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Electroanalytical Study of Actinide Ions

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Abstract

Transfer reactions at the interface of aqueous/organic solutions and redox reactions of actinide ions, such as U, Np and Pu, were investigated electrochemically as fundamental studies for the development of separation and speciation of such ions. A method to investigate ion transfer at a liquid/liquid interface based on controlled potential electrolysis and radioactivity measurement was developed and applied to determine standard ion transfer potential and complex formation constant of facilitated actinide ions transfer with an ionophore in the organic phase. A separation method was developed on the basis of the fundamental ion transfer data. Electrode redox reactions of actinide ions were also investigated. A mediator reaction and electrocatalysis were found to be involved in the reduction processes of actinide ions. In addition, a method to control the valence of actinide ions was successfully developed.

Keywords: actinide, liquid/liquid interface, ion transfer, reduction mechanism, valence control

Introduction

Among actinide (abbreviated as An in chemical notation) ions, U, Np, and Pu, which are the most important elements for nuclear power, exist as trivalent to hexavalent ions in an aqueous solution (rarely Np(VII) in a basic solution). Interactions of these ions with other species, such as complex and ion-pair formation, significantly differ depending on the valence of the ion. Consequently, understanding and controlling the state of the ion in a solution is necessary for precise analysis and selective separation. Although An ions are successively reduced or oxidized between trivalent and hexavalent forms, the redox reactions are not

simple; some are electrochemically irreversible, large overpotentials are observed in some cases, and redox potentials are significantly affected by complex formation. Transfer reactions of An ions at the interface of aqueous (W)/organic (O) solutions are also interesting because they are elementary processes of distribution of the ions between two phases of solvent extraction, which is widely employed or investigated to separate actinides. Electroanalysis is promising for the development of precise adjustments of the oxidation state or transfer at the interface because the reaction is expected to be controlled by applied potential. Therefore, a fundamental study can lead to the development of a

novel separation and speciation method for actinides. Fundamental and applicable aspects of electrochemical studies of An ions at liquid/liquid and liquid/solid interfaces are summarized in this study.

Actinide transfer by controlled potential electrolysis at the W/O solutions interface

An ions form a stable complex in O solution and can be extracted to O phase using many types of extractants. Facilitated transfers of An ions have been studied by polarography at the interface between two immiscible electrolyte solutions (PITIES), which will be described later. However, An ions are so hydrophilic that the transfer reactions are difficult to observe by conventional electrochemical methods because most An ions can only stably dissolve in an acid solution. In highly concentrated acidic solutions, the transfer currents of An ions inevitably overlap with the residual current of coexisting H^+ ions. To solve this problem, the development of a method based on measurement of radioactivity in two phases rather than the transfer current was attempted to investigate actinide transfer at a W/O solutions interface¹⁾. The procedure was as follows: controlled potential electrolysis at a W/O solutions interface (CPEITIES) was performed to attain ion transfer equilibrium using a bulk electrolysis cell, as illustrated in Fig. 1; the amount of ion transfer was determined by radioactivity measurement, and the relation between applied potential (E_{app}) and the distribution ratio (D) of the ion was plotted. Usually, a fairly long time is required to achieve electrolysis equilibrium at the W/O solutions interface due to the small ratio of interfacial area to the volume of two phases. To attain equilibrium more efficiently, a stirring rod was used to stir the W/O solutions interface, as shown in Fig. 1. As a result, the time required to attain electrolysis equilibrium was successfully reduced from more than 4 h to 20 min.

Fig. 1 Apparatus for controlled potential electrolysis at W/ O solutions interface.

The standard ion transfer potential (E^0) can be determined from the plot of the relationship between E_{app} and D of the ions transferred by electrolysis in both phases after attaining equilibrium. The method is applicable to ion transfers that compete with other ions, such as supporting electrolytes. Furthermore, radioactivity measurement is effective for low ion concentration.

