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**Modelling of the Am(III) - Cm(III) kinetic separation effect observed
during metal ion extraction by bis-(1,2,4)-triazine ligands**

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Shortened version of a title: Modelling of the Am-Cm kinetic separation

Modelling of the Am(III) - Cm(III) kinetic separation effect observed during metal ion extraction by bis-(1,2,4)-triazine ligands

Abstract

The kinetic separation effect was observed leading to a separation factor for Am(III) over Cm(III) as high as 7.9 by using 2,9-bis-(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhen) ligands in our recent study. In an attempt to explain the observed tendencies, several kinetic models were tested. A model based on mass transfer as the rate-controlling process was found to best describe the kinetic data and allowed to simulate the dependence of Am/Cm separation factor on time. The calculated values of the overall mass-transfer coefficients confirmed that the observed kinetic effect was caused by the different rates of Am(III) and Cm(III) extraction. This kinetic separation phenomenon and its explanation paves the way for potential new approaches to separation of metal ions with very similar properties, such as the adjacent minor actinides Am(III) and Cm(III).

Keywords: liquid-liquid extraction; bis-(1,2,4)-triazine ligands; Am(III); Cm(III); kinetic separation effect; BTPhen ligands

Introduction

The separation of substances with similar properties, such as various isotopes of one element, lanthanide or actinide elements (both within and among the series), or for example Co(II)-Ni(II), Zr(IV)-Hf(IV)), or U(VI) separation from some nuclear impurities, may be accomplished in many ways. Chemical separation processes usually rely upon an equilibrium separation effect realized by means, e.g., of High-Performance Liquid Chromatography or liquid-liquid extraction in mixer-settler cascades or in columns. Many separation processes are described in the literature and are used not only on the laboratory or pilot plant scale but also under operating conditions on a large scale. As an example of the latter, the preparation of nuclear-grade zirconium and uranium may be cited [1]. As for the

U-235/U-238 isotope separation, two chemical processes have been developed and brought up to pilot plant scale, in Japan (the ASAHI-process) based on the application of classical solid anion exchangers [2], and in France (the CHEMEX-process), based on the application of liquid-liquid extraction with tri-*n*-butyl-phosphate [3].

The equilibrium separation effect between two components depends on the values of the corresponding distribution coefficients; the greater the difference in their values, the higher the separation effect, and *vice versa*. Consequently, the most difficult to achieve is the separation of isotopes, especially of the isotopes of heavy elements such as uranium, where the separation factors range from 1.001 to 1.003 for the best performing aqueous systems. However, processes based on these systems are still regarded as being able to compete in the enrichment of uranium with the gaseous diffusion process, although the latter has significantly higher separation factors [4].

In the 1980s, the so called “kinetic concentration isotope effect” was discovered [5] at the Czech Technical University in Prague (CTU), and its application to the separation of isotopes or substances with similar properties was patented [6]. According to this discovery, the kinetic (time-dependent) effect occurs in two-phase systems, such as liquid-liquid extraction or ion-exchange systems, comprising at least three exchangeable components; namely two substances with similar properties (e.g. isotopes or chemically similar metal ions) in one phase (usually aqueous) and a counter-ion (counter-component) in the second phase (usually liquid organic or solid polymer). The results of the respective kinetic experiments can be evaluated and depicted as dependencies $\alpha = f(t)$ that go through an extreme (usually through a maximum); the values of α_{extr} then characterize the kinetic concentration isotope effect. In the case of uranium isotope separation studies, maximum values of the separation factor were found to range *ca.* from 1.020 to 1.040 – even for systems that converge to $\alpha=1.001-1.000$ at equilibrium [7,8] . This principle was

experimentally verified in study of the kinetics of uranium isotope separation by uranium extraction into tri-*n*-octyl-amine (TOA) and tri-*n*-butyl-phosphate [7], by uranium sorption onto both cation and anion exchangers [5-8], or in the study of the kinetics of ion exchange in the ternary systems Na^+ - Co^{2+} - Ni^{2+} + strong-acid cation exchanger [9], or Na^+ - Mg^{2+} - UO_2^{2+} + strong-acid cation exchanger [10,11].

These studies revealed that the occurrence and magnitude of the kinetic separation effect depends on many parameters such as the nature of the second (non-aqueous) phase, especially its functional groups and corresponding counter-ions, the concentration of the separated species and time. In the course of the experiments mentioned above, attention was focused mainly on ion-exchange systems, and only two types of liquid-liquid extraction system were considered.

