

7-6 How Hydrophilic are Actinide Ions?

— Determination of Standard Gibbs Energy of Transfer at Aqueous/Organic Interface —

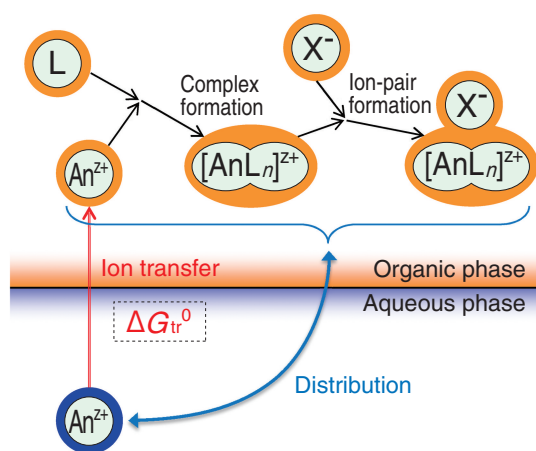


Fig.7-16 Ion transfer at aqueous/organic interface

In a solvent extraction system, the actinide ions transferred from an aqueous phase to an organic phase form complexes with ligands (L) and ion pairs with counter ions (X^-) in the organic phase, and they are then stabilized. The distribution of the ions is determined by the Gibbs energy of transfer (ΔG_{tr}^0), complex formation, and ion-pair formation.

The transferability of an ion at the interface between aqueous and organic phases depends on the chemical potentials of the ion in both phases. Separation of ions by solvent extraction and analysis by using an ion-selective electrode are conducted by utilizing the difference in the ion transferability. Many metal ions require a large energy for their transfer from an aqueous phase to an organic phase (the standard Gibbs energy of transfer at the interface, ΔG_{tr}^0) because they are highly hydrophilic and hardly dissolve in an organic solvent. In solvent extraction, ions are extracted into the organic phase by stabilizing them through complex formation and ion-pair formation in the organic phase (Fig.7-16). Accordingly, the distribution of the ions is determined by ΔG_{tr}^0 of the ions and counter ions, as well as complex formation and ion-pair formation.

First, we determined ΔG_{tr}^0 of the hydrogen ion (H^+) by the electrochemical method for use as a reference, in order to estimate ΔG_{tr}^0 of actinide ions at the interface precisely. Then, we estimated ΔG_{tr}^0 of trivalent- to hexavalent-actinide ions such as uranium, neptunium, and plutonium from the ratio between the concentrations of actinide ion and H^+ in both phases for an equilibrium ion distribution.

ΔG_{tr}^0 values of actinide ions for five types of organic solvents are plotted against those of H^+ in Fig.7-17. It can be

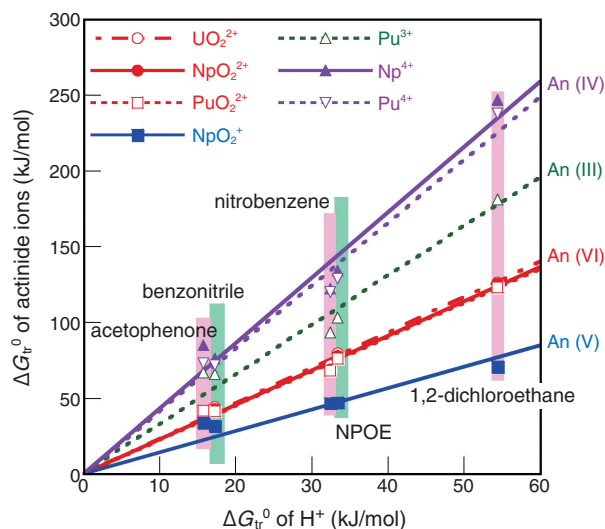


Fig.7-17 Relation between standard Gibbs energies of transfer (ΔG_{tr}^0 s) of actinide ions and those of H^+

ΔG_{tr}^0 values of actinide ions in each oxidation state are almost proportional to those of H^+ regardless of the type of solvent, suggesting that solvation of actinide ions is not special, but similar to that of H^+ .

observed that the ΔG_{tr}^0 values of actinide ions in the same oxidation state are similar to each other irrespective of the type of organic solvent. The ΔG_{tr}^0 values of hexavalent actinide ions (AnO_2^{2+}) are larger than that of the magnesium ion (Mg^{2+}), which is the most hydrophilic among divalent ions whose ΔG_{tr}^0 values are known. ΔG_{tr}^0 values of actinide ions having a lower charge number are smaller. A comparison of the ratios of ΔG_{tr}^0 to the charge number for actinide ions shows that the values of pentavalent neptunium ions (NpO_2^+) are much larger than those of other actinide ions. Thus, NpO_2^+ is particularly hydrophilic among actinide ions. It is considered that this high hydrophilicity is one of the reasons why a large distribution ratio of NpO_2^+ is hardly obtained in any solvent extraction system.

The ΔG_{tr}^0 values of actinide ions determined in this study were for organic solvents with relatively large dielectric constants. If more sensitive methods are applied to determine the concentration of actinide ions, the procedure can be extended to organic solvents having low dielectric constants. Accumulated data on ΔG_{tr}^0 might be useful for developing guidelines for the selection of a solvent for the extraction of actinide ions and for designing an extraction reagent selective for actinide ions.

Reference

Kitatsuji, Y. et al., Standard Gibbs Energies for Transfer of Actinyl Ions at the Aqueous/Organic Solution Interface, The Journal of Chemical Thermodynamics, vol.43, issue 6, 2011, p.844-851.