DE
G
DE GRUYTER
OPEN

Characterization of solvents containing CyMe₄-BTPhen in selected cyclohexanone-based diluents after irradiation by accelerated electrons

**Petr Distler,
Jana Kondé,
Jan John,
Zuzana Hájková,
Jaroslav Švehla,
Bohumír Grüner**

Abstract. Radiation stability of CyMe₄-BTPhen was examined in systems with three selected cyclohexanone-
-based diluents. Accelerated electrons were used as a source of ionizing radiation. The CyMe₄-BTPhen radiation
degradation identification and characterization of the degradation products were performed by high performance
liquid chromatography (HPLC) and mass spectrometry (MS) analyses. Residual concentrations of tested ligand
were determined. Moreover, extraction properties of the solvents irradiated at two different doses were compared
with the extraction properties of non-irradiated solvents to estimate the influence of the presence of degradation
products in the organic phase.

Key words: accelerated electrons • CyMe₄-BTPhen • irradiation • radiation stability • solvent extraction

P. Distler, J. Kondé, J. John✉
Department of Nuclear Chemistry,
Czech Technical University in Prague,
Břehová 7, 11519 Prague 1, Czech Republic,
E-mail: jan.john@fjfi.cvut.cz

Z. Hájková, J. Švehla, B. Grüner✉
Institute of Inorganic Chemistry, Academy of Sciences
of the Czech Republic,
Hlavni 1001, 25068 Husinec-Rež, Czech Republic,
E-mail: gruner@iic.czs.cz

Introduction

A significant portion of the long-lived radiotoxicity of spent nuclear fuel is due to the presence of transplutonium elements. Even though the plutonium and uranium reduction extraction (PUREX) process is currently used to separate uranium and plutonium from spent nuclear fuel, the resulting high level liquid waste (PUREX raffinates/concentrate) still contains minor actinides (Am, Cm, and Np) [1–3]. Partitioning and transmutation (P&T) is a concept aiming at decreasing the long-term radiotoxicity of used nuclear fuel. It focuses on chemical treatment of spent nuclear fuel by separating out e.g. the long-lived minor actinides by means of some separation process, e.g. liquid-liquid extraction. Once removed, these elements can be transformed into stable or more short-lived isotopes [4, 5].

A wide range of molecules have been proposed and tested as extractants for solvent extraction in the separation for transmutation processes [6]. The annulated ligand CyMe₄-BTBP (**1** in Fig. 1) has solvent extraction properties suitable for An(III)/ Ln(III) separations, as was demonstrated under process conditions [7–9]. However, it has been shown that the extraction properties of CyMe₄-BTBP can be increased by intra-molecular preorganization of the molecule, in which the 2,2′-bipyridine moiety of the BTBPs has been replaced with a 1,10-phen--anthroline (BTPhen) moiety [10–12]. The CyMe₄-
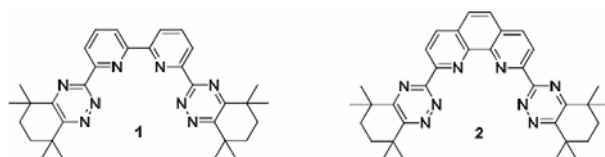
Fig. 1. Structures of CyMe$_4$-BTBP (**1**) and CyMe$_4$-BTPhen (**2**).

-BTPhen (**2** in Fig. 1) ligand can be considered as a more pre-organized quadridentate ligand. The modification of the molecule has a significant effect on extraction properties. Also, the kinetics of extraction is significantly faster for CyMe$_4$-BTPhen, the equilibrium is reached within 15 minutes of contact time [12–14].

The CyMe$_4$-BTPhen molecule is a promising extractant for the European SANEX and/or GANEX processes for the recovery of minor actinides from a genuine spent nuclear fuel solution. In such applications, it is necessary to demonstrate not only good extraction properties of the solvent, but also radiation stability of the extractants and the influence of solvent irradiation on its extraction properties. The effects of irradiation on solvent extraction might result in: (1) decreased ligand concentrations; (2) decreased selectivity due to the production of ligand radiolysis products; (3) decreased selectivity due to the production of diluent radiolysis products; and (4) altered solvent performance due to films, precipitates, and increased viscosity [15].

