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Citation for the original published paper (version of record):
Lyseid Authen, T., Tebikachew, B., Foreman, M. et al (2022). A comparison on the use of DEHBA or TBP as extracting agent for tetra- and hexavalent actinides
in the CHALMEX Process. Journal of Radioanalytical and Nuclear Chemistry, 331(12): 5137-5145.
http://dx.doi.org/10.1007/s10967-022-08481-0

Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-022-08481-0

A comparison on the use of DEHBA or TBP as extracting agent for tetra- and hexavalent actinides in the CHALMEX Process

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Received: 22 April 2022 / Accepted: 3 August 2022

Abstract
The Chalmers Grouped ActiNide EXtraction process is a solvent extraction process for the homogeneous recycling of spent nuclear fuel. The use of TBP for the extraction of tetra- and hexavalent actinides can be problematic for several reasons, including troublesome degradation products causing crud formation, decreased extraction yield and the possibility of explosive red oil reactions. Here, the substitution of TBP by a *N,N*-dialkyl monoamide, DEHBA, is investigated. The findings suggest that DEHBA can be a suitable extracting agent for use in the CHALMEX solvent, although identified drawbacks need to be further investigated.

Keywords GANEX · CHALMEX · DEHBA · Spent nuclear fuel recycling

Introduction

The recovery of tetra- and hexavalent actinides, predominantly uranium and plutonium, from irradiated nuclear fuel using the extractant tri-*n*-butyl phosphate (TBP) has been done on an industrial scale since the early 1950's [1, 2]. TBPs high affinity and loading capacity for U(VI) and Pu(IV) made it the benchmark molecule for the separation of uranium and plutonium from fission products in the *P*lutonium *U*ranium *R*eduction *Ex*traction (PUREX) process [1, 3, 4]. The molecules structure can be seen in Fig. 1 (left). TBP has a high resistance towards both radiolysis and hydrolysis. Its degradation products are primarily mono-butyl phosphate and dibutyl phosphate, and other less abundant degradation products. They are known to cause both red oil reactions and promote crud formation. Both aspects can have serious implications in reprocessing plants [5–9]. Furthermore, the presence of phosphor in the molecule is often referred to as being problematic in modern processes, in which the aim is typically to develop CHON-abiding processes. Adhering to the CHON-principle (only molecules containing C, H, O and N) allows for complete incineration of the final, spent solvent, thus minimizing the volume of the final waste [10]. However, the Chalmers GANEX (CHALMEX) diluent, phenyl trifluoromethyl sulfone (FS-13), which is seen in Fig. 1 (right), is both fluorinated and sulfonated. Here, solidifying the final organic waste has been suggested as a treatment option [11].

Possible alternatives to TBP as an extracting agent have received a lot of research efforts in the past decades. A promising group of extractants include the *N,N*-dialkyl monoamides, and especially the monoamide *N,N*-di-(2-ethylhexyl) butyramide (DEHBA), as seen in Fig. 2 [12–16]. Not only has the monoamide class of extractants been shown to be comparable or better than TBP in terms of U(VI) and Pu(IV) separation from the fission products, but they also have comparable radiolytic stability, compared to TBP [17–23]. Additional benefits of the *N,N*-dialkyl monoamide extractants are the less problematic degradation products. While TBP does not extract the lanthanides to any significant extent in the CHALMEX system, DEHBA yields D-ratios > 1 for both Sm and Eu in cyclohexanone [24]. Similar trends are seen for the corrosion products, where DEHBA consistently yielded higher D-ratios than TBP. Especially for Co and

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Published online: 02 September 2022

