



Kinetics study of fission products' extraction with attenuated total internal reflection IR spectroscopy

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Abstract

A new method for extraction kinetics studying in a biphasic system using time-lapse recording of IR absorption spectra in the attenuated total internal reflection (ATR IR) geometry is developed. The method is examined by studying the extraction process of europium, yttrium and cesium ions with various extractants both from acidic and carbonate media. The mechanism of step-wise coordination with functional groups of the ligand is proposed. The extraction kinetics constants are calculated for the extraction systems with europium. The main advantages of the new method are miniaturization and rapidity, compared to classical methods.

Keywords Extraction · Kinetics · Europium · Cesium · ATR IR spectroscopy

Introduction

Currently, one of the important tasks of the industry is the separation of metals with similar properties, for example, in hydrometallurgy it is necessary to separate metal pairs to obtain individual rare earth elements such as Zr/Hf, Nb/Ta, Ni/Co. Also, the rapid development of the nuclear industry in the world requires close attention to the problems of spent nuclear fuel (SNF) processing and high-level waste (HLW) fractionation. First of all, it is necessary to increase the efficiency and radiation safety of the nuclear industry. In this regard, there is a need for continuous improvement of technologies for the separation and concentration of rare earth element and actinide radionuclides, as well as a number of high-energy isotopes such as cesium-137 and strontium-90.

One of the most common methods for separating and concentrating radionuclides is solvent extraction. Information on the required phase contact time is of great importance in modern radiochemistry, as it allows to reduce the one-time

loading of active components and, thereby, significantly reduce the radiation impact on the extractant. The ability of rapid studying the extraction kinetics can allow the selection of effective extractants used in centrifugal extractors, where the phase contact time is extremely short [1, 2]. There are currently many methods used to study extraction kinetics, the most common of them are the single drop technique [3–5], the Lewis diffusion cell method [6–10], microfluidic extraction [11, 12], and the AKUFVE apparatus (“apparatus for continuous measurement of distribution factors in solvent extraction”) [13]. The main disadvantages of these methods are the use of large volumes of aqueous and organic phases to be studied, the long duration of the analysis or the complexity of processing the obtained data [11]. In this paper, we propose a new method for studying extraction kinetics using attenuated total reflection infrared spectroscopy (ATR IR). The ATR-IR method is based on the phenomenon of total internal reflection of light, propagating through an optically dense internal reflecting element (crystal). At the interface between the crystal and the sample, an evanescent wave is generated, penetrating the sample to a depth of several nanometers to several microns. This wave interacts with molecules adsorbed on the surface, allowing to study their spectra [14]. ATR IR is a convenient method for studying both solid and liquid samples, when the sample is in direct contact with the ATR crystal attachment. It becomes possible to use small amounts of samples and study various

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samples without any sample preparation. Due to these properties, the IR ATR method allows to study the kinetics of chemical processes of the widest spectrum [15, 16]. The IR ATR method was developed and examined on various extraction systems (phosphine oxides, crown ethers, heterocyclic phenols) proposed for the fission products extraction from nitric acid and carbonate media. We compared the IR ATR experimental results with those, obtained by the classical method—with a Lewis diffusion cell.

Experimental

Materials and techniques

Extractants (Table 1)—triarylphosphine oxide (TAPO), octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO), di-tert-butylbenzo-18-crown-6 ether (DTBDB18C6), N,N,N',N'-tetraoctyldiamide diglycolic acid (TODGA), and 8-hydroxyquinoline (8-HQ) were obtained from Khlopin Radium Institute (Russia), organic

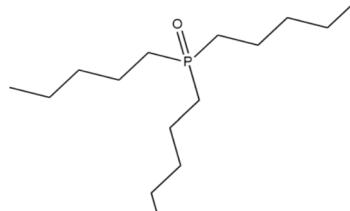
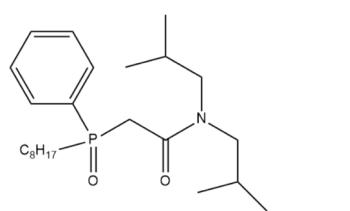
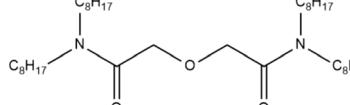
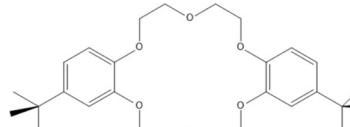
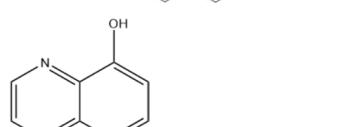
solvents—dichloroethane (DCE) and tetrachloroethylene (TCE) were purchased from Ekos (Russia), europium and cesium nitrates— $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and CsNO_3 were produced by Vekton (Russia), yttrium carbonate $\text{Y}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$ was from Chemcraft (Russia).

The FTIR absorption spectra were measured on a Simex FT-800 spectrometer (Simex, Russia) using a Simex ATR-A attachment (Simex, Russia) with a diamond crystal (operating surface diameter 2.4 mm). The measurements were carried out in the spectral range 500–4000 cm^{-1} with a resolution 2 cm^{-1} . Calorimetric mixing studies were carried out on a Setaram C80 Calvet calorimeter (Setaram, France). A TA Instruments Nano ITC 2G titration microcalorimeter (TA Instruments, USA) was used for calorimetric titration.

Solutions preparation

An aqueous solution of europium with a concentration of 0.6 mol·L⁻¹ was prepared by dissolving 6.69 g of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in a 25 mL volumetric flask. To study the kinetics of extraction from nitric acid media, cesium

