

# Deep Eutectic Solvents: Promising Co-solvents to Improve the Extraction Kinetics of CyMe<sub>4</sub>-BTBP

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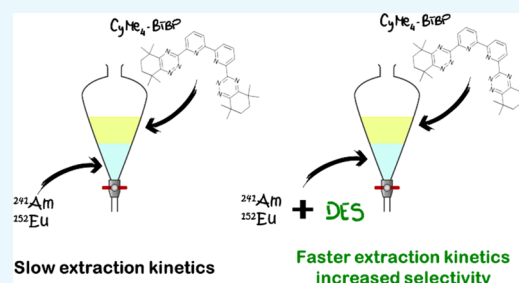
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**ABSTRACT:** In this communication, we report on the use of deep eutectic solvents (DESs) for processing nuclear waste, with a view to selectively recovering minor actinides (MA) from highly active raffinate solutions. DESs are an interesting new class of green and eco-sustainable solvents. Herein, a representative family of DES was tested as a co-solvent for MA/lanthanides partitioning based on Selective ActiNide EXtraction (SANEX)-like hydro-metallurgical processes. The reference system exploits the CyMe<sub>4</sub>-BTBP lipophilic extractant for selective MA recovery, but the slow kinetics is the main limitation toward the industrial implementation. A selection of hydrophilic DESs has been proposed as a phase transfer catalyst and tested to improve the process performances. In this work, the radiochemical stability and the extraction behavior of these DESs have been ascertained. Moreover, a preliminary optimization of system composition has been achieved. This study underlines a catalytic effect of DES that can be proficiently exploited to enhance CyMe<sub>4</sub>-BTBP extraction and selectivity.



## 1. INTRODUCTION

The global energy demand is estimated to grow at a CAGR (compound annual growth rate) of over 4% in the next 5 years.<sup>1</sup> Given the depletion of fossil fuel resources and to reduce greenhouse gases in the atmosphere in which fossil fuel is one of the major responsible, nuclear energy is considered to be one of the most viable options.<sup>2</sup> Limited emissions are generated during the entire nuclear power plant life, from construction to decommissioning, including the fuel fabrication stage. For this reason, nuclear energy is considered an environmentally friendly and green energy source.<sup>3</sup> However, the problem of using nuclear energy is the inevitable production of high-level radioactive waste (HLW).<sup>2</sup> Many researchers in the world are studying a better and safer management of this radioactive waste.<sup>4</sup>

The PUREX (Plutonium and Uranium Reduction EXtraction) process is currently used in many plants to recover uranium and plutonium from spent nuclear fuel to use them as a new fuel for nuclear plants.<sup>5</sup> One of the most important goals should be selectively removing (partitioning) the radiotoxic minor actinides (MA) from the PUREX raffinate using a hydrometallurgical process. Several approaches have been proposed, such as TALSPEAK (USA), SETFICS (Japan), TRPO (China), and the European SANEX (Selective ActiNide EXtraction) processes.<sup>6</sup> It is an interesting challenge because the separation of MA from lanthanides (Ln), also present in solution as trivalent cations, is a difficult task for their similar

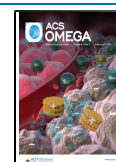
chemical and physical properties (such as size and coordination capabilities). Once removed, MA may be converted by fast neutrons into less radiotoxic or even stable elements (transmutation). This strategy, known as partitioning and transmutation, permits to reduce the environmental footprint and improve the sustainability of nuclear energy production also for the treatment of the existing HLW.<sup>7</sup>

At the beginning of this century, the promising SANEX-like processes have been proposed and then further developed in the framework of European collaborative research projects.<sup>8,9</sup> Basically, a lipophilic ligand is exploited to selectively extract MA(III) from an acidic aqueous solution containing also Ln(III).<sup>10</sup> So far, hundreds of polydentate S- and N-donor ligands have been tested.<sup>11,12</sup> Soon, the highly selective and efficient dithiophosphinic acids were abandoned since they do not contain just C, H, O, and N atoms (CHON principle), *i.e.*, they would imply secondary waste generation as they are not fully incinerable. Consequently, most efforts have been focused on CHON and N-donor extractants. In this context, the bis-triazinyl-pyridine (BTP) class of ligands showed outstanding

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extraction capability directly from highly acidic solutions and without a lipophilic anion source as a synergist.<sup>13</sup> Differently from earlier BTPs, CyMe<sub>4</sub>-BTP (bis-2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-benzo-1,2,4-triazin-3-yl)pyridine) showed better chemical and radiolytical stability, which would favor longer lifecycle and easier recyclability.<sup>14,15</sup> However, it was affected by slow extraction kinetics and too strong ligand–cation complexation. The first drawback would entail higher number of extraction stages (*i.e.*, larger facility, larger volumes, higher costs...), while the second one would hamper cation back-extraction before conversion and fuel fabrication steps. In order to overcome this latter issue, the slightly less efficient bis-triazinyl-bipyridine (BTBP) class of ligands was proposed. In particular, the CyMe<sub>4</sub>-BTBP (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2'-bipyridine) ligand is endowed with high, but reversible, extraction affinity for MA and satisfactory hydrolytical and radiolytical stability.<sup>16</sup> However, it still suffers from scarce solubility, kinetics, and loading capability. In order to improve these important features, octanol was proposed as a diluent and DDMOHEMA (*N,N'*-dimethyl,*N,N'*-dioctylhexylethoxymalonamide) or TODGA (*N,N,N',N'*-tetraoctyl diglycolamide) extractants were added to the organic phase as phase transfer catalysts.<sup>16,17</sup> Anyhow, centrifugal contactor tests once again resulted in unsatisfactory extraction kinetics, meaning that several stages would be required to achieve the desired decontamination.<sup>18</sup> Several other attempts have been made, rarely with decent results, to improve CyMe<sub>4</sub>-BTBP kinetics, such as different alkyl-substitutions on the BTBP backbone<sup>19,20</sup> and use of different diluents than octanol.<sup>21</sup>

A real breakthrough has been the discovery of the outstanding extraction and stability properties of the pyridine-bis-triazolyl (PyTri) class of ligands<sup>22–26</sup> that has prompted the development of a lipophilic PyTri endowed with unprecedented features, including high solubility and rather fast kinetics.<sup>27</sup> Since this extractant is relatively recent, several basic studies are still ongoing to ascertain its full applicability to SANEX-like processes.

