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Effect of diluent on the extraction of europium(III) and americium(III) with N,N,N',N'-tetraoctyl diglycolamide (TODGA)

Ivan Kajan, [ID] *[a] Markéta Florianová,[b] Christian Ekberg[c] and Artem V. Matyskin [ID] †[c]

Solvent extraction of Eu^{3+} and Am^{3+} *via* N,N,N',N'-tetraoctyl diglycolamide (TODGA) dissolved in different molecular diluents was studied. The diluent types used in this work were primary and secondary alcohols, secondary ketones and alkanes. Effects of concentration of extracting agent, temperature, diluent type and its carbon chain length on the extractions were determined. Distribution ratios of Eu^{3+} and Am^{3+} showed high dependence on the diluent type as well as the carbon chain length within the same type of diluent. The highest distribution ratios for both Eu^{3+} and Am^{3+} as well as the separation factors of Eu^{3+} over Am^{3+} were observed in the alkane diluents. Unexpectedly high distribution ratios for Eu^{3+} and Am^{3+} were observed in polar diluents with 5 carbon atoms in the chain, clearly standing out against the general trends. It was found that Eu^{3+} and Am^{3+} extraction *via* TODGA is enthalpy driven in all the studied diluents and that extraction is more exothermic in alkane diluents. Analysis of the stoichiometry of the extracted complexes shows that the average ligand number of TODGA molecules in the extracted complex is lower for Am^{3+} compared to Eu^{3+} except for with alkane diluents.

1 Introduction

Solvent extraction is a separation technique commonly used in many various industries including mining and nuclear fuel reprocessing, as well as being one of the foreseen methods for recycling rare earth elements from nickel-metal hydride batteries, permanent magnets or modern electronics.[1–4] Its ease of use for industrial application offers efficient application and high purity of extracted metal. A tremendous effort during the last decades has been put into the development of new, more selective, extracting agents for the extraction processes. At the same time basic phenomena in the particular solvent extraction processes are poorly understood. One of them is the effect of the diluent on the extraction process. Diluent is defined as: "the liquid or homogeneous mixture of liquids in which extractant(s) and possible modifier(s) may be dissolved to form the solvent phase."[5] The organic diluent is the major constituent of the organic phase in the solvent extraction systems. It was already shown in the past that diluent has a substantial effect on the outcome of the extraction with respect to both distribution ratios as well as separation factors between different elements.[6–15] Despite the strong experimental evidence of diluent effect, its full theoretical explanation is challenging and predictions are still very uncertain. Few theoretical explanations for the diluent effect were proposed. The first introduction of diluent effect to the predictions of distribution ratios in solvent extraction was proposed by Schmidt.[15] An empirical diluent parameter was included to predict the distribution ratios of zinc extracted by tri-*n*-octyl-amine in different diluents. Unfortunately, the proposed predictions were valid only for a limited number of diluents even with only one extracting agent. Another explanation of diluent effect is based on the energetic balance between the cost of cavity formation within the diluent into which the extracted molecule is placed and the energetic gain from interaction between the diluent and the extracted molecule.[3,16] In order to get a deeper understanding into the energetic cost of the cavity creation Hildebrand used the heat of vaporization to predict the cohesive forces within liquids. The model is based on the proportionality of the heat of vaporization to the intermolecular binding energy.[17,18] This idea was further developed by Hansen dividing the solubility parameter into three vectors consisting of the hydrogen bonding, polar and dispersion interactions.[19] Hansen's model has been successfully applied on mutual solubility of polymers in solvents or plasticizers. However, in solvent extraction, simple correlations of extraction constants (K_d) against solubility

[a]Laboratory of Radiochemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland. E-mail: ivan.kajan@psi.ch

[b]Department of Nuclear Chemistry, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Brehova 7, 11519 Prague 1, Czech Republic

[c]Nuclear Chemistry and Industrial Material Recycling Group, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Gothenburg, Sweden

† Present address: Chemistry Division, Los Alamos National Laboratory, P. O. Box 1663, 87545 Los Alamos, New Mexico, United States of America.

parameters are not sufficient for predictions of the extraction outcome.[20] At the same time systematic experimental studies on the diluent effect are very scarce.[21]

In order to further investigate the effects of diluent on extraction, the aim of this study is the systematic evaluation of the molecular diluent effect on the extraction of trivalent europium and americium from nitric acid solutions with N,N,N',N'-tetraoctyl diglycolamide as an extracting agent. The family of diglycolamides are known extracting agents for trivalent lanthanides and actinides in solvent extraction, with expected application in partitioning and transmutation of a nuclear fuel[22–25] and in radiopharmaceutical industry for [225]Ac production.[26–29] While the behavior of diglycolamides with respect to equilibrium distribution ratios, acid extraction and kinetics was extensively evaluated,[30–42] the effect of the diluent on the extraction was evaluated only in a few studies.[42–47] From the available data, correlations of diluent properties against the distribution ratios seems rather difficult. It was shown that in nonpolar diluents benzene rings give decrease in the extraction of americium.[32,43] At the same time, distribution ratios of americium and lanthanides in the polar nitrobenzene media are high.[32,48]

Correlations of distribution ratios against dielectric constants of used diluents seem to be also non-conclusive.[49] Dielectric constant of the diluent appears to have effect on the stoichiometry of the extracted americium complex giving lower ligand number in diluents with higher dielectric constants.[32,43,44,48,49] In the diluents with higher polarity (e.g. dichloroethane, octanol) 1 : 2 metal : TODGA complex was observed whereas in low polarity diluents (e.g. chloroform, toluene, dodecane) 1 : 3 or 1 : 4 metal : TODGA molecules were detected.[43,44] At the same time it was shown that the nature of the diluent does not affect the results of time resolved laser fluorescence measurements luminescence spectra of Eu^{3+}.[38,45]

In order to bring deeper insight into diluent effects, we performed a systematic study of the molecular diluent influence on solvent extraction of americium and europium by N,N,N',N'-tetraoctyl diglycolamide (TODGA) from nitric acid media. Three different groups of diluents consisting of alkanes, long chained alcohols and ketones were studied. The effect of the carbon chain length, was evaluated from 5 to 10 carbons in order to target the subtle changes in the polarity of used diluents. Moreover, standard molar Gibbs energy ($\Delta G^0_{298\ K}$), enthalpy ($\Delta H^0_{298\ K}$), and entropy ($\Delta S^0_{298\ K}$) changes for the extraction of Eu^{3+} and Am^{3+} from 4 M HNO_3 into TODGA dissolved in different diluents was

studied to get better understanding of thermodynamic effect of molecular diluent on these solvent extraction processes.

