EXTRACTION KINETICS OF METAL CHELATES

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ABSTRACT

The factors which in the authors' opinion are most important in determining the rates of extraction processes are considered. These include: site of metal chelate formation: extraction of metal chelates as a homogeneous heterophase process (quantitative characteristics); role of replacement of water in the aquo-complex; catalysis by the ligand; influence of the method of reagent introduction; and kinetics of exchange extraction reactions. The urgent need for further development of the kinetic investigation of extraction seems incontrovertible. Suitable apparatus is needed for rapid mixing and separation of phases.

INTRODUCTION

Metal chelate extraction is usually investigated under equilibrium conditions. The results of such investigations are of importance both for the theory of extraction and for practical applications in analytical chemistry. For instance, extraction coupled with spectrophotometry is widely used for metal determinations. Extraction of metal chelates is used for concentration of trace elements, for the separation of elements similar in properties, for substoichiometric extraction, etc. Extraction of metal chelates is also an important method for investigation of complex formation in aqueous solution.

Against the progress made in the theoretical study and practical use of equilibrium extraction the successes in the field of kinetics of extraction processes look much more modest. This is obviously connected with a number of objective experimental difficulties. First, equilibrium is generally rather rapidly established during extraction. Hence, appropriate apparatus and methods of investigation are needed for the study of relatively rapid extraction reactions. Secondly, as extraction systems are heterogeneous, it is necessary to take into account the contribution of rate of mass transfer to the total rate of the process. At a low rate of phase mixing, the rate of mass transfer may determine the rate of the whole process (region of 'diffusion-controlled' extraction). Under such conditions it is impossible to obtain information about the rate of individual chemical stages of the process. However, such information can become available if the rates of mass transfer and of the chemical reactions are comparable in magnitude (region of

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'mixed' kinetics) and especially if the rate of chemical reaction is substantially lower than the rate of mass transfer ('kinetic' region). The kinetic region may be reached by increasing the rate of phase mixing and by lowering the temperature; the latter factor always influences the rate of chemical reactions more than does the rate of mass transfer. As criteria for the kinetic region having been reached in an extraction, we may use the independence of the extraction rate on mixing rate, or, the dependence of extraction rate on the pH of the aqueous phase if the extraction reagent is an acid.

Up to the present almost all investigations of extraction kinetics have been accomplished on systems in which equilibrium is relatively slowly established (> 5 min). The most important results of these investigations of the kinetic region of extraction have been summarized by us in a review[1] published in 1964. The conclusions drawn in that review and data from more recent investigations prove the importance of studying the kinetics of extraction processes, for the following reasons.

First, kinetic investigations provide information about the mechanism of extraction, especially the rate-determining steps and where the compound extracted is actually formed. This, together with data on the equilibrium reaction, makes it possible to obtain a more complete idea of the mechanism of the process as a whole. The study of the influence of experimental conditions on the extraction rate is then of great practical importance as it makes it possible, in principle, to control the rate of the process. This may be of importance in working out new schemes of separation and concentration of elements by extraction methods. Elucidation of the kinetic parameters of extraction processes furthers the reasonable choice of extraction time in extraction-photometric determinations of metals, in theoretical investigations of equilibrium extraction, etc. Finally, the kinetics of complex formation of metal ions with various organic and inorganic ligands in aqueous solution can also be studied by the extraction method.

We have extensively investigated the extraction kinetics of a great number of metal chelates—β-diketonates (for instance, iron, indium, cobalt, uranium), cupferronates, complexes with N-benzoyl-N-phenylhydroxylamine (BPHA), 8-hydroxyquinoline, 1-(2-pyridylazo)-2-naphthol (PAN), etc. In most cases experimental data have been obtained for the kinetic region. The systems were investigated at a definite temperature. If a temperature-controlled air-bath was used, the phases were mixed by means of an apparatus for intensive shaking: 140 vibrations/min with a 25mm amplitude. Otherwise, the phases were mixed with a rotatory mixer at 8000 rev/min.

