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Influence of diluent alkyl substitution on the extraction of Am(III) and Eu(III) by a 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine ligand dissolved in alkylated cyclohexanone diluents

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Summary. Several alkylated cyclohexanones were investigated as potential diluents for the selective extraction of Am(III) from Eu(III) from nitric acid solutions by the CyMe₄-BTBP ligand. No significant extraction of either of the metal ions was observed for these diluents themselves. In the extractions from 1 M HNO₃, 3-methylcyclohexanone and 4-methylcyclohexanone gave comparable results to cyclohexanone whereas in the extractions from 4 M HNO₃, 2-methylcyclohexanone, 3-methylcyclohexanone and 4-methylcyclohexanone all gave superior results. For the monomethylated diluents, D_{Am} and $SF_{Am/Eu}$ decreased in the order of alkyl substitution 2 > 4 ~ 3. However, alkyl substitution of cyclohexanone significantly slows down the extraction kinetics compared to cyclohexanone, and the position of alkyl substitution was found to play an important role in the solvents properties. 3-Methylcyclohexanone was identified as the most promising of the diluents.

1. Introduction

The long-lived radiotoxicity of waste nuclear fuel is largely due to the presence of the transplutonium elements. Currently, the PUREX process is used worldwide [1, 2] to remove plutonium and uranium but the remaining waste also contains the minor actinides americium, curium and neptunium which are highly radiotoxic. Once removed, these elements can be fissioned or transmuted into shorter-lived radionuclides by neutron bombardment in fast reactors or dedicated transmuters, enabling safer geological disposal of the remaining waste [3, 4]. A highly selective solvent extraction process (SANEX process) has been

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proposed for the future reprocessing of waste solutions produced in the PUREX process, involving the selective separation of the minor actinides from the lanthanides and fission products which make up the bulk of the waste [5, 6]. A large number of ligands have been synthesized and tested in recent years as potential candidates in such a process [7–11]. Currently, the quadridentate nitrogen heterocyclic 6,6'-bis-(1,2,4-triazin-3-yl)-2,2'-bipyridine ligands (BTBPs) [12–15] show the most promising results. An important feature of these ligands is the pronounced effect of the type of diluent on the extraction properties of the solvent. The annulated BTBP ligand CyMe₄-BTBP **1** (Fig. 1) is the benchmark ligand [16, 17] and was successfully tested on genuine waste solution in a laboratory SANEX demonstration test [18].

One drawback of the BTBPs, including **1**, is the need to use additional phase-transfer agents such as *N,N'*-dimethyl-*N,N'*-dioctylhexoxyethylmalonamide [19], *N,N,N',N'*-tetraoctyldiglycolamide [20] or bidentate triazine-based aromatic ligands [21] to improve the otherwise slow extraction kinetics in suitable diluents such as 1-octanol, dodecane or hydrogenated tetrapropene (TPH). However, rapid extraction kinetics have been observed using the BTBPs dissolved in cyclohexanone in the absence of a phase-transfer agent [22–24]. Unfortunately, cyclohexanone presents several drawbacks for process implementation; its high solubility in aqueous nitric acid solutions, its known oxidation by nitric acid [25] and its low flash point (44 °C compared to 81 °C for 1-octanol). In this study, we thus decided to evaluate several more hydrophobic alkyl-substituted cyclohexanones as potential new diluents for the separation of actinides from lanthanides using CyMe₄-BTBP **1** as the extractant.

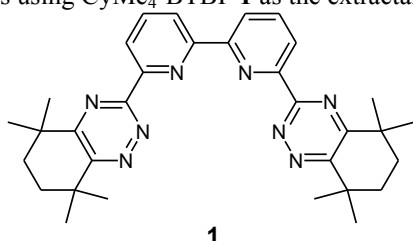


Fig. 1. Structure of CyMe₄-BTBP **1**.

2. Experimental

CyMe₄-BTBP **1** was synthesized as previously described [16, 17] with the modification that the final step in the synthesis was performed in dioxane at reflux for 24 h, rather than in THF at reflux. 3,3,6,6-Tetramethylcyclohexane-1,2-dione (the aliphatic diketone precursor to **1**) was synthesized using a new procedure [26, 27]. All reagents and solvents were purchased from Aldrich Chemical Company Inc. and used as received.