Retegan *et al.* studied γ-irradiated solutions of CyMe$_4$-BTBP, dissolved in cyclohexanone or hexanol, for americium and europium solvent extraction experiments. They reported that there was no apparent decrease in performance up to the maximum absorbed dose of 12–14 kGy. The related compound C5-BTBP exhibited a significant decrease in the extraction efficiency for americium over the absorbed dose range 0–28 kGy [16].

Fermvik *et al.* investigated varying γ-dose-rates for the irradiation of MF2-BTBP in cyclohexanone in the absence of aqueous phase during irradiations. While the solutions were irradiated up to absorbed dose of 100 kGy at low dose rate (15 Gy/h), the solvent extraction efficiency for americium and europium remained more or less at the same level. During high dose rate irradiation (1.2 kGy/h) the extraction efficiency for americium and europium decreased significantly (approx. 60% of initial value) with increasing absorbed dose. The lower degradation during low dose rate experiments was not necessarily a dose-rate effect. The authors commented that at the low dose rate irradiation, the oxygen concentration in the solutions was most likely higher, due to repeated sampling over the 5400 hours required to deliver the 100 kGy [17].

Radiolysis of CyMe$_4$-BTBP has been studied in several papers. Magnusson studied radiation stability of CyMe$_4$-BTBP dissolved in hexanol or cyclohexanone and in the absence of aqueous phase/nitric acid during the irradiation. Samples were irradiated at lower dose rate (220 Gy/h) and significant radiolytic degradation was observed [18]. The radiolysis of CyMe$_4$-BTPhen has not yet been studied.

Methodology

Irradiation procedure

The solutions of the CyMe$_4$-BTPhen (synthesized by the University of Reading, United Kingdom, the group of Prof. Harwood) ligand dissolved in cyclohexanone or alkylated cyclohexanone derivatives were irradiated by pulse linear electron accelerator LINAC 4-1200 (Tesla v.t. Mikroel). The mean electron energy was 4.5 MeV, pulse width 3 μs, and repeating frequency 500 Hz. The maximum total dose was 200 kGy.

Residual concentrations of tested ligand determination – HPLC analyses

Samples were analyzed using HPLC system LaChrom series 7000 (Merck-Hitachi) equipped with HPLC Pump D7100, Diode Array detector D7450, Programmable Autosampler D7250, Interface Module D7100 and LaChrom 7000 Data Manager. Chromatographic conditions column: Gemini C18 RP (150 × 3 mm I.D., Phenomenex), which enabled operation at higher pH values up to pH 12 necessary to limit peak broadening. Buffer: the buffer was prepared by mixing 150 mL of aqueous triethylamine carbonate solution (TAAC, component A) (20.0 mL of 1.0 mol/L TEAC solution (Aldrich) was poured into 120 mL of water (HPLC grade, Biosolve BV), pH was adjusted 10.2 by 1.0 mol/L triethylamine and water was added to set the final volume 150.0 mL) and 850 mL of acetonitrile (gradient grade, Aldrich, component B). Elution: isocratic, flow rate 0.6 mL/min; detection DAD in the range 237–300 nm, selected wavelengths 245, 259, 262 and 292 nm. The CyMe$_4$-BTPhen sample of concentrations 5 mmol/L in cyclohexanones were diluted by CH$_3$CN: 50 μL of the sample syringed and the final volume was adjusted to 1.0 mL by acetonitrile. Injection volume 6 μL, injection statistics over 6 injections from 2 vials containing each irradiated sample was performed from peak areas on chromatograms integrated at 259 nm.

Calibrations

The calibrations were performed using samples of three non-irradiated standards of CyMe$_4$-BTPhen dissolved in the particular solvents; 50 μL of the solution of the three standards of specified concentration 5 mmol/L CyMe$_4$-BTBP in different solvents were diluted with 950 μL of CH$_3$CN (for HPLC, gradient grade, Aldrich). The calibration curves for samples in each of the three solvents were constructed separately from peak areas measured at 259 nm using data from injection statistics over 6 injections for volumes 1, 2, 3, 5, and 7 μL from 3 vials (two injections from each vial and for each volume). The calibration plots exhibited very good linear fit over the whole range; $R^2 = 0.985$, 0.9893, and 0.9892 for standards diluted by cyclohexanone, 3-methylcyclohexanone, and 2,6-dimethylcyclohecanone, respectively. The

data for calibration were used for calculations of the residual concentrations in the irradiated samples.

