



Steric effects of trialkyl phosphates on the extraction of uranyl cation

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ABSTRACT

We report gas phase calculations on uranyl ions (UO_2^{2+}) complexes with symmetrical trialkyl phosphates, $(\text{RO})_3\text{PO}$, as ligand (L), where, R is a linear or branched propyl, butyl and amyl groups. Density functional theory (DFT) using double numerical polarization (DNP) basis set with restricted scalar relativistic effect is used to validate the structural features of $\text{UO}_2(\text{NO}_3)_2\text{L}_2$ complexes against experimental XRD data. The interaction energy and extraction ability of the trialkyl phosphates are compared for uranyl (VI) ion. Steric effect of the extracting agent that governs the metal extraction is explained in terms of cone angles made by ligands towards metal ion. The complexation behaviour of straight chain and branched chain ligands is well understood by this study. The relative order of cone angles and interaction energies from DFT simulation follow the trend with the experimentally determined distribution coefficients. An interesting approach of this work is the importance of cone angle in the solvent extraction.

Keywords: Steric effect; Uranyl(VI) ions; Cone angle; Trialkyl phosphates; Density functional theory; Molecular modeling; Interaction energy; Partition coefficient

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