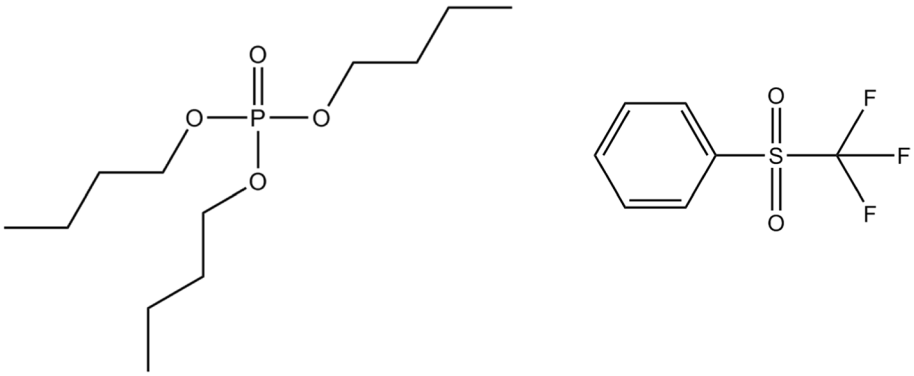

Fig. 1 The molecular structure of **a** tri-*n*-butyl phosphate (TBP) and **b** phenyl trifluoromethyl sulfone (FS-13)

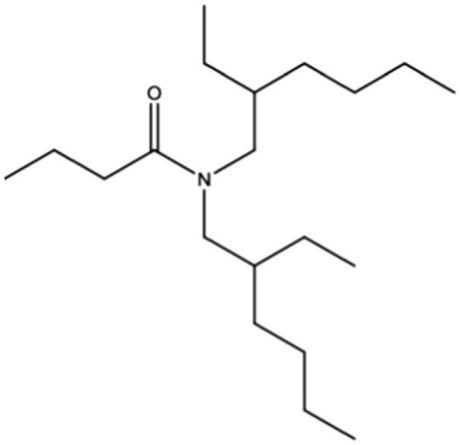

Fig. 2 The molecular structure of *N,N*-di-(2-ethylhexyl)butyramide (DEHBA)

Mn, the D-ratios were > 1. For the fission product extraction however, DEHBA yields lower D- ratios than TBP for all the fission products with D > 1 (Mo, Pd, Ag, Cd and Sb), except for Zr [24].

The use of DEHiBA in the GANEX 1st cycle has been proven to recover more than 99.99% of the uranium, and so the main focus in this work is the ability of DEHBA to recover uranium and plutonium [25, 26].

Theory

The surface tension is a measure of the force required to form a surface on a liquid. Since liquid molecules at the surface are surrounded by fewer liquid molecules than the bulk liquid molecules, the surface molecules interact with each other to a higher extent than in the bulk liquid. Interfacial tension is practically the same force as surface tension, but between two liquids rather than between a liquid and air as for surface tension.

Both surface tension and density are important parameters to consider in solvent extraction as they play an important role in the formation and size of droplets. Generally, the smaller the droplet, the greater the surface area of contact between the two liquids and also the greater the mass transfer rate, at least up to a certain point. At one point the droplet size becomes so small that the droplets start behaving more like individual spheres and the rate of mass transfer will start to decrease again [27].

Density is an important parameter for the coalescence and separation of the organic and the aqueous phase. A sufficiently large density difference in a two-phase system will cause the two phases to spontaneously separate into two distinct layers. For systems with too similar densities between the phases, different phenomena can occur: phases can be "layered" vertically, i.e. side by side, or formation of a three-phase system can happen. In the latter, you'll see parts of the heavy phase layered over the aqueous phase. It is also important to keep in mind that in solvent extraction processes in which the metal content is high, the density of the organic phase will increase as extraction proceeds, while it will decrease for the aqueous phase. In systems with a heavier aqueous phase and lighter organic phase, the density difference will thus decrease [28].

Surface active agents (surfactants) are molecules with a polar- and non-polar part, or hydrophobic and hydrophilic, respectively. In a solvent extraction system, a surfactant can be added to lower the surface tension. The surfactant will then dissolve its hydrophobic part in the organic phase, and its hydrophilic part in the aqueous phase. In systems in which the surfactant is also an extractant, an increase in surfactant/extractant concentration is typically associated with an increased rate of extraction [29].

Experimental

Unless otherwise stated, the DEHBA solvent constitutes 30% v/v DEHBA and 70% v/v FS-13, and the TBP solvent 30% v/v TBP and 70% v/v FS-13, pre-equilibrated with 4 M HNO_3. The pre-equilibration is necessary to minimize

effects of mutual solubility of the organic and aqueous phases in each other.

