Preliminary Solubility Assessment of M–UO_2–2-Methoxybenzoate Precipitates (M = Li, K, Rb, Cs) under Acidic Conditions

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1. Introduction

Liquid radioactive waste containing uranium(VI) is generated from diverse waste streams, including nuclear fuel cycle operations [1,2] and industrial processes that employ uranium(VI) as a catalytic agent [3,4]. Given its high treatment cost and radiological hazard, strategies aimed at volume reduction of the radioactive waste—specifically through the selective separation and recovery of uranium(VI)—have received considerable attention. In particular, precipitation methods utilizing inorganic ligands such as hydroxide and phosphates, which form stable solid complexes with uranium(VI), have been extensively investigated as effective approaches for uranium immobilization [4,5]. We attempted to extend the scope of uranium(VI) complexation and precipitation studies to organic ligands [6-8], and we first observed that 2-methoxybenzoate (2-mba) readily complexes with uranium(VI) in the presence of sodium, precipitating as a crystalline compound sodium uranyl tri-2-methoxybenzoate dodecahydrate ($Na[UO_2(2\text{-}mba)_3]\cdot 12H_2O(s)$) under acidic conditions [8]. The structural stability of this compound arises from parallel-displaced π-π stacking interactions among the aromatic rings in the $[UO_2(2\text{-}mba)_3]^-$ complex unit, while sodium ions and water molecules are arranged within a one-dimensional channel framework (Fig. 1). This finding highlights the potential of developing organic complexants capable of efficiently precipitating uranium(VI) under acidic conditions. Building on this, the present work extends the investigation beyond sodium to a broader set of coprecipitating monovalent cations—specifically lithium, potassium, rubidium, and cesium—and reports preliminary solubility assessment of the alkali-metal uranyl 2-mba precipitates. Such comparative analysis provides critical insight into how cation identity influences the stability and recovery efficiency of uranium(VI), thereby informing their applicability in the radioactive waste treatment.

2. Experimental

All experiments were conducted under ambient conditions at a temperature of 22 ± 2 ºC. Aqueous batch samples were prepared with deionized water (Millipore, Direct-Q), and chemical reagents—including $HClO_4$ (99.999 % trace metals basis), LiOH (99.995 % trace metals basis), KOH (ACS reagent), RbOH (99.9 % trace metals basis), CsOH (99.95 % trace metals basis), and 2-methoxybenzoic acid (99 %)—were purchased from Sigma-Aldrich. Preparation of de-nitrated uranium(VI) stock solution and solubility experiment followed the procedures described in our previous works [6-8]. Initial concentrations of alkali metals, uranium(VI), and 2-methoxybenzoic acid were controlled to be 100, 2.6, and 23.3 mM, respectively, while the pH of batch samples was adjusted within the range of 3–5. After equilibration, supernatant samples were separated and analyzed using inductively coupled plasma-mass spectrometry (Thermo Scientific, iCAP RQ), inductively coupled plasma-optical emission spectrometry (Perkin Elmer, Optima 8300), and UV-vis spectrophotometry (Analytik Jena, SPECORD S600).

3. Results and discussions

In all batch samples, the formation of crystalline uranyl(VI) complexes was observed instantly. As the precipitation progressed, pH values showed a common tendency to decrease by approximately 0.1 to 0.2 compared to the initial states, which is explained by the Le Chatelier's principle regarding the protonation-deprotonation of dissolved 2-mba species [8].

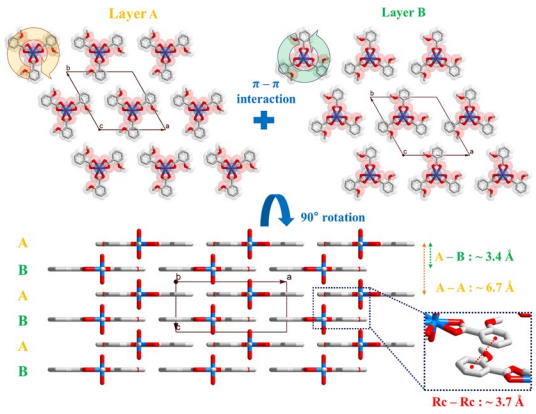

Fig. 1. Crystal structure of the $Na[UO_2(2\text{-}mba)_3]\cdot 12H_2O(s)$.

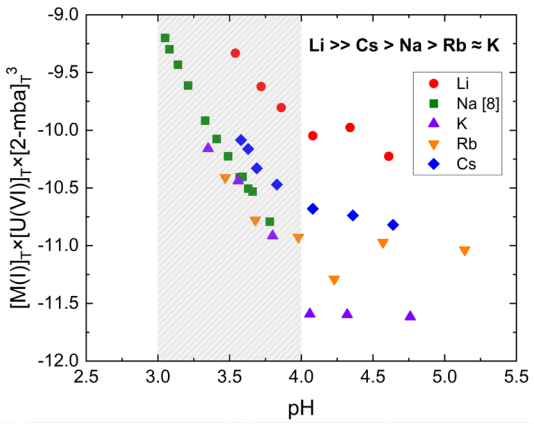

Fig. 2. Comparison of pH-dependent solubility variations of M–UO_2–2-mba precipitates (M = Li, Na, K, Rb, and Cs).

Furthermore, the ratio of decreased total concentrations of dissolved 2-mba to uranium(VI) (i.e., $\Delta[\text{2-mba}]_T/\Delta[\text{U(VI)}]_T$) was approximately 3, with an overall average of 2.8 across all samples, confirming that the 2-mba ligand bind to uranyl in a 3:1 stoichiometry within the crystalline precipitates. Fig. 2 presents the product of total concentrations of remaining alkali-metals, uranium(VI), and 2-mba species after the reaction, showing that the solubility of uranyl(VI)-organic compounds decrease in the order lithium >> cesium > sodium > rubidium ≈ potassium. In summary, rubidium and potassium appear to be the most efficient counter-cations and therefore merit further consideration. Future work will include a detailed analysis of the supernatant data, including calculation of relevant species distribution to determine the solubility product of each precipitate, as well as direct structural characterization of the crystalline uranyl compounds obtained.

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