SITE OF METAL CHELATE FORMATION

The general equation for extraction of a simple metal chelate is

$$\text{Me}^{n+} + n\,\text{HR}_{(o)} \rightleftharpoons \text{MeR}_{n(o)} + n\text{H}^+ \tag{1}$$
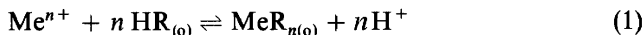
This equation describes the final result of extraction, which is independent of where the compound being extracted is actually formed, viz. at the interface of the phases or in the aqueous phase. However, the site of formation is of great importance when the kinetics of extraction are considered.

Definition of the notion of the extraction rate depends on whether the chemical reactions during extraction are homogeneous or heterogeneous.

One of the methods of approaching this question was proposed by Irving et al.[2]. The method was further developed in our own work[3]. The essence of the method is as follows. If the reactions involved in formation of a compound proceed in the aqueous phase, then, all other conditions being equal, the extraction rate must be highest when that organic solvent is used for which the distribution constant of the reagent is the lowest (for a series of solvents similar in chemical nature). On the contrary, if the compound is formed at the interface, then the solvent with the greatest distribution constant for the reagent must extract the complex the most rapidly (in this case the concentration of the reagent is higher in the organic phase).

This principle was taken as the basis for identifying the zone where chemical reactions proceed during the extraction of some metal chelates of acetylacetone, benzoylacetone, dibenzoylmethane, thenoyltrifluoracetone, BPHA, PAN and 8-hydroxyquinoline. Chloroform, benzene and carbon tetrachloride were used as organic solvent. The distribution constants of these reagents between organic solvent and water decrease in the order $CHCl_3 > C_6H_6 > CCl_4$. It turns out that metals are more rapidly extracted by the reagent solutions in CCl_4 than those in C_6H_6 and more slowly extracted by solutions in $CHCl_3$. As an illustration, *Figures 1* and *2* give data on the extraction of the scandium dibenzoylmethane complex[3] and iron(III) benzoylphenylhydroxylamine complex[4]. The conclusion may be drawn that these metal chelates are formed in the aqueous phase.
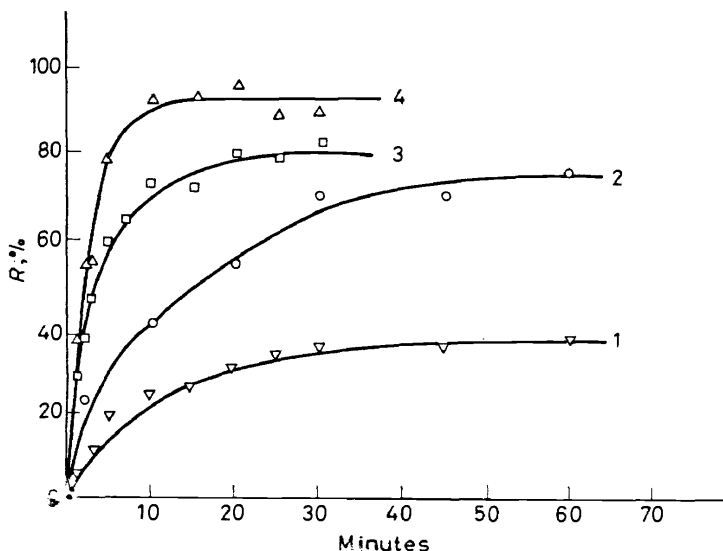