When the ion transfer reaction between W and O solutions is at equilibrium by controlled potential electrolysis, the distribution ratio of the ion is defined by the applied potential based on the Nernst equation as follows.

$$E_{app} = E^0 + \left(\frac{RT}{zF} \right) \ln(\alpha_O / \alpha_W) \\ = E^0 + \left(\frac{RT}{zF} \right) \ln(\gamma_O / \gamma_W) + \left(\frac{RT}{zF} \right) \ln D \quad (1)$$

where R , T , z , and F denote the gas constant, absolute temperature, electric charge, and the Faraday constant, respectively.

Results of UO_2^{2+} and Am^{3+} transfer at the interface between W and nitrobenzene (NB) phases are shown in Fig. 2 as an example of CPEITIES measurement. Linear relations between E_{app} and $\log D$ of the ions were obtained at a potential less than +0.32 V. The E^0 of ion transfer is determined by the extrapolation of the linear portion to the potential at which $D = 1$.

Fig. 2. Log D versus E_{app} plots for the transfer of UO_2^{2+} and Am^{3+} with and without BDPPM. W: 0.05 M MgCl_2 , pH 3.0. NB: 0.05 M THepATFPB (ref. 1).

Determination of ΔG_{tr}^0 of An ions

To understand the ion transfer reaction at the W/O solutions interface, solvation (hydration in the W phase) of the ion in solutions, complex formation of the ion with ligand, and ion-pair formation between the ion and counter ions should be determined quantitatively. As the standard Gibbs energy for the transfer of an ion (ΔG_{tr}^0) shows the difference between the hydration and solvation energies in both solution phases, the determination of ΔG_{tr}^0 of An ions will provide the necessary data for the solvation of the transferred ions.

An attempt was made to determine the ΔG_{tr}^0 of An ions of various oxidation states using the by partition method^{2,3)} and CPEITIES,¹⁾ as described previously. Figure 3 shows the ΔG_{tr}^0 of trivalent to hexavalent U, Np, and Pu ions between W/O phases. Here five types of organic solvents having relatively high permittivity were employed as the O phase (i.e., NB, 1,2-dichloroethane, benzonitrile, acetophenone, and 2-nitrophenyl octyl ether). The ion pair formations of pentavalent and hexavalent ions were corrected on the basis of formation constants

Fig. 3. Relationship between ΔG_{tr}^0 of actinide ion and that of H^+ (ref. 2).

determined by conductivity measurements.

The values indicated that ΔG_{tr}^0 values for the same oxidation state were similar irrespective of the type of O solutions. The ΔG_{tr}^0 values of NpO_2^{2+} were much larger than those for other An ions divided by the electric charge (z) or ΔG_{tr}^0 of H^+ . Thus, ΔG_{tr}^0 values for NpO_2^{2+} with any organic solvents investigated are considered to be particularly large. The pentavalent Np ion is known to be hardly extracted into the organic solvent due to weak complex formation with any ligand. However, it can be concluded that the particularly high hydrophilic nature is also a reason for its poor extractability. In addition, ΔG_{tr}^0 of An ions was found to be almost proportional to ΔG_{tr}^0 of H^+ regardless of the type of An ions. This suggests that solvations of An ions in various oxidation states in W and various O solutions that control ΔG_{tr}^0 are not unique. Therefore, it is considered that An ions are partly hydrated even after transfer to O phase and that the ion-solvent interaction in O phase is through water molecules.

Facilitated transfer of An ions

Several types of ligands (e.g., phosphine oxide

derivatives) were employed as an ionophore to facilitate the transfer of An ions.⁴⁻⁶⁾ The transfer of trivalent and hexavalent An ions from W to O phases was found to be facilitated by (bis(diphenyl phosphoryl) methane) (BDPPM), which was added to O solution. Plots of D versus E_{app} for facilitated transfer of UO_2^{2+} and Am^{3+} in the presence of 10^{-4} M BDPPM measured by CPEITIES are shown as broken lines in Fig. 2. The ion transfer potentials were determined from the plots. The shift of the ion transfer potential with and without an ionophore was attributed to the facilitation of the transfer by the complex formation of an An ion and a ligand. The composition of an actinide complex formed in O solution and the complex formation constant was estimated on the basis of the difference of ion transfer potentials.

