R^{+} + (RH)_{ad} \rightleftharpoons (Cu\,R_2)_{ad} + H^{+} \qquad \text{slow} \qquad (166)$$

$$(Cu\,R_2)_{ad} \rightleftharpoons \overline{Cu\,R_2} \qquad \text{fast} \qquad (167)$$

when only LIX 65 N is present.

However, it seems quite unlikely that the proposed mechanisms can give rise to rate laws yielding reaction orders in agreement with those experimentally found both in the case of ideal and saturated interfaces.

Although the use of unpurified products and the *a priori* assumption of a rate law having the form of a product of concentrations, each one raised to an integer power, has somehow limited the validity of the conclusions reported, the authors have correctly pointed out the relevant importance of interfacial reactions in controlling the extraction rate and have emphasized the need of a physico-chemical characterization of the interface in order to reach unequivocal conclusions on the reaction mechanisms.

The extraction kinetics of $Cu^{2+}$ by LIX reagents has also been investigated in Reference 39 using the moving drop method. Also in this work, unpurified compounds have been used. The organic diluent was xylene, and the aqueous phase contained nitrate ions. Since no buffer was used in the aqueous phase, the copper concentration variations have been indirectly evaluated by pH measurements. In this work, the system has been studied far from the equilibrium condition, and initial rates have been measured. From the slopes of the straight lines obtained by plotting log ([Cu]/[Cu]$_0$) vs. t, the following rate law has been derived:

$$V_0 = K[Cu]\,[\overline{LIX\ 65\ N}]^{0.5}[\overline{LIX\ 63}]^{0.5} \qquad (168)$$

Due to the very low water solubility of the LIX reagents and claiming high internal drop circulations, homogeneous aqueous phase reactions as well as diffusional processes have been excluded by the authors as rate determining steps. A mechanism based on rate determining interfacial chemical reactions has been therefore proposed. This mechanism can be summarized as follows:

1. Fast interfacial adsorption of both LIX compounds
2. Fast interfacial protonation of the $\alpha$-oxime at the expense of the $\beta$-oxime

$$(RH)_{ad} + (BH)_{ad} \rightleftharpoons (R^{-})_{ad} + (BH_2^{+})_{ad} \qquad (169$$

3. Slow reaction of $Cu^{2+}$ with $(R^{-})_{ad}$

$$Cu^{2+} + (R^{-})_{ad} \rightleftharpoons (Cu\,R^{+})_{ad} \qquad (170)$$

4. Fast formation of the final interfacial complex through the reaction of $(CuR^+)_{ad}$ with $(RH)_{ad}$ or $(R^-)_{ad}$, followed by the fast desorption from the interface and the fast deprotonation of $(BH_2^+)_{ad}$

By considering the equilibrium constant of Reaction 169 and the slow Reaction 170, Equation 168 is easily obtained, provided a direct proportionality between the bulk and interfacial LIX concentrations is assumed. No experimental support to this evidence has been given, however. The lack of $[H^+]$ dependence shown in Equation 168 is probably due to a lack of proper data treatment as indicated in Reference 105. Furthermore, also in this case, no direct evidence of the interfacial kinetic regime has been obtained.

The same authors[104] have also tried to find an explanation of the $[H^+]$ dependence met in Reference 103 by assuming that it was caused by the back reaction, whose influence was strongly evident near equilibrium conditions. They have therefore claimed that the data of Reference 103 could be represented by the rate equation

$$V = K_f[\overline{RH}][\overline{BH}]^{0.5}[Cu] - K_r[H^+][\overline{R_2Cu}] \qquad (171)$$

which was consistent with their mechanism when the following slow step was assumed:

$$(Cu\,R^+)_{ad} + (RH)_{ad} \underset{K_r}{\overset{K_f}{\rightleftharpoons}} \overline{R_2Cu} + H^+ \qquad (172)$$

From Reaction 172 and the equilibrium conditions applied to Reactions 169 and 170, and the following rate law has been in fact derived, assuming ideal adsorption,

$$V = K_f[\overline{RH}]^{1.5}[\overline{BH}]^{0.5}[Cu] - K_r[H^+][\overline{R_2Cu}] \qquad (173)$$

This rate law could take into account the reaction orders higher than one occasionally found in Reference 103. However, this interpretation was later rejected in Reference 105 on the argument that Reaction 171 gave rise, by setting V = 0, to an equilibrium relationship inconsistent with that experimentally determined by equilibrium measurements in Reference 103. Still, in Reference 105, interfacial tension measurements on both LIX 65N and LIX 63 have been used to demonstrate that the interface was occupied only by LIX 65 N molecules. The authors have therefore concluded that the mechanisms represented by Reactions 159 to 167, and 169 to 170 were unrealistic. The alternative mechanism, first suggested in Reference 107, was then proposed:

$$Cu^{2+} + (BH)_{ad} \rightleftharpoons (CuB^+)_{ad} + H^+ \qquad \text{fast} \qquad (174)$$

$$(CuB^+)_{ad} + (RH)_{ad} \rightleftharpoons (Cu\,BR)_{ad} + H^+ \qquad \text{slow} \qquad (175)$$

$$(Cu\,BR)_{ad} + (RH)_{ad} \rightleftharpoons (Cu\,R_2)_{ad} + \overline{BH} \qquad \text{fast} \qquad (176)$$

$$(Cu\,R_2)_{ad} \rightleftharpoons \overline{Cu\,R_2} \qquad \text{fast} \qquad (177)$$

However, it seems quite questionable that even with such a mechanism the experimentally found reaction orders could be explained.

The role of interfacial chemical reactions in the extraction process of $Cu^{2+}$ by LIX compounds has also been evidenced in Reference 22, where a correlation has been found between the rate of extraction and the area occupied by each molecule of the extracting reagent at the interface. The investigation has been performed with conditions such that the interface was saturated with the extractant molecules. The area

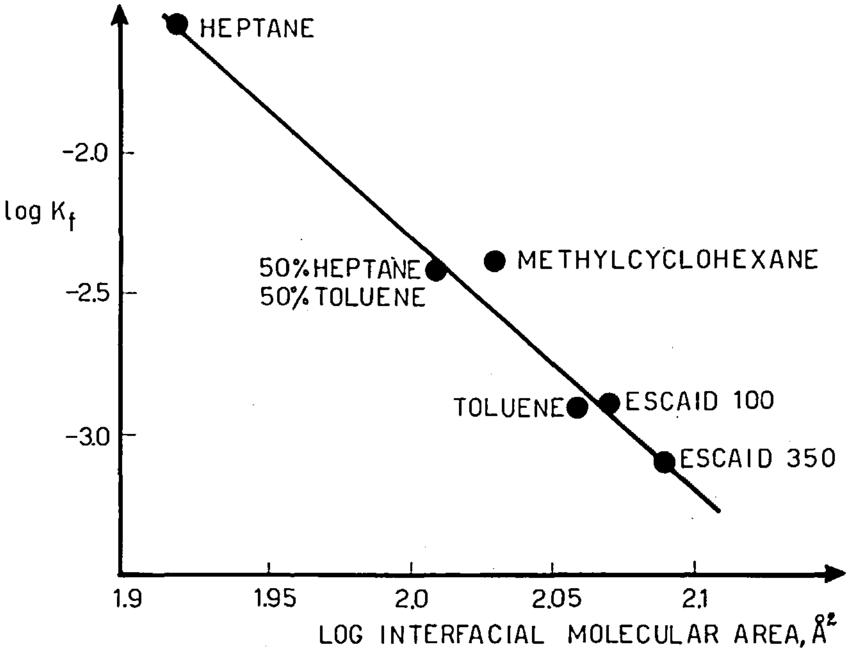


FIGURE 44. Dependence of the forward rate constant of copper extraction (from 1.0*M* $Na_2SO_4$ solutions into organic solutions of LIX 65 N $10^{-3}$*M*) from the interfacial molecular area of the extractant. (From Flett, D. S., *Acc. Chem. Res.*, 10, 99, 1977. With permission.)

occupied by each molecule has been derived from interfacial tension measurements. Figure 44 shows that the logarithm of the forward rate constant of copper extraction decreases by increasing the logarithm of the interfacial area occupied by each extracting reagent molecule. This area has been varied by changing the nature of the organic diluent dissolving the extractant. The plot of Figure 44 seems to indicate that the reactions ruling the extraction kinetics are interfacial, with the rate law being proportional to the number of interfacial active sites. A further support to the presence of interfacial rate determining reactions has been obtained by the acceleration of the extraction reaction which was occurring when the strongly interfacially adsorbed dinonylnaphthalenesulfonic acid was added to the organic phase. The authors have explained this acceleration in terms of a fast interfacial reaction with the sulfonic acid followed by a fast ligand-exchange reaction in the organic phase. In spite of all these indications pointing out the presence of rate determining interfacial chemical reactions, no derivation of an unambiguous interfacial reaction mechanism has been obtained, however. This comment also holds for the work performed in Reference 106, where the rate of $Ni^{2+}$ extraction from nitrate solutions by a mixture of a $\alpha$-hydroxyoxime (HOx) and lauric acid (HL) dissolved in hexane has been investigated. In this work, highly stirred phases have been studied using the AKUFVE apparatus. Initial forward and reverse rates have been measured, and the reaction orders have been evaluated through linear plots, following the same procedure described in Reference 103. These reaction orders, which have been found quite close to integer numbers, have allowed the authors to formulate the following rate law

$$V = K_f[Ni] \frac{[\overline{HOx}][\overline{HL}]}{[H^+]} - K_r[\overline{Ni}] \frac{[H^+]}{[\overline{HOx}][\overline{HL}]} \qquad (178)$$

Equation 178 has been tentatively explained with the following reaction mechanism occurring at the interface:

$$Ni^{2+} + HL \rightleftharpoons NiL^{+} + H^{+} \qquad \text{fast} \qquad (179)$$

$$NiL^{+} + HOx \xrightleftharpoons[K_r]{K_f} NiLHOx \qquad \text{slow} \qquad (180)$$

$$NiLHOx + HOx \rightleftharpoons NiOx_2LH + H^{+} \qquad \text{fast} \qquad (181)$$

$$NiOx_2LH + HL \rightleftharpoons NiOx_2(LH)_2 \qquad \text{fast} \qquad (182)$$

However, as the authors have correctly deduced, this mechanism, although capable of explaining the experimental reaction orders, does not provide any explanation to the fact that the much more surface-active HL does not participate in the slow interfacial Reaction 180. In fact, HL should replace at the interface the less surface-active HOx.

The kinetics of $Cu^{2+}$ extraction from sulfate media by LIX 64 N in Escaid 100 (a kerosene diluent of low aromatic content) has been studied in References 37 and 108 through 110 by the single drop method using a commercial unpurified reagent. The dependence of the initial rate of forward extraction on the composition of the aqueous phase[37] has shown a proportionality between $V_0$ and the ratio $[Cu]_{total}$: $[H^+]_{free}$, at least up to a rate value of 0.1 mol $m^{-2}$ $sec^{-1}$. The dependence of $V_0$ on the LIX 64 N concentration[108] has instead led to a noninteger and variable reaction order suggesting that a mechanism based on interfacial chemical reactions (see Section V.A.1.c) could be rate controlling. Concerning the reverse rate of extraction, a direct proportionality has been found in Reference 37 between $V_0$ and $[Cu]_{total} \cdot [H^+]_{free}$, while no dependence on [LIX 64 N] was found. The authors have then concluded that the interface had to be involved in the extraction reaction since

1. In methanolic homogeneous solutions, the reaction between LIX 64 N and $Cu^{2+}$ was instantaneous.
2. The initial extraction rate was directly proportional to the interfacial area.

In order to get information on the rate controlling process, the authors have also measured the extraction activation energy.[108] A much higher value than that of Reference 103 has been found. Since the work of Reference 103 was performed in conditions close to equilibrium, while the work of Reference 108 referred to initial rates, the conclusion has been reached that the extraction reaction was chemically controlled at the early stage and diffusion controlled as equilibrium was approached. In this last instance, the authors have suggested that the slowest diffusional process could be the diffusion of the copper-loaded reagent away from the interfacial zone. Unfortunately, the measurement of the diffusivity of the copper-extractant complex of LIX 65 N in different organic diluents[111] has not allowed final conclusions to be drawn on this point.

As far as the catalytic role of LIX 63 is concerned, in Reference 109 it has been hypothesized that an "interfacial zone" had to exist where both the LIX reagents could be present at concentrations related to the bulk ones by means of either adsorption isotherms or partition relations. In this interfacial zone, the α-oxime could be protonated at the expense of the β-oxime causing an increase in the concentration of LIX 65 N anions which in turn could enhance the extraction rate. This hypothesis has been formulated on the basis of the higher interfacial activity of LIX 65 N as compared to that of LIX 63 and of the much lower acid strength of LIX 63[112] compared to LIX 65

N. This explanation is somewhat similar to that reported in References 39 and 104, with the difference that in this case a simultaneous adsorption of both LIX 63 and LIX 65 N on the interface was not required.

Another important contribution to the understanding of the kinetic behavior of the LIX compounds has been obtained by the experimental evidence of the deleterious effect that nonylphenol, always present in small amounts in commercial reagents, had on the copper extraction equilibrium isotherms as well as on the initial extraction rates.[110] The depressive kinetic effect of nonylphenol has been attributed to the preferential solvation that this compound exerted on unionized $\beta$-hydroxyoximes, thus reducing the availability of these molecules with respect to the reaction with copper ions. For this reason, chemically pure compounds should be used in solvent extraction kinetics experiments aiming at the elucidation of the extraction mechanism. Purification procedures have been suggested in References 112 and 158. Due to the great importance that the interface has been shown to have in the extraction kinetics of copper ions by means of LIX products, the interfacial behavior of purified LIX compounds, making use of various techniques, has been also investigated.[113,114] Contrary to the findings reported in Reference 3 (no variation of interfacial tension with pH up to pH 9), the authors of this investigation have found that the interfacial tension vs. pH plots for different oximes showed a maximum between pH ≃3 and pH ≃5. The decrease in interfacial tension at higher acidities has then been attributed to the possibility of LIX compounds becoming protonated, while the decrease at lower $[H^+]$ was ascribed to the dissociation of the oximes to give anions with higher surface activity. A surface dissociation constant or alternatively a surface pH value different from the bulk one, taken into account in evaluating the complexing free anion concentration, has been therefore hypothesized. Unfortunately, no direct evaluation of interfacial dissociation constants has been reported until now. The determination of the interfacial tension of various oximes at fixed pH as a function of the oxime concentration in various diluents has led to the following results:

1. Oximes are more interfacially active in aliphatic (hexane) than in aromatic (toluene) diluents in agreement with previous findings.[22,106]
2. In the diluent hexane, LIX 65 N is more interfacially active than LIX 63 in agreement with References 3 and 105.
3. In the diluent toluene, the situation is reversed, LIX 63 being slightly more interfacially active than LIX 65 N.
4. The bulk LIX 65 N or LIX 63 concentration at which the interface can be considered saturated (estimated on the basis of the Gibbs equation) is $<10^{-2}M$ in toluene, in good agreement with Reference 22.

This last consideration has particuarly puzzled the authors who have been unable to explain why the rate of copper extraction was strongly dependent on the bulk concentration of LIX 65 N, while the interfacial concentration was, on the contrary, virtually independent of it. The conclusion has been then reached that either the extraction kinetics were unrelated to the interfacial concentrations or these were wrongly estimated. An alternative explanation linking together interfacial concentrations and the rate dependence on the bulk concentrations can probably be attempted following a treatment based on interfacial steady state conditions similar to that presented in Section V.A.1.c.

More recently, the same authors[115] have presented a somewhat different reaction mechanism regarding the extraction of copper by LIX 65 N. Due to the inverse dependence of the rate on $[H^+]$ and the small but finite concentration of hydroxy-oximes in the aqueous phase, they held the view that the reaction zone was on the aqueous side of the interface. In this case, the suggested possible homogeneous reactions have been

$$Cu^{2+} + R^- \rightleftharpoons CuR^+ \qquad \text{fast} \qquad (183)$$

$$Cu^{2+} + HR \rightleftharpoons CuR^+ + H^+ \qquad \text{fast} \qquad (184)$$

$$CuR^+ + HR \rightleftharpoons CuR_2 + H^+ \qquad \text{slow} \qquad (185)$$

$$CuR^+ \cdot xH_2O \rightleftharpoons CuR^+ \cdot (x-n)\,H_2O + n\,H_2O \qquad \text{fast} \qquad (186)$$

$$CuR_2 \cdot y\,H_2O \rightleftharpoons CuR_2 \cdot (y-m)\,H_2O + m\,H_2O \qquad \text{fast} \qquad (187)$$

where HR here denotes the aqueous monomer of LIX 65 N. Reaction 185 has been chosen as rate determining on the basis of the hydrogen dependence, the acid dissociation constant, and the HR solubility in the aqueous phase. Since the low value of the activation energy determined in both the forward and reverse extraction indicated diffusion control, Reaction 185 leading to the kinetic equation

$$V = K\ [Cu^{2+}][HR]^2[H^+]^{-1} \qquad (188)$$

has been coupled to the diffusion process of HR in the aqueous reaction zone. Following the method reported in Section VI.B.1, the rate equation

$$N = \left(\frac{2}{3}\,K\,D_{HR}\right)^{0.5} K_{D,R}^{-1.5} \left(\frac{[Cu^{2+}]}{[H^+]}\right)^{0.5} [\overline{HR}]^{1.5} \qquad (189a)$$

has been derived, where N is the rate of transfer for unit interfacial area referred to HR. The reaction orders with respect to $[Cu^{2+}]/[H^+]$ and $[\overline{HR}]$ have been found in partial agreement with the experimental findings of Reference 37.