2. Experimental

2.1. Organic and aqueous phase preparation

Aliphatic organic diluents (ACS grade, ≥99.0%) were obtained from Sigma Aldrich and were used as supplied. TODGA (>99% by HPLC) was obtained from Technocomm Ltd (Scotland). Organic phases for experiments were prepared volumetrically by mixing TODGA with various diluents. For the primary and secondary alcohols as well as ketones the TODGA concentration in the organic phase was 20 mmol L^{-1}. For the alkane diluents the TODGA concentration was 2 mmol L^{-1}. Aqueous phases were prepared by gravimetrical dilution (Sartorius, 98648-018-34) of 65 volume% HNO_3 (purris. p.a. grade, J.T. Baker) with deionized water (18 MΩ cm at 25 °C from Milli-Q system) to 4 mol L^{-1}. The aqueous phases were spiked with trace amounts of radioactive [152]Eu and [241]Am (approximately 10^{-7} mol L^{-1} and 10^{-8} mol L^{-1}, respectively) obtained from PSI stocks. The complete composition of extraction systems and extraction conditions studied in this work are shown in the Table 1.

2.2. Measurements of distribution ratios

The distribution ratios for the trace amounts of [152]Eu and [241]Am were determined by contacting 1 mL of the aqueous phase containing 4 mol L^{-1} HNO_3 (as the representative HNO_3 concentration in the high active raffinate solution[50]) and europium and americium tracers with the same volume of organic phase containing TODGA dissolved in respective diluent. Contacting was done by the shaking of the organic and aqueous phases for 120 minutes in shaking machine (IKA Vibrax VXR Basic) at 1000 rpm. This time (120 min) was determined in the initial tests to be sufficient in order to reach distribution equilibrium for both europium and americium. Shaking machine was equipped with sample holder coupled with a heated circulating water bath (Julabo, F250) to maintain constant temperature. After the contacting, the samples were allowed to settle by gravity for 120 minutes. After phase separation, 500 μL and 800 μL aliquots were taken from organic and aqueous phases, respectively. Aqueous phase (800 μL) was transferred to the second vial from which a second 500 μL aliquot was taken in order to avoid cross contamination with the organic phase. The samples were kept in the temperature-controlled setup from the phase contacting stage till the first sampling of 500 μL and 800 μL aliquots for organic and aqueous phases respectively. This

Table 1 Composition of extraction systems and extraction conditions used

Diluent family	Length of the carbon chain	TODGA concentration (mmol L^{-1})	Temperature (K)	Nitric acid concentration (mol L^{-1})
Alkanes	6–10	1, 2, 5	288, 298, 308	4
Primary alcohols	5–10	5, 20, 40	288, 298, 308	4
Secondary alcohols	5–10	5, 20, 40	288, 298, 308	4
Secondary ketones	5–10	5, 20, 40	288, 298, 308	4

decreases the possible experimental errors in the determination of the extraction constants that are highly temperature sensitive.

After the sampling, count-rates of ^{152}Eu at 121.8 keV and ^{241}Am at 59.6 keV in aqueous and organic phases were measured via a p-type High Purity Germanium detector (HPGe) coupled with digital spectrum analyzer. Genie 2000 software was used to analyze obtained gamma spectra. Dead time during the data acquisition was kept below 5%. The effect of density differences between the aqueous and organic phases on transmission of γ-rays from the samples was evaluated by EFFTRAN code[51] and was found to be less than 0.5% thus below the random uncertainty originating from the counting statistics. The extraction of americium and europium by pure diluent in the absence of TODGA was investigated in the screening experiments which were performed in the same manner as experiments with TODGA described above.

The distribution ratios were calculated as the ratio of equilibrium concentration of solute (Eu^{3+} and Am^{3+}) in the organic phase over its concentration in the aqueous phase represented by its measured radioactivity (eqn (1)).

$$D_m = \frac{[M]_{(org)}}{[M]_{(aq)}} = \frac{A_{M(org)}}{A_{M(aq)}} \qquad (1)$$

The separation factors were subsequently calculated as the ratio of the distribution ratios of europium and americium as shown in eqn (2)

$$SF_{Eu/Am} = \frac{D_{Eu}}{D_{Am}} \qquad (2)$$

Experiments were performed in duplicates or triplicates and the uncertainties of all data are given as one standard deviation.

It is well known that extraction of HNO_3 via some organic phases containing TODGA occurs.[33,38–41,49,52] Therefore, two sets of experiments were performed – with the organic phase pre-saturated with 4 M HNO_3 as well as with a non-preconditioned set of diluents. Saturation of the organic solvent (diluent and TODGA) was performed by contacting the solvent with the same volume of 4 M HNO_3 by shaking machine for 60 minutes and then the phases were let to separate by gravity for 120 minutes. This procedure was performed only with polar diluents, as alkanes did not show any appreciable extraction of nitric acid thus behaving like true inert diluents.

2.3. Extraction of nitric acid into diluent

In order to obtain insight into the ability of the pure diluent to extract nitric acid from the aqueous solutions experiments were performed in the similar way as described in the work by Geist.[53] Organic diluent (25 mL) was contacted with the equal volume of water and shook for 30 minutes. Phases were separated by centrifugation and 25 mL of organic phase was then transferred and contacted with the equal volume of nitric acid solutions of varied concentration (0.1–4 mol L^{-1}) in shaking machine at 2000 rpm.

