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Thermodynamic Parameters of Am(III), Cm(III) and Eu(III) Extraction by CyMe$_4$-BTPhen in Cyclohexanone from HNO$_3$ Solutions

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Shortened version of title: Thermodynamic parameters of extraction systems with CyMe$_4$-BTPhen

Abstract: The thermodynamic parameters of the extraction system consisting of CyMe$_4$-BTPhen dissolved in cyclohexanone and Am(III), Cm(III) and Eu(III) in HNO$_3$ in the aqueous phase have been determined. Kinetic extraction experiments were carried out under various temperatures (15 – 45 °C) and the corresponding over-all mass transfer coefficients were used for the calculation of apparent activation energy and frequency factor values. The values of reaction enthalpy and entropy were also calculated using the distribution coefficients resulting from the experiments mentioned above. Based on the calculated data, the rate-controlling processes and the exothermic character of the studied extractions were determined.

Introduction

Thermodynamic parameters such as apparent activation energy, reaction enthalpy and entropy can be obtained via evaluation of kinetic and equilibrium data determined experimentally under different temperatures. The experimental procedure, in principle, is relatively simple but the evaluation of experimental data requires the reaction conditions, mechanism, and the composition of the system studied to be taken into account – especially if it deals with a two-phase system.

For the determination of *apparent activation energy*, E_a (or E_k), in most of the literature, the procedure generally deals with homogenous systems where reversible monomolecular or bimolecular chemical reactions occur. More complicated situations are heterogeneous systems, for instance two phase systems such as liquid-liquid and liquid-solid extraction, because more than one kind of rate process can participate in the over-all transport process. Then, strictly speaking, each partial process has its own inherent activation energy [1], the independent determination of which may not be simple. Only if one of the processes is experimentally identified as the rate-determining step, can the activation energy be associated with it. Of course, as regards equilibrium quantities, i.e., enthalpy and entropy, these do not depend on the rate-controlling process. From the point of view of reaction thermodynamics, they depend on the equilibrium state of the given system only, even if the equilibrium state is a result of several mutual reactions. In the literature, information on the determination of thermodynamic quantities for such two-phase systems is relatively abundant [1–13].

As for the liquid-liquid extraction systems, an article by Simonin *et al*. [1] addressed the problem of Eu(III) extraction kinetics by two malonic diamides. A simple model for turbulent transport in a Lewis-type cell was used for the evaluation of experimental data obtained at 11 °C, 22 °C and 33 °C, and the apparent activation energy, E_a, was calculated by means of the Arrhenius equation, i.e., by means of a linear regression procedure of the dependence $k = f(1/T)$, where k is the global rate constant at the temperature T. The determined value of the apparent activation energy amounted to 17.6 $\mathrm{kJ \cdot mol^{-1}}$, which was a rather low value, typical of a diffusion controlled process (as a general rule of thumb, the boundary value of apparent activation energy dividing the diffusion and chemical reaction processes ranges from *ca.* 20 to 40 $\mathrm{kJ \cdot mol^{-1}}$. Values below this interval suggest diffusion as the rate-controlling process, while it is the chemical reaction for higher values. Of course, this situation holds true only in the case of the two-phase systems mentioned above).

In another work, the extraction kinetics of lanthanum with purified Cyanex 923 from nitrate medium was described [2]. The kinetic model was based on the assumption that the rate-controlling process is chemical reaction. The experiments were accomplished in temperature intervals 25 to 45 °C (in total, 6 experimental kinetic dependences under 6 different temperatures were obtained). Again, the Arrhenius equation was used to evaluate the experimental data; the apparent activation energy amounting to 32 $\mathrm{kJ \cdot mol^{-1}}$. In this instance, it can be suggested that the extraction rate is controlled by both chemical reaction and diffusion.

The activation energy in solid-liquid systems has also been determined [3–6]. Analogous to liquid-liquid systems, the Arhenius equation was used to evaluate experimental data in all cases and the significant values of the apparent activation energy for both types of rate-controlling processes were found, namely for diffusion (1.1-7.4 kJ·mol^{-1}) [4] and for chemical reaction (193 kJ·mol^{-1}) [5].

Determination of *reaction enthalpy* in a two-phase liquid-liquid system has been disclosed in an article devoted to the study of the extraction of uranium from Egyptian phosphoric acid using a synergistic D2EHPA-DBBP mixture [7]. The influence of temperature, as well as various factors such as extraction agents, phosphoric acid concentrations, contact time and aqueous(aq)-organic(org) phase ratio on the degree of extraction were studied. The effect of temperature on uranium extraction, especially its effects on the values of the distribution coefficients, between 25-70 °C, was quantified by means of the modified van't Hoff equation, in the form: $\ln D = (-\Delta H/R)(1/T)$ where D denotes the distribution coefficient [$L_{aq}^{3}\cdot L_{org}^{-3}$], ΔH reaction enthalpy [J·mol^{-1}], R gas constant [J·mol^{-1}·K^{-1}], and T absolute temperature [K]. In such a way, a value of $\Delta H = -23.12$ kJ·mol^{-1} was determined, which indicates that the extraction is an exothermic process. Unfortunately, this modified van't Hoff equation does not allow determination of the value of ΔS.