The rate of copper extraction from a nitrate medium by a LIX 65 N - LIX 63 mixture in chloroform has also been studied in Reference 67 by a constant interfacial area stirred cell. The copper extraction has been indirectly evaluated by monitoring pH variations with a glass electrode. The authors have here found a proportionality between the rate of extraction and both the interfacial area and the stirring speed of the only organic phase in the range of 20 to 150 r/min. These results suggest that the rate is controlled by diffusion in the organic phase. The determination of the apparent reaction orders at 60 r/min, that is in a diffusional or mixed regime, as a function of the concentrations has led to the following results:

1. The rate increased with increasing copper concentration up to $[Cu^{2+}] = 0.05\,M$, then becoming independent.
2. The rate was independent of $[H^+]$ at high pH values and showed a nonlinear inverse dependence on $[H^+]$ at lower pH values.
3. The rate had a first order dependence on $[\overline{\text{LIX 65 N}}]$ at high pH values and an almost second-order dependence in more acidic solutions; these dependences occurred also in the presence of a constant concentration of LIX 63.
4. At constant $[\overline{\text{LIX 65 N}}]$, the reaction order with respect to $[\overline{\text{LIX 63}}]$ was variable (zero at low $[\overline{\text{LIX 63}}]$ and one at high $[\overline{\text{LIX 63}}]$).

These results have been explained in terms of extraction kinetics controlled by diffusional processes, with the interfacial chemical reactions being fast. This model, based on the coupling of diffusional processes and an equilibrium state at the interface, has already been described in Section VI.B.2. The derived Equations 96 and 97 have been able to explain sufficiently well the experimental data. In addition, Equation 98 also is used to explain the data of Reference 103.

In order to get a clearer picture of the extraction kinetics by hydroxy-oximes, very pure compounds have been used in Reference 158. In this work, the rate law

$$V = K_f[(\overline{RH})_2][H^+]^{-1}[Cu] - K_a[H^+][\overline{R_2Cu}] \qquad (189b)$$

has been deduced from experimental forward and reverse extraction kinetics data of copper from $Na_2SO_4$ aqueous solutions obtained in experimental conditions very similar to those of Reference 103. In Equation 189b, $(\overline{RH})_2$ represents the free dimer of a 5-alkyl-2-hydroxyphenol alkyl ketoxime. Toluene and heptane have been used as diluents. The authors have then concluded that the following interfacial mechanism was operative:

$$(\overline{RH})_2 \rightleftharpoons (\overline{RH})_{2ad} \qquad \text{fast} \qquad (189c)$$

$$Cu^{2+} + (\overline{RH})_{2,ad} \rightleftharpoons (CuR_2\,H^+)_{ad} + H^+ \qquad \text{fast} \qquad (189d)$$

$$(CuR_2H^+)_{ad} \rightleftharpoons (CuR_2)_{ad} + H^+ \qquad \text{slow} \qquad (189e)$$

$$(CuR_2)_{ad} \rightleftharpoons \overline{CuR_2} \qquad \text{fast} \qquad (189f)$$

the interface being completely saturated with monomeric RH molecules. Although the interfacial nature of the proposed steps was not experimentally demonstrated, the use of very pure and specifically prepared compounds makes the suggested rate law and mechanism rather sound. The faster kinetics obtained in n-heptane have been explained considering the larger dimer concentrations of the extractant in this diluent. The influence of highly purified compounds which act as accelerators or retardants has also been investigated. A complete explanation of their action was not, however, found.

Another extracting reagent which will be included in this section because of its similarities with the hydroxy-oxime compounds as far as the kinetic behavior and the practical applications are concerned is KELEX 100. This compound, which chemical name is 7-dodecenyl-8-hydroxyquinoline, is a derivative of the well-known reagent oxine. In Reference 107, its properties and extracting behavior are reviewed. A study of the extraction kinetics of $Cu^{2+}$ from a $1\,M\,Na_2SO_4$ medium by KELEX 100 in toluene has been performed in Reference 116 using the same experimental technique and method of handling the data as in Reference 103. The results obtained have indicated that the rate equation could be formulated as follows:

$$\vec{V}_0 = K_f[Cu^{2+}][\overline{HR}][H^+]^{-1} \qquad (190)$$

where HR represents KELEX 100. Experimental reaction orders slightly different from +1 and −1 have been determined, however. The authors, following the same reasoning as in Reference 103, have proposed a mechanism based on the interfacial rate determining step

$$(CuR^+)_{ad} + (HR)_{ad} \longrightarrow (CuR_2)_{ad} + H^+ \qquad , \qquad (191)$$

The same criticisms already formulated for the LIX reagents therefore apply here also. Nevertheless, in the case of the KELEX reagents also, the importance of the interfacial properties in determining the rate of extraction has been emphasized. This fact is in line with the high surface activity of these extracting reagents.

This section concerning the extraction kinetics of LIX and KELEX reagents can then be concluded by summarizing the results obtained as follows:

1. In spite of the amount of work performed, neither the extraction mechanism nor the catalytic role of LIX 63 have been unambiguously identified; however, the outstanding role of the interface has been well elucidated.
2. The different techniques used to study extraction kinetics have evidenced that, even when kinetic regimes could be hypothesized, noninteger reaction orders with respect to the extractant concentration are often obtained. This finding suggests that an approach based on interfacial chemical reactions, following the lines reported in Section V.A.1.c, could be attempted to provide a quantitative explanation of the rates.
3. When different hydrodynamic conditions are established in the apparatus used to study the extraction kinetics, the approach followed in Reference 21 and already reported in Section VII appears as a very useful tool to understand the reasons of the different extraction kinetics.
4. The extraction kinetics by pure β-hydroxy-oximes is not extremely fast. The addition of a second component is then required to make the kinetics sufficiently rapid to be applied to industrial processes. This fact, together with the need to obtain information on extracting reagents used in industrial practice having a limited degree of purity, has been up to this point a drawback in the elucidation of the mechanism of the extraction reactions.

### *3. Hydroxamic Acids*

The use of hydroxamic acids as extracting reagents in analytical chemistry has been intensively investigated.[77] Recently, trialkylacetohydroxamic acids have been proposed as new extractants to be exploited in the reprocessing of nuclear fuel, in the treatment of nuclear wastes, as well as in hydrometallurgical processes for the recovery and purification of metals.[117,118] In spite of the high selectivity which can be achieved by these extractants, a major drawback to their use lies in the slow kinetics of extraction. The forward and reverse kinetics of iron(III) extraction from an aqueous 2*M* nitrate medium by means of tri-n-butylacetohydroxamic acid (HB) dissolved in toluene has been studied in Reference 24. The aggregation, extraction equilibriums, and interfacial behavior of the extractant have also been investigated. The aim of this study was to understand the reasons of the slow extraction kinetics and possibly to find a way to enhance it. The same cell, stirrer, and amperometric concentration monitoring as shown in Figure 17 have been used. In this case, the two phases were highly mixed at the constant stirring speed of 2150 r/min, where the extraction of Fe(III) has been assumed to proceed in a kinetic regime. The results obtained from the kinetic experiments have shown that

1. The reaction order with respect to [Fe(III)] and $[\overline{\mathrm{Fe(III)}}]$ in the forward and reverse extraction is equal to one.
2. $\overrightarrow{V}^*_o = -\, d[\mathrm{Fe(III)}]/dt\ 1/[\mathrm{Fe(III)}]$ is an increasing function of the analytical concentration of HB and a decreasing function of $[H^+]$. These functions are reported in Figure 45.
3. $\overleftarrow{V}^*_o = d[\mathrm{Fe(III)}]/dt\ 1/[\mathrm{Fe(III)}]$ is, on the contrary, an increasing function of the analytical concentration of $H^+$ and a decreasing function of the analytical $\overline{\mathrm{HB}}$ concentration.

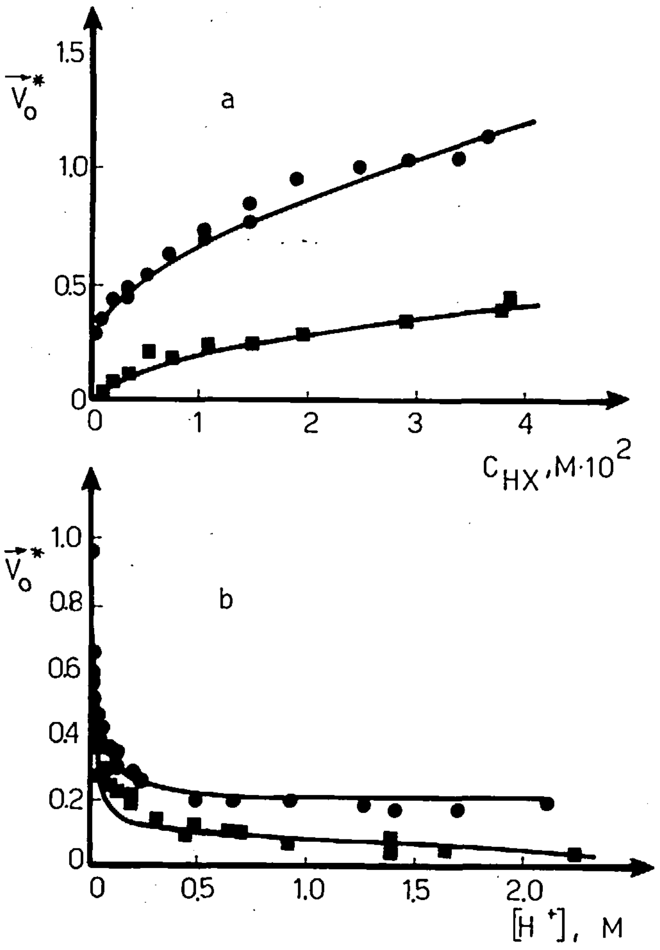


FIGURE 45. Dependence on the normalized rate of iron extraction $\vec{V}_0^* = \vec{V}_0/[Fe^{3+}]$ by toluene solutions of tri-n-butylacetohydroxamic acid HX, from the analytical concentration of HX, $C_{HX}$, and hydrogen ion concentration. (a) ● $[Fe^{3+}] = 8.73 \cdot 10^{-4} M$, $[H^+] = 2.00 \cdot 10^{-2} M$, $[NO_3^-] = 2M$; ■ $[Fe^{3+}] = 8.73 \cdot 10^{-4} M$, $[H^+] = 2.00 \cdot 10^{-1} M$, $[NO_3^-] = 2M$, and (b) ● $[Fe^{3+}] = 8.73 \cdot 10^{-4} M$, $[NO_3^-] = 2M$, $C_{HX} = 1.95 \cdot 10^{-2} M$ in toluene; ■ $[Fe^{3+}] = 8.73 \cdot 10^{-4} M$, $[NO_3^-] = 2M$, $C_{HX} = 5.33 \cdot 10^{-3} M$ in toluene. (From Chiarizia, R., Danesi, P. R., and Fornarini, S., *J. Inorg. Nucl. Chem.*, 41, 1465, 1979. With permission.)

On the basis of the relatively large concentration of HB in the aqueous phase (a partition coefficient of HB, $K_D \simeq 40$, has been determined in the experimental conditions used) and the quite strong surface active properties of HB (see Figure 8), the following reaction mechanism has been suggested:

1. The two aqueous reacting species are the $Fe^{3+}$ (hydrated) and the $Fe(OH)^{2+}$ (hydrated) cations. Although $Fe(OH)^{2+}$ is always present at very low concentrations, its very high reactivity makes this species kinetically very important even at relatively high acidities. Both Fe(III) species can slowly react with the undissociated HB molecules to form the 1:1 complex. The reactions occur through two parallel

paths: (a) in the aqueous phase with the HB molecules which have been solubilized by the electrolyte and (b) at the interface where an adsorbed layer of molecules has been shown to exist.

2. The $FeB^{2+}$ complex formed both in the aqueous phase and at the interface is rapidly transformed to an interfacial uncharged complex $(FeB_3)_{ad}$.
3. The interfacial uncharged complex, $(FeB_3)_{ad}$, is slowly transferred into the bulk organic phase through a desorption-adsorption reaction. The less surfactive $(FeB_3)_{ad}$ is replaced at the interface by three molecules of the stronger surfactant, HB.
4. The $FeB_3$ complex is rapidly solvated by an HB molecule in the bulk toluene phase to yield the final product of the extraction reaction $\overline{FeB_3 \cdot HB}$.
5. The opposite sequence (5 to 1) occurs when the reverse (organic iron(III) aqueous iron(III)) reaction takes place, providing [Fe(III)]:[HB] is sufficiently low. When this condition is not present, the occurrence of organic polynuclear complexes can introduce further complications.

The quantitative treatment of this mechanism, following the procedure already reported in Section V.A.1.c.iv has led to the rate Equations 67 and 68, valid for a saturated interface, i.e., for an analytical bulk concentration of $\overline{HB} \geqslant 1.10^{-3} M$. Equations 67 and 68, with the following values of the kinetic and equilibrium parameters,

$$K_1 / K_{D,R} = (17 \pm 2)\, M^{-1}\, \mathrm{min}^{-1}$$

$$K_2 K_h / K_{D,R} = (0.65 \pm 0.05)\, \mathrm{min}^{-1}$$

$$K_3 \alpha_2 a = (3.0 \pm 0.3) \cdot 10^{-2}\, \mathrm{min}^{-1}$$

$$K_4 \alpha_2 a K_h = (6.0 \pm 0.5) 10^{-3} M\, \mathrm{min}^{-1}$$

$$\left( \frac{K_{-4} a}{K_{e,2}} + \frac{K_{-2}}{K_{e,1}} \right) / K_5 = (3.0 \pm 0.5) \cdot 10^{-9}$$

$$\left( \frac{K_{-3} a}{K_{e,2}} + \frac{K_{-1}}{K_{e,1}} \right) / K_5 = (7 \pm 1) \cdot 10^{-9}$$

have been found to fit the experimental data. The solid lines reported as an example in Figure 45 show the fit of the data $\vec{V}_o^*$ vs. $[H^+]$ and $\vec{V}_o^*$ vs. analytical HB concentration. A further support to the validity of the hypothesized mechanism has been obtained by the comparison between the biphasic overall extraction reaction equilibrium constant ($K_{eq} = (5.0 \pm 0.7) \cdot 10^8 M^{-1}$), experimentally determined, and the equilibrium constants calculated from the kinetic parameters applying the principle of microscopic reversibility, i.e., $K_{eq} = (10 \pm 3) \cdot 10^8 M^{-1}$ (for the reaction path involving the nonhydrolyzed cation) and $K_{eq} = (4.5 \pm 1.5) \cdot \times{:}^{8} M^{-1}$ (for the reaction path involving the hydrolyzed cation), respectively.

In addition, the values of the rate constants $K_1$ and $K_2$ referring to the reaction with HB in the aqueous phase of $Fe^{3+}$ and $FeOH^{2+}$ ($K_1 = 11 M^{-1}\, \mathrm{sec}^{-1}$ and $K_2 = 2.7 \cdot 10^2 M^{-1}\, \mathrm{sec}^{-1}$, respectively) have been found to fall in the range expected for the homogeneous reaction of a ligand with iron(III).[97] The possibility that the acid dependence of $V^*_o$ could be ascribed to the reaction between $Fe^{3+}$ and $B^-$ has been excluded on the basis of the too high value which would have been obtained for the rat constant of this reaction ($\sim 10^{10} M^{-1}$ $sec^{-1}$). The numerical values of the rate constants $K_1$ and $K_2$ have indicated that the substitution of a water molecule in the inner coordination sphere of the metal ion is the rate determining process of the complex formation reaction. This consideration can of course be extended to the same reaction taking place at the interface and consequently to the overall process of extraction of Fe(III) from the aqueous to the organic phase by tri-n-butylacetohydroxamic acid.

The complex formation reaction, occurring simultaneously in the bulk aqueous phase and at the interface, has been interpreted as following Eigen's mechanism,[120] where the fast formation of an outer-sphere complex is followed by the slow substitution of a water molecule coordinated to the metal ion:

$$Fe(H_2O)_6^{3+} + HB \rightleftharpoons Fe(H_2O)_6^{3+} \text{ ---- } HB \rightleftharpoons FeB(H_2O)_5^{2+} + H_2O + H^+$$

$$FeOH(H_2O)_5^{2+} + HB \rightleftharpoons FeOH(H_2O)_5^{2+} \text{ ---- } HB \rightleftharpoons FeB(H_2O)_5^{2+} + H_2O$$

The faster rate of reaction of $FeOH(H_2O)_5^{2+}$ compared to that of $Fe(H_2O)_6^{3+}$ can be explained by considering that the electron donation from the hydroxide ion can make the dissociation of coordinated water molecules from $FeOH(H_2O)_5^{2+}$ faster than from the aquoferric ion.

This section can be concluded by remarking that the extraction of Fe(III) with tri-n-butylacetohydroxamic acid is the only case reported in the literature where two parallel reaction paths, one homogeneous and the other heterogeneous, have been simultaneously proposed to control the extraction rate in a kinetic regime. These two paths are probably a consequence of the nonnegligible solubility in the aqueous phase and the quite strong interfacial activity of the extractant. It is therefore plausible to foresee that, apart from possible steric complications, a reaction mechanism entirely based on interfacial reactions could explain the kinetic behavior of other less water-soluble hydroxamic acids.

The rather slow extraction kinetics of iron(III) is the result of the slow water substitution reaction. Similarly to the case of HTTA, it is therefore possible that the extraction reaction could be made more rapid by the introduction of iron complexing anions in the water phase.

### *4. Thiocarbazones*

In spite of the well known and wide analytical applications of solvent extraction procedures utilizing thiocarbazones, relatively little attention has been paid to the quantitative study of the kinetic behavior of these compounds. The first quantitative investigation of the extraction kinetics of $Zn^{2+}$ from 1 $M$ perchlorate solutions by means of dithizone (diphenylthiocarbazone) dissovled in $CCl_4$ or $CHCl_3$ has been reported in Reference 121.

Separatory funnels, mechanically shaken, with discontinuous sampling and radiochemical analysis of the tracer $^{65}Zn$ have been used to obtain rate data. Similar to other studies, it has been observed that the rate of extraction increased with the shaking speed up to a plateau region. The kinetics measurements were then performed at a shaking speed falling within this plateau region, where it was assumed that the extraction occurred in a kinetic regime. The analysis of the experimental data, after establishing that the plots of log ([Zn]$_0$/[Zn]) vs. t were straight lines, i.e., the reaction was first order with respect to the zinc concentration, has been performed evaluating the slopes of the plots. The following rate law has been obtained:

$$V_0 = K[Zn^{2+}][\overline{HDz}][H^+]^{-1} \qquad (192)$$

where HDz represents dithizone.

