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Radiation influencing of the extraction properties of the CyMe4-BTBP and CyMe4-BTPhen solvents with FS-13

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Abstract

The radiolytic stability of two ligands, CyMe4-BTBP and CyMe4-BTPhen in system with the FS-13 (phenyl trifluoromethyl sulfone) diluent was investigated under irradiation by accelerated electrons to study impact of the degradation products on the separation process efficiency and safety. Irradiation experiments were carried out up to the absorbed dose of 200 kGy.The irradiated samples were analysed by HPLC for the degree of extractant degradation. In addition, the effect of the presence of HNO_3 during the irradiation was studied.Extraction properties of the irradiated solvents were evaluated and compared with the extraction properties of non-irradiated solvents to assess the impact of the degradation products on extractions properties.

The results obtained show that the stabilities of these ligands are higher in FS-13 than in the cyclohexanone-type solvents. The extraction properties are significantly influenced by degradation products contained in these systems. Surprisingly, both the distribution ratios for americium and europium, and the Am/Eu separation factor increase with the absorbed dose for the system withCyMe4-BTPhen in FS-13. Obviously, the degradation products of this ligand are efficient extractants too. In the next phase, an attempt will be done to identify the main degradation products, synthesise them and study their extraction properties.

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Keywords:$CyMe_4$-BTBP; $CyMe_4$-BTPhen; radiolytic stability; accelerated electrons; FS-13

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1. Introduction

The used nuclear fuel from nuclear power plants is highly radiotoxic and has to be stored for more than 100,000 years. The radiotoxicity is mainly dominated by transuranics (TRUs), particularly plutonium isotopes and decay products of Pu-241.For the recovery of uranium and plutonium from spent nuclear fuel is widely used the PUREX[1] (Plutonium and Uranium Reduction EXtraction) process. Liquid high radioactive waste (PUREXraffinates / concentrate) generated from nuclear fuel reprocessing still contains long-lived actinides namely Np, Pu, Am and Cm. If these actinides are separated from the rest of waste, long term radiological risks of the high radioactive waste would be reduced very effectively. So recycling (reprocessing) of the used nuclear fuel could decrease the long-term radiotoxicity, reduce the heat load of the waste and shorten the storage time of waste[2,3].

Partitioning and Transmutation (P&T) is an advanced reprocessing option which focuses on decreasing the long-term radiotoxicity of used nuclear fuel. Partitioning is aimed at chemical separation of long-lived minor actinides from the high-level liquid waste and transmutation by means of the nuclear conversion of these actinides into more short-lived or even stable ones[4–7].

There are several methods to separate minor actinides from spent nuclear fuel, such as solvent extraction or pyroprocessing. In recent years, many ligands have been tested and studied, which can be used as extracting agents for liquid-liquid extraction[8]. Any extractant used in such processes must fulfill several criteria. The extractant must show a sufficient selectivity toward the actinides, good solubility in organic phase, must be resistant toward hydrolysis and radiolysis and any problematic degradation products formed must be eliminated in the process[9].

One of the most important classes of prospective extractants are soft N donor ligands, BTBP-type molecules - (6,6ʺ-(5,6-dialkyl-1,2,4-triazin-3-yl)- 2,2ʺ-bipyridines. The BTBP-type molecules are polyaromatic nitrogen donor ligands that have a common core of two aromatic pyridine rings and two triazine rings but with different side groups. The BTBPs ligands are able to separate trivalent and pentavalent actinides from trivalent lanthanides[10,11], but exhibit low resistance towards radiolysis and low solubility in aliphatic industrial diluents which imposes the use of long-chain alcohol or cyclohexanone which are not really suitable for an industrial process. Therefore, alternative diluents for these ligands are sought.

The current reference molecule for An(III)/Ln(III) separation is CyMe$_4$-BTBP (**1** in Figure 1) ligand with good extraction properties that have been already demonstrated under process conditions[12–14]. The stability of BTBPs depended on the dose rate and the type of radiation. γ-irradiated solutions of CyMe$_4$-BTBP dissolved in cyclohexanone or hexanol diluent proved good stability up to absorbed dose of 12-14 kGy[15]. The extraction efficiency for americium and europium remained more or less at the same level for the solutions of MF2-BTBP (4-tert-butyl-6,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2]bipyridine)in cyclohexanone irradiated up to absorbed dose of 100 kGy at low dose rate (15 Gy h^{-1}). On the other hand the extraction efficiency for americium and europium decreased significantly with increasing absorbed dose after irradiation at high dose rate (at 1.2 kGy h^{-1})[16].Radiolysis experiments of CyMe$_4$-BTBP in n-octanol show that the radiolytic degradation rate is higher (40%) for gamma radiation (0.22 kGy/h) than it is for alpha radiation(1 kGy/h). So CyMe$_4$-BTBP ligand proved good resistance towards alpha radiolysis and gamma radiolysis at the low dose rates[17].

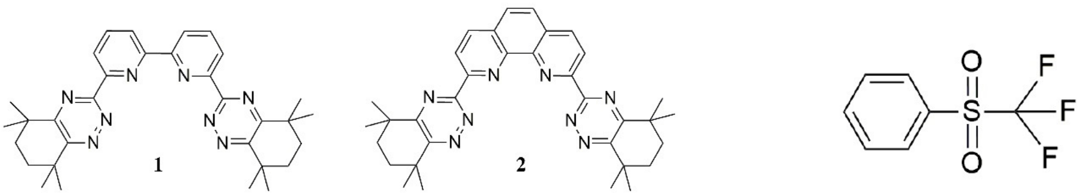

Fig.1. Structures ofCyMe$_4$-BTBP**1**, CyMe$_4$-BTPhen**2**, and phenyl trifluoromethyl sulfone

By replacing the 2,2′-bipyridine moiety of the BTBPs with a 1,10-phenanthroline moiety the new more pre-organized quadridentate ligand CyMe$_4$-BTPhen (**2** in Figure 1) is formed[18,19].

This simple modification improved extraction properties of the ligand. The extraction efficiency for americium is by about 2 orders of magnitude higher for the solutions of CyMe$_4$-BTPhen in 1-octanol than for those of CyMe$_4$-