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# Voltammetric study on the transfer of U, Np, and Pu ions at the aqueous–organic interface facilitated by phosphine oxides

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## Abstract

Transfer of U, Np, and Pu ions across the interface between aqueous and 1,2-dichloroethane phases, which was facilitated by bidentate phosphine oxide, was studied by ion transfer polarography using an aqueous electrolyte dropping electrode. The ionic species participating in the transfer reaction were determined on the basis of wave analyses of the polarograms and results of the dependence of half-wave potential or limiting current on the concentration of metal ion in the aqueous phase or phosphine oxide in the organic phase. Applicability of the ion transfer reaction to the electrolytic separation of ions or the liquid-membrane-type ion selective electrode was investigated.

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## 1. Introduction

Voltammetry for ion transfer across the interface of two immiscible electrolyte solutions has become one of the most powerful methods for investigating the dynamic features of the ion transfer phenomenon [1]. The transferring ion can be specified and its transfer energy can be determined from the potential at which the voltammetric wave appears, and the number of ions transferred can be determined by the current. Ion transfer voltammetry has been applied not only to the elucidation of such fundamental problems in analytical chemistry as the distribution mechanism of an ion at a liquid–liquid interface [2] and the potential-generating process at an ion-selective electrode [3] but also to the understanding of the electrochemical phenomena occurring in living organisms [4]. Theoretical equations for analysing the voltammogram have been proposed [5].

In the present paper, the transfer of such actinide ions as U, Np, and Pu ions from aqueous solution to organic solution such as 1,2-dichloroethane (DCE), facilitated by phosphine oxide derivatives, was investigated by ion transfer polarography [6] using the aqueous electrolyte dropping electrode (AEDE), which is one of the branches of the ion transfer voltammetry.

## 2. Experimental details

### 2.1. Polarographic measurement

A polarogram at the AEDE was recorded using cells as shown in Fig. 1(a) [6]. The aqueous electrolyte solution was forced to flow upward dropwise through a glass capillary into the DCE phase containing crystal violet tetraphenylborate ($CV^+$ $TPhB^-$) as a supporting electrolyte. The supporting electrolyte of the aqueous solution was sulphuric acid or ammonium sulphate solution. The flow rate *m* of the aqueous solution was controlled by a plunger-type pump. A potentiostat, a function generator, and an IR compensator (HA501, HB105, and HI203 respectively; Hokuto Denko Co. Ltd.) as well as an *X–Y* recorder employed for the measurement of the polarogram were similar to those employed in the previous work [6, 7]. The potential difference $\Delta V$ at the aqueous solution–DCE interface was measured using an Ag–AgCl/1 M LiCl electrode (WE) placed in the aqueous solution and a tetraphenylborate-ion-selective electrode (TPhBE; RE) in DCE. The potential in the present paper refers to an imaginary potential denoted as TPhE, at which the transfer energy equals zero. The potential of TPhBE at the aqueous solution–DCE interface was +0.390 V *vs.* TPhE (at 25 °C) [6].

### 2.2. Chemicals

Uranium metal (JAERI-U4), neptunium dioxide (CEA, Fontenay-aux-Roses), and plutonium metal (NBS-949c) were dissolved with nitric acid. After addition of 0.5 M $H_2SO_4$ the solution was heated to remove the excess of nitric acid and the residue was dissolved with 0.5 M $H_2SO_4$ to prepare stock solutions of metal ions. The oxidation states of actinide ions were adjusted by controlled-potential electrolysis using