After subsequent centrifugation, 20 mL of the organic phase was transferred to the different vial and contacted with distilled MQ water in order to back-extract nitric acid from the organic phase. The acid concentration in the back-extracted solutions as well as in the initial aqueous solutions was determined by potentiometric titrations using Metrohm Titrino and 0.01 mol L^{-1} and 0.1 mol L^{-1} standard NaOH solutions. These experiments were performed in triplicates. The mass balance calculations showed that single contacting of the loaded organic phase with distilled water is sufficient for the complete back-extraction of HNO_3 into aqueous phase.

2.4. Determination of the stoichiometry of the extracted species

The stoichiometry of extracted complexes with respect to average number of TODGA ligand surrounding the extracted metal was determined by the conventional slope analysis. The slope analysis was performed by the least squares linear regression of the logarithmic plots of distribution ratios against the logarithmic values of TODGA concentration in the organic phase for each diluent. As only trace amounts of Eu^{3+} and Am^{3+} were used in the tests (10^{-7} mol L^{-1} and 10^{-8} mol L^{-1}, respectively), the concentration of the free TODGA at the equilibrium was assumed to be equal to its initial value. For the calculations of apparent extraction constants, activities in the aqueous phase rather than concentrations were used. Extended Specific ion Interaction Theory (ESIT) developed by Ciavatta[34] was used to compute activity coefficients of free nitrate ions in aqueous phase. According to the mechanism of Eu and Am extraction via TODGA (eqn (4) below), only neutral, uncharged species exist in organic phase. It can be assumed that activity coefficients of neutral species are equal to one,[54] therefore concentrations of $M(NO_3)_n(TODGA)_{m(org)}$ were used for all computations.

In order to interpret the linear regression results following assumptions were applied:

- Tracer amounts of Am^{3+} and Eu^{3+} don't contribute to the ionic strength.

- Eu^{3+} and Am^{3+} are not hydrolyzed in 4 mol L^{-1} HNO_3.[55]

- Activity coefficients for neutral species are equal to one.[54]

There is some evidence from experimental spectroscopic data (mostly Raman and Infra-Red), Nuclear Magnetic Resonance data and molecular dynamic simulations for the existence of weak HNO_3^0 ion pairs in relativity concentrated aqueous solutions of nitric acid.[56–61] Comprehensive review of the experimental data is available[62] and according to this review values of HNO_3^0 stability (dissociation) constants at infinite dilution (K_a^0) vary significantly, from 10 to 40. Such a large difference in K_a^0 can be explained by the problems associated with experimental or theoretical determination of stability constants of weak ion pairs and strongly indicates that uncertainty associated with this value is large.[63,64] In this work apparent stability constant of HNO_3^0 at 4 mol L^{-1} (K_a) and its 1σ standard deviation was estimated based on literature data as 25 ± 10. This value is in a good agreement with most of the literature values discussed by Levanov and co-workers.[62] The degree

of HNO_3 dissociation at 4 mol L^{-1} (α) can be calculated from estimated dissociation constant ($K_a = 25$) using Ostwald dilution law and it can be shown that 88% of HNO_3 is dissociated.

The assumed extraction mechanism is presented in eqn (3):[30]

$$M_{(aq)}{}^{n+} + 3NO_{3(aq)}{}^- + m\text{TODGA}_{(org)} \leftrightarrow \\ M(NO_3)_3(\text{TODGA})_{m(org)} \quad (3)$$

where m (number of TODGA molecules) in the extracted specie was determined by slope analysis.

The apparent equilibrium extraction constant (K_{ex}) for the reaction in eqn (3) is defined as:

$$K_{ex} = \frac{\left[M(NO_3)_3\text{TODGA}_{m\,(org)}\right]}{\left[\gamma_{M^{n+}}M_{(aq)}{}^{n+}\right]\left[\gamma_{NO_3^-}\left[NO_{3(aq)}{}^-\right]\right]^n\left[\text{TODGA}_{(org)}\right]^m} \\ \sim \frac{D_m}{\left[\right.} \quad (4)$$

Activity coefficients of free nitrate in the aqueous phase were calculated with extended SIT theory according to ref. 65:

$$\log_{10} \gamma_{NO_3^-} = -z_i{}^2 D_H + \sum_j \varepsilon_{H^+}(i,j,I_m) \\ + \varepsilon_{NO_3^-}(i,j,I_m)\log_{10}(I_m)m_j \quad (5)$$

where $\varepsilon(H^+, NO_3^-) = 0.07$.[66]

Thus when combined with distribution ratio (eqn (1)) the equation can be rearranged into the form of eqn (6).

$$\log D_m = m \log\left[\text{TODGA}_{(org)}\right] + n \log\left[\gamma_{NO_3^-}NO_{3(aq)}{}^-\right] \\ + \log K_{ex} \quad (6)$$

For the polar diluents, TODGA concentration of 5, 20 and 40 mmol L^{-1} were used, whereas for alkanes concentration of TODGA was 1, 2 and 5 mmol L^{-1}. All the extraction experiments for stoichiometry determination were performed at 298 ± 0.2 K. For the free nitrate concentration in the aqueous phase equilibrium values obtained from the nitric acid extraction experiments were used.

The activity coefficients of TODGA in the organic diluents taken to be equal to unity in this work. However, the transport of water, nitric acid and nitrate groups into the organic phase during the contacting could possibly lead to the binding of the free TODGA ligand. Therefore, the determined stoichiometry from the slope analysis has only limited validity within the range of tested TODGA concentrations. The uncertainties of the linear regression are presented as one standard deviation.