In another study, the standard enthalpy and entropy of dissolution of CyMe$_4$-BTBP in cyclohexanone at temperatures of 10, 20 and 30 °C were determined. Classical experimental set-up (glass vials with both components were shaken at the desired temperature for approximately two days and were then left for (2 to 3) days in a water bath of the same temperature to allow settling) was used [8]. The values of enthalpy and entropy were calculated by means of equation (12) (see below) where instead of D the solubility constant, K_s, was used. It is evident, that the positive values of both quantities reflect the endothermic character of the process studied, i.e., the amount of energy which has to be delivered into the system, ($\Delta H = 38.9\pm0.7$ kJ·mol^{-1} and $\Delta S = 98.0\pm2.5$ J·mol^{-1}·K^{-1}).

The literature data given above can therefore be summarized as follows:

a) The Arhenius equation is generally used for the calculation of apparent activation energy, E_a, in two-phase systems, such as in liquid-liquid or liquid-solid extraction. Of course, at first, it is necessary to determine the kinetic dependences at different temperatures and then evaluate them using the corresponding kinetic model. The resulting kinetic parameters, such as the global rate constants or over-all mass transfer coefficients at temperatures T, are used as the input data into the calculation procedure of E_a. Not only does this quantity indicate the influence of temperature on the reaction kinetics, but also the type of rate-controlling process.

b) The thermodynamic quantities ΔH and ΔS, characterizing the chemical reactions taking place in the same type of two-phase systems, can be determined by means of microcalorimetric titration or by the evaluation of equilibrium parameters (constants, distribution coefficients), obtained at different temperatures T, using the modified van't Hoff equation.

Recently, *N*-donor ligands containing the 1,2,4-triazine moiety, such as BTPhen, BTP and BTBP, have attracted much attention as potential ligands capable of separating the trivalent minor actinides (Am, Cm) from trivalent lanthanides or even for mutual separation within the minor actinides. These compounds have been designed to be used in the Selective Actinide Extraction (SANEX) process, which has been suggested for the reprocessing of irradiated nuclear fuel [9].

To understand the origin of the selectivity of these ligands better, more fundamental studies are needed. Indeed, the studies of the thermodynamic parameters ΔH and ΔS of Am(III), Eu(III) and Cm(III) extraction with the above-mentioned *N*-donor-extracting compounds (BTBPs or BTPhens) are still in their infancy. The overview of currently known data for Am(III) and Eu(III) is summarized in Table 1. As can be seen from this table, the values of ΔH and ΔS are strongly dependent on the diluent used. The structures of the ligands mentioned in Table 1 are shown in Figure 1.

Table 1. The overview of enthalpy ΔH and entropy ΔS for extraction of Am(III) and Eu(III) with BTPhen and BTBP ligands

Ligand	Method, temperature	Solvent	ΔH [kJ·mol^{-1}]		ΔS [kJ·mol^{-1}·K^{-1}]		Ref.
			Am(III)	Eu(III)	Am(III)	Eu(III)	
BQPhen	TMC, 25 °C	$(CH_3)_4N(ClO_4)$/DMF	-14.7 ± 0.6	-7.6 ± 0.1	220 ± 18	-221 ± 10	[10]
CyMe$_4$-BTPhen	TMC, 25 °C	acetonitrile	-	-113 ± 6	-	-224 ± 23	[11]
C5-BTBP	TMC, 25 °C	methanol	-	-28 ± 1	-	107 ± 13	[12]
t-Bu-C2-BTBP	TRLFS, 20 °C	propan-2-ol/H_2O (1:1 vol)	-	-23 ± 4	-	99 ± 12	[13]

*TMC = titration microcalorimetry.

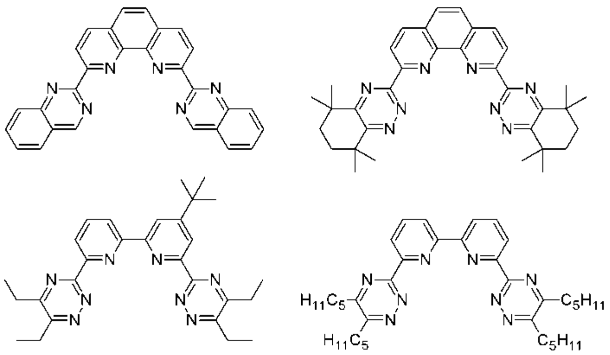

Figure 1. Structures of BQPhen (top, left), CyMe$_4$-BTPhen (top, right), *t*-Bu-C2-BTBP (bottom, left) and C5-BTBP (bottom, right)

As can be seen from Table 1, no data are available for the extraction systems with cyclohexanone even though it is, in general, one of the well described diluents for lanthanides and minor actinides separation. The extraction properties, kinetics and radiation stability of solvents based on this diluent were already described previously [14-19].

Since no research has been carried out to determine the thermodynamic parameters of extraction systems with cyclohexanone, it was decided to direct this study to this area. The approach selected was based on the evaluation of the liquid-liquid extraction kinetic experimental data obtained under different temperatures. Speciation of the respective metal ions in nitric acid solutions had to be calculated to account for their complexation with nitrate ions.

Theory

Kinetic models and extraction rate-controlling process

For the description of sorption/extraction taking place in two-phase systems, several kinetic models have been developed and are widely used. They are usually characterised by the transfer-controlling process. The most important models are: mass transfer or two-film (DM), film diffusion (FD), diffusion in inert layer (ID), diffusion in reacted layer (RLD), chemical reaction (CR), and gel diffusion (GD). A detailed discussion and description of these models, including the respective differential equations, has been summarised in our earlier paper. [20] Since the preliminary evaluation of the experimental data obtained by using the quantities WSOS/DF [21] revealed that our system is best described by the mass transfer (DM) model, only this model was used for a detailed data treatment and is described below.