Recently, many new triazinylpyridine *N*-donor ligands have been studied for the liquid-liquid extraction separation of minor actinides from used nuclear fuel solutions [13]. In our recent study of Am(III) – Cm(III) separation by these ligands, the kinetic separation effect was observed leading to separation factors for Am(III) over Cm(III) as high as 7.9 [12]. Therefore, it seemed useful and even necessary to attempt to simulate this kinetic separation effect by means of mathematical-physical modelling. Therefore, the ultimate goal of this contribution to model the kinetics of the separation of Am(III) – Cm(III) in liquid-liquid extraction systems using the *N*-donor 2,9-bis(1,2,4-triazin-3-yl)-1,10-phenanthroline (BTPhen) ligand CyMe_4 -BTPhen, C4-BTPhen and C5-BTPhen families under given reaction conditions. The progressive goals were formulated as follows:

- Initially, to evaluate the time dependent concentrations of Am(III) and Cm(III) with the aim of identifying the rate-controlling extraction process and to find the corresponding kinetic model.

- In the second step, to model the experimental data, evaluated as a time-dependent separation factor, $SF = f(t)$, where $SF \equiv \alpha$; for this task, the corresponding kinetic model has first to be constructed and verified.
- To assess the results from the point of view of separation efficiency of the liquid-liquid extraction systems studied, and to assess and quantify the influence of the basic reaction parameters.

Theory

Kinetic models for two-phase systems

As regards the first step of the experimental data evaluation, the kinetic models summarized in Table 1 are available from the literature, e.g. from [14]: mass transfer (DM), film diffusion (FD), diffusion in inert layer (ID), diffusion in reacted layer (RLD), chemical reaction (CR) and gel diffusion (GD); the rate-controlling processes being evident from their names. All of these models are given by ordinary first order differential equations where the numerical solution is relatively simple.

Here, the DM-model is used for a demonstration of the detailed account of the liquid-liquid extraction kinetics; for example of the system Am(III) – extraction agent, as follows:

$$\text{control process – mass transfer: } (C_{aq})_{Am} \leftrightarrow (C_{org})_{Am} \quad (1)$$

$$\text{rate equation: } r_{Am} = -d(C_{aq})_{Am} / dt = (K_{DM})_{Am} / Rv \cdot ((C_{org})_{Am}^* - (C_{org})_{Am}) \quad (2)$$

$$\text{equilibrium equation: } (C_{org})_{Am}^* = (C_{aq})_{Am} \cdot D_{Am} \quad (3)$$

$$\text{balance equation: } (C_{org})_{Am} = Rv \cdot ((C_{0aq})_{Am} - (C_{aq})_{Am}) + (C_{0org})_{Am} \quad (4)$$

modified rate equation:

$$-d(C_{aq})_{Am} / dt = (K_{DM})_{Am} / Rv \cdot ((C_{aq})_{Am} \cdot D_{Am} - Rv \cdot ((C_{0aq})_{Am} - (C_{aq})_{Am}) + (C_{0org})_{Am}) \quad (5)$$

The meaning of the symbols:

$(c_{aq})_{Am}$ - concentration of Am(III) in the aqueous phase at time t ; $(c_{org})_{Am}$ - concentration of Am(III) in the organic phase at time t (see Eq. (4)); $(c_{org})_{Am}^*$ - equilibrium concentration of Am(III) in the organic phase corresponding to the concentration in the aqueous phase (see Eq. (3)); D_{Am} - distribution coefficient of a given component; R_v - volume ratio of aqueous to organic phase; $(c_{0aq})_{Am}$ and $(c_{0org})_{Am}$ - starting (initial) concentration in the given phase at $t = 0$; $(K_{DM})_{Am}$ - over-all mass transfer coefficient.

It is evident that the rate equation (2) describes the extraction (mass transfer) of Am(III) from the aqueous into organic phase. Its mathematical solubility assumes that Eqs. (3) and (4) have to be inserted into Eq. (2). Then, Eq. (5) is obtained which can be used for the direct evaluation of experimental data (of course, the quantities D_{Am} and R_v , and starting concentrations have to be known). For this evaluation, in the course of which the value of the over-all mass transfer coefficient is sought, a non-linear regression procedure, combined with the solution of differential equation (5) under given boundary conditions (Runge-Kutha method used), is applied.