2.5. Determination of the thermodynamic parameters

Solvent extraction of Am^{3+} and Eu^{3+} *via* TODGA was studied at different temperatures (288 K, 298 K and 308 K). Distribution ratios determined at these temperatures were used to compute extraction constant (K_{ex}). For the calculation of K_{ex} in different diluents the stoichiometry of Eu(Am):TODGA complexes for each type of diluent derived from slope analysis presented in the Table 3 were used. Natural logarithm of K_{ex} was plotted as a function of temperature (T^{-1}) and standard enthalpy change and the standard entropy change were derived from this plot (Van't Hoff's plot) using eqn (7). The standard change of Gibbs energy was thereafter calculated using eqn (8).

$$\ln K_{ex} = \frac{-\Delta H_R^0}{RT} + \frac{\Delta S_R^0}{R} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

3. Results and discussion

3.1. Distribution ratios and separation factors

Experiments with pure diluents without TODGA showed that extraction of europium or americium into pure diluent doesn't occur.

The obtained distribution ratios for Eu^{3+} and Am^{3+} in the different pristine diluents at 298 ± 0.2 K are presented in Fig. 1A and B, respectively. The results for the diluents pre-saturated with acid are shown in Fig. 2A and B. As it is shown in Fig. 1A and B, and Fig. 2A and B in extraction experiments performed
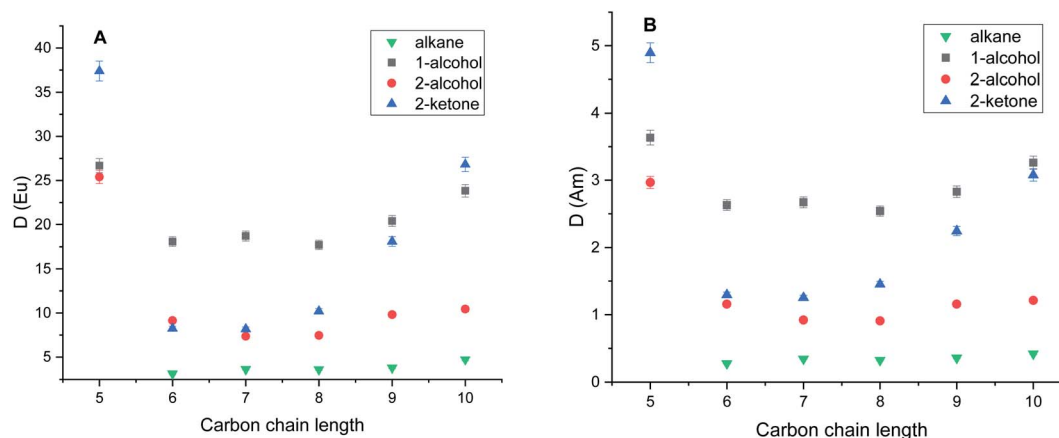

Fig. 1 Dependence of distribution ratios of Eu^{3+} (A) and Am^{3+} (B) on the diluent type and its carbon chain length in pristine solvents. The concentration of TODGA was 20 mmol L^{-1} for polar diluents and 2 mmol L^{-1} for alkanes.
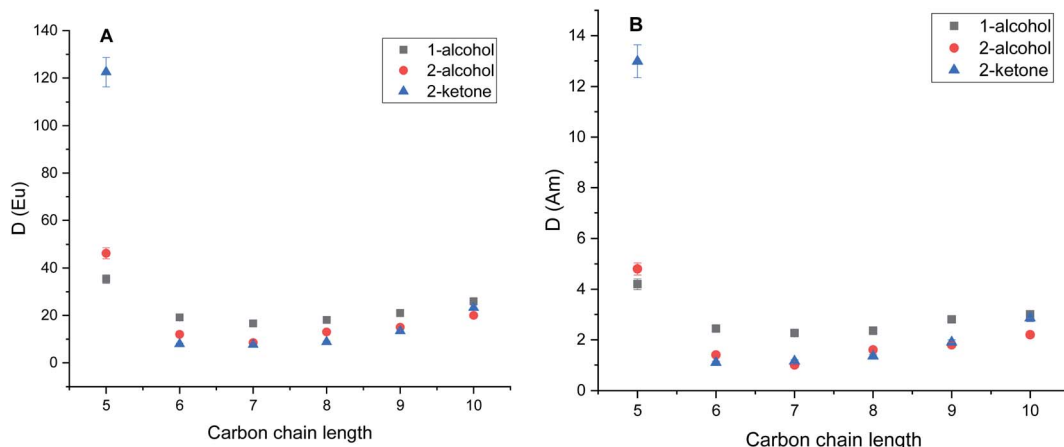
Fig. 2 Dependence of distribution ratios of Eu^{3+} (A) and Am^{3+} (B) on the diluent type and its carbon chain length in solvents, pre-saturated with HNO_3.

with TODGA dissolved in polar diluents, the distribution ratios of both europium and americium showed significant dependence on the diluent type as well as carbon chain length. This behavior was observed in both pre-conditioned as well as pristine solvents. Significant increase of the distribution ratios was observed in diluents with 5 carbon atoms in chain, regardless of the diluent type used. Concentration of TODGA in alkane diluents was kept 2 mmol L^{-1} in order to keep D-ratios below 150. In the case of alkanes, pentane was not used as diluent due to its low viscosity.

It is clear from Fig. 1A and B that the type of diluent as well as the length of the carbon chain have a substantial effect on the distribution ratio of europium and americium. Generally, the distribution ratio in polar diluents increases with the increase of the carbon chain length except for chain with 5 carbon atoms. Carbon chain length has a profound effect in the case of ketone diluents. It is note-worth to point out on the difference between primary and secondary alcohols with respect to distribution ratios while position of the hydroxyl group further in carbon chain leads to the significant decrease of the

distribution ratio. In the case of alkane diluents, the change of the distribution ratios was insignificant with the increase of the carbon chain length. In solvents pre-saturated with nitric acid a slight increase of the distribution ratio was observed while penta-2-one showed significant increase in distribution ratios for both Am^{3+} and Eu^{3+}. The increase of distribution ratios can be addressed to the higher free nitrate concentration in the aqueous phase at the extraction equilibrium. However, the trends regarding the diluent type as well as the carbon chain were the same as in pristine solvents. The separation factors between Eu^{3+} and Am^{3+} presented in the Fig. 3 show a similar behavior as the distribution ratios of Eu and Am with respect to their dependence on carbon chain length.