In general, the mass transfer kinetic model can by described by the differential equation

$$\frac{dq}{dt} = k_{\mathrm{DM}} \cdot (q^* - q)\ , \tag{1}$$

where k_{DM} is an over-all mass transfer coefficient, q is concentration of the component in the organic phase at time t and q^* is equilibrium concentration of the component in the organic phase at time t, as well (see Eq. (4)). The difference (q^* - q) is the driving force of the given transport process.

Next, the mass transfer model is used for a demonstration of the detailed account of the liquid-liquid extraction kinetics – for the system Am(III) – CyMe$_4$-BTPhen. As was already mentioned, the control process is mass transfer between aqueous and organic phase:

$$(c_{\mathrm{aq}})_{\mathrm{Am}} \leftrightarrow (c_{\mathrm{org}})_{\mathrm{Am}}\ , \tag{2}$$

where $(c_{\mathrm{aq}})_{\mathrm{Am}}$ is a concentration of Am(III) in the aqueous phase at time t; $(c_{\mathrm{org}})_{\mathrm{Am}}$ is a concentration of Am(III) in the organic phase at time t. The rate equation can be written as:

$$r_{\mathrm{Am}} = -\frac{d(c_{\mathrm{aq}})_{\mathrm{Am}}}{dt} = \frac{(k_{\mathrm{DM}})_{\mathrm{Am}}}{Rv} \cdot \left(\left(c_{\mathrm{org}}\right)^*_{\mathrm{Am}} - \left(c_{\mathrm{org}}\right)_{\mathrm{Am}}\right)\ , \tag{3}$$

where $(c_{\mathrm{org}})^*_{\mathrm{Am}}$ is an equilibrium concentration of Am(III) in the organic phase and Rv is a volume ratio of aqueous to organic phase. Next, equilibrium equation (4) and balance equation (5) can be formed:

$$(c_{\mathrm{org}})^*_{\mathrm{Am}} = (c_{\mathrm{aq}})_{\mathrm{Am}} \cdot D_{\mathrm{Am}}\ , \tag{4}$$

$$(c_{\mathrm{org}})_{\mathrm{Am}} = Rv \cdot \left(\left(c_{0\mathrm{aq}}\right)_{\mathrm{Am}} - \left(c_{\mathrm{aq}}\right)_{\mathrm{Am}}\right) + \left(c_{0org}\right)_{\mathrm{Am}}\ , \tag{5}$$

where D_{Am} is a distribution coefficient of a given component, $(c_{0\mathrm{aq}})_{\mathrm{Am}}$ and $(c_{0\mathrm{org}})_{\mathrm{Am}}$ is a starting (initial) concentration in the given phase at $t = 0$.

Mathematical solubility of Eq. (3) assumes that Eqs. (4) and (5) have to be inserted into Eq. (3). Then, Eq. (6) – modified rate equation – is obtained which can be used for the direct evaluation of experimental data:

$$-\frac{d(c_{\mathrm{aq}})_{\mathrm{Am}}}{dt}=\frac{(k_{\mathrm{DM}})_{\mathrm{Am}}}{Rv}\cdot\left((c_{\mathrm{aq}})_{\mathrm{Am}}\cdot D_{\mathrm{Am}}-Rv\cdot\left((c_{0\mathrm{aq}})_{\mathrm{Am}}-(c_{\mathrm{aq}})_{\mathrm{Am}}\right)+(c_{0\mathrm{org}})_{\mathrm{Am}}\right). \tag{6}$$

For Eq. (6), 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 (6) under given boundary conditions (e.g. Runge-Kutha method), is applied.

Calculation of activation energy

The temperature dependence of the rate constants, k, or over-all mass transfer coefficients, k_{DM}, characterizing the kinetics of many chemical reactions and transport processes, can be described by the Arrhenius equation (7), [22] derived by analogy with the van't Hoff equation in 1889 [23] in the following form:

$$k_{\mathrm{DM}}\equiv k=k_0\cdot e^{-E_{\mathrm{a}}/RT}, \tag{7}$$

where k_0 is the frequency factor (pre-exponential or steric factor) and E_{a} is the activation energy; the meanings of R and T were defined above. The dependence of the natural logarithm of k (or k_{DM}) on $1/T$ is a straight line with the slope equal to E_{a}/R, i.e.:

$$\ln k_{\mathrm{DM}}\equiv\ln k=-\left({}^{E_{\mathrm{a}}}/_{R}\right)\cdot\left({}^{1}/_{T}\right)+\ln k_0. \tag{8}$$

From the previous literature data, equation (8) is suitable for the determination of activation energy of many reactions studied. Furthermore, it may be used for the determination of the value of the apparent activation energy if it does not relate to a specific elementary reaction.

In addition, two other models describing the temperature dependence of rate constants exist, based on collision theory and transition state theory [22]. These models are more sophisticated than the Arrhenius-based approach and their advantage is the possibility to assess the meaning of the frequency factor (pre-exponential factor). According to collision theory, the frequency factor relates to T^m ($m = 0 \leq 1$), and, in accordance with the transition state theory, it is a function of the activation entropy and hence of T, R, Planck and Boltzmann constants. Detailed background information can be found in the specialized physical chemistry literature [22].

Speciation of Am^{3+}, Cm^{3+} and Eu^{3+} in HNO_3 solution

The speciation diagram of NO_3^- complexes of radionuclides (M^{3+}) as a function of NO_3^- (HNO_3) concentration was calculated using stability constants taken from the databases HATCHES [24] and THERMO-CHIMIE [25] for the complexation reactions $M^{3+} + NO_3^- = MNO_3^{2+}$ (where M = Am^{3+}, Cm^{3+}, Eu^{3+}) for $I = 0$ that are: $\log\beta_{\mathrm{Am}} = 1.33$; $\log\beta_{\mathrm{Cm}} = 1.13$; $\log\beta_{\mathrm{Eu}} = 1.22$ [24, 25].