The quantities $WSOS/DF$ (weighted sum of squares divided by the degrees of freedom) [15] were used as criteria of the goodness-of-fit. $WSOS/DF$ is evaluated by the χ^2 -test, which is based on calculating the quantity χ^2 according to equation:

$$\chi^2 = \sum_{i=1}^N \frac{(SSx)_i}{(s_q)_i^2} \quad (6)$$

where $(SSx)_i$ is the i^{th} -square of deviation of experimental from calculated value, $(s_q)_i$ is the relative standard deviation of the i^{th} experimental point and N ($\equiv n_p$) is number of the experimental points.

The value of χ^2 is then used for the calculation of $WSOS/DF$ criterion as:

$$WSOS / DF = \chi^2 / n_i \quad n_i = n_p - n \quad (7)$$

where n_i is the number of degrees of freedom, n_p is the number of experimental points and n is the number of model parameters sought during the regression procedure.

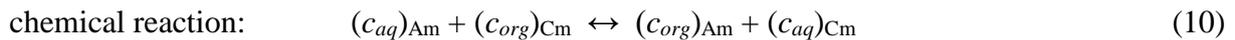
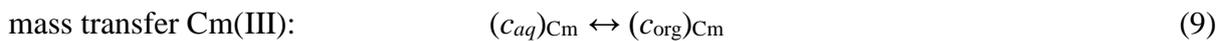
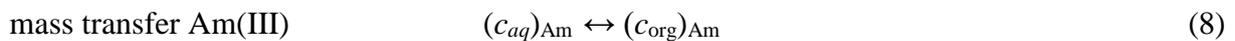
For this specific criterion, it holds that the fit is acceptable if $0.1 < WSOS/DF < 20$.

Kinetic model of the time-dependent separation factor, $SF(t)$

The modelling of the time dependent separation of two components having similar chemical properties in a liquid-liquid extraction system, is based on the findings obtained in the kinetic studies of isotope systems [5-8] as well as non-isotope systems [9-12]. The time-dependent kinetic separation effect then exists in the two-phase system as a result of the antagonistic action of two processes:

- Different transfer rates of the separated substances from one phase (usually from aqueous) into the second phase.
- Heterogeneous isotope or reversible chemical reaction that aims at returning the system to the equilibrium state.

In principle, such a model consists of three differential rate equations. For example, if it deals with the system Am(III) – Cm(III) – liquid extraction organic agent, e.g. [13,14], then there are two mass transfer rate equations of type Eq. (2) – see Eqs (9) and (10). The third one is the rate equation describing the reversible chemical reaction of the 2nd order – see Eqs. (10) and (11):



The corresponding first order rate equations are defined above (Eqs (2) – (5)) for americium; analogous equations may be written for curium.

The rate equation of the 2nd order reaction will then be:

$$r_{Am-Cm} = d(C_{aq})_{Am} / dt = k_3 \cdot ((C_{aq})_{Am} \cdot (C_{org})_{Cm} - (C_{aq})_{Cm} \cdot (C_{org})_{Am} / K_{AC}) \quad (11)$$

Where: k_3 is the rate constant of the forward reaction (taking place from left to right- of chemical reaction (10) mentioned above) and K_{AC} ($= k_3/k_4$) is the corresponding equilibrium constant (k_4 is the rate constant of the reverse reaction). It is assumed that K_{AC} tends to the ratio of distribution coefficients, D_{Am} / D_{Cm} , or to the equilibrium value of the separation factor (see Eq. (14)).

Therefore, the system can be described by differential equations (10) and (12), where equation (12) is the sum of differential equations (9) (see r_{Am}) and (11) (see r_{Am-Cm}):

$$r_{Am\Sigma} = r_{Am} + r_{Am-Cm} \quad (12)$$

The experimental time-dependent values of the separation factor, $SF_{(Am/Cm)}(t)$ – see eq. (13), are evaluated and simulated by means of the non-linear regression procedure combined with the mathematical (numerical) solution of differential equations (10) and (12) by means of the Runge-Kutha method.

$$SF_{(Am/Cm)}(t) = ((c_{org})_{Am} \cdot (c_{aq})_{Cm}) / ((c_{aq})_{Am} \cdot (c_{org})_{Cm}) \quad (13)$$

In equilibrium, it holds: $SF_{(Am/Cm)} = D_{Am} / D_{Cm}$ (14)

Again, the quantities *chi-squared* (χ^2) and *WSOS/DF* [15] can be used as a criterion of the goodness-of-fit.