This rate equation has led the authors to conclude that the mechanism ruling the extraction process is that reported in Section V.A.1.a, i.e., the fast distribution and dissociation of HDz, the slow formation of the 1:1 complex in the aqueous phase, according to the reaction

$$Zn^{2+} + Dz^- \xrightarrow{K} ZnDz^+ \qquad (193)$$

followed by the fast formation and distribution of the final $ZnDz_2$ complex. Although the distribution of HDz has been reported in Reference 122 to be rather slow, the partition of the reagent between the two phases has been excluded as a possible rate determining step on the basis of the very high interfacial area which resulted from the very vigorous stirring of the phases. Different values of the rate constants K′ have been obtained in $CCl_4$ and $CHCl_3$. However, the authors have not been able to explain the experimentally observed differences between the K′ values. In fact, from Equations 192 and 193 it follows

$$K' = K \frac{K_a}{K_{D,R}} \qquad (194)$$

with $k_a$ the acid dissociation constant and $k_{D,R}$ the distribution constant of $HD_z$. Therefore, the ratio between the rate constants in the two diluents was expected to be equal to

$$K_a/K_{D,R(CCl_4)}/K_a/K_{D,R(CHCl_3)} = 15$$

The experimentally found ratio between the K′ values was instead

$$K'_{(CCl_4)}/K'_{(CHCl_3)} = 58$$

A tentative explanation of this difference can be found if a reaction mechanism, based on the reaction between $Zn^{2+}$ and $Dz^-$ at the interface, is assumed. In this case in fact, following the same kind of reasoning reported in Section V.A.1.c, the apparent kinetic constant would include Langmuir adsorption constants which could be quite different in the two solvents. Unfortunately, no information is available on the interfacial behavior of HDz in the two diluents to support this hypothesis.

In spite of the uncertainty of the localization of the rate controlling step, a strong support to the correctness of its formulation (Equation 193) has been given by the numerical value of K ($\sim 3 \cdot 10^7 M^{-1}$ sec$^{-1}$), found in good agreement with that expected for a water substitution reaction in the zinc ion inner coordination sphere.[94]

The extraction kinetics of $Zn^{2+}$, $Ni^{2+}$, and $Co^{2+}$ have been successively studied using dithizone, 2,2′-dimethyl-dithizone (HMeDz), and di$\alpha$-naphthylthiocarbazone ($\alpha$-NHDz) in $CHCl_3$ as extracting reagents.[123] The experimental conditions and the procedure followed have been the same as those of Reference 121. The results obtained have been expressed by the same rate law (Equation 192) in spite of some small deviations of the reaction orders from integer numbers. The rate law (Equation 192) has been found to not hold for $Cd^{2+}$, where the reactions occurred too rapidly and for the system $Zn^{2+}$-$\alpha$-NHDz, where the reaction orders with respect to [$H^+$] and the extractant concentration were found equal to −2 and 2, respectively. The unexpected result that the bulky groups on the phenyl rings of dithizone increased the rate of formation of the zinc chelates has also been found. On the basis of the higher stability of the 1:1 Zn-dithizonate complex compared to that of the 1:1 Zn-methyl-substituted chelate, the authors have then concluded that Reaction 193 had to be more complex than previously formulated. The following mechanism was then assumed for the aqueous reaction between $Zn^{2+}$ and HDz:

$$Zn(H_2O)_6^{2+} + Dz^- \xrightleftharpoons{K_{eq,1}} Zn(H_2O)_4Dz^+ + 2H_2O \qquad \text{fast} \tag{195}$$

$$Zn(H_2O)_4Dz^+ \xrightarrow{K_1} Zn(H_2O)_2Dz^+ + 2H_2O \qquad \text{slow} \tag{196}$$

$$Zn(H_2O)_2Dz^+ + Dz^- \xrightarrow{K_2} ZnDz_2 + 2H_2O \qquad \text{slow} \tag{197}$$

where the rate determining step (Reaction 196) can now explain the increased rate observed with substituted dithizones. The authors in fact state that these substituted compounds have a greater tendency to remove water molecules after the addition of the first ligand since the steric strain due to the substituents is energetically compensated for by the change in structure from octahedral to tetrahedral. The reaction orders −2 and 2 obtained with $Zn^{2+}$ and $\alpha$-NHDz have been explained assuming that for this system it was $K_1 > K_2$, with Reaction 197 now becoming rate determining. The following values of the rate constant $K_1$ have been reported: $6.3 \cdot 10^3$ min$^{-1}$ for HDz and $4.5 \cdot 10^5$ min$^{-1}$ for HMeDz. Also in this case, the importance of the lability of the metal-ion-water bond in determining the reaction rate has been evidenced by comparing the K values calculated by Equation 194 for the different cations and extractants, with the rates of water substitution reported in Reference 94. The series of the rate constants has been found equal to that of water substitution, i.e., $K_{Cd^{2+}} > K_{Zn^{2+}} > K_{Co^{2+}} > K_{Ni^{2+}}$. A series of substituted dithizones in $CHCl_3$ (di-*p*-fluoro, di-*p*-chloro, di-*p*-bromo, di-*p*-iodo, di-*m*-trifluoromethyl, di-*p*-methyl, and di-*p*-methoxyphenyl) have been also kinetically investigated[124] as extractants of $Zn^{2+}$ and $Ni^{2+}$ using the technique already described.[121] Also in this case, the overall rate determining step (Reaction 193) has been found to explain the reaction orders experimentally determined. The rate constants have instead been found always higher than those evaluated for the unsubstituted dithizone. Furthermore, their wide variation in the extractant series has been taken as a strong indication that the formation of the 1:1 metal dithizonate complex involved a metal-ligand bonding rather than a simple ion-pair formation.

The effect of auxiliary aqueous ligands on the extraction rate of $Ni^{2+}$ and $Zn^{2+}$ by dithizone in $CHCl_3$ has been studied in Reference 125. When the concentration of these ligands was such that only 1:1 complexes were formed in the aqueous phase, the experimental results have shown that the extraction rate of both cations was increased by the presence of thiocyanate and mercaptoacetate anions. When acetate ions were added, only the rate of $Zn^{2+}$ extraction was increased. These effects have been attributed to the increased rate of water release when the net charge on the metal ion was reduced as a consequence of the complex formation. On the other hand, when the 1:2 complexes were formed, they reacted with dithizone more slowly than the hydrated metal ions, indicating that in this case the coordination sphere of the central ion was saturated by the auxiliary ligand molecules, hindering the reaction with dithizone. On the basis of these considerations, the authors have suggested useful analytical applications and an interesting kinetic method to obtain reliable values of stepwise formation constants.

The extraction of $Zn^{2+}$ from a $Cl^-$ medium in an acetic buffer by dithizone in $CCl_4$ and $CHCl_3$ has been also studied in References 8 and 14 by the moving drop technique and the constant interfacial area stirred cell shown in Figure 14. From the straight-line dependence of the initial transfer rate on the interfacial area, evaluated by the moving drop method, the authors have concluded that the rate controlling processes had to be heterogeneous. In addition, the results obtained with the constant interfacial area cell have shown that the dependence of the transfer rate in both diluents on the stirring speed of the aqueous phase exhibited both a flow-dependent and a flow-independent (plateau area) region. This plateau region started at stirring speeds increasingly lower when the $Zn^{2+}$ concentration was decreased. On the contrary, when the $Zn^{2+}$ concentration was very high compared to that of the extractant concentration ($10^{-2}M$ and $1.5\cdot10^{-1}M$ for $[\overline{HDz}] = 1.25\cdot10^{-4}M$ in $CCl_4$ and in $CHCl_3$, respectively), the plateau was not reached at all.

In the flow-dependent region, the extraction rate has been found to be described by the equation

$$\frac{d[\overline{ZnDz_2}]}{dt}\frac{V}{A} = -\frac{1}{2}\frac{d[\overline{HDz}]}{dt}\frac{V}{A} = \text{const}\cdot[\overline{HDz}] \qquad (198)$$

that is proportional only to the extractant concentration. This equation has been explained considering that only the transport process of HDz out of the organic bulk phase to the interface was rate controlling. In this case, the transport equation

$$\frac{d[\overline{ZnDz_2}]}{dt}\frac{V}{A} = \frac{1}{2}\beta_{HDz}([\overline{HDz}] - [HDz]_i) \qquad (199)$$

had to hold since $[\overline{HDz}]_i$ was always negligible as demonstrated by the authors of Reference 8. In the flow-independent region, due to the very well-characterized hydrodynamic conditions, a kinetic regime has been unambiguously assumed. The determination of the reaction orders with respect to the concentrations of $Zn^{2+}$, $H^+$, and $\overline{HDz}$ has led to the same rate law (Equation 192) previously reported. To take into account the heterogeneous character of the rate controlling process, the authors have concluded that Reaction 193 assumed as the rate determining step, occurred at the interface and not in the aqueous bulk phase as suggested in References 121 and 123 through 125. In this case, similar to Equation 194, it followed that

$$K' = K\,K_{a,i} \qquad (200)$$

with $K_{a,i}$ the interfacial acid dissociation constant of HDz. However, also in this case, the authors have not been able to explain the much faster extraction reaction occurring with $CCl_4$ compared to $CHCl_3$ since they have not taken into consideration possible variations of $K_{a,i}$ with the organic diluent properties.

The transient region, where transport processes and interfacial reactions were both controlling the extraction kinetics, has been treated in terms of mass-transfer resistances, as already reported in Section VII. The same kinetic behavior of the $Zn^{2+}$-dithizone-$CCl_4$/$CHCl_3$ system has been also experimentally observed in the case of the systems $Cd^{2+}$-dithizone-$CCl_4$/$CHCl_3$ and $Co^{2+}$-dithizone-$CCl_4$, with different values of the rate constants.[126]

The results reported in this section can be summarized as follows: in kinetic regime conditions it seems quite well established that the rate determining step of the extraction process is the reaction between the unhydrolyzed metal cations and the dithizonate anion, although discordance of opinions still exists on the localization of the rate determining step, i.e., whether interfacial or in the bulk aqueous phase. The determination of the interfacial properties of the systems could probably help to better clarify this point.

### *5. Alkylphosphoric Acids*

This class of compounds has received much attention due to their potentiality in the fields of the reprocessing of nuclear fuel, the selective hydrometallurgical recovery of metals, and in analytical chemistry. The first detailed investigations on the kinetics of metal extraction by organophosphorous acids have been performed by Russian workers.[27,127,128] Their works as well as the previous literature on the subject up to 1970 have been reviewed in Reference 129. Therefore, only the main conclusions reached in these investigations will be briefly reported in this section. In reference 128, where the extraction of iron(III) from perchloric acid into di(2-ethylhexyl) phosphoric acid (HDEHP) in n-octane has been studied, a mechanism has been proposed involving, as the rate determining step, the homogeneous reaction between $Fe^{3+}$ ions and the anion $DEHP^-$, solubilized in the aqueous phase. In References 27 and 127, the extraction rate of the same cation from various mineral acid media by di-isopentyl-phosphoric acid in benzene has been studied. On the basis of the discovered proportionality between the extraction rate and the specific interfacial area, both in quiescent interface systems and stirred tanks, the conclusion has been reached that the rate limiting stage of the extraction process occurred at the interface. The importance of the interfacial reactions has also been recognized in Reference 130, where the extraction kinetics of copper and cobalt from sulfate solutions by HDEHP, in a Lewis-type cell, were analyzed in terms of mass-transfer resistances and the suggestion was made that an interfacial reaction such as

$$M^{2+} + H_2B_2 \longrightarrow MB_2H^+ + H^+$$

(with HB representing HDEHP) could be the rate determining process. The system iron(III)-perchlorate, HDEHP-n-octane has been also extensively studied in Reference 31. The rate of Fe(III) extraction was investigated both by the constant interfacial area stirred cell, shown in Figure 15, and by a baffled dispersion tank having standardized hydrodynamics.[100,101] This standardization has allowed the authors to determine the interfacial area by means of published correlations.[99] The results obtained with the constant interfacial area stirred cell have shown that the initial extraction rate was independent of the impeller speed over a rather wide range and proportional to the specific interfacial area. It was then concluded that neither homogeneous bulk reactions nor diffusion processes were rate determining and that the mechanism controlling the overall extraction process was based on interfacial chemical reactions. Concerning the dependence of the rate on the chemical parameters, it has been shown that a first reaction order with respect to $Fe^{3+}$ concentration was not always obtained. Further, the reaction order varied in a complex way as a function of $\overline{\mathrm{HDEHP}}$ and $H^+$ concentrations, with widely varying power dependences. The mechanism which has been proposed to explain the experimental results consisted of a series of two groups of parallel interfacial reactions. The first group of reactions accounted for the formation of the 1:1 interfacial complex via reaction of the hydrated $Fe^{3+}$ with the monomer and dimer of the ionized $\overline{\mathrm{HDEHP}}$:

$$\begin{tikzcd}
\mathrm{Fe(H_2O)_6^{3+}} + \mathrm{B^-} \arrow[r, "K_{1,m}"] & \mathrm{(H_2O)_5FeB^{2+}} + \mathrm{H_2O} \arrow[d, shift left] & (201) \\
\mathrm{Fe(H_2O)_6^{3+}} + \mathrm{HB_2^-} \arrow[r, "K_{1,d}"] & \mathrm{(H_2O)_5FeB^{2+} \cdot HB} + \mathrm{H_2O} \arrow[u, shift left, "+\,\mathrm{HB}"] & (202)
\end{tikzcd}$$

The second group, in series with the first one, consisted of the formation of the 1:2 interfacial complex through the following simplified parallel reactions:

$$(H_2O)_5FeB^{2+} \cdot HB \rightleftharpoons (H_2O)_5FeB^{2+} \cdot H^+ + B^- \xrightarrow{K_{2,s}} (H_2O)_4FeB_2^+ + H_2O + H^+ \qquad (203)$$

$$(H_2O)_5FeB^{2+} + HB_2^- \xrightarrow{K_{2,d}} (H_2O)_4FeB_2^+ \cdot HB + H_2O \qquad (204)$$

$$(H_2O)_5FeB^{2+} \cdot HB + HB_2^- \xrightarrow{K'_{2,d}} (H_2O)_4FeB_2^+ \cdot HB + HB + H_2O \qquad (205)$$

where the subscripts m and d refer to the reaction with the HDEHP monomer and dimer, respectively and the subscript s refers to saturation of the interface with monocomplexed iron. The intermediate hydroxospecies, hypothesized by the authors are transiently formed along each of the Reactions (201 to 205), have been omitted for the sake of simplicity.

The series (Reactions 201 to 202 and 203 to 205) was then followed by the fast desorption of the interfacial 1:2 complex and the fast formation in the organic phase of the final complex $\overline{FeB_3(HB)_3}$. The combination of the parallel and series steps has then allowed the authors to derive the following normalized overall extraction rate:

$$-\frac{d[Fe]}{dt}\frac{1}{[Fe]} = \frac{(V_{1,m} + V_{1,d})(V_{2,s} + V_{2,d} + V'_{2,d})}{V_{1,m} + V_{1,d} + V_{2,s} + V_{2,d} + V'_{2,d}} \qquad (206)$$

which fit the experimental data in a wide range of HDEHP, $H^+$ and $Fe^{3+}$ concentrations, with the following expressions for the single step rates:

$$V_{1,m} = 5.5 \cdot 10^{-4} C^{0.5}/[H^+]$$

$$V_{1,d} = 1.8 \cdot 10^{-3} C/[H^+]$$

$$V_{2,s} = 1.5 \cdot 10^{-7}/[H^+][Fe^{3+}]$$

(assuming the interface saturated with the monocomplex)

$$V_{2,d} = 9.0 \cdot 10^{-6} C^{1.5}/[H^+]^2$$

$$V'_{2,d} = 1.2 \cdot 10^{-5} C^2/[H^+]^2$$

where C represents the analytical concentration of HDEHP.

The alternative acid-dependent steps involving the reaction of $FeOH^{2+}$ with the undissociated extractant, very often encountered in the previous sections, were excluded by the authors because they could not explain the dependence of the extraction rate on the iron concentration.

The experiments performed in a stirred tank, while confirming the proportionality existing between the extraction rate and the calculated interfacial area, have evidenced the absence of Reaction 203 and that the contribution of Reactions 204 and 205 was smaller compared to the constant interfacial area cell case. These differences have been attributed to the increased rate of desorption of the monocomplex into the organic phase due to the rapid expansions and contractions of the interface as the droplets formed and coalesced. The rate of extraction was found equal to

$$-\frac{d[Fe]}{dt}\frac{1}{[Fe]} = \frac{(V_{1,m} + V_{1,d})V_2}{V_{1,m} + V_{1,d} + V_2} \qquad (207)$$

Rate Equation 207 implies a series of the parallel Reactions 201 and 202 with an unidentified step having the rate

$$V_2 = 4 \cdot 10^{-4}/[H^+]^2 \qquad (208)$$

accounting for the contribution of the introduction of the second anion ligand. As previously mentioned, Reactions 201, 202, 204, and 205 were considered by the authors to proceed through transient intermediate hydroxospecies, analogous to the formation of the ferric chloride complex assumed by Eigen,[131] i.e.,

$$Fe(H_2O)_6^{3+} + Cl^- \longrightarrow (H_2O)_5FeOH^{2+} + H^+Cl^- \longrightarrow (H_2O)_5FeCl^{2+} + H_2O \qquad (209)$$

This hypothesis has been supported by the enhancement of the extraction rate in presence of $Cl^-$ and other aqueous, soluble, proton-accepting complexing ions such as nitrate, acetate, citrate, and phosphate.[129]

It has to be mentioned that in the review on the kinetics of metal extraction by organophosphorous acids previously quoted[129] the extraction of beryllium from perchloric solutions by HDEHP has been reported to also behave kinetically in a way similar to iron (III); no evidence of Reaction 203 was, however, found.