At the same time, it seems more worthwhile further investigating the well-studied and well-established CyMe<sub>4</sub>-BTBP reference system in order to improve its extraction kinetics. The scope of this work is pursuing this challenging result by a novel approach based on green chemistry reagents.

Over the past 20 years, green chemistry has developed rapidly in every branch of chemistry, focusing on the development of green solvents. Ionic liquids, as a class of green solvents, have attracted great attention for their special physical and chemical properties.<sup>28</sup> On the other hand, some studies have highlighted their limitations, such as toxicity, poor biodegradability, and high cost, that limit the industrial applications. To overcome these limitations, a new type of green solvent, called deep eutectic solvents (DESs), has emerged. The concept of DES was first described by Abbot *et al.* in 2001.<sup>29</sup> Generally, a DES is a type of solvent usually obtained by mixing, in a suitable molar ratio, two components acting as a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). The DES components give rise to a mixture showing a depression of the melting point much deeper than that expected on the basis of ideal mixing, often providing homogeneous liquids at room temperature with unique solvent properties.<sup>30</sup> The most studied DES reported in the literature is the eutectic mixture of choline chloride (ChCl) and urea in a molar ratio 1:2.<sup>31</sup> Choline chloride is a

quaternary ammonium salt that belongs to the vitamin B group (vitamin B4). It is a biodegradable and nontoxic salt. Many new DESs have been rapidly developed by a combinatorial approach of HBD and HBA. In general, DESs have some recognized properties, such as poor conduction, high viscosity, low vapor pressure, high thermal stability,<sup>32</sup> and no-toxicity.<sup>33</sup> In recent years, DESs have received increased attention in a variety of synthetic,<sup>34</sup> catalytic,<sup>35</sup> and electrochemical<sup>36,37</sup> applications due to their potential as green and versatile solvents. Some applications about extraction of dissolved metal,<sup>38,39</sup> removal of pollutants from water,<sup>40</sup> and promotion of speciation and redox chemistry<sup>41</sup> were reported. Recently, DES has been successfully proposed for advanced spent nuclear fuel reprocessing processes.<sup>39,41</sup> In this work, we propose a new family of DES based on choline acetate, in compliance to the CHON rule to avoid secondary waste production at the end of life. For the sake of comparison, and in order to have a first evaluation of the performance of the acetate-based DESs, two analogues based on choline chloride are also considered and discussed. The main purpose of this communication is to report on the application of such a DES class as co-solvents in liquid–liquid extraction of MA in SANEX-like processes.

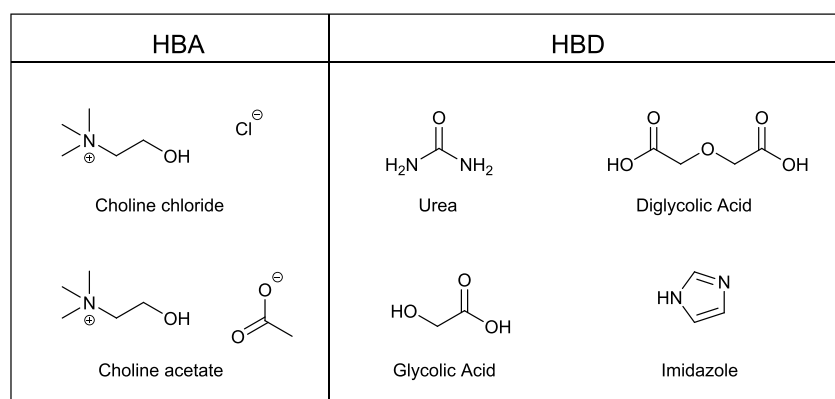
## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** Choline chloride (99%), urea, glycolic acid (99%), diglycolic acid (98%), imidazole (99%), and 1-octanol were purchased from Sigma-Aldrich. Choline acetate (98%) was purchased from Iolitech. Nitric acid (65% w/w) was purchased by FLUKA. CyMe<sub>4</sub>-BTBP was kindly provided by the University of Reading (School of Chemistry).

**2.2. Preparation of DESs.** DESs were prepared according to the most used procedure reported in the literature. Briefly, the preparation involved the combination of choline chloride or acetate (HBA) with the different HBDs, urea, glycolic acid, diglycolic acid, or imidazole at 80 °C for 30 min stirring until a homogeneous and transparent solution was formed. The prepared DESs were cooled to 22 °C and used for the extraction tests without any purification.

**2.3. Preparation of Solution.** For the liquid–liquid extraction experiments, a simplified feed solution was prepared by diluting concentrated nitric acid (purchased from FLUKA, ≥65% w/w) with ultrapure water (Millipore, Billerica, USA; 18.2 MΩ·cm). Weighed amounts of DES, or of its pure components if otherwise specified, were added to the aqueous phase. Then, these solutions were spiked with trace amounts of certified standard solutions: <sup>241</sup>Am(NO<sub>3</sub>)<sub>3</sub> in 1 M HNO<sub>3</sub> and <sup>152</sup>EuCl<sub>3</sub> in 1 M HCl solutions supplied by Eurostandard CZ (Czech Republic) and LEA-CERCA (France), respectively. If not otherwise specified, the final concentration of HNO<sub>3</sub> was 3 M and the specific activity of each radionuclide was about 2.5 kBq/mL. The organic solvent was prepared by dissolving weighed quantities of extractant in pure 1-octanol (purity of ≥99%, purchased from Sigma-Aldrich) to obtain 0.015 M CyMe<sub>4</sub>-BTBP concentration. The organic phase was pre-equilibrated with equal volume of 3 M HNO<sub>3</sub> before being used in the extraction experiment in order to avoid aqueous phase acidity alteration during the tests.