Physical properties of the solvents were measured using a tensiometer (Sigma 700, Attension, using a du Noüy ring). Each measurement was repeated at least twice, and the average measured value is reported here. Surface tension was measured against air, while interfacial tension (IFT) was measured between the solvent and 4 M HNO_3. All measurements were performed at room temperature of 295 K.

The DEHBA solvent was irradiated using a ^{60}Co gamma-source (Gamma cell 220, Atomic Energy of Canada ltd). To replicate process conditions, the solvent was irradiated aerated and in contact with 4 M HNO_3. After irradiation, the organic phase was used for extractions from 4 M HNO_3 immediately after collection.

For the acid extraction experiments, equal volumes (500 µL) of the respective organic phases were contacted with an equal volume of nitric acid with varying concentrations ranging from 0.01 to 4 M using an IKA Vibrax VXR, 1500 rpm shaker. The contact time was 15 min and the temperature controlled by a thermostatic bath (Grant Instruments, TC120 Heated Circulating Bath) at 298 K. Both initial acid concentration and the resulting acid concentration after contacting with the organic phase were titrated at least twice. The organic phase was then contacted with MQ water for 5 min, and the MQ water was titrated for mass balance purposes. Errors were taken as the mass balance deviation.

Batch solvent extraction was performed always using a phase ratio $\Theta = 1$ and a minimum volume of each phase of 400 µL. Contacting was done using an IKA Vibrax VXR, 1500 rpm shaker and thermostatic bath. The radionuclides were added at trace concentrations and all radionuclides were investigated in isolated systems, except for Am and Eu which were investigated together. The activity of the radionuclides were 323 kBq mL^{-1} for Pu, 281 kBq mL^{-1} for Am, 278 kBq mL^{-1} for Eu and 30 kBq mL^{-1} for Np. The concentration of the U-stock solution was 1.1 M, diluted to 10^{-4} M using 4 M HNO_3. All data points represent the average of triplicate samples, where the uncertainty is taken as the standard deviation of the series. Unless otherwise stated, the temperature was kept at 298 K. Save for the kinetics experiments, the contact time was 1 h for all the experiments which was enough to reach extraction equilibrium. After contacting, the samples were centrifuged for 5 min to ensure complete phase separation.

Analysis

Both ^{238}Pu and ^{237}Np were analysed by taking a 100 µL aliquot of each phase and measuring them using a liquid scintillation counter (LSC, Wallac 1414 WinSpectral). The samples were dissolved in 5 mL Ultima Gold. The aqueous phase of the ^{nat}U-samples was diluted and measured using ICP-MS (Perkin Elmer NexION 2000C). 100 µL of each phase of the $^{241}Am/^{152}Eu$ system was measured on a high purity germanium detector (HPGe).

Results and discussion

The physical properties such as density, surface tension and interfacial tension plays a crucial role in solvent extraction. Here, the mentioned parameters have been measured for various versions of both the DEHBA- and the TBP-solvent, and the results are presented in Table 1.

DEHBA has a lower density than TBP, and when diluted in FS-13 the solvent density of the DEHBA solvent showed a lower density than the TBP solvent for the pre-equilibrated system. The density difference is significant with 1.28 g cm^{-3} for the TBP solvent and 1.12 g cm^{-3} for the DEHBA solvent, while the density difference is less pronounced for the pristine solvents with 1.26 g cm^{-3} for the TBP-solvent and 1.20 g cm^{-3} for the DEHBA solvent. The density of nitric acid is approximately 1.15 g cm^{-3} at 295 K and so the density difference to the pre-equilibrated DEHBA solvent is only 0.03 g cm^{-3} [30]. This can be a source of issues with phase separation under process conditions. Especially considering that metal extraction will cause a density increase of the solvent and a density decrease of the aqueous phase. This may in the worst case even lead to phase

Table 1 The density, surface tension and interfacial tension measured for various versions of the DEHBA- and TBP-solvent respectively

Solvent	Density (g cm^{-3})	Surface tension (mN m^{-1})	IFT (mN m^{-1})
DEHBA	0.837	28.70	–
30%DEHBA + 70%FS-13	1.20	27.46	–
30%DEHBA + 70%FS-13, pre-equilibrated	1.12	29.19	7.23
TBP	0.971	25.5	–
30%TBP + 70%FS-13	1.26[a]	28.5[a]	
30%TBP + 70%FS-13, pre-equilibrated	1.28[a]	25.8	12.8
FS-13	1.41	22.9	-

[a]Values reproduced from Halleröd et al. [32]

inversion, and so further hydrodynamic tests are necessary to determine the suitability of the DEHBA solvent for reprocessing applications.