Identification and characterization of the degradation products by mass spectrometry

Mass spectra were measured Finnigan LCQ Fleet™ spherical Ion Trap LC/MS$_n$ instrument (Thermo Scientific) with atmospheric pressure chemical ionization (APCI) in positive mode using direct infusion of the samples from a syringe pump. 50 μL of the samples were diluted to volume 1.0 mL by acetonitrile (for HPLC, gradient grade, Chemlab NV), flow rate 10 μL/min. Conditions used for APCI interface: MS measurements: flow rate from a syringe infusion pump: 10 μL/min; sheath gas flow 20 L/min; auxiliary gas flow at 9 L/min; source voltage: 4.17 kV; vaporizer temperature 400°C; capillary temperature 250°C; capillary voltage 3 V and mass range from 50 to 2000. The signals of the degradation products of lower relative intensities were measured in enhanced mode.

Solvent extraction studies

The aqueous solutions were prepared by spiking 0.98 mL of 1 mol/L HNO₃ solutions subsequently with 10 μL of each of the working solutions of ²⁴¹Am and ¹⁵²Eu tracers. Organic phase solutions of each of the ligands (initial concentration before irradiation was 5 mmol/L) were prepared by dissolution of the ligand in the respective diluent. In each case, 1.0 mL of labelled aqueous phases were prepared, from which 150 μL standards were taken (to allow for mass balance calculations) prior to the contacts of aqueous phase with the organic phase in plastic ampoules. Organic phase (0.85 mL) was shaken with aqueous phase for 6 hours at ambient temperature (ca. 23°C, non-thermostated) using a horizontal GFL 3005 Orbital shaker at 250 min⁻¹.

Usually, in solvent extraction experiments with cyclohexanone, the phases are pre-equilibrated with the HNO₃ or cyclohexanone, respectively, prior to the extraction experiments to limit the influence of mutual miscibility of cyclohexanone with aqueous solution. In the experimental set-up used this was not possible. However, since all the data are related to their respective standards, any potential influences are suppressed.

Radioactivity measurements of ²⁴¹Am and ¹⁵²Eu were performed with a γ-ray spectrometer EG&G Ortec equipped with the PGT HPGe detector. The γ-lines at 59.5 keV, and 121.8 keV were used for ²⁴¹Am and ¹⁵²Eu, respectively.

Results

CyMe₄-BTPhen radiation degradation

Three series of samples were irradiated by total absorbed doses 12, 24, 48, 100, and 200 kGy. The
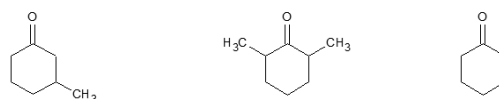
3-methylcyclohexanone   2,6-dimethylcyclohexanone   cyclohexanone
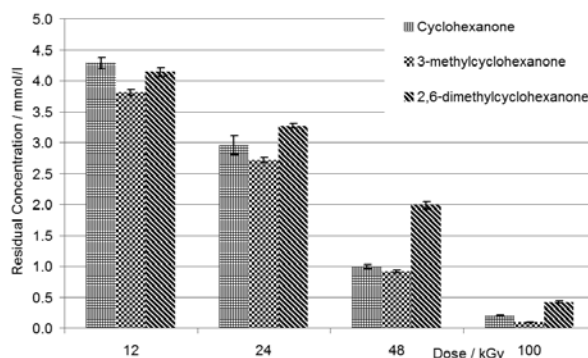
Fig. 2. Structure of tested diluents.

Fig. 3. Residual concentration of CyMe4-BTPhen after irradiation in cyclohexanone, 3-methylcyclohexanone, and 2,6-dimethylcyclohecanone. Initial concentration of CyMe4-BTPhen was 5 mmol/L.

series differed by the diluent used – cyclohexanone, 3-methylcyclohexanone, 2,6-dimethylcyclohexanone. The structures of these diluents are shown in Fig. 2.