The observed separation factors in the secondary alcohols were higher for all carbon chain lengths when compared to primary alcohols despite aforementioned lower distribution ratios. We observed the significant increase in the separation factors in the alkane diluents when compared to the polar ones. In alkane diluents, the separation factor did not show statistically significant variations with the increase of carbon chain
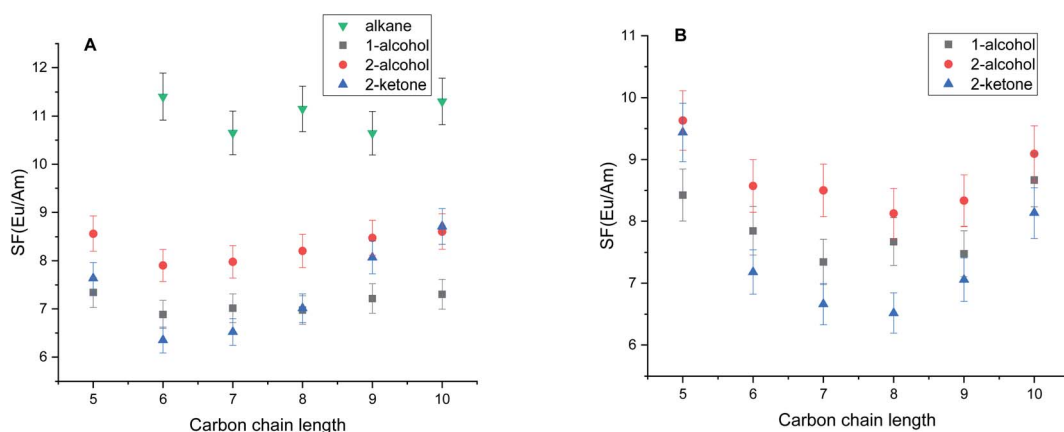

Fig. 3 The dependence of separation factors between Eu^{3+} and Am^{3+} on the diluent type and its carbon chain length (A) pristine solvent (B) pre-saturated solvent. The concentration of TODGA was 20 mmol L^{-1} for polar diluents and 2 mmol L^{-1} for alkanes.

unlike in other diluent types. In solvents pre-saturated with nitric acid slight increase of separation factors for Eu³⁺ from Am³⁺ was observed in all three polar diluent families while maintaining the similar visual trend over the carbon chain length as in non-conditioned solvents.

3.2. Extraction of nitric acid into the diluent

The extraction of nitric acid into various diluents is shown in Fig. 4. Alkane diluent type is omitted in presented results, as this diluent type did not extract nitric acid and behaves like an inert diluent. As shown in Fig. 4, the extraction of nitric acid into organic phase always increases with its initial concentration in aqueous phase, and decreases with the carbon chain length of the diluent. The non-linear behavior (Fig. 4) could be an effect of the organic phase dielectric properties changes due to the pre-saturating of the diluent with the water before the nitric acid introduction. The water extraction by diluents was clearly visible when following the water level in graduated cylinder during contacting, however not quantified by *i.e.* Karl Fischer titrations. The data for the water absorption quantities in the pure diluents are known and available from the IUPAC compilations.[67–74]

Higher concentrations of nitric acid in organic phase may result in change of intermolecular interactions and thus contribute to deviation from linearity. Therefore, it cannot be assumed that the same forces will act on the nitric acid in the case of different diluents.

While differences of acid extraction between primary and secondary alcohols are minor (if any), ketones with more than 6 carbon atoms in the alkyl chain extract significantly less nitric acid than alcohol diluents. For example the equilibrium concentration of nitric acid in the organic phase is *ca.* 11% lower for 2-heptanone when compared to 2-heptanol and 20% lower in case of 2-decanone *versus* 2-decanol. The lower concentration of nitric acid in long carbon chained ketones yielding to lower dielectric constant of the saturated diluent. This behavior might explain the increase of the distribution ratios for Eu³⁺ and Am³⁺ for the longer carbon chained ketones as shown in Fig. 1. The lower extraction of nitric acid is presumably caused by the inability of longer carbon chain ketones to act as a hydrogen bonding donors. In general, the extraction of acid followed the order according to alkyl chain length 5 > 6 > 7 > 8 > 9–10 for all diluent types. Equilibrium concentrations of nitric acid in the aqueous phase after contacting with each diluent was determined and are listed in the Table 2.