The rate of extraction of lanthanide(III) ions from aqueous solutions containing a strong chelating agent, diethylenetriaminepentaacetic acid (DTPA), and an additional carboxylic acid, latic acid, by HDEHP solutions in n-dodecane has been studied in References 132 and 133 in the frame of the investigations on the actinide-lanthanide separation procedure denoted TALSPEAK. By using stirred vessels where the phases were thoroughly dispersed, on the basis of the proportionality between extraction rate and stirring velocity up to 2400 r/min, the conclusion has been reached that the rate was determined by interfacial reactions. A proportionality between the stirring speed and the interfacial area was in fact assumed. As the rate determining step, the interfacial dissociation of the complex $LnY^{2-}$ (where $Y^{5-}$ is the anion of DTPA) followed by the reaction at the interface of the metal ion with the extracting HDEHP molecules to give the final complex of the extraction, has been proposed. The authors also report that the dissociation of $LnY^{2-}$ was catalyzed by $H^+$ and lactate anions through the formation of intermediate species such as $EuH_2Y$ and $Eu(lactate)Y^{3-}$. A saturation of the interface by HDEHP interfacial species was also assumed, at least for HDEHP $\geqslant$ 1*M*; no experimental independent evidence of this saturation has been given however.

Completely different conclusions have been reached instead by the authors of Reference 134 who have studied the kinetics of scandium extraction from 0.5 and 8*M* HCl solutions by HDEHP in a kerosene diluent by means of a constant interfacial area stirred cell. The extraction reaction has been found first order with respect to the metal concentration. From the variations of the rate constant with temperature, the activation energies of the extraction reactions from both weak (5.4 kcal/mol) and strong (1.8 kcal/mol) acidic solutions have been evaluated. On the basis of these data only, the authors have concluded that the scandium extraction rate was controlled by diffusion processes. The limited validity of such a conclusion, not supported by other physico-chemical measurements, has been already discussed in Section III.

The extraction kinetics of $Ca^{2+}$ from nitric aqueous solutions into dodecane solutions of HDEHP has been thoroughly investigated in Reference 23, making use of a constant interfacial area stirred cell. The results obtained in this work can be summarized as follows:

1. The rate of mass transfer was proportional to the interfacial area and increased with the stirring speed in both phases up to 100 r/min (no plateau region was reached).

2. The transfer rate was affected only by the aqueous phase stirring.
3. The experimental logarithmic plots of the forward and reverse transfer rates vs. $H^+$ and $\overline{HDEHP}$ concentrations had shapes very similar to those reported in Figure 28 (Section V.A.1.c.iii).
4. HDEHP showed surface active properties at the interface dodecane-aqueous $HNO_3$, and the plot of the interfacial tension vs. the logarithm of HDEHP concentration (Figure 6) allowed to establish, by means of the Gibbs equation, that a saturated interface was obtained when the molar concentration of the extractant was about 0.025*M*.

From these results, the authors have concluded that the extraction of $Ca^{2+}$ by HDEHP was limited both by diffusion through a viscous water layer adjacent to the interface and chemical reactions taking place at the interface. This conclusion appears rather convincing because of the low degree of stirring of the solutions. The slowness of the crossing of the viscous water layer has been attributed to the presence of a highly structured, "ice-like" water layer several molecules thick formed through hydrogen bonding with the HDEHP interfacial monolayer. The increased rates observed by raising the stirring speed has then been explained as caused by eddies which could break up this water structure.

From the concentration dependences of the forward and reverse extraction rates, the following interfacial reaction mechanism has been proposed:

$$Ca^{2+} + (HB)_{2,ad} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} (CaB_2)_{ad} + 2H^+ \qquad (210)$$

$$(CaB_2)_{ad} + 2(\overline{HB})_2 \underset{K_2}{\overset{K_{-2}}{\rightleftharpoons}} \overline{CaB_2(HB)_4} \qquad (211)$$

that is, formation of the interfacial neutral complex followed by its desorption from the interface through the reaction with extractant bulk molecules to form the final complex of the extraction process. This mechanism has allowed to derive expressions for the aqueous to organic ($\beta_w$) and organic to aqueous ($\beta_{org}$) mass-transfer coefficients in terms of concentrations and stirring-dependent parameters. The following equations have been so obtained:

$$\beta_w = \frac{K_1[(HB)_2]_{ad}K_{-2}[(\overline{HB})_2]^2}{K_{-2}[(\overline{HB})_2]^2 + K_{-1}[H^+]^2} \qquad (212)$$

$$\beta_{org} = \frac{K_2K_{-1}[H^+]^2}{K_{-2}[(\overline{HB})_2]^2 + K_{-1}[H^+]^2} \qquad (213)$$

where $\beta_w$ and $\beta_{org}$ were referred to the pseudo first order rate law

$$V = A(\beta_w[Ca^{2+}] - \beta_{org}[\overline{Ca}]) \qquad (214)$$

which was always followed by the extraction rate data. An expression for the $Ca^{2+}$ partition coefficient E has been also derived in terms of concentrations and rate parameters by using the equilibrium condition V = 0:

$$E = \frac{K_1[(HB)_2]_{ad}K_{-2}[(\overline{HB})_2]^2}{K_2K_{-1}[H^+]^2} \qquad (215)$$

It has to be mentioned that while $K_2$ and $K_{-2}$ are stirring-independent parameters, $K_1$and $K_{-1}$ are functions of the stirring speed. However, the validity of the equilibrium relationship (Equation 215) was warranted by the same stirring dependence of $K_1$ and $K_{-1}$. Equations 212, 213, and 215 have been found to fit the experimental data well with the following numerical values of the rate parameters referring to 60 r/min: $K_1$ $[(HB)_2]_{ad}$ = $6.7 \cdot 10^{-4}$ cm sec$^{-1}$ (for a saturated interface), $K_2$ = $1.85 \cdot 10^{-4}$ cm sec$^{-1}$, $K_{-2}/K_{-1} = 5.0 \cdot 10^{-3}$.

The extraction kinetics of titanium from sulfuric acid media by HDEHP in benzene at 30°C has also been investigated by means of agitated separatory funnels.[135] No information has been reported in this work on the dependence of the extraction rate on the agitation speed. The authors have determined that the extraction reaction stoichiometry was

$$1/3\,(TiO^{2+})_9 + 3\,\overline{H_2B_2} \overset{K_{eq}}{\rightleftharpoons} \overline{(TiOB_2)_3} + 6H^+; K_{eq} = 4.36 \cdot 10^3 \qquad (216)$$

where HB stands for HDEHP, $\overline{(TiOB_2)_3}$ is the final equilibrium titanium complex, and $(TiO^{2+})_9$ the initial polymerized aqeous titanium species. The kinetic measurements have been analyzed following a procedure similar to that already reported in References 89 through 93, i.e., hypothesizing that the rate law could be expressed simply by a product of concentrations each one elevated to an integer value and then determining the reaction orders with respect to the various chemical species by means of logarithmic plots. The authors have concluded that the following rate laws held for the forward and reverse extraction, respectively:

$$\vec{V} = -\frac{d[Ti]}{dt} = K_f[Ti]^3[H^+]^{-6}[\overline{H_2B_2}]^3 \qquad (217)$$

$$\overleftarrow{V} = \frac{d[Ti]}{dt} = K_r[\overline{Ti}][H^+]^2[\overline{H_2B_2}]^{-1} \qquad (218)$$

with $K_r = 1.36 \cdot 10^{-6}$ sec$^{-1}$.

To explain the rate law (Equation 217), a trimeric titanyl complex has been assumed as a reacting species. The following mechanism was proposed for the forward reaction:

$$(TiO^{2+})_9 \rightleftharpoons 3(TiO^{2+})_3 \qquad \text{fast} \qquad (219)$$

$$\overline{H_2B_2} \rightleftharpoons H_2B_2 \qquad \text{fast} \qquad (220)$$

$$(TiO^{2+})_3 + 3H_2B_2 \longrightarrow (TiOB_2)_3 + 6H^+ \qquad \text{slow} \qquad (221)$$

$$(TiOB_2)_3 \rightleftharpoons \overline{(TiOB_2)_3} \qquad \text{fast} \qquad (222)$$

For the reverse extraction the mechanism proposed has been

$$1/3\,\overline{(TiOB_3)_3} \rightleftharpoons \overline{TiOB_2} \rightleftharpoons TiOB_2 \qquad \text{fast} \qquad (223)$$

$$TiOB_2 + 2\,H^+ \longrightarrow H_2B_2 + TiO^{2+} \qquad \text{slow} \qquad (224)$$

$$9\,TiO^{2+} \rightleftharpoons (TiO^{2+})_9 \qquad \text{fast} \qquad (225)$$

The proposed mechanisms however, appear, quite in disagreement with the rate laws (Equations 217 and 218) experimentally found. In fact if Equation 221 is assumed as the rate determining step, Equation 217 should be acid independent since the treatment of the kinetic data adopted by the authors applies to initial rates, that is, when the effect of the counterreaction is negligible. An alternative explanation of the dependence of Equation 217 on $[H^+]$ could instead be given by the rate determining step

$$(TiO^{2+})_3 + 3\,B_2^{2-} \longrightarrow (TiOB_2)_3$$

Concerning the reverse extraction, it is also highly improbable that the rate determining step (Equation 224) can explain the HDEHP dependence of Equation 218. Moreover, the rate controlling reactions have been arbitrarily assumed to occur in the aqueous phase, in spite of the already reported large number of experimental evidence concerning the importance of interfacial reactions in extraction rates with HDEHP. Finally, it has to be reported that considerable discrepancies have also been seen when equilibrium constants derived from equilibrium measurements and from kinetic measurements have been compared.

In conclusion, the results reported in this section seem to indicate that in the extraction kinetics of metal species by alkylphosphoric acids, interfacial chemical reactions also play a predominant role. In fact, they have been clearly found by all investigators who have been using appropriate research methodologies. Only a few systems ($Fe^{3+}$ and $Ca^{2+}$) have led to the identification of sound reactions mechanisms. Too few results therefore are available to draw any generalization on the type of mechanisms. It seems, however, that the interfacial mechanism is strongly dependent on the chemical nature of the metal species which are involved in the extraction.

### 6. *Sulfonic Acids*

High-molecular-weight sulfonic acids dissolved in water-immisible organic diluents have been utilized in solvent extraction chemistry, mainly to investigate the properties of aqueous electrolyte solutions. The solvent extraction properties of these extractants have been reviewed in Reference 136. The only organic sulfonic acid which has been used in solvent extraction kinetics studies is dinonylnaphthalenesulfonic acid (HD). In References 21, 32, 74, and 75, the interfacial properties of HD at a water-toluene interface[21] and the extraction kinetics of $Fe^{3+}$,[32] $Eu^{3+}$,[74] and other lanthanide cations[75] from aqueous perchloric acid solutions into toluene solutions of HD have been studied. The interfacial pressure data shown in Figure 9 have indicated that, as expected, this compound is a very strong surfactant which forms a completely saturated interface when its organic concentration is as low as $6 \cdot 10^{-7}$ *M*. The strong tendency toward polymerization of HD has also been demonstrated.[21]

The initial extraction rates of $Fe^{3+}$ and $Eu^{3+}$ have been studied in References 32 and 74 by using constant interfacial area stirred cells. The cell shown in Figure 17 has been used to study the $Fe^{3+}$ rate of extraction, while the radiometric monitoring technique has been employed to study the rate of $Eu^{3+}$ extraction. Since the rates of extraction have been evaluated at stirring speed values where the contribution of diffusional processes was assumed as negligible,[76] and a direct proportionality between $V_0$ and the specific interfacial area was measured, it has been concluded that the extraction kinetics could be described by a kinetic regime controlled by interfacial chemical reactions. The extraction mechanism and rate laws reported in Section V.A.1.c.iii have been therefore used to quantitatively describe the extraction kinetics. The experimental rate data which have been obtained with HD in toluene are reported in Figures 46, 47, and 48. The rate data refer to the direct and reverse extraction rates of Fe(III) at time zero, $\overrightarrow{V}_0$ and $\overleftarrow{V}_0$, as functions of the chemical composition of the system, i.e., $HClO_4$, HD, and the aqueous and organic Fe(III) concentrations. Since the reaction orders with respect to both the aqueous and organic metal concentrations have always been found equal to 1, the data have been plotted as normalized rates $\overrightarrow{V}_0^*$ and $\overleftarrow{V}_0^*$, that is, the initial rates divided by the initial metal concentrations. For $Eu^{3+}$ only the direct extraction rates have been obtained. These are reported in Figure 48. The reaction mechanism based on interfacial chemical reactions and described in Section V.A.1.c.iii for this specific extractant, consists of the following steps:

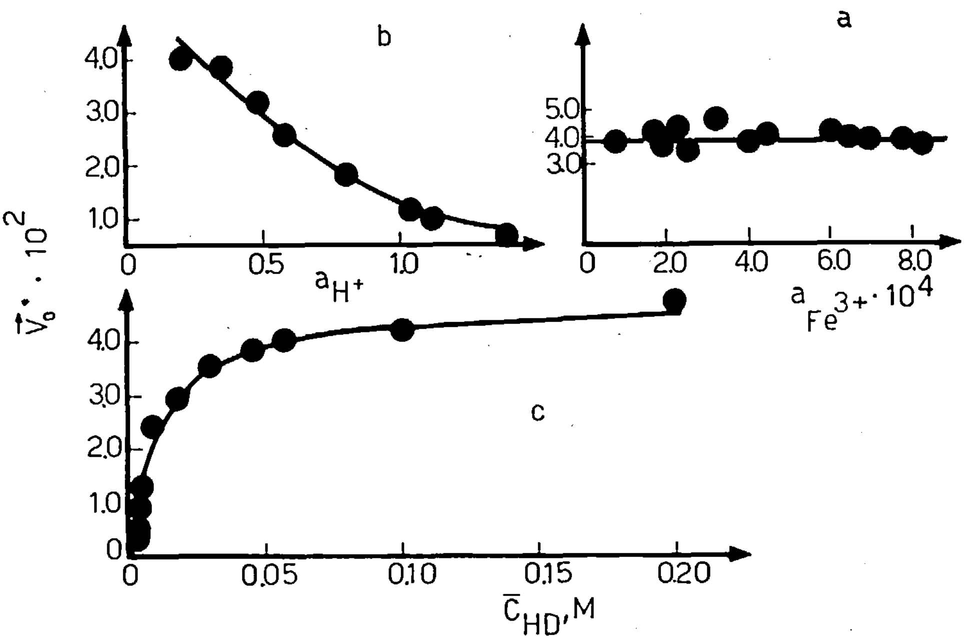


FIGURE 46. Normalized initial forward extraction rate of Fe(III), $\vec{V}_0^* = \vec{V}_0/[Fe^{3+}]$, from aqueous $HClO_4$ solutions into toluene solutions of dinonylnaphthalene sulfonic acid, HD. $\vec{V}_0^*$ vs. concentrations (or activity) plots: (a) $\vec{V}_0^*$ vs. $\cdot Fe^{3+}$ ($\bar{C}_{HD}^\circ = 0.046 M$, $[HClO_4] = 0.451 M$, (b) $\vec{V}_0^*$ vs. $a_{H^+}$. ($\bar{C}_{HD}^\circ = 0.046 M$, $[Fe^{3+}] = 6.87 \cdot 10^{-4} M$; (c) $\vec{V}_0^*$ vs. $\bar{C}_{HD_0}$ ($[HClO_4] = 0.451 M$, $[Fe^{3+}] = 6.87 \cdot 10^{-4} M$). $\bar{C}_{HD_0}$ = analytical concentration of organic HD. Solid lines calculated through Equation 231 and rate constants reported in the text. (From Danesi, P. R. and Chiarizia, R., Paper 9b, Proc. Int. Solv. Extr. Conf. ISEC 77, Toronto, 1977; Danesi, P. R. and Chiarizia, R., *J. Appl. Chem. Biotechnol.*, 28, 581, 1978. With permission.)

1. When water to organic phase transfer takes place the hydrated and/or partially ion-paired metal cations react with the layer of extractant molecules which are strongly adsorbed at the interface. A zero charge interfacial complex is formed in this way.
2. The interfacial complex is transferred into the organic phase by reacting with the polymerized molecules of the sulfonic acid present in the organic phase. The interfacial complex molecules leaving the interface are replaced on the interface by the extractant molecules.
3. When organic-to-water transfer is occurring, the organic complex formed between the sulfonic acid and the metal reacts with the monolayer of extractant molecules present at the interface forming the same zero charge interfacial complex.
4. The interfacial complex releases metal ions into the aqueous phase leaving the extractant molecules on the interface.