Table 1 Extraction systems and recovered cations

Nº	Cation	Extraction system	Structural formula of the extractant
1	Eu^{3+}	triarylphosphine oxide (TAPO) in dichloroethane	
2		octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) in dichloroethane	
3		N,N,N',N'-tetraoctyldiamide diglycolic acid (TODGA) in tetrachloroethylene	
4	Cs^+	di-tert-butylbenzo-18-crown-6 ether (DTBDB18C6) in dichloroethane	
5	Y^{3+}	8-hydroxyquinoline (8-HQ) in dichloroethane	

solutions with a cesium concentration of $0.3 \text{ mol}\cdot\text{L}^{-1}$ and nitric acid concentrations of $1 \text{ mol}\cdot\text{L}^{-1}$ and $2.5 \text{ mol}\cdot\text{L}^{-1}$ were prepared. For this purpose, 1.46 g samples of CsNO_3 were dissolved in 25 mL volumetric flasks, then 1.79 mL and 4.46 mL of $14 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 were added to the resulting solutions, respectively. To study the kinetics of extraction from carbonate-alkaline media, an yttrium solution with yttrium concentration of $0.1 \text{ mol}\cdot\text{L}^{-1}$ and a potassium carbonate concentration of $3 \text{ mol}\cdot\text{L}^{-1}$ was prepared. In this case, 10.37 g of K_2CO_3 were dissolved in a 25 mL volumetric flask and 0.89 g of $\text{Y}_2(\text{CO}_3)_3$ were added to the resulting solution. After complete dissolution of the reagents, the resulting solutions were saturated with an organic solvent (DCE or TCE) by adding 0.5 mL of the organic solvent and stirring on a shaker for 10 min. Then the solutions were centrifuged and the aqueous phases were used for experiments. A $0.6 \text{ mol}\cdot\text{L}^{-1}$ TAPO solution was prepared by dissolving a precise weighed portion of TAPO (3.9 g) in DCE in a 25 mL volumetric flask. The $0.6 \text{ mol}\cdot\text{L}^{-1}$ solutions of CMPO, DTBD18C6, and 8-HQ were also prepared in 25 mL volumetric flasks by dissolving in DCE. A $0.6 \text{ mol}\cdot\text{L}^{-1}$ TODGA solution was prepared by dissolving the precise weighed portion in TCE, because the TODGA solution in DCE has a lower density than the $\text{Eu}(\text{NO}_3)_3$ solution. It is critical for the ATR IR method, since it is necessary for the organic phase to contact the ATR diamond of the attachment. After preparation, all extractant solutions were saturated with water by adding 0.5 mL of distilled water and shaking for 10 min on a shaker. The solutions were then centrifuged and the organic phases were used for the experiments.

Measurement of ATR FTIR spectra

The measurements were performed in the spectral range $500\text{--}3500 \text{ cm}^{-1}$ with a resolution 2 cm^{-1} . When studying the kinetics of europium extraction in different systems, the spectra were recorded every 3 s, and when studying the extraction rate in the system of cesium and DTBDB18C6—every 10 s. This difference in the recording rates was chosen according to the preliminary experiments, showed that in the system of cesium and DTBDB18C6 the equilibrium is attained in at least 90 min.

The kinetic experiments were carried out in a microcell (Fig. 1), a polypropylene tube ($d=4.6$ or 8 mm) with a hole in the upper side part for the liquid samples injection.

Samples were injected with a 50 μL chromatographic syringe or with a 100 μL dispenser. During the experiments, the microcell was positioned so that the cell material did not contact with the ATR crystal and was pressed using the ATR press attachment to reduce liquid evaporation. The extractant solution was injected into the cell and the initial spectrum was recorded. Then the aqueous phase was injected into the cell and the spectra recording turned on (one spectrum every

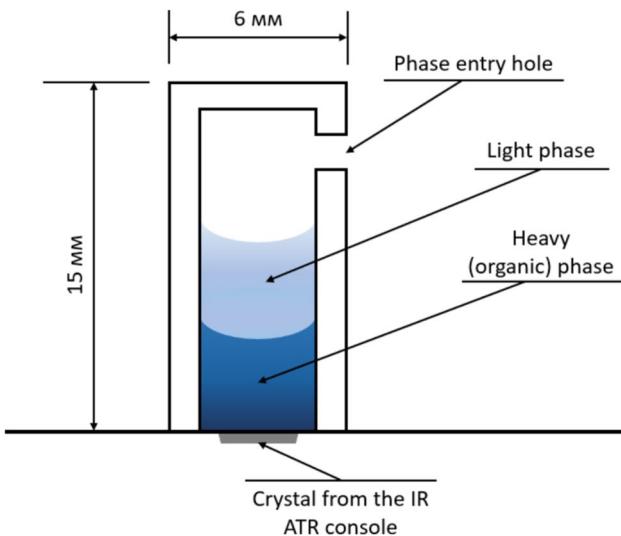


Fig. 1 A microcell for the extraction kinetics studying using the ATR IR method

3 or 10 s). The spectra recording continued until no changes were observed at the characteristic wavelengths over 4–5 scans.

Extraction kinetics studying by the Lewis diffusion cell method

A Lewis cell was made to study the extraction kinetics by the classical method (Fig. 2). For this purpose, a 50 mL graduated faulcon was cut to a volume of 15 μL . The organic phase was stirred with a magnetic stirrer, and the aqueous phase was stirred with an overhead stirrer. The volume of each phase during the Lewis cell extraction study was 10 μL . Sampling was performed from the aqueous phase using a 100 μL dispenser (the volume of each sample was 50 μL). The samples were diluted 2500 times with $0.1 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 solution and then analyzed by inductively coupled plasma atomic emission spectroscopy.

Results and discussion

Extraction kinetics in the system of europium and TAPO

The ATR IR spectra in the extraction system of europium ($0.6 \text{ mol}\cdot\text{L}^{-1}$ $\text{Eu}(\text{NO}_3)_3$) and TAPO ($0.6 \text{ mol}\cdot\text{L}^{-1}$) in dichloroethane were recorded for 150 s (Fig. 3).

As one can see from the overall IR spectra, the greatest changes occur in the region $2400\text{--}2300 \text{ cm}^{-1}$ (peaks of carbon dioxide) and the region $1200\text{--}1080 \text{ cm}^{-1}$ (Fig. 4). This region contains a band of $\nu_{\text{P=O}}$ stretching vibrations

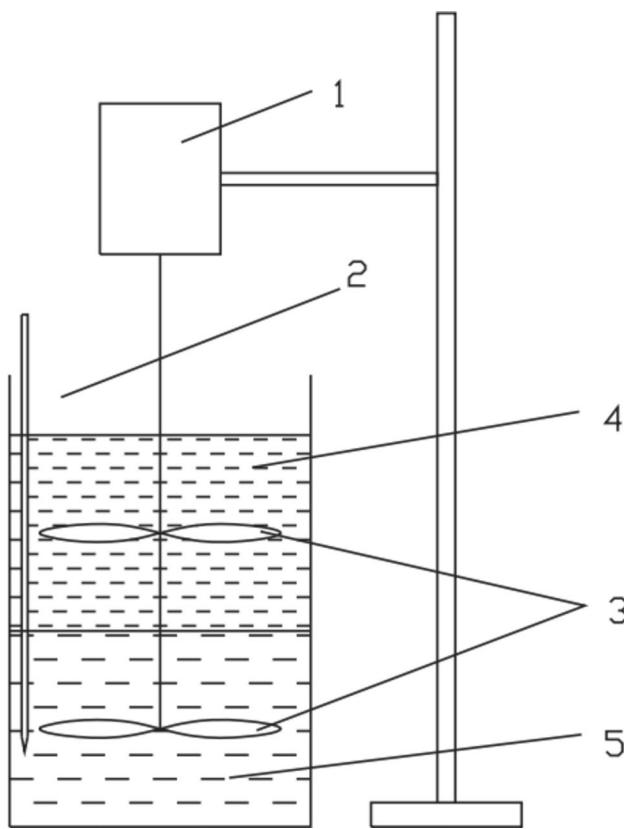


Fig. 2 A Lewis diffusion cell. 1—frequency mixing motor, 2—sampler, 3—agitating vane, 4—aqueous phase, 5—organic phase. [17]