3.3. Stoichiometry of the extracted species

The stoichiometry of the extracted species were determined by the slope analysis of the distribution ratios plotted against the
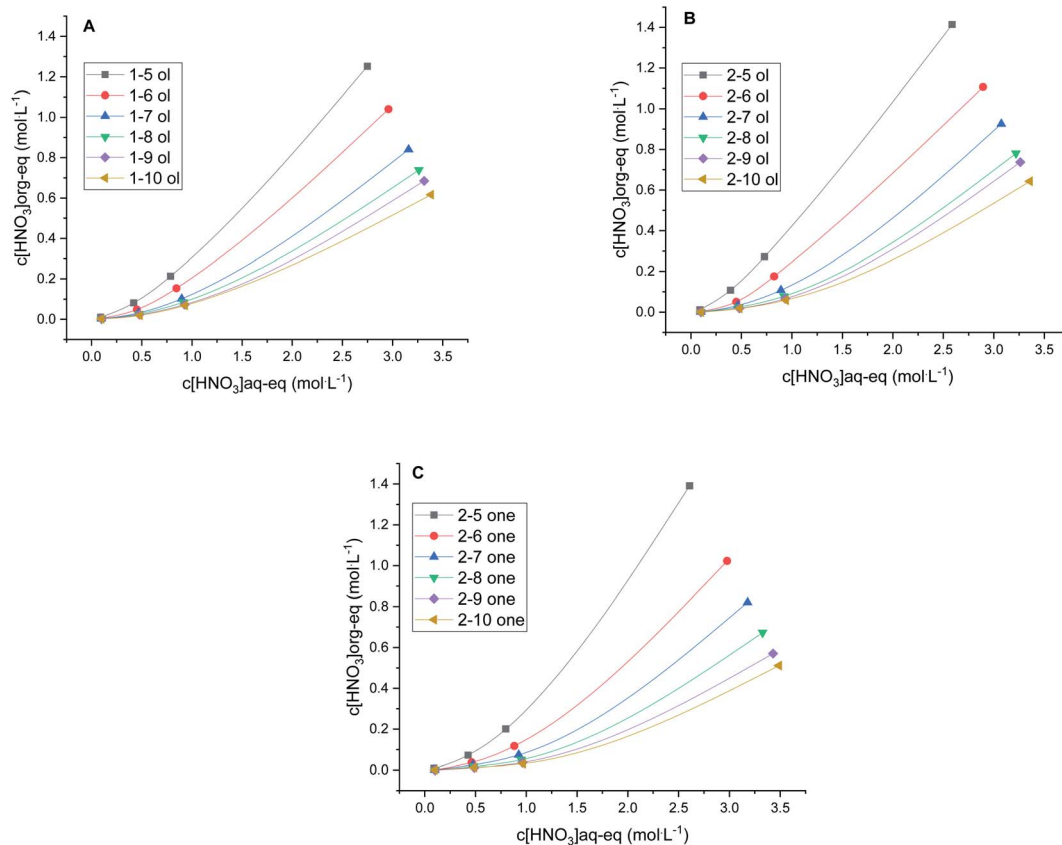

Fig. 4 Equilibrium concentrations of nitric acid in organic phase against its equilibrium concentration in the aqueous phase (A) primary alcohols, (B) secondary alcohols, (C) secondary ketones. Full lines in plots are only for the eye guidance.

Table 2 Equilibrium concentrations of nitric acid in the aqueous phase after contacting 4 mol L^{-1} HNO$_3$ solution with different diluents

Diluent	$C_{(eq)}$HNO$_{3(aq)}$ (mol L^{-1})	Diluent	$C_{(eq)}$HNO$_{3(aq)}$ (mol L^{-1})	Diluent	$C_{(eq)}$HNO$_{3(aq)}$ (mol L^{-1})
1-Pentanol	2.75 ± 0.03	2-Pentanol	2.59 ± 0.03	2-Pentanone	2.60 ± 0.03
1-Hexanol	2.96 ± 0.03	2-Hexanol	2.90 ± 0.03	2-Hexanone	2.98 ± 0.03
1-Heptanol	3.16 ± 0.03	2-Heptanol	3.09 ± 0.03	2-Heptanone	3.19 ± 0.03
1-Octanol	3.25 ± 0.03	2-Octanol	3.22 ± 0.03	2-Octanone	3.33 ± 0.03
1-Nonanol	3.31 ± 0.03	2-Nonanol	3.27 ± 0.03	2-Nonanone	3.42 ± 0.03
1-Decanol	3.39 ± 0.03	2-Decanol	3.36 ± 0.03	2-Decanone	3.43 ± 0.03

TODGA concentration in the organic phase in the logarithmic scale. By this method the apparent stoichiometry of the extraction reaction was determined with respect to the TODGA molecules surrounding the extracted metal complex. The obtained results are presented in the Table 3.

The obtained data indicate that stoichiometry of extracted europium and americium complexes differ from each other in all the types of polar diluents. However, the apparent stoichiometry does not variate significantly with the change of the carbon chain length within the same diluent type. The slope analysis shows that Eu^{3+} is extracted predominantly as 1 : 3 complex whereas Am^{3+} as a mix of 1 : 2 and 1 : 3 complexes in the polar diluents. The determined stoichiometry in alkane diluents indicates extraction of 1 : 3 and 1 : 4 complexes within the presented concentration range of TODGA for both Eu^{3+} and Am^{3+}. In general, the observed values are consistent with the previously reported stoichiometries of extracted complexes of An^{3+} and Ln^{3+} with diglycolamides.[38,45,75–78] Its noteworthy that 1 : 4 coordination, although observed also in other works[30,38,79] is not possible within the first solvation shell of Eu^{3+} and Am^{3+} due to geometrical hindering.[80] As spectroscopic methods *i.e.* Time Resolved Laser Fluorescence Spectroscopy (TRLFS) target the inner coordination sphere of the extracted ion the outer sphere coordination remains unresolved. One can therefor speculate about the explanation of the observed effect due to additional complexation by TODGA molecule in the second

solvation shell[81] or as the consequence of TODGA aggregation into the form of micelles.[82]

3.4. Thermodynamic parameters

The extraction of europium as well as of americium was exothermic in all tested diluents. In alkane diluents, the decrease of distribution ratios with increasing temperature was the steepest. This behavior is in agreement with previously reported results.[44,75] The derived thermodynamic parameters for the extraction of Eu^{3+} and Am^{3+} from 4 mol L^{-1} HNO$_3$ by TODGA dissolved in various diluents are shown in Tables 4 and 5. The values of nitrate concentrations listed in Table 2 were used to calculate activity coefficients of free nitrate using extended SIT. In general, the observed values show similar behavior as in the previously published studies mainly with respect to exothermic behavior and negative entropy change values.[75,83,84] From the derived thermodynamic parameters, the Gibbs energy change $(-\Delta G^0)$ follows the order alkanes $\gg$ primary alcohols $\approx$ secondary alcohols $\approx$ ketones. However the change of enthalpy of extractions shows difference between primary or secondary alcohols and ketones, where the latter show smaller exothermic nature of extraction. This also leads to the different $(\Delta H^0/\Delta S^0)$ ratios for each diluent family probably according to the disturbances in the structure of diluents during the extraction process. This explanation is feasible when taking in account more ordered structure of alcohol diluents