The aqueous solutions for the solvent extraction experiments were prepared by spiking pre-conditioned nitric acid solutions (0.01–4 mol dm⁻³) with stock solutions of ²⁴¹Am and ¹⁵²Eu tracers in nitric acid. The stock solution of ²⁴¹Am in 0.5 M HNO₃ was prepared by dissolving

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americium oxide in 5 M HNO₃ and subsequent dilution with water. The stock solution of ¹⁵²Eu was prepared by appropriate dilution of a commercial preparation (REu-2) supplied by Polatom (Poland). Solutions of CyMe₄-BTBP **1** (0.005 mol dm⁻³) were prepared by dissolving in the appropriate cyclohexanone-based diluent (see Fig. 2) without an additional phase modifier. Prior to labelling, the aqueous phases were pre-equilibrated with the neat diluents by shaking them for 4 h at 250 min⁻¹ and volume ratio of 4 : 1. Prior to contacting with the labelled aqueous phases, the organic phases were pre-equilibrated with the respective non-labelled, non-preconditioned aqueous phases by shaking them for 4 h at 400 min⁻¹ and volume ratio of 1 : 1. In each case, 1.2 mL of labelled aqueous phases were prepared from which 200 µL standards were taken (to allow for mass balance calculations) prior to contacting the aqueous phases with the organic phases. Each organic phase (1 mL) was shaken separately with each of the aqueous phases for 6 h at ambient temperature (ca. 25 °C, non-thermostatted) using a GFL 3005 Orbital Shaker (250 min⁻¹). **The ambient temperature was determined using a standard room thermometer.** After phase separation by centrifugation, two parallel 200 µL aliquots of each phase were withdrawn for analysis. The same procedure was used to investigate the kinetics of ²⁴¹Am extraction. Activity measurements of ²⁴¹Am and ¹⁵²Eu were performed with a γ-ray spectrometer EG&G Ortec (USA) with a PGT (USA) HPGe detector. The γ-lines at 59.5 keV and 121.8 keV were examined for ²⁴¹Am and ¹⁵²Eu, respectively. The errors shown in the figures and/or throughout the text are 1 σ and are based on counting statistics, only. **In the experimental setup used, the values of the minimum detectable distribution ratios, $D_{\min}(\text{Am})$ and $D_{\min}(\text{Eu})$, were approximately 0.002 for all systems.**

3. Results and discussion

The alkylated cyclohexanone diluents shown in Fig. 2 were each evaluated as potential new diluents for the selective extraction of Am(III) in the presence of Eu(III) from nitric acid solutions by CyMe₄-BTBP **1**. Since cyclohexanone itself extracts to a small degree both Am(III) and Eu(III) in a non-selective manner [28], each diluent was first examined for the background extraction of both metal ions in the absence of CyMe₄-BTBP **1**. When each of the diluents was contacted with 4 M HNO₃ solutions of Am(III) and Eu(III) for 6 h, no changes in the volume of either phase were observed. For the monoalkylated cyclohexanone derivatives, **the measured distribution ratios for Am(III) and Eu(III) (D_{Am} and D_{Eu}) were 0.002–0.003 (just above the detection limit).** The cyclohexanones with more alkyl chains or those with (one or more) longer alkyl-groups yielded D values below the detection limits. Thus no significant extraction of either metal ion was observed by the neat diluents themselves, in contrast to cyclohexanone [28].

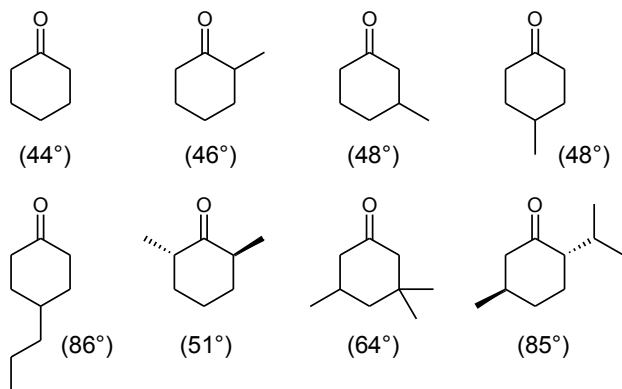


Fig. 2. Cyclohexanone-based diluents examined in this study. Flash points (in °C) are shown in parentheses.

The extraction of Am(III) and Eu(III) from nitric acid solutions by CyMe₄-BTBP **1** dissolved in each of the cyclohexanone diluents shown in Fig. 2 (5 mmolar) was then evaluated. Three different concentrations of the aqueous phase were examined; 0.1 M, 1 M and 4 M HNO₃. The distribution ratios (*D*) and separation factors (SF_{Am/Eu}) for the extraction from 0.1 M HNO₃ are shown in Fig. 3. Cyclohexanone gave the best results compared to its alkylated derivatives ($D_{Am} = 0.101 \pm 0.004$, SF_{Am/Eu} = 11.2 ± 1.4) at this acidity. In contrast, significantly lower *D* values and Am/Eu selectivities were found in the other diluents. No selectivity was observed in the case of 3,3,5-trimethylcyclohexanone, although the *D* values were close to the detection limit.