Figure 1. Extraction of scandium $(3.1 \times 10^{-6}$ M) by 0.05 M dibenzoylmethane in $CHCl_3$ and CCl_4 at 25°C. 1—$CHCl_3$, pH 5.1: 2—$CHCl_3$, pH 5.3: 3—CCl_4, pH 5.1: 4—CCl_4, pH 5.3.
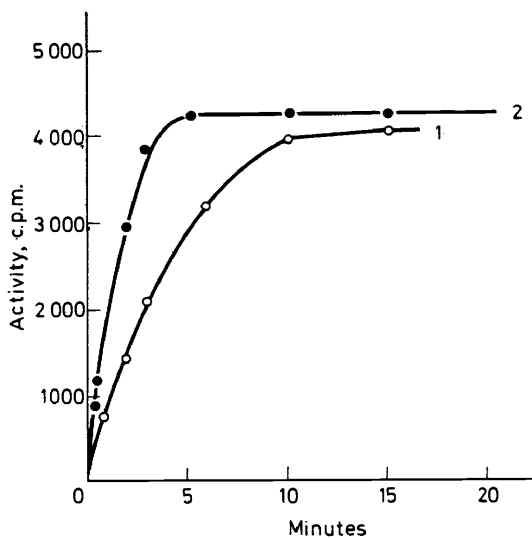
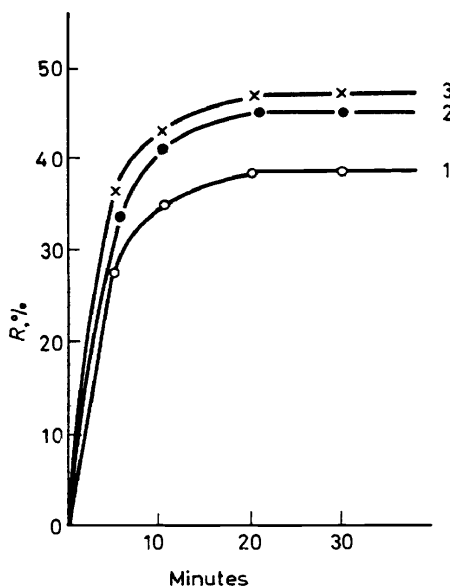*Figure 2.* Extraction of iron (III) by 0.01 M N-benzoyl-N-phenylhydroxylamine in C_6H_6 and $CHCl_3$ at 25°C (pH 2.6). 1—$CHCl_3$; 2—C_6H_6.

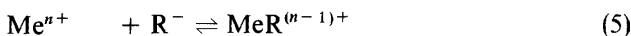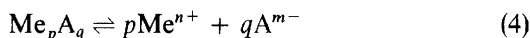*Figure 3.* Extraction of nickel (5.1×10^{-4} M) by 6.3×10^{-3} M 8-hydroxyquinoline in $CHCl_3$ at 15°C. 1—pH 3.3; 2—pH 4.2; 3—pH 5.0.

Another approach consists in investigation of the dependence of extraction rate on the pH of the aqueous phase under otherwise similar conditions. Here the initial extraction rate has to be taken into account, because as the extraction time increases the extent of the reverse reaction (back-extraction) also increases; therefore kinetic curves obtained at different pH values must differ. However, if distribution and dissociation of the chelating agent precedes formation of the chelate in the aqueous phase, the initial rate of extraction will depend on the pH. If the chelate is formed at the interface and the undissociated form of the reagent participates in the reaction, the initial rate does not depend on the pH. The data obtained for the above-mentioned systems confirm that the metal chelates extracted are formed in the aqueous phase. As an example. *Figure 3* gives data on nickel—in 8-hydroxyquinoline extraction in the system water–chloroform[5].

The results obtained by other investigators also generally confirm the conclusion that the metal chelates extracted are formed in the aqueous phase.

EXTRACTION OF METAL CHELATES AS A HOMOGENEOUS HETEROPHASE PROCESS; QUANTITATIVE CHARACTERISTICS

On the basis of what has been stated above the general scheme of metal chelate extraction may be represented as:

