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Alkyl chains effects on uranium(VI) and plutonium(IV) speciation in organic phases containing tetra-alkylcarbamides

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The separation of uranium(VI) and plutonium(IV) by solvent extraction from spent nuclear fuels has already been studied with several families of extractants such as trialkyl phosphate, phosphine oxides or monoamides. A new family of extractant containing the carbamide function (also called urea with the general formula $R_1R_2NC(O)NR_3R_4$) is currently studied in our laboratory. Only few extraction studies of uranium(VI) and plutonium(IV) by carbamide extractants can be found in the literature. They show the high potential of those molecules to extract actinides(IV) and (VI). The objective of this study is to evaluate the effect of alkyl chains length on actinide extraction. Our results show that the chain length (from butyl to octyl chain) does not influence significantly uranium(VI) extraction while it has a strong impact on plutonium(IV) extraction. In order to better understand the relationship between the alkyl chains length and extraction performances, U(VI) and Pu(IV) complexes formed in the organic phase were characterized by spectroscopic techniques. First, to gain information on the coordination sphere of U(VI) and Pu(IV) complexes with carbamide, single crystals were synthesized with short alkyl chain carbamide ($R_1=R_2=R_3=R_4=$ iso-butyl). An octahedron complex and a bicapped dodecahedron complex are obtained for $UO_2(NO_3)_2L_2$ and $Pu(NO_3)_4L_2$ (with L: N,N,N',N'-tetra-iso-butylcarbamide) respectively. Then, the analysis of organic phases after uranyl extraction confirmed the participation of the carbonyl function and the nitrate anions denticity (bidentate) to uranyl coordination, and showed that the coordination sphere of uranyl is not modified by a change in the alkyl chains length of the carbamide. At the opposite, the speciation of plutonium(IV) depends on alkyl chain length of the carbamide and acidity of the solution. UV-Vis-NIR and EXAFS spectroscopy indicate that two different complexes are formed: a neutral complex $Pu(NO_3)_4L_2$ and an anionic complex $Pu(NO_3)_6^{2-}$ and their proportion varies with the length of the alkyl chain. The organic phase containing the higher proportion of anionic complex is associated to the higher Pu(IV) distribution ratio. These results suggest that the anionic complex is more extracted than the neutral complex and that increasing alkyl chain length enhances its organic phase solubility.

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