The values of the activity coefficients, which are usually calculated by the Davies equation, were in this case obtained by the SIT (Special Interaction Theory) method [26] because the ionic strength exceeded the value 0.1 $\mathrm{mol\cdot kg^{-1}}$. The corresponding calculated speciations are presented in Figure 2 as molar fractions of MNO_3^{2+}, F_{MNO3} [10^2], on the NO_3^- concentration, [$\mathrm{mol\cdot kg^{-1}}$]. Here, the software product FAMULUS [27] and the proper code PAmNit_S.fm (code package STAMB 2019) were used. It has to be added that the molar fraction of M^{3+}, F_{M} [10^2], equals 100 – F_{MNO3}.

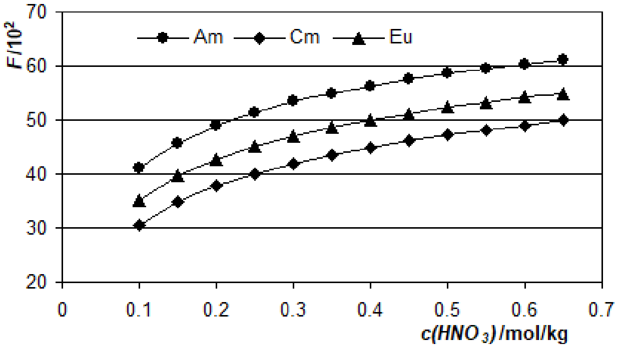

Figure 2. Molar fractions, $F/10^2$, of the given complexes MNO_3^{2+} as a function of NO_3^- concentration /$\mathrm{mol\cdot kg^{-1}}$.

It is evident that at the experimental concentration of NO_3^- equal to 0.5 $\mathrm{mol\cdot kg^{-1}}$, the complexation attains approx. 52 % in the case of Eu^{3+}. The highest value, approx. 58 %, concerns Am^{3+}, while in the case of Cm^{3+} it is approx. 47 %. These results were taken into account while formulating the extraction reactions equations (11b) and (11c) below.

Calculation of reaction enthalpy and entropy

The enthalpy change (ΔH) and the entropy change (ΔS) of liquid-liquid extraction of metal ions can be determined from the dependences of the natural logarithm of D ($\ln D$) on $1/T$, as demonstrated below (see Equations (9), (10), (14) – (18)):

The change in Gibbs free energy is defined as

$$\Delta G=R\cdot T\cdot\ln K \tag{9}$$

or

$$\Delta G = \Delta H - T \cdot \Delta S\ ; \tag{10}$$

where K is the equilibrium constant of the given reaction, ΔH is the enthalpy change, and ΔS is the entropy change [22, 28]. Under certain conditions, Equation (9) can be converted to a form applicable to the solvent extraction processes studied herein.

Assuming that the complexation stoichiometry between (M^{3+} + 3 NO_3^-) and CyMe$_4$-BTPhen (abbreviated to BTPhen in the following equations) is 1 : 2 [29,30], the reaction, in the course of which the charge neutral complex originates, is usually written as follows:

$$\mathrm{M^{3+}}_{\mathrm{aq}} + 3\ \mathrm{NO_3^-}_{\mathrm{aq}} + 2\ \mathrm{BTPhen}_{\mathrm{org}} \leftrightarrow [\mathrm{M(BTPhen)_2(NO_3)_3}]_{\mathrm{org}}\ . \tag{11a}$$

But, since the complexation of the metal ion with nitrates proceeds as described in Figure 2, the following two reactions should actually be considered:

$$(\mathrm{F_{MNO3}}/100)\left\{\mathrm{MNO_3^{2+}}_{\mathrm{aq}} + 2\ \mathrm{NO_3^-}_{\mathrm{aq}} + 2\ \mathrm{BTPhen}_{\mathrm{org}} \leftrightarrow [\mathrm{MNO_3(BTPhen)_2(NO_3)_2}]_{\mathrm{org}}\right\} \tag{11b}$$

$$(\mathrm{F_M}/100)\left\{\mathrm{M^{3+}}_{\mathrm{aq}} + 3\ \mathrm{NO_3^-}_{\mathrm{aq}} + 2\ \mathrm{BTPhen}_{\mathrm{org}} \leftrightarrow [\mathrm{M(BTPhen)_2(NO_3)_3}]_{\mathrm{org}}\right\} \tag{11c}$$

Because both reactions proceed in the given system, we can sum them as:

$$\mathrm{a} \cdot \mathrm{MNO_3^{2+}}_{\mathrm{aq}} + \mathrm{b} \cdot \mathrm{M^{3+}}_{\mathrm{aq}} + (2\mathrm{a}+3\mathrm{b})\mathrm{NO_3^-}_{\mathrm{aq}} + (2\mathrm{a}+2\mathrm{b})\mathrm{BTPhen}_{\mathrm{org}} = \mathrm{a} \cdot [(\mathrm{MNO_3})(\mathrm{BTPhen})_2(\mathrm{NO_3})_2]_{\mathrm{org}} + \mathrm{b} \cdot [\mathrm{M(BTPhen)_2(NO_3)_3}]_{\mathrm{org}}\ (= \mathrm{A_{org}} + \mathrm{B_{org}}) \tag{12}$$