Table 3 Values of slopes from log–log plots of the extraction of Eu^{3+} and Am^{3+} from 4 M HNO$_3$ by TODGA in various organic diluents. Uncertainties are given as two standard deviations. Pearson's R was >0.99 for all performed regressions

Diluent	Eu^{3+} : TODGA	Am^{3+} : TODGA	Diluent	Eu^{3+} : TODGA	Am^{3+} : TODGA
Hexane	3.40 ± 0.05	3.40 ± 0.05	2-Pentanol	2.82 ± 0.02	2.46 ± 0.02
Heptane	3.7 ± 0.1	3.7 ± 0.1	2-Hexanol	2.81 ± 0.02	2.43 ± 0.02
Octane	3.7 ± 0.1	3.7 ± 0.1	2-Heptanol	2.80 ± 0.02	2.44 ± 0.03
Nonane	3.5 ± 0.1	3.4 ± 0.1	2-Octanol	2.80 ± 0.01	2.44 ± 0.04
Decane	3.3 ± 0.1	3.3 ± 0.1	2-Nonanol	2.83 ± 0.05	2.46 ± 0.02
			2-Decanol	2.82 ± 0.03	2.53 ± 0.03

Diluent	Eu^{3+} : TODGA	Am^{3+} : TODGA	Diluent	Eu^{3+} : TODGA	Am^{3+} : TODGA
1-Pentanol	2.80 ± 0.01	2.35 ± 0.03	2-Pentanone	2.84 ± 0.01	2.40 ± 0.05
1-Hexanol	2.74 ± 0.01	2.28 ± 0.02	2-Hexanone	2.84 ± 0.09	2.40 ± 0.05
1-Heptanol	2.74 ± 0.005	2.32 ± 0.02	2-Heptanone	2.90 ± 0.05	2.40 ± 0.05
1-Octanol	2.74 ± 0.005	2.25 ± 0.02	2-Octanone	3.00 ± 0.05	2.50 ± 0.05
1-Nonanol	2.77 ± 0.01	2.31 ± 0.02	2-Nonanone	3.00 ± 0.02	2.50 ± 0.05
1-Decanol	2.86 ± 0.01	2.33 ± 0.02	2-Decanone	3.00 ± 0.03	2.50 ± 0.05

Table 4 Standard molar Gibbs energy $\Delta G_{298\ K}^0$ enthalpy $\Delta H_{298\ K}^0$, and entropy $\Delta S_{298\ K}^0$ changes and natural logarithm of apparent extraction constants for the extraction of Eu^{3+} in tested systems. In polar diluents, concentration of TODGA was 20 mmol L^{-1}, whereas in alkanes 2 mmol L^{-1} concentration of TODGA was used

Diluent	$\ln K_{ex298\ K}$	$\Delta G_{298\ K}^0$ (kJ mol^{-1})	$\Delta H_{298\ K}^0$ (kJ mol^{-1})	$\Delta S_{298\ K}^0$ [J $(mol\ K)^{-1}$]
1-Pentanol	11.6 ± 0.5	-28.6 ± 2.0	-41.8 ± 2.1	-44.2 ± 2.2
1-Hexanol	10.6 ± 0.4	-26.3 ± 1.9	-40.4 ± 2.0	-47.3 ± 2.4
1-Heptanol	10.4 ± 0.4	-25.7 ± 1.8	-40.2 ± 2.0	-48.4 ± 2.4
1-Octanol	10.2 ± 0.4	-25.3 ± 1.8	-46.6 ± 2.3	-71.5 ± 3.6
1-Nonanol	10.4 ± 0.4	-25.7 ± 1.8	-45.7 ± 2.3	-67.2 ± 3.4
1-Decanol	10.6 ± 0.4	-26.3 ± 1.9	-43.2 ± 2.2	-56.9 ± 2.8
2-Pentanol	11.8 ± 0.5	-29.3 ± 2.1	-46.4 ± 2.3	-57.4 ± 2.9
2-Hexanol	10.3 ± 0.4	-25.5 ± 1.8	-40.5 ± 2.0	-50.3 ± 2.5
2-Heptanol	9.7 ± 0.4	-24.2 ± 1.7	-41.4 ± 2.1	-57.8 ± 2.9
2-Octanol	9.6 ± 0.4	-23.8 ± 1.7	-42.3 ± 2.1	-62.3 ± 3.1
2-Nonanol	9.9 ± 0.4	-24.6 ± 1.7	-36.4 ± 1.8	-39.5 ± 2.0
2-Decanol	10.0 ± 0.4	-24.8 ± 1.8	-40.0 ± 2.0	-51.1 ± 2.6
2-Pentanone	12.3 ± 0.5	-30.4 ± 2.1	-46.3 ± 2.3	-53.4 ± 2.7
2-Hexanone	10.2 ± 0.4	-25.3 ± 1.8	-28.4 ± 1.4	-10.4 ± 0.5
2-Heptanone	10.2 ± 0.4	-25.2 ± 1.8	-30.1 ± 1.5	-16.5 ± 0.8
2-Octanone	10.6 ± 0.4	-26.2 ± 1.9	-23.1 ± 0.12	10.3 ± 0.5
2-Nonanone	$11.0 \pm 0.$	-27.3 ± 1.9	-29.5 ± 1.5	-7.3 ± 0.4
2-Decanone	11.4 ± 0.5	-28.2 ± 2.0	-32.9 ± 1.6	-15.6 ± 0.8
Hexane	18.2 ± 0.7	-45.0 ± 3.2	-126.7 ± 6.3	-273.9 ± 13.7
Heptane	19.5 ± 0.8	-48.4 ± 3.4	-124.4 ± 6.2	-255.0 ± 12.8
Octane	19.2 ± 0.8	-47.7 ± 3.4	-125.1 ± 6.3	-260.0 ± 13.0
Nonane	19.4 ± 0.8	-48.1 ± 3.4	-124.2 ± 6.2	-255.3 ± 12.8
Decane	18.8 ± 0.8	-46.7 ± 3.3	-120.3 ± 6.0	-247.2 ± 12.4