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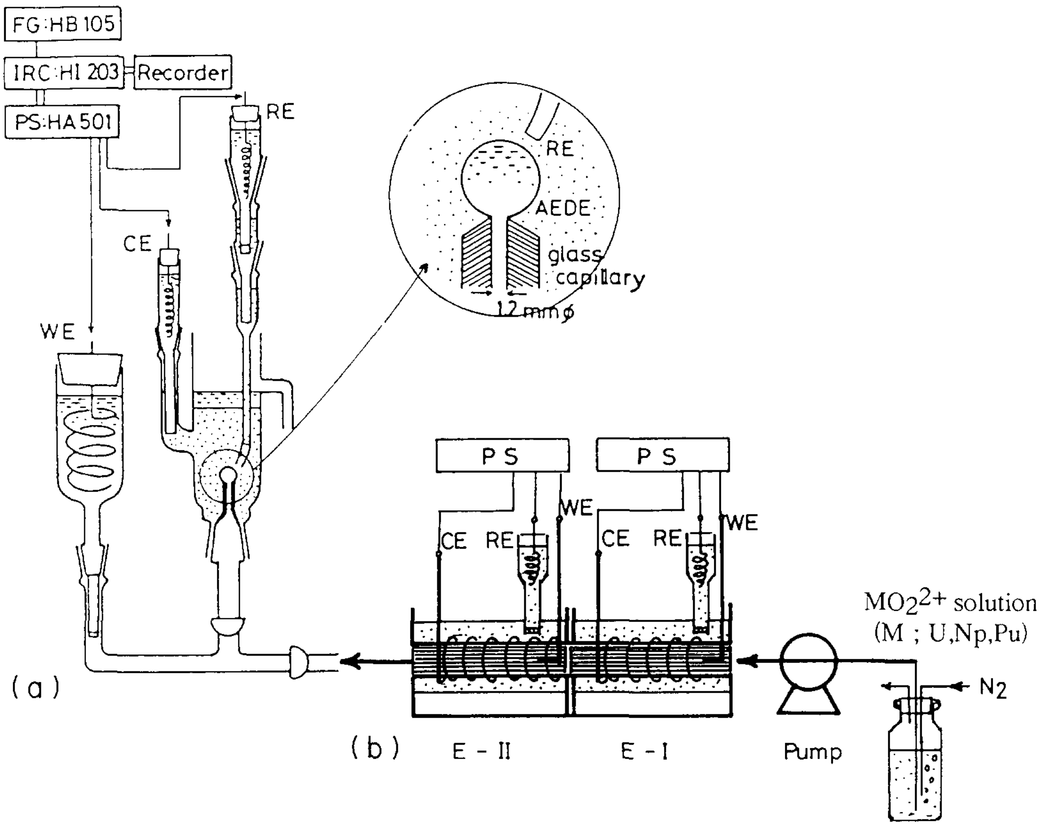

Fig. 1. Polarographic cell for the measurement of the transfer of actinide ions across the aqueous–organic interface: (a) polarographic cell with AEDE [6]; (b) flow electrolysis system with column electrodes for the preparation of the oxidation state of actinide ions [8].

flow-through column electrodes [8] as shown in Fig. 1(b). Bis(diphenylphosphoryl)methane (BDPPM) and bis(diphenylphosphoryl)ethane (BDPPE) were prepared according to the proposed method [9]. Other chemicals were of reagent grade.

## 3. Results and discussion

### *3.1. Polarograms for the transfer of U, Np, and Pu ions from aqueous solution to 1,2-dichloroethane solution facilitated by phosphine oxide*

Polarograms illustrated in Fig. 2 were measured at the aqueous solution–DCE interface between an aqueous solution of 0.2 M $H_2SO_4$ + 0.1 M $UO_2SO_4$ and a DCE solution of 0.05 M $CV^+$ $TPhB^-$ + $(1–5)\times10^{-4}$ M BDPPM. Curve 4 is the residual polarogram obtained with aqueous solution in the absence of $UO_2^{2+}$. The anodic final rise in the residual current is due to the transfer of $H^+$ from the aqueous solution to DCE. Anodic waves in polarograms 1–3 correspond to the transfer of $UO_2^{2+}$ from aqueous to DCE solution facilitated by the formation of the stable complex of $UO_2^{2+}$ with BDPPM. The limiting current $I_l$, of the anodic wave was proportional to the concentration $C_L^0$ of the ligand BDPPM in DCE in the range from $1\times10^{-4}$ to $2\times10^{-3}$ M and did not depend on the concentration $C_M^0$ of $UO_2^{2+}$ in aqueous solution in the range from $10^{-2}$ to $10^{-1}$ M. Since $I_l$ was proportional also to the square root of the flow rate $m$ of the aqueous phase to prepare the AEDE, it was found that the facilitated transfer of $UO_2^{2+}$ is reversible and controlled by the diffusion of BDPPM in DCE.