The surface tension of the different solvents appears to be dominated by the extracting agent added. For both solvents, the surface tension is closer in value to that of the pure extractant, rather than to that of the pure diluent. The lower surface tension for FS-13 is somewhat surprising as it is not known to be very surface active despite its polar nature. The TBP solvent sees an increase in its surface tension upon pre-equilibration with 4 M HNO_3, which can suggest a reorientation of the TBP molecule in the solvent. Any acid extracted by the ligand will not only occupy ligand, taking it away from the phase boundary, it can also change the charge density of the solvent. For the DEHBA solvent, the opposite trend is observed; an increase in the surface tension from the pristine solvent to the pre-equilibrated solvent. This could be due to the presence of water-soluble amine impurities, which is removed upon pre-equilibration.

Interfacial tension (IFT) is perhaps more interesting than the surface tension, as the former shows the force between the solvent and the nitric acid (4 M). In contrast to earlier work reported on DEHBA and TBP in cyclohexanone, the interfacial tension of the TBP solvent is higher than that of the DEHBA solvent, while for *n*-dodecane it is the other way around [16, 31]. It has previously been shown that DEHBA has a much larger IFT towards nitric acid compared to TBP, which indicates a much higher degree of surface activity for TBP [16]. Here, the higher interfacial tension of the TBP solvent can indicate that the interaction between TBP and FS-13 to some degree prevents the TBP molecule acting like a surfactant, through e.g. micelle formation. Micelle formation is a phenomenon in which the concentration of a surfactant becomes so high that they self-assemble in colloidal aggregates. The lower IFT for the DEHBA solvent also suggests a quicker mass transfer rate compared to the TBP solvent. A lower IFT produces smaller droplets and increased surface area of contact, which is known to promote faster mass transfer rates [27].

In earlier published work, it was found that DEHBA extracts acid to the same extent as TBP, although it was mainly attributed to extraction by the diluent cyclohexanone. In later work, acid extraction by TBP was investigated, and found to be relatively high, while no acid is extracted by the current FS-13 diluent [33]. Published results have also found that nitric acid extraction by TBP occurs by both a 1:2 and a 1:1 complex formation for HNO_3:TBP [34, 35]. Here we show that the acid extraction by DEHBA is indeed comparable to the acid extraction by TBP, at least up until 2 M [HNO_3], as shown in Fig. 3. A slope analysis of the log(HNO_3) vs log(D(DEHBA)) plot yields no conclusive dependency with a slope of 0.73 and $R^2 = 0.85$. This indicates mixed complexes of HNO_3-DEHBA. At [HNO_3] > 2 M, extraction is still significant, but the extraction by TBP exceeds that of DEHBA. For both solvents, the acid extraction is a function of the acid concentration, although it appears that the acid extraction of TBP reaches its maximum at 4 M