where: a = F_{MNO3}/100, b = F_M/100, a + b =1

And if we substitute $\mathrm{a} \cdot \mathrm{MNO_3^{2+}}_{\mathrm{aq}} + \mathrm{b} \cdot \mathrm{M^{3+}}_{\mathrm{aq}}$ for $\sum M_{aq}$ and $\mathrm{a} \cdot [(\mathrm{MNO_3})(\mathrm{BTPhen})_2(\mathrm{NO_3})_2]_{\mathrm{org}} + \mathrm{b} \cdot [\mathrm{M(BTPhen)_2(NO_3)_3}]_{\mathrm{org}}\ (= \mathrm{A_{org}} + \mathrm{B_{org}})$ for $\sum M_{org}$, then the equilibrium constant of reaction (6) can be expressed as

$$K_{\Sigma} = \sum \mathrm{M_{org}} / \left(\sum \mathrm{M_{aq}} \cdot [\mathrm{NO_3^-}]_{\mathrm{aq}}^{(2a+3b)} \cdot [\mathrm{BTPhen}]_{\mathrm{org}}^{4b}\right) \tag{13}$$

Further, comparing the concentration of BTPhen (between 1 – 5 mmol·kg_{org}^{-1}) and NO_3^- (0.5 mol/kg_{aq}) with the concentration of radionuclides in question, i.e. M^{3+} (tracer quantities, roughly 10^{-7} – 10^{-10} mol·kg_{aq}^{-1}, see Table 3), we can assume that the concentrations of BTPhen and NO_3^- do not change during the extraction (the difference between BTPhen and [M^{3+}] is 4 – 7 orders of magnitude, in a case of NO_3^- it amounts to 6-9 orders of magnitude). Under such conditions, Equation (13) can be converted to

$$K_{\Sigma} \cdot [\mathrm{NO_3^-}]_{\mathrm{aq}}^{(2a+3b)} \cdot [\mathrm{BTPhen}]_{\mathrm{org}}^{4b} = \sum \mathrm{M_{org}} / \sum \mathrm{M_{aq}} = D = \mathrm{const.} \tag{14}$$

We see from this that the extracted component exists in two forms in the organic phase, for example A_{org} and B_{org}, and in two forms in the aqueous phase, for example $(MNO_3^{2+})_{aq}$ and $(M^{3+})_{aq}$. Then, the product of the equilibrium constant K_{Σ} and constant concentrations of $NO_3^-{}_{aq}$ and $BTPhen_{org}$ is equal to the experimental distribution coefficient, D [kg_{org}/kg_{aq}]. It has to be added that this holds in cases where the extracted component exists in more than two forms. Under these conditions, the thermodynamic quantities can be calculated by means of Equation (18) obtained using Equations (9), (10) and (14) – (17) as follows:

$$D = e^{-\Delta G/RT} \tag{15}$$

from where

$$\Delta G = -R \cdot T \cdot \ln D\ . \tag{16}$$

Combining Equations (10) and (16), a new equation (17)

$$-R \cdot T \cdot \ln D = \Delta H - T \cdot \Delta S \tag{17}$$

is obtained, where ΔH and ΔS represent changes in enthalpy and entropy of the extraction of the metal ion. The last step involves expressing the dependence of natural logarithm of D (ln D) on $1/T$:

$$\ln D = -\left({}^{\Delta H}/_{R}\right) \cdot \left({}^{1}/_{T}\right) + {}^{\Delta S}/_{R}\ . \tag{18}$$

Using data from the linear regression of the plot of ln D *vs. 1/T*, the ΔH and ΔS changes for the studied extraction can be calculated by equation (18). In contrast to the paper by Abdel-Khalek *et al* [7], where – the reaction enthalpy was calculated by means of the modified van't Hoff equation, Equation (18) was derived here in such a way that both the quantities ΔH and ΔS can be obtained. In addition, it can be used in cases when the component in question exists in the system as more than one species.

Experimental

The common reagents were used as received and they are listed in the Table 2. The aqueous solutions were prepared by spiking 0.5 mol·kg_{aq}^{-1} HNO^3 with stock solutions of ^{152}Eu, ^{241}Am, and ^{244}Cm tracers prepared by double-dilutions of the original preparations to 0.5 mol·kg_{aq}^{-1} nitric acid; the initial metal ion concentrations, applied at given temperatures, can be found in Table 3. The count rates were converted into molality (mol·kg_{aq}^{-1}) of ^{152}Eu, ^{241}Am, and ^{244}Cm. These molalities of metal cations in the aqueous phase were used for the evaluation of kinetic and equilibrium quantities at the temperatures studied.

Table 2. CAS Registry Number, Suppliers, and Mass Fraction Purity of the Chemicals

Component	CAS Reg. No.	Suppliers	Mass Fraction / Specific Activity
nitric acid	7697-37-2	Sigma-Aldrich	0.65 / –
cyclohexanone	108-94-1	Sigma-Aldrich	≥0.99 / –
CyMe$_4$-BTPhen	1276186-76-5	University of Reading	0.98 / –
americium-241 oxide	12005-67-3	Cesio, Czech Republic	>0.99 / 111 MBq/mg
curium-244 nitrate	35311-12-7	TENEX, Russia	≥0.995 / 2.4 GBq/mg
europium-152 chloride	10025-76-0	Polatom, Poland	>0.99 / 917 MBq/mg

Table 3. Aqueous and organic phase initial concentrations applied at given temperatures

