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2 - 35 An Solvent Extraction and Complexation Study on Americium(III) and Europium(III) with Tridentate N,N-diethyl-1, 10-Phenanthroline-2-Amide

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In the spent fuel reprocessing, the high-level liquid waste (HLLW) from PUREX process is the major environmental concern of its high radiotoxicity level[1]. The partitioning and transmutation (P&T) strategy, aiming at transforming the minor actinides into short-lived or stable isotopes with neutron bombardment, is one of the most perspective technology to solve this problem. However, the lanthanides in HLLW have very high neutron capture cross-sections, and need to be removed before the transmutation.

We proposed a new soft-hard combined 1, 10-phenanthroline-2-carboxamide ligand, N, N-diethyl-1, 10-phenanthroline-2-carboxamide (C2-PTA). Its extraction behavior for Am(III) and Eu(III) in HNO_3 solution was investigated. The extraction models were studied by slope analysis and the UV-vis titration. The synthesis route of N, N-dialkyl-2-amide-1, 10-phenanthroline-derived ligands is similar to that of EtTolDAPhen, MePhPTA[2,3]. The products are characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and ESI-MS. The distribution ratios are deduced by the isotopic tracer technique in both organic and aqueous phase after an extraction equilibrium.

It can be seen from Fig. 1 that the distribution ratios of both Am(III) and Eu(III) as well as $SF_{\mathrm{Am/Eu}}$ decrease with the increase of nitric acid concentration. This is due to the protonation of donor N atoms on 1, 10-phenanthroline moiety. This means that C2-PTA shows a much higher extraction selectivity of Am(III) over Eu(III). The maximum values of D(Am) and D(Eu) reach (25.2 ± 0.2) and (3.3 ± 0.1), respectively. As lower acid concentration will cause the hydrolysis of Am(III) and Eu(III) in aqueous, the highest $SF_{\mathrm{Am/Eu}}$ is determined to be (7.6 ± 0.3) at the acidity of around $10^{-4.0}$ mol/L. In Fig. 2, as the concentration of nitrate ions increases, D(Am) and D(Eu) clearly increase at identical rates, while $SF_{\mathrm{Am/Eu}}$ remains about the same. On the fact of the appearance in the experiment, it can be inferred that nitrate ions promote the formation of the complexes at high concentration, acting as counter-ions or binding ligands of the metal ions[4].

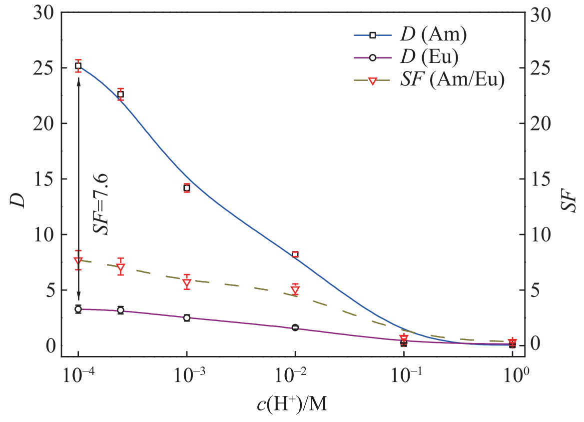

Fig. 1 (color online) Effect of initial acidity in aqueous phase by C2-PTA. Organic phase: 0.2 mol/L PTA in chloroform. Aqueous: HNO_3 + ^{241}Am/^{152}Eu radiotracers. T = 293 K.

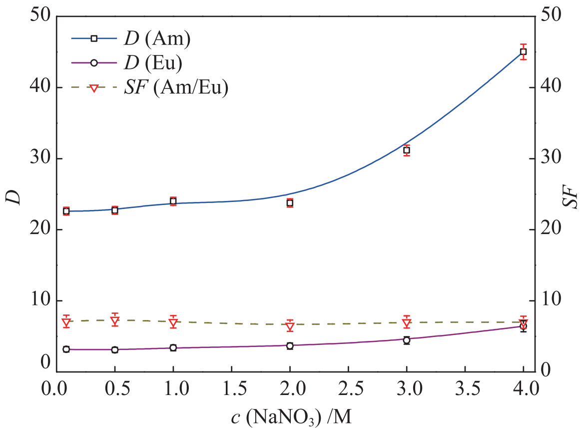

Fig. 2 (color online) Effect of nitrate ion concentration. Organic phase: 0.2 mol/L C2-PTA in chloroform. Aqueous phase: $10^{-3.63}$ mol/L HNO_3 + ^{241}Am/^{152}Eu radiotracers + $NaNO_3$. T = 293 K.

UV-vis titration is carried out to determine the stable constant of the Eu-(C2-PTA) complexes. The change of absorption during the UV-vis titration of C2-PTA by Eu(III) is shown in Fig. 3. It can be seen that a free ligand has a strong absorption peak at 268 nm in methanol solution. With the addition of Eu(III) the absorption at 268 nm gradually decreases, while the new peak at 287 nm corresponding to EuL complexes increases. Only one isosbestic point is found at 276 nm, denoting the 1:1 complexes formed. By fitting the data at the wavelength of

287 nm, the stable constants ($K_{\mathrm{Eu(C2-PTA)}}$) were determined to be (4.00 ± 0.01), indicating that C2-PTA has a strong trend of complexing with metal ions in solution.

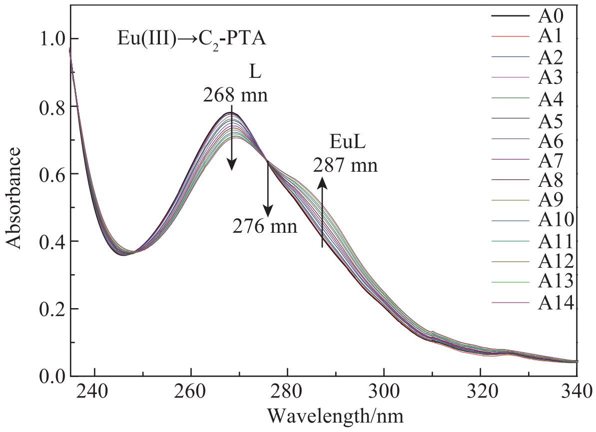

Fig. 3 (color online) The UV-vis titration of C2-PTA by Eu(III) in methanol medium. $c_L = 3.0\times10^{-5}$ mol/L, c_M = 0-3.7$\times10^{-5}$ mol/L, T = 293 K.

The conclusions may shed light on the research of the designing of improved PTA ligands, and contribute to the improvement of structural modifications to develop novel extractants for the separations of actinides from lanthanides in the treatment and disposal of HLLW.

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