**2.4. Irradiation Condition.** The solutions were stored in 1 mL glass vials closed with a plastic lid and sealed with Parafilm in order to avoid sample leakage during irradiation. Between the preparation and the analysis, the samples were kept in the dark. Irradiations were performed at ambient temperature



**Figure 1.** Molecular formulae of the components of DESs used.

using a  $^{60}\text{Co}$  gamma source with a 2.5 kGy/h dose rate, up to 100 kGy of absorbed dose. At the end of the irradiation of the sample with the highest absorbed dose, all samples were stored in the dark at  $4\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  until further analyses, namely, ESI-MS (electrospray ionization–mass spectrometry) and solvent extraction. Therefore, the same thermal treatment was used for all samples.

**2.5. Electrospray Ionization–Mass Spectrometry (ESI–MS) and NMR Spectroscopy Conditions.** ESI–MS spectra were acquired on a Bruker Esquire 3000 PLUS instrument (ESI Ion Trap LC/MSn System), equipped with an ESI source and a quadrupole ion trap detector (QIT). Samples were diluted in acetonitrile to  $10^{-2}$  g/L before being directly infused in the ESI–MS at a  $4\text{ }\mu\text{L}/\text{min}$  rate. After each experiment, both the syringe and loop used for the infusion were abundantly rinsed with acetonitrile and methanol in order to avoid sample cross-contaminations. The analyses were performed in positive ion mode after optimization of the acquisition parameters: 4.5 kV needle voltage, 10 L/h  $\text{N}_2$  flow rate, 40 V cone voltage, trap drive set to 46, 115.8 V capillary exit, and 13,000 ( $m/z$ )/s scan resolution over the 35–900  $m/z$  mass/charge range. The signals of the pristine ligand and byproducts were identified in the spectra of fresh, aged, and irradiated solutions. The assignment of some detected byproducts was confirmed by collision-activated decomposition (CID) tandem mass spectrometry experiments ( $\text{MS}^2$ ), with an isolation width of 1 mass unit and a duly optimized collisional fragmentation amplitude between 0.5 and 1.00 V. All data were analyzed using Bruker Daltonics Data Analysis software (version 5.1, 2002).

NMR spectra were acquired at 11.74 T on a Bruker NEO 500 instrument equipped with a direct observe BBFO probe. The spectra were collected at 298 K in  $\text{D}_2\text{O}$ . The chemical shift scale is referenced to external sodium trimethylsilylpropanesulfonate (DSS).

**2.6. Liquid–Liquid Extraction Experiments.** All batch extraction experiments were performed by contacting equal volumes (300  $\mu\text{L}$ ) of aqueous and organic solutions in closed single-use Eppendorf microtubes. In order to keep the aqueous phase acidity unchanged during the tests, the organic solutions were pre-equilibrated with equal volumes of 3 M  $\text{HNO}_3$  prior to use. The phases were vigorously mixed at room temperature ( $22 \pm 1\text{ }^{\circ}\text{C}$ ) using an orbital shaker (Eppendorf ThermoMixer, 1100 rpm). If not otherwise specified, the mixing time was set to 1 h, even if certainly not enough to achieve the chemical equilibrium. In order to ensure complete phase disengagement, all samples were centrifuged at 4000 rpm for 10 min. Then,

200  $\mu\text{L}$  aliquots were sampled from each phase and measured by  $\gamma$ -spectrometry ( $2'' \times 2''$  NaI(Tl), Silena SNIP N MCA). The activity concentrations of  $^{241}\text{Am}$  and  $^{152}\text{Eu}$  were quantified by exploiting the  $\gamma$ -lines at 59.5 and 121.8 keV, respectively. System performance was evaluated by calculating distribution ratios ( $D_A$ , where A is the cation) and separation factors ( $SF_{A/B}$ , where A and B are the different cations). In particular, the extraction efficiency is evaluated by  $D_A$ , calculated as the ratio between the concentration of A in the organic and in the aqueous phases. Selectivity is assessed by the  $SF_{A/B}$ , calculated as the ratio between  $D_A$  and  $D_B$ . In a SANEX-like process,  $D_{\text{An}}$  should be above unit and  $D_{\text{Ln}}$  below unit to obtain the required separation between these cations. The selectivity for Am toward Eu is expressed by the  $SF_{\text{Am}/\text{Eu}}$ . In a SANEX-like process,  $SF_{\text{An}/\text{Ln}}$  should be greater than 10 to achieve the required  $\text{An}/\text{Ln}$  separation by a reasonable number of extracting stages. These performance parameters were calculated only if no third-phase formation was observed during the extraction experiments and are considered reliable if the activity balances are  $100 \pm 10\%$ . In the 0.01 and 100 distribution ratio range, the uncertainty is about  $\pm 5\%$ . Consequently, the uncertainty of the SF calculated from these  $D$ -ratios is about  $\pm 7\%$ .

### 3. RESULTS AND DISCUSSION

**3.1. Deep Eutectic Solvents.** The family of DES based on choline acetate combined with urea, glycolic acid, diglycolic acid, and imidazole is shown in Figure 1, along with the molecular formula of ChCl. The list of the DESs tested in this work and the corresponding abbreviations are reported in Table 1. Such a list is based on a collection of ChAc-based DES along with two specific choline chloride-based DESs, ChClU and ChClGlyA, here considered in spite of the fact that they have already been extensively studied in literature for different applications.<sup>42–46</sup> The latter DESs were chosen on

**Table 1.** DESs Prepared and Used in this Work, Abbreviation, and Molar Ratio

HBA	HBD	name	molar ratio
choline acetate	urea	ChAcU	1:2
choline acetate	glycolic acid	ChAcGlyA	1:1
choline acetate	diglycolic acid	ChAcDigA	1:1
choline acetate	imidazole	ChAcIm	1:1
choline chloride	urea	ChClU	1:2
choline chloride	glycolic acid	ChClGlyA	1:2

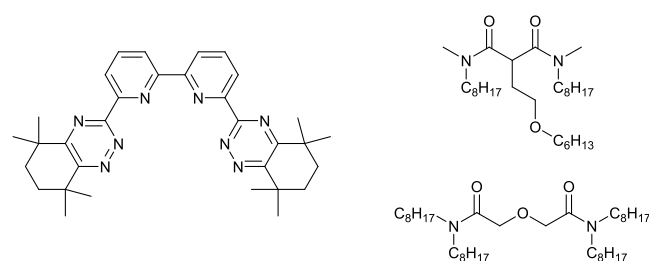


the basis of the following facts: (i) ChCIU is the most popular and the most investigated DES, thus deserving a role of “reference” also in the context of the present investigation. (ii) ChClGlyA can provide information on the role of the HBA—chloride vs acetate—beneficial for the discussion of the partitioning results.

