Extraction of Actinide and Lanthanide From Nitric Acid Medium Using Ionic Liquid

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1. Introduction

Ionic Liquids (ILs) are receiving increased attention in the area of nuclear fuel cycle and waste management because they have several attractive properties suitable for aqueous and non-aqueous reprocessing applications. ILs are being evaluated as an alternative to the conventional diluent in aqueous reprocessing and as a substitute to the traditional high-temperature molten salts in the non-aqueous reprocessing of spent nuclear fuels [1, 2]. In this study, the application of ILs, 1-alkyl-3-methyl imidazolium bis(trifluoromethylsulfonyl) imide (C_nmimTf_2N, n = 4, 6, 8), in the extraction of Am(III) and Eu(III) ions from nitric acid medium using n-octyl(phenyl)-N,N-diisobutylcarbamoyl methyl phosphine oxide (CMPO) and tri-n-butyl phosphate (TBP) as extractants was investigated. The distribution ratios of Am(III) and Eu(III) in CMPO-TBP/C_nmimTf_2N were measured as a function of various parameters such as the concentrations of nitric acid, CMPO, and TBP. Extraction experiments were also carried out at varying temperatures to determine the influence of temperature on the extraction process

2. Experimental

2.1 Chemicals and equipment

All the chemicals and reagents used in the study were of analytical grade and used without further purification. Ionic liquid, C_nmimTf_2N, was procured from C-TRI, Korea. CMPO and TBP were obtained from Merck. [241]Am(III) and [152]Eu(III) were obtained from IPL. To remove the water and volatile impurities, C_nmimTf_2N was dried under a reduced pressure at 373 K, and the residual water concentrations measured using a Karl Fisher moisture content meter (Metrohm 831 KF Coulometer) were below 100 ppm.

2.2 Experimental method

All the extraction studies were carried out at 298 K. The organic phase (1 mL) was equilibrated with the same volume of aqueous phase for 3 hr. Extraction of Am(III) and Eu(III) as a function nitric acid was studied by equilibrating the organic phase with aqueous phase containing desired concentrations of CMPO and nitric acid spiked with [241]Am(III) and [152]Eu(III) tracer. After 3 hr of equilibration, the radioactivity of [241]Am(III) and [152]Eu(III) distributed between organic and aqueous phases was measured using MCA (Canberra DSA-1000, HPGe detector). The distribution ratio (D_M) and separation factor (SF) were determined using Eq. (1) and (2).

$$D_M = [M]_{org}/[M]_{aq}, M = {}^{241}Am \text{ or } {}^{152}Eu \quad (1)$$

$$SF = D_{Am}/D_{Eu} \quad (2)$$

3. Results and discussion

The distribution ratio of [241]Am(III) and [152]Eu(III) in a solution of 0.05 M CMPO-1.1 M TBP/C_nmimTf_2N as a function of concentration of nitric acid is shown in Fig. 1. It also shows the distribution ratio obtained in a solution of 0.05 M CMPO-1.1 M TBP/n-dodecane (n-DD). In cases where ILs (C_nmimTf_2N) are used as the diluent, increasing aqueous phase acidity causes a decrease in the extraction of Am and Eu on the contrary to the case of using n-DD as the diluent. Extraordinary extractions of Am and Eu are observed when ILs are used as diluents. D values of ILs are much greater than those of n-DD. The use of ILs enhances the extraction of Am and Eu. D decreases with increase in the chain length of alkyl group of the cationic part of the ILs, which is attributed to the hydrophobicity of the ILs. Higher aqueous solubility of the butyl form is responsible for the higher metal ion extraction.
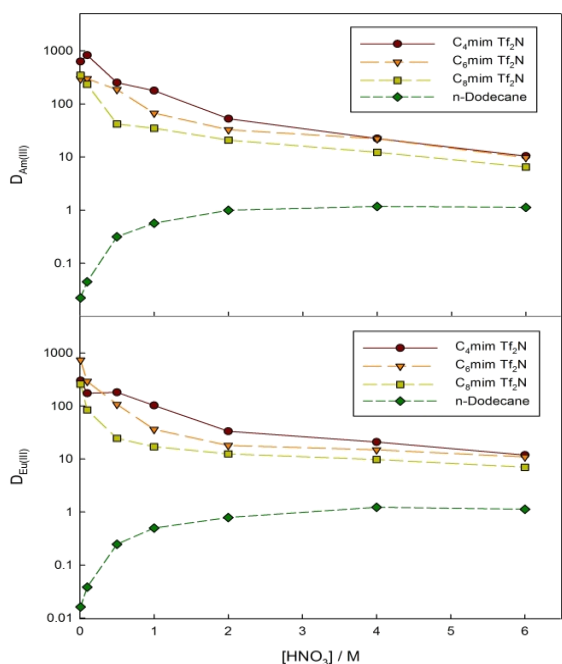
Fig. 1. Distribution ratio of Am and Eu with [HNO$_3$].