If it is assumed that the reversible facilitated transfer of a metal ion $M^{z+}$ by a neutral ligand L in organic solution proceeds through an electrochemical mechanism, through which $M^{z+}$ transfers from aqueous to organic phases (electrochemical process) and then complexes with L in the organic phase to form $ML_n^{z+}$ (chemical process), and the polarogram is measured under the condition that $C_M^0 \gg C_L^0$, the following equations for the polarogram can be derived [2]:

$$\begin{aligned}\Delta V = {} & \Delta\phi_M^0 + (RT/zF)\ln\{1/(\beta_n C_M^0)\} \\ & + (RT/zF)\ln(S_L^n/S_{ML_n}) \\ & + (RT/zF)\ln(\gamma_{\pm,\mathrm{org}}/\gamma_{\pm,\mathrm{w}}) \\ & + (RT/zF)\ln[I/(I_l - I)^n] \qquad (1)\end{aligned}$$

with

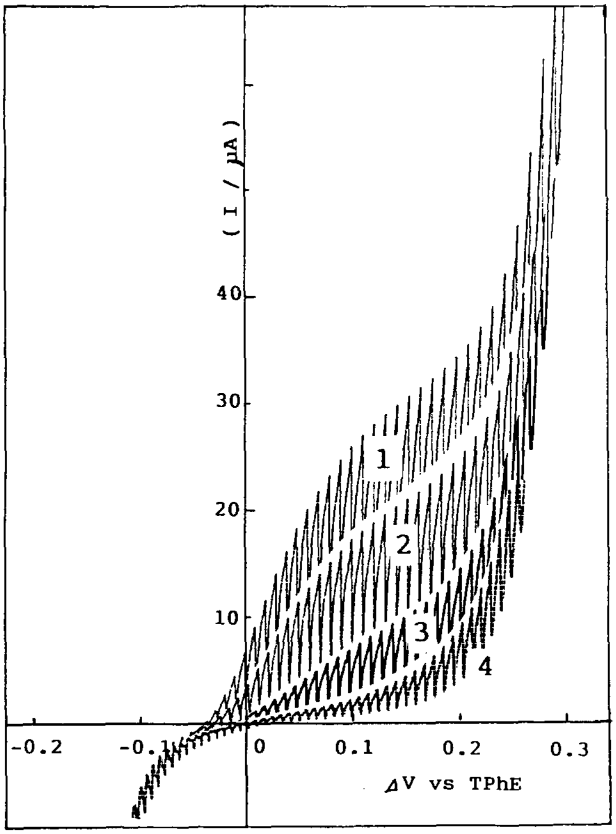

Fig. 2. Polarograms for the ion transfer of $UO_2^{2+}$ from aqueous to DCE phases facilitated by BDPPM. The aqueous phase contained 0.1 M $UO_2SO_4 + 0.2$ M $H_2SO_4$ (curves 1–3) or 0.2 M $H_2SO_4$ (curve 4); the DCE phase contained 0.05 M $CV^+ TPhB^- + 5\times10^{-4}$ (curve 1), $3\times10^{-4}$ (curve 2) or $1\times10^{-4}$ (curves 3 and 4) M BDPPM. The flow rate of the aqueous phase was 1.1 ml $min^{-1}$ and the potential scan rate was 3 mV $s^{-1}$.

$$S_L = KF(z/n)D_L^{1/2}m^{2/3}t_d^{1/6} \tag{2}$$

and

$$S_{ML_n} = KF(z/n)D_{ML_n}^{1/2}m^{2/3}t_d^{1/6} \tag{3}$$

and the subscript "w" indicates aqueous solution. By defining the half-wave potential $\Delta V_{1/2}$ as $\Delta V$ at $I = I_l/2$,

$$\begin{aligned}\Delta V_{1/2} = {} & \Delta\phi_M{}^0 + (RT/zF)\ln\{1/(\beta_n C_M{}^0)\} \\ & + (RT/zF)\ln(D_{ML_n}/D_L)^{1/2} \\ & + (RT/zF)\ln(\gamma_{\pm,\mathrm{org}}/\gamma_{\pm,\mathrm{w}}) \\ & - (n-1)(RT/zF)\ln(C_L{}^0/2)\end{aligned} \tag{4}$$

In these equations, $\Delta\phi_M{}^0$, $\beta_n$, $\gamma_\pm$, and $D$ are the standard Galvani potential difference for the transfer of $M^{z+}$, the constant for the complex formation of $ML_n$ in the organic phase, the mean activity coefficient of a salt in the solution, and the diffusion coefficient in organic phase respectively.