Exp. No.	T °C]	c [mol·kg^{-1}]			
		Am	Cm	Eu	org
1	15	$8.33\cdot10^{-8}$	$3.18\cdot10^{-9}$	$4.20\cdot10^{-10}$	0.001
2	25	$9.09\cdot10^{-8}$	$3.08\cdot10^{-9}$	$4.23\cdot10^{-10}$	
3	35	$8.33\cdot10^{-8}$	$3.18\cdot10^{-9}$	$4.20\cdot10^{-10}$	
4	45	$9.09\cdot10^{-8}$	$3.08\cdot10^{-9}$	$4.23\cdot10^{-10}$	

Then, a solution of 0.001 mol·kg$_{org}^{-1}$ CyMe$_4$-BTPhen ligand was prepared by dissolving the requisite amount of the ligand in cyclohexanone. Prior to adding the radiolabels, 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 (aqueous:organic). The cyclohexanone phases were pre-equilibrated with the respective non-labelled aqueous phases by shaking them for 4 hours at 400 min^{-1} with a volume ratio of 1:1. In each case, 1210 µL$_{aq}$ of labelled aqueous phases were prepared from which 10 µL$_{aq}$ standards (for alpha measurements) and 200 µL$_{aq}$ standards (for gamma measurements) were taken (to allow mass balance calculations) prior to contacting the aqueous phases with the organic phases. Each organic phase (1 mL$_{org}$) was shaken separately with each (1 mL$_{aq}$) of the aqueous phases for the specified time at a thermostatted temperature (15, 25, 35, and 45 °C) using a GFL 3005 Orbital Shaker (250 min^{-1}). Before contacting the phases for shaking, each phase was separately equilibrated at the desired temperature. A Peltier effect based thermostatted shaker was used.

After phase separation by centrifugation, two parallel 10 µL and 200 µL aliquots of each phase were withdrawn for alpha and gamma measurements. The aliquots for alpha analysis were deposited on stainless steel planchets, evaporated to dryness under an infra-red lamp, and heated in a burner flame until the sample glowed to dull red heat. Activity measurements of ^{244}Cm were performed with an ORTEC® OCTETE Plus Integrated Alpha-Spectroscopy System equipped with an ion-implanted-silicon ULTRA Alpha Detector, Model BU-020-450-AS. The ^{244}Cm peaks were evaluated by AlphaVision-32 Alpha Analysis Software (ORTEC, Advanced Measurement Technology, Inc., USA). The aliquots for gamma analysis were placed in glass ampoules. The walls of the glass ampoules were washed with 1 mL of distilled water or 1 mL of cyclohexanone; and the ampoules were covered with paraffin wax sealant. Activity measurements of ^{152}Eu and ^{241}Am were performed with a γ-ray spectrometer EG&G Ortec (USA) using a PGT (USA) HPGe detector and evaluated by Maestro for Windows.

Results and Discussion

The experiments performed were aimed at the following:

- Determination of the thermodynamic quantities, namely, the heat of reaction, i.e. reaction enthalpy and reaction entropy of the extractions studied for the system Am/Cm/Eu-CyMe$_4$-BTPhen based on the reaction (12).
- Assessment of the extraction rate control process and the values of apparent activation energies and frequency factors.

Extraction kinetics

Each kinetic curve consisted of 10, 20, 30, 60, 90, and 120 minutes points (the equilibrium state was achieved within 60 minutes for all the tested ions). As an example, the experimental curves obtained at temperature 25 °C for Am(III), Cm(III), and Eu(III) extraction by CyMe$_4$-BTPhen, are shown in Figure 3. To elucidate the rate-controlling process, the kinetic curves were fitted by the six kinetic models mentioned above; the goodness-of-fit was assessed by using the WSOS/DF quantity (weighted sum of squares of residuals divided by the degree of freedom) the values of which has to be between approx. 0-20. [21] The mass transfer (DM) model showed the best fits of all the experimental data yielding the WSOS/DF values about or below 20 (e.g., Am(III): 26.8, Cm(III): 8.01, and Eu(III): 0.03 for the curve shown in Fig. 3). The obtained values of the over-all mass transfer coefficients, k_{DM} ($\equiv k$), together with the equilibrium distribution coefficients, D, are shown in Table 4 and were used as input data for the subsequent calculations.

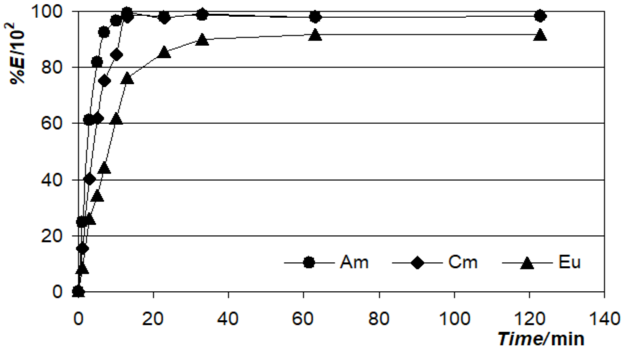

Figure 3. Dependency of the extraction percentage, %E/10^2, on time for the tested system at 25 °C.