The number of CMPO molecules involved in the extraction can be determined by slope analysis method. This was obtained by measuring the distribution ratio of Am and Eu as a function of CMPO concentration in ionic liquid phase, and plotting the logarithmic value of the measured distribution ratio against CMPO concentration and the results are shown in Fig. 2. Linear regression analysis of the data results in a slope of 2.5 for Am
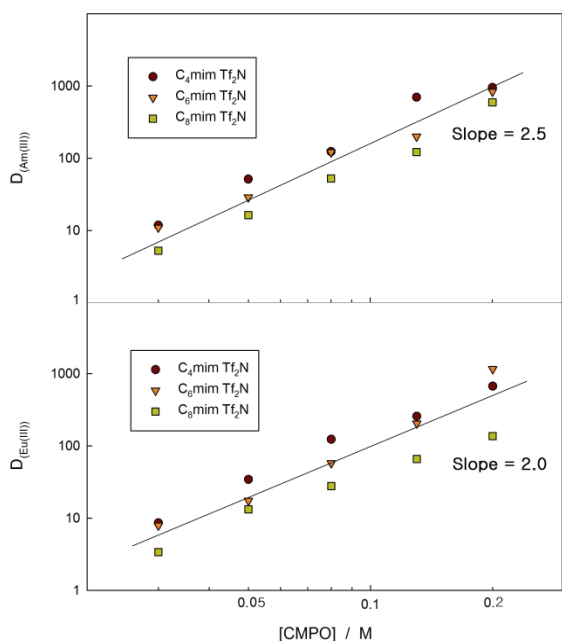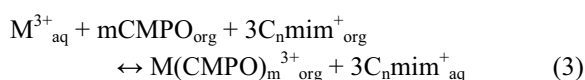
and 2.0 for Eu, indicating that 2 or 3 molecules of CMPO are involved in the extraction step.

A change of the chain length of the alkyl group of the RTILs did not influence the stoichiometry of the extracted complex. The results suggest that the extraction of Am and Eu by CMPO in RTILs from nitric acid medium proceeds through the following cation-exchange mechanism.

$$M^{3+}_{aq} + mCMPO_{org} + 3C_nmim^+_{org}$$
$$\leftrightarrow M(CMPO)_m{}^{3+}_{org} + 3C_nmim^+_{aq} \qquad (3)$$

Extraction experiments were also carried out at varying temperatures to determine the influence of temperature on the extraction process, and the thermodynamic parameters were calculated. The distribution ratios were found to decrease with increasing temperature, indicating that the extraction process is exothermic.

4. Conclusion

Feasibility of ILs as novel media for the extraction of Am and Eu was examined. CMPO dissolved in IL showed much high extraction ability compared to in an ordinary diluent, n-DD. Partitioning of the metal cations into the IL with CMPO proceeds through cation exchange mechanism, which is different from that of the conventional solvent extraction system. The results suggest that ILs are a promising medium for Ln/An elements separation.

References

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[2] T. Prathibha, K.A. Venkatesan, B. Robert Selvan, M.P. Antony and P.R. Vasudeva Rao, "Anomalous extraction behavior of americium(III) in some diglycolamide isomers present in ionic liquid medium", Radiochim. Acta 100, 907-913(2012).

Fig. 2. Distribution ratio of Am and Eu with [CMPO].