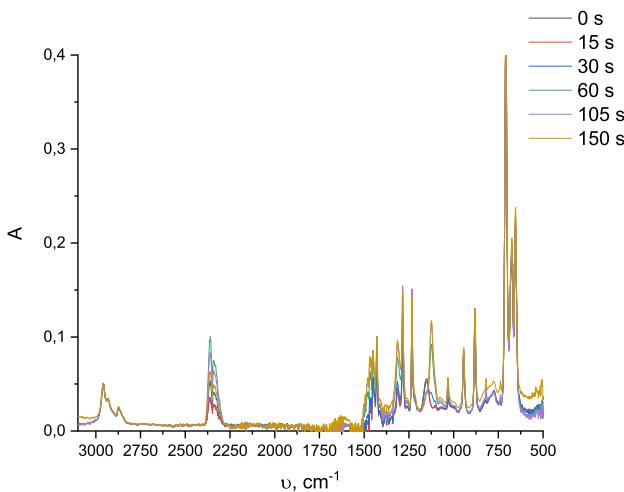


Fig. 3 IR spectra of the organic phase for europium extraction with a TAPO solution in DCE

of intact TAPO molecules at 1152 cm^{-1} , and its intensity decreases with the increasing of phase contact time. Also, with the beginning of extraction, a band of $\nu_{P=O}$ stretching vibrations of TAPO solvates with the Eu^{3+} ion at 1124 cm^{-1} appears in this region.

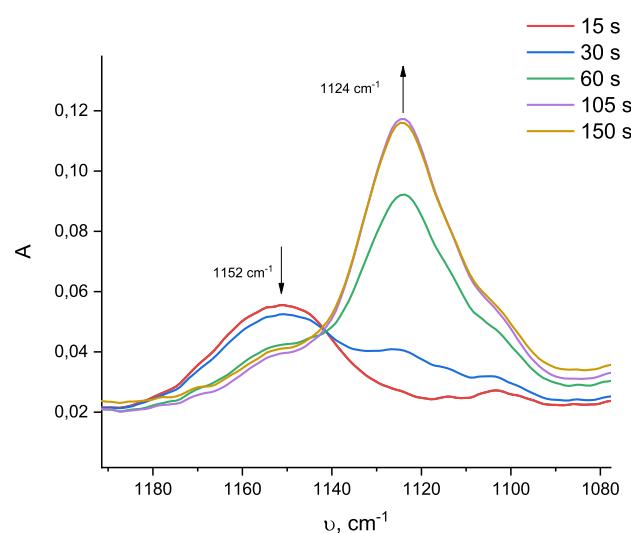


Fig. 4 IR spectra variations for the organic phase in the process of europium extraction with a TAPO solution in DCE

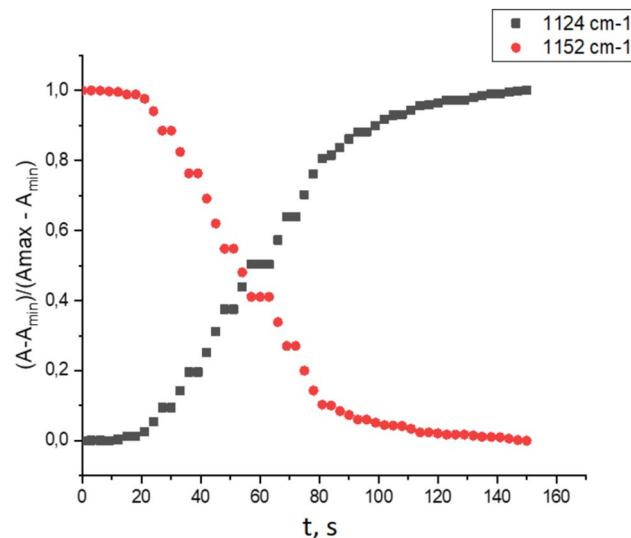


Fig. 5 Kinetic curves for europium extraction with a TAPO solution in DCE

Taking into account the experimental data for the extraction system of europium and TAPO, we constructed kinetic curves in the coordinates $(A - A_{\min}) / (A_{\max} - A_{\min})$ vs t , presented in Fig. 5.

The kinetic straight lines correspond to the curves of successive reactions: up to approximately 65 s, the extraction rate increases, which can be explained by the stage of TAPO accumulation at the phase boundary due to its surface activity or by the diffusion of TAPO solvates with the Eu^{3+} ion from the surface layer to the surface of the ATR crystal. After 65 s from the moment of contact, the

extraction rate can be described similarly to the rate of a first-order reversible reaction (Fig. 6) [18].

For this system, the extraction rate constant was calculated ($k=7.5 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$), which is consistent with the literature data for a similar system of neodymium and triocetylphosphine oxide ($k=4.8 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$) [19].

A hypothesis was proposed that the kinetic curve in Fig. 3 corresponds to two successive reactions $A \rightarrow B \rightarrow C$, where $A \rightarrow B$ is a reaction of formation of TAPO solvates with Eu^{3+} ions, and $B \rightarrow C$ is a diffusion of solvates from the surface layer to the surface of the ATR crystal. In order to study only the extraction kinetics, we minimized possible volumes of the extractant and the extracted substance. An additional experiment was conducted to study the kinetics of Eu^{3+} extraction with a TAPO solution at phase volumes of 10 μL (Fig. 7).

This kinetic curve we also reconstructed in linearizing coordinates and found the extraction kinetics constant (Fig. 8).