In the irradiated samples, residual concentrations of the CyMe₄-BTPhen were determined by HPLC. The data obtained for all these series are summarized in Fig. 3.

It can be seen that the degradation of the CyMe₄-BTPhen proceeds quite fast with the absorbed dose – for cyclohexanone or 3-methylcyclohexanone, almost 50% of the ligand is degraded already at 24 kGy (44 and 49%, respectively), whereas the system in 2,6-dimethylcyclohexanone shows only 34% degradation. Almost complete degradation occurs at the applied dose of 100 kGy, when only 4, 2 and 8% of the original ligand concentration could be found in the systems with cyclohexanone, 3-methylcyclohexanone, and 2,6-dimethylcyclohexanone, respectively. There was no CyMe₄-BTPhen determined at the dose of 200 kGy in any of tested diluents. As an interesting new phenomenon, a clear radioprotective action of the 2,6-dimethylcyclohexanone can be seen from these results. It could be caused by blocking both sites in α-position to the carbonyl group by two methyl groups or by sterical shielding of the carbon of carbonyl group itself.

According to MS, the peaks corresponding to products originating from reactions of CyMe₄-BTPhen (m/z = 559) with solvent molecules are detected across the series (for example see Fig. 4). The pattern observed in all spectra of irradiated samples over the whole series is quite uniform and consists from well distinguishable peaks corresponding to addition of one, two or eventually three molecules of the diluent to CyMe₄-BTPhen scaffold. The uniform chemical origin of the degradation products in all three systems is also indicated by incremental increase of 15 mass units between systems with cyclohexanone and 3-methylcyclohexanone and
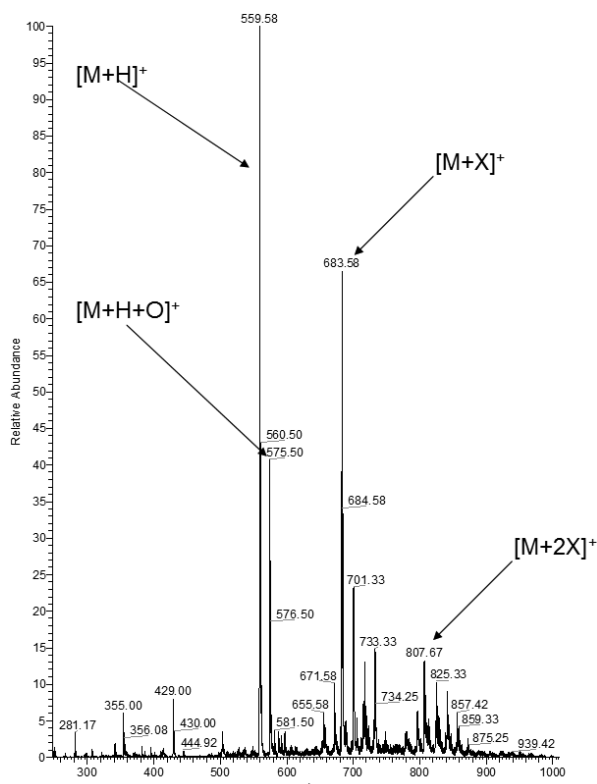
Fig. 4. MS spectrum of CyMe$_4$-BTPhen irradiated in 2,6-dimethylcyclohexanone irradiated by dose 100 kGy (M = CyMe$_4$-BTPhen, X = 2,6-dimethylcyclohexanone).

30 mass units between cyclohexanone and 2,6-dimethylcyclohexanone observable between base peaks with mass [M + X]$^+$ and [M + 2X]$^+$, corresponding to main degradation products (where M stands for the ligand and X for a diluent used). This incremental mass clearly corresponds to presence of one methyl group in 3-methylcyclohexanone and two methyl groups in 2,6-dimethylcyclohexanone system. With increased doses, the relative abundances of peaks clearly move to higher mass adducts with solvent.

The main peaks in the spectra of the irradiated samples are accompanied by smaller peaks with mass increased by 16 or 17 mass units, which probably corresponds to an addition of oxygen or OH groups. Their relative abundances of peaks corresponding to higher mass products increase depending on the absorbed dose. Some peaks with lower molecular mass than the parent molecule could be seen, but their relative intensities in the system irradiated in neat diluent are relatively low (see Fig. 4). This suggests about good stability of the annulated system of CyMe$_4$-BTPhen towards bonds breaking and extrusions of smaller fragments.