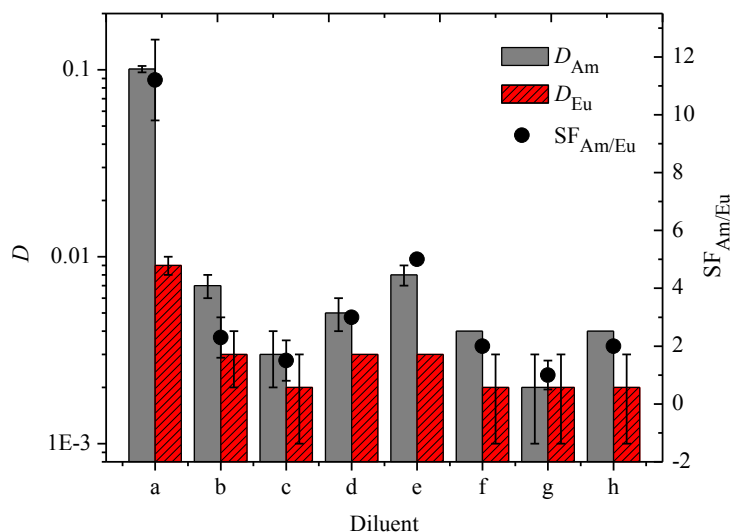


Fig. 3. Extraction of Am(III) and Eu(III) from 0.1 M HNO₃ by CyMe₄-BTBP **1** (5 mM) dissolved in various diluents at 25 °C (non-thermostatted). Contact time = 6 h (a = cyclohexanone, b = 2-methylcyclohexanone, c = 3-methylcyclohexanone, d = 4-methylcyclohexanone, e = 4-propylcyclohexanone, f = 2,6-dimethylcyclohexanone, g = 3,3,5-trimethylcyclohexanone, h = menthone).

The extraction of Am(III) and Eu(III) from 1 M HNO₃ by solutions of CyMe₄-BTBP **1** in the various diluents is shown in Fig. 4. The results for 3-methylcyclohexanone and 4-methylcyclohexanone are both similar to those for

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cyclohexanone. The D values for Am(III) and the separation factors are comparable to the values observed in cyclohexanone. The remaining diluents gave inferior results compared to cyclohexanone, although useful selectivities were observed in some cases (eg: $SF_{Am/Eu} = 101.4 \pm 16.1$ for 3,3,5-trimethylcyclohexanone).

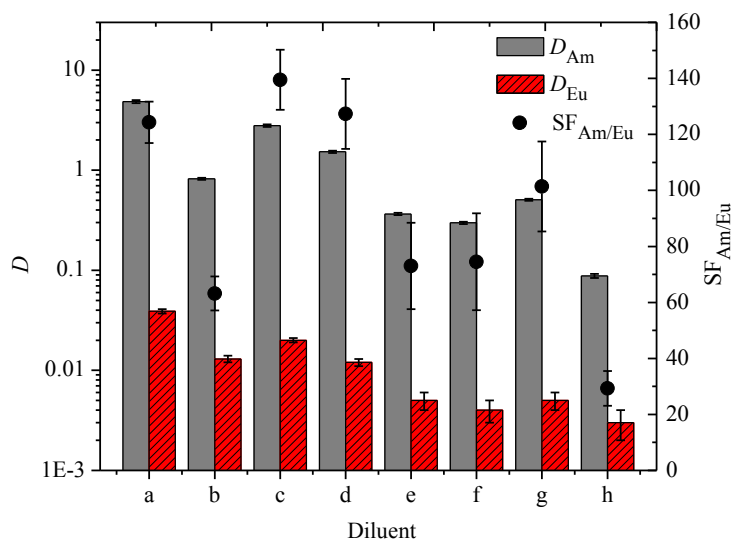


Fig. 4. Extraction of Am(III) and Eu(III) from 1 M HNO_3 by $CyMe_4$ -BTBP **1** (5 mM) dissolved in various diluents at 25 °C (non-thermostatted). Contact time = 6 h (a = cyclohexanone, b = 2-methylcyclohexanone, c = 3-methylcyclohexanone, d = 4-methylcyclohexanone, e = 4-propylcyclohexanone, f = 2,6-dimethylcyclohexanone, g = 3,3,5-trimethylcyclohexanone, h = menthone).