The calculated extraction rate constant ($k=3.3 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$) is in better agreement with the literature data for a similar system of neodymium and triocetylphosphine oxide ($k=4.8 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$) [19] than that with phase volumes of 50 μL . This is due to the fact that in a system with a 10 μL phase volume, the diffusion of TAPO- Eu^{3+} solvates in the lay of the organic phase to the surface of the diamond ATR makes a much smaller contribution to the kinetics, and the extraction approaches the kinetic regime. Thus, when studying the kinetics in systems with fast extraction, it is necessary to use small phase volumes. To verify the obtained results, we also investigated the kinetics by the Lewis cell method. A kinetic curve was constructed (Fig. 9)

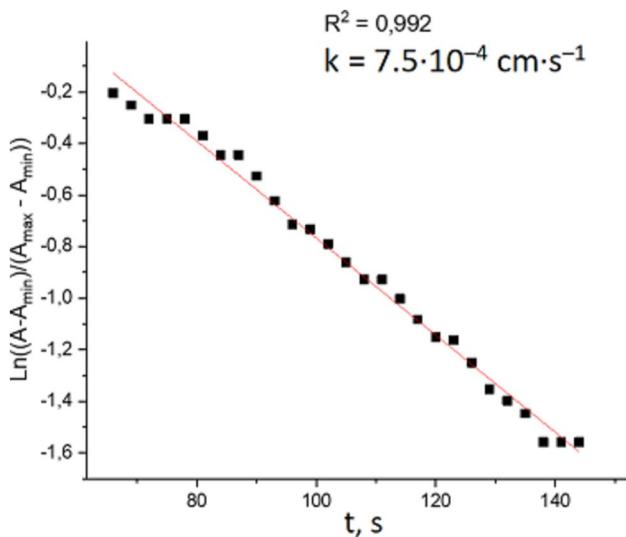


Fig. 6 The rate of europium extraction with a TAPO solution in DCE. Phase volumes are 50 μL

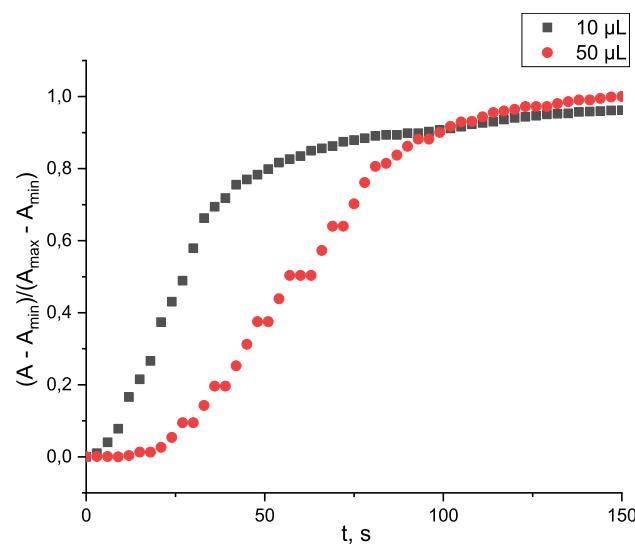


Fig. 7 Kinetic curves for europium extraction with a TAPO solution in DCE. Phase volumes are 10 μL and 50 μL , respectively

and the extraction rate constant was calculated, consistent with our data and with similar extraction rate constant ($k=4.3 \cdot 10^{-4} \text{ cm} \cdot \text{s}^{-1}$) (Fig. 10).

Thus, using the system of europium and TAPO, it was shown that the new ATR IR method for studying the extraction kinetics allows to carry out the experiment faster than in the Lewis cell method (the experiment time is 150 s and 1800s, respectively), while the calculated extraction rate constants are close to each other. It was also shown that the process of solvates diffusion from the surface layer to the surface of the ATR crystal has a great influence on the

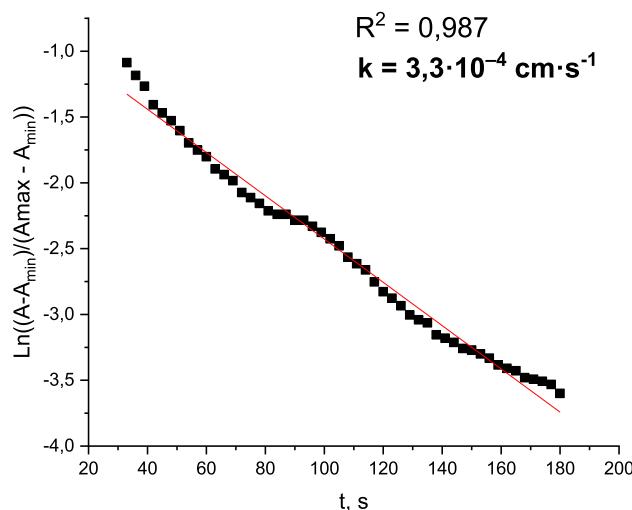


Fig. 8 Europium extraction rate with a TAPO solution in DCE. Phase volumes are 10 μL

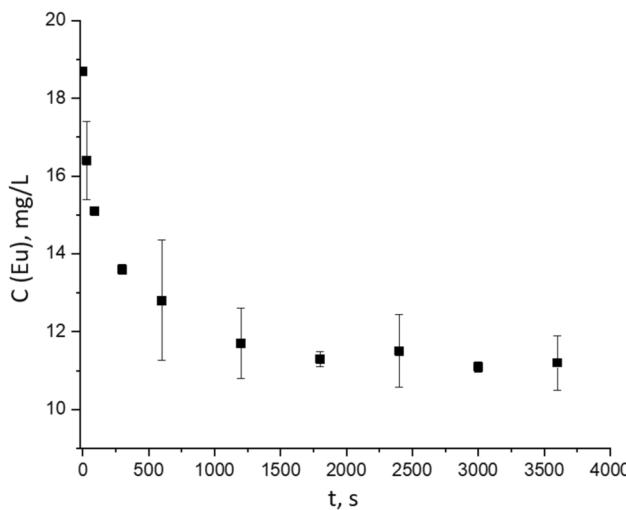


Fig. 9 Kinetic extraction curve for the system of europium and a TAPO solution in DCE, constructed for a Lewis cell

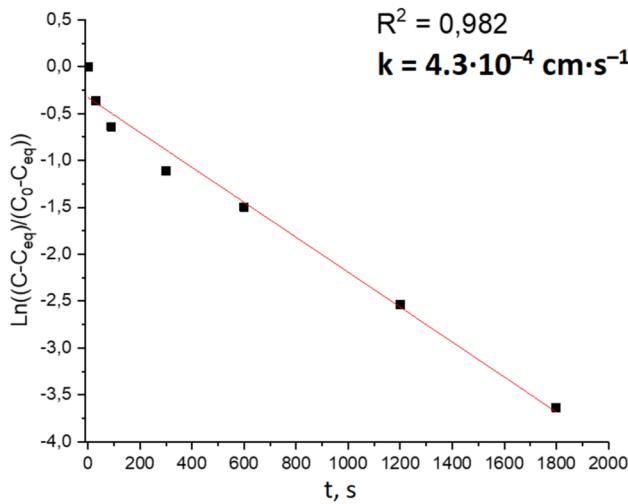


Fig. 10 Europium extraction rate for a TAPO solution in DCE, calculated for a Lewis cell

study of the kinetics, but it can be neutralized by reducing the volumes of the contacting phases.