By assuming that only a very small fraction of the interfacial extractant molecules were converted into interfacial complexes and that an interfacial steady-state condition was instantaneously established for the interfacial complex, i.e., its concentration did not vary with time, the following reaction steps have been assumed for the extraction of the trivalent metal cation $M^{3+}$:

$$M(H_2O)_n X_p^{3-p} + (3-p)(HD)_{ad} \underset{K_3}{\overset{K_1}{\rightleftharpoons}} (M(H_2O)_i X_p D_{3-p})_{ad} + (3-p)H^+ \qquad (226)$$

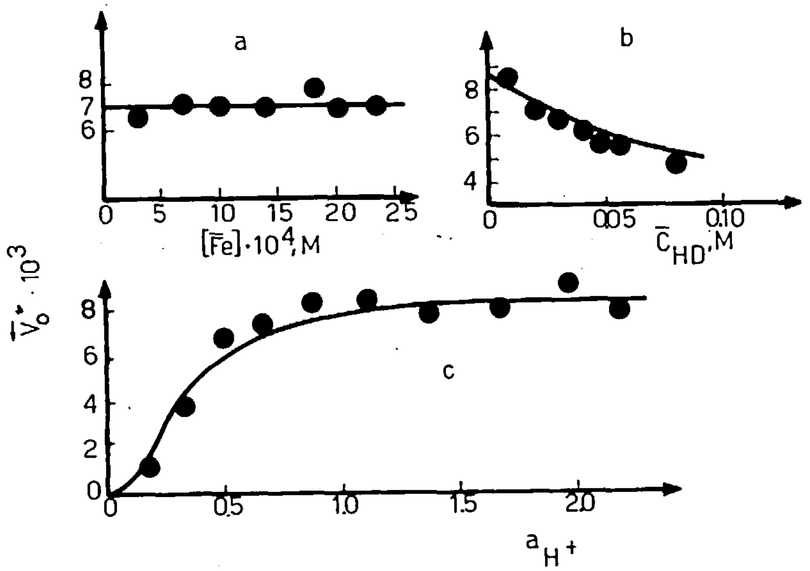


FIGURE 47. Normalized initial reverse extraction rate of Fe(III, $\vec{V}_0^* = \vec{V}_0/[\overline{Fe}]$, from toluene solutions of dinonylnaphthalene sulfonic acid, HD, into aqueous $HClO_4$ solutions. $\vec{V}_0^*$ vs. concentrations (or activity) plots: (a) $\vec{V}_0^*$ vs. $[\overline{Fe}]$ ($\bar{C}^o_{HD}$ = 0.025*M*, $[HclO_4]$ = 1.11*M*); (b) $\vec{V}_0^*$ vs. $\bar{C}_{HD}$ ($[HClO_4]$ = 1.18*M*, [Fe] = 7.01 $10^{-4}$ *M*); (c) $\vec{V}_0^*$ vs. $a_H$. ($\bar{C}^o_{HD}$ = 0.0125*M*, $[\overline{Fe}]$ = $1.16 \cdot 10^{-3}$*M*). $\bar{C}^o_{HD}$ = analytical concentration of organic HD. Solid lines calculated through Equation 231 and rate constants reported in the text. (From Danesi, P. R. and Chiarizia, R., Paper 9b, Proc. Int. Solv. Conf. ISEC 77, Toronto, 1977; Danesi, P. R. and Chiarizia, R., *J. Appl. Chem. Biotechnol.*, 28, 581; 1978. With permission.)

where n and i represent the number of solvated water molecules around the cation in the aqueous and in the organic phase (i can be substantially different from zero since it has been shown that cations which are extracted by HD retain at least some of their hydration water[138]), $X^-$ represents the $ClO_4^-$ anion, which in the case of iron can be bound to the aqueous cation as an ion-pair, i.e., p = 1. The rate of this process is

$$\vec{V}_1 = K_1[M] - K_1[M]_{ad}[H^+]^{3-p} \qquad (227)$$

where $K_1 = K_1'[HD]_{ad}^{3-p}$ since the interfacial concentration of the extractant was constant, [M] = activity of M $(H_2O)_nX_p^{3-p}$ which was practically constant with the concentration of $HClO_4$ in the range 0.2 to 1.5 *M* which was experimentally explored since both the activity coefficient of $M^{3+}$ and the fraction of ion-paired $M^{3+}$ were practically constant, $[M]_{ad}$ = interfacial concentration of $M(H_2O)_iX_pD_{3-p}$, and $[H^+]$ = mean activity of $HClO_4$.

The next step of the reaction has been then written as

$$(M(H_2O)_iX_pD_{3-p})_{ad} + (\overline{HD})_m \underset{\bar{K}_1'}{\overset{K_2'}{\rightleftharpoons}} \overline{M(H_2O)_i\,X_pH_{m-3+p}D_m} + (3-p)(HD)_{ad} \qquad (228)$$

where m is the degree of polymerization of the sulfonic acid in the organic phase. The rate of this step is

$$\vec{V}_2 = K_2[M]_{ad}\bar{C}_{HD} - \bar{K}_1[\bar{M}] \qquad (229)$$

where $K_1 = K_1'[HD]_{ad}^{3-p}$, $K_2 = K_2'/m$, $C_{HD}$ = analytical concentration of the sulfonic

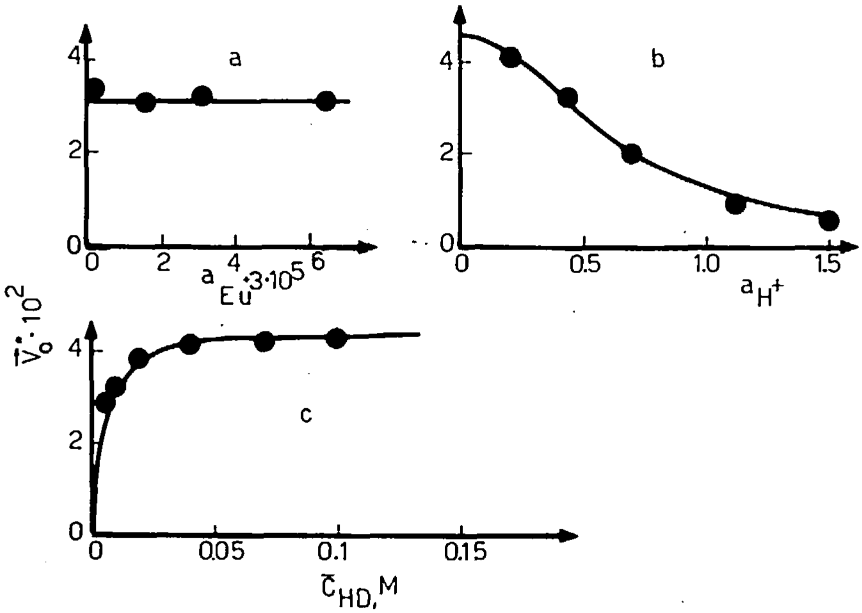


FIGURE 48. Normalized initial forward extraction rate of Eu(III), $\vec{V}_0^* = \vec{V}_0/[Eu^{3+}]$, from aqueous $HClO_4$ solutions into toluene solutions of dinonylnaphthalenesulfonic acid, HD. $\vec{V}_0^*$ vs. concentration (or activity) plots: (a) $\vec{V}_0^*$ vs. $\cdot Eu^{3+}$ ($\bar{C}_{HD}^{\circ} = 0.01 M$, $[HClO_4] = 0.545 M$); (b) $\vec{V}_0^*$ vs. $a_{H^+}$ ($\bar{C}_{HD}^{\circ} = 0.01 M$, $[Eu^{3+}] = 1.58 \cdot 10^{-6} M$); (c) $\vec{V}_0^*$ vs. $\bar{C}_{HD}^{\circ}$ ($[HClO_4] = 0.545 M$, $[Eu^{3+}] = 1.58 \cdot 10^{-6} M$) $\bar{C}_{HD}^{\circ}$ = analytical concentration of organic HD. Solid lines calculated through Equation 231 and rate constants reported in the text. (From Danesi, P. R. and Chiarizia, R., Paper 9b in Proc. Int. Solv. Extr. Conf. ISEC 77, Toronto, 1977; Danesi, P. R., and Chiarizia, R., *J. Appl. Chem. Biotechnol.*, 28, 581, 1978. With permission.)

acid $\cong m[(HD)_m]$, and $\overline{[M]}$ = activity of $\overline{M(H_2O)_iX_pH_m\text{-}3_{+p}D_m}$ which was set equal to the organic concentration of the metal, assuming ideal behavior or organic species.

From the interfacial steady-state condition, it followed that $\vec{V}_1 = \vec{V}_2$ and $[M]_{ad}$, evaluated through Equations 227 and 229, has been inserted into either Equation 227 or 229 to obtain

$$\vec{V} = \frac{K_1 [M] \bar{C}_{HD} - \bar{K}_1 K_R [\bar{M}] [H^+]^{3-p}}{\bar{C}_{HD} + K_R [H^+]^{3-p}} \quad \text{with } K_R = K_3/K_2 \tag{230}$$

for the overall transfer rate valid at any time, and

$$\vec{V}_0^* = \frac{K_1 \bar{C}_{HD}}{\bar{C}_{HD} + K_R [H^+]^{3-p}} \tag{231}$$

and

$$\overleftarrow{V}_0^* = \frac{\bar{K}_1 K_R [H^+]^{3-p}}{\bar{C}_{HD} + K_R [H^+]^{3-p}} \tag{232}$$

for the direct and reverse transfer rate at time equal to zero.

The derived rate equations have been able to represent well the experimental data as shown by the comparison between the experimental points and the curves calculated with Equations 231 and 232 reported in Figures 46, 47, and 48. In the case of iron(III), the curves have been calculated with p = 1 and with the following rate constants (referring to a specific interfacial area of 0.47 $cm^{-1}$): $K_1 = (4.8 \pm 0.1) \cdot 10^{-2}$ $min^{-1}$, $\overline{K}_1 = (8.57 \pm 0.5) \cdot 10^{-3}$ $min^{-1}$, and $K_R = (1.16 \pm 0.1) \cdot 10^{-2} M,^{-1}$ evaluated by best fit of the experimental points. A slightly poorer fit was obtained for the data of Figure 47b when p was set equal to zero. For $Eu^{3+}$ the best fit of the experimental points has been obtained with p = 0 and the following rate constants (referring to a specific interfacial area of 0.042 $cm^{-1}$): $K_1 = (4.6 \pm 0.2) \cdot 10^{-2}$ $min^{-1}$, $\overline{K}_1 = (1.4 \pm 0.5) \cdot 10^{-2}$ $min^{-1}$, and $K_R = (3.0 \pm 0.5) \cdot 10^{-2} M^{-2}$. Similar results have been also obtained for the other lanthanide cations: $Ce^{3+}$, $Gd^{3+}$, and $Tm^{3+}$.[75] It can then be concluded that the following extraction mechanism, where interfacial chemical reactions play a predominant role, seems to control the extraction of the trivalent lanthanide cations $M^{3+}$ (hydration water is omitted) by toluene solutions of HD:

$$M^{3+} + 3(HD)_{ad} \rightleftharpoons (MD_3)_{ad} + 3H^+ \qquad (233)$$

$$(MD_3)_{ad} + (\overline{HD})_m \rightleftharpoons \overline{MH_{m-3}D_m} + 3(HD)_{ad} \qquad (234)$$

For iron(III), instead of the possible mechanism given by Reaction 233 and 234, the following one best explains the experimental results:

$$FeClO_4^{2+} + 2(HD)_{ad} \rightleftharpoons (FeClO_4D_2)_{ad} + 2H^+ \qquad (235)$$

$$(FeClO_4D_2)_{ad} + (\overline{HD})_m \rightleftharpoons \overline{FeClO_4H_{m-2}D_m} + 2(HD)_{ad} \qquad (236)$$

The validity of rate Equation 230 has been supported by the significant distribution data which have been obtained by setting $\vec{V} = 0$.[137] The following relationship has been obtained:

$$E = \frac{[\overline{M}]}{[M(III)]} = \frac{K_1 \overline{C}_{HD}}{\overline{K}_1 K_R [H^+]^{3-p}} \qquad (237)$$

which has allowed the calculation of the partition coefficients, E, from rate constants, in good agreement with experimental ones.

The extraction rate of $Eu^{3+}$ at low stirring speeds where a diffusional contribution was present has been also studied in Reference 74. The results have been discussed in Section VII. Regarding the possible influence of diffusion processes, it is interesting to notice that an equation formally similar to Equation 231 has been derived in Section VI.B.2 (Equation 98), where the rate was assumed to be controlled only by mass-transport processes. The possibility that, because of the presence of some of the plateau-simulating effects described in Section III, the extraction rate (Equation 231) could be alternatively explained in terms of diffusional processes cannot therefore be excluded. Diffusion processes have been in fact assumed as rate determining in the extraction of $Fe^{3+}$ by HD.[139]

## B. Basic Extractants

The only basic extractants which have been studied from the extraction kinetics point of view are long-chain alkylamines. The extraction properties of these extractants have been extensively described in References 1 and 2. An attempt to obtain a qualitative picture of the reaction mechanism involved in the extraction of $UO_2^{2+}$ from aqueous sulfate solutions by benzene solutions of di-n-decylamine sulfate has been performed in Reference 140 through interfacial tension studies and by measuring the transfer rate of $^{35}SO_4^{2-}$. By studying the interfacial tension of both the amine sulfate and the amine sulfate uranyl complex, the authors of this work have concluded that an interfacial complex between the interfacially adsorbed amine salt and the aqueous uranium sulfate was formed during the extraction. This complex was then transferred into the bulk organic phase since it was less surface active than the amine salt. The extraction kinetics studies have been performed with a Lewis type cell where the two phases were stirred at the very low and fixed stirring speed of 24 r/min. Although at this stirring speed a very large contribution of the diffusional processes was present, this fact did not interfere with the meaningfulness of the experiments whose aim was to get information on the number of sulfate ions accompanying each uranyl group in the extraction process as a function of the total sulfate aqueous concentration. From the rate of $^{35}SO_4^{2-}$ transfer from the organic to the aqueous phase, it was then concluded that at high aqueous sulfate concentrations (>0.025 *M*) the extraction followed an ion-exchange mechanism,

$$UO_2(SO_4)_2^{2-} + 3\overline{(R_2NH_2)_2SO_4} \rightleftharpoons \overline{(R_2NH_2)_6UO_2(SO_4)_4} + SO_4^{2-} \quad (238)$$

while when the sulfate concentration was less than 0.01 *M* the extraction took place through the addition mechanism,

$$UO_2SO_4 + 3\overline{(R_2NH_2)_2SO_4} \rightleftharpoons \overline{(R_2NH_2)_6UO_2(SO_4)_4} \quad (239)$$

or

$$UO_2^{2+} + SO_4^{2-} + 3\overline{(R_2NH_2)_2SO_4} \rightleftharpoons \overline{(R_2NH_2)_6UO_2(SO_4)_4} \quad (240)$$

The three interfacial mechanisms (Reactions 238, 239, and 240) could of course take place simultaneously, their importance depending on the level of sulfate concentrations.

The extraction kinetics of $^{181}Hf$ from sulfuric acid solutions by xylene solutions of tri-n-octylamine sulfate ($TOAHHSO_4$) has been investigated in Reference 141 also using a constant interfacial area stirred cell. The authors have reported that the extraction rate showed a plateau region as a function of the stirring speed starting at 1500 r/min. A kinetic regime was therefore established from this stirring value. Moreover, the typical linear dependence of $\vec{V}_0$ on a, reported in Figure 5, was measured. The dependence of $\vec{V}_0$ on the extractant concentration, [$TOAHHSO_4$], was also analyzed, and a curve similar to that of Figure 27, $\vec{V}_0^{\ddagger}$ vs. $[\overline{HB}]$, was obtained. Although no attempt has been made to derive a rate law and a reaction mechanism, it has been correctly concluded, even if only in a qualitative way, that for r/min >1500 the reaction was controlled by an interfacial resistance originated by interfacial adsorption phenomena. However, for the reasons reported in Sections III and IV.B, it is probable that the mechanism and the rate laws which control this extraction process are of the type described in Section V.A.2., i.e., involving slow interfacial chemical reactions. Finally, in agreement with the simplest expectations, the values of the measured activation energies of the extraction processes have been found equal to 10 kcal/mol in the kinetic regime (r/min >1500) and 4 kcal/mol in the diffusional (or mixed) regime (r/min<1500). The meaning of the information which can be derived from the activation energy has been discussed in Section III.

The rate of extraction of Mo in the form of molibdosilicic acid (MSA) from aqueous solutions containing both $NaNO_3$ and $HNO_3$ by solutions of trioctylamine (TOA) in toluene and trichloroethane has been studied in Reference 142 using a Lewis type cell. Similar to the previously mentioned work,[141] the authors found that the rate of extraction was proportional to the interfacial area and became independent of the rate of stirring beyond a given value. It was therefore correctly concluded that the reaction took place at the interface, with the rate being kinetically controlled provided the stirring speed was higher than 400 r/min. Further support of this hypothesis was also obtained by using the reference substance method described in Section III, while the activation energy of the extraction process, equal to 6.7 kcal/mol, could not provide an unambiguous indication on the type of regime. Unfortunately, the authors have not realized that in a kinetic regime controlled by interfacial reactions, as that described in Section V.A.2, variable reaction orders with respect to TOA had to be expected and have not provided any explanation to the measured variable reaction orders with respect to both $[\overline{TOA}]$ and [MSA]. They have in fact assumed a rate law,

$$\vec{N}_0 = K[\overline{TOA}]^a[MSA]^b \tag{241}$$

and have consequently found a = 1.0 ± 0.3 (toluene), a = 0.3 ± 0.11 (dichloroethane) and b = 1.4 ± 0.2 (toluene), and b = 1.2 ± 0.25 (dichloroethane). No attempt has been made to work out a reaction mechanism. The following rate constants (T = 19°C) have been reported: $K = 2.7 M^{-1} sec^{-1} cm^{-2}$ (toluene) and $K = 6.9 \cdot 10^{-3} M^{-1} sec^{-1} cm^{-2}$ (dichloroethane). The influence of the ionic strength and pH on the rate of extraction has also been investigated in the same work. The decrease of the rate constant by increasing the ionic strength has been attributed to the increasingly competing reaction between TOA and nitrate ions. The decrease of the rate observed at pH 2.77 has instead been explained in terms of reduced protonation of the amine.

The extraction rate of pertechnetate ions from aqueous nitric acid solutions by trioctylmethylammonium nitrate and tridodecylammonium nitrate in *o*-xylene has been studied in Reference 159 using a constant interfacial area stirred cell, at the constant stirring speed of 60 r/min. The data have been then analyzed following a treatment very similar to that reported in Reference 23 for the extraction of $Ca^{2+}$ by HDEHP solutions (see Section VIII.A.5). The authors have also shown that in the region 20 to 200 r/min, the extraction rate was linearly dependent on the stirring speed. This result seems to indicate that at 60 r/min the extraction kinetics were occurring in a diffusional regime. Consequently, the derived mechanism, based on interfacial chemical reactions of the type reported in Section V.A.2 does not seem to be here fully demonstrated.