The kinetics of a facilitated transfer of An ions with BDPPM was investigated using PITIES. The transfer current wave of UO_2^{2+} and Pu^{3+} appeared to be quasi-irreversible. The adsorption of the species at the W/O solutions interface was investigated on the basis of the results of drop-time measurements of a dropping aqueous solution electrode. Figure 4 shows the drop time and the applied potential relationship during the polarographic measurement of UO_2^{2+} transfer facilitated by BDPPM⁴⁾. The drop time decreased with the addition of BDPPM to O solution and increased slightly during UO_2^{2+} transfer to O phase. It could be concluded that the transfer of An ions from W to O phases consisted of three steps: (1) adsorption of BDPPM at the interface; (2) complex formation of the An ion and the ionophore adsorbed at the interface; (3) desorption of the complex from the interface through the transfer of the actinide ion.

Separation based on ion transfer

Based on ion transfer data, a novel separation method (i.e., electrolytic solvent extraction) was developed. In this method, the ion was selectively

Fig. 4. Drop-time versus potential relations during polarographic measurements for facilitated transfer of UO_2^{2+} by BDPPM (ref. 4).

transferred from W to O phases utilizing the differences in ion transfer potential. By using a CPEITIES cell, described above, it was found that UO_2^{2+} could be separated from Am^{3+} with a separation factor of more than 10^3 when E was -0.035 V (Fig. 2).¹⁾

To improve the efficiency and speed of electrolytic solvent extraction, a flow electrolysis cell for rapid ion transfer (FECRIT)⁷⁾ was applied to the separation of An ions. The cell was composed of a porous Teflon tube, a silver wire inserted into the tube, and a platinum wire placed outside the tube. The tube was immersed in O solution, and W solution containing An ions flowed through the narrow gap between the tube and silver wire. All of the target An ions could be transferred to O phase by electrolysis until the solution exited through the tube. UO_2^{2+} was successfully separated from other An ions and lanthanide ions within 1 min by using (bis(diphenylphosphoryl) ethane) (BDPPE) as the ionophore.⁸⁾ Although the An ions in the same oxidation state, such as NpO_2^{2+} and PuO_2^{2+} , could not be separated, a successive separation method for

Fig. 5. Schematic diagram of the flow electrolytic solvent extraction system for actinide separation.

U, Np, and Pu using a column electrode for valence control, and FECRIT was proposed (Fig. 5). Valence control will be described in a subsequent section.

It is thought that a large separation factor achieved by the precise control of the applied potential based on ion transfer data and rapid transfer of the ions by flow electrolysis would contribute to the development of a practical separation method.

Pu ion-selective electrode

Actinide ion transfer that satisfies the Nernst relation can be applied to develop an ion-selective electrode (ISE). Based on the ion transfer data of Pu^{3+} facilitated by BDPPM, a Pu^{3+} -ISE was designed.⁵⁾ NB containing BDPPM and a Pu^{3+} -BDPPM complex was prepared by solvent extraction and employed as a Pu^{3+} -ISE liquid membrane. Figure 6 shows the ISE potential generated between the ISE and a reference electrode plotted against the concentration of Pu^{3+} ($c_{\text{Pu(III)}}$) in a test solution of a 10^{-3} M HCl medium. A slope of 19 mV per decade of $c_{\text{Pu(III)}}$, which is in agreement with the theoretical Nernstian response, was obtained. The proposed ISE exhibited the Nernstian response from 1×10^{-7} to 1×10^{-2} M Pu^{3+} in a 10^{-3} M HCl medium.