Extraction kinetics in the system of cesium and DTBDB18C6

The study of the extraction kinetics in the system of cesium and $0.6 \text{ mol} \cdot \text{L}^{-1}$ DTBDB18C6 in DCE was carried out using the ATR IR method. The phase contact time was 4 h. No changes were detected in the spectra before and after extraction, so it was decided to add a salting-out agent, a substance that increases the activity of the extracted compound in the aqueous phase and also

releases the extracted ions from their hydrate shell. The addition of a salting-out agent ($2.5 \text{ mol} \cdot \text{L}^{-1}$ and $1 \text{ mol} \cdot \text{L}^{-1}$ HNO_3) made it possible to obtain satisfactory experimental data. Based on them, the corresponding kinetic curves were constructed (Fig. 11).

In this system the kinetic curves are not distorted by diffusion or chelate interaction. This can be explained by the long extraction process: in the system with DTBDB18C6, equilibrium is established over 90 min, while diffusion occurs much faster. This kinetic dependence also confirms the great influence of the salting-out agent on the extraction process, and is consistent with the literature data [20], showing that the optimal concentration of HNO_3 for Cs^+ extraction with DTBDB18C6 is $2-3 \text{ mol} \cdot \text{L}^{-1}$.

Extraction kinetics in the system of europium and CMPO

The experiments were carried out in a medium cell ($d=4.6 \text{ mm}$) with $50 \mu\text{L}$ of $0.6 \text{ mol} \cdot \text{L}^{-1}$ CMPO solution and $50 \mu\text{L}$ of $0.6 \text{ mol} \cdot \text{L}^{-1}$ $\text{Eu}(\text{NO}_3)_3$. Due to the more complex structure of the extractant, $4 \nu_{\text{P}=\text{O}}$ stretching vibration bands were chosen for determining the kinetics of europium extraction. Thus, the region $1220-1080 \text{ cm}^{-1}$ was regarded (Fig. 12).

This region of the spectrum contains a $\nu_{\text{P}=\text{O}}$ stretching vibration band of free CMPO molecules at 1194 cm^{-1} , with the intensity decreasing with increase of phase contact time, and a $\nu_{\text{P}=\text{O}}$ stretching vibration band at 1150 cm^{-1} , which is responsible for the vibrations of coordinated $\text{P}=\text{O}$ groups in the solvates of the extractant with the Eu^{3+} ion.

The region of $1660-1570 \text{ cm}^{-1}$ (Fig. 13) was also considered. It contains the band of $\nu_{\text{C}=\text{O}}$ stretching vibrations of

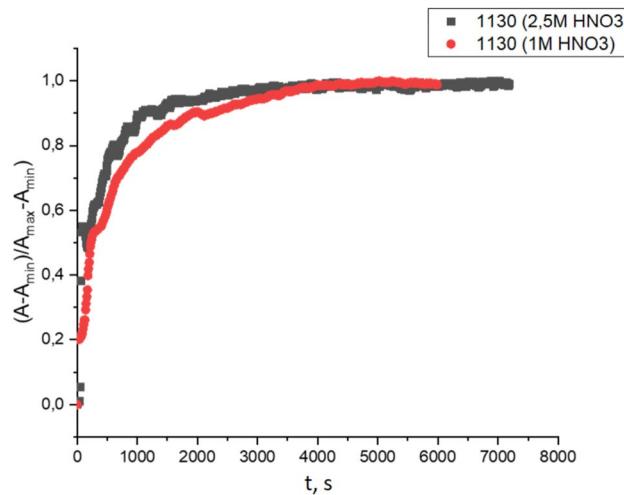


Fig. 11 Kinetic curves for cesium extraction from the aqueous phase ($0.6 \text{ mol} \cdot \text{L}^{-1}$ $\text{CsNO}_3 + 2.5 \text{ mol} \cdot \text{L}^{-1}$ HNO_3 and $0.6 \text{ mol} \cdot \text{L}^{-1}$ $\text{CsNO}_3 + 1 \text{ mol} \cdot \text{L}^{-1}$ HNO_3) with a solution of DTBDB18C6 in DCE

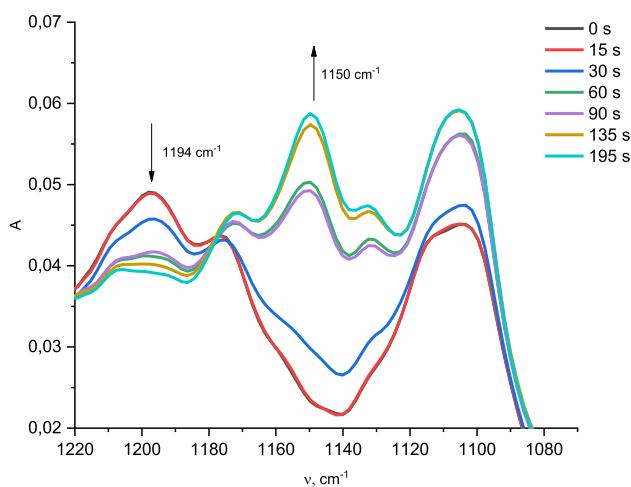


Fig. 12 IR spectra variations for the organic phase in the process of europium extraction with a CMPO solution in DCE