$$HR_{(o)} \rightleftharpoons HR \tag{2}$$

$$HR \rightleftharpoons H^+ + R^- \tag{3}$$

$$Me_pA_q \rightleftharpoons pMe^{n+} + qA^{m-} \tag{4}$$

$$Me^{n+} + R^- \rightleftharpoons MeR^{(n-1)+} \tag{5}$$

$$MeR^+_{(n-1)} + R^- \rightleftharpoons MeR_n \tag{6}$$

$$MeR_n \rightleftharpoons MeR_{n(o)} \tag{7}$$

Here HR is the chelating agent, used in the form of a solution in an organic solvent, R is its anion, Me^{n+} is the hydrated cation of the metal, Me_pA_q is the charged or neutral complex of the metal with ligands present in the aqueous phase (hydroxyl ions, buffer components, etc); the subscript (o), indicates species in the organic phase. Stages 2 and 7 describe the mass transfer of the reagent and the extracted compound between the phases. Stages 3 to 6 describe the chemical reactions occurring during extraction. In the kinetic region the rate-determining step must be one of the stages 4–6 as reaction 3 very rapidly comes to equilibrium during extraction. This, for instance, follows from kinetic investigations of 8-hydroxyquinoline[6] and dithizone[7] extractions.

Thus the extraction of metal chelates may be thought of as a homogeneous heterophase process. It must be considered as being homogeneous because the chemical interaction occurs within the aqueous phase, and as hetero-phase because the initial and final products of chemical interaction are found in different phases. The determination of the rate of such a process is identical

to the determination of the rate of the homogeneous chemical reaction, the sole difference being that the concentration of all compounds participating in the chemical interaction has to be related to the phase in which the reaction takes place, i.e. the aqueous phase.

We have used such an approach in the study of the kinetics of nickel extraction by 8-hydroxyquinoline solutions in chloroform[5,8]. The step which determines the extraction rate of the $NiOx_2 \cdot 2HOx$ chelate is the second stage of complexation

$$NiOx^+ + HOx \rightleftharpoons NiOx_2 + H^+ \qquad (8)$$
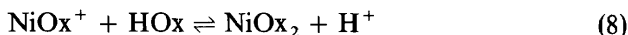
i.e. the extraction reaction proves to be third order, first-order in metal ion and second order in the molecular form of the reagent. During the treatment of the kinetic data the so-called 'conventional' concentrations of molecular 8-hydroxyquinoline in the aqueous phase were used. These concentrations were calculated from the amount of the molecular form in the organic phase as related to the volume of the aqueous phase. The resulting value of the extraction rate constant [$(1.4 \pm 0.2) \times 10^3$ 1^2 mol^{-2} min^{-1} at pH = 3.3, 15°C and 0.1 M $NaNO_3$] characterizes the initial complexing rate in the heterogeneous system water–chloroform and is determined by the following expression

$$K_{ex} = K_t \cdot K_p/[H^+] \qquad (9)$$

where K_t is the rate constant of the direct reaction 8, and K_p the equilibrium constant for the $NiOx^+$ complex formation.

Under the same conditions the complexing rate in the aqueous solution would obviously be substantially greater.

If we assume that in the homogeneous medium the reaction of nickel with 8-hydroxyquinoline will also be second-order with respect to the molecular form of the reagent, it may be seen that

$$K_{hom} = K_{ex} \cdot P^2 \qquad (10)$$

where K_{hom} is the complex-formation rate constant in the aqueous solution and P the distribution constant of the molecular form of the reagent between the two phases. The expression 10 shows that the complex-formation rate in heterogeneous systems is substantially lower than that in the homogeneous system. It must be noted that the higher the value of the distribution constant of the reactive form of the reagent in the system water–organic solvent, the slower complex-formation proceeds in the same system.

ROLE OF REPLACEMENT OF WATER IN THE AQUO-COMPLEX

As is now established, the main factors which determine the extraction rate are temperature, nature and concentration of the metal in the aqueous phase, pH, nature and concentration of the chelating agent, nature of the organic solvent, and composition of the aqueous phase, i.e. the nature and concentration of those compounds contained in it which formally do not participate in the extraction reaction.

Without dwelling in detail on the significance of most of the factors mentioned, the role of which is obvious, we should like to consider in more detail the following question.