Table 5 Standard molar Gibbs energy $\Delta G_{298\ K}^0$ enthalpy $\Delta H_{298\ K}^0$, and entropy $\Delta S_{298\ K}^0$ changes and natural logarithm of apparent extraction constants for the extraction of Am^{3+} in tested systems. In polar diluents, concentration of TODGA was 20 mmol L^{-1}, whereas in alkanes 2 mmol L^{-1} concentration of TODGA was used

Diluent	$\ln K_{ex298\ K}$	$\Delta G_{298\ K}^0$ (kJ mol^{-1})	$\Delta H_{298\ K}^0$ (kJ mol^{-1})	$\Delta S_{298\ K}^0$ [J $(mol\ K)^{-1}$]
1-Pentanol	7.8 ± 0.3	-19.3 ± 1.4	-31.6 ± 1.6	-41.3 ± 2.1
1-Hexanol	6.9 ± 0.3	-17.1 ± 1.2	-30.5 ± 1.5	-45.1 ± 2.3
1-Heptanol	6.8 ± 0.3	-16.8 ± 1.2	-29.4 ± 1.5	-42.3 ± 2.1
1-Octanol	6.4 ± 0.3	-15.8 ± 1.1	-34.7 ± 1.7	-63.7 ± 3.2
1-Nonanol	6.6 ± 0.3	-16.4 ± 1.2	-34.6 ± 1.7	-61.1 ± 3.1
1-Decanol	6.7 ± 0.3	-16.6 ± 1.2	-34.5 ± 1.7	-60.0 ± 3.0
2-Pentanol	8.3 ± 0.3	-20.5 ± 1.4	-35.1 ± 1.8	-49.2 ± 2.5
2-Hexanol	6.7 ± 0.3	-16.7 ± 1.2	-27.2 ± 1.4	-35.3 ± 1.8
2-Heptanol	6.3 ± 0.3	-15.5 ± 1.1	-28.8 ± 1.4	-44.6 ± 2.2
2-Octanol	6.1 ± 0.2	-15.0 ± 1.1	-29.7 ± 1.5	-49.1 ± 2.5
2-Nonanol	6.4 ± 0.3	-15.8 ± 1.1	-24.2 ± 1.2	-28.3 ± 1.4
2-Decanol	6.6 ± 0.3	-16.2 ± 1.1	-22.3 ± 1.1	-20.4 ± 1.0
2-Pentanone	8.6 ± 0.3	-21.2 ± 1.5	-35.8 ± 1.8	-48.7 ± 2.4
2-Hexanone	6.5 ± 0.3	-16.1 ± 1.1	-16.7 ± 0.8	-1.9 ± 0.1
2-Heptanone	6.3 ± 0.3	-15.7 ± 1.1	-18.8 ± 0.9	-10.5 ± 0.5
2-Octanone	6.8 ± 0.3	-16.7 ± 1.2	-13.2 ± 0.7	12.0 ± 0.6
2-Nonanone	7.2 ± 0.3	-17.7 ± 1.3	-18.1 ± 0.9	-1.2 ± 0.1
2-Decanone	7.2 ± 0.3	-17.8 ± 1.3	-23.7 ± 1.2	-19.8 ± 1
Hexane	15.5 ± 0.6	-38.5 ± 2.7	-121.1 ± 6.1	-277.4 ± 13.9
Heptane	16.6 ± 0.7	-41.0 ± 2.9	-114.7 ± 5.7	-247.2 ± 12.4
Octane	16.8 ± 0.7	-41.6 ± 2.9	-116.8 ± 5.8	-252.2 ± 12.6
Nonane	16.8 ± 0.7	-41.7 ± 3.0	-118.5 ± 5.9	-257.5 ± 12.9
Decane	15.7 ± 0.6	-39.0 ± 3.0	-112.4 ± 5.6	-246.4 ± 12.3

when compared to ketones, due to the ability alcohols to form hydrogen bonds within the diluent.

4. Conclusions

The performed studies indicate that diluent plays significant role in the solvent extraction of Eu^{3+} and Am^{3+} with TODGA as

an extracting agent. Examinations of the effect of carbon chain length revealed that carbon chain length has significant impact on the extraction outcome in the polar diluents. Diluents with 5 carbon atoms in aliphatic chain showed higher distribution ratios as well as separation factors than longer chained homologues, leading to the concave shaped distribution ratios dependence on the carbon chain length. However, the extraction behavior in 5 carbon chain diluents could not be reasonably explained. It was shown that the diluents apart from alkanes extract a significant amount of nitric acid during the contacting with aqueous phase. This in conjunction with water absorption will lead to significant changes of the dielectric constant organic phase and the electrical forces affecting the solubility of the extracted species in the organic phase. The determined D-values and separation factors correlate with the amount of extracted HNO_3 and water into the organic phase for diluents with carbon chain C6–C10. However, this correlation is not straightforward between the different diluent types as well as for C5 diluents which could mean that more than one phenomenon might take place.

Extraction process for both Eu^{3+} and Am^{3+} with TODGA is enthalpy driven in all studied diluent types. Performed studies suggest that in the alkanes extractions behave significantly more exothermic than in the other diluents. Moreover, in the case of alkanes, both distribution ratios as well as separation factors are significantly higher than in any other type of diluents.

The stoichiometry investigation indicates that at least three different metal complexes are extracted into the organic phase dependable on the used diluent. The average ligand number of TODGA molecules in the extracted complex was typically lower for Am^{3+} when compared with Eu^{3+} except for alkane diluents.

Author contributions

I. K.: conceptualization, resources, methodology, formal analysis, investigation, visualization, writing – original draft, writing – review & editing. M. F.: methodology, investigation, writing – review & editing. C. E.: formal analysis, writing – review & editing. A. V. M. methodology, formal analysis, investigation, writing – original draft, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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