AQUEOUS COMPLEXATION AND INTERACTIONS OF ND(III) AND AM(III) WITH CITRATE IN PERCHLORATE MEDIA

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Abstract

Carboxylic acids have played an important role in the field of separating actinides (An) from lanthanides (Ln) using liquid-liquid extractions to develop effective and economical means to reducing the volume, toxicity, and lifetime of irradiated nuclear fuel in the United States.[1, 2] Studies have now shown that negligent control of the carboxylate concentration in advanced liquid-liquid reprocessing of high-level waste can jeopardize the solubility of Ln and An.[3] Recent bench-scale experiments have demonstrated that the more soluble 3-carboxy-3-hydroxypentanedioic acid (citric acid) is a propitious aqueous complexant that can effectively aid in the separation of transition metals from f-elements mixtures using a combined solvent mixture of di(2-ethylhexyl) phosphoric acid (HDEHP) and octyl(phenyl) - N',N',-diisobutylcarbamoylmethyl phosphine oxide (CMPO).[4] The complexation of Ln with anions of citric acid has been previously studied with conflicting results regarding the coordination of metal ions between carboxylic groups, the feasibility of protonated metal complexes, and the formation constants themselves.[5]

Using potentiometric and spectrophotometric measurements as well as specific ion interaction modeling (SIT) we report protonation equilibria of citric acid and its complexes with Nd(III) and ^{243}Am(III) using least-squares fitting of the experimental data. For trivalent metal (M^{3+}) complexation, the best model included mononuclear and protonated species

$$M^{3+} + iH^{+} + jCit^{3-} \rightleftharpoons MH_iCit_j^{3+i-3j} \quad (1)$$

The calculated formation constants showed enhanced stability relative to other carboxylic complexes with Ln elements which was attributed to some coordination of the α-hydroxyl group of citric acid to the metal ion. Protonated metal complexes demonstrated an overall lower stability than that of the neutral charged $MCit^{0}$(aq) species. A comparison of the Nd(III) and Am(III) formation constants with citrate showed very little discrepancy which is consistent given their similar charge, ionic radii, and affinity for hard oxygen-donor ligands.

References:

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