Extraction properties of the irradiated solvents

The impact of CyMe$_4$-BTPhen degradation products and adducts (and remaining concentration of CyMe$_4$-BTPhen) on extraction properties was tested. The 5 mmol/L CyMe$_4$-BTPhen solutions in all tested diluents were irradiated by accelerated electrons by the dose of 24 kGy and 100 kGy. The

Table 1. Extraction of Am and Eu by non-irradiated and irradiated 5 mmol/L CyMe$_4$-BTPhen in 3-methylcyclohexanone

Dose [kGy]	D(Am)	D(Eu)	SF(Am/Eu)
0	201 ± 47	2.43 ± 0.06	83 ± 19
24	112 ± 16	1.16 ± 0.03	97 ± 14
100	7.4 ± 0.4	0.132 ± 0.005	56 ± 4

Table 2. Extraction of Am and Eu by non-irradiated and irradiated 5 mmol/L CyMe$_4$-BTPhen in 2,6-dimethylcyclohexanone

Dose [kGy]	D(Am)	D(Eu)	SF(Am/Eu)
0	9.0 ± 0.5	0.111 ± 0.004	81 ± 6
24	4.9 ± 0.2	0.098 ± 0.004	50 ± 3
100	0.92 ± 0.02	0.053 ± 0.003	17 ± 1

Am and Eu distribution coefficients were determined as described above.

The influence of ionizing radiation on the extraction properties of solvents with 3-methylcyclohexanone diluent are summarized in Table 1. As can be seen from these data, D(Am) and D(Eu) decrease rapidly with the absorbed dose. Already at 24 kGy, they decreased approximately twice, and at 100 kGy they decreased 30 and 20 times, respectively. The values of separation factors at first remain practically constant; they decrease to about one half of the original value at 100 kGy.

The values for 2,6-dimethylcyclohexanone diluent are shown in Table 2. The decrease in distribution coefficients in this diluent is slightly less than in 3-methylcyclohexanone. Even at 100 kGy the D(Am) values dropped only to approx. 10% for Am extraction and to 50% for Eu extraction compared to the drop to approx. 5% for both the D(Am) and D(Eu) values in 3-methylcyclohexanone. However, the decrease in the separation factor is more noticeable in 2,6-dimethylcyclohexanone (decrease by a factor of 5) than in 3-methylcyclohexanone.

Finally, as can be seen from Table 3, the values of distribution ratios for both Am and Eu also decreased with increasing doses in cyclohexanone. The rates of D values decrease were slower for Am than for Eu extraction; it led to an increase of a separation factor by 4.5 at dose the of 100 kGy.

The dependences of the relative D(Am) and D(Eu) values on the absorbed doses are shown in Fig. 5. It was shown that the D(Am) values decreased by more than 80% at the dose of 100 kGy in each of the diluents used. When related to the decrease of D(Am) values in cyclohexanone, it can be seen that neither of the alternative diluents showed a signifi-

Table 3. Extraction of Am and Eu by non-irradiated and irradiated 5 mmol/L CyMe$_4$-BTPhen in cyclohexanone

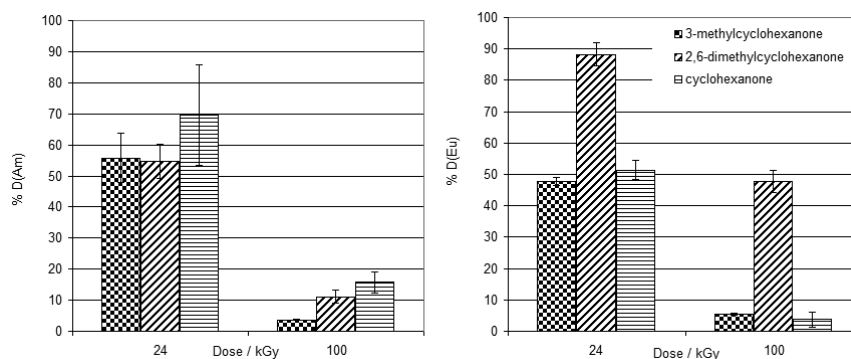| Dose [kGy]	D(Am)	D(Eu)	SF(Am/Eu)
0	447 ± 113	10.2 ± 0.2	44 ± 12
24	310 ± 70	5.22 ± 0.15	59 ± 15
100	70 ± 15	0.381 ± 0.009	184 ± 40