Table 4. Values of over-all mass transfer coefficients $(k_{DM})_{Am,Cm,Eu} \pm \sigma$ and distribution coefficients $D_{Am,Cm,Eu} \pm \sigma$ for temperatures 15–45 °C

Exp. No.	T [°C]	$(k_{DM})_{Am}$ [min^{-1}]	D_{Am} [kg$_{aq}$·kg$_{org}^{-1}$]	$(k_{DM})_{Cm}$ [min^{-1}]	D_{Cm} [kg$_{aq}$·kg$_{org}^{-1}$]	$(k_{DM})_{Eu}$ [min^{-1}]	D_{Eu} [L$_{aq}$·L$_{org}^{-1}$]
1	15	$2.29\cdot10^{-3}$ $\pm 3.7\cdot10^{-4}$	43.90 ± 1.10	$4.48\cdot10^{-3}$ $\pm 9.6\cdot10^{-4}$	19.80 ± 0.99	$2.32\cdot10^{-2}$ $\pm 4.6\cdot10^{-3}$	0.17 ± 0.01
2	25	$9.17\cdot10^{-3}$ $\pm 1.10\cdot10^{-3}$	20.90 ± 0.97	$7.64\cdot10^{-3}$ $\pm 1.99\cdot10^{-3}$	8.80 ± 0.44	$3.96\cdot10^{-2}$ $\pm 1.31\cdot10^{-2}$	0.16 ± 0.01
3	35	$3.15\cdot10^{-3}$ $\pm 2.8\cdot10^{-4}$	23.60 ± 1.00	$4{,}87\cdot10^{-3}$ $\pm 3.2\cdot10^{-4}$	12.10 ± 0.60	$5.32\cdot10^{-2}$ $\pm 1.30\cdot10^{-2}$	0.13 ± 0.01
4	45	$3{,}33\cdot10^{-3}$ $\pm 8.7\cdot10^{-4}$	15.60 ± 0.90	$1.03\cdot10^{-2}$ $\pm 1.3\cdot10^{-3}$	7.60 ± 0.38	$1.04\cdot10^{-1}$ $\pm 2.6\cdot10^{-2}$	0.12 ± 0.01

It should be noted here that the kinetic equations, e.g. (1) and (6), are functions not only of the mass-transfer, but also of the distribution coefficient and thus the distribution coefficient takes part in the transport driving force. In consequence of their mutual interaction, both these parameters affect the rate of extraction/sorption. This is exemplified by the correlation of the decreasing rate of extraction from Am(III) to Eu(III) seen in Figure 3 with the order of the values of the respective distribution coefficients given in Table 4. This also reflects the important role of these equilibrium parameters or the values of driving forces, if different systems are evaluated.

As the most important result of the above described kinetic data evaluation, we regard the determination, on one hand, of the over-all mass-transfer coefficients by means of which the values of apparent activation energy can be calculated, and, on the other hand, elucidation of the extraction rate-controlling process. The mass transfer kinetic model (DM), generally characterizing the rate-controlling process in the studied system, is based on the assumption that on both sides of the interphase boundary exist films of the given phases and the interphase transfer of the given component takes place by diffusion through these films [31]. Therefore, in principle, the rate-controlling process should be the diffusion. In most cases, the value of apparent activation energy can validate the rate controlling process as shown also below.

Reaction enthalpy and entropy

The values of the equilibrium distribution coefficients and temperatures from Table 4 were used as input data into the linear regression procedure based on Equation (18). The graphical evaluation of the experimental data is demonstrated in Figure 4 for Am(III), Cm(III) and Eu(III), and the calculated values of ΔH and ΔS of the extraction reactions are listed in Table 5.

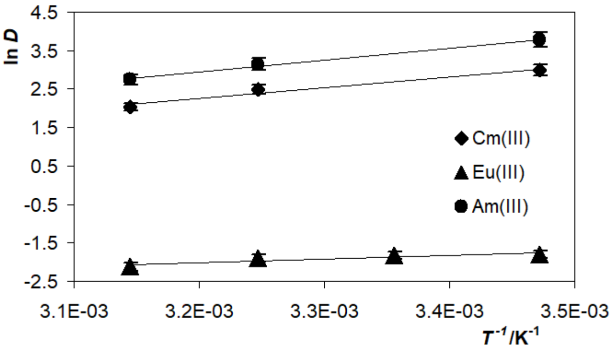

Figure 4. Dependency of ln $D_{Am,Cm,Eu}$ ± σ on 1/T used for the calculation of the reaction enthalpy, ΔH, and entropy, ΔS, by means of Equation (12)

Table 5. Values of reaction enthalpy, ΔH ± σ, and entropy, ΔS ± σ, and corresponding regression coefficients, R^2, of extraction systems studied

Nuclide	ΔH [kJ·mol^{-1}]	ΔS [kJ·mol^{-1}.K^{-1}]	R^2 [-]
Am	-25.4 ± 2.0	-0.057 ± 0.007	0.99
Cm	-23.3 ± 4.7	-0.056 ± 0.015	0.96
Eu	-7.7 ± 2.6	-0.041 ± 0.008	0.82

It is evident, that the values of the enthalpy change, ΔH, reflect the exothermic nature of metal ion extraction, particularly Am(III) and Cm(III) extraction (in this case, corroborated by the values of regression coefficients, R^2). As for the entropy change, ΔS, its negative value in all three cases points to the increase of the order in the liquid-liquid extraction system studied. While the negative values of ΔH are generally comparable with the literature data in Table 1, this does not hold for our values of ΔS presented above. A reason for the differences between our data and the literature ΔS values can possibly lie in the properties of the cyclohexanone used as the organic solvent for CyMe$_4$-BTPhen in this study.