An Eu^{3+} -ISE was developed and used to estimate complex formation constants of lanthanide

Fig. 6. Potential measured at Pu^{3+} -ISE. Test solution: 10^{-3} M HCl (ref. 5).

and organic ligands.⁹⁾ The composition of the Eu^{3+} -ISE was similar to that of the Pu^{3+} -ISE.

Electrode redox reaction of An ions

U, Np, and Pu exist as trivalent to hexavalent ions in acids such as HCl, HNO_3 , and HClO_4 . It is well known that An(III) and An(IV) are hydrated ions (An^{3+} and An^{4+} , respectively), while An(V) and An(VI) form dioxo ions (AnO_2^+ and AnO_2^{2+} , respectively). Although the redox of $\text{An}^{4+}/\text{An}^{3+}$ and $\text{AnO}_2^{2+}/\text{AnO}_2^+$ couples in various types of acid solutions have been well studied and reported to be reversible or quasi-reversible reactions¹⁰⁾, the investigation of electrode redox reactions of

$\text{AnO}_2^+/\text{An}^{4+}$ couples has been limited. Electrode reactions of $\text{AnO}_2^+/\text{An}^{4+}$ couples include the formation or breaking of An–O bonds; consequently, they are so irreversible that the voltammetric observation of the redox current is difficult. The detailed clarification of the reaction mechanisms of the irreversible redox of An ions can provide information that would contribute to the development of a reliable method to control the oxidation state of An ions.

Reduction processes of irreversible reduction of Np(V)

Bulk electrolysis was employed to investigate the irreversible reduction of NpO_2^{2+} .¹¹⁾ The reduction currents of NpO_2^{2+} and NpO_2^+ in 1 M HClO_4 at a gold gauze electrode during controlled potential electrolysis were compared. The results are shown in Fig. 7. The reduction current of NpO_2^{2+} by applying +0.6 V versus SSE decreased

exponentially with time (Curve 1) and reached the background level observed in the absence of NpO_2^{2+} after 20 min. This reduction behavior is consistent with a first-order reaction, i.e., the current decays exponentially with time during electrolysis. The electric charge during electrolysis was the same as the theoretical value for the one-electron reduction of NpO_2^{2+} to NpO_2^+ :

On the other hand, unique reduction behavior was observed when NpO_2^+ was electrolyzed at a gold electrode by applying –0.175 V (Curve 2 in Fig. 7b). At the beginning of electrolysis, the current was close to the background level. It increased gradually for approximately 30 min and then decreased to the background level. After the completion of bulk electrolysis, Np^{3+} and Np^{4+} were produced in the electrolyzed solution. The electric charge during electrolysis agreed with the theoretical value for the mixture solution of Np^{3+} and Np^{4+} whose concentrations were determined by spectrophotometry. Although the reduction current of NpO_2^+ could not be observed by voltammetry at a gold electrode, NpO_2^+ was reduced to Np^{4+} or Np^{3+} by controlled-potential bulk electrolysis.

The reduction mechanism of NpO_2^+ to Np^{4+} and Np^{3+} can be explained by the combination of the electrode reduction of Np^{4+} to Np^{3+} (Eq. 3) and the electron exchange reaction between Np^{3+} and NpO_2^+ in a bulk solution (Eq. 4).

That is, $\text{Np}^{4+}/\text{Np}^{3+}$ acts as a mediator for the reduction of NpO_2^+ . Here the initial solution of NpO_2^+ contains a very small amount of Np^{4+} , which was produced by the disproportionation of NpO_2^+ (Eq. 5).

Fig. 7. Current–time curve observed by controlled potential electrolysis at a gold or platinum electrode for reduction of (a) NpO_2^{2+} and (b) NpO_2^+ in 1 M HClO_4 (ref. 11).

The coexisting Np^{4+} becomes a trigger for the mediator reaction.

This reduction mechanism of NpO_2^+ occurs at any electrode material, such as carbon and platinum. The reaction proceeds as a matter of course at the potential at which Np^{4+} is reduced to Np^{3+} , and reaction rates increase at more negative potentials up to -0.175 V.