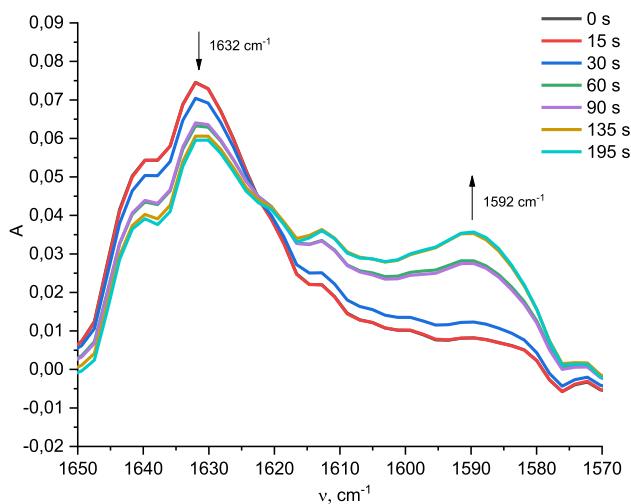


Fig. 13 IR spectra variations for the organic phase in the process of europium extraction with a CMPO solution in DCE

$\text{C}=\text{O}$ groups uncoordinated to the metal ion at 1632 cm^{-1} , with the intensity decreasing as a result of the formation of solvates with Eu^{3+} ions, and the band of $\nu_{\text{C}=\text{O}}$ stretching vibrations at 1592 cm^{-1} , responsible for the vibrations of $\text{C}=\text{O}$ groups of the CMPO molecule coordinated to Eu^{3+} ions.

Based on the experimental data, we constructed the kinetic curves (Fig. 14).

As it is seen from the kinetic curves, the growth of the peak responsible for the association of europium with CMPO molecules via the $\text{P}=\text{O}$ bond is faster at the initial moment of extraction than the growth of the peak responsible for the association of europium with CMPO via the $\text{C}=\text{O}$ bond, and then the system comes to equilibrium. The

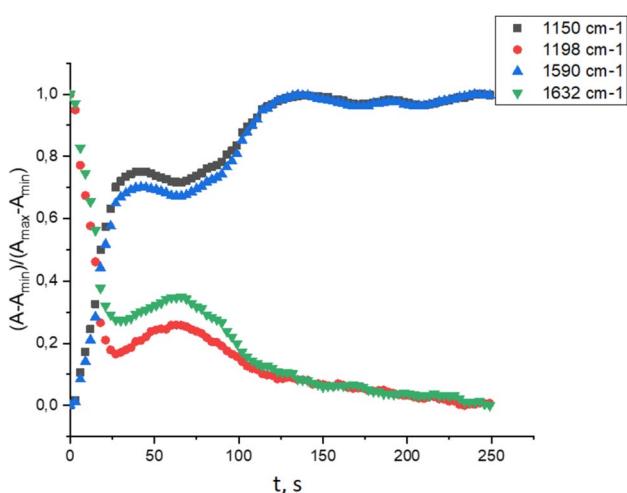


Fig. 14 Kinetic curves for europium extraction with a CMPO solution in DCE

presence of two steps on the kinetic curve can be explained by the sequential addition of Eu^{3+} ions to the $\text{C}=\text{O}$ or $\text{P}=\text{O}$ bonds due to the chelating effect of the extractant (Fig. 15). Also, based on the fact that the peak at 1150 cm^{-1} grows faster than the peak at 1590 cm^{-1} at the initial moment of time, it can be assumed that most of the Eu^{3+} ions are primarily coordinated via the $\text{P}=\text{O}$ bond in CMPO.

This system was also studied by calorimetric methods. 1 mL of $0.1\text{ mol}\cdot\text{L}^{-1}$ CMPO solution in DCE and 2 mL of $0.1\text{ mol}\cdot\text{L}^{-1}$ aqueous $\text{Eu}(\text{NO}_3)_3$ solution were put into the cell of a Setaram C80 Calvet calorimeter, being separated from each other by aluminum foil. After thermal equilibrium in the system was attained, the aluminum foil was pierced with a buoy and stirring was turned on. The resulting graph of thermal effects in the system is presented at Fig. 16.

The left peak is attributed with the sample, the right one with a blank experiment without CMPO. The sharp drop at the beginning of the experiment is caused by the expansion of DCE when the buoy pierced the foil, and the subsequent exothermic effect is due to the complexation of Eu^{3+} with CMPO. It can be noted that the exo-effect of complex formation also has two steps, which confirms the theory of stepwise formation of the chelate complex. The enthalpy of complex formation when subtracting the blank experiment was $-6.1\text{ kJ}\cdot\text{mol}^{-1}$.

This experiment was also carried out on a TA Instruments Nano ITC 2G titration microcalorimeter by a CMPO solution titration with a $\text{Eu}(\text{NO}_3)_3$ solution. Taking into account the blank experiment, the titration curve was obtained (Fig. 17), and it also clearly shows two titration steps.

The enthalpy of complex formation in this system, calculated with the titration curve, was $-24.6\text{ kJ}\cdot\text{mol}^{-1}$, which is in good agreement with literature data [21]. At the same time, the low enthalpy value in the study on a Calvet-type

