

Studies on Transfer Energy of Actinide and Lanthanide Ions between Aqueous and Organic Phases and Solvation State of the Ion Transferred into Organic Phase

Yoshihiro Kitatsuji ^a, Ryuji Nagaishi ^a, Takaumi Kimura ^a,
Zenko Yoshida ^a, Sorin Kihara ^b
^a Japan Atomic Energy Research Institute,
Tokai, Ibaraki 319-1195, Japan
^b Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

The standard Gibbs energy for ion transfer (ΔG_{tr}°) which is defined as the difference of the solvation Gibbs energy of the ion between two phases is a significant parameter for understanding the strength of ion-solvent interaction. Authors have developed the new method (i.e., controlled-potential electrolysis at liquid-liquid interface, CPEITIES) to study ion transfer and have measured the ΔG_{tr}° of various oxidation states of actinide ions. In the present paper, transfer of trivalent actinide and lanthanide ions between aqueous (W) and organic (Org) phases was investigated. Further, to understand the solvation state of ions transferred from W to Org, luminescence properties of Eu(III) in Org were investigated by time-resolved laser-induced fluorescence spectroscopy (TRLFS).

ΔG_{tr}° OF ACTINIDE AND LANTHANIDE IONS

Ion transfer equilibrium of trivalent actinide and lanthanide ions between W and nitrobenzene (NB) phases was attained by CPEITIES. An electrolysis cell consisted of inner and outer vessels and procedures were identical to those reported previously [1]. Definite volumes of W and NB in the inner vessel were taken after electrolysis, and concentrations of the metal ions in both phases were determined by an NaI scintillation counter or an inductively coupled plasma-atomic emission spectrometer. The standard potential and the Gibbs energy for ion transfer were obtained from the relationship between interfacial potential and distribution ratio (*D*) of the ion at electrolysis equilibrium based on the Nernst equation.

The ΔG_{tr}° of Am(III) and lanthanides(III) determined are listed in Table 1. The difference in ΔG_{tr}° between La(III) and Lu(III) is smaller than 21 kJ mol⁻¹ which is expected from the ionic radii (i.e., 0.105 and 0.086 nm for La(III) and Lu(III), respectively) based on the Born theory.

SOLVATION STATE OF Eu(III) TRANSFERRED FROM AQUEOUS INTO ORGANIC PHASES

Europium(III) ion in the sample solution was excited by a pulse laser beam (394 nm). Eu(III) in NB and NPOE solution was excited by the 464 nm laser beam, because these solvents absorb light of less than 450 nm. The emission light of Eu(III) was detected by a multichannel photodiode array analyzer to obtain emission spectrum. The light due to the emission of Eu(III) from the lowest luminescent level to the ground state manifold (⁵D₀→⁷F₁; 591 nm) was measured to obtain luminescence lifetime, and the luminescence decay curves observed were fitted to single exponential curves with correlation coefficients 0.99-0.999. The equipments and procedures for the TRLFS measurement of Eu(III) in solution were identical to those reported previously [2].

The emission spectra of Eu(III) in NB and aqueous solution are shown in Fig. 1. The Eu(III) transferred from W into NB (spectrum 1) showed a similar emission

spectrum as of that in aqueous solution (2). On the other hand, the spectrum of Eu(III) dissolved in dehydrated NB (3) showed different characteristics; the ratio of the emission intensity of 591 nm peak to 615 nm is remarkably changed. Hydration number (*N*_{H2O}) of inner-sphere of Eu(III) transferred from W into NB was nearly the same as that in aqueous solution, which was determined from luminescence lifetime. Similar results were obtained in the case of other organic solvents such as 1,2-dichloroethane, NPOE.

These results mean that at least inner-sphere of Eu(III) transferred from W into Org is completely occupied by water molecules, and that hydration environment of inner-sphere of Eu(III) is retained after ion-transfer. Thus, it is supposed that the ΔG_{tr}° determined by CPEITIES is for lanthanide ions keeping (at least) first hydration shell. In this connection, the difference in ΔG_{tr}° between hydrated La(III) and Lu(III) can be estimated to be 2.7 kJ mol⁻¹ from radii of first hydration shell of these ions (i.e., 0.323 and 0.297 nm for La(III) and Lu(III), respectively).

REFERENCES

[1] Y. Kitatsuji, Z. Yoshida, H. Kudo and S. Kihara, *J. Electroanal. Chem.*, **520**, 133(2002).
[2] T. Kimura and Y. Kato, *J. Alloy Comp.*, **275-277**, 806(1998).

Table 1. Standard potential and the Gibbs energy for transfer of trivalent lanthanide and actinide ions between aqueous and nitrobenzene phases.

	E° V	ΔG_{tr}° kJ mol ⁻¹
La ³⁺	0.390 ± 0.003	113
Eu ³⁺	0.393 ± 0.003	114
Lu ³⁺	0.397 ± 0.002	115
Am ³⁺	0.390 ± 0.004	113

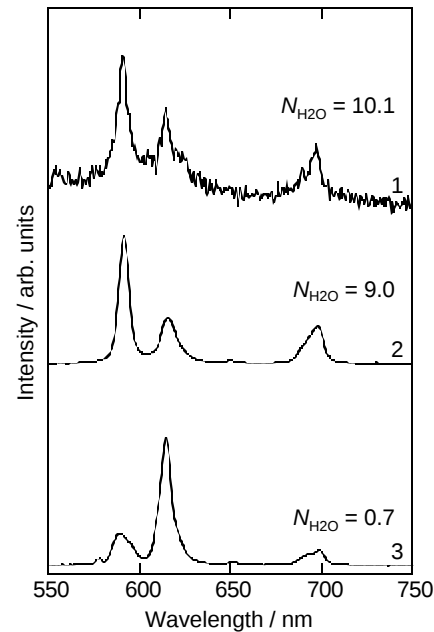


Fig. 1. Emission spectra and *N*_{H2O} of Eu(III) in aqueous and organic solutions. (1) transferred from W into NB by CPEITIES, (2) in 1mM HCl, (3) dissolved in dehydrated NB.