A peculiar reduction was observed when a platinum gauze was used as the working electrode (Curve 3, Fig. 7b). Although a current peak was observed at approximately 10 min of electrolysis time, a relatively large Faradaic current was observed even at the beginning of electrolysis. It should be noted that the potential of electrolysis was more positive than that of electrolysis at a gold electrode (Curve 2, Fig. 7b).

H^+ is reduced, forming adsorbed hydrogen on the platinum surface, when the applied potential is more negative than approximately 0 V. At this potential range, a small current resulting from the reduction of NpO_2^+ was observed by voltammetry. Therefore, it is suggested that the hydrogen atom on the electrode surface reduces NpO_2^+ .

Fig. 8. Two reaction schemes for NpO_2^+ reduction by bulk electrolysis.

The Np^{4+} produced by the reaction shown in Eq. 6 functions as an electron transfer mediator to reduce NpO_2^+ (Eqs. 3 and 4), similar to the reaction at a gold electrode. These two NpO_2^+ reduction schemes are illustrated in Fig. 8. The combination of the mediator reaction of $\text{Np}^{4+}/\text{Np}^{3+}$ and the electrocatalytic reduction of the platinum electrode resulted in the rapid formation of Np^{4+} by bulk electrolysis with a platinum electrode.

Electrolytic control of the oxidation state of An ions

Since it is not necessary to add any reagents and as electrolysis potential can be controlled precisely and freely, controlled potential electrolysis is a promising method for the adjustment of the oxidation state of ions. Flow electrolysis enables the rapid control of ion valence, even in a slow electrode reaction because the ions are repeatedly electrolyzed as they flow through the flow path. The author employed flow electrolysis with glassy carbon (GC) column electrodes for the precise and selective control of the oxidation state of An ions.¹²⁾

The column electrode was a working electrode comprising a bundle of very thin GC fibers tightly packed in a cylindrical electrolytic diaphragm cell of porous glass. Fabrication procedures and the pretreatment of GC fiber have been described in the literature.¹³⁾ Electrolysis is performed by passing the electrolyte solution containing An ions through the narrow paths between the GC fibers.

An example of the electrolysis behavior of An ions by flow electrolysis (current (I) –potential (E) curves for the redox of Np ions in various oxidation state in 1 M HClO_4 ¹²⁾) is shown in Fig. 9. The curves were charted after correction for the residual current observed in the absence of Np ions. Here the ordinate of the figure indicates n , which is the number of electrons involved in the redox reaction.

Fig. 9. I - E curves for redox of Np ions in 1 M HClO_4 (ref. 12).

On the flow electrolysis, the limiting current (I_l) is the function of n , F , the concentration of the ions (c) and the flow rate of the solution (f).

$$I_l = nFcf \quad (7)$$

Therefore, n is calculated by dividing the measured I by the product of F , c , and f .

One-electron redox currents due to $\text{Np}^{4+}/\text{Np}^{3+}$ and $\text{NpO}_2^{2+}/\text{NpO}_2^+$ couples are observed at approximately -0.2 V and $+0.8$ V, respectively. These redox waves show the reversible nature of the reactions. In addition, the two-electron reduction current of NpO_2^+ , which, as described previously, is not clearly observed by voltammetry, can be observed at -0.2 V in the I - E curve. This reduction potential is close to that of the reduction of Np^{4+} to Np^{3+} . This reduction of NpO_2^+ proceeds by a mediator reaction with $\text{Np}^{4+}/\text{Np}^{3+}$, as described above. An oxidation current of Np^{4+} is observed at approximately $+1.0$ V; however, it is overlapped with the residual current and is somewhat unclear.