Fig. 15 Coordination and formation of the Eu^{3+} chelate complex with CMPO

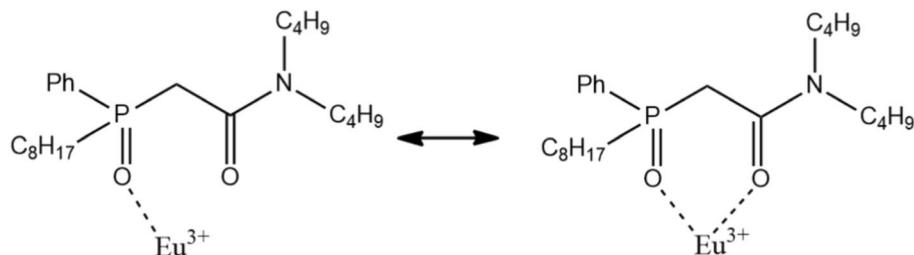
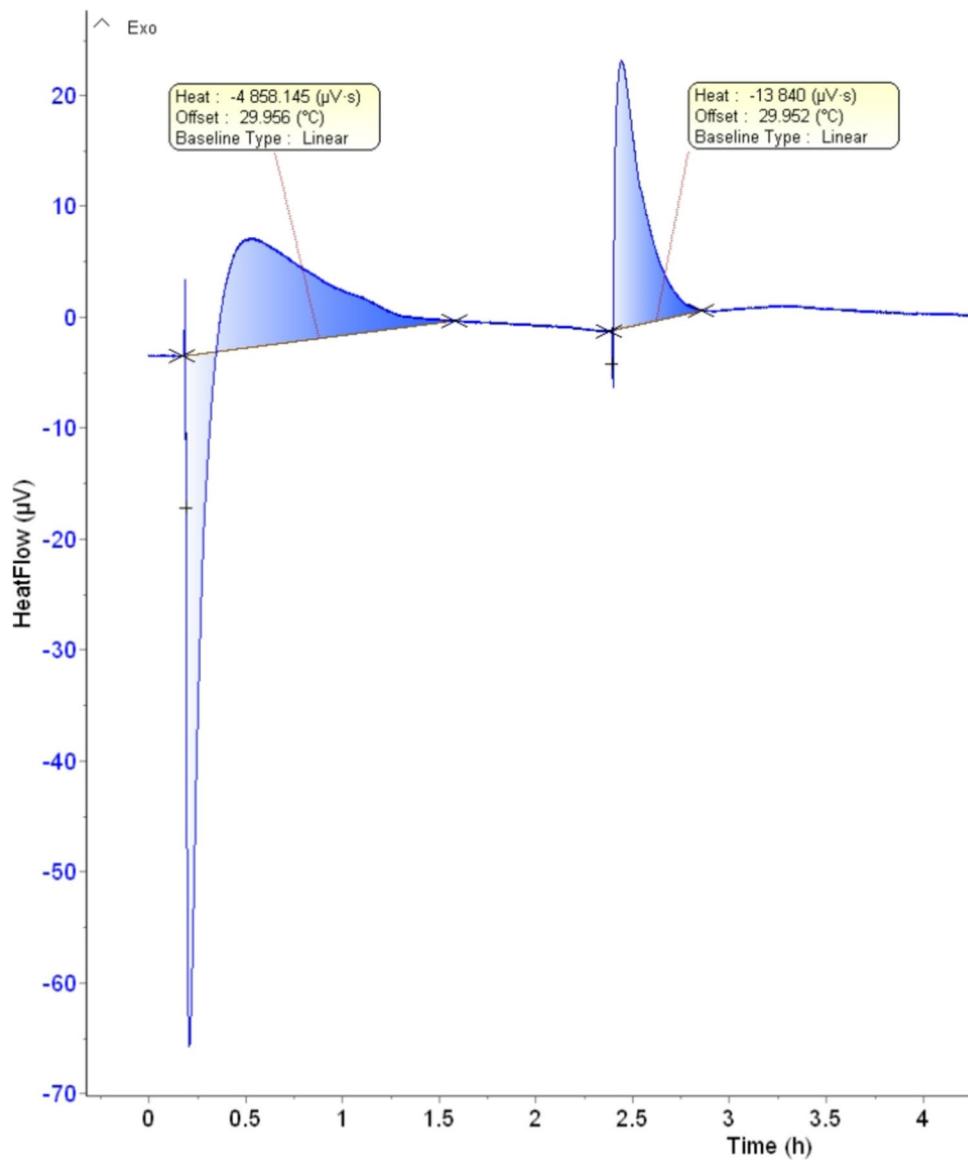


Fig. 16 Thermal effects in the system of europium and CMPO in DCE



calorimeter may be due to the weak mixing in the system, as well as the significant influence of the evaporation and expansion of DCE.

Extraction kinetics in the system of europium with TODGA

The experiments were carried out in a medium cell ($d=4.6$ mm) with 50 μL of a $0.6 \text{ mol}\cdot\text{L}^{-1}$ TODGA solution in TCE and 50 μL of $0.6 \text{ mol}\cdot\text{L}^{-1}$ $\text{Eu}(\text{NO}_3)_3$. The spectrum region

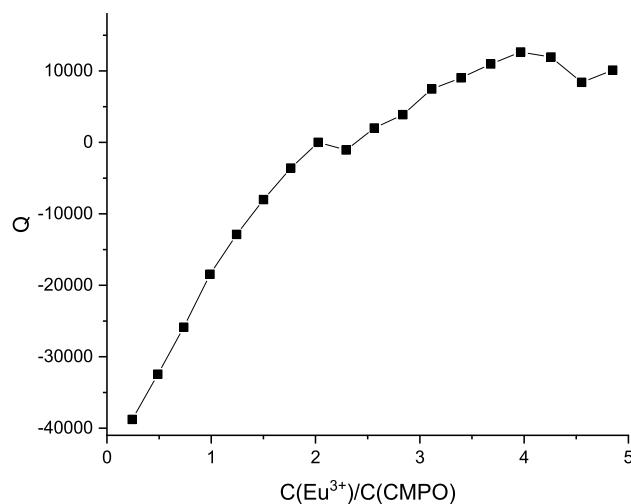


Fig. 17 Calorimetric titration curve for the system of europium and CMPO in DCE

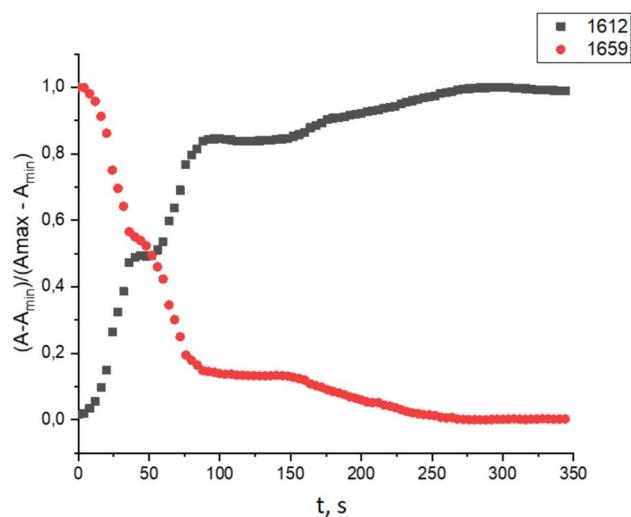
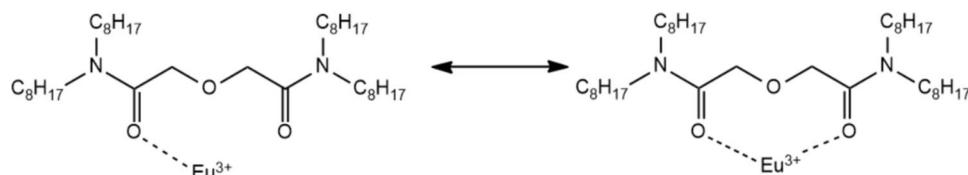


Fig. 18 Kinetic curves for europium extraction with a TODGA solution in TCE

1710–1530 cm^{-1} was analyzed. It contains a band of $\nu_{\text{C=O}}$ stretching vibrations, which is not associated with the Eu^{3+} ion of C=O groups at 1659 cm^{-1} , with the intensity decreasing during the experiment due to the formation of solvates with Eu^{3+} ions, and a band of $\nu_{\text{C=O}}$ stretching vibrations at 1612 cm^{-1} , which is responsible for the vibrations of TODGA

Fig. 19 Coordination and formation of the chelate complex of Eu^{3+} with TODGA



solvates with Eu^{3+} ions. Based on the obtained experimental data, we constructed the kinetic curves in the coordinates $(A - A_{\min}) / (A_{\max} - A_{\min})$ vs t (Fig. 18).

