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EPR measurements on N-bearing ligands used in spent nuclear fuel reprocessing for An(III)/Ln(III) partitioning

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A future goal for the reprocessing of spent nuclear fuel is the transmutation of long-lived minor actinides, such as americium and curium, into short-lived isotopes by means of neutron irradiation. In order to develop an effective transmutation process, it is necessary to separate the trivalent minor actinides, An(III), from the trivalent lanthanides, Ln(III) by means of two subsequent solvent extraction processes: i) DIAMEX to extract both Ln(III) and An(III) from PUREX raffinate and ii) SANEX to obtain the selective extraction of An(III) from the output of DIAMEX process.

The present work concerns the degradation due to ionizing radiation released by radionuclides to the selected solvent system involved in the SANEX process. The high-energy radiations are able to modify the ligands molecules structures changing their extractant capabilities. In particular, several aspects must be considered when selecting a molecule to be used in the mentioned process: chemical stability; solubility in organic diluents; extraction capability of metal ions with appropriate distribution ratios; and resistance towards irradiation. Some aza-heterocyclic extractant molecules C2-BT (5,6 diethyl (1,2,4 bis-triazine), C2-BTP (2,6-diethyl(1,2,4-triazine-3-yl)pyridine), C5-BTBP (6,6'-bis-(5,6-dipentyl-[1,2,4]triazine-3-yl)-[2,2']bipyridinyl) and CyMe4BTBP (2,6-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)-[2,2']bipyridinyl), constituted by pyridine and triazine aromatic rings with chelating nitrogen donor atoms, have been studied during the European Research Project EUROPART. Furthermore, the mentioned molecules present aliphatic side groups as, n-carbon alkyl substituents (methyl, ethyl or pentyl chains), or cyclohexyl moieties to ensure their lipophilic behavior after coordination of trivalent metal ions during liquid-liquid extraction processes. To carry out studies concerning radical mechanisms, the abovementioned molecules were irradiated in a Co-60 gamma irradiation facility (up to 113 kGy with a dose rate of 0.5 kGy/h), at 77 K to reduce radicals reactivity before investigations by EPR Spectrometry. A preliminary EPR screening on the four ligand molecules shows the presence of radiation-induced radicals on both the aromatic and aliphatic sides of the ligands. In particular, irradiation of C2-BTP in alcoholic solutions highlighted the formation of azacyclohexadienyl radical as intermediated specie. The azacyclohexadienyl radical has been recognized by simulated spectra using appropriate hyperfine constants, and similar signals have been collected also for irradiated solution of C5-BTBP. The EPR spectra collected on samples of C5-BTBP powder, irradiated in air, disclosed the formation of peroxide radical species ROO•. Further simulations on the EPR spectrum collected at 208 K revealed definitively the presence of peroxide species on C5-BTBP.

In conclusion, taking into account the peroxide radical formation proven on C5-BTBP powder, it was possible to propose several radical mechanisms able to modified the extractant capabilities of the investigated molecules.

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