Based on the I - E curve, electrolytic preparation of Np^{3+} , Np^{4+} , NpO_2^+ , and NpO_2^{2+} can be proposed. Np^{3+} and NpO_2^{2+} can be prepared by single column electrode electrolysis. However, Np^{4+} and NpO_2^+ require two-step column electrode electrolysis to

adjust the oxidation state, i.e., to prepare Np^{4+} , all Np is reduced to Np^{3+} at the first column electrode and then Np^{3+} is oxidized to Np^{4+} at the second electrode.

The concentration of Np^{4+} , NpO_2^+ , and NpO_2^{2+} could be successfully determined by measuring the electrolysis current. The method is applicable to the detection of Np^{3+} ; however, Np^{3+} is not stable in an acid solution.

When a platinum electrode is employed as a working electrode, the reduction overpotential of NpO_2^+ is expected to decrease because of the electrocatalytic reduction, as described previously. The author tried to add an electrocatalytic function to the column electrode.¹⁴⁾ Figure 10 shows the effect of platinization on the I - E curve for the reduction of NpO_2^+ at a column electrode with platinized GC (Pt/GC) fiber prepared by the electrodeposition of platinum on a GC surface. The overpotential of reduction of NpO_2^+ to Np^{4+} was significantly decreased relative to the degree of platinization. The reduction-current wave of the I - E curve changed from a one-step two-electron curve at normal GC to successive two-step one-electron waves of $\text{NpO}_2^+ \rightarrow \text{Np}^{4+} \rightarrow \text{Np}^{3+}$ at a Pt/GC

Fig. 10. Effect of the platinized surface area on I - E curves for reduction of NpO_2^+ (ref. 14).

electrode. This successive reduction means that preparation of Np^{4+} can be achieved by electrolysis at approximately +0.15 V using only a single column electrode.

The I - E curve for the reduction of U, Np, and Pu at normal GC and Pt/GC is compared in Fig. 11. In the case of Pu, the reduction wave of PuO_2^{2+} changed from a two-step wave (i.e., $\text{PuO}_2^{2+} \rightarrow \text{PuO}_2^+ \rightarrow \text{Pu}^{3+}$) to a one-step three-electron wave (i.e., $\text{PuO}_2^{2+} \rightarrow \text{Pu}^{3+}$). This result indicates that the reduction overpotential of PuO_2^+ to Pu^{4+} was decreased.

The one-step two-electron reduction of UO_2^{2+} to U^{4+} was observed at the Pt/GC electrode as well as

Fig. 11. I - E curves for redox of U, Np, and Pu ions at a platinized GC fiber electrode (ref. 14).

at normal GC. The reduction potential was hardly affected by platinization because the reduction of UO_2^+ results from very rapid disproportionation producing NpO_2^{2+} and U^{4+} .

Based on these unique characteristics of a Pt/GC column electrode, the selective adjustment of the valence of An ions can be achieved successfully. When Pt/GC electrode is employed, U, Np, and Pu ions in different oxidation states (i.e., UO_2^{2+} , Np^{4+} , and Pu^{3+}) can be prepared by electrolysis at +0.15 V; UO_2^{2+} , NpO_2^+ and Pu^{3+} were also prepared at +0.5 V.

Conclusions

The electroanalysis of liquid/solid and liquid/liquid electrodes provides useful information about the solution chemistry of An ions.

Elementary processes of the transfer of An ions at a W/O solutions interface and the solvation state of actinide ion after interfacial transfer could be clarified by PITIES and CPEITIES. Fundamental studies of ion transfer were applied to develop a separation method for An ions. The electrochemical method enables precise control with a high separation factor; however, the solvents that can be used with electrolytic solvent extraction are limited. Therefore, in future, the application of the methodology to common organic solvents will be investigated.

With regard to redox reactions of An ions, the irreversible reduction mechanisms of AnO_2^+ have been clarified and a method to control valence was developed. However, the details of the irreversible oxidation process of An^{4+} are unexplained as yet. Redox reactions of An ions in non-acidic solutions are interesting and significant, because they involve hydrolysis forming a hydroxide complex, a colloid, and a precipitate.

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