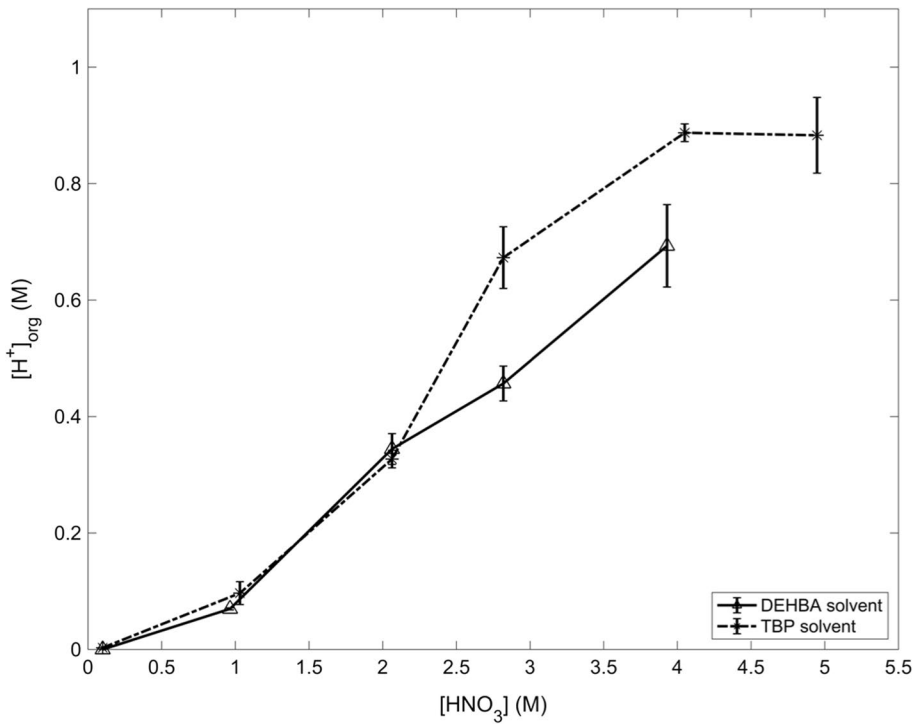

Fig. 3 [H^+] extracted by the organic phase versus initial acid concentration. Data points for TBP solvent at 1, 4 and 5 M HNO_3 are reproduced from [33]

HNO_3. Therefore, with the use of the DEHBA solvent, an additional acid scrubbing step would need to be included within the process.

Extraction tests were performed for all the actinides of interest, irrespective of expected oxidation state in the spent nuclear fuel raffinate. The results at equilibrium are presented in Table 2. None of the trivalent or pentavalent actinides are extracted to any significant degree, with D-ratios < 0.01 for Np(V), Am(III) and Eu(III). This was expected as DEHBA is known to extract the tetra- and hexavalent actinides. It has previously been found that Np(VI) is extractable with D > 1 by DEHBA from nitric acid solutions with nitrate concentration above 1 M, while D-ratios of Np(V) remained < 1 for the nitric acid range investigated [36]. While the oxidation state of Np(V) was confirmed by UV–VIS for these experiments, the speciation of Np has been shown to spontaneously distribute between Np(V, VI). Furthermore, Np is sensitive to both oxidizing and reducing agents (i.e., nitrous acid), and temperature- and acid concentration changes. The oxidation state of Np was challenging to control under the given process conditions [37–42]. In conclusion, it is expected that the Np oxidation state will be a mixture of + 5 and + 6 in spent nuclear fuel raffinate.

The distribution ratios, at equilibrium, for Pu(IV) and U(VI), were 11 and 9.4, respectively. These D-ratios yield a high separation factor over the lanthanides, here represented by Eu(III). Compared to TBP, the D-ratios are once again comparable. Halleröd et al. [43] reported D(Pu) of approximately 12 and D(U) of approximately 10.5, while D(Am) and D(Eu) were < 0.1. The D-ratios of Np cannot be directly compared as Np(V,VI) was used for the extraction by TBP in FS-13.

Pu has been shown to form both a 2:1 and a 1:1 complex with TBP. In the CHALMEX FS-13 system, the slope of Pu extraction as a function of TBP concentration is 1.27, which could be a product of co-extraction by $CyMe_4$-BTBP or adduct formation with nitric acid [33]. For the DEHBA solvent, the slope of Pu extraction shows a 2:1 complex formation, as seen in Fig. 4. This agrees with results published earlier [44]. In addition, this publication provided evidence for a 3:1 complex, which is not seen for the CHALMEX system. For uranium, a slope of 1 is seen which suggests a 1:1 complex formation with the DEHBA ligand, while a thorough study by Acher et al. showed that uranium is coordinated by two DEHBA molecules and 4 nitrate ions [44]. Slope analysis is a less robust method compared to

Table 2 The distribution ratios measured for Pu, U, Np, Am and Eu for the extraction by the DEHBA solvent from 4 M HNO_3.