Fig. 5. Dependences of percentage D(Am) and D(Eu) values on doses.

cant radioprotective effect regarding the extraction properties of the solvent. On the contrary, for both 3-methylcyclohexanone and 2,6-dimethylcyclohexanone, the decrease of D(Am) value with the absorbed dose was slightly faster than in cyclohexanone diluent. Surprisingly, a slower decrease in Eu extraction (when comparing with Am) was observed from the solvent with 2,6-dimethylcyclohexanone.

These figures give also a visual explanation of the reasons of unexpected dependences of the separation factors SF(Am/Eu) on the absorbed doses. As seen in the Tables 1–3, while the SF(Am/Eu) does not significantly depend on the absorbed dose for the solvents with cyclohexanone or 3-methylcyclohexanone, a marked decrease of SF(Am/Eu) with the absorbed dose is observed for the solvents with 2,6-dimethylcyclohexanone diluent. The clear reason for this is the different behavior of the systems for Am and Eu extractions. While no significant difference in the influence of the diluents on the D values measured for Am is observed, a markedly slower decrease of D(Eu) is observed in irradiated solvents with 2,6-dimethylcyclohexanone diluent when compared with those with cyclohexanone or 3-methylcyclohexanone diluents. Even though the D(Eu) values in the 2,6-dimethylcyclohexanone diluent are generally rather low, here, they are well above the limit of detection and their precision is well below 10%. Also, it is known from earlier studies that, contrary to the neat cyclohexanone, virtually no Am or Eu is extracted into the neat 2,6-dimethylcyclohexanone [19]. Hence, no explanation of this experimentally observed phenomenon is available at this moment.

Semiquantitative assessment of the extraction properties of radiolysis products

The assessment of the extraction properties of the products of radiolysis was performed by comparing the experimental D values measured for the irradiated solvents with the theoretical values calculated from the experimental D value measured for the non-irradiated solvent and the residual CyMe₄-BTPhen concentration measured in the irradiated samples. For this calculation, the 1 : 2 stoichiometry of the Am : CyMe₄-BTPhen complexes was assumed.

The results of these comparisons for all three solvents are shown in Table 4. It can be seen that in all the systems studied, the experimental D values are significantly higher than their theoretical values calculated from the residual concentrations of CyMe₄-BTPhen in these samples. The only plausible explanation for this effect is that the products of radiolysis of CyMe₄-BTPhen solvents are relatively efficient extractants for Am, too. This is in good agreement with the finding from MS that the most abundant products of the radiolysis of CyMe₄-BTPhen solvents in cyclohexanone-based diluents are CyMe₄-BTPhen + diluent adducts. Based on the fact that the D(Am) values decrease slowly anyway; it can be estimated that compared to the neat CyMe₄-BTPhen ligand, the CyMe₄-BTPhen + diluent adducts are less efficient Am extractants.

Conclusions

The CyMe₄-BTPhen radiation stability has been studied in the three selected cyclohexanone-type diluents. HPLC data displayed a continuous decrease in the concentration with the applied dose. In particular, the 2,6-dimethylcyclohexanone diluent proved some stabilizing effect, apparently due to the blocking of either both sites in α-position to the carbonyl group by two methyl groups or due to the sterical shielding of the carbon of carbonyl group itself. The pattern observed in MS spectra correspond to reaction of CyMe₄-BTPhen with cyclohexanones producing main degradation products that contain from one up to three molecules of diluents, depending

Table 4. Experimental and calculated values of D(Am)

Dose [kGy]	D(Am) values in different diluents					
	3-methylcyclohexanone		2,6-dimethylcyclohexanone		Cyclohexanone	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
0	201	–	9	–	447	–
24	112	55	4.9	3.7	310	139
100	7.4	0.080	0.92	0.061	70	0.72

on the applied dose. It seems that the diluent is co-valently bound in these species, similarly as has been supposed previously for the CyMe$_4$-BTBP series [20]. Ongoing are further experimental studies with the aim to determine a site of reaction and the structure of degradation products. Minor products containing oxygen atoms were also observed along with a relatively small extent of CyMe$_4$-BTPhen degradation to low molecular mass species.

