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Structural Investigation of the Extracted Complexes of Am(III) and Ln(III) with Cyanex301 by EXAFS

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Cyanex301, a dithiophosphinic acid, selectively extracts trivalent actinides (e.g., Am(III)) over trivalent lanthanides (Ln(III)) in solvent extraction. To understand the underlying principle governing the selectivity, the structures of the extracted complexes of Am(III) and Ln(III) in organic solvent solutions were investigated using EXAFS. The data show that the structure of the Am(III) complex is different from that of the Ln(III) complexes. The coordination number of Ln(III) in the complexes is 8 (seven sulfur atoms from four Cyanex301 molecules and one oxygen atom from a water molecule), suggesting the Ln(III) complex with Cyanex301 has one H_2O molecule with a molecular formula of $HLnL_4 \bullet H_2O$, where L stands for the anion of Cyanex301. On the contrary, the Am(III) complex with Cyanex301 does not contain H_2O with the molecular formula of $HAmL_4$, in which only the eight sulfur atoms from Cyanex301 coordinated to Am(III). The results suggest that the high selectivity of Cyanex301 in the extraction of An(III) over Ln(III) arises from the difference in the hydration state of the extracted complexes and thus their affinity to the organic phase.

The coordination bond lengths in the extracted complexes are also determined by EXAFS. As the atomic number increases from La(III), through Nd(III) to Eu(III), the bond lengths of Ln-O and Ln-S gradually decrease: Ln-O, 2.70, 2.56, and 2.50 Å; Ln-S, 3.01, 2.91, and 2.84 Å. The average Ln-P distances are 3.60 (La), 3.53 (Nd), and 3.46 Å (Eu). In comparison, the bond length of Am-S is 2.98 Å, and the average Am-P distance is 3.58 Å.