	Pu(IV)	U(VI)	Np(V)	Am(III)	Eu(III)
D	11.4 ± 0.31	9.41 ± 0.51	$< 0.01 \pm < 10^{-4}$	$< 0.01 \pm < 10^{-4}$	$< 0.01 \pm < 10^{-4}$

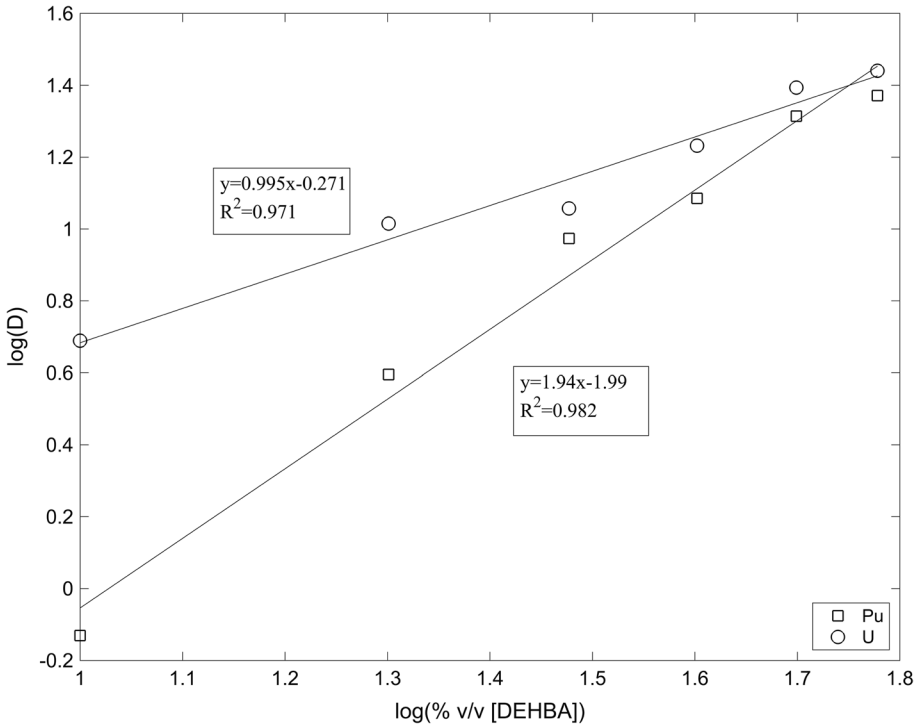

Fig. 4 The distribution ratio (D) of Pu and U as a function of % v/v DEHBA in FS-13. A linear fit to the data points, with equation and R^2, is also displayed

spectroscopic evidence such as those used by Acher et al. Furthermore, the use of different diluents can affect the complexation of ligand to metal.

The nitric acid dependency was also investigated, and the results are presented in Fig. 5. As can be seen, the D-ratios increase with increasing nitric acid for both U and Pu. The slope of D(Pu) is steeper (0.994) compared to the slope of D(U) (0.535), suggesting a stronger dependency on the nitrate content of the aqueous solution. The same tests were performed by changing the nitrate concentration only (using $NaNO_3$), which yielded the same slope for Pu. This confirms that the extraction is dependent on the nitrate concentration, rather than the acid concentration.

Earlier studies have shown that the presence of TBP in the solvent more readily promotes the hydrolytic degradation of the BTBP-molecule [17]. For comparison, no BTBP degradation products were detected in the DEHBA solvent for the same conditions and exposure time. Although not relevant for the extraction of the tetra- and hexavalent actinides, the degradation of $CyMe_4$-BTBP led to a significant decrease in both Am and Eu D-ratios. A decrease of Am and Eu D-ratios were seen also for the DEHBA solvent in the presence of $CyMe_4$-BTBP, which was attributed to water soluble DEHBA degradation products acting like masking agents for Am and Eu. For both solvents, a more problematic decrease in Np D-ratios was seen as hydrolysis progressed, mainly due to the low original D(Np) [17].