Two maxima on the kinetic curves can be explained by the formation of a chelate complex (Fig. 19) and correlate with the same shape of the kinetic curves in the system with CMPO.

Thus, the above described shows that for the systems with chelate extractants, bearing functional groups of the same nature, two steps are also observed on the kinetic curve, demonstrating a chelate complex formation over the time.

Extraction kinetics for the system of yttrium and 8-HQ

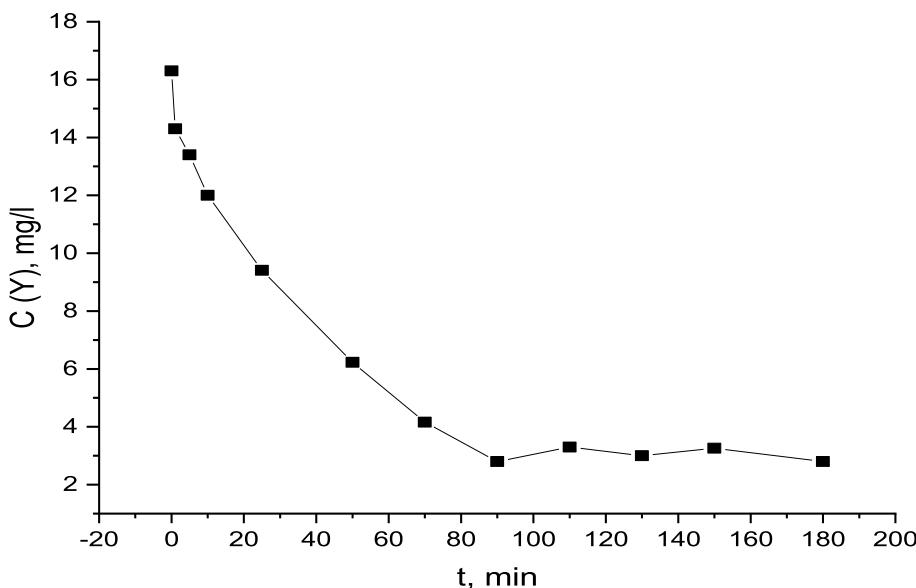
Since the solubility of $\text{Y}_2(\text{CO}_3)_3$ in water is extremely low, to dissolve yttrium carbonate, a 3 mol·L⁻¹ solution of K_2CO_3 was preliminarily prepared, where yttrium carbonate was then dissolved [22, 23]. A 0.01 mol·L⁻¹ aqueous solution of $\text{Y}_2(\text{CO}_3)_3$ and a 0.1 mol·L⁻¹ solution of 8-HQ in DCE were obtained. The spectra of 0.1 mol·L⁻¹ 8-HQ solution in DCE and 8-HQ solution after extraction at 25 °C by stirring 0.5 mL of 0.01 mol·L⁻¹ yttrium solution and 0.5 mL of 0.1 mol·L⁻¹ 8-HQ solution were recorded, the contact time of the phases was 4 h. Since there were no visible changes in the spectra before and after extraction, it was supposed that the yttrium concentration was too low to study the kinetics in this system by the ATR IR method. This limits the new method for studying the extraction kinetics. The kinetics was studied in a Lewis cell, and a kinetic curve was constructed (Fig. 20).

Thus, on this system one can see that the ATR IR method, suggested for the extraction kinetics studying, has some limitations, for example, it can't be applied for the systems with low concentrations of the extractant and the extracted metal.

Conclusions

It is experimentally stated that the new ATR IR based method of studying the extraction kinetics allows reducing the analysis time (2–3 min instead of an hour) and significantly reducing the volume of the required aliquot of the studied solution (0.01 mL instead of tens of mL) compared to the classical methods.

Fig. 20 Kinetic curve for yttrium extraction from $3 \text{ mol}\cdot\text{L}^{-1} \text{K}_2\text{CO}_3$ with $0.1 \text{ mol}\cdot\text{L}^{-1}$ 8-HQ solution, obtained by the Lewis diffusion cell method



With this method some patterns of the extraction process in different extraction systems are studied. It is shown that the rate of the process can be affected both by the diffusion of the metal-extractant solvates in the extractant solution to the surface of the ATR and the mechanism of solvate formation itself. Thus, in the system of europium and CMPO the kinetic curve with two steps is explained by the stepwise formation of a chelate complex. This is confirmed by the calorimetric titration method. It is shown that for the system of europium and TAPO, the values of the extraction kinetics constants ($k_{50} = 7.5 \cdot 10^{-4} \text{ cm}\cdot\text{s}^{-1}$, $k_{10} = 3.3 \cdot 10^{-4} \text{ cm}\cdot\text{s}^{-1}$ for the ATR IR method at different phase volumes and $k = 4.3 \cdot 10^{-4} \text{ cm}\cdot\text{s}^{-1}$ in a Lewis cell) are in good agreement with the extraction kinetics constant for a similar extraction system of neodymium and triocetylphosphine oxide ($k = 4.8 \cdot 10^{-4} \text{ cm}\cdot\text{s}^{-1}$).

For the system of cesium and DTBDB18C6 the possibility of studying the extraction kinetics by the ATR IR method in the presence of a salting-out agent in the system is shown, and the effect of the salting-out agent (HNO_3) concentration on the distribution ratio of cesium and on the kinetics of the extraction process is stated. It is experimentally confirmed that when extracting cesium with DTBDB18C6 from aqueous solutions it is preferable to use a $2\text{--}3 \text{ mol}\cdot\text{L}^{-1}$ nitric acid solution. The study of the extraction kinetics in the system of yttrium and 8-HQ points out some limitations of the proposed method, namely, the potential impossibility of conducting an experiment in the case of extraction of metal cations from solutions of their poorly soluble salts. Also, for the ATR IR method, it is important for the organic phase to be denser than the aqueous one in order to contact with the ATR crystal of the attachment. The above mentioned, thus, imposes a number of restrictions on the solvents used.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

Declarations

Conflict of interest All authors declare that they have no conflicts of interest.

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