D(Am) and D(Eu) decrease rapidly with the absorbed dose delivered by accelerated electrons. Already at 24 kGy, the D values decreased approximately twice for all three investigated systems. Neither of the diluents alternative to cyclohexanone exhibited a significant radioprotective effect regarding the extraction properties of the solvent except for the surprising case of Eu extraction from the solvent with 2,6-dimethylcyclohexanone diluent. Based on the semiquantitative assessment, the CyMe$_4$-BTPhen+diluent adducts extract Am and Eu, too, even though they are weaker extractants than the parent molecule itself. In the next phase, these adducts should be synthesized and their extraction properties studied in detail. Moreover, in the subsequent experiments, the results obtained will be compared with the effect of irradiation by gamma rays and with the behavior of CyMe$_4$-BTBP under irradiation at the same conditions.

References

1. Lanham, W. G., & Runion, T. C. (1949). *Purex process for plutonium and uranium recovery*. Oak Ridge: Oak Ridge National Laboratory. (USAEC Report ORNL-479/TN).

2. Rydberg, J., Cox, M., Musikas, C., & Choppin, G. R. (2004). *Solvent extraction principles and practice.* 2nd ed., revised and expanded (pp. 507–558). New York: Marcel Dekker.

3. Sood, D. D., & Patil, S. K. (1996). Chemistry of nuclear fuel reprocessing: Current status. *J. Radiat. Chem.*, *203*, 547–573. DOI: 10.1007/BF02041529.

4. Greneche, D., Quiniou, B., Boucher, L., Delpech, M., Gonzalez, E., Alvarez, F., Cunado, M. A., Serrano, G., Cormenzana, J. L., Kuckshinrichs, W., Odoj, R., Lensa, W., Wallenius, J., Westlén, D., Zimmerman, C., & Marivoet, J. (2007). *Red impact – impact of partitioning, transmutation and waste reduction, synthesis report, technologies on the final nuclear waste disposal.* Jülich: Forschungszentrum Jülich GmbH.

5. Salvatores, M., & Palmiotti, G. (2011). Radioactive waste partitioning and transmutation within advanced fuel cycles: Achievements and challenges. *Progr. Part. Nucl. Phys.*, *66*, 144–166. DOI: 10.1016/j.ppnp.2010.10.001.

6. Lewis, F. W., Hudson, M. J., & Harwood, L. M. (2011). Development of highly selective ligands for separations of actinides from lanthanides in the nuclear fuel cycle. *Synlett.*, 18, 2609–2632. DOI: 10.1055/s-0030-1289557.

7. Magnusson, D., Christiansen, B., Foreman, M. R. S., Geist, A., Glatz, J. P., Malmbeck, R., Modolo, G., Serrano-Purroy, D., & Sorel, C. (2009). Demonstration of a SANEX process in centrifugal contactors using the CyMe$_4$-BTBP molecule on a genuine fuel solution. *Solvent Extr. Ion Exch.*, *27*, 97–106. DOI: 10.1524/ract.2009.16478.

8. Wilden, A., Modolo, G., Schreinemachers, Ch., Sadowski, F., Lange, S., Sypula, M., Magnusson, D., Geist, A., Lewis, F. W., Harwood, L. M., & Hudson, J. M. (2013). Direct selective extraction of actinides(III) from PUREX raffinate using a mixture of CyMe$_4$-BTBP and TODGA as 1-cycle SANEX solvent Part III: Demonstration of a laboratory-scale counter-current centrifugal contactor process. *Solvent Extr. Ion Exch.*, *31*, 519–537. DOI: 10.1080/07366299.2013.775890.

9. Modolo, G., Wilden, A., Daniels, H., Geist, A., Magnusson, D., & Malmbeck, R. (2013). Development and demonstration of a new SANEX partitioning process for selective actinide(III)/lanthanide(III) separation using a mixture of CyMe$_4$-BTBP and TODGA. *Radiochim. Acta*, *101*, 155–162. DOI: 10.1524/ract.2013.2016.

