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Thermodynamic study on the U(VI) complexation with “aliphatic” and “aromatic” di-carboxylic acids by micro-calorimetry

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The thermodynamics of complex formation of U(VI) with oxydiacetic acid (ODA), thiodiacetic acid (TDA), iminodiacetic acid (IDA), isophthalic acid (IPA), 2,5-frandicarboxylic acid (FDA) and dipicolinic acid (DPA) were studied by the micro-calorimetric titration technique. So far, extensive data on stability constant have been obtained and summarized in databases for a variety of combinations of actinide ions and complexants which could be found in the geosphere to predict the migration behavior of actinides in deep underground for the safety assessment of radioactive waste disposal. However, enthalpy and entropy data of actinide elements are scarce in comparison with stability constants. These data are indispensable not only for understanding of the reaction mechanism but also for the estimation of stability constants at elevated temperatures outside the range of 20-30 °C by the extrapolation from those at a room temperature with using thermodynamic models. Following our previous study reporting thermodynamic data (ΔG , ΔH and ΔS) of complexation of 8 di-carboxylates with U(VI) [1], this paper presents the thermodynamic quantities of U(VI) complexation with three “aliphatic” di-acetic acids and three “aromatic” di-acetic acids. Those ligands have a different center atom between two carboxylic groups, i.e., oxygen for ODA and FDA, sulfur for TDA and nitrogen for IDA and DPA, which may coordinate with a metal cation. The obtained thermodynamic quantities are compared with those of U(VI) complexation with glutaric acid (GA) for the discussion of the effect of structural difference, i.e., aliphatic- and aromatic structure and types of central atom in the ligands on the complex formation thermodynamics.

From the thermodynamic quantities, i.e., ΔG , ΔH and ΔS determined by the potentiometric and calorimetric titration techniques, it is indicated that these reactions are mainly driven by the entropy change while the enthalpy change is not promoting the progress of the reaction. The ΔG , ΔH and ΔS of 1:1 IDA complex show remarkable difference from those of GA complex, while those of ODA and TDA complex are almost equal to those of GA complex. ΔG of 1:1 IDA complex with U(VI) was 30 kJ/mol larger than that of GA complex, which is generally referred to the chelate effect of the ligand. Our calorimetric measurement has revealed that this “chelate effect” should be ascribed to the “entropy effect” since the entropy change ($T\Delta S$) of IDA complex was 50 kJ/mol larger than that of GA complex. The origin of this large entropy effect is discussed in the presentation with the help of structural information of the complex calculated using density functional theory (DFT).

[1] A. Kirishima, Y. Onishi, N. Sato and O. Tochiyama, Radiochim. Acta 96 (2008) 581–589.

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