Experimental

The aqueous solutions were prepared by spiking 0.5 mol/L_{aq} HNO₃ with stock solutions of ²⁴¹Am and ²⁴⁴Cm tracers. Solutions of the 0.005 mol/L_{org} hydrophobic BTPPhen ligands, namely CyMe₄-BTPPhen (**1**), C4-BTPPhen (**2**) and C5-BTPPhen (**3**), were prepared by dissolving the ligands in cyclohexanone. The structures of the ligands are shown in Figure 1. Prior to labelling, the aqueous phases were pre-equilibrated with neat cyclohexanone by shaking them for 4 hours at 400 min⁻¹ and volume ratio of 4:1 ($= R_v$). The cyclohexanone phase was pre-equilibrated with the respective non-labelled aqueous phases by shaking them for 4 hours at 400 min⁻¹ and a volume ratio of 1:1 ($= R_v$). In each case, 1020 μ L_{aq} of labelled

aqueous phases was prepared from which two 10 μL_{aq} standards were taken (to allow for mass balance calculations) prior to contacting the aqueous phases with the organic phases. Initial concentrations of americium and curium in the aqueous phase can be found in Table 2. Each organic phase (1 mL_{org}) was shaken separately with each of the aqueous phases for the desired time at a thermostatted temperature (22 ± 1 °C) using a GFL 3005 Orbital Shaker (250 min^{-1}). Each kinetic run consisted of 10 experimental points at different contact times: 1, 3, 5, 7, 10, 20, 30, 60, 90, and 120 minutes.

After phase-separation by centrifugation, two parallel 10 μL aliquots of each phase were withdrawn for analysis. Aliquots were deposited on stainless steel planchets, evaporated to dryness under an infra-red lamp, and heated in a burner flame until the sample glowed dull red. Activity measurements of ^{241}Am and ^{244}Cm were performed with ORTEC® OCTETE Plus Integrated Alpha-Spectroscopy System equipped with an ion-implanted-silicon ULTRA Alpha Detector Model BU-020-450-AS. The Am and Cm peaks were evaluated by AlphaVision-32 Alpha Analysis Software (ORTEC, Advanced Measurement Technology, Inc., USA). The count rates were converted into molar concentrations (mol/L) of ^{241}Am and ^{244}Cm and the molar concentrations in the aqueous phase were used for the evaluation by means of the kinetic models listed in Table 1.

Results and Discussion

Evaluation of kinetic dependences

The experimental dependences of $D = f(t)$ measured for all the systems under evaluation have been previously discussed in detail [12]. Here, $F = f(t)$ dependences are shown only in comparison with the data predicted by the models (see Figs 1a and 1b). It is evident from the description of the experimental procedure, that extraction kinetics of both nuclides, i.e. Am(III) and Cm(III), were determined simultaneously (in one experiment), which means

that any mutual interaction of nuclides mentioned was not considered. In our opinion, such a supposition is correct and reasonable in view of the very low concentrations of Am(III) and Cm(III) (see Table 2).

As is evident from the lowest values of quantity $WSOS/DF$ in Table 3, the DM model proved to describe our liquid-liquid extraction systems the best. It has to be noted, that the DM model is the classical mass transfer model based on the so-called two-film theory of interphase diffusion [16], according to which “films” exist on both sites of the interphase boundary of a given two phase system. In some cases, FD and CR models can be applied as well; whereas the ID, RLD and GD models, usually used for solid-liquid systems, are practically inapplicable for the description of the kinetics in our liquid-liquid systems.

As mentioned above, the kinetic experimental data were also evaluated with the aim of establishing the values of over-all-mass transfer coefficients, $(K_{DM})_{Am}$ and $(K_{DM})_{Cm}$. In addition, the values of the distribution coefficients, D_{Am} and D_{Cm} , were obtained from the equilibrium states of the kinetic experiments. The values of these parameters are summarized in Table 4.