All the DESs were prepared according to the traditional methodology<sup>31</sup> and by using the molar ratios reported in Table 1.

As shown in Table 1, DESs with different HBAs and HBDs were studied to evaluate the possible role of the components and to evaluate the performance of choline acetate-based DESs. The proposed choline acetate-based DESs have been designed in accordance with the CHON rule so that at the end of their life, the DES-containing solvents are completely incinerable without producing secondary waste.

**3.2. Screening of Partitioning Properties.** The CyMe<sub>4</sub>-BTBP molecule (Figure 2, left)<sup>47</sup> is one of the most promising



**Figure 2.** Molecular structures of CyMe<sub>4</sub>-BTBP (left), DMDOHEMA (top right), and TODGA (bottom right).

current European reference ligands for the development of An(III) separation processes. It has been designed to have good radiolytic and hydrolytic stability, retaining high selectivity for actinides over lanthanides. It has already been successfully tested in continuous lab-scale counter-current solvent extraction process tests.<sup>48</sup> Unfortunately, the kinetics of extraction of the CyMe<sub>4</sub>-BTBP system is rather slow and requires the addition of a phase-transfer agent. This molecule can improve the transfer kinetics of species of interest across a phase boundary. The most promising in literature are DMDOHEMA<sup>49</sup> and TODGA<sup>18</sup> (see structures in Figure 2, right).

In order to shed light on possible benefits from the introduction of DES, it was decided to preliminarily test ChAcDigA as a DES model for the similar structure of dicarboxylic acid to TODGA. Liquid–liquid extraction was performed following a standard procedure (described in the Experimental Section) to evaluate the performances of the extracting system in the presence or the absence of DES. The aqueous phase contained trace amounts of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), used as representatives of MA and Ln families present in the aqueous feed to be decontaminated, 3 M HNO<sub>3</sub>, and 5% v DES as a co-solvent. The organic phase was the CyMe<sub>4</sub>-BTBP lipophilic ligand dissolved in 1-octanol (0.015 M).

As shown in Table 2 and as already known from the literature, the results of CyMe<sub>4</sub>-BTBP alone (blank sample) are consistent with SANEX-like process requirements:  $D_{Am}$  is above unit and  $D_{Eu}$  is below unit, resulting in  $SF_{Am/Eu}$  around 10.

By comparing all the results obtained, a noticeable beneficial effect is observed in each formulation by introducing DES in

**Table 2.** Distribution Ratios of Trivalent Am and Eu and Am/Eu Separation Factors in the Absence/Presence of Different DESs<sup>a</sup>

sample ID	aqueous phase	$D_{Am}$	$D_{Eu}$	$SF_{Am/Eu}$
1 D	blank (no DES)	2.88	0.35	8.17
2 D	ChAcDigA	10.86	0.50	21.60
3 D	ChAcGlyA	13.06	0.53	25.00
4 D	ChAcU	10.28	0.55	18.66
5 D	ChAcIm	9.56	0.67	14.24
6 D	ChCIU	5.22	0.43	12.13
7 D	ChClGlyA	5.12	0.37	13.89

<sup>a</sup>Organic phases: 0.015 M CyMe<sub>4</sub>-BTBP in 1-octanol, pre-equilibrated with equal volume of 3 M HNO<sub>3</sub>. Aqueous phases: 3 M HNO<sub>3</sub> spiked with <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), in the absence (blank, 1 D) or in the presence of 5% v DES (2 D–7 D). Mixing time of 60 min.

the aqueous phase as a co-solvent (just 5% v). In particular,  $D_{Am}$  considerably increases with respect to that of the blank sample, while those of Eu remain constant or slightly increase, still remaining below the unit. Hence, the presence of DES improves both the Am extraction efficiency and the Am/Eu selectivity, as expressed by the reported  $SF_{Am/Eu}$  values.

The best results were obtained with choline acetate-based DES and in particular with choline acetate glycolic acid and diglycolic acid. The use of ChAcDigA allows to increase  $D_{Am}$  by more than four times with respect to the blank. On the contrary,  $D_{Eu}$  is almost constant. This is important because a more efficient extraction process seems to be feasible without complicating the system or introducing expensive reagents and maintaining a good An/Ln selectivity. The presence of acid contributes to increasing the chelation capability of the system.<sup>50</sup> Urea and imidazole have different chelation properties, and the different behavior suggests a different mechanism for the system that should be further investigated.

**3.3. Role of DESs in the Extraction System.** To better understand the mechanism of the enhanced extraction capability using the DESs as co-solvents, it was decided to perform two types of control experiments: (i) extraction tests using the individual components of DES and (ii) extraction tests with the mixture of the best performing DES components—i.e., choline acetate and glycolic acid, for the sake of brevity indicated as “physical mixture”—independently and separately added to the aqueous solution in the same molar proportion as in Table 1. In test (i), the individual components, choline acetate, diglycolic acid, and glycolic acid were thus added at the same molar concentration of the tests as DES, namely, at 0.2 M. In test (ii), the physical mixture was added to the aqueous medium, maintaining the same molar ratio of the individual DES components and at the same concentration 0.2 M. In assessing the molar concentration, the MW of DES was calculated by considering it as a single compound. A brief discussion of the possible way of calculating the MW of DES is reported by Agieienko and Buchner.<sup>51</sup> These results are reported in Table 3 and compared with those of the blank (no added DES) and of corresponding DES (i.e., ChAcDigA and ChAcGlyA).