The extraction of Am(III) and Eu(III) from 4 M HNO_3 by solutions of $CyMe_4$ -BTBP **1** in the various diluents is shown in Fig. 5. In this case, the results in 2-methylcyclohexanone, 3-methylcyclohexanone and 4-methylcyclohexanone were all superior to those observed in cyclohexanone. The D values for Am(III) were very similar to those found in cyclohexanone but the separation factors were all significantly higher in these diluents. This is due to the small but non-negligible, non-selective extraction of both Am and Eu from 4 M HNO_3 by the neat cyclohexanone diluent itself ($D_{Eu} \sim D_{Am} = 0.06$) [28]. This property of cyclohexanone is obviously connected to its significant miscibility with nitric acid solutions, particularly at high acidities, as evidenced by changing phase volumes after phase contact. This non-selective extraction results in decreased separation factors in neat cyclohexanone. Both the extraction of the ions by the neat 2-, 3- or 4-methylcyclohexanone and the the miscibility of these diluents with the aqueous phase is lower which results in higher Am/Eu separation factors. Lower D values for Am(III) and lower separation factors were observed in the other diluents tested. Thus 2-methylcyclohexanone, 3-methylcyclohexanone and 4-methylcyclohexanone might be promising new diluents for the separation of Am(III) from Eu(III) using $CyMe_4$ -BTBP **1**.

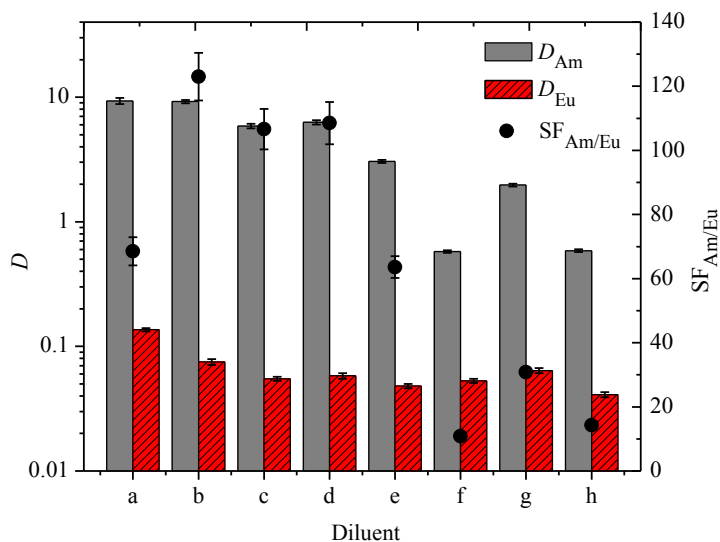


Fig. 5. Extraction of Am(III) and Eu(III) from 4 M HNO₃ by CyMe₄-BTBP **1** (5 mM) dissolved in various diluents at 25 °C (non-thermostatted). Contact time = 6 h (a = cyclohexanone, b = 2-methylcyclohexanone, c = 3-methylcyclohexanone, d = 4-methylcyclohexanone, e = 4-propylcyclohexanone, f = 2,6-dimethylcyclohexanone, g = 3,3,5-trimethylcyclohexanone, h = menthone).

We then examined the influence of contact time on the extraction of Am(III) and Eu(III) by CyMe₄-BTBP **1** dissolved in the various diluents in order to determine the effect of alkyl substitution of the diluent on the extraction kinetics. The D values for the extraction of Am(III) from 4 M HNO₃ as a function of contact time are presented in Fig. 6. The fastest extraction kinetics were found for 3-methylcyclohexanone and 4-methylcyclohexanone, and equilibrium was reached after 1 h of contact time in each case. However, these kinetics are still considerably slower than those found in cyclohexanone (equilibrium reached after 20 minutes). The difference between these kinetics and the results observed for related BTBP ligands dissolved in cyclohexanone (where equilibrium was reached after 5 minutes) [22–24], may be explained by the different experimental conditions (namely intensity of shaking). Interestingly, the kinetics are much slower in 2-methylcyclohexanone than in either 3-methylcyclohexanone or 4-methylcyclohexanone, and equilibrium was not reached even after 3 h of phase contact. This suggests that the position of the methyl group plays an important role in the diluents properties. Methylation at the 2-position of cyclohexanone could hinder processes such as metal ion ligation, acid-catalyzed enolization or acetal formation by the carbonyl-group which may possibly play a role in the extraction mechanism. The kinetics in 4-propylcyclohexanone were much slower than in 4-methylcyclohexanone, suggesting that the length of the alkyl chain considerably influences the rates of extraction. The other remaining diluents (2,6-dimethylcyclohexanone, 3,3,5-trimethylcyclohexanone and menthone) showed the slowest extraction kinetics.