The graphical evaluations of the CyMe₄-BTPPhen extraction system, namely the experimental and calculated results, are depicted in Figure 2a (extraction kinetics of Am(III)) and Figure 2b (extraction kinetics of Cm(III)). From the comparison of both figures and the respective overall mass transfer coefficient values shown in Table 4, it is clear that the rate of extraction of americium is higher than the rate of extraction of curium. From the ligands studied, the difference between the rates of extraction of Am(III) and Cm(III) is by far the largest in the case of CyMe₄-BTPPhen (compare the values of coefficients and their relations in Table 4). The reason for this fact is not clear at this moment, although differences in the kinetic labilities of the Am(III) and Cm(III) aqua complexes toward ligand substitution, similar to those observed for the lanthanide series [e.g. 17–19], have been suggested as one of the

possible reasons in our earlier paper [12]. Moreover, the side-groups can also have an effect on rates of extraction, for example due to steric effects or their influence on the electron densities at the binding sites.

On the other hand, from the point of view of equilibrium extraction properties, it is the C5-BTPhen ligand that exhibits the best selectivity for Am(III) according to the D_{Am}/D_{Cm} values. For CyMe₄-BTPhen, the $SF_{(Am/Cm)}$ limits to 1.00 in equilibrium.

Evaluation of time dependent separation factor $SF_{(Am(III)/Cm(III))}$

The experimental time dependent values of the separation factor, $SF_{(Am(III)/Cm(III))}$, were evaluated and simulated by means of the model described above. Again, a non-linear regression procedure combined with numerical solution of the corresponding differential equations (by means of the Runge-Kutha method) was applied. Of course, it related to the DM – model (Eqs. (2) and analogous equations for Cm, Eqs. (11) and (12)) and new values of the kinetic parameters, $\{(K_{DM})_{Am}\}_{SF}$ and $\{(K_{DM})_{Cm}\}_{SF}$, were sought in the course of the non-linear regression procedure. The quantity $WSOS/DF$ was used as a criterion of the goodness of fit. The corresponding kinetic parameters, $(K_{DM})_{Am}$ and $(K_{DM})_{Cm}$, from Table 4 were used as initial estimates of the parameters sought. As regards the initial values of k_3 and K_{AC} , they were estimated as $k_3=1E-03$ and $K_{AC}=D_{Am}/D_{Cm}$ (taken from Table 4), respectively, on the basis of trial-and-error.

The resulting new values of the kinetic coefficients and $WSOS/DF$ obtained for the extraction systems with CyMe₄-BTPhen, C4-BTPhen and C5-BTPhen can be found in Table 5, and a graphical evaluation of Eq. (13), i.e. $SF_{(Am/Cm)}(t)$, in Figures 3 a, b and c. If we compare the new values of the kinetic coefficients, $\{(K_{DM})_{Am}\}_{SF}$ and $\{(K_{DM})_{Cm}\}_{SF}$, and K_{AC} ($\equiv D_{Am}/D_{Cm}$) with the previous ones in Table 4, it is evident that these values do not differ. This can be regarded as good confirmation, because it means that input data into the code for

the simulation of time dependent separation factor of extraction systems can be obtained on the basis of the evaluation of individual kinetic experiments.

Equally interesting is the mutual relationship of Figures 3a, b and c where the experimental and calculated dependences of separation factor on time for all three extraction agents studied are demonstrated. Here, CyMe₄-BTPPhen extraction system having the highest value of SF appears to be the most promising candidate for kinetic separation of Am(III) and Cm(III). On the other hand, how best to utilize this kinetic separation effect for Am(III)-Cm(III) separation is not known at this point, and consequently, further studies will need to be carried out in future.

The model of the time dependent separation factor determination consists of concentration, kinetic, equilibrium and balance parameters. The contribution of individual parameters can be studied by means of a so-called parametric study. On the basis of preliminary calculations, we suppose that the overall mass transfer coefficient, K_{DM} , and equilibrium constant of the reversible reaction, K_{AC} , are among the important parameters. Therefore, two 3D-graphs (Figure 4a and 4b) demonstrating the functions $SF_{(Am(III)/Cm(III))} = f(t, (K_{DM})_{Am})$ and $SF_{(Am(III)/Cm(III))} = f(t, K_{AC})$, were constructed for the CyMe₄-BTPPhen extraction system. The conditions of these constructions are as follows:

Figure 4a: function $Z = f(X, Y)$, i.e. $SF_{(Am(III)/Cm(III))} = f(t, (K_{DM})_{Am})$,

$$Z = SF, X = t \text{ [min}^{-1}\text{]}, Y = (K_{DM})_{Am} \cdot 10^2 \text{ [min}^{-1}\text{]},$$

further it holds (see Table 4 and 5): $(K_{DM})_{Cm} = (K_{DM})_{Am} / 1.83 \text{ [min}^{-1}\text{]} ; K_{AC} = 1.00;$

$$R_V = 1 \text{ [L}_{aq}\cdot\text{L}_{org}^{-1}\text{]};$$

$$D_{Am} = 58.00 \text{ [L}_{aq}\cdot\text{L}_{org}^{-1}\text{]} ; D_{Cm} = D_{Am} / K_{AC} \text{ [L}_{aq}\cdot\text{L}_{org}^{-1}\text{]} ; (c_{0aq})_{Am} = 3.49\text{E-}07 \text{ [mol}\cdot\text{L}_{aq}^{-1}\text{]} ;$$

$$(c_{0aq})_{Cm} = 1.31\text{E-}08 \text{ [mol}\cdot\text{L}_{aq}^{-1}\text{]}.$$

Figure 4b: function $Z = f(X, Y)$, i.e. $SF_{(Am(III)/Cm(III))} = f(t, K_{AC})$,

$$Z = SF, X = t \text{ [min}^{-1}\text{]}, Y = K_{AC},$$

further it holds (see Table 4 and 5): $(K_{DM})_{Am} = 8.68E-03$ [min^{-1}]; $(K_{DM})_{Cm} = 4.74E-03$ [min^{-1}]; $R_V = 1$ [$\text{L}_{\text{aq}} \cdot \text{L}_{\text{org}}^{-1}$]; $D_{Am} = 58.00$ [$\text{L}_{\text{aq}} \cdot \text{L}_{\text{org}}^{-1}$]; $D_{Cm} = D_{Am}/K_{AC}$ [$\text{L}_{\text{aq}} \cdot \text{L}_{\text{org}}^{-1}$]; $(c_{0aq})_{Am} = 3.49E-07$ [$\text{mol} \cdot \text{L}_{\text{aq}}^{-1}$]; $(c_{0aq})_{Cm} = 1.31E-08$ [$\text{mol} \cdot \text{L}_{\text{aq}}^{-1}$].

As Figure 4a clearly demonstrates, an interaction between the both parameters, time and overall mass transfer coefficient, exists and can be regarded as important and unexpected. This unexpected behaviour of the given system lies in the sudden change of the separation factor from 1.0 to 4.0 if $Y (=K_{DM})$ is smaller than *circa* $4 \cdot 10^{-3}$ [min^{-1}] and $X (=t)$ is greater than *circa* 30 minutes. Of course, this deals only with the results of calculations executed under conditions that are not be fully relevant to the time and mass transfer coefficients of real systems.

The interpretation of Figure 4b is easier – it is evident that the increase of K_{AC} is favourable for the separation process; we see that if the value of this parameter increases from 1 to 1.5, the separation factor increases from *ca.* 4 to 8.

In any case, such simulations of the influence of selected parameters on the separation efficiency of given system enable the results of research to be optimized before their application in practice.

Conclusions

In the present paper, we have tried to model the different behaviour of Am(III) and Cm(III) during liquid-liquid extraction by three 2,9-bis-(1,2,4-triazin-3-yl)-1,10-phenantroline (BTPPhen) derivatives published by Lewis et al. [12], who observed that extraction of Am(III) by CyMe₄-BTPPhen into cyclohexanone is significantly faster than extraction of Cm(III) resulting in higher-than-equilibrium SF(Am/Cm) values after 7 minutes of shaking. Computational modelling has helped to explain the observed dependences. A DM model, based on mass transfer as the rate-controlling process, was chosen as the best model for the

kinetic data. The value of the overall mass-transfer coefficients confirmed that extraction of Am(III) by the CyMe₄-BTPhen is approximately twice as fast as the extraction of Cm(III). Moreover, a dependence of SF(Am/Cm) on time was simulated and the obtained good fit of the calculated transfer-coefficients to the determined experimental values confirmed the validity of the theoretical model.

This kinetic separation phenomenon and its explanation paves the way for potential new approaches to separation of metal ions with very similar properties, such as the adjacent minor actinides Am(III) and Cm(III). In addition to a more detailed study of related systems, the next challenge is to engineer processes and devices that will be able to make practical use of this separation effect.

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