In References 143 through 146, the rate of extraction of Nb(V) from 10.8*M* HCl aqueous solutions into chloroform, carbon tetrachloride, and benzene solutions of di-(3,5,5-trimethylhexyl) ammonium chloride ($R_2NHHCl$) has been studied by using the moving drop technique. The authors have claimed that with their experimental setup, the hydrodynamic conditions were such to preclude diffusion as a rate determining factor, i.e., a kinetic regime was certainly established. However, for the reasons reported in Section IV.C this assertion should be taken rather cautiously. Further, the authors have reported that the extraction reaction occurred at the interface with the formation of an interfacial complex and that with their experimental conditions a steady state was never attained. No experimental support has been given to these assumptions which then appear rather arbitrary. By using log $N_0$ vs. log of concentration plots, referring to both the forward (aqueous to organic) and reverse (organic to aqueous) initial interfacial fluxes, it was concluded that in $CCl_4$ and in $CHCl_3$ the extraction mechanism could be described by the following interfacial reaction:

$$NbCl_6^- + (R_2NHHCl)_{ad} \underset{K_r}{\overset{K_f}{\rightleftharpoons}} (R_2NHHNbCl_6)_{ad} + Cl^- \tag{242}$$

with log $K_f$ = −4.40 ± 0.10 ($CHCl_3$), log $K_f$ = −2.74 ± 0.1 ($CCl_4$), log $K_r$ = −5.56 ± 0.05 ($CHCl_3$), and log $K_r$ = −6.2 ± 0.2 ($CCl_4$).

The authors have supported this mechanism on the fact that the slopes of the plots log $\overrightarrow{N}_0$ vs. log [Nb], log $\overrightarrow{N}_0$ vs. log $[\overline{R_2NHHCl}]_{monomer}$, log $\overleftarrow{N}_0$ vs. log $[\overline{Nb}]$, and log $\overleftarrow{N}_0$ vs. log $[\overline{R_2NHHCl}]_{monomer}$ were found equal to +1, +1, +1, and 0, respectively. The excess acid extraction and the aggregation of the extractant, forming a dimer in $CHCl_3$ and a trimer in $CCl_4$, were taken into account to calculate the reaction orders. However, a closer inspection of the log $\overrightarrow{N}_0$ vs. log extractant concentrations plots of References 143 and 144 reveals that serious deviations are present, particularly pronounced in chloroform, which indicate that the data could also conform to a curve of the type shown in Figure 27. The same also holds for the log $\overleftarrow{N}_0$ vs. log $[\overline{R_2NHHCl}]$ curves where the claimed independence from the extractant concentration could be a result of the range of extracting reagent concentration used, as indicated in the log $\overleftarrow{V}_0^*$ vs. log $[\overline{HB}]$ curve of Figure 28. These comments, together with the consideration that the extractant used is a very strong surfactant which could give rise to a constant interfacial concentration in the whole experimental range used for this kinetics investigation, indicate that the obtained results are probably more consistent with the reaction mechanism described in Section V.A.2, where interfacial reactions are taken into consideration. The same considerations also hold for the work of Reference 146, where benzene has been used as the organic diluent. With this diluent, the possibility of dealing with a completely saturated interface, however, has been taken into account. The aggregation behavior of the extractant has been investigated also in this work, and the following rate equations have been experimentally determined:

$$\overrightarrow{N}_0 = K_f[\overline{R_2NHHCl}]^0[NbCl_6^-] \qquad (243)$$

with log $K_f = -5.56 \pm 0.06$, and

$$\overleftarrow{N}_0 = K_r[\overline{R_2NHHNbCl_6}][\overline{R_2NHHCl}]^{-1} \qquad (244)$$

with log $K_r = -7.3 \pm 0.1$ and $[\overline{R_2NHHCl}]$ representing the stoichiometric concentration of the alkylammonium salt. The derivation of rate Equation 244, however, must be considered quite questionable since only two $\overline{R_2NHHCl}$ concentrations have been examined. The authors have then explained rate laws (Equations 243 and 244) with the following reaction mechanism:

$$(NbCl_5)_{ad} + (R_2NHHCl)_{ad} \rightleftharpoons (R_2NHHNbCl_6)_{ad} \qquad (245)$$

where $[(R_2NHHCl)_{ad}]$ has been assumed as constant due to the interface saturation of the extracting reagent. Unfortunately, this saturation has notbeen experimentally demonstrated. Although the reaction mechanism proposed with benzene appears more realistic than the ones concerning $CCl_4$ and $CHCl_3$, its quantitative formulation is open to some criticism. In fact, it has been proposed that the uncertain inverse dependence of the alkylammonium salt concentration shown in Equation 244 was generated either by an unspecified interfacial resistance proportional to the extractant concentration or by the rapid dissociation of an hypothesized organic Nb complex,

$$\overline{(R_2NHHCl)_2\ (NbCl_5)} \xrightleftharpoons{\text{fast}} \overline{R_2NHHCl} + \overline{R_2NHHNbCl_6} \qquad (246)$$

which presence has not been demonstrated.

Moreover, as the authors report, the interface saturation model did not allow the correct estimation of the distribution equilibrium relationship. Finally, it has to be mentioned that due to the experimental technique used, which does not prove in an unambiguous way the type of regime controlling the extraction kinetics, the alternative exists that the reaction orders of References 143 through 146 could simply reflect a mass-transport controlled extraction kinetics.

The rate of extraction of Pu(IV) from nitric acid solutions by solutions of trioctylammonium nitrate in a n-dodecane-octylalcohol diluent mixture has been studied in Reference 160 using a constant interfacial area stirred cell. The experimental data have been here analyzed by plotting $y = \ln [Pu] - [Pu]_{eq}/[Pu]_0 - [Pu]_{eq}$ as a function of time, where $[Pu]$, $[Pu]_0$, and $[Pu]_{eq}$ represent the Pu(IV) concentrations at time t, zero and at equilibrium, respectively. Since the y vs. t plots were characterized by an initial curved part followed by a somewhat straight line behavior at $t > 150$ min, the authors have concluded that a change of regime and mechanism occurred as long as the extraction proceeded. From the shape of the curves at the two stirring speeds of 100 and 300 r/min and at the two interfacial areas of 5.2 and 10.0 $cm^2$, and using two amine salt and $HNO_3$ concentrations, it has been qualitatively concluded that the first part of the extraction was occurring in a mixed kinetic-diffusional regime and the second one in a kinetic regime controlled by aqueous phase bulk reactions. However, the explanation proposed has to be taken only as tentative since too few experimental data have been obtained and the bending of the curves could be caused by the presence of octylalcohol which can modify the interface structure. The alternative explanation of an extraction occurring, at least at 200 r/min, in a kinetic regime controlled by interfacial chemical reactions in the absence of alcohol cannot be then ruled out.

The extraction rate of Fe(III) and PU(IV) from aqueous acid solutions by trilaurylammonium salts (TLAHX) dissolved in aromatic diluents has been studied in References 119 and 147 by using a constant interfacial area stirred cell. The dependence of the forward and reverse initial rates on the stirring speed of the two phases has shown that, with the Lewis cells used, a kinetic regime could be assumed when the stirring speed was larger than a given value characteristic of each cell. Furthermore, a linear relationship between the extraction rate and the specific interfacial area such as that reported in Figure 5 has been measured. These experimental results, added to the very strong surface-active properties of the alkylammonium salts[20] have been taken as an indication that the kinetic regime was controlled by interfacial chemical reactions.

The direct and reverse initial transfer rates of Fe(III) as function of the initial iron(III) aqueous and organic concentrations are reported in Figure 49 for the diluent toluene. Similar results have been obtained in benzene. The straight lines indicate that, as usual, both the forward and the reverse rates are first order with respect to the metal concentration. Figures 50 and 51 show how the rates vary with the concentration of TLAHCl in the organic phase (Figure 50) and with the HCl aqueous concentration (Figure 51). In all cases the normalized rates $\overrightarrow{V}_0^* = \overrightarrow{V}_0/$[aqueous metal concentration] and $\overleftarrow{V}_0^* = \overleftarrow{V}_0/$[organic metal concentration] have been plotted. Equal results have been obtained both with benzene and toluene solutions of TLAHCl. The forward and reverse initial transfer rates of Pu(IV) in the system water-$HNO_3$-*o*-xylene-$TLAHNO_3$ have been also found to be straight lines when plotted as a function of the initial aqueous and organic Pu(IV) concentrations. Figure 52 shows the dependence of the normalized rates $\overrightarrow{V}_0^*$ and $\overleftarrow{V}_0^*$, referring to the Pu(IV) transfer, on the $TLAHNO_3$ concentration in *o*-xylene. The reaction mechanism which has been elaborated to explain the experimental data is basically that described in Section V.A.2. In addition, the polymerization of the alkylammonium salts and the participation of multiple reactive species to the mechanism have been taken into account. The mechanism can be described schematically as follows:

1. In the water-to-organic transfer, the kinetically active aqueous metal complex reacts with the monolayer of extractant molecules which are adsorbed at the interface. An interfacial complex with zero charge is thus formed.

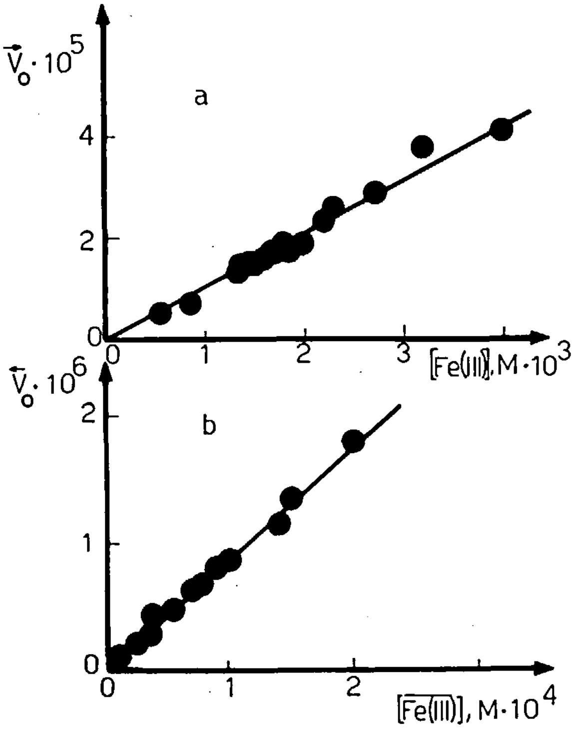


FIGURE 49. Initial forward (a) and reverse (b) extraction rate of Fe(III) ($\vec{V}_0 = -d[\text{Fe(III)}]/dt$; $\overleftarrow{V}_0 = +d[\text{Fe(III)}]/dt$) vs. aqueous iron concentration (a) and toluene iron concentration (b). [HCl] = 1 *M*, [$\overline{\text{TLAHCl}}$] = 0.2*M*(a) and 0.01*M*(b). (From Chiarizia, R. and Danesi, P. R., *J. Inorg. Nucl. Chem.*, 40, 1811, 1978.

2. The interfacial complex is then transferred into the organic bulk by reacting with the alkylammonium salt molecules in the organic phase. The interfacial complex molecules leaving the interface are replaced on the interface by the molecules of the extractant. Since different aggregated species can be simultaneously present in equilibrium with each other in the organic phase and various complexes containing the alkylammonium salt and the extracted metal can be formed as final products of the extraction process, it has not been *a priori* excluded that any of the alkylammonium aggregates present in the organic diluent could be reactive with respect to the interfacial complex, each alkylammonium aggregate reacting with more than one molecularity. However, since the organic aggregation reactions of the alkylammonium salts are characterized by fast equilibria,

$$m(\overline{\text{TLAHX}}) \overset{\text{fast}}{\rightleftharpoons} \overline{(\text{TLAHX})}_m$$

it follows that, from a kinetic point of view, the reaction of the interfacial complex with m monomeric $\overline{\text{TLAHX}}$ molecules will be indistinguishable from that with one m-mer, $\overline{(\text{TLAHX})}_m$, even though the latter will be more probable, especially when m > 3. Consequently, for the sake of simplicity, in the general reaction mechanism, the reaction steps concerning the removal of the interfacial complex from the interface have been formally attributed to the alkylammonium salt monomers. For each specific system, on the basis of the aggregated alkylam-

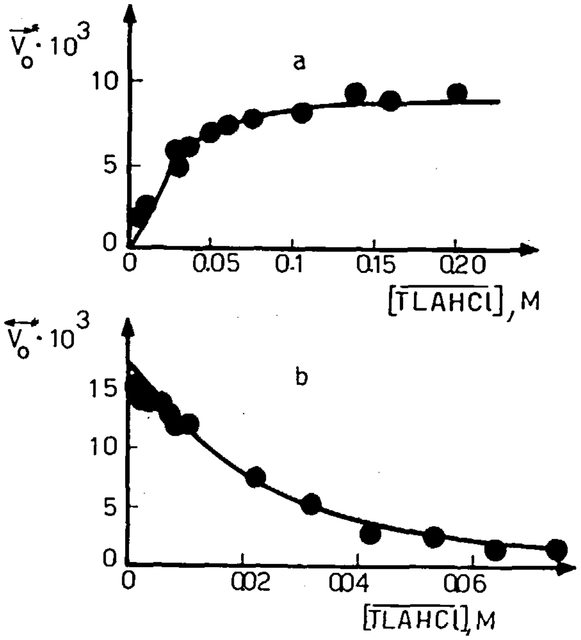


FIGURE 50. Normalized extraction rate of Fe(III), $V_0^*$ = $V_0$/[Fe(III)], from: (a) aqueous solutions into benzene solutions of TLAHCl; and (b) benzene TLAHCl into aqueous HCl solutions. $\vec{V}_0^*$ and $\overleftarrow{V}_0^*$ vs. $[\overline{\text{TLAHCl}}]$ plots, aqueous phase = 1*M* HCl. Solid lines calculated using Equations 252 and 254 and rate and equilibrium constants reported in the text. (From Chiarizia, R. and Danesi, P. R., *J. Inorg. Nucl. Chem.*, 40, 1811, 1978. With permission.)

monium salt species formed in a given diluent and of the stoichiometry of the alkylammonium salt-extracted metal complexes, hypothesis on the actually reacting species and their molecularity have been formulated.

3. The opposite step to that just described takes place when the metal, initially present in the organic phase, reacts with the monolayer of extractant molecules present at the interface to form the interfacial complex.
4. The interfacial complex releases the complex metal species in the aqueous phase leaving the alkylammonium molecules on the interface.

By assuming that only a very small fraction of the interfacial extractant molecules were converted into the interfacial complex and that an interfacial steady-state condition was instantaneously established for the interfacial complex, the following reaction steps and rates have been written for the extraction of a $M^{z+}$ cation:

$$MX_z + q\,B_{ad} \underset{K_3}{\overset{K_1'}{\rightleftharpoons}} (MX_zB_q)_{ad} \tag{247}$$

$$\vec{V}_1 = K_1[M] - K_3[M]_{ad} \tag{248}$$

where B represents the alkylammonium salt extractant $R_3NHX$, $K_1 = K_1'[B]_{ad}^{q}$ since *the interfacial concentration of the extractant is constant,* $[M]_{ad}$ *is the concentration* of the interfacial complex $(MX_zB_q)_{ad}$, and [M] is the activity of the complex $MX_z$. Since an aqueous constant-ionic medium has been used in most of the experiments ([HCl] = 1*M* for Fe(III) and [$HNO_3$] = 4*M* for Pu(IV)), activities have been replaced by the

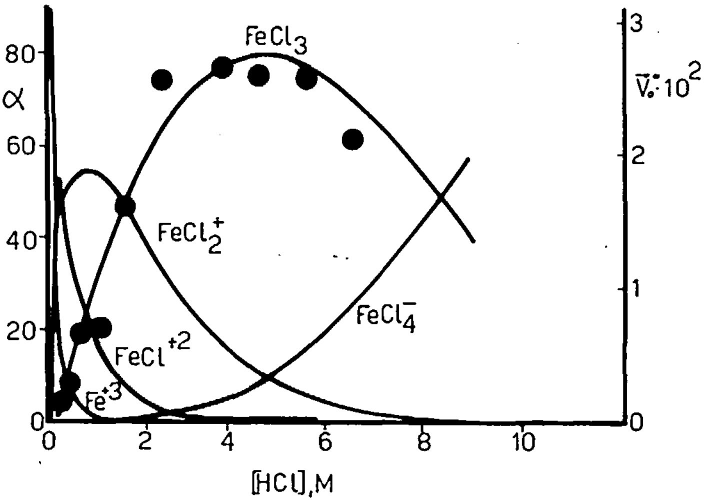


FIGURE 51. Fraction of iron-chloride complexes in solution α (left scale, solid lines) and normalized direct extraction rate, $\vec{V}_o^* = V_o/[Fe(III)]$, (full points) as function of the total aquous HCl concentration. Aqueous and organic phase as in Figure 50. (From Chiarizia, R. and Danesi, P. R., *J. Inorg. Nucl. Chem.*, 40, 1811, 1978. With permission.)