As it can be observed from the data of Table 3, it is the presence of the preformed DES added as a co-solvent that leads to the major enhancement of the extraction capability of the system. In fact, neither the individual components (HBA or HBD alone) nor the physical mixture added to the aqueous

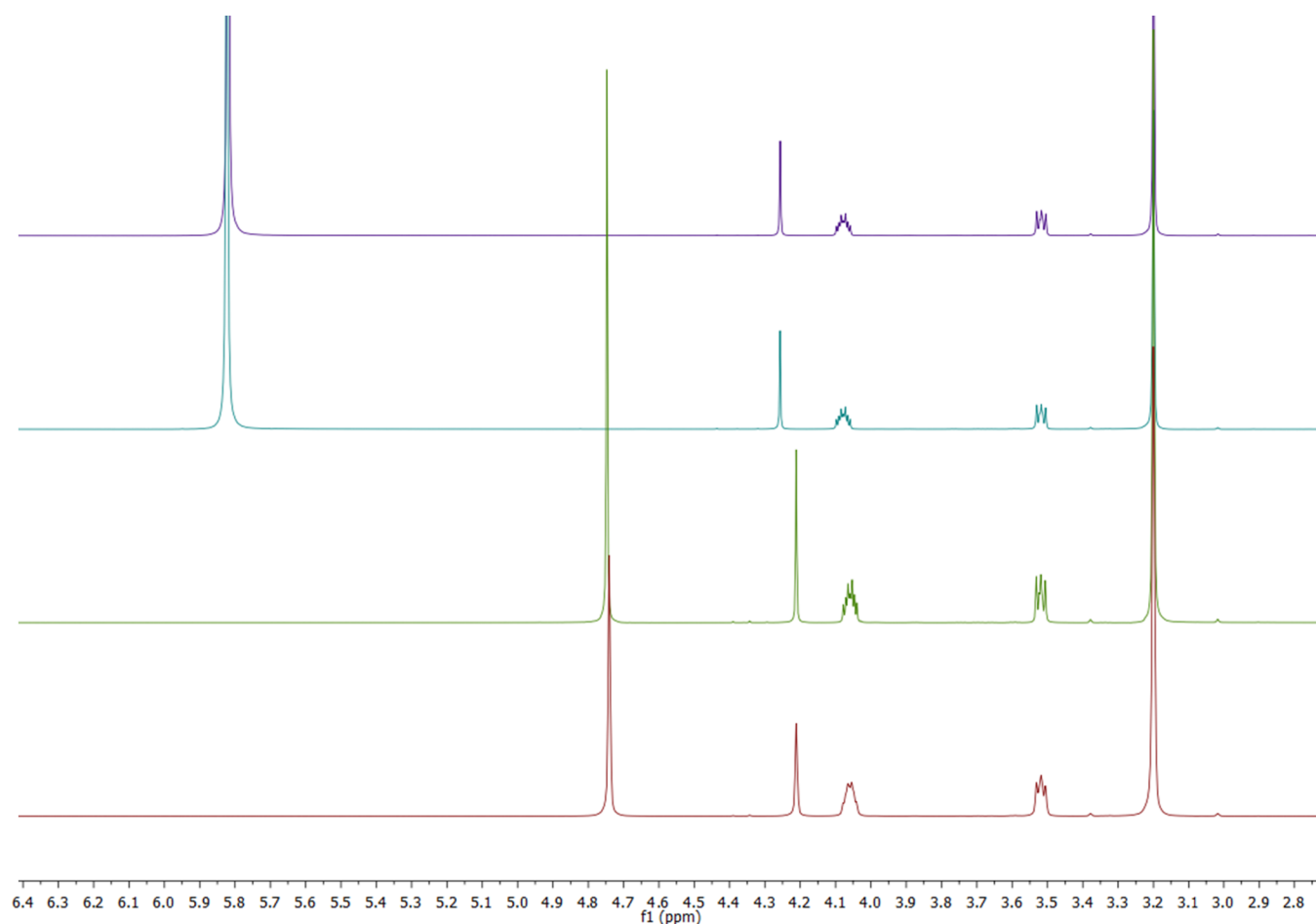
**Table 3. Distribution Ratios of Trivalent Am and Eu and Am/Eu Separation Factors in the Absence/Presence of Different DESs, Single DES Components, or the Physical Mixture<sup>a</sup>**

sample ID	aqueous phase	$D_{Am}$	$D_{Eu}$	$SF_{Am/Eu}$
1 D	blank (no DES)	2.88	0.35	8.17
8 D	diglycolic acid	3.15	0.37	8.59
9 D	choline acetate	3.84	0.42	9.10
10 D	glycolic acid	3.15	0.37	8.60
2 D	ChAcDigA	10.86	0.50	21.60
3 D	ChAcGlyA	13.06	0.53	25.00
11 D	physical mixture	4.83	0.42	11.6

<sup>a</sup>Organic phases: 0.015 M CyMe<sub>4</sub>-BTBP in 1-octanol, pre-equilibrated with equal volume of 3 M HNO<sub>3</sub>. Aqueous phases: 3 M HNO<sub>3</sub> spiked with <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) in the absence (blank, 1 D) or in the presence of 0.2 M diglycolic acid (8 D), 0.2 M choline acetate (9 D), 0.2 M glycolic acid (10 D), and 5% v DESs (0.2 M, ChAcDigA and ChAcGlyA, 2 D and 3 D, respectively) and 0.2 M of physical mixture (11 D, *vide supra* for the definition). Mixing time of 60 min.