Similar, though accelerated, trends were seen for the radiolytic stability of the DEHBA solvent, whether it be linked to the loss of extracting agent or the presence of water soluble "complexing agents" (DEHBA degradation products), as shown in Table 3. For Pu, a higher D-ratio than the unirradiated value ($D_{eqm} = 11.4$) is observed for all doses. The highest D-ratio is seen after only 5 kGy, with D = 27.2, with consistently decreasing D-ratios with increasing doses. For the distribution ratio of U, the observations are less consistent. At 5 kGy, D = 13.8, which is higher than its equilibrium value ($D_{eqm} = 9.41$). This is also observed for a dose of 100 kGy, where D = 9.51 compared to D = 8.12 for 75 kGy. This could be due to the formation of less stable degradation products, which have a higher affinity for U than the original DEHBA molecule.

For the extraction of uranium and plutonium as a function of time, both ligands reach extraction equilibrium within five minutes of contact time. A surprising trend is seen in Fig. 6 for the extraction of U and Pu by DEHBA. The standard deviations of the triplicates were generally below 5% for

Table 3 The D-ratios of Pu and U respectively after gamma irradiation of the DEHBA solvent in contact with 4 M HNO_3

Dose (kGy)	D(Pu)	D(U)
5	27.2 ± 0.37	13.8 ± 0.35
20	21.6 ± 0.47	8.24 ± 0.71
75	19.9 ± 0.21	8.12 ± 0.31
100	17.5 ± 0.27	9.51 ± 0.41
250	17.7 ± 0.63	6.41 ± 0.15

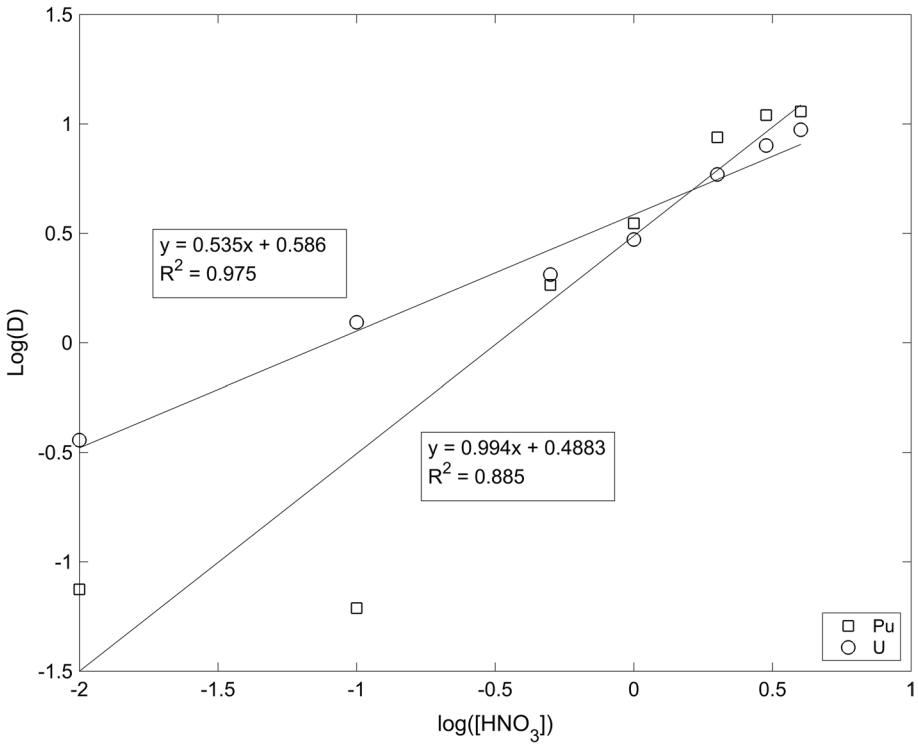

Fig. 5 The log(D) of Pu and U vs. log([HNO_3]), with linear regression lines fitted to the data points. Line equations with R^2 values are also shown

