

STRUCTUREAL STUDIES ON EXTRACTED SPEICES BY USING DIAMIDE COMPOUNDS AS EXTRACTANT FOR ACTINIDE/LANTHANIDE SEPARATION

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Abstract

Diamide compounds have been examined as extractants for separating actinide(III) and lanthanide(III) from high level liquid waste (HLLW) by solvent extraction. *N,N,N',N'*-tetraoctylglycoldiamide (TODGA) and *N,N,N',N'*-tetraoctyl-3,6-dioxaoctanediamide (DOODA) have been reported to extract trivalent metal ions with large *D* values into *n*-dodecane from nitric acid solutions. TODGA is one of the most extensively studied and promising extractant. Recently, it was reported that DOODA also has similar *D* values and shows different affinity to heavier lanthanide(III). In the most of extraction of metal ions from aqueous phase to organic phase, metal ions are extracted through the formation of uncharged complexes with the extractant and anions such as nitrate. The number of extractants and nitrate ions participating in solvent extraction, which are usually obtained from $\log D$ - $\log[L]$ plots ($[L]$: the concentrations of the extractant or nitric acid), are not always compatible with those in the crystal structures. Several structural studies were made in this area, however the nature of extracted complexes is still not elucidated. In order to understand the extraction mechanism and the factors for controlling selectivity, the stoichiometry and the structure analysis of the extracted species in the solution should be essential.

In this paper, in order to elucidate the structures of the extracted species, the complex formation with lanthanide(III)-diamide were studied. Multinuclear NMR spectroscopy was used to obtain information about the stoichiometry, the symmetry and the structural parameters of lanthanide(III)-diamide complexes in acetonitrile. ¹H-, ¹³C-, and ¹⁵N-NMR signals were assigned by using 2D COSY and HMQC correlation spectroscopies and nuclear Overhauser effects (NOE). By increasing the metal to ligand ratios from 2:1 to 1:10. In the DOODA system, when the ratio metal/DOODA is less than 1, the ¹H NMR spectra showed that the metal and DOODA form 1:1 complex, and DOODA retains C_{2v} symmetry in the 1:1 complex in the solution. Broad signals appeared between free DOODA and coordinated in the 1:1 complex when the ratio is more than 2. This indicate that the existence of a fast ligand exchange process on the NMR timescale. Paramagnetic metal ion complexes gave separate broad signals of free and coordinated DOODA, and the signals were resolved at lower temperature. The signals assigned to two coordinated DOODA molecules suggest that two DOODA are in symmetric positions but both of them coordinate asymmetrically. This result is in agreement with the solvent extraction result which has shown two DOODA molecules participate in the extracted species. The results of the TODGA system are also discussed from the viewpoint of the stoichiometry and the symmetry of the extracted species. Our study demonstrates that the structure analyses of the extracted species in the solution by using NMR can interpret well solvent extraction mechanism of lanthanide(III) by diamide compounds as an extractant.