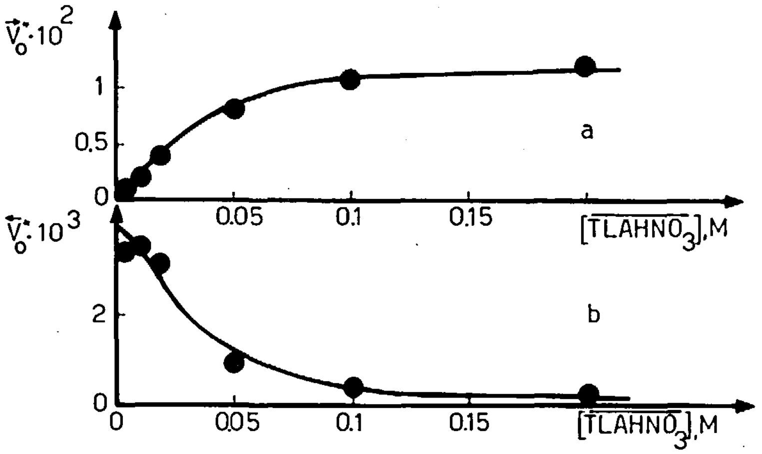


FIGURE 52. Normalized initial forward ($\vec{V}_o^* = -d[Pu(IV)]/dt\,[Pu(IV)]$) and reverse ($\overleftarrow{V}_o^* = d[Pu(IV)]/dt[Pu]$) extraction rates of $\overline{Pu(IV)}$ vs. $[TLAHNO_3]$ plots from: (a) aqueous $HNO_3$ solutions into o-xylene solutions of $TLAHNO_3$; (b) o-xylene $TLAHNO_3$ solutions into aqueous $HNO_3$ solutions. Aqueous phase: $HNO_3$ 4*M*. Solid lines calculated using Equations 259 and 260 and rate and equilibrium constants reported in the text. (From Chiarizia, R., Danesi, P. R., and Domenichini, C., *J. Inorg. Nucl. Chem.*, 40, 1409, 1978. With permission.)

concentrations in Equation 248. Further, some evidence has been obtained that the aqueous kinetically active complex in the case of Fe(III) was $FeCl_3$. Extrapolating this result to plutonium, i.e., assuming that $Pu(NO_3)_4$ was the kinetically active species and considering that a constant $X^-$ concentration was used, a direct proportionality always existed between the total aqueous metal concentration and the concentration of any other metal-containing species in the aqueous phase. Consequently, the total concentration of the aqueous metal has been inserted at the place of the activity of the aqueous reacting species in Equation 248.

$$(MX_zB_q)_{ad} + \left\{ \begin{array}{l} \bar{B} \underset{\bar{K}'_{1,1}}{\overset{K_{2,1}}{\rightleftharpoons}} \overline{MX_zB} + q(B)_{ad} \\ 2\bar{B} \underset{\bar{K}'_{1,2}}{\overset{K_{2,2}}{\rightleftharpoons}} \overline{MX_zB_2} + q(B)_{ad} \\ 3\bar{B} \underset{\bar{K}'_{1,3}}{\overset{K_{2,3}}{\rightleftharpoons}} \overline{MX_zB_3} + q(B)_{ad} \\ \vdots \qquad\qquad\qquad \vdots \qquad\qquad \vdots \\ n\bar{B} \underset{\bar{K}'_{1,n}}{\overset{K_{2,n}}{\rightleftharpoons}} \overline{MX_zB_n} + q(B)_{ad} \end{array} \right. \qquad (249)$$

$$\vec{V}_2 = [M]_{ad} \sum_1^n {}_i K_{2,i}[\bar{B}]^i - \sum_1^n {}_i \bar{K}_{1,i}[\overline{MX_zB_i}] \qquad (250)$$

where $\bar{K}_{1,i} = \bar{K}_1{}'_{,i}[\bar{B}]^q_{ad}$ and $[\bar{B}]$ is the monomer concentration of the alkylammonium salt. From the interfacial steady state condition, $\vec{V}_1 = \vec{V}_2$, it followed

$$\vec{V} = \frac{K_1[M] \sum_1^n {}_i K_{R,i}[\bar{B}]^i - \sum_1^n {}_i \bar{K}_{1,i}[\overline{MX_zB_i}]}{1 + \sum_1^n {}_i K_{R,i}[\bar{B}]^i} \qquad (251)$$

where $K_{R,i} = K_{2,i}/K_3$. Rate Equation 251 has been found to explain well the experimental data reported in Figures 50 and 52, as shown by the comparison between experimental points and calculated curves. For the cases of Fe(III)-HCl, benzene-TLAHCl and Fe(III)-HCl, toluene-TLAHCl,[119] the forms of Equation 251 which were found to best represent the experimental results of Figure 50 are

$$\vec{V}_0^* = \frac{K_1(K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3)}{1 + K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3} \qquad (252)$$

and

$$\overleftarrow{V}_0 = \frac{\bar{K}_{1,1}[\overline{FeCl_3B}] + \bar{K}_{1,3}[\overline{FeCl_3B_3}]}{1 + K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3} \qquad (253)$$

or

$$\overleftarrow{V}_0^* = \frac{(\bar{K}_{1,1} + \bar{K}_{1,3}\bar{K}_{ass}[\bar{B}]^2)/(1 + \bar{K}_{ass}[\bar{B}]^2)}{1 + K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3} \qquad (254)$$

since the following equilibrium

$$\overline{FeCl_3B} + 2\bar{B} \rightleftharpoons \overline{FeCl_3B_3}\,; \quad \bar{K}_{assoc.} = 4 \times 10^4\ M^{-2} \qquad \text{Un. eq. PP}$$

has been found to take place in *o*-xylene.[148]

The monomer concentrations in benzene and toluene have been calculated taking into consideration the following aggregation equilibriums and formation constants:

$$\text{benzene}^{149} \quad 2\,\overline{\text{TLAHCl}} \rightleftharpoons \overline{(\text{TLAHCl})_2}; \quad K_2 = 44.7\ M^{-1}$$

$$\text{toluene}^{150} \quad 2\,\overline{\text{TLAHCl}} \rightleftharpoons \overline{(\text{TLAHCl})_2}; \quad K_2 = 56\ M^{-1}$$

$$7\,\overline{\text{TLAHCl}} \rightleftharpoons \overline{(\text{TLAHCl})_7}; \quad K_7 = 5.2 \times 10^7\ M^{-6}$$

$$\text{o-oxylene} \quad 2\,\overline{\text{TLAHNO}_3} \rightleftharpoons \overline{(\text{TLAHNO}_3)_2}; k_2 = 26.5\ M^{-1}$$

The following rate constants have been used to obtain the calculated curves in benzene of Figure 50:$_1$ = (9.0 ± 0.5) × $10^{-3}$ min$^{-1}$, $\overline{K}_{1,1}$ = (1.6 ± 0.1) × $10^{-2}$ min$^{-1}$, $\overline{K}_{1,3}$ = (1.3 ± 0.1) × $10^{-2}$ min$^{-1}$, $K_{R,1}$ = (1.0 ± 0.3) × 10$M^{-1}$, and $K_{R,3}$ = (5 ± 1) × $10^5 M^{-3}$. For toluene, very close values of the rate constants have been used, i.e., $K_1$ = (9.5 ± 1.5) × $10^{-3}$ min$^{-1}$, $\overline{K}_{1,1}$ = (1.7 ± 0.2) × $10^{-2}$ min$^{-1}$, $\overline{K}_{1,3}$ = (1.4 ± 0.2) × $10^{-2}$ min$^{-1}$, $K_{R,1}$ = (2 ± 1) × 10$M^{-1}$, and $K_{R,3}$ = (10 ± 5) × $10^5 M^{-3}$.The rate constants have been evaluated by best fit of the experimental points of Figure 50 with Equations 252 and 254.

As far as the aqueous species kinetically reactive with the interfacial molecules of TLAHCl is concerned, some indications have been obtained from the data reported in Figure 51 where, in the same plot, the dependence of $\vec{V}_0^*$ on [HCl] and of the fraction of each complex in solution, $\alpha$, on [Cl$^-$] have been plotted. The fraction of each complex in solution was calculated from

$$\alpha = \frac{K_n a_{Cl}^n}{1 + \sum_{1}^{4}{}_i K_i a_{Cl}^i} \tag{255}$$

where $a_{Cl}$ = chloride activity function, $K_n$ = formation constant of $\text{FeCl}_n^{(3-n)+}$, and $K_i$ = formation constant of $\text{FeCl}_i^{(3-i)+}$. Although the fraction of complexes gives only a rough indication of the complexes really predominating in solution since the oversimplification of assuming the ratio of the activity coefficients equal to one has to be introduced, the plots of Figure 51 seem to indicate that the neutral trichloride complex, $\text{FeCl}_3$, could be the aqueous, kinetically active species. Consequently, the following extraction mechanism, based on interfacial chemical reactions, was suggested as the one which controls the direct and reverse extraction of $\text{Fe}^{3+}$ from HCl solutions into benzene and toluene solutions of TLAHCl:

$$\text{FeCl}_3 + q(\text{TLAHCl})_{ad} \rightleftharpoons (\text{FeCl}_3(\text{TLAHCl})_q)_{ad} \tag{256}$$

$$(\text{FeCl}_3(\text{TLAHCl})_q)_{ad} + \overline{\text{TLAHCl}} \rightleftharpoons \overline{\text{FeCl}_3(\text{TLAHCl})} + q(\text{TLAHCl})_{ad} \tag{257}$$

$$(\text{FeCl}_3(\text{TLAHCl})_q)_{ad} + 3\,\overline{\text{TLAHCl}} \rightleftharpoons \overline{\text{FeCl}_3(\text{TLAHCl})_3} + q(\text{TLAHCl})_{ad} \tag{258}$$

For the system Pu(IV)-$\text{HNO}_3$, *o*-xylene-$\text{TLAHNO}_3$, the forms of Equation 251 which were found to best represent the experimental results of Figure 52 have been the following:

$$\vec{V}_0^* = \frac{K_1(K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3 + K_{R,10}[\bar{B}]^{10}}{1 + K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3 + K_{R,10}[\bar{B}]^{10}} \tag{259}$$

and

$$\overleftrightarrow{V}_0^* = \frac{\bar{K}_1}{1 + K_{R,1}[\bar{B}] + K_{R,3}[\bar{B}]^3 + K_{R,10}[\bar{B}]^{10}} \qquad (260)$$

This means that the condition $\bar{K}_{1,1} = \bar{K}_{1,3} = \bar{K}_{1,10} = \bar{K}_1$ held. The monomer concentration in *o*-xylene has been calculated by the following aggregation equilibria and formation constants:[151]

$$3\,\overline{\mathrm{TLAHNO_3}} \rightleftharpoons \overline{(\mathrm{TLAHNO_3})_3} \;;\; K_3 = 4 \times 10^5\ M^{-2}$$

$$10\,\overline{\mathrm{TLAHNO_3}} \rightleftharpoons \overline{(\mathrm{TLAHNO_3})_{10}} \;;\; K_{10} = 2.6 \times 10^{13}\ M^{-9}$$

The following rate constants have been used in Reference 147 to obtain the calculated curves of Figure 52: $K_1 = (1.2 \pm 0.1) \times 10^{-2}\ \mathrm{min}^{-1}$, $\bar{K}_1 = (4.0 \pm 0.5) \times 10^{-3}\ \mathrm{min}^{-1}$, $K_{R,1} = (5 \pm 3) \times M^{-1}$, $K_{R,3} = (4 \pm 2) \times 10^5 M^{-3}$, and $K_{R,10} = (1.0 \pm 0.5) \times 10^{17}\ M^{-10}$. They have been evaluated by best fit of the experimental points of Figure 52 with Equations 259 and 260. The following extraction mechanism, based on interfacial chemical reactions, was then suggested as the one which controls the direct and reverse extraction of $Pu^{4+}$ from $HNO_3$ solutions into *o*-xylene solutions of $TLAHNO_3$:

$$\mathrm{Pu(NO_3)_4} + q(\mathrm{TLAHNO_3})_{ad} \rightleftharpoons (\mathrm{Pu(NO_3)_4(TLAHNO_3)}_q)_{ad} \qquad (261)$$

$$(\mathrm{Pu(NO_3)_4(TLAHNO_3)}_q)_{ad} + \overline{\mathrm{TLAHNO_3}} \rightleftharpoons \overline{\mathrm{Pu(NO_3)_4(TLAHNO_3)}} + q(\mathrm{B})_{ad} \qquad (262)$$

$$(\mathrm{Pu(NO_3)_4(TLAHNO_3)}_q)_{ad} + \overline{(\mathrm{TLAHNO_3})_3} \rightleftharpoons \overline{\mathrm{Pu(NO_3)_4(TLAHNO_3)_3}} + q(\mathrm{B})_{ad} \qquad (263)$$

$$(\mathrm{Pu(NO_3)_4(TLAHNO_3)}_q)_{ad} + \overline{(\mathrm{TLAHNO_3})_{10}} \rightleftharpoons \overline{\mathrm{Pu(NO_3)_4(TLAHNO_3)_{10}}} + q(\mathrm{B})_{ad} \qquad (264)$$

Equations 263 and 264 have been written assuming that the trimer and decamer of $TLAHNO_3$ were the kinetically active species. Reactions with three and ten monomeric units would have been in fact highly improbable. The validity of the derived rate equation containing the contribution of both the direct and the reverse interfacial chemical reactions has also been checked by using it to obtain a distribution law. This can be easily obtained by setting $\vec{V} = 0$ at equilibrium. The following distribution law has been so obtained:

$$E = \frac{\sum_{1}^{n}{}_i\,[\overline{MX_zB_i}]}{[M]} = \sum_{1}^{n}{}_i\,K_{R,i}[\bar{B}]^i \cdot (K_1/\bar{K}_1) \qquad (265)$$

for the extraction of Fe(III) from HCl solutions by benzene and toluene solutions of TLAHCl and for the extraction of Pu(IV) from $HNO_3$ solutions by *o*-xylene solutions of $TLAHNO_3$. The solid lines reported in Figure 53 have been calculated using Equation 265 and the rate constants of the interfacial chemical reactions and the equilibrium constants of the organic aggregation reactions reported previously. The comparison between the experimental distribution ratios and the calculated curves shows that the developed kinetic model and the evaluated rate constants have allowed the prediction of the equilibrium distribution data with a good degree of reliability. We can then conclude this section concerning the rate of extraction with basic extractants by summarizing the results obtained as follows:

1. The interfacial tension studies have shown that, due to the very strong surface active properties of all alkylammonium salts even at very low bulk organic con-

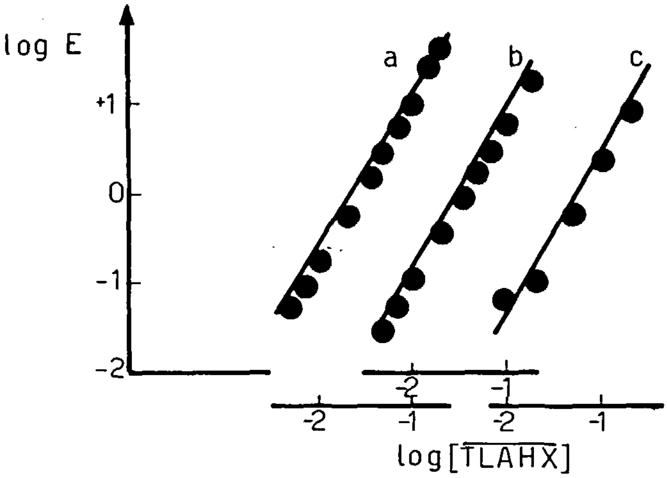


FIGURE 53. Logarithmic plot of ditribution ratio E vs. organic extractnt cocentration, [$\overline{\text{TLAHX}}$]. (a) extraction of Fe(III) from 1*M* HCl solutions as a function of total TLAHCl concentration in toluene; (b) extraction of Fe(III) from 1*M* HCl solutions as a function of total TLAHCl concentration in benzene; and (c) extraction of Pu(IV) from 4*M* $HNO_3$ solutions as a function of total $TLAHNO_3$ concentration in *o*-xylene. Solid lines calculate with Equation 265 and rate and equilibrium constants reported in the text. (From Chiarizia, R. and Danesi, P. R., *J. Inorg. Nucl. Chem.*, 40, 1811, 1978; Chiarizia, R., Danesi, P. R., and Domenichini, C., *J. Inorg. Nucl. Chem.*, 40, 1409, 1978. With permission.)

centrations, the interfacial plane gets completely saturated with a strongly adsorbed layer of the extractant. A constant interfacial extractant concentration is therefore generally established in the whole bulk organic concentration ranges which are used in practical extraction studies.

2. The extraction kinetics experiments performed in kinetic regimes have shown that the extraction rates are directly proportional to the specific interfacial area. It follows then that the rate determining steps of the extraction process take place at the interface.
3. Rate determinations, performed in kinetic regimes as a function of the chemical composition of the system, have shown that the reaction mechanisms and the rate laws generally conform to those described in Section V.B. The reaction mechanisms basically consists in the following steps:

   a. Formation of an interfacial complex between the interfacially adsorbed molecules of the extracting reagent and the metal complex present in the aqueous solutions.
   b. Replacement at the interface of the interfacial complex with bulk organic molecules of the extractant; this process, which rate is proportional to the organic concentration of the extractant, occurs through reaction with bulk molecules of the extractant.
   c. The reverse of these steps occurs when organic-to-water transfer takes place.

4. The extraction kinetics, when performed in stirred tanks, are quite fast, i.e., equilibrium is established within a few seconds. These fast kinetics are due to the fact

that slow water substitution reactions are not involved since the metal species react at the interface as complexed species and the polymerization-depolymerization reactions occurring in the organic diluents are fast processes.

### C. Neutral Extractants

The most widely studied neutral extracting reagent is tributylphosphate, TBP. This compound has been largely studied because of its great technological importance. It is in fact used in the solvent extraction plants for the reprocessing of the spent nuclear fuel. The physico-chemical and extraction properties of TBP have been thoroughly reviewed in Reference 1. The rate of extraction of $UO_2^{2+}$ from aqueous nitrate solutions into n-dodecane solutions of TBP has been studied in Reference 33 at various temperatures using the constant interfacial area stirred cell of Figure 18. The very rapid stirring of the phases has allowed the author to assume that diffusion was not a controlling factor of the extraction kinetics. By evaluating the interfacial flux as a function of the uranium, nitrate, and TBP concentrations, the following rate equation has been so obtained at 25°C:

$$\overrightarrow{N}_0 = K[UO_2^{2+}][NO_3^-]^{1.2}[\overline{TBP}]^{1.8} \qquad (266)$$

with $K = 2.2 \cdot 10^{-4}$ mol cm$^{-2}$ sec$^{-1}$.

Rate Equation 266 has been explained by assuming that the rate determining step was the interfacial reaction,

$$UO_2NO_3^+ \cdot TBP + TBP \underset{K_2}{\overset{K_1}{\rightleftharpoons}} UO_2NO_3^+ \cdot 2\,TBP \qquad (267)$$

In fact, the slow step (Reaction 267), combined with the fast equilibria taking place in the solutions, with the assumption that $UO_2NO_3^+$ 2TBP was in a steady state and had a very low concentration, and with the hypothesis that $K_2$ had a very low value, has led the authors to derive the rate equation,

$$\overrightarrow{N}_0 = K[UO_2^{2+}][NO_3^-][\overline{TBP}]^2$$

The noninteger values of the reaction orders with respect to $[NO_3^-]$ and $[\overline{TBP}]$ have been explained by the presence of other competing mechanisms becoming predominant at higher and lower temperatures. In fact, it has been observed that at temperatures higher than 33°C the rate became

$$\overrightarrow{N}_0 = K[UO_2^{2+}][NO_3^-][\overline{TBP}] \qquad (268)$$

while at 6°C it was

$$\overrightarrow{N}_0 = K[UO_2^{2+}][NO_3^-] \qquad (269)$$

However, an alternative explanation to the noninteger reaction orders could be found either in the nonideal behavior of the solutes participating in the reaction or in an interfacial mechanism of the type described in Section V.A.3. Moreover, it has to be noticed that although the possibility of an interfacial rate determining step appears rather probable, the experimental technique used has not allowed it to be demonstrated experimentally. The observed independence of the extraction rate from the stirring speed can be instead taken as a strong evidence that the rate of extraction was occurring in a kinetic regime.