As is known, metal ions in aqueous solutions form hydrated aquo-complexes, for instance, $Me(H_2O)_6^{n+} \cdot aq$, where aq represents the secondary hydration sphere. Owing to this, complex-formation reactions must be considered as replacement reactions of aquo-complexes. The aquo-complexes, like other metal complexes, are classified as labile and inert, but it is not possible to draw a sharp boundary line between the two groups. Besides typically inert aquo-complexes [for instance, chromium(III), rhodium(III)] and typically labile ones [alkaline-earth metals], there are aquo-complexes of an intermediate type, for instance, $Fe(H_2O)_6^{3+}$. The inertness or lability chiefly depends on the electronic structure of the aquo-complex and is in the main determined by the change in ligand field stabilization energy when an activated complex is formed during the replacement reaction.

The expediency of such an approach for comprehending the extraction mechanism was first demonstrated by Honaker and Freiser in their kinetic investigation of zinc dithizonate extraction[9]. McClellan and Freiser[10] have also established that for a number of metal ions (Ni, Co, Zn, Cd) the rate of their extraction by dithizone is, other conditions being equal, paralleled by the rate of exchange of water molecules between the inner coordination sphere of the aquo-complexes and the bulk solvent (water).

The nature of the atoms at the reaction centre, the number of donor atoms and the charge of the reactive form of the ligand, the size of the chelate ring and the ease of closing it, the nature and disposition of substituents in the reagent molecule should also be taken into account. For β-diketones the transition from keto to enol form is important kinetically[11].

In choosing the organic solvent in investigations of extraction kinetics, it is necessary to take into account its chemical nature. For instance, solvents containing oxygen atoms may compete with reagent molecules during complex-formation, favouring the formation of mixed-ligand complexes. This may substantially influence the general rate of the process. For instance, nickel is extracted by 8-hydroxyquinoline solutions in chloroform at a considerably slower rate than by solutions in isopentanol[5].

The extraction rate strongly depends on the composition of the aqueous phase. Of importance here are such factors as the nature and concentration of the electrolytes used to create the required ionic strength and those of the components of buffer solutions, and masking agents, etc.

CATALYSIS BY THE LIGAND

We should like to dwell in more detail on the phenomenon which in the literature is called 'catalysis by the ligand'. In essence it consists of acceleration of complex-formation by participation of inert aquo-ions in the presence of a 'foreign' ligand which, as a rule, forms with the metal ion a less stable metal complex than does the chief ligand. Many such cases have been described, and may be exemplified by chromium(III) reactions. Such effects also occur in extraction systems. Thus, McKavaney and Freiser[12] have found that chromium(III) extraction by a mixture of acetylacetone and

isopentanol (1:1) is greatly accelerated when an acetate buffer solution is introduced into the aqueous phase, especially if this solution is introduced into the system just before the beginning of the extraction. In our laboratories an investigation[13] was made which showed the influence of fluoride on the rate of chromium(III) thenoyltrifluoracetonate extraction. It turns out that the catalytic action of fluoride is mostly displayed immediately after its introduction into the aqueous phase (*Figure 4*). If the aqueous Cr(III) solution with fluoride added is kept for a long time and the extraction is then carried out, hardly any chromium is extracted; the EPR spectrum shows the appearance of CrF_6^{3-} in the aqueous phase, a complex which is both thermodynamically and kinetically stable.
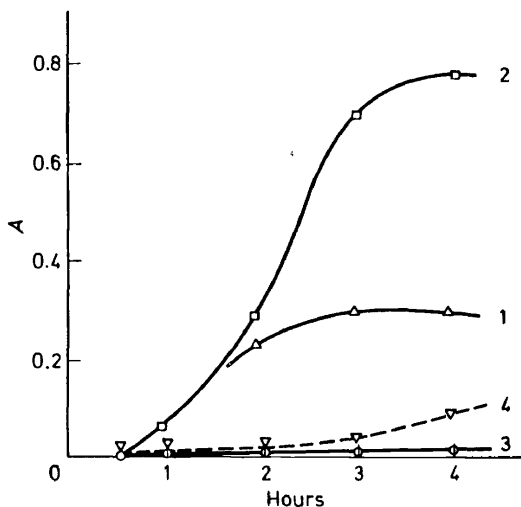

Figure 4. Rate of chromium(III) extraction (1.9×10^{-3} M) as a function of pH and NH_4F concentration. Curves 1 and 2 were obtained immediately after mixing the solutions; curves 3 and 4 during extraction 6 and 14 days, respectively, after preparation of the solutions. NH_4F concentration, 1—1.9×10^{-2} M, pH 5.7; 2—9.5×10^{-2} M, pH 5.4; 3—1.9×10^{-2} M, pH 5.2; 4—9.5×10^{-2} M, pH 5.7.

This effect was investigated in detail for the chromium(III)–8-hydroxyquinoline extraction in the systems water–chloroform and water–isopentanol at different temperatures[8, 14]. Sodium salts of some inorganic and organic acids (hydrofluoric, hydrobromic, hydrochloric, carbonic, formic, acetic, tartaric and ascorbic) were tested. The salts were introduced into the aqueous phase by two methods. In method A the complexing agents were introduced into the aqueous chromium solution before the extraction, which was then carried out after the complex-formation reactions in the aqueous solution had been completed. In method B these compounds were introduced into the extraction system at the moment the extraction was started.

For ligands which do not form stable complexes with chromium(III), for

instance, Cl⁻ or Br⁻, the catalytic effect is very feeble at temperatures of 20°–30°C. If, however, the ligand-catalyst forms stable complexes with chromium, the catalytic effect is already evident at room temperature, depends on the method of catalyst introduction, and increases with temperature. For ligands such as $HCOO^-$ and CH_3COO^-, the catalytic effect increases with increase in their concentration; on the other hand increase of fluoride concentration reduces the extraction rate irrespective of the method of its introduction into the aqueous phase. These differences may obviously be explained by the change in the ratio of the stabilities of the chromium(III)–8-hydroxyquinoline complex and the chromium complexes with the ligand-catalysts.
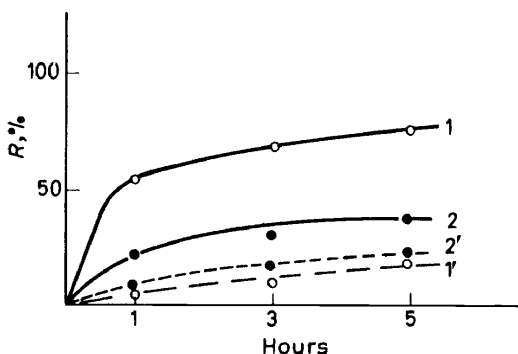

Figure 5. Extraction of chromium(III) (6 × 10⁻⁴ M) by 0.1 M 8-hydroxyquinoline in isopentanol at 25°C. Ionic strength 1.5 (NaNO₃). Dashed curves show method A, continuous curves method B. 1— 1.5 M CH₃COONa ; 2— 0.02 M NaF.

Catalysts which form stable complexes with chromium(III) have in common a sharp difference in their catalytic effect depending on whether they are introduced by method A or B (*Figure 5*). Our results accordingly allow us to assume the existence of different mechanisms for the catalytic effect. When catalyst is introduced by method A, the acceleration of extraction may be explained by the formation, at the start of extraction, of chromium complexes with the catalyst which are more labile and less stable than chromium(III) aquo-ions and interact with the reagent to give the chelate to be extracted. When the ligand-catalysts are introduced by method B, the accelerating mechanism is apparently connected with initial formation of an ion-association complex between the aquo-ion and the catalyst. Later on, striving to occupy one of the places in the internal coordination sphere of the aquo-ion, the ligand-catalyst activates it, thus facilitating the introduction of the chief ligand into the internal sphere. Hence, it may be assumed that during the reaction an activated complex is formed which includes the chief ligand and the ligand-catalyst. This assumption still requires further verification.