10. Lewis, F. W., Harwood, L. M., Hudson, M. J., Drew, M. G. B., Desreux, J. F., Vidick, G., Bouslimani, N., Modolo, G., Wilden, A., Sypula, M., Vu, T. H., & Simonin, J. P. (2012). From BTBPs to BTPhens: The effect of ligand pre-organization on the extraction properties of quadridentate bis-triazine ligands. *Procedia Chem.*, *7*, 231–238. DOI: 10.1016/j.proche.2012.10.038.

11. Lewis, F. W., Harwood, L. M., Hudson, M. J., Drew, M. G. B., Desreux, J. F., Vidick, G., Bouslimani, N., Modolo, G., Wilden, A., Sypula, M., Vu, T. H., & Simonin, J. P. (2011). Highly efficient separation of actinides from lanthanides by a phenanthroline-derived bis-triazine ligand. *J. Am. Chem. Soc.*, *133*, 13093–13102. DOI: 10.1021/ja203378m.

12. Hudson, M. J., Harwood, L. M., Laventine, D. M., & Lewis, F. W. (2013). Use of soft heterocyclic N-donor ligands to separate actinides and lanthanides. *Inorg. Chem.*, *52*, 3414–3428. DOI: 10.1021/ic3008848.

13. Lewis, F. W., Harwood, L. M., Hudson, M. J., Drew, M. G. B., Hubscher-Bruder, V., Videva, V., Arnaud-Neu, F., Stamberg, K., & Vyas, S. (2013). BTBPs versus BTPhens: Some reasons for their differences in properties concerning the partitioning of minor actinides and the advantages of BTPhens. *Inorg. Chem.*, *52*, 4993–5005. DOI: 10.1021/ic3026842.

14. Afsar, A., Westwood, J., Harwood, L. M., Hudson, J. M., Laventine, D. M., & Geist, A. (2014). The effect of alkyl substitution on the extraction properties of BTPhen ligands for the partitioning of trivalent minor actinides and lanthanides in spent nuclear fuels. *JJC*, *9*, 50–58.

15. Mincher, B. J., Modolo, G., & Mezyk, P. S. (2010). Review: The effects of radiation chemistry on solvent extraction 4: Separation of the trivalent actinides and considerations for radiation-resistant solvent systems. *Solvent Extr. Ion Exch.*, *28*, 415–436. DOI: 10.1080/07366299.2010.485548.

16. Retegan, T., Ekberg, C., Englund, S., Fermvik, A., Foreman, M. R. S., & Skarnemark, G. (2007). The behaviour of organic solvents containing C5-BTBP and CyMe$_4$-BTBP at low irradiation doses. *Radiochim. Acta*, *95*, 637–642. DOI: 10.1524/ract.2007.95.11.637.

17. Fermvik, A., Ekberg, C., Englund, S., Foreman, M. R. St J., Modolo, G., Retegan, T., & Skarnemark, G. (2009). Influence of dose rate on the radiolytic stability of a BTBP solvent for actinide(III)/lanthanide(III) separation. *Radiochim. Acta*, *97*, 319–324. DOI: 10.1524/ract.2009.1615.

18. Magnusson, D., Christiansen, B., Malmbeck, R., & Glatz, J. P. (2009). Investigation of the radiolytic stability of a CyMe$_4$-BTBP based SANEX solvent. *Radiochim. Acta, 97*, 497–502. DOI: 10.1524/ract.2009.1647.

19. Distler, P., Špendlikova, I., John, J., Harwood, L. M., Hudson, M. J., & Lewis, F. W. (2012). 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. *Radiochim. Acta, 100*, 747–752. DOI: 10.1524/ract.2012.1949.

20. Aneheim, E., Ekberg, C., Fermvik, A., Foreman, M. R. St J., Grüner, B., Hájková, Z., & Kvičalová, M. (2011). A TBP/BTBP-based GANEX separation process – Part 2: Ageing, hydrolytic and radiolytic stability. *Solvent Extr. Ion Exch., 29*, 157–175. DOI: 10.1080/07366299.2011.539462.