The forward and reverse rates of extraction of both $UO_2^{2+}$ and $Pu^{4+}$ from nitrate aqueous solutions into TBP solutions in dodecane have been studied in Reference 36 by the moving drop method (Section IV.C). The rates were studied as functions of the actinide metal cation, nitrate, and TBP concentrations. On the basis of the assumptions that the rate of extraction was occurring in a kinetic regime, controlled by interfacial chemical reactions, the authors have explained their data in terms of the two following rate laws:

$$\vec{N}_0 = \frac{\frac{\text{const}}{f_w}\,[\overline{\text{TBP}}]^2[\text{NO}_3^-]^x\,K_w[\text{M}]}{1 + \frac{\text{const}}{f_w}\,[\overline{\text{TBP}}]^2[\text{NO}_3^-]^x + \frac{K_w\sigma_w}{f_w}\,[\text{M}]} \qquad (270)$$

and

$$\overleftarrow{N}_0 = \frac{K_{org}[\overline{\text{M}}]}{1 + \frac{\text{const}}{f_w}\,[\overline{\text{TBP}}]^2\,[\text{NO}_3^-]^x + \frac{K_{org}\,\sigma_{org}}{f_{org}}\,[\overline{\text{M}}]} \qquad (271)$$

where, according to the authors, x = 1.75 for uranium and 2.5 for plutonium. $f_w$ and $f_{org}$ are probabilities of removal of the interfacial complex from the interface into the aqueous ($f_w$) and organic ($f_{org}$) phase, $\sigma_w$ and $\sigma_{org}$ are effective cross sections for the metal entering the interface, K are probabilities of entering the interface from the aqueous ($K_w$) and the organic ($K_{org}$) phase and [M] and $[\overline{\text{M}}]$ are the initial aqueous and organic metal concentrations. Equations 270 and 271 have been successfully fitted to the experimental data, obtained at constant nitrate concentration, by finding suitable values to the parameters defined above. Equations 270 and 271 have been able to explain fractional reaction orders with respect to all the chemical species involved in the extraction reaction. Their derivation on the basis of a postulated slow step leading to the formation of an interfacial complex of unknown composition is basically similar to the procedures described in Section V when the cross section for the metal entering the interface $\sigma$ is set equal to zero. $\sigma \neq 0$ means that the fraction of interfacial extractant molecules bound to the actinide cation is not negligible. However, since in this investigation both the interfacial area and the hydrodynamic conditions have not been varied, the hypothesis that the extraction was occurring in a kinetic regime controlled by interfacial chemical reactions cannot be considered as fully demonstrated experimentally. The noninteger values of x could in fact signify that diffusion processes were still operative in controlling the rate of extraction. Finally, it has to be mentioned that all the constant paramters of equations 270 and 271, which the authors refer to as probability factors, can be alternatively regarded as rate constants, in line with widely used terminology.

A centrifugal extractor has been used in Reference 152 to obtain qualitative information on the extraction kinetics of uranium, plutonium, ruthenium, and zirconium from nitric acid solutions into TBP solution in various diluents, i.e., n-dodecane, mixtures of aliphatic hydrocarbons and $CCl_4$. The authors have found that the extraction rate of uranium and plutonium was dependent on the rate of mixing of the phases and on this evidence have concluded that the extraction was diffusion controlled. They bring, as further support to this hypothesis, the rather low value of the activation energy measured in terms of temperature dependence of the extraction rate. This conclusion is, however, open to the serious criticism that by increasing the rate of mixing the specific interfacial area was also simultaneously growing. Therefore, the observed increase of the rate of extraction with the stirring speed could also occur in a kinetic regime with interfacial rate determining reactions. Concerning the low reliability of the activation energy criterion, the considerations reported in Section III hold. The reductive stripping of plutonium from the organic to the aqueous phase using Fe(II) as well as the extraction of ruthenium and zirconium have instead been reported to occur in a kinetic regime controlled by aqueous phase slow reactions. The authors derive their explanations on the basis of graphs showing how the percentage of extraction varies with contact time. The slow steps are claimed to be the aqueous phase reduction of Pu(IV) to Pu(III) and the slow transformation of nonextractable ruthenium and zirconium complexes into extractable ones. In this case, the chemical regime has been supported by the rather large values of the measured activation energies.

A constant interfacial area stirred cell was used in Reference 155 to study the extraction rate of vanadium from hydrochloric acid aqueous solutions into pure TBP as functions of the stirring speed of the phases and temperature. From experiments performed at constant temperature, where the rate was observed to increase with the rotation speed of the stirrers, the authors have concluded that the extraction kinetics were diffusion controlled, with the aqueous and organic film resistances having the same order of magnitude. The activation energy, calculated from the mass-transfer coefficients obtained at different temperatures, amounting to only about 5 kcal/mol, has also been taken in this case as support for the extraction occurring in a diffusion regime. However, the validity of the information obtained in this investigation is very limited because of the few experimental data examined and is restricted to the experimental extraction apparatus used by the authors.

Test tubes shaken at a speed where the extraction rate is at a plateau have been used in References 153 and 154 to study the extraction rate of Fe(III) from aqueous perchloric solutions into hexane solutions of trioctylphosphine oxide (TOPO). In spite of the lack of hydrodynamic characterization of the system and the unknown solubility of the extractant in the aqueous phase, the authors have explained their kinetic results in terms of a kinetic extraction regime controlled by aqueous phase slow reactions.

The influence of accelerating water-soluble anions has also been studied. By plotting the logarithm of the Fe(III) concentration as a function of time, straight lines have been obtained which have allowed the derivation of both the reaction orders with respect to all components and the rate constants. The following rate equation has been so derived:

$$V_0 = K_O[Fe^{3+}][\overline{TOPO}][H^+]^{-1} + K_{1,X}[Fe^{3+}][\overline{TOPO}][X^-] \qquad (272)$$

where $X^-$ represents the concentation of the accelerating anions $Cl^-$, $Br^-$, and $NO_3^-$. Since TOPO is not an acidic extractant, the authors have attributed the inverse $[H^+]$ dependence appearing in the rate Equation 272 to the reactivity of the $FeOH^{2+}$ species, which, as has been discussed with regard to the acidic extractants, is the most likely kinetic reactive species. Similarly, the authors have explained the acceleration effect produced by the $X^-$ anions with the fast formation of the more reactive $FeX^{2+}$ species. Therefore Equation 272 has been rewritten in the form,

$$V_0 = K_{OH} K_{D,R}^{-1}[FeOH^{2+}][\overline{TOPO}] + K_X K_{D,R}^{-1}[FeX^{2+}][\overline{TOPO}] \qquad (273)$$

where $K_{D,R} = [\overline{TOPO}]/[TOPO]$. The following rate constants have been evaluated: $K_{OH} K_{D,R}^{-1} = 1.58 \cdot 10^2 M^{-1}$ sec$^{-1}$, $K_{NO_3} K^{-1}_{D,R} = 1.02 \cdot 10 M^{-1}$ sec$^{-1}$, $K_{Br} K^{-1}_{D,R} = 7.08 M^{-1}$ sec$^{-1}$, and $K_{Cl} K^{-1}_{D,R} = 4.47 M^{-1}$ sec$^{-1}$. These rate constants have been explained in terms of an increase in the rate of association of iron with TOPO in the aqueous phase following the order

$$FeOH^{2+} > FeNO_3^{2+} > FeBr^{2+} > FeCl^{2+}$$

where the rate determining steps of the extraction kinetics are

$$FeOH^{2+} + TOPO \longrightarrow Fe(TOPO)^{3+} + OH^-$$

and

$$FeX^{2+} + TOPO \longrightarrow Fe(TOPO)^{3+} + X^-$$

The extraction kinetics of $K^+$ ions from aqueous picrate solutions into 1,2-dichloroethane solutions of the macrocyclic polyether dibenzo-18-crown-6 (DBC) has been studied in Reference 25 using the constant interfacial area stirred cell shown in Figure 16. It has been shown that the rate of $K^+$ extraction became independent from the stirring speed of the phases when this exceed 270 r/min. A curve similar to that reported in Figure 3 has been in fact obtained. Rate data obtained as a function of the specific interfacial area have also shown that a linear dependence, such as that shown in Figure 5, was followed. A first order reaction with respect to both $K^+$ and the picrate anion has been evaluated. The slope of the curve describing the dependence of the initial rate of extraction on the DBC organic concentration has been found instead to vary with the DBC concentration, allowing the calculation of reaction orders varying from one to zero. This dependence is shown in Figure 54. Information about the surface activity of DBC has also been obtained. Unfortunately, a different diluent, i.e., benzene, has been used. The interfacial pressure, $\pi$, vs. the logarithm of the benzene concentration of DBC has been shown in Figure 11. Although the different organic diluent dissolving DBC in the interfacial pressure measurements did not allow the calculation at which bulk concentration in 1,2-dichloroethane a constant interfacial concentration of DBC was obtained, the data of Figure 11 have suggested that also this extractant was adsorbed at the interface. Therefore, on the basis of these experimental data it has been assumed that beyond the stirring speed of 270 r/min the extraction rate was occurring in a kinetic regime controlled by interfacial chemical reactions. An extraction mechanism similar to that described in Section V.A.3 has been suggested. However, since no information was available on the interfacial DBC concentration, two alternative reaction mechanisms have been proposed. The first one considers, as slow steps, the two reactions

$$K^+ + P^- + (S)_{ad} \underset{K_{-1}}{\overset{K_1'}{\rightleftharpoons}} (KPS)_{ad} \tag{274}$$

and

$$(KPS)_{ad} + \bar{S} \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} \overline{KPS} + (S)_{ad} \tag{275}$$

and assumes a constant interfacial concentration of DBC. In Equations 274 and 275, $P^-$ represents the aqueous picrate anion and S the DBC.

The following rate law was so derived:

$$V_0 = \frac{K_1[K^+][P^-][\bar{S}]}{K_R + [\bar{S}]} \tag{276}$$

with $K_1 = K_1'[(S)_{ad}] = 2.7 \pm 0.5\ M^{-1}\ min^{-1}$ and $K_R = K_{-1}/K_2 = (6 \pm 1)\ 10^{-3}\ mol\ cm^2$ for an interfacial area of 19.6 cm$^2$.

The second mechanism replaced the slow step described by Equation 275 with the following

$$(KPS)_{ad} \longrightarrow \overline{KPS} \tag{277}$$

and arrived to the rate law

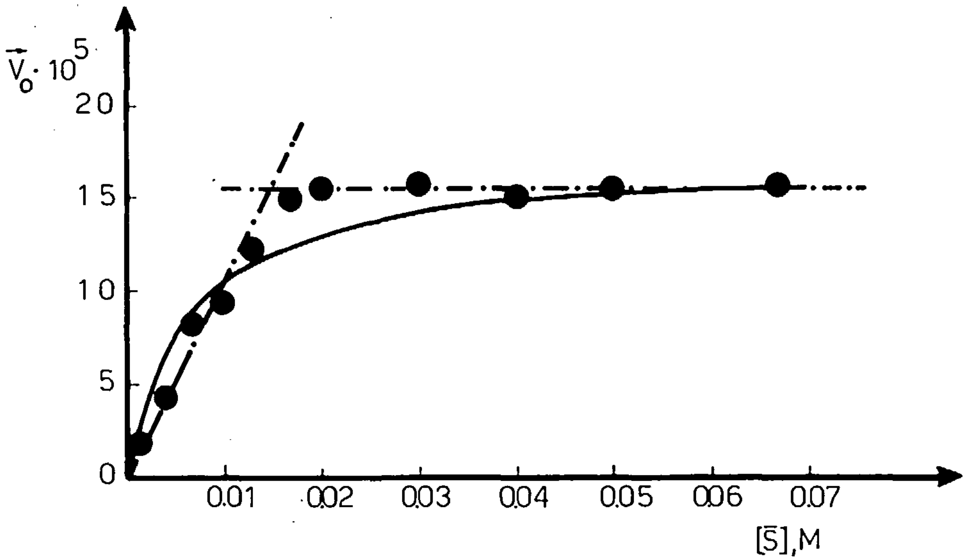


FIGURE 54. Initial extraction rate of $K^+$, $\vec{V}_0$, vs. $[\bar{S}]$ (molar concentration of DBC in 1,2 dichloroethane). $[K^+] = [P^-] = 8$ m*M*. Data obtained with the cell of Figure 16. Solid line calculated using Equation 279. Dashed line calculated through Equation 279 with $\alpha = 1.6 \cdot 10^{-2} [\bar{S}]$ ) ($M^{-1} min^{-1}$) for $[\bar{S}]$ <0.015 *M* and $\alpha = 2.4$ ($M^{-1}$ $min^{-1}$) for $[\bar{S}] > 0.015$ *M*.

$$V_0 = \alpha [P^-][K^+] \qquad (278)$$

with

$$\alpha = \frac{K_1 K_2}{K_{-1} + K_2} [(S)_{ad}] \qquad (279)$$

However, the results of this investigation also cannot be considered as very conclusive.

The following concluding remarks can be then drawn concerning the extraction kinetics by neutral extractants:

1. Provided the two phases are vigorously shaken, interfacial chemical reactions seem to control the rate of extraction, at least when TBP diluted in a water-immersible organic diluent is used as extractant and uranium and plutonium are the extractable metals.
2. This hypothesis is somewhat supported by the surface activity of TBP, shown in Figure 12.
3. The detailed interfacial chemical mechanism is, however, far from being completely identified.

   Conclusions regarding other neutral extractants such as TOPO or DBC are still controversial; probably both aqueous phase and interfacial chemical reactions can control the extraction kinetics, the predominance of one type of reaction on the other being strictly dependent on the system involved.

## IX. CONCLUSIONS

The reviewed works seem to indicate that whenever the rate of extraction was thoroughly investigated in the kinetic regime as functions of both the specific interfacial area and the chemical composition, interfacial rate controlling chemical reactions were often found.

Recently, Russian workers[156] have also reported that in a systematic investigation of the extraction kinetics with the extractants dibutyl, diisoamyl, di (2-ethyl-hexyl) phosphoric acids, di (2-ethyl-hexyl) dithiophosphoric acid, acetylacetone, benzoylacetone, dibenzoylmethane, dithizone, 2-thenoyltrifluoroacetone, pyridylazonaphthol, 8-hydroxyquinoline and derivatives with the metals iron, cobalt, nickel, copper, zinc, indium, beryllium, titanium, and chromium, 65 out of 82 systems have shown to be rate limited by interfacial chemical reactions. Although this support is of only qualitative nature, little doubt seems to exist that, as was expected for an heterogeneous system, the interface is the most probable locale of the chemical reactions. However, when the solubility of the extractant in the water phase becomes appreciable, the contribution of aqueous phase rate determining reactions can become competitive. The case of 2-thenoyltrifluoroacetone is in this respect significant.

Concerning the actual reaction mechanisms which rule the extraction processes, the data are too insufficient to elaborate general patterns. Although the reaction mechanisms described in Section V seem to be representative of many systems, several exceptions are probably present. This is, however, an expected result because of the very different chemical nature of the extractants and metal species which can be involved. With regard to the techniques available to study the extraction kinetics, constant interfacial area stirred cells seem to be very versatile. It is desirable that in the future more and more systems will be investigated also with this technique, exploring how the extraction rate varies when the following parameters are varied in the widest possible range: (1) stirring speed, (2) interfacial area, and (3) chemical composition. Further, the interfacial properties of the system, the water solubility of the extractant, as well as the chemical equilibriums occurring in the biphasic system should be always determined.

It is in this way hoped that many more reaction mechanisms as well as significant rate constants will become available. This is of course not a very easy job due to the very large amount of experimental data which are necessary to obtain and analyze. It is, however, hoped that the progressive introduction of continuous concentration monitoring devices as well as on-line computerized systems to collect and analyze the data will make this task easier.

## LIST OF FREQUENTLY USED SYMBOLS

A = interfacial area
a = specific interfacial area = interfacial area/volume
C = molar concentration
D = diffusivity, diffusion coefficient
K = rate constant
$K_{D,R}$ = partition coefficient of extracting reagent
$K_c$, $K_{eq}$ = equilibrium constant
$K_{D,C}$ = partition coefficient of neutral complex
$K_h$ = hydrolysis constant
$K_a$ = acid dissociation constant
M = moles/liter
N = interfacial flux = V/a
N* = normalized interfacial flux = interfacial flux/initial metal concentration
$n_w$, $n_{org}$ = stirring speed of aqueous and organic phase
R = mass-transfer resistance
$R_i$ = interfacial resistance
$R_e$ = Reynolds number

r/min = revolutions per minute
t = time
V = extraction rate = $-dC/dt$
V* = normalized extraction rate = extraction rate/initial metal concentration
[ ] = molar concentration

Greek symbols:
$\alpha_1$ = $\alpha_2/\gamma$ = ratio of Langmuir adsorption constants
$\alpha_2$ = Langmuir adsorption constant
$\gamma$ = Langmuir adsorption constant or interfacial tension at the organic-water interface
$\beta$ = mass-transfer coefficient
$\bar{\beta}$ = overall mass-transfer coefficient
$\delta$ = thickness of diffusion (stagnant) film
$\pi$ = interfacial pressure at the organic-water interface

Superscripts:
— over chemical symbols indicates organic phase species
→ over V and N indicates aqueous to organic transfer
← over V and N indicates organic to aqueous transfer

Subscripts:
e, eq = equilibrium
ad = interfacially adsorbed species
i = near the interface
w = pertaining to the aqueous phase
org = pertaining to the organic phase
o = referring to time zero
f = forward (aqueous to organic) reaction
r = reverse (organic to aqueous) reaction

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