$\Delta V_{1/2}$ of anodic waves in polarograms 1–3 in Fig. 2 depend on both $C_M{}^0$ and $C_L{}^0$. The $\Delta V_{1/2}$ shifted to negative linearly with an increase in $C_M{}^0$ in the range $10^{-2}$–$10^{-1}$ M, and the slope of the $\Delta V_{1/2}$ *vs.* $\log C_M{}^0$ plot was found to be 28±3 mV. Also, the $\Delta V_{1/2}$ shifted linearly with $\log C_L{}^0$ in the range $1\times10^{-4}$–$5\times10^{-4}$ M, and the slope of the $\Delta V_{1/2}$ *vs.* $\log(C_L{}^0/2)$ plot was 52±3 mV. On the basis of these results and eqn. (4), it was found that the ionic species participating in the ion transfer reaction giving the anodic wave in Fig. 2 was $UO_2(BDPPM)_3{}^{2+}$.

Since the experiments for Np and Pu ions under the condition that $C_M{}^0 \gg C_L{}^0$ were unpractical, the polarographic behaviour of these ions was studied under the condition that $C_L{}^0 \gg C_M{}^0$. A similar anodic wave was observed in polarograms which were recorded with an aqueous phase of 0.2 M $H_2SO_4 + (1\text{–}5)\times10^{-4}$ M $UO_2^{2+}$ and DCE solution containing $1\times10^{-3}$–$1\times10^{-2}$ M BDPPM. Even under the condition that $C_L{}^0 \gg C_M{}^0$, the transfer of $UO_2^{2+}$ facilitated by BDPPM is reversible. In this case, $I_l$ was proportional to $C_M{}^0$, and $\Delta V_{1/2}$ shifted 90 mV more negatively with an increase of one order of magnitude in $C_L{}^0$. Wave analysis, *i.e.* $\Delta V$ *vs.* $\log[I/(I_l - I)]$ plots [2], revealed a linear relation with a slope of 32±3 mV. These results confirm that the ionic species participating in the transfer reaction is $UO_2(BDPPM)_3{}^{2+}$.

The $\Delta V_{1/2}$ values of anodic waves for the transfer of $UO_2^{2+}$, $U^{4+}$, $NpO_2^{2+}$, $NpO_2^{+}$, $Np^{4+}$, $Np^{3+}$, $PuO_2^{2+}$, $Pu^{4+}$, and $Pu^{3+}$, which were determined with DCE solution containing $1\times10^{-2}$ M BDPPM, were −0.116 V, −0.020 V, −0.056 V, +0.023 V, +0.012 V, −0.004 V, −0.030 V, −0.014 V, and −0.064 V respectively. Referring to the $\Delta V_{1/2}$ for relatively stable species, *i.e.* $UO_2^{2+}$, $NpO_2^{+}$, $Pu^{4+}$, and $Pu^{3+}$, it was observed that the transferability of actinide ions from aqueous to DCE phases facilitated by BDPPM is in the following sequence: M(VI) > M(III) > M(IV) > M(V).

When BDPPE was employed instead of BDPPM, anodic waves due to the facilitated transfer of actinide ions were not clearly observed in the polarograms, indicating the lower stabilities of BDPPE complexes of actinide ions than those of BDPPM complexes. For example, $\Delta V_{1/2}$ for the transfer of $UO_2^{2+}$ with BDPPE was about 100 mV more positive than that with BDPPM.

### *3.2. Separation of ions based on ion transfer electrolysis*

Diffusion-controlled transfer of $UO_2^{2+}$ from aqueous to DCE phases containing $10^{-2}$ M BDPPM takes place at −0.065 V where neither $Pu^{4+}$ nor $NpO_2^{+}$ transfers into DCE. When the controlled-potential electrolysis at −0.065 V was performed with a 0.2 M $H_2SO_4$ solution containing these three ions and DCE containing $10^{-2}$ M BDPPM, $UO_2^{2+}$ was separated from $Pu^{4+}$ and

$NpO_2^+$. Such a method based on the electrolytic ion transfer reaction has the unmatchable advantages that it is not required to add a hydrophobic counteranion, which is indispensable for conventional ion pair extraction, and that the selectivity can be increased by the precise control of the electrolytic potential.

### *3.3. Ion-selective electrode of $UO_2^{2+}$*

The potential-generating process at an ion-selective electrode (ISE) of the liquid membrane type has been interpreted on the basis of the voltammograms for the ion transfer across the aqueous–organic interface [3]. In order to obtain a stable nernstian response the test solