Translated from *Uspekhi Khimii* **61** 1515–1549 (1992) U.D.C. 66.061

The dynamic separation of substances by liquid–liquid extraction

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ABSTRACT. Experimental data on the separation of substances by extraction, based on differences in the rates of their extraction, have been given. The physicochemical principles of dynamic separation have been examined. Approaches to the mathematical modelling of the process have been described, and specific models have been analysed.

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I. Introduction

The method for separating substances based on differences in the rates of their liquid–liquid extraction has been known for a long time. As early as 1947, Barnes[1] showed that copper(II) and mercury(II) can be separated by extracting them with a chloroform solution of dithizone at low pH values. Mercury dithizonate was extracted rapidly, and the equilibrium state was reached in less than 1 min under the conditions of the experiments,[1] whereas the extraction of copper dithizonate took place slowly. Few such examples were known, however, and they were regarded as a possible way of improving the separation of substances in analytical determinations.[2]

In the last two decades, there has been a sharp increase in interest in the study of the kinetics of extraction. This has been due to the need to solve a number of theoretical problems, and also to an extension of the range of practical application of extraction methods. A large number of studies have been carried out, important reviews have been published,[3–9] and a new scientific field has developed, namely the kinetics of the extraction of inorganic substances. The kinetic studies have revealed many systems in which equilibrium is established slowly, and these can be used in practice. However, the separation of substances under non-equilibrium conditions, based on the use of kinetic factors (subsequently, the term "dynamic separation" will be used), has not been widely employed, for the following reasons.

Studies of separation by extraction have involved mainly the search for (synthesis of) effective extracting agents giving the required degree of separation as a result of differences in the thermodynamic parameters of the processes. In the list of factors influencing the separation (the nature of the extracting agent and the diluent, the composition of the aqueous solution, pH), the rate of extraction occupied one of the last places. In fact, there were definite grounds for this. The kinetic studies were at the stage of the development of the experimental procedure and the accumulation of data. For the most part, the kinetics of the extraction of individual substances were studied. Because of differences in the experimental conditions and the indeterminate nature of the hydrodynamic conditions close to the inter-phase boundary, the results of studies of the same extraction system were often inconsistent, and even contradictory. The situation was complicated considerably by the wide range of inter-phase phenomena (chemical reaction, adsorption, the formation of inter-phase films, spontaneous surface convection, electrical phenomena) in the extraction of inorganic substances, the non-uniformity of the inter-phase layer, and the consequent complexity of inter-phase mass exchange. Theoretical studies were based on extensive simplifications, and did not have sufficient predictive power.

At the same time, the determination of the factors leading to differences in rates of extraction and the discovery of criteria for identifying those systems for which the application of kinetic factors would lead to a significantly higher selectivity of separation require the systematic study of the kinetics of the simultaneous extraction of several components. However, the still unresolved fundamental problems of the kinetics of the extraction of individual elements, related mainly to the identification of the rate-determining stage and the location of the reaction, make it impossible for research workers to concentrate their attention on more complex systems. The study of the simultaneous extraction of several components is of considerable interest for a deep understanding of the mechanism of multicomponent liquid–liquid extraction and the general mechanism of the transfer of substances through the interface between two immiscible liquids. Moreover, the practical importance and the possibility of further improvement in the separation of substances is increasing interest in the dynamic separation method. The effective application of this method requires fundamentally new apparatus, but definite results can also be achieved using the equipment traditionally employed.[10–17]

The present review gives the results of experimental and theoretical studies of the dynamic separation of substances by liquid–liquid extraction.

II. Experimental data

1. Systems with dynamic separation

The separation of Cu^{II} from Hg^{II} by extraction with a chloroform solution of dithizone at low pH values, based on the difference in their rates of extraction, has been noted not only by the author cited above[1] but also by other workers.[18] The slow extraction of copper(II) dithizonate has been used in the determination of gold.[19]

Gold is extracted rapidly from 0.5 N H_2SO_4 by a chloroform solution of dithizone, whereas copper is extracted slowly and does not interfere in the determination of gold. The difference in the rates of extraction of zinc, cobalt, and nickel by dithizone solution has been made the basis of a method for their separation. In the extraction under the conditions of the experiments,[20] the extraction equilibrium is established in 15 min for zinc, 20 h for cobalt(II), and 10 d for nickel(II). The optimum conditions for separating the pairs Ni–Zn, Zn–Co, and Ni–Co have been determined.[20] It has been suggested that the high rate of extraction of vanadium(V) by β-isopropyltropolone solution could be used to separate vanadium(V) and iron(III).[21] The influence of kinetic factors on the selectivity of separation in the extraction of chelates has been examined by Freiser.[22]

The rate of extraction of Cu^{II} by Kelex 100, the active component of which is a β-alkenyl-8-quinolinol, is much greater than the rate of extraction of Fe^{III}, so that the selective extraction of Cu^{II} in the presence of Fe^{III} is possible.[23,24] For short phase contact times (less than 2 min) and an equilibrium pH of 0, the extraction of copper is not suppressed by iron. On prolonged mixing (up to 48 h), the ratio of the concentrations of copper(II) and $Fe^{(III)}$ in the organic phase at first increases from 20 to 80 (in 0.5–1 h), and then decreases to 18. Without stirring (after preliminary contact between the phases for 1 min), this ratio remains constant;[25] this is important when the extraction assembly is stopped unexpectedly.

In the range far from equilibrium, the rate of extraction of copper by Kelex 100 is 2.81×10^{-7} mol $cm^{-2} s^{-1}$, and that of iron(III) is 2.24×10^{-8} mol $cm^{-2} s^{-1}$. In the extraction from a nitrate solution (pH 2) by a 0.02 mol dm^{-3} solution of Kelex 100 in chloroform, 85% Cu^{II} is extracted after 2 min, whereas only 7% Fe^{III} is extracted.[26] On prolonged contact between the phases (48 h), Fe^{III} displaces Cu^{II} and the extract is saturated with Fe^{III} to the extent of 92%. The selectivity of the extraction of Cu^{II} is explained by kinetic factors.[26] This is indicated by the fact that for the maximum time of mixing, the degree of extraction of Fe^{III} in the absence of Cu^{II} is 98.9% and above, and the extent of the extraction of Cu^{II} in the absence of iron is 72.7%.

The results of an experimental study of the separation of copper from iron have been published.[27] A solution containing 1.3×10^{-2} mol dm^{-3} Cu^{II}, 1.6×10^{-2} mol dm^{-3} Fe^{III}, and 1 mol dm^{-3} Cl^- was shaken for 4 min with an organic phase consisting of a mixture of 2% Kelex 100 and 8% n-dodecanol in kerosene. The acidity was adjusted so that the final pH of the aqueous solution was 0.9; the separation factor was 30. Thus the system formed by Kelex 100 with the metal chlorides is similar to the corresponding sulphate system[23,25] in that the selectivity of the extraction of copper is also due to kinetic factors. Since $pH_{0.5}$ for Fe^{III} is lower than that for Cu^{II}, it might have been expected that Fe^{III} would be extracted more rapidly, but because of the large difference in the rates of extraction, Cu^{II} is extracted preferentially.[27] Determination of the equilibrium constants and rates of extraction showed that the introduction of the modifier nonylphenol into the organic phase leads to an increase in the distribution coefficient of Cu^{II}, but decreases the rate of extraction. The addition of Fe^{III} ions to the solution leads to an almost ten-fold further decrease in the rate of extraction of Cu^{II}, but has practically no influence on the rate of re-extraction of Cu^{II}. In all cases where Kelex 100 and Kelex 120 (20% Kelex 100 and 80% nonylphenol) are used, the rate of extraction of Cu^{II} remains 10^2 times higher,[28] and this ensures the separation of Cu^{II} and Fe^{III}. In the extraction by a solution of Kelex 100 in chloroform with a phase contact time of 0.5 h, the ratio of the concentrations of Cu^{II} and Fe^{III} in the organic phase was 38, whereas the value after stirring for 276 h was 0.5.[29]

The aminophenol extracting agents 7-(t-butylbenzyl)-8-quinolinol and a mixture of isomeric 7-β-decenyl-8-quinolinols are kinetically selective in the extraction of Cu^{II} from iron-containing solutions.[30] With short phase contact times (6–12 min), the selective extraction of Cu^{II} is possible. When equilibrium is reached, however, Fe^{III} is extracted more effectively than Cu^{II}, so that after prolonged contact between the phases, Fe^{III} begins to displace Cu^{II} from the organic phase.

In the extraction of copper, nickel, zinc, and cobalt(II) from ammoniacal solutions containing 300 g $litre^{-1}$ $(NH_4)_2SO_4$ by a 0.5 kmol m^{-3} solution of Kelex 100 and 10% isodecyl alcohol in Solvesso 150, the extraction and separation are influenced significantly by the phase contact time and temperature.[31] The ease of extraction of Cu^{II} at 323 K is higher than that at room temperature for short phase contact times, but with increase in the time of contact the extraction of Cu^{II} becomes less effective, and less Cu^{II} is extracted with increase in temperature. The extraction of Co^{II} increases regularly with increase in the phase contact time and temperature. The extraction of zinc(II) is higher at room temperature for short phase contact times, and with increase in the contact time, zinc(II) is displaced from the organic phase. Almost no nickel(II) is extracted. The optimum conditions for separating copper(II) and cobalt(II) are achieved for a phase contact time of 30 s at 323 K, or 2 min at room temperature. The separation of copper(II) and zinc(II) is improved by increasing the temperature and the phase contact time. Increase in the concentration of the extracting agent increases the efficiency of separation, but the degree of extraction is decreased. The authors cited[31] point out that the extraction of these elements depends on the nature of the anion and its concentration, the pH of the solution, the concentration of the extracting agent, temperature, and the phase contact time, so that the order of extraction may change: zinc(II) and cobalt(II) or zinc(II) and copper(II) may change positions.

In the extraction from the sulphate solution from the leaching of manganese nodules containing copper, nickel, cobalt(II), iron(III) and manganese(II) at pH 0–9 by a 10–15% Kelex 100 solution, the rate of extraction of copper(II) is greater than that of iron(III). The degree of extraction of iron(III) at pH 0.5–1.5 is greater than that of copper.[32] At pH 2, however, the degree of extraction of iron(III) is 80%, and that of copper(II) is 100%. With increase in the phase contact time and decrease in the ratio of the volumes of the organic and aqueous phases, there is a marked increase in the degree of extraction of copper(II) and an increase in the degree of extraction of iron(III). For a phase contact time of 2 min, the degree of extraction of copper is 93.2%, and the ratio of the concentrations of iron(III) and copper(II) in the organic phase is 0.142.[32] A study of the extraction of cobalt(II) and nickel(II) from sulphate solutions containing 0.25 kmol m^{-3} $(NH_4)_2SO_4$ at pH 4.72 by a 0.03–0.62 kmol m^{-3} solution of Kelex 100 in Shellsol containing added isodecyl alcohol established that at 298 K the rate of extraction of nickel(II) is very low, and equilibrium is not established even after mixing the phases for 120 min.[33] Increase in temperature leads to an increase in the rate of extraction. The addition of dinonylnaphthalenesulphonic acid (DNSA) has an even greater effect on the rate of extraction. For Ni^{2+} in the presence of 0.01 kmol m^{-3} DNSA, equilibrium is established in 1.5 h at 298 K, and in 20 min at 323 K. In all cases the rate of extraction of cobalt(II) is higher than that of nickel(II). At 323 K in the presence of 0.005 kmol m^{-3} DNSA, equilibrium in the extraction of cobalt(II) is achieved in

8 min. The data obtained can be used to improve the separation of Co^{II} and Ni^{II}.

Lix extracting agents are also kinetically selective. In the range far from equilibrium, the rate of the extraction of copper(II) from a nitrate solution with pH 2 by a solution of 0.02 kmol m^{-3} Lix 65N in chloroform is 4.42×10^{-9} mol $cm^{-2} s^{-1}$, and that of iron(III) is 3.01×10^{-11} mol $cm^{-2} s^{-1}$. In the extraction of copper(II) and iron(III), equilibrium is not established even after 6 weeks. The displacement of copper(II) from the organic phase by iron(III) is observed only after 140 h from the start of the experiment: this is much longer than in the extraction of these elements by a 0.02 kmol m^{-3} solution of Kelex 100 in chloroform.[26] When the solutions are mixed for a long time, the degree of extraction of iron(III) in the absence of copper reaches 53.7% and above, and the degree of extraction of copper(II) in the absence of iron(III) is 37.5%, indicating that the selectivity is due to kinetic factors.

In the extraction of copper(II) from a sulphate solution containing 5.13 g dm^{-3} copper(II) and 4.9 g dm^{-3} iron(III) (pH 2) by a 10% solution of Lix 63 in kerosene with the addition of 10% α-bromolauric acid and 3% isodecyl alcohol, a slight decrease in the extraction of copper(II) and a gradual increase in the extraction of iron(III) with increase in the phase contact time from 0 to 60 min is observed.[34] The decrease in the extraction of copper(II) is greater for a mixture containing 10% Lix 63 and 10% di-2-ethylhexyl hydrogen phosphate (D2EHHP) in kerosene with the addition of 3% isodecyl alcohol. The extraction of iron(III) increases sharply in the range 0–20 min, and for phase contact times greater than 45 min the degree of extraction of iron(III) becomes greater than that of copper(II).[34]

In the extraction of copper(II) from acid solutions containing iron(III) by a 20% solution of Lix 64N in the diluent Shell 140 with prolonged stirring (0–48 h), the ratio of the concentrations of copper(II) and iron(III) in the organic phase increases from 28 to 107.[25] Without mixing, this ratio remains constant.

For the extraction from the sulphate solution from the leaching of manganese nodules by a 10–15 vol.% solution of Lix 64N[32] it was established that the rate of extraction of copper(II) is greater than that of iron(III) throughout the pH range studied (0–9). At pH 2, the degree of extraction (E) of copper(II) is 75%, and that of iron(III) is 20%. A study of extraction from a solution modelling the leachings and containing 6 g dm^{-3} copper(II), 6 g dm^{-3} nickel(II), 0.15 g dm^{-3} cobalt(II), and 15 g dm^{-3} iron(III) for a phase contact time of 2 min showed that E_{Cu} is 52.1%, and the ratio of the concentrations of iron(III) and copper(II) in the organic phase is 0.007.[32]

It is also known that there is a difference in the rates of the extraction of non-ferrous metals and iron(III) by solutions of chelating extracting agents such as Hostarex DK-16 and SME-529. The extraction of iron(III) by DK-16 solutions takes place very slowly; the other metals are extracted rapidly, except nickel,[35] for which the rate of extraction by SME-529 is determined by the second stage of complex formation or by the diffusion of the complex being extracted.[36] Equilibrium is established in 30–35 min in the extraction of copper(II), and in 60 min in the extraction of iron.[37] Lix 63 is a kinetically synergetic additive to Lix 65N.[38,39]

A separation based on kinetic factors can be acheived in the extraction of zinc(II) and nickel(II) by solutions of dialkyl and diaryl hydrogen dithiophosphates.[40,41] Thus in the extraction by a 0.475 kmol m^{-3} solution of bis(di-isobutylmethyl) hydrogen dithiophosphate in Solvesso-150 containing 160 g dm^{-3} octanol, equilibrium is established in 1 h for zinc(II), and in 6 h for nickel.[40] In the extraction by 0.475 kmol m^{-3} solutions of di-n-butyl, di-isobutyl, di-n-octyl, di-(2-ethylhexyl), di-n-dodecyl, dicyclohexyl, and diphenyl hydrogen dithiophosphates in Solvesso-150 containing 160 g dm^{-3} octanol, equilibrium is established in 15 min for zinc(II), and in 120 min for nickel(II).[40] A study of the combined extraction of zinc(II) and nickel(II) by a 0.475 kmol m^{-3} solution of D2EHHDTP in the same mixed solvent at a ratio of the aqueous and organic phases of 1:1 established that the distribution of coefficient of Zn^{II} increases at first ($t \leqslant 2$ min), and then decreases, whereas the distribution coefficient of nickel(II) increases, indicating in the opinion of the authors cited,[41] the possibility of dynamic separation. For a phase contact time shorter than 2 min, the distribution coefficient (α) is greater than 6 for zinc(II), and less than 0.15 for nickel(II); when equilibrium is established, $\alpha_{Zn} = 0.68$, and $\alpha_{Ni} = 3.4$.

The difference in the rates of extraction of cobalt(II) and nickel(II) by dialkyl hydrogen dithiophosphates[42,43] can be used to increase the efficiency of their separation. Studies of the extraction of cobalt(II) and nickel(II) by solutions of di-(2-ethylhexyl) hydrogen dithiophsphate (D2EHHDTP) in n-decane showed that under equilibrium conditions the separation is not effective; the separation factor $\beta_{Ni/Co} < 2$. Since the extraction equilibrium is established in 10–45 h for cobalt(II) and in 0.5–2 h for nickel(II), it is possible to select conditions under which their effective separation is possible.[44,45] The extraction by a 0.3–0.5 kmol m^{-3} solution of D2EHHDTP in n-decane from a 1–2 kmol m^{-3} solution of $Co(NO_3)_2$ at a phase ratio of 1:1 with stirring for 0.5–2 h gave $\beta_{Ni/Co} = 150-200$. In these systems, the rate of extraction of Ni^{II} is much slower in acidic solutions, whereas the rate of extraction of Co^{II} remains high. By using kinetic factors under conditions close to equilibrium for Co^{II} and far from equilibrium for Ni^{II}, that is by using short phase contact times, it is possible to obtain high separation factors. In the extraction of Co^{II} and Ni^{II} from sulphate solutions by a 0.5 kmol m^{-3} solutions of D2EHHDTP in the presence of 1 kmol m^{-3} tri-n-butyl phosphate (TEP) for a definite phase contact time and a definite intensity of stirring, the separation factor reaches 20–100.[46] A method for separating Co^{II} and NI^{II} by extracting with a monoalkyl alkylphosphonate has been described.[47] The rate of transfer of Co^{II} into the organic phase is restricted by controlling the pH.

It is possible in principle to achieve higher separation factors ($\sim 10^4$) in systems containing D2EHHDTP.[48,49] The addition of oxygen-containing electron-donor additives (TBP, TOPO, etc.) to the system makes it possible to obtain a high efficiency of separation of cobalt and nickel at the re-extraction stage. With phase contact times restricted to several minutes it is possible to achieve effective separation with preferential re-extraction of cobalt.[50] After re-extraction for 2 min, cobalt is extracted to the extent of 99%, and nickel to the extent of less than 0.2%, corresponding to a separation factor of about 10^5. With long phase contact times, the separation factor decreases. Nickel can be re-extracted by an aqueous 9 kmol m^{-3} solution of HCl. With traces of cobalt at a high nickel concentration, partial separation at the extraction stage is appropriate.

A study of the re-extraction of cobalt(II) and nickel(II) from the extracts obtained in the system formed by D2EHHP and aqueous sulphuric acid solution using a single-stage centrifugal extractor[51] established the existence of a kinetic effect. Thus in the re-extraction from an organic phase containing 5.86 g dm^{-3} Co^{II} and 1.71 g dm^{-3} Ni^{II} (concentration of extracting agent in the original solution 0.58 kmol m^{-3}) with a 0.4 kmol m^{-3} aqueous H_2SO_4 solution at a

ratio of the volumes of the aqueous and organic phases of 1:1, the separation factor (β) decreases with increase in the phase contact time (t_c). At 294 K, β = 1.61 for t_c = 0.33s, β = 1.35 for t_c = 0.86 s, and β = 1.27 for t_c = 7.03 s.[51] A kinetic effect at the re-extraction stage is also possible for the pair copper–nickel,[52] cobalt, and nickel.[53]

The increase in selectivity for short phase contact times has been discussed[54] for the extraction of scandium(III), yttrium(III), and the lanthanides from a solution, after the extraction of uranium, containing up to 5 g dm^{-3} Fe_2O_3 as Fe^{2+} ions, using a solution of D2EHHP in kerosene. The extraction of iron(II), thorium(IV), and titanium(II) depends on t_c, but the extraction of scandium(III) and the lanthanides is almost independent of t_c in the range 2–30 s. For t_c = 2 s, non-intensive stirring (185 r.p.m.) in a turbine mixer gives more selective extraction of scandium(III), yttrium(III), and the lanthanides in the presence of iron(II), compared with their extraction in an ordinary mixer–settler for t_c = 30 s.[54]

A difference in the rates of extraction of iron(III) and uranium(VI) by D2EHHP solutions has been noted.[55] The low rate of extraction of Fe^{III} makes it possible to separate it from the lanthanides and yttrium by extraction with D2EHHP solutions in a centrifugal counter-current extractor. For t_c = 10 s and pH 2, yttrium is extracted from the clarified solution to the extent of more than 95% by a 10–12 vol.% solution of D2EHHP in Shell 140 kerosene. For this value of t_c, almost no Fe^{III} is extracted.[56] Increase in t_c leads to a sharp increase in the extraction of Fe^{III}, which suppresses the extraction of the lanthanides.[57] A concentrate of lanthanide oxides containing 30–60% Y can be obtained[58] by extracting with a 0.1 kmol m^{-3} solution of D2EHHP in kerosene at a ratio of the streams of the aqueous and organic phases of 4:1 with stirring for a short time, by varying the pH and the concentration of the extracting agent.

The significant difference in the rates of the extraction of indium and tin(IV) by alkyl hydrogen phosphates [in the extraction of tin(IV), equilibrium is established only after 60–70 min] led to the conclusion[59] that a considerable quantity of tin can be left in the aqueous phase by controlling the phase contact time. 4-t-Butylphenol-2-azo-1′-benzene-carboxylic acid and its mixture with 4-t-butylphenol-2-azo-1′-methoxybenzene are kinetically selective extracting agents for the extraction of copper(II) from iron-containing solutions. In the extraction of Cu^{II}, equilibrium is established in 10 min. The distribution coefficient of iron is higher than that of copper, so that the separation factor decreases with increase in the phase contact time.[60]

In their extraction by solutions of TBP in n-hydrocarbons, the behaviour of zirconium(IV) differs sharply from that of uranium(VI), for which a weak dependence of the rate of extraction on the TBP concentration was established. At low concentrations of TBP and nitrate ions, the separation of these elements under non-equilibrium conditions is much more effective than extraction under equilibrium conditions.[61]

A separation of the lanthanides has been based on the difference in the rates of extraction of these elements from concentrated solutions of salts of nitric and hydrochloric acids in the presence of an excess of acid by TBP containing a small quantity of di-n-butyl hydrogen phosphate.[62] The rate of extraction increases with increase in the atomic mass or atomic number of the element.

A difference in the rates of extraction of uranium(IV), uranium(VI), neptunium(IV), and plutonium(IV) was established[63] in their extraction by a 30% solution of TBP in hydrogenated tetrapropylene using a centrifugal extractor (phase contact time 0.4–2 s). At a high rate of rotation of the cylinder, complete extraction of uranium nitrates is achieved in 2 s. The rate of extraction of uranium(IV) is lower than that of uranium(VI), and only half the rate of extraction of neptunium(IV) and plutonium(IV).

A study[64] of the extraction of thiocyanate complexes of zinc and nickel from aqueous solution using droplet-dispersed n-butanol established that for short extraction times there is appreciable enrichment of the organic phase in zinc. Thus for t_c = 5 min the ratio of the concentrations of zinc(II) and nickel(II) in the organic phase is 6:1, although in the original aqueous solution the ratio of the concentrations was 1:1.

The differences in the rates of the extraction can be increased by adding complex-forming reagents to the system. Sakka and co-workers[65] studied the extraction of cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) from their 2 × 10^{-4} kmol m^{-3} aqueous buffer solutions with an ionic strength of 0.1 kmol m^{-3} (KNO_3) and pH 1–9 by 0.02 kmol m^{-3} solutions of 5-(4-dodecylphenylazo)-8-quinolinol (HL) in chloroform in the presence and absence of complex-forming reagents. In the absence of complex-forming reagents, the extraction of Ni^{II} is slow, and equilibrium is not established even after 10 h. The order of extraction from equilibrium data, Ni→Co→Zn, is reversed when the rates of extraction are compared.

For weak water-soluble complex-forming reagents (polyacrylic acid and citric acid), the extraction curves are displaced slightly to higher pH values. In the stronger reaction when triethylenetetramine (TETA) is added, the value of $pH_{1/2}$ is displaced considerably to higher values, and the slope of the $\lg \alpha = f(pH)$ relationship, where α is the distribution coefficient, differs considerably from 2, which is observed in the absence of complex formation.[65] In extraction by the "rapid mixing–rapid separation" method or in rate-controlled extraction, as can be seen from the published illustrations,[65] when polyacrylic acid ($\overline{m}$ = 2000) is present, zinc(II) is extracted preferentially, the extraction of cobalt is complex, and the extraction of nickel(II) decreases considerably (pH 4–8). When citric acid is added to the system, similar changes are observed, but the position of cobalt in the order of ease of extraction at pH 7–8.5 is rigorously defined. Its extraction under the conditions indicated (concentration of M^{n+} in the original aqueous solution 2 × 10^{-4} kmol m^{-3}, concentration of HL in the original organic phase 2 × 10^{-3} kmol m^{-3}) does not exceed 25%, whereas the extraction of zinc(II) reaches almost 100%, and that of nickel is close to zero.

The addition of a stronger complex-forming reagent (TETA) leads to a decrease in the rate-controlled extraction of zinc and cobalt, and practically no cobalt is extracted. At pH 8, nickel is extracted preferentially, the extraction of zinc is much lower, and practically no cobalt is extracted. Thus the correct combination of complex-forming reagent, concentration of extracting agent, and pH makes possible the effective separation of zinc, cobalt, and nickel on the basis of kinetic factors.[65]

An analysis of data on the kinetics of the extraction of the trans-plutonium elements (TPE) in systems containing D2EHHP in the presence and absence of complex-forming reagents[66] led to the conclusion that in the absence of a complex-forming reagent the TPE are extracted under diffusion conditions, and the rates of their extraction are approximately equal. The addition of a complex-forming reagent increases the contribution of chemical resistance and produces a difference in the rates of extraction. A Lewis diffusion cell was used to study the kinetics of the extraction of the TPE and various lanthanides by D2EHHP solutions from solutions containing a complex-forming reagent. It was shown for the extraction system

10^{-2} kmol m^{-3} EDTA – 1 kmol m^{-3} ($NaNO_3$, HNO_3) – H_2O – CCl_4 – 1 kmol m^{-3} D2EHHP that extensive purification of the macro-component from micro-impurities is possible. Terbium is extracted more readily than europium, so that the separation of macro-quantities of the former from micro-quantities of the latter is difficult in an equilibrium extraction system. The rate of extraction of europium is much higher than that of terbium, and is independent of the terbium concentration, so that dynamic separation may be effective. Under emulsion conditions, only 15% terbium is transferred to the organic phase in the extraction of 90% europium. The authors cited[66] consider that effective purification of terbium from europium is achieved.

To determine the separation conditions, a study was made of the extraction of a number of TPE (Am, Cm, Cf, Bk), and also La, Ce, Sm, Eu, Gd, Th, Pa, U, Pu, Zr, Nb, Cs, Ru, and Fe using a solution fo 4-(α,α-dioctylethyl)pyrocatechol (Q) in toluene from strongly alkaline solutions in the presence of diethylenetriaminepenta-acetic acid (DETAPA).[67] It was shown that the degree of separation of the elements can be increased by varying the phase mixing time, the alkalinity of the medium, and the concentration of the extracting agent. The degree of extraction of Eu^{III} in the system 10^{-4} kmol m^{-3} Eu^{3+}, 2 kmol m^{-3} NaOH, 5×10^{-3} kmol m^{-3} diethylenetriamine-penta-acetic acid – 0.04 kmol m^{-3} Q in toluene increases from 60% to 100% with increase in t_c from 10 min to 45 – 60 min.[68] The separation of europium from americium can be improved by decreasing t_c. Thus in their extraction from 2 kmol m^{-3} NaOH for a contact time of 10 min, the degree of extraction of europium into the organic phase is 98%, and that of americium only 48%. With increase in the europium concentration, the distribution coefficient decreases, but by varying t_c, the concentration of alkali in the original aqueous solution, and the concentration of the extracting agent it is possibe to find the optimum conditions for their separation.

For 2 kmol m^{-3} NaOH, 10^{-4} kmol m^{-3} DETAPA, 10^{-2} kmol m^{-3} extracting agent, and t_c = 10 min, the degree of extraction of europium into the organic phase is 97%, and that of americium only 10%.[68] Americium(III) is subsequently extracted into the organic phase by a 0.04 kmol m^{-3} solution of Q in toluene with a phase contact time of 45 min.

A decrease was observed[69] in the rate of the extraction of fragment lanthanides from radioactive wastes to which complex-forming reagents (tartrate or citrate ions) had previously been added, in the presence of the ions of various metals (Fe^{3+}, Al^{3+}, Cr^{3+}). The magnitude of the retardation effect is different for different lanthanides. In the presence of Fe^{3+} the extraction of europium(III) and neodymium(III) is suppressed to a greater extent than that of cerium(III), whereas the presence of chromium(III) has a greater influence on the extraction of cerium(III) than on that of europium(III). The undesirable influence of interfering ions is partly eliminated by increasing the concentration of the complex-forming reagent.

The rate of the extraction of the TPE from aqueous solutions containing citric acid by D2EHHP solution is much higher than the rates of extraction of aluminium, iron, and zirconium, and it should be possible to increase the efficiency of separation by carrying out the process under non-equilibrium conditions.[10] The experiments were carried out on a stand of gravitational extractors. The phase contact time was lowered to 1 min, which made it possible to suppress the extraction of impurities. The purification factors achieved were ~10 for the removal of iron and aluminium, and greater than 50 for the removal of zirconium. The losses of the TPE do not exceed 1%. The authors cited[10] pointed out that purification from the elements indicated is not achieved when the process is carried out under equilibrium conditions.

The separation of yttrium and the lanthanides in the D2EHHP – DETAPA system is based on the difference in the rates of extraction; the rate for yttrium is higher than that for the lanthanides.[70]

The degree of extraction of zirconium and niobium from mineral acid solutions containing oxalic acid by solutions of di-n-octyl-methylenediphosphoric acid in petroleum spirit depends on the concentration of the reagents, the acid, and the time of shaking. In their extraction from 0.5 kmol m^{-3} H_2SO_4 solution containing 0.1 kmol m^{-3} $H_2C_2O_4$ and less than 10^{-4} kmol m^{-3} zirconium and niobium, for a concentration of the extracting agent of 2×10^{-3} kmol m^{-3} and a time of shaking of 10 min, the degree of extraction into the organic phase is 95% for zirconium, and 4.9% for niobium.[71]

The separation of zinc and cadmium using dithizone and Complexone III is based on the difference in the rates of their extraction. Thus at pH 8, a ratio of the volumes of the aqueous and chloroform phases of 9:1, and a Complexone concentration of 0.01 kmol m^{-3}, cadmium is practically completely transferred to the aqueous phase in 35 s, whereas significant transfer of zinc is observed only after 90 s.[72] The influence of water-soluble complex-forming reagents on the rate of the extraction of zinc and nickel by a solution of dithizone in chloroform has been studied.[73]

2. Cases where the extraction equilibrium is established slowly

The study of the kinetics of extraction has revealed a whole series of extraction systems, characterised by a sufficiently low rate of attainment of extraction equilibrium, which can be used to develop dynamic separation processes or which must be taken into account in the construction of apparatus for the process.

In the extraction of chromium(III) by a 0.1 kmol m^{-3} solution of 8-quinolinol in isopentyl alcohol at 328 K with a low concentration of sodium acetate (0.3 kmol m^{-3}), equilibrium is not reached even after phase contact for 7 h.[74] The rate is equally slow for the extraction of germanium by 0.01 – 0.1 kmol m^{-3} solutions of 8-quinolinol in chloroform, benzene, nitrobenzene, or isobutyl alcohol from nitrate media with an ionic strength of 0.1 ($LiNO_3$, $NaNO_3$).[75] Nickel is extracted slightly more rapidly.[76] Slow attainment of equilibrium is observed in systems containing dithizone in the extraction of zinc, cobalt, copper,[1,18,19] and bismuth (the equilibrium state at pH 1.0 and a concentration of dithizone in chloroform of 10^{-4} kmol m^{-3} is established in 3 h).[2] The rate of extraction of selenium(IV) by a solution of dithizone in CCl_4 is low. In the extraction from 5 kmol m^{-3} HCl solution by 5×10^{-5} kmol m^{-3} dithizone solution, 98 – 99% selenium is extracted after stirring for 1 – 3 h.[77]

A study of the extraction of indium by 1-(2-pyridylazo)-2-naphthol (PAN) revealed a characteristic feature of the dependence of the degree of extraction on the phase contact time.[78] The form of the kinetic curves depended on the method used to introduce the reagent into the system. When a chloroform solution of PAN was used, the kinetic curves had the usual form, but several hours were required for maximum extraction. When an ethanol solution of the reagent was added to the aqueous phase followed by extraction of the resulting compound with chloroform, indium was extracted almost instantaneously, but with increase in the time of shaking the degree of extraction reached the same values as observed for chloroform solutions of PAN. True equilibrium is established very

slowly. The extraction of indium with the addition of the reagent to the aqueous phase and shaking for 1–3 min[79,80] is carried out under non-equilibrium conditions, although it gives the maximum possible extraction.

Similar relationships were obtained for the extraction of gallium, zinc, iron(III), and manganese(II), but in the extraction of nickel, curves with a maximum were not observed.[78] The extraction of copper by indium and zinc dithizonates, and the extraction of iron(III) by indium, copper, and gallium cupferronates, take place slowly.[76,81] Under conditions in which all the reagent is present in the organic phase as a complex with the macro-element, the rate of extraction of a micro-element is independent of the acidity of the aqueous phase. The rate of exchange extraction decreases with decrease in the concentration of the reagent and with increase in the concentration of the macro-component.[81]

The extraction of iron(III) by a 0.2 kmol m^{-3} solution of thenoyltrifluoroacetone (TTA) in benzene is slow, and equilibrium is established in 12 h.[82] The rate of extraction depends on the composition of the aqueous phase and the acidity.

In the extraction of samarium from nitric acid solutions by a solution of TTA in kerosene with the addition of TBP, carried out in an Erlenmeyer flask with subsequent separation of the phases by centrifuging, the time taken to establish the equilibrium state in all the cases studied[83] is 60 min.

The rate of equilibration in the extraction of gallium, iron(III), zinc, nickel, and manganese depends on the method used to introduce PAN.[78] When a solution of PAN in chloroform is used, equilibrium is established very slowly (in several hours). When PAN is added to the aqueous phase (solution in ethanol) with subsequent extraction of the complexes by the pure solvent, the complexes are transferred instantaneously to the extract, but with increase in the time of shaking the degree of extraction decreases until equilibrium is established. In the extraction of the complexes of zinc, nickel, and manganese(II) by butanol, isopentyl alcohol, and nitromethane, equilibrium is established very rapidly. According to Kuznik's data,[84] in the extraction of dysprosium(III) and ytterbium(III) by PAN, equilibrium is established in 20 min.

A study[85] of the extraction of gallium by bidentate chelating reagents from a solution modelling the liquor of the Bayer process, containing 0.75 g dm^{-3} Ga_2O_3, showed that gallium can be extracted with a distribution coefficient of ~1 for a phase contact time of 2 h only by 7-nonyl-8-quinolinol.

There are only a few cases of the slow extraction of metal ions by organic acids. Thus in the extraction of iron(II) from 10^{-3} kmol m^{-3} HCl solution by a 0.5 kmol m^{-3} solution of D2EHHP in kerosene in a nitrogen atmosphere, equilibrium is established in 100 min;[86] in the extraction of titanium from sulphate solutions by D2EHHP the time taken for equilibration is greater than 14 h;[87] equilibrium is also established slowly in the extraction of niobium from fluoride–sulphate media;[88] and in the extraction of tin by a 0.5 kmol m^{-3} solution of D2EHHP in heptane, equilibration requires more than 20 h.[89] Anomalously slow transfer through an impregnated membrane using D2EHHP as the transferring reagent has been detected.[90]

The distribution of europium in the two-phase system Eu^{III}–0.1 kmol m^{-3} (Na,H)ClO_4/D2EHHP–toluene is slow, and equilibration takes ~4 h.[91] In the extraction of europium from nitric acid solutions by D2EHHP in a diffusion cell with stirring, equilibrium is established in 7 h.[92] In the extraction of yttrium, europium, thulium, lutetium, and americium at an ionic strength of 1 (NaCl, HCl) by a 1 kmol m^{-3} solution of D2EHHP in n-heptane, the time taken for equilibration does not exceed 20 min.[93] The influence of the composition of the aqueous phase on the rate of the extraction of praseodymium(III) by 2-ethylhexyl 2-ethylhexylphosphonate has been noted.[94]

The time taken for equilibration in extraction depends on the method used to bring the phases into contact. Thus in the extraction of uranium from sulphate solutions by D2EHHP the time taken for equilibration is 10 mins in an annular flow reactor, and 1 min in a reactor with mechanical stirring.[95] The kinetic character of the extraction of molybdenum(VI) in the presence of tungstates by D2EHHP solutions has been noted. The extraction of Mo^{VI} from sulphate solutions under emulsion conditions is fairly rapid, and equilibrium is established in 1.5–2 min.[96] The presence of W^{VI} in the acidic solution decreases the rate of extraction of Mo^{VI} by D2EHHP solutions. Equilibration requires phase contact times from 10 min to 6–7 h, depending on the process conditions.[97] The very low rate of equilibration has been attributed[98] to the formation of mixed tungsten–molybdenum polyanions, leading to a sharp decrease in the free concentration of molybdenum(VI).

Cases of slow equilibration in systems with basic extracting agents are known. For example, in the extraction of polymolybdates and the products of their protonation from aqueous solutions with an initial molybdenum concentration of about 0.25 kmol m^{-3} by solutions of trioctylammonium (TOA) chloride in chloroform, the time taken for equilibration increases from 4 h to 24 h with decrease in the pH of the solution from 4 to 1.[99] In the extraction of molybdenum from aqueous solutions containing HNO_3 and $NaNO_3$ by solutions of tri-n-decylamine (TDA) in benzene, the distribution coefficient increases with increase from 5 min to 20 h in the time for which the phases are stirred.[100] The phase contact time influences the distribution coefficient in the extraction of molybdenum(VI) by TBP solutions.[101]

In the extraction of chromium(III) by a 20% solution of Primene JMT in xylene, equilibration requires a phase contact time of 1 h at 80 °C, or 20 d at room temperature.[102] Iron(III) is extracted more rapidly. In the $Fe_2(SO_4)_3$–$(NH_4)_2SO_4$–Primene JMT sulphate–toluene system, equilibrium is established in about 1 h, although some changes take place for 20 h.[103] As a consequence of the higher rate of extraction of iron(III) and the suppression of the extraction of chromium(III), Fe^{III} can be separated from Cr^{III}.[102] A complex dependence of the distribution coefficient (D) on t_c was established for the extraction of Rh^{III} and Pd^{II} by a solution of an alkylthiuronium chloride,[104] of Ir^{IV} by a solution of TBP and diantipyrinylmethane,[105] and of Sb^{III} and Sb^{V} by non-polar solvents.[106] For t_c greater than 1 h, a decrease in D is observed, and the extraction stops after 12 h.[104] Increase in t_c above the value required to establish equilibrium for Sb^{V} leads to an increase in D in the extraction from concentrated H_2SO_4 solution, as a result of the reduction of Sb^{V} to Sb^{III}.[106] The dependence of the extraction of yttrium and strontium by octanoic acid on t_c,[107] and that of the re-extraction of aluminium and iron from aliphatic acids,[108] on the magnitude of t_c have been studied. Hydrolysis and polymerisation of the ions in aqueous solutions have a significant influence on the extraction of Nb, Ta, and Zr. The plot of the degree of extraction against pH shows maxima which disappear with increase in t_c.[109] Systems characterised by a long equilibration time have been noted by a number of authors.[110–118]

III. Physicochemical principles of dynamic separation

In principle, any factor capable of bringing about a difference in the rates of extraction of substances may be responsible for dynamic separation. The factors bringing about dynamic separation can be divided into four groups: differences in mechanisms, differences in conditions, differences in transport and kinetic parameters, and external factors. The following factors lead to dynamic separation.

1. Differences in mechanisms

1.1. Type of reaction
homogeneous/heterogeneous
simple/complex (multistage homogeneous, multistage surface)
1.2. The existence of intermediate steps and stages (in particular surface association, polymerisation, the formation of inter-phase films)
1.3. Colloid-chemical phenomena and processes (micelle formation, solubilisation, etc.)
1.4. The addition of complex-forming reagents, oxidising agents, and surface-active agents to the system

2. Differences in conditions

2.1. Kinetic/diffusion
extraction with a surface reaction
extraction with a bulk reaction
2.2. Intermediate conditions with bulk reaction/diffusion condition
2.3. Intermediate conditions with bulk reaction/kinetic condition

3. Differences in transport and kinetic parameters

3.1. Diffusion mobility
3.2. Rate of chemical reaction
3.3. Adsorption–desorption processes
3.4. The accumulation of intermediate products in the inter-phase region, their aggregation, the formation of a new phase

4. External factors

4.1. The application of external fields
4.2. Change in the process conditions (for example the type of extractor, degree of dispersion, etc.)

The proposed classification of the factors is to some extent arbitrary, but it is sufficiently general. Additional details can be introduced. In particular, in the examination of processes with surface reactions it is possible to note the factors influencing the rate of the surface reaction: adsorption, orientational and steric hindrance, catalysis by the surface, and spatial separation of the charges, leading to the formation of strong electric fields in the region of the phase interface. The ability of charged inter-phase surfaces to accelerate or inhibit extraction has been noted.[5,119] In the examination of differences in mechanisms, when the extraction of one substance can be described by a scheme with a simple reaction, and that of the other by a scheme with a complex reaction, we also have in mind bulk reactions taking place in the aqueous phase and associated with the formation of an extractable form of the substance, for example the displacement of a hydrolytic equilibrium or a monomer–polymer equilibrium, including stable polynuclear compounds. A difference between the relaxation times of these reactions in the extraction of each substance may bring about dynamic separation, but in the proposed classification of factors it will be included in section 3.2. Section 1.4. includes so-called inter-phase transfer catalysts,[120] which are also capable of bringing about differences in the rates of extraction.

Theoretical estimates of the attainable separation effects have been carried out.[121–123] These effects may be considerable when there are differences in the mechanisms and conditions of the processes.

In publications giving the results of experimental studies of the kinetics of the simultaneous extraction of two or more components, insufficient attention is often paid to the description of the method and the apparatus. Unfortunately, this makes it difficult to identify the factors responsible for dynamic separation, and prevents an unambiguous solution of the inverse problem of dynamic separation. At the same time there are publications in which either the authors themselves interpret the factors responsible for dynamic separation or the systems dealt with have been sufficiently well studied from both the thermodynamic and the kinetic viewpoints, and in these cases it is possible to identify the factors responsible for the separation.

The difference between the rates of extraction of U^{VI} and Fe^{III} by D2EHHP[124] is due to a difference in the extraction conditions. At an H_2SO_4 concentration less than 1 M, U^{VI} is extracted under diffusion conditions,[125] and Fe^{III} under kinetic conditions.[126,127] In the opinion of Sato and co-workers,[127] the rate-determining stage includes the reaction of the hydroxo-complex $Fe(H_2O)_3(OH)^{2+}$ with D2EHHP dimers, but in the opinion of Karpacheva and Ilozheva,[126] the rate of extraction of Fe^{III} is limited by the reaction

$$Fe^{3+} + X^-_{(aq)} \rightleftarrows FeX^{2+},$$

which apparently takes place in the aqueous phase. The fairly high activation energy, which according to Sato[128] is 37.8 kJ mol^{-1}, confirms that Fe^{III} is extracted under kinetic conditions.

The separation of Zn^{II} and Co^{II} in their extraction by dithizone, based on kinetic factors,[129] is due to a difference in the mechanisms.[130] It is considered that the limiting stage for the reaction of both Zn^{II} and Co^{II} is the replacement of a water molecule in the inner coordination sphere of the ion by the anion of the extracting agent,[130,131] since its formation is accompanied by the rupture of four coordinate bonds with water molecules. It is suggested that for an aqueous solution with pH 4, the extraction of Zn^{II} is accompanied by a surface reaction,[130,132] and that of Co^{II} by a homogeneous reaction.[130] Other authors,[133,134] however, in a study of the kinetics of the extraction of Zn^{II} and Co^{II} by solutions of dithizone in chloroform with rapid mixing of the aqueous and organic phases, concluded that the rate-determining stage is the formation of the metal chelate in the aqueous phase, and not a surface reaction. The conclusions reached by the authors cited[132] from the results of a study of the kinetics of the extraction of Zn^{II} by the single-drop method do not agree with other conclusions.[134] This difference of opinion makes it impossible to reach an unambiguous conclusion about the mechanism of the dynamic separation of Zn^{II} and Co^{II}. If however it is assumed that in the extraction of both Co^{II} and Zn^{II} the rate-determining reaction takes place in the aqueous phase, it may be assumed that the separation is due to a difference in the rates of the removal of water molecules from the hydration layers of the metal ions. Freiser[135] gives Eigen's

data on the rate constants of the above reaction; the rate constant is 5×10^7 s^{-1} for Zn^{II}, and 5×10^5 s^{-1} for Co^{II}.

Fleming,[26] on the basis of a study of the kinetics of the extraction of iron and copper by Kelex 100 and 8-quinolinol,[24,25,27,136] considers that the selectivity is determined by kinetic factors and is due to the fact that the extraction of copper takes place under diffusion conditions, and that of iron(III) under kinetic conditions. It is known that 8-quinolinol forms much more stable (by factors of $\sim 10^{10}$) complexes with Fe^{3+} than with Cu^{2+}, and that alkyl-substituted 8-quinolinol – Kelex 100 extracts copper(II) more effectively than iron(III).[26] Other authors[23,24,28] reach the same conclusion about the nature of the selectivity. This view is confirmed by the decrease in the rate of the extraction of copper when nonylphenol is added to the organic phase. The decrease in the rate of extraction with increase in the concentration of nonylphenol takes place in parallel with an increase in the inter-phase tension, indicating the formation of hydrogen complexes by Kelex 100 and nonylphenol.[28] The rate of extraction of Cu^{II} remains 10^2 times greater than that of Fe^{III}. At the same time, other authors[137] consider that the rate of the extraction of Cu^{II} from sulphate solutions by Kelex 100 is determined by a surface reaction.

In a study of the difference in the rates of the extraction of Ni^{II}, Co^{II}, and Zn^{II} by HL solutions,[65] it was noted that the rates of extraction change in the same sequence as the rate constants for the replacement of water molecules from the hydration layers of the metal ions, and the difference in the rates of extraction was attributed to a difference in the rates of the chemical reactions, and not to a difference in the rates of "physical" distribution. According to other works,[138] the rate-determining stage is the addition of the second 8-quinolinol molecule. Thus the dynamic separation of Ni, Co, and Zn in their extraction by HL is due to the difference in the reaction rate constants.

The selectivity of the extraction of Cu^{II} compared with Fe^{III} by solutions of hydroxyoximes is attributed to kinetic factors.[26,29,139] If it is assumed, following Danesi and co-workers,[140] that the rate-determining stages in both the extraction of copper(II) and the extraction of Fe^{III} are reactions taking place on the phase interface,

$$Cu(H_2O)_{6-n}Cl_n^{(2-n)+} + Ox^- \rightarrow CuOx^+ + (6-n)H_2O + nCl^-,$$

$$Fe(OH)(H_2O)_{5-n}Cl_n^{(2-n)+} + HOx \rightarrow FeOx^{2+} + (6-n)H_2O + nCl^-,$$

$$Fe(H_2O)_{6-n}Cl_n^{(3-n)+} + HOx \rightarrow FeOx^{2+} + (6-n)H_2O + nCl^- + H^+,$$

it may be assumed that the separation is due to a difference in the rates of these reactions; a possible reason for this difference may be that the copper ions, as a consequence of their small radius, bring about the polarisation of the phenolic oxygen in the hydroxyoxime and facilitate the ionisation of a proton, whereas the Fe^{3+} ions, despite their smaller radius, cannot rapidly form a square-planar complex with hydroxyoximes.[141] A different view of the rate-determining stage in the extraction of copper(II) by Lix 34 has been put forward.[142]

The difference in the rates of extraction of the dithizonates has been used to separate Zn^{II}, Co^{II}, and Ni^{II}.[20] It has been established[130] that the separation of Zn^{II} and Co^{II} is due to a difference in the reaction mechanisms; at pH 4, Zn^{II} is extracted by a heterogeneous mechanism, and cobalt by a homogeneous mechanism. Thus more complete separation, based on the higher rate of extraction of zinc, requires more intensive stirring.[130] The localisation of the reaction is due to the increase in the reactivity of the dithizone ions adsorbed on the phase interface, as a result of the influence of adsorption forces.[130] Other authors[132] also consider that in the extraction of Zn^{II} by dithizone the reaction is localised at the inter-phase surface. In Freiser's opinion,[133,134] the rate-determining stage is the formation of 1:1 chelates in the aqueous phase, but in the case of cobalt(II) at concentrations greater than 8×10^{-5} M the process is limited by the chemical reaction at the phase boundary.[143] The rate constants for the formation of the chelates of zinc, cobalt, and nickel are closely related to the rate constants for the removal of water from the hydration layer of the metal ion.[135] Although the position of the reaction zone has not been finally determined, there is no doubt that the separation is due to kinetic factors, since the thermodynamic approach cannot explain the observed separation effects, even if only because the stability constants of the neutral dithizonate complexes of zinc(II) and cobalt(II) are practically identical.[144] Studies of the kinetics of extraction by halogenated dithizones led to the conclusion[145] that the rate-determining stage is the formation of the metal dithizonate (1:1), which takes place mainly on the surface in the extraction of Ni^{II} and in the bulk of the aqueous phase in the extraction of Zn^{II}.

The rates of the extraction of multivalent ions such as Zr^{IV}, Ru^{IV}, Al^{III}, Ga^{III}, Cr^{III}, and the platinum metals (Pt^{II}, Rh^{III}, Ir^{III}) are often low, so that the separation of these ions from others which are rapidly extracted has been verified under laboratory conditions. The slow extraction of the ions is due to hydrolysis and polymerisation in the aqueous phase and the low rate of formation of the extractable form. The low rate of equilibration in the extraction of molybdates by solutions of tri-n-octylamine in chloroform is due to the existence of polymeric ions, detected by osmometry and chemical analysis.[99] Noting that at low concentrations of TBP and HNO_3 the separation of zirconium and uranium is much more effective under non-equilibrium conditions than under equilibrium conditions, Mailen and co-workers[61] examined the chemistry of the extraction of Zr^{IV}. They assume that of the four complexes present, namely Zr^{4+}, $Zr(OH)^{3+}$, $Zr_3(OH)_4^{8+}$, and hydroxo-polymers, the species extracted are Zr^{4+} and $Zr(OH)^{3+}$, which are present in equilibrium with the other two forms. At $[HNO_3] \geqslant 3$ M, Zr^{4+} ions predominate in the solution, and the rate of extraction is proportional to $[TBP]^2$. At $[HNO_3] \leqslant 1$ M, $Zr(OH)^{3+}$ predominates, and the rate of extraction is proportional to $[NO_3^-]^3$. The behaviour of zirconium differs sharply from that of uranium, which is only weakly dependent on the TBP concentration and which is not influenced by $[NO_3^-]$. The presence in solution of chemical forms of ruthenium with different extraction properties is responsible for the two-stage character of its extraction by TBP — a rapid first stage (~ 0.6 s) and a slow second stage (> 1 h).[146]

The complexity of the ionic equilibria of Sn^{IV} in aqueous solution and the slow transformation of the complexes into the extractable form can be used to separate indium and tin(IV) by extraction using alkyl hydrogen phosphates. By controlling the phase contact time, a large quantity of tin(IV) can be left in the aqueous phase.[59]

The existence of the kinetic factor in the separation of Co^{II} and Ni^{II} in their re-extraction[51] can be attributed to the polymerisation of the Ni^{II} complex in the organic phase.[147] It is known,[148] however, that the view that polymers are formed is not consistent with experimental data on the kinetics of the combined extraction of Co^{II} and Ni^{II} by D2EHHP.

The separation of cobalt(II) and nickel(II) in their extraction by D2EHHDTP is due to a difference in the reaction mechanisms. The extraction of Co^{II} is determined by two factors — the rate of the reaction of Co^{II} with D2EHHDTP and the rate of its oxidation in

the organic phase by atmospheric oxygen. The kinetics of the extraction of Ni^{II} are determined only by the rate of its reaction with the DTP.[48] A study of the extraction of Ni^{II} by solutions of D2EHHDTP in decane showed that nickel is extracted as the diamagnetic complex $Ni[(C_8H_{17}O)_2P(S)S]_2$, which has a low-spin square-planar configuration,[44] whereas in the extraction of cobalt an equilibrium is established in the organic phase between the tetrahedral paramagnetic complex $Co[(C_8H_{17}O)_2P(S)S]_2$ and the diamagnetic low-spin complex $Co[(C_8H_{17}O)_2P(S)S]_3$ with a configuration close to octahedral. The stage of Co^{II} oxidation is relatively slow, and the extraction equilibrium is established in 10–45 h, depending on the conditions, whereas for nickel, equilibrium is established in 0.5–2 h.[44] This provides a basis for separating cobalt and nickel by the preferential extraction of nickel(II).

The addition of donor–acceptor reagents (TBP, TOPO) decreases considerably the rate of oxidation of cobalt. When the phase contact time is restricted, it is possible in principle to separate cobalt and nickel by the preferential extraction of cobalt(II).[46,48] The oxidation of cobalt(II), however, gives kinetically inert complexes,[149] making re-extraction difficult. Various donor–acceptor additives decrease the rate of this process.[50] If the phase contact time is restricted to a few minutes, separation is achieved by the preferential re-extraction of cobalt. The system containing TOPO is preferable to that containing TBP. Re-extraction for 2 min makes it possible to achieve separation factors of $\sim 10^5$.[50]

The separation of zinc and nickel in their extraction by dialkyl hydrogen dithiophosphates (DAHDTP), in particular D2EHHDTP, is due to the difference in the rates of dehydration of zinc and nickel ions.[40,41] Since the rate of extraction is influenced by the nature of the group in the DAHDTP,[150] this may facilitate the choice of separation conditions.

Rates of extraction can be differentiated by adding complex-forming reagents to the system.[65,66,151] The influence of complex-forming reagents is two-fold. On the one hand, complex formation leads to changes in the equilibrium parameters; for example, by adding citrate ion and keeping the solution for 24 h it is possible to suppress the extraction of chromium(III) by D2EHHP almost completely,[152] and in an acetate solution kept for up to 2 d the distribution coefficient of chromium(III) is lowered by a factor of ~ 200.[153] When very weak complex-forming reagents are used, the extraction curves of transition metals are displaced to high pH values, and the $\lg D = f(\mathrm{pH})$ relationship usually studied is linear with a slope differing little from 2, which is characteristic of extraction systems in the absence of complex formation. For a stronger reaction with the complex-forming reagent, the value of $pH_{1/2}$ is displaced considerably to high pH values, and in the case of the strong interaction which takes place, for example, in the Fe^{III}–citrate ion system, the extraction is completely suppressed.[65] Cases are known, however, where the addition of a complex-forming reagent has a levelling action. Increase in the time for which an aqueous solution containing Ni^{II} is kept leads to a three-fold decrease in the distribution coefficient of nickel. The presence of the citrate ion decreases the difference in the distribution coefficients to 1.5. Further increase in the concentration of citrate ions generally counterbalances the effect of keeping the solution beforehand.

On the other hand, the addition of complex-forming reagents influences the rate of extraction.[154] The addition of lactate ion leads to a decrease in the coefficient of mass transfer in the extraction of europium,[155] and produces a marked change in the rate of extraction of copper by SME-529.[156] The extraction of Eu^{III} and Am^{III} by solutions of (α,α-dioctylethyl)-pyrocatechol (Q) in the presence of diethylenetriaminepenta-acetic acid (DETAPA) takes place more slowly, the higher the stability of their complexes in the aqueous phase. Thus in their extraction from 2 kmol m^{-3} NaOH solution by a solution of 0.04 kmol m^{-3} Q in toluene, Eu^{III}, which forms a less stable complex with DETAPA, is extracted into the organic phase to the extent of 98% after 10 min, whereas the degree of extraction of Am^{III} is only 48%.

The transplutonium elements are extracted by D2EHHP under diffusion conditions, and their rates of extraction are identical. In the presence of a complex-forming reagent, the contribution of chemical resistance should be greater, and the rates of extraction will be different.[66] The addition of a complex-forming reagent leads to a change in the extraction conditions for Eu^{III}. With increase in the concentration of the complex-forming reagent, the extraction conditions change from diffusion to kinetic. The authors cited[66] consider that the rate of extraction is determined by the chemical reaction in the aqueous phase or in the inter-phase layer. The results show that to achieve the maximum difference in the rates of extraction of europium(III) and terbium, it is necessary to use the highest possible concentrations of the Complexone. The nature of the functional group of the Complexone has no significant influence, but when the complexes have high stability constants, the concentration of Complexone required to achieve a given effect is lower.[66] In the presence of a Complexone (EDTA), the rate of extraction of europium is much higher than that of terbium, giving effective dynamic separation; under emulsion conditions, only 15% terbium is transferred to the organic phase in the extraction of 90% Eu^{III}.[66]

The dynamic separation of nickel and zinc can be achieved using polyacrylate and citrate as complex-forming reagents.[65] In the extraction of the metal ions from aqueous solutions, the rate of the process is determined by the rate of the removal of water molecules from the hydrated ions. This mechanism does not change significantly in the presence of weak complex-forming reagents, since most of the ions remain hydrated in solution. Greater differences in the rates of the processes may be expected at the re-extraction stage. It appears possible to select catalysts for the decomposition of the complexes.[65] The decrease in the rate of extraction when a complex-forming reagent is added to a system may be due to the appearance of double complexes. For example,[69] in the presence of tartrate ion the addition of chromium(III) for a phase contact time of 3 min lowers the distribution coefficient of Eu^{III} from 1000 to 88 if the concentration of chromium(III) in the solution is 0.001 kmol m^{-3}. A decrease in the rate of the process when a mixture of extracting agents is used has been noted.[157]

IV. Mathematical models

A basis for the mathematical modelling of dynamic separation is provided by the general theory of inter-phase multi-component mass transfer accompanied by inter-phase phenomena. The variety of inter-phase phenomena (adsorption, chemical reaction, inter-phase film formation, spontaneous surface convection, micro-emulsification, association, dissociation, etc.) and the need to take account of the mutual influence of the components being extracted create insuperable mathematical difficulties in this approach, so that a rigorous quantitative calculation of the dynamic separation coefficient is not yet possible.

The simultaneous extraction of several components is complicated by their mutual influence.[158,159] Even in the case of the "physical" distribution of each component, it is necessary in the mathematical modelling of the process to take account of the interaction of the diffusion fluxes in each phase, since it follows from the thermodynamics of irreversible processes that the flux of each component depends on the gradients of the chemical potential of each component of the mixture. The methods described earlier[160–166] can be used. If one of the components is present in the system in micro-quantities and the other in macro-quantities, the analysis developed earlier[167,168] can be used. The development of this approach is being held up, however, by the absence of published data on diffusion cross coefficients in the organic phase and the extremely limited amount of such data for the aqueous phase. Moreover, allowance for the whole variety of inter-phase phenomena accompanying the extraction of inorganic substances[173–215] practically excludes the possibility of obtaining an analytical solution.

In most cases for specific mechanisms of the process the estimation of the expected value of the dynamic separation factor is carried out using mathematical models based on the assumption that the extraction processes of the separate components are independent, that is that the extraction of one component does not influence the extraction of the other. Naturally, it is assumed that the principle of independence applies at all stages of the extraction process, irrespective of the complexity of the macroscopic process. If it is assumed that the diffusion cross coefficients tend to zero with decrease in the concentrations of the components being extracted, better agreement can be expected between calculation and experiment for dilute solutions containing the extractable components in equal concentrations. With increase in the concentration of the components extracted, the errors in the estimates of the dynamic separation factor will increase not only as a result of the neglect of the mutual influence of the extraction processes but also as a result of the neglect of the non-ideal character of the system and the use of concentrations instead of activities. Nevertheless, this approach is useful for estimating possible values of the dynamic separation factor. When the loading of the organic phase is low, the separation factor can be calculated if the mutual influence of the ions is neglected.[216]

The possibility of a determinate description of the transport stages in non-stirred systems means that an exact analytical solution can be obtained for the flux of the component being extracted by the construction of a mathematical model of the dynamic separation process. For simplicity we shall assume that the phases are semi-infinite, that the diffusion coefficients are independent of the coordinate and of time, that the components being distributed are initially present in only one phase, and that rapid reversible reactions take place at the interface, complicating the processes involved in the distribution of each component. The system of equations with initial and boundary conditions is written in the form[121,122]

$$\frac{\partial C_{ij}}{\partial t} - D_{ij}\frac{\partial^2 C_{ij}}{\partial x^2} = 0, \quad j = \begin{cases} 1, \text{ if } x \in (-\infty, 0) \\ 2, \text{ if } x \in (0, \infty) \end{cases} \qquad (1)$$

for $x = 0$

$$D_{i1}\frac{dC_{i1}}{dx} - D_{i2}\frac{dC_{i2}}{dx} = 0,$$

$$\alpha_i = C_{i1}/C_{i2},$$

$$C_{i1}(x,0) = C_{i1}^0, \qquad C_{i2}(x,0) = 0,$$

where C_{ij}, $C_{ij}(x,0)$ are the current and initial concentrations of the ith component in the jth phase, D the diffusion coefficient, t the time, x the coordinate, and α the local distribution coefficient. The equation† for the flux of the ith component[217]

$$j_i = \frac{C_{i1}^0}{R_i}\left(\frac{D_{i1}}{\pi t}\right)^{1/2},$$

where $R_i = 1 + \alpha_i(D_{i1}/D_{i2})^{1/2}$, determines the quantity of the ith substance (M_i) transferred into phase 2 in a time t through a phase interface F if the integration is carried out in the range from 0 to t,

$$M_{i2} = \frac{2C_{i1}^0 F}{R_i}\left(\frac{D_{i1}t}{\pi}\right)^{1/2}.$$

Adopting for the dynamic separation factor the expression:[121]

$$\beta = \frac{M_{12}}{C_{11}^0} \Big/ \frac{M_{22}}{C_{21}^0},$$

gives

$$\beta = \left(\frac{D_{11}}{D_{21}}\right)^{1/2}\frac{R_2}{R_1}.$$

For a pair of elements with similar properties, the ratio R_2/R_1 can hardly differ greatly from 1, so that high values of β cannot be expected.

The separation of the extractable components may be greater if the extraction of one of the substances is accompanied by a reversible reaction of first order with rate constants k_1 for the forward reaction and k_2 for the back reaction, taking place in the donor phase, while the extraction of the other takes place by a "physical" distribution mechanism. The mathematical formulation of the problem is then altered considerably. The equation for the diffusion of the substance A in the donor phase will be replaced by the equation for diffusion with chemical reaction

$$D_{11}C''_{11xx}(x,t) - \dot{C}_{11t}(x,t) - k_1 C_{11}(x,t) + k_2 C_{21}(x,t) = 0,$$

† It should be noted that the equation for the flux of a substance leads to a situation which cannot be realised physically when $j \to \infty$ as $t \to 0$. This is due on the one hand to the restricted character of the application of the equation of Fick's second law to the description of molecular diffusion when there are large concentration gradients, and on the other hand to the use of the boundary condition $\alpha_i = C_{i1}/C_{i2}$, which reflects an unchanged ratio of the pre-boundary concentrations. As a result, the equation is inapplicable at $t = 0$. If the non-stationary diffusion is described using the hyperbolic equation

$$\frac{\partial C}{\partial t} + \tau\frac{\partial^2 C}{\partial t^2} - D\frac{\partial^2 C}{\partial x^2} = 0,$$

where τ is the relaxation time of the diffusion flux, the divergence of the flux as $t \to 0$ is eliminated. The attainable accuracy of the calculation has been discussed briefly.[5] The unique role of the boundary conditions in the analysis of the kinetics of diffusion-controlled processes has been examined in detail in monographs[169,170] and articles.[171,172]

where C''_{1xx} is the second partial derivative with respect to the coordinate, and C_{1t} the partial derivative with respect to time, and an analogous equation taking account of the diffusion of the reaction product in the donor phase is added. The boundary condition should take account of the fact that there is no accumulation of the reaction product in the inter-phase region.

The time dependence of the dynamic separation factor (β_t) is described by expressions determined by the values of the parameter a_0

$$a_0 = \frac{r_1}{\alpha_1} + \left(1 + \frac{r_1}{\alpha_1}\right) K_c,$$

where D_{11}, D_{21} are the diffusion coefficients of the original substance and the reaction product in the donor phase, α_1 the distribution coefficient of the reaction product at the phase interface, and K_c the equilibrium constant of the chemical reaction:

a, for $a_0 < 1$

$$\beta_t = a_{11} / F_1(t),$$
$$F_1(t) = 1 + a_{12} F_{11}(t) - F_{12}(t),$$
$$F_{11}(t) = \left\{ \mathrm{erf}\left[(k_{12} + b_0)t\right]^{1/2} - \mathrm{erf}\left(b_0 t\right)^{1/2} \right\} \exp(b_0 t),$$
$$F_{12}(t) = \left[\sqrt{\pi}\, \mathrm{erfz}(t)\right] / 2a_0 z(t),$$
$$a_{11} = a_2 r_{31} \Big/ \left(1 + \frac{r_2}{\alpha_2}\right), \quad a_{12} = \frac{\sqrt{\pi}}{2} \frac{\left(1 - a_0^2\right)^{1/2}}{a_0},$$
$$a_2 = 1 + \frac{r_1}{\alpha_1} \frac{1 + K_c}{K_c}, \quad b_0 = a_0^2 k_{12} / \left(1 - a_0^2\right),$$
$$k_{12} = k_1 + k_2, \quad K_c = k_1 / k_2, \quad r_1^2 = D_{11} / D_{21},$$
$$r_2^2 = D_{31} / D_{32}, \quad r_{31}^2 = D_{31} / D_{11}, \quad z(t) = \sqrt{k_{12} t},$$

where $\mathrm{erf}\,\xi$ is the probability integral;

b, for $a_0 > 1$

$$\beta_t = a_{11} / F_2(t),$$
$$F_2(t) = 1 + a_{13} F_{21}(t) - F_{12}(t),$$
$$F_{21}(t) = \left[I_1(t) - I_2(t)\right] \exp(-bt) / z(t),$$
$$I_i(t) = \int_0^{\pi_i^2(t)} e^{\lambda^2} d\lambda, \quad \pi_1^2(t) = (b - k_{12})t, \quad \pi_2^2(t) = bt,$$
$$a_{13} = \left(k_{12} / b\right)^{1/2}, \quad b = a_0^2 k_{12} / \left(a_0^2 - 1\right);$$

c, for $a_0 = 1$

$$\beta_t = \frac{K_c r_{31}}{1 + r_2 / \alpha_2} \Big/ \left[1 - F_{12}(t)\right].$$

From the last expression it follows that for short phase contact times, β_t increases with decrease in the time and is given approximately by the expression

$$\beta_t \approx r_{31} F_3(t) \Big/ \left[k_1 \left(1 + \frac{r_2}{\alpha_2}\right) t \right],$$

where

$$F_3(t) = \left[\frac{2}{3} - \frac{1}{5} k_{12} t + \frac{1}{21} (k_{12} t)^2 \right]^{-1}.$$

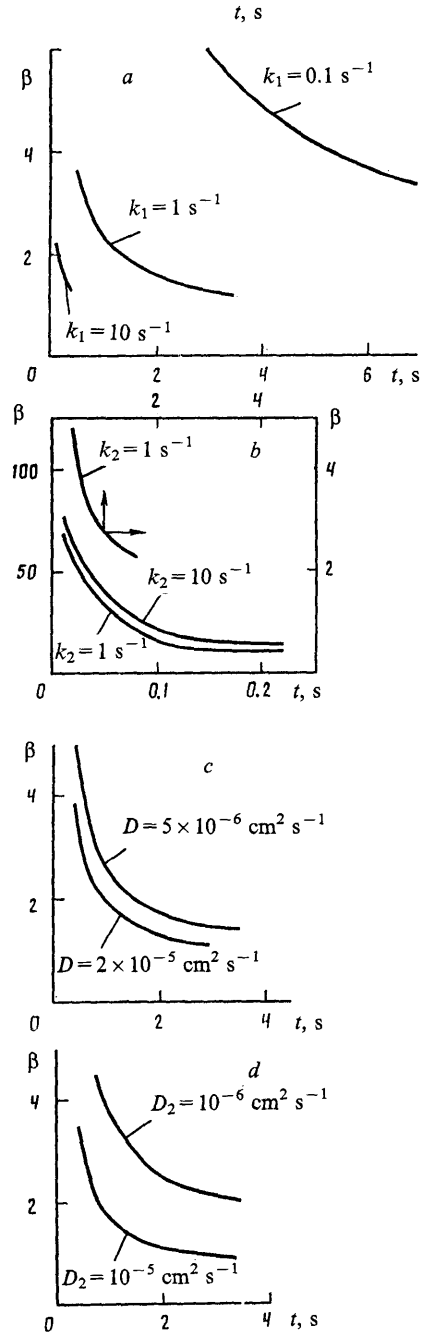


Figure 1. Influence of the rate constants of the forward (*a*) and back (*b*) reactions and the diffusion coefficients of the original substance in the donor phase (*c*) and of the extracted substance in the acceptor phase (*d*) on the time dependence of the dynamic separation factor.

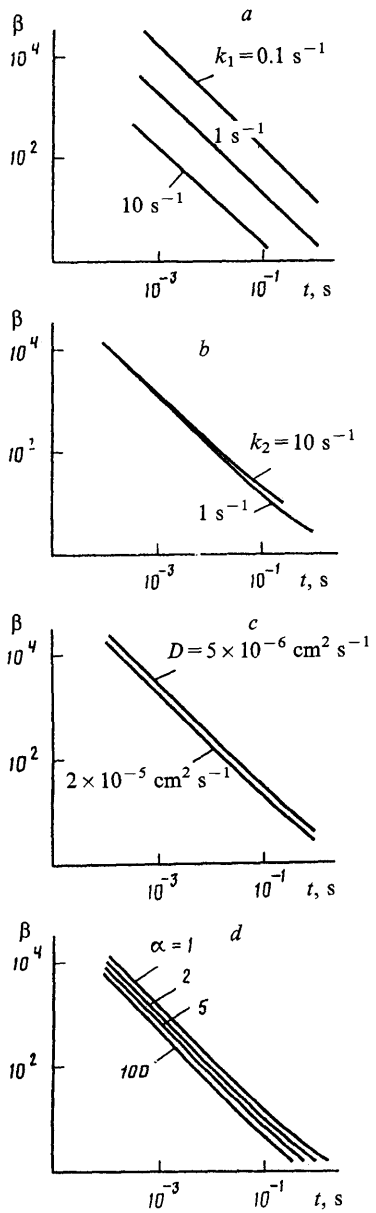


Figure 2. Influence of the rate constants of the forward (*a*) and back (*b*) reactions, the diffusion coefficient of the original substance in the donor phase (*c*), and the distribution coefficient of the reaction product at the phase inter-phase (*d*) on the time dependence of the dynamic separation factor for a short phase contact time; the numbers on the curves give the values of the parameters.

With increase in the time, β_t decreases, and for high values of the time, when $k_{12}t > 25$, the expression for β_t becomes

$$\beta_t = K_c r_{31} \Big/ \left[\left(1 - \frac{\sqrt{\pi}}{2} \frac{1}{z(t)} \right) \left(1 + \frac{r_2}{\alpha_2} \right) \right] .$$

It is obvious that as $k_{12}t \to \infty$, β_t tends to a limiting value equal to $K_c r_{31}/(1 + r_2/\alpha_2)$. Restricting the examination to the simplest case ($a_0 = 1$), we note that the range of possible values of β_t is extremely wide. The influence of various parameters on the time dependence of β_t is shown in Figs. 1 and 2. For a slow homogeneous reaction taking place in the donor phase ($k_1 \leqslant 0.1\ s^{-1}$), appreciable dynamic separation factors can be achieved with relatively long phase contact times (~ 10 s).

If the extraction of one of the substances is accompanied in the acceptor phase by a first or pseudo-first order reaction with rate constants of the forward and back reactions k_1 and k_2 respectively, and the extraction of the other takes place under diffusion conditions, the system of equations describing this process has a similar form and an analytical solution is possible.

The expression for β_t depends on the value of the parameter $\bar{a}_0$

$$\bar{a}_0 = K_c / [1 + \alpha_1 r_1 (+ K_c)] ,$$

where K_c is the chemical equilibrium constant ($K_c = k_1/k_2$):

a, for $\bar{a}_0 < 1$

$$\beta_t = a_1 / F_5(t),$$

$$a_1 = (1 + R_{11}) r_{31} \Big/ \left(1 + \frac{1}{\alpha_2 r_2} \right),$$

$$F_5(t) = 1 + \frac{a_2}{\sqrt{1 - \bar{a}_0^2}} F_{51}(t) - F_{52}(t),$$

$$F_{51}(t) = \exp(-bt) \left[\Phi \sqrt{bt} - \Phi \left(\sqrt{(b - k_{12})t} \right) \right],$$

$$F_{52}(t) = a_3 \operatorname{erf}\left(\sqrt{k_{12} t} \right), \quad a_2 = \bar{a}_0 a_3, \quad a_3 = \frac{\sqrt{\pi}}{2} \frac{\bar{a}_0}{\sqrt{k_{12} t}},$$

$$b = k_{12} / \left(1 - \bar{a}_0^2 \right), \quad k_{12} = k_1 + k_2, \quad r_1^2 = D_{12} / D_{11},$$

$$r_2^2 = D_{32} / D_{31}, \quad r_{31}^2 = D_{31} / D_{11}, \quad R_{11} = \frac{1}{\alpha_1 r_1 (1 + K_c)},$$

$\Phi(\xi)$ is the Kramp function;

b, for $\bar{a}_0 > 1$

$$\beta_t = a_1 / F_6(t),$$

$$F_6(t) = 1 + \frac{a_2}{\sqrt{\bar{a}_0^2 - 1}} F_{61}(t) - F_{52}(t),$$

$$F_{61}(t) = \exp(b_0 t) \left[\operatorname{erf}\left(\sqrt{(k_{12} + b_0)t} \right) - \operatorname{erf}\left(\sqrt{b_0 t} \right) \right];$$

c, for $\bar{a}_0 = 1$

$$\beta_t = a_1 / F_7(t),$$

$$F_7(t) = 1 + \frac{1}{2k_{12}t} \left(1 - e^{-k_{12}t} \right) - F_{52}(t).$$

In particular, it can be seen from the last expression that for low values of t ($k_{12}t \ll 1$)

$$\beta_t \approx a_1 \Big/ \left(\frac{1}{2} + \frac{1}{3} k_{12} t \right).$$

Thus as $t \to 0$, β_t increases and tends to a limiting value $2a_1$. With increase in $k_{12}t$, the value of β_t decreases, and when $k_{12}t \gg 1$ the time dependence of β_t can be approximated by the expression

$$\beta_t \approx a_1 \Big/ \left(1 + \frac{1}{2k_{12}t} - \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{k_{12}t}}\right).$$

From this it can be seen that with further increase in $k_{12}t$ the second term in brackets can be neglected, so that

$$\beta_t \approx a_1 \Big/ \left(1 - \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{k_{12}t}}\right).$$

Finally, as $k_{12}t \to \infty$, β_t reaches its lower limiting value a_1.

It can be shown that in cases a and b also, the lower limiting value of β_t, reached as $k_{12}t \to \infty$ and $bt \to \infty$, will also be a_1. Other values of β_t are also possible, however. For example, if $k_c \gg 1$, then $\alpha_1 r_1 < 1$, and the limiting value for β_t is $r_{31}/(1 + 1/\alpha_2 r_2)$, that is $\beta_{t\to\infty}$ is greater, the greater the difference in the diffusion coefficients of the substances in the donor phase and the lower the distribution coefficient of the second substance. By continuing the analysis of the expressions given for β_t, it is possible to establish other particular cases observed for definite ratios of the parameters α_1, r_1, K_c, and t.

The two models of dynamic separation examined above are united by the fact that one of the stages in the extraction of the substance is a homogeneous chemical reaction. This approach, based on the homogenous formation of the complex extracted, is widely used in the description of the kinetics of extraction processes.[5] At the same time, any workers (as indicated, in particular, by discussions of the location of the reaction in the extraction of zinc by dithizone and its derivatives, of various metals by organophosphorus acids, and of copper by extracting agents of the Kelex type) conclude that the chemical reaction involved in the formation of the complex extracted is heterogeneous‡.

In an examination of models of dynamic separation with surface reactions,[122] six models of this type were analysed in considerable detail. A characteristic feature of the mathematical formulation of problems with a surface reaction is that the reaction rate is included in the boundary condition, and not in the equation describing the diffusion from sources and sinks, as has been the case for homogeneous reactions of formation of the complex extracted.

In the mathematical modelling, the accumulation of a substance at the phase interface, leading to the formation of self-generating inter-phase films, can be taken into account formally by the introduction into the boundary condition of an additional term determined by the difference in the fluxes of the substance to the phase interface and from the interface into the depth of the phase. The quantity of substance containing the element being extracted in the acceptor phase can be calculated from the equation

$$m_2(t)/C_2^0 = A_1\sqrt{t} + A_2\left[\exp(\varphi^2 t)\operatorname{erfc}(\varphi\sqrt{t}) - 1\right] - A_3\exp(-k_2 t)\int_0^t \exp(\alpha\tau)\operatorname{erfc}(\varphi\sqrt{\tau})\,d\tau,$$

where A_1, A_2, A_3, α are constants, $\alpha = \varphi^2 + k_2$; $\varphi = k_1\sqrt{D_1}$; k_1 and k_2 are the rate constants for the accumulation of the substance in the inter-phase region and its consumption respectively.

‡ In publications on the kinetics of extraction it is often described as a surface reaction.

Analysis shows that the accumulation of a substance is extremal in character (Fig. 3*a*), in qualitative agreement with experimental data.[212,214] If in the extraction of two elements, one of them can accumulate in the inter-phase region while the extraction of the other takes place by a "physical" distribution mechanism under diffusion conditions, the separation brought about this this difference may be considerable, particularly for short phase contact times (Fig. 3*b*). As expected, the value of β is influenced mainly by the rate constant k_2.

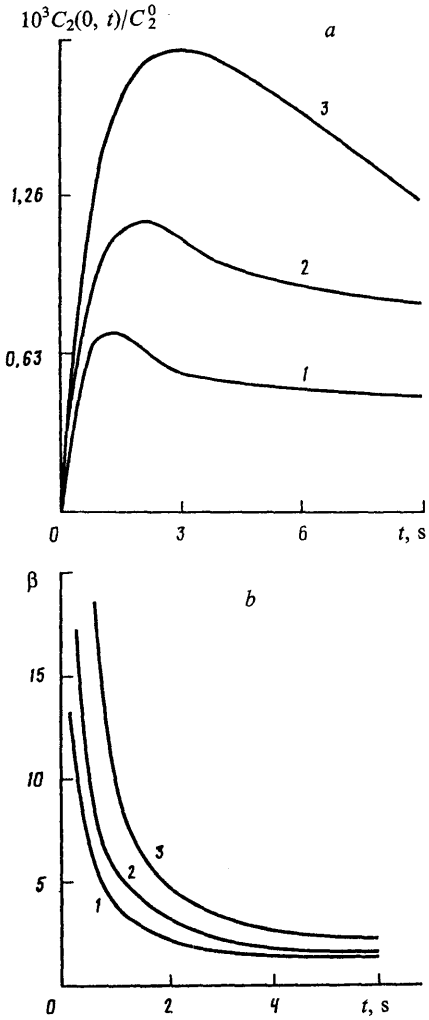


Figure 3. Kinetics of the accumulation of the intermediate product (*a*) and the time dependence of the dynamic separation factor (*b*); calculated for $k_1 = 3.16 \times 10^{-3}$ cm s^{-1}, $D_1 = 10^{-5}$ cm^2 s^{-1}, k_2, s^{-1}: *1*, 2; *2*, 1; *3*, 0.5.

All the above models were based on the distribution of the substance in a system consisting of two semi-finite phases. These models can be used either for comparatively short times, if the phases in contact are finite, or for any values of the time, if the

extent of the phases in the direction of the diffusion flux is considerable.

If the liquid films in contact are sufficiently thin, so that the diffusion front reaches the back boundary in the time of the experiment, it is necessary to include in the mathematical formulation the additional conditions at these boundaries (l_1 and l_2). We can consider, for example, the distribution of two substances (indices 1 and 2) with the assumption that the transfer of the first substance is accompanied by a rapid reversible surface reaction, and that of the second by a fairly slow surface reaction with rate constants k_1 and k_2 for the forward and back reactions respectively. The rate of the surface reaction is taken into account by introducing the additional boundary condition

$$D_{21}C'_{21x}(0,t) - k_1C_{21}(0,t) + k_2C_{22}(0,t) = 0.$$

The conditions for the back boundaries of the phases are written as

$$D_{i1}C'_{i1x}(l_1,t) = 0; \quad -D_{i2}C'_{i2x}(l_2,t) = 0; \quad i = 1;2.$$

It is convenient to express the dynamic separation factor as follows:

$$\bar{\beta}_{12}(t) = \frac{\langle C_{12}(t)\rangle}{\langle C_{11}(t)\rangle} \Big/ \frac{\langle C_{22}(t)\rangle}{\langle C_{21}(t)\rangle},$$

where $< C_{ij}(t) >$ represents the averaged concentrations of the ith component in the jth phase

$$\langle C_{ij}(t)\rangle = \frac{1}{l_j}\int_0^{l_j} C_{ij}(x,t)dx.$$

The expression for the averaged concentrations can be written as the series

$$\langle C_{11}(t)\rangle = \frac{C_{11}^0}{1+K_1l_0} - \sum_{n=1}^{\infty} \frac{C_{11}^0F_4(\mu_n)}{\mu_nF_2(\mu_n)}\exp\left(-\frac{D_{11}}{l_1^2}\mu_n^2t\right),$$

$$\langle C_{12}(t)\rangle = \frac{C_{11}^0}{l_0+K_1^{-1}} + \sum_{n=1}^{\infty}\frac{2C_{11}^0K_1\sin(\mu_n)\sin(\mu_nl_0r)}{\mu_nl_0F_2(\mu_n)}\exp\left[-\frac{D_{12}}{l_2^2}(rl_0\mu_n)^2t\right],$$

$$\langle C_{21}(t)\rangle = \frac{C_{21}^0 + C_{22}^0l_0}{1+K_cl_0} + \sum_{n=1}^{\infty}\frac{a_0\sin(\bar{\mu}_n)\sin(\bar{\mu}_nl_0\bar{r})}{\bar{\mu}_nF_6(\bar{\mu}_n)}\exp\left(-\frac{D_{21}}{l_1^2}\bar{\mu}_n^2t\right),$$

$$\langle C_{22}(t)\rangle = \frac{K_c\left(C_{21}^0 + C_{22}^0l_0\right)}{1+K_cl_0} + \sum_{n=1}^{\infty}\frac{(-a_0)\sin(\bar{\mu}_n)\sin(\bar{\mu}_nl_0\bar{r})}{\bar{\mu}_nl_0F_6(\bar{\mu}_n)}\exp\left[-\frac{D_{22}}{l_2^2}(\bar{\mu}_n\bar{r}l_0)^2t\right],$$

where

$$F_2(\mu_n) = \mu_n\left[(1+K_1l_0)r\cos(\mu_n)\cos(\mu_nl_0r) - \left(K_1+r^2l_0\right)\sin\mu_n\sin(\mu_nl_0r)\right],$$

$$F_4(\mu_n) = 2K_1\sin\mu_n\cdot\sin(\mu_nl_0r),$$

$$F_6(\bar{\mu}_n) = \frac{1}{2}\bar{\mu}_n\left(\frac{3D_{21}}{l_1} + k_1 + k_2\bar{r}^2l_0\right)\sin\bar{\mu}_n\cdot\sin(\bar{\mu}_n\bar{r}l_0) +$$

$$+\left(\frac{1}{2}\frac{D_{21}}{l_1}\bar{\mu}_n^2 - k_1\right)\cos\bar{\mu}_n\cdot\cos(\bar{\mu}_n\bar{r}l_0) +$$

$$+\bar{r}\left(\frac{1}{2}\frac{D_{21}}{l_1}l_0\bar{\mu}_n^2 - k_2\right)\sin\bar{\mu}_n\cdot\cos(\bar{\mu}_nl_0\bar{r}) -$$

$$-\frac{1}{2}\bar{r}\bar{\mu}_n(k_1l_0+k_2)\cos\bar{\mu}_n\cdot\cos(\bar{\mu}_nl_0\bar{r}),$$

$$a_0 = k_1C_{21}^0 - k_2C_{22}^0, \quad l_0 = l_2/l_1,$$

$$r^2 = D_{11}/D_{12}, \quad \bar{r}^2 = D_{21}/D_{22}, \quad K_c = k_1/k_2,$$

μ_n are the roots of the equation

$$(K_1/r)\mathrm{tg}\mu rl_0 + \mathrm{tg}\mu = 0,$$

$\bar{\mu}_n$ are the roots of the transcendental equation

$$\sin\bar{\mu}\left(\bar{\mu}\frac{D_{21}}{k_1l_1}\sin\bar{\mu}l_0\bar{r} - \frac{k_2\bar{r}}{k_1}\cos\bar{\mu}l_0\bar{r}\right) - \cos\bar{\mu}\sin(\bar{\mu}\bar{r}l_0) = 0.$$

In some particular cases it is convenient to represent the solution in a different form (for example, using an additional probability integral). Analysis of the given expressions made it possible to distinguish the principal factors influencing $\bar{\beta}_t$. Fig. 4 gives the calculated relationships $\bar{\beta}_t = f(t)$ for the most probable values of the parameters. A noteworthy feature is the complex character of the relationships (curves *6*, *11*) which are realised for definite ratios between the parameters and which are due to the difference in the relaxation times of the diffusion and chemical processes.

A knowledge of the thermodynamic and kinetic parameters of an extraction process (obtained, for example, using the reference literature[218–223] and reviews[3–5]) makes it possible to estimate the possible value of a dynamic separation coefficient without resorting to experiments on the combined extraction of the components.

A formal-kinetic approach was used by Danesi and Chiarizia[224] in an estimation of the dynamic separation factor of Cu^{II} and Fe^{III} in their extraction by a hydroxyoxime. It was based on the kinetic equations describing the extraction of these substances

$$-\frac{d[\mathrm{Cu}]}{dt} = a_ik^*_{1\mathrm{Cu}}\left[\mathrm{Cu}^{2+}\right] - k^*_{-1\mathrm{Cu}}\left[\overline{\mathrm{CuOx}_2}\right],$$

$$-\frac{d[\mathrm{Fe}]}{dt} = a_ik^*_{1\mathrm{Fe}}\left[\mathrm{Fe}^{3+}\right] - k^*_{-1\mathrm{Fe}}\left[\overline{\mathrm{FeOx}_3}\right].$$

The authors cited took as the kinetic parameter of the separation (S_t) the following ratio

$$S_t = \frac{[\overline{\mathrm{Cu}}]_t}{[\overline{\mathrm{Fe}}]_t} \Big/ \frac{[\mathrm{Cu}]_0}{[\mathrm{Fe}]_0},$$

which after integration of the kinetic equations[224] was brought to the form

$$S_t = \left\{1 - \frac{k^*_{-1Cu} + k^*_{1Cu}\exp\left[-\left(k^*_{1Cu} + k^*_{-1Cu}\right)a_i t\right]}{k^*_{1Cu} + k^*_{-1Cu}}\right\} \times$$

$$\times \left\{1 - \frac{k^*_{-1Fe} + k^*_{1Fe}\exp\left[-\left(k^*_{1Fe} + k^*_{-1Fe}\right)a_i t\right]}{k^*_{1Fe} + k^*_{-1Fe}}\right\}^{-1}. \quad (2)$$

For short phase contact times with allowance for the values of the reaction rate constants, the expression for the parameter S_t is simplified considerably:

$$S_0 = \frac{2.83}{0.194 + 9.23\left[H^+\right]},$$

indicating that the separation is influenced by only one factor, namely the acidity of the aqueous phase. For high values of the time, the parameter S_t degenerates into the thermodynamic separation parameter S_∞

$$S_\infty = \frac{\left[\overline{Cu}\right]_\infty}{\left[\overline{Fe}\right]_\infty} \Big/ \frac{[Cu]_0}{[Fe]_0} = \frac{K_{eq(Cu)}K^{-1}_{eq(Fe)}\left[H^+\right]^3 + K_{eq(Cu)}\left[\overline{HOx}\right]_m}{\left[\overline{HOx}\right]_m\left[H^+\right]^2 + K_{eq(Cu)}\left[\overline{HOx}\right]^3_m}.$$

For very low acidities, $S_\infty \simeq 1$, that is separation of Cu^{II} and Fe^{III} does not take place. On the other hand, at a very high acidity, S_∞ becomes large, since the equilibrium for the extraction of Fe^{III} is displaced to the left to a much greater extent than that for Cu^{II}. According to published data,[224] $k_{eq(Cu)} = 0.55$ and $k_{eq(Fe)} = 5.5 \times 10^{-4}$. The authors cited introduce the concept of critical kinetic acidity (CKA), which is defined as the abscissa of the point of intersection of the $S_\infty = f([H^+])$ curve with the $S_0 = f([H^+])$ curve. At acidities lower than the CKA, $S_0 > S_\infty$, and the separation based on kinetic factors is preferable. At acidities greater than CKA, kinetic factors cannot be used, and at an acidity equal to CKA the separation is independent of time. The kinetic separation parameter S_t has been calculated for different values of a_i and t.[224] For acidities lower than CKA, Eqn. (2) can be used to calculate the time necessary to obtain a specified separation; the following quantities must be determined: the chemical composition of the system ($[\overline{HOx}]_m$) and $[H^+]$ and the specific inter-phase surface, which depends on the geometry of the extractor, the intensity of mixing of the phases, the viscosity, density, inter-phase tension, etc. For example, if $[\overline{HOx}]_m = 0.1$ M, $[H^+] = 3 \times 10^{-3}$ M, and $a_i = 5$ cm^{-1}, then after stirring the phases for 2 min, $S_t > 5$ and copper is separated almost completely from iron. After stirring for 5 min, $S_t \simeq 2.5$, and an appreciable quantity of Fe^{III} is transferred into the extract.

If the distribution coefficient of the component extracted and the value of the specific surface (a) of contact between the phases are assumed to be unchanged during the process, the equation for its rate can be written as

$$\frac{dC}{dt} = ka\left(C^* - C\right),$$

where C ad C^* are the current and equilibrium values of the concentration of the component extracted in the acceptor phase, and k the coefficient of mass transfer. Integration of this equation gives

$$\ln(1 - E) = -kat, \quad (3)$$

where $E = C/C^*$ is the degree of completion of the process.

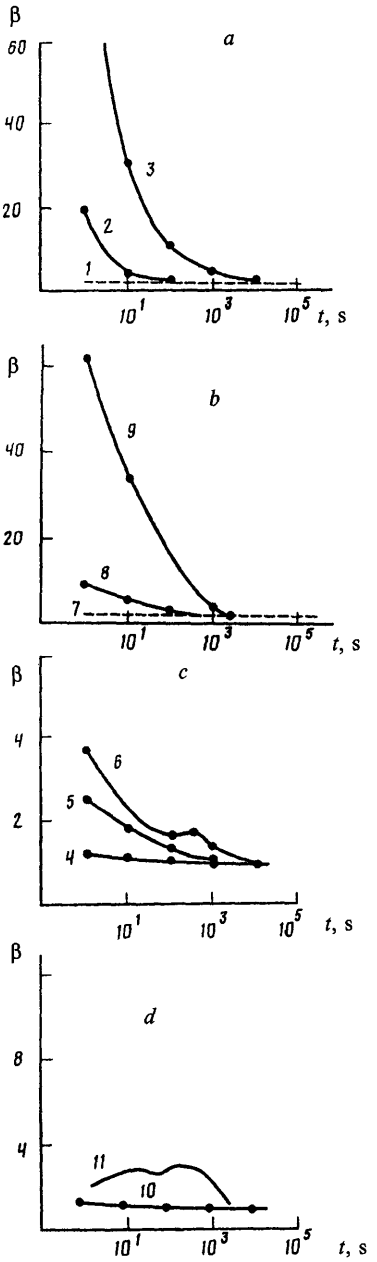


Figure 4. Influence of the equilibrium constant of the surface reaction (a), the rate constants of the forward (b) and back reactions, and the diffusion coefficient (D_{12}) of the substance (d) on the time dependence of the dynamic separation factor; k_1, cm s^{-1}: *1,4–6,7,10,11*, 10^{-3}; *2,8*, 10^{-4}; *3,9*, 10^{-5}; k_2, cm s^{-1}: *7–11*, 10^{-3}; *2,5*, 10^{-4}; *3,6*, 10^{-5}; D_{12}, cm^2 s^{-1}: *1–10*, 10^{-6}; *11*, 10^{-5}.

Relationship (3) is widely used in the treatment of the results of kinetic experiments. If Eqn. (3) is written for each component extracted, it is possible, neglecting the mutual influence of the extraction processes, to obtain expressions for estimating the magnitude of the dynamic separation factor.

If at the initial moment there is a certain amount of substance in the acceptor phase, the equation for the rate of the process becomes[225]

$$1-E=(1-E_0)\exp(-kt),$$

or, expressing E in terms of the extraction coefficient D_e,[226]

$$1-\frac{1+1/D_e^*}{1+1/D_e}=\left(1-\frac{1+1/D_e^*}{1+1/D_0}\right)\exp(-kt).$$

if $E_0 = 0$, the value of D_e attainable at a given stage is determined by the values of D_e^*, t, and k, which the authors cited call the effective rate constant. In general, D_e depends on D_e^0. For a cascade, since the values of D^0 are different for different stages, the values of D will also be variable. From the material balance equation with allowance for the expressions for the extraction coefficients it is possible to obtain relationships between the extraction coefficients in adjacent stages[226]

$$D_{e(i-1)}^{-1}=\frac{1/D_e^*+e^{-kt}}{1+(1/D_e^*)e^{-kt}-(1+1/D_e^*)e^{-kt}A},$$

where

$$A=1-\frac{e^{-kt}(1+1/D_e^*)/(1+1/D_{ei})}{1+(1/D_e^*)e^{-kt}-(1+1/D_e^*)/(1+1/D_{ei})}.$$

The value of D at any of the stages is determined experimentally, after which the values for the other stages of the cascade are calculated.

A mathematical model of the dynamics of counter-current multi-stage extraction in a cascade of mixer–settlers, constructed with allowance for the kinetics of the reactions of the components extracted with the extracting agent, has been published.[227] The introduction of kinetic factors into the model showed that it is possible to increase the selectivity of separation as a result of differences in the kinetics and that there exists an optimum residence time in each stage of the process to give the maximum value of the separation factor. The influence of the constructional parameters of the extraction column on selectivity has been noted.[228]

V. Summary

The present review shows that there exist real possibilities for increasing the efficiency of the extraction separation of substances by making use of kinetic factors. Here it is important to make effective use of differences in the mechanisms of the extraction of the components from a multi-component mixture, or differences in the conditions of the processes, or existing differences in the kinetic or transport parameters of the separate stages of the process. The possibilities for dynamic separation are greatly increased by creating or increasing differences in the parameters of the individual stages under the influence of external factors.

The forms of time dependence of the dynamic separation factor given in the present review show that the efficiency of dynamic separation is greater, the farther the system from the equilibrium state. Thus the realisation of the possibilities of dynamic separation requires a different non-traditional, approach to the construction of equipment for carrying out the process. It is necessary to ensure a short contact time between the phases and effective separation of the phases. The injected flow method which has recently been widely introduced in analytical chemistry would appear to be useful here. It cannot be used to achieve "rapid mixing–separation", however, since only 10–20% of the organic phase is separated from the aqueous phase.[65] The rapid separation of the phases remains a serious problem in the construction of apparatus for carrying out the process. The film systems of Boyadzhiev[229,230] and other methods[231] are of interest in this connection.

The mathematical modelling of the process of dynamic separation is based on a phenomenological and formal-kinetic description, and is greatly simplified. Frequently, no account is taken of the mutual influence of the components in their extraction from a multi-component system; this may be acceptable when modelling the extraction of components from dilute solutions. In the models developed, full account is not taken of the variety of inter-phase phenomena exerting a significant influence on the selectivity of separation. It is important to carry out a detailed analysis of the processes, accompanied by homogeneous and heterogeneous chemical reactions, adsorption–desorption phenomena, the formation of inter-phase films, change in the electrical properties of the phase interface, and spontaneous surface convection. Allowance for inter-phase phenomena or processes complicates the mathematical modelling considerably. The restricted nature of analytical methods can be overcome, however, by using numerical methods, widely employed in the modelling of liquid–liquid extraction processes.

To develop the theoretical ideas it is necessary to establish the relationships between the nature and state of the component extracted and the kinetic parameters of the process, and to select and substantiate criteria for identifying extraction systems for which dynamic separation is preferable to separation based on differences in the thermodynamic parameters of the process.

The solution of these problems associated with dynamic separation will undoubtedly facilitate the practical development of a method which is one of the most promising ways of increasing the selectivity of extraction processes.

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Received 19th April 1991