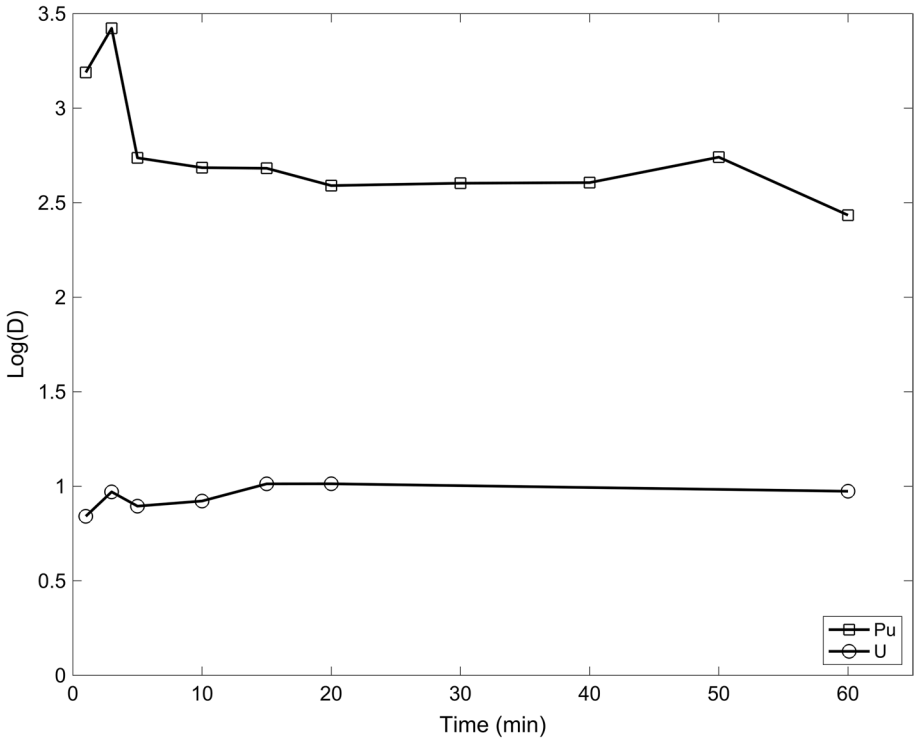

Fig. 6 The log(D) of Pu and U as a function of contact time (min). The extraction was by the pre-equilibrated DEHBA solvent from 4 M HNO_3

all dose rates, except for D(Pu) at t = 1 min, for which the uncertainty was 13% and D(U) at t = 3 min and t = 10, for which the uncertainties were 11% and 25% respectively. The uncertainties make little to no difference in the trends seen for either Pu or U. The highest D-ratios are seen after 3 min of contacting, before the D-ratios drop to values close to their equilibrium values. This is quite unexpected behavior, but it could be partially due to difficulties in ensuring accurate contact times. Another possibility is that unknown and less controlled chemical reactions are happening during the first minutes of contacting. If so, it is probably a reaction between the metal and the solvent, as the solvent is already pre-equilibrated with 4 M nitric acid. Further investigations are required to understand what is causing this phenomenon. Overall, the distribution ratios are high for the DEHBA solvent and can be compared to those of the TBP solvent published by Halleröd et al. [43].

Conclusions

In this study, a comparison of DEHBA and TBP was made for the extraction of the tetravalent and hexavalent actinides, namely U(VI) and Pu(IV). Several performance criteria were investigated, including the physical properties of the solvents, acid extraction by the ligands, distribution ratios at extraction equilibrium, extraction kinetics, extraction as a function of ligand concentration and nitric acid concentration, and radiolytic stability. While the ligands are comparable for most of the evaluation criteria investigated here, some differences were identified. The acid extraction by the TBP solvent is higher than that of the DEHBA solvent at $[HNO_3] > 2$ M. Some concerns were identified in the current work for the DEHBA solvent; its low density and the low interfacial tension between the solvent and 4 M nitric acid. Both these properties can cause serious phase inversion issues and/or phase separation issues under process conditions. It is thus suggested that future work focuses on investigations of the hydrodynamics of the DEHBA solvent to determine its suitability for use in the CHALMEX process. Subsequently, further studies can also include investigations of co-extraction of fission products in the FS-13 diluent as well as investigations of the radiolytic degradation products.

Acknowledgements H2020 Euratom Research and Innovation Programme under Grant agreement no 755171 is acknowledged for funding this research.

Funding Open access funding provided by Chalmers University of Technology.

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