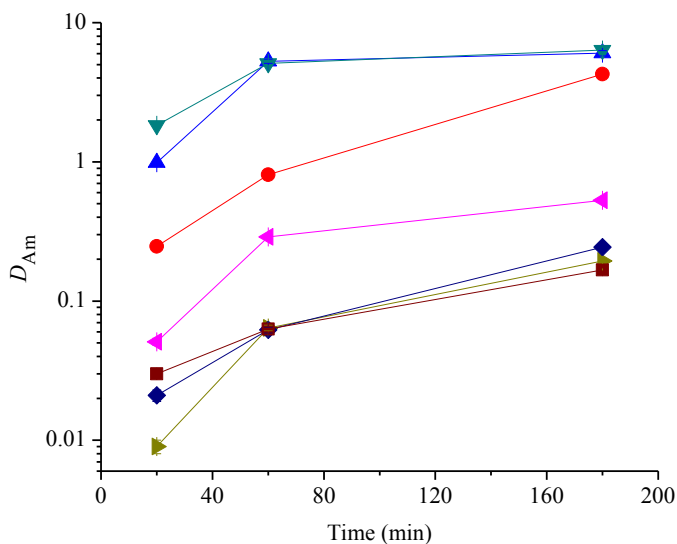


Fig. 6. Extraction of Am(III) from 4 M HNO₃ as a function of contact time by CyMe₄-BTBP **1** (5 mM) dissolved in various diluents at 25 °C (non-thermostatted, ● = 2-methylcyclohexanone, ▲ = 3-methylcyclohexanone, ▼ = 4-methylcyclohexanone, ◀ = 4-propylcyclohexanone, ► = 2,6-dimethylcyclohexanone, ◆ = 3,3,5-trimethylcyclohexanone, ■ = menthone).

Considering the results of the extraction experiments from 4 M HNO₃ solution, some general observations can be made regarding the effect of alkyl substitution of cyclohexanone on its properties as a diluent. For the monomethylated diluents, the values of D_{Am} and $SF_{Am/Eu}$ slowly decrease in the order of methyl positions 2 > 4 ~ 3. However, the position of the methyl group profoundly influences the kinetics; the rate of Am extraction from 4 M HNO₃ is fastest if the substituent is in position 3 and slowest if the substituent is in position 2. When comparing 2,6-dimethylcyclohexanone with 2-methylcyclohexanone, addition of a second methyl group markedly deteriorates the properties of the diluent and further reduces its extraction ability, Am/Eu selectivity and kinetics of extraction. Alkyl substitution in positions 2 and 6 is clearly responsible for slow kinetic properties. Overall, methylation of cyclohexanone in position 3 seems to yield the best properties.

The length of the alkyl chain does not significantly influence the equilibrium values of D or $SF_{Am/Eu}$; the values of D_{Am} and $SF_{Am/Eu}$ measured in 4-propylcyclohexanone were only approximately twice lower than the values of D_{Am} and $SF_{Am/Eu}$ measured in 4-methylcyclohexanone. However, the length of the alkyl chain significantly influences the kinetics of the extraction. When comparing 3,3,5-trimethylcyclohexanone with 3-methylcyclohexanone, the additional methyl groups cause a decrease of the distribution ratio by a factor of three and a dramatic deterioration of the kinetics, indicating that increasing the number of alkyl groups generally causes rather slow kinetics. On the other hand, when comparing 3,3,5-trimethylcyclohexanone with 2,6-dimethylcyclohexanone, the values of D_{Am} and $SF_{Am/Eu}$ for 3,3,5-trimethylcyclohexanone are approximately four times

higher. Thus the positions of the alkyl groups on the cyclohexanone molecule are more important for the extraction properties of the diluent than the number of alkyl groups in the molecule.

4. Conclusion

The effects of alkyl substitution of cyclohexanone on the extraction of Am(III) and Eu(III) by CyMe₄-BTBP **1** dissolved in various cyclohexanone-based diluents have been investigated. Alkylated cyclohexanones are promising potential new diluents for the partitioning of minor actinides and lanthanides by the BTBP molecules. Compared to cyclohexanone, the alkylated derivatives showed lower miscibilities with the aqueous phase, but slower extraction kinetics. Overall, 3-methylcyclohexanone was found to have the best properties as a diluent. When compared with the results obtained in neat cyclohexanone, D_{Am} in 4 M HNO₃ is lower by **approximately** one third, $SF_{Am/Eu}$ is higher by 50% and the kinetics of extraction are about three times as slow. The results are similar in the extraction from 1 M HNO₃. Alkylation of cyclohexanone in position 2 and long alkyl substituents are disadvantageous for the extraction properties of the solvent.

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