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INFLUENCE OF THE METHOD OF REAGENT INTRODUCTION MAXIMA ON KINETIC CURVES

To reduce the time needed to reach equilibrium during extraction, the reagent is often introduced directly into the aqueous phase in the form of a solution in alcohol, acetone and similar solvents, and not as a solution in an organic solvent immiscible with water. The equilibrium state of the system, all other conditions being equal, most frequently proves to be the same for both cases, but the kinetics of the process may differ substantially. This was shown during investigation of the extraction of complexes of some metals [In, Ga, Fe(III), Zn, Mn(II), Ni] with 1-(2-pyridylazo)-2-naphthol (PAN)[15, 16]. The differences in the extraction kinetics, observed when different methods of reagent introduction are used, show common features for all the elements tested except nickel and are illustrated by *Figure 6*. When the reagent is introduced into the aqueous phase, the extraction rate is high at the beginning, but after prolonged extraction the degree of extraction has the same value as it has when the reagent is introduced in the organic phase.
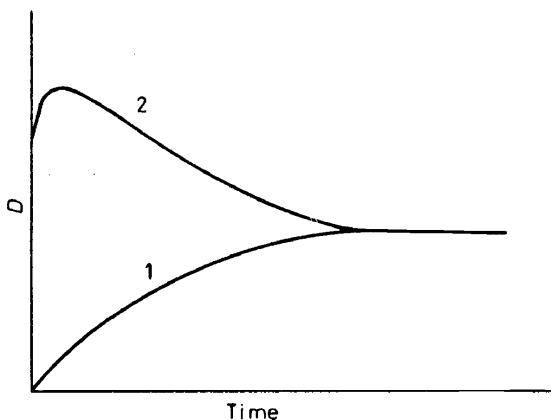

Figure 6. Schematic kinetic curves for the 1-(2-pyridylazo)-2-naphthol complex of indium. 1—PAN introduced as its chloroform solution; 2—PAN introduced in the aqueous phase.

The extraction of indium using different methods of reagent introduction has been investigated in more detail[15]. With PAN this element forms a cationic metal chelate and is extracted into the organic phase in the form of a mixed complex with acetate, which is added as a component of the buffer solution. This example shows once more the importance of taking into account the influence of 'foreign' components of the aqueous phase on the extraction kinetics.

Kinetic curves with a maximum have already been described in the literature (see references cited in ref. 16). It is difficult to give an unambiguous explanation of this phenomenon. In the case of complexes with PAN it

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would be possible to explain it by the tendency of PAN solutions to form colloids, or by hydrolysis of metal ions. However, data on nickel extraction do not fit into such a scheme. Perhaps the appearance of maxima on the kinetic curves is connected with the fact that at the beginning the high concentration of PAN in the aqueous phase creates favourable conditions for a rapid and effective extraction of metal complexes. Later on, PAN itself is extracted, its concentration in the aqueous phase is sharply lowered, and then, depending on the stability of the complex formed, the nature of the solvent and other factors, the degree of extraction can remain at its previous level or decrease. The elucidation of the causes of maxima on the kinetic curves for extraction systems is of great interest from the theoretical and practical points of view. In this connection it may be noted that many methods of extraction-photometric determination with the use of PAN recommend working under non-equilibrium conditions.