phase improves the  $D$ -ratios and  $SF$  to a level comparable to the entries related to samples 2 D and 3 D. Interestingly, the data of sample 11 D indicate that the presence of the DES components in the correct molar ratio is *di per sé* not sufficient

to reproduce the effect of the DES added as a co-solvent. Overall, the data of Table 3 clearly show that DES is responsible for the increase in separation capability of the system, with a synergistic action of its components. In turn, the individual components of DES do not yield comparable results in the absence of the partner. These results permit to underline that the DES impact on process performance is not only due to an ionic contribution of HBA, but also it seems to be related to a synergic effect of the two components. The comparison of entry 3 D with 11 D highlights unexpected and unprecedented aspects of DES behavior. The current literature proposes distinct regimes of DES/water mixtures that can be sketched as water-in-DES and DES-in-water. The former is characterized by a relatively low water content (up to 42% wt H<sub>2</sub>O in ChCl-urea DES), which, nevertheless, does not induce the full disruption of the DES nanostructure. The latter, on the contrary, is dominated by water-water and DES-water interactions, leading to disruption of the DES structure.<sup>52</sup> These findings prompted the DES community to focus on the water-in-DES dilution range, neglecting the higher dilution regime, DES-in-water, because “after the rupture of HB complexes, the system becomes a simple aqueous solution of the individual components”.<sup>53</sup> The data of Table 3, in particular the case of 11 D, seem to indicate that the solvation features of DES, rather than the network of intermolecular H-bonds responsible for the DES nanostructuration and largely

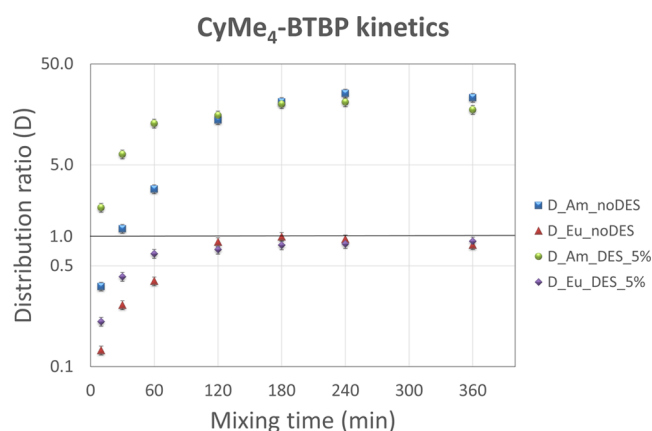


**Figure 3.** <sup>1</sup>H NMR spectra of DES solutions. From bottom to top: (i) ChAcGlyA in D<sub>2</sub>O; (ii) ChAcGlyA in D<sub>2</sub>O after 48 h; (iii) ChAcGlyA in D<sub>2</sub>O + 3 M HNO<sub>3</sub>; and (iv) ChAcGlyA in D<sub>2</sub>O + 3 M HNO<sub>3</sub> after 48 h. The large downfield shift of the HOD signal (from 4.74 to ca. 5.85 ppm) is due to the different pH of the two solutions.

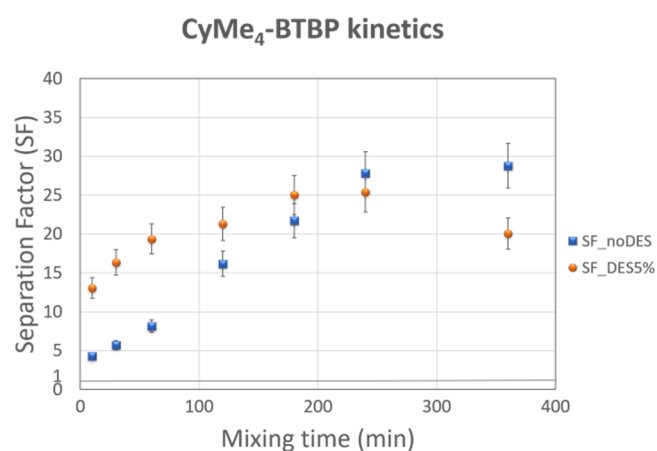
disrupted at the used dilution, may play a role in the partitioning here investigated. Although at this stage, we do not speculate on a possible general model providing a clear-cut rationalization of the results of Table 3, these findings suggest that the DES in water systems might have been overlooked, thus calling for further investigation on the dilution range commonly believed lacking of interest.

As a final remark, it is worth mentioning that the ester formation<sup>54</sup> between choline and the organic acids used in this work (glycolic and diglycolic acid) was not observed under the experimental conditions used in this work. In their work,<sup>54</sup> Rodriguez Rodriguez *et al.* showed that in the <sup>1</sup>H NMR spectrum of ChClGlyA, there is a satellite peak downfield the intense singlet assigned to the trimethylammonium group (see Figure S8 of ref 54). The authors indicated such a satellite singlet as a marker of the ester formation, along with two other, less intense signals due to higher multiplicity. Figure 3 shows the comparison of the NMR spectra in D<sub>2</sub>O and in D<sub>2</sub>O + HNO<sub>3</sub> 3 M of 5% v ChAcGlyA from the present work. The spectra were recorded immediately after the DES dissolution and after 48 h. The spectra clearly show the absence of products other than the DES components and, noticeably, indicate that the satellite peak mentioned above is not detectable. The NMR spectrum of the acid solution repeated after 48 h confirmed the result mentioned above. In all of the spectra, the reporter NMR signals for the formation of the ester between the cholinium ion and the glycolic acid were not observed. This result is also in line with our recent results on acetate-based DES.<sup>55</sup>

**3.4. Extraction Kinetics.** As above reported, the addition of a small amount of DES as a co-solvent permits to increase the extraction and selectivity of the system. A possible role of the DES in the extraction kinetics could be hypothesized. In order to corroborate this hypothesis, the system with ChAcGlyA DES at 5% v, being the best performing DES as shown in Table 3, was tested at different mixing times (10, 30, 60, 120, 180, and 360 min). For proper comparison, the blank system (*i.e.*, without DES) is tested under the same experimental conditions. The comparison between the obtained *D*-ratios and *SF* is reported in Figure 4 and in Figure 5, respectively. The major difference is evident for the shorter



**Figure 4.** Distribution ratios of trivalent Am and Eu as a function of the mixing time. Organic phases: 0.015 M CyMe<sub>4</sub>-BTBP in 1-octanol, pre-equilibrated with equal volume of 3 M HNO<sub>3</sub>. Aqueous phases: 3 M HNO<sub>3</sub> spiked with <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), with/without 5% v DES (*i.e.*, ChAcGlyA).



