The Influence of Rare Earth Metal Cations on the Coordination, Aggregation, and Transport of Trivalent Uranium in the LiCl-KCl Eutectic

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Abstract:

Both on-line and post-processing electrorefining methods for used nuclear fuel propose the use of chloride-based molten salts containing a variety of fission product species which complicates the coordination environment and, consequently, the associated transport properties of ion species. The high-temperature, radioactive nature of dissolved fuel complicates experimental investigations, making classical molecular dynamics a useful tool in understanding the thermophysical and transport properties alongside ionic behavior at the atomic scale. This work employs a polarizable Born-Mayer-Huggins potential within CP2K to investigate the coordination environment and its influence over aggregation and transport properties of U^{3+} in the presence of fission products such as Fp^{3+} = Sc^{3+}, Y^{3+}, La^{3+}, and Tb^{3+} at 5 mol% MCl_3 and 773 K.

Fission products influence the uranium coordination environment and aggregation trends in several ways. Evaluation of M^{3+}-Cl^- coordination number distributions reveals that the addition of Fp^{3+} reduces the commonality of the five and six coordinate UCl_x^{3-X} complexes. Contrarily, U^{3+} induces negligible effect on the strict, orthogonal coordination of Sc^{3+}, Y^{3+}, and Tb^{3+}, but reduces the tendency of La^{3+} to form the CN = 7 complex anion. Meanwhile, all M^{3+} cations coordinate with each other via shared Cl^- anions to form homogeneous aggregates; however, they show preferential coordination to K^+ by the same anion sharing mechanism. Further analysis reveals that cations loosely form heterogeneous aggregates comprising of solvent bridged complex anions (MCl_x^{3-X}) where K^+ acts as the primary bridging cation. The addition of small trivalent cations (Sc^{3+}, Y^{3+}, and Tb^{3+}) breaks down both the homogeneous and heterogeneous aggregates. The effects of coordination and aggregation on ion transport are studied through the impacts on the viscosity and a spatially decomposed diffusion coefficient.