KINETICS OF EXCHANGE EXTRACTION REACTIONS

The kinetics of exchange extraction reactions, i.e. reactions in which another metal chelate is used as reagent[17], deserve some attention. The importance of these reactions in analytical chemistry has increased because their application often improves the selectivity of extraction. Besides the factors considered earlier the exchange extraction rate must depend on the kinetic and thermodynamic stability of the complex-reagent and on its concentration. During the theoretical consideration of the problem[17] the interesting conclusion was drawn that the rate of the exchange extraction itself should be independent of pH and must increase with decrease in $K^{1/n}$, where K is the extraction constant for the reagent MeR_n. These hypotheses were confirmed experimentally. In *Figure 7* are shown kinetic curves for the
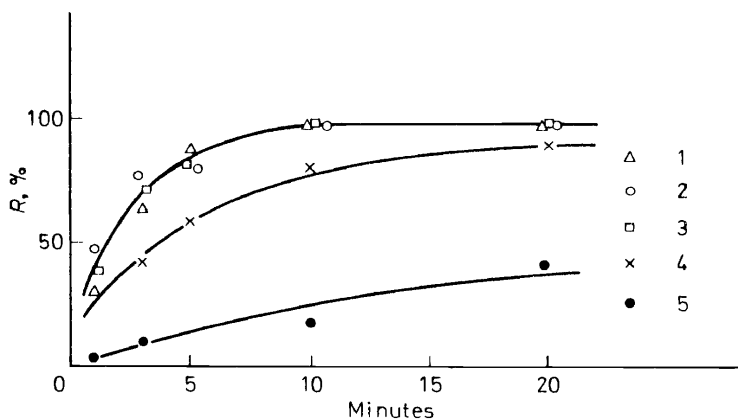

Figure 7. Extraction of copper by 3.3×10^{-6} M indium dithizonate in $CHCl_3$ at 25°C. pH: 1—5.5; 2—5.2; 3—3.0; 4—2.0; 5—1.1.

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exchange extraction of copper by indium dithizonate. It is seen that once the pH has been reached at which all the indium is present as its dithizone complex in the organic phase, i.e. when the exchange process begins, the rate of copper extraction ceases to depend on the pH of the aqueous phase. *Figure 8* demonstrates the other effect predicted by the authors. It is seen that
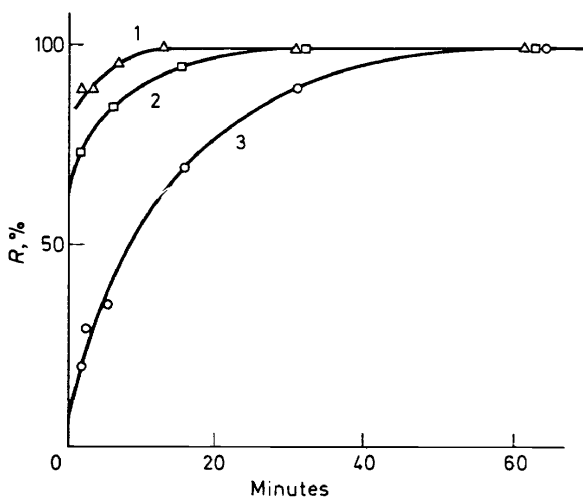

Figure 8. Rate of iron(III) extraction (10^{-5} M) by cupferronates of In, Cu and Ga at pH 4.0. 1—5 × 10^{-3} M In(Cup)$_3$, [In]$_{aq}$ = 2.5 × 10^{-3} M; 2—7.5 × 10^{-3} M Cu(Cup)$_2$, [Cu]$_{aq}$ = 3.75 × 10^{-3} M; 3—5 × 10^{-3} M Ga(Cup)$_3$, [Ga]$_{aq}$ = 2.5 × 10^{-3} M.

the rate of Fe(III) extraction increases with the series of reagents gallium cupferronate [$(1/n) \log K = 1.64$], copper cupferronate [$(1/n) \log K = 1.33$], indium cupferronate [$(1/n) \log K = 0.81$]. It is interesting that on the basis of these investigations a conclusion has been drawn about the formation, in the aqueous phase, of the compounds being extracted by the exchange extraction, at least for the systems studied. The considerations above apply to cases where the reagent-complex is labile. If this complex is kinetically inert, the rate of the exchange extraction will be determined by the rate of dissociation of the complex. In such cases there is often no exchange extraction at all.

CONCLUSION

We have briefly considered the factors which in our opinion are the most important in determining the rate of extraction processes. It seems to us that the expediency of further development of kinetic investigations of extraction is unquestionable.

In this connection there arises the question of the need to develop suitable apparatus for rapid mixing and separation of phases. The classic method of sampling for analysis at intervals during the course of the process is not suitable for the study of rapid processes. At present this limits the range of

systems available for kinetic investigation and reduces the possibility of reaching general theoretical conclusions.

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