Extraction rate-controlling process and evaluation of apparent activation energy, E_a, and frequency factor, k_0

As detailed above, the procedure for the assessment of the extraction rate-controlling process initially consisted of the evaluation of the temperature-dependent kinetic experimental data. It was found that the mass-transfer (or, more exactly, two-film) model gave the best fit of the experimental data and therefore this model generally characterizes the diffusion as the rate-controlling process. The obtained values of the over-all rate constants or over-all mass transfer coefficients, k_{DM} (≡k), were used as input data into the Arrhenius equation (8) with the aim of deriving the apparent activation energies, E_a, and frequency factors, k_0. Their values for Am(III) and Cm(III) as representatives of the minor actinides, and Eu(III) as a representative of the lanthanides, are summarized in Table 6. The dependences of ln(k_{DM})$_{Am,Cm,Eu}$ on 1/T, evaluated by the Arrhenius equation (2), are shown in Figure 5.

Table 6. Values of apparent activation energy, (E_a)$_{Am,Cm,Eu}$ ± σ, frequency factor, (k_0)$_{Am,Cm,Eu}$, and of corresponding regression coefficients, R^2

Nuclide	E_a [kJ·mol^{-1}]	k_0 [min^{-1}]	R^2 [-]
Am	31.71 ± 3.80	$1.14 \cdot 10^3$	0.75
Cm	18.15 ± 2.54	7.96	0.64
Eu	36.43 ± 8.38	$9.20 \cdot 10^4$	0.98

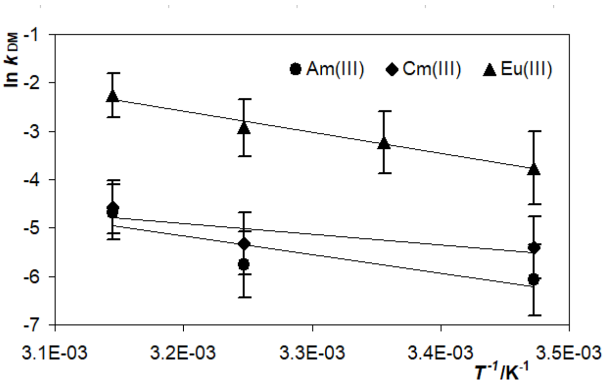

Figure 5. Dependence of $\ln(k_{DM})_{Am,Cm,Eu} \pm \sigma$ on $1/T$ used for the calculation of the apparent activation energy, E_a, and the frequency factor, k_0, by means of the Arrhenius equation (8)

The measured values of the apparent activation energy, E_a, seem to point to the conclusion that the principle rate-controlling process for liquid-liquid extraction of the investigated nuclides by CyMe$_4$-BTBPhen into cyclohexanone is a combination of diffusion and chemical reaction, because the values of E_a range from almost 20 to almost 40 kJ·mol^{-1}. The contribution of diffusion seems to be highest for Cm(III) where the value of E_a is slightly smaller than 20 kJ·mol^{-1}.

Regarding the frequency factors, $(k_0)_{Am,Cm,Eu}$, it is difficult to judge their true meaning because, not only are their values different, but also the regression coefficients, R^2, are low (especially in the case of Am(III) and Cm(III)). According to transition state theory, they should reflect the different values of the activation entropy, $\Delta S^{\#}$, characterizing the orientation of the activated complex of molecules taking part in the given extraction reaction [22]. According to this theory, the frequency factor is proportional to $\exp(\Delta S^{\#})$ and therefore, probably, the value of E_a also depends, at least in part, on $\Delta S^{\#}$. This assumption seems to correspond with the calculated E_a for Am(III), Cm(III) and Eu(III), the relative values of which are $(E_a)_{Am} \approx (E_a)_{Eu} >> (E_a)_{Cm}$, which are comparable with the following values of k_0: $(k_0)_{Am} \approx (k_0)_{Eu} >> (k_0)_{Cm}$ (see Table 6). Of course, such interpretation requires verification by additional studies.

In addition, if the individual values of $(k_{DM})_{Am,Cm,Eu}$ and $D_{Am,Cm,Eu}$ found for individual temperature points are taken into account (see Table 4), it is evident that their values increase and decrease respectively: in the case of Eu(III), in the interval 15-45 °C. The reason for this anomalous behavior is not clear at this point. Among the potential reasons, slightly different initial aqueous phase concentrations at temperatures 15 and 35 °C, and at 45 °C (see Table 3), or the experimental error in the course of temperature regulation can be considered. Additionally, this could be a result of anomalous behavior of the actinide system studied in the very low molality region (it deals with the values about 10^{-8}-10^{-10} mol·kg^{-1}) as it is known from colloid and tracer chemistry [32]. However, this does not fully explain the role of temperature.

Conclusions

We have determined the distribution and over-all mass-transfer coefficients at 15, 25, 35 and 45 °C and the thermodynamic parameters of Am(III), Cm(III) and Eu(III) extraction by the CyMe$_4$-BTPhen ligand dissolved in cyclohexanone. Based on the values of the apparent activation energy, it was found that the extractions are probably driven by both the chemical reaction and by diffusion (values of E_a between almost 20 and almost 40 kJ·mol^{-1}); the contribution of diffusion seems to be the highest for Cm(III) (E_a < 20 kJ·mol^{-1}). Extractions of all the studied metals, present as (at least) two species (as MNO_3^{2+} and M^{3+}), were exothermic and all calculated values of the entropy change were negative.

The obtained data can help to understand better the extraction systems based on CyMe$_4$-BTPhen and extractions of An(III) and Ln(III) more generally. To be specific, the results can find application in laboratory studies of reaction mechanism taking part in the analogous systems, but also in the course of the technological tasks solution such as modelling of the process based on this solvent including the determination of extraction apparatuses parameters (type of mixer-settlers, extraction centrifuges or extraction columns).

Acknowledgments

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