**Figure 5.** Am/Eu separation factor as a function of the mixing time. Organic phases: 0.015 M CyMe<sub>4</sub>-BTBP in 1-octanol, pre-equilibrated with equal volume of 3 M HNO<sub>3</sub>. Aqueous phases: 3 M HNO<sub>3</sub> spiked with <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), with (red symbols) or without (blue symbols) 5% v DES (*i.e.*, ChAcGlyA).

mixing times, *i.e.*, between 10 and 120 min. Under these conditions, the *D*<sub>Am</sub>—and *D*<sub>Eu</sub> at a lower extent—increases several times in the presence of DES, if compared with the control, *i.e.*, without DES, as reported in Table 4. The ratios of

**Table 4. Extraction Efficiency and Selectivity Variations as a Function of Different Mixing Times<sup>a</sup>**

mixing time [min]	Am extraction efficiency variation $\frac{D_{Am}(DES)}{D_{Am}(no DES)}$	Eu extraction efficiency variation $\frac{D_{Eu}(DES)}{D_{Eu}(no DES)}$	Am/Eu selectivity variation $\frac{SF_{Am/Eu}(DES)}{SF_{Am/Eu}(no DES)}$
10	6.0 ± 0.4	2.0 ± 0.1	3.0 ± 0.3
30	5.5 ± 0.4	1.9 ± 0.1	2.9 ± 0.3
60	4.5 ± 0.3	1.9 ± 0.1	2.4 ± 0.2
120	1.1 ± 0.1	0.8 ± 0.1	1.3 ± 0.1
180	1.0 ± 0.1	0.8 ± 0.1	1.2 ± 0.1
240	0.8 ± 0.1	0.9 ± 0.1	0.9 ± 0.1
360	0.8 ± 0.1	1.1 ± 0.1	0.7 ± 0.1

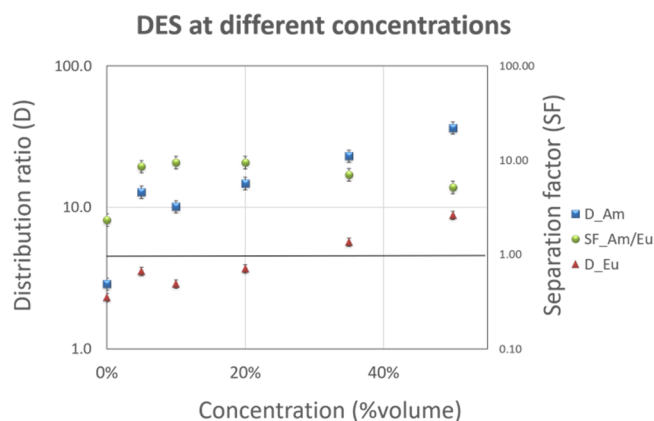
<sup>a</sup>These ratios have been calculated, respectively, by dividing *D*<sub>Am</sub>, *D*<sub>Eu</sub>, and *SF*<sub>Am/Eu</sub> obtained in the presence and absence of DES. Experiment details are reported in the captions of Figures 5 and 6.

Table 4 represent the extraction efficiency (or selectivity) variations since they are calculated by dividing the *D*-ratios (or the *SF*) obtained in the presence of the DES by those obtained without the DES. In particular, the extraction efficiency of both Am and Eu improves by a factor greater than 1 for mixing times below 120 min. Moreover, the extraction efficiency variation tends toward the unit as the mixing time increases. This means that the extraction equilibrium is reached at shorter mixing times if DES is introduced in the system. This suggests the effect of DES as the phase transfer catalyst in the extraction system and is a first confirmation of the hypothesized improved kinetics. The steeper increase in Am extraction efficiency toward Eu entails the improved selectivity of the system for shorter mixing times (up to three times better), as shown by the *SF* reported in Figure 5 and in Table 4. On the other hand, a reversal *SF* trend could be noticed at mixing times above 240 min. This could be indicative of a more complex phenomenon, as selectivity is dominated by short-term kinetic factors and long-term thermodynamic

factors. This intriguing phenomenon could be the subject of a further targeted study.

The above-described outcomes are supposed to show interesting fall-out in view of the implementation of an industrial process. In fact, a sufficiently fast extraction kinetics is a key requirement for a hydrometallurgical separation process on an industrial scale since centrifugal contactors are endowed with residence times of around 2–5 min, depending on flow rate and dimensions.<sup>56</sup> By way of example, the reduction of aqueous and organic phases flow rates may be helpful in obtaining satisfactory results with slow kinetics systems. On the other hand, under these circumstances, improvement of extraction kinetics is preferably pursued by modifying the system composition (*e.g.*, by adding phase transfer catalysts), rather than by excessively reducing the flow rate, otherwise the processing capability would also be compromised.

**3.5. DES Concentration.** The previous sections showed the identification of the optimal conditions to proficiently improve the extraction process using CyMe<sub>4</sub>-BTBP as a selective extractant of An(III) and the DES as a phase transfer catalyst. The next step was the evaluation of the effect of DES concentration on the extraction capability of the system. The ChAcGlyA DES was added at 5, 10, 20, 35, and 50% v, maintaining the final concentration of HNO<sub>3</sub> at 3 M. These experiments were performed by keeping 1 h as the mixing time, which is a good compromise for efficiency and selectivity. The results are summarized in Figure 6.



**Figure 6.** Distribution ratios of trivalent Am and Eu and Am/Eu separation factors as a function of different ChAcGlyA concentrations. Organic phases: 0.015 M CyMe<sub>4</sub>-BTBP in 1-octanol, pre-equilibrated with equal volume of 3 M HNO<sub>3</sub>. Aqueous phases: 3 M HNO<sub>3</sub> spiked with <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), in the absence (0% v) or in the presence (5–50% v) of DES (*i.e.*, ChAcGlyA). Mixing time of 60 min.

As shown in the graphic, both  $D_{Am}$ ,  $D_{Eu}$  and  $SF_{Am/Eu}$  are nearly constant at low DES concentrations, namely, in the 5–20% v range, indicating the robustness of the system toward undesired fluctuation of this parameter that may occur during process operation. Under these conditions, good performance in terms of Am extraction capability and Am/Eu selectivity is obtained. At the same time,  $D_{Eu}$  remains below the unit, thus allowing the implementation of a selective separation process, resulting in a pure Am product. By further increasing the ChAcGlyA DES concentration, both  $D_{Am}$  and  $D_{Eu}$  increase, while the  $SF_{Am/Eu}$  slightly decreases. Consequently, even if Am extraction efficiency improves, the Am product is not as pure,

being also the Eu extraction more favored, resulting in a loss of process selectivity. The results shown in Figure 6 point out that the favorable effect of DES as a co-solvent seems to be independent of the DES nanostructure but rather connected to the solvation properties of the DES components under the process conditions.

**3.6. Radiolytic Stability.** The radiolytic stability of the DESs used in the present work was tested according to the following protocol: electrospray ionization mass spectrometry (ESI–MS) analyses were performed on fresh and irradiated (integrated absorbed dose of 25–100 kGy with a 2.5 kGy/h dose rate <sup>60</sup>Co source) ChAcDigA as a DES representative, pure and diluted with 3 M HNO<sub>3</sub> aqueous solutions (5–50% v). For all the samples, the ESI–MS spectra of irradiated solutions resulted to be unaltered with respect to fresh ones. The irradiated solutions of 5–50% v ChAcDigA dissolved with 3 M HNO<sub>3</sub> were spiked with trace amounts of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), leading to the final 3.75% v and 37.5% v ChAcDigA concentration, respectively. The final acidity of the aqueous phases was 2.9 and 2.3 M, respectively. The irradiated aqueous phases were in contact with the CyMe<sub>4</sub>-BTBP-based organic solvent, previously pre-equilibrated with HNO<sub>3</sub>. These extraction experiments were performed in order to ascertain if the performances of the system are influenced by radiolysis. For proper comparison, not irradiated ChAcDigA solutions were also tested. The results are reported in Table 5. As it

**Table 5.** Distribution Ratios of Trivalent Am and Eu and Am/Eu Separation Factors as a Function of the Absorbed Dose<sup>a</sup>

DES [% v]	HNO <sub>3</sub> [M]	absorbed dose [kGy]	$D_{Am}$	$D_{Eu}$	$SF_{Am/Eu}$
3.75	2.9	0	10.39	0.49	21.03
3.75	2.9	25	10.54	0.47	22.24
3.75	2.9	100	5.73	0.43	13.39
37.5	2.3	0	24.39	1.82	13.37
37.5	2.3	25	15.37	0.93	16.51
37.5	2.3	100	15.52	0.86	17.97

<sup>a</sup>Two different HNO<sub>3</sub> and DES concentrations were tested. Organic phases: 0.015 M CyMe<sub>4</sub>-BTBP in 1-octanol, pre-equilibrated with equal volume of 3 M HNO<sub>3</sub>. Aqueous phases: 2.9 and 2.3 M HNO<sub>3</sub> spiked with <sup>241</sup>Am(III) and <sup>152</sup>Eu(III), in the presence of 3.75 and 37.5% v ChAcDigA. The DES solution was previously irradiated to 25 and 100 kGy using a <sup>60</sup>Co source with a 2.5 kGy/h dose rate. Mixing time of 60 min.

could be evinced, at low DES concentration, the distribution ratios of Am and Eu and the Am/Eu separation factor remain stable up to 25 kGy, and they decrease at higher absorbed dose. On the other hand, at higher DES concentration, both Am and Eu distribution ratios already decrease at the lowest absorbed dose tested, but then they remain almost constant up to 100 kGy. This different behavior may be explained by the possibly higher concentration of radiolytic byproducts when high DES concentration solution is irradiated. The reduction of cation extraction into the organic phase may be due to competing complexation capability between CyMe<sub>4</sub>-BTBP and DES radiolytic byproducts. The apparent contradiction between solvent extraction and ESI–MS experiments may be justified by the intrinsic spectrometer's limitations in the detection of these byproducts. Even if this is just a preliminary screening of DES radiolytic behavior, a promising radiation resistance has been highlighted, especially at low DES



concentration. Moreover, CyMe<sub>4</sub>-BTBP extraction performance in the presence of the DES is still largely better than that without adding the DES to the aqueous phase, further supporting the introduction of this innovative reagent.

In conclusion, the results of the present work suggest that the addition of only 5% v DES is sufficient to reach optimal conditions for both Am extraction and Am/Eu selectivity. This result suggests a perspective of implementation in industrial processes. The addition of 5% v DES acting *de facto* as a phase transfer catalyst permits to reduce the contact time and to improve the process performance. In addition, the DES is not a classical catalyst or ligand. It is obtained by simple mixing of two components commercially available without synthesis and purification steps required.

#### 4. CONCLUSIONS

In summary, we have demonstrated the proficient applicability of the selected DESs in SANEX-like processes as co-solvents. A novel extraction system, in which the added DES shows catalytic activity, improved the extraction kinetics and the performance of CyMe<sub>4</sub>-BTBP extractant. The role of DES was investigated, resulting in not only an increase in ionic contribution to the system but also mainly a synergic effect of the two components. The use of a preformed DES co-solvent, rather than the independent DES components added separately to the aqueous phase, was demonstrated to play a role in the efficiency and selectivity of the extraction. A selection of DES was tested, and in all the cases, an improvement of extraction capability was observed. The best results were obtained with choline acetate-based DES, in particular with ChAcGlyA. The present study on this new system suggests the capability of DESs to improve the extraction kinetics of CyMe<sub>4</sub>-BTBP, which is one of the main weak points of this ligand. This would introduce a more efficient, selective, and compact An(III) extraction stage. Further investigation about the mechanism should be followed but the results herein reported are a good starting point. Moreover, the DES-containing aqueous phase showed promising stability toward radiolysis. Concerning future works, the performance of the proposed system should be verified with a more realistic feed, at least including also Cm(III), all of the Ln and the main fission and corrosion products at real concentration. This will allow to ascertain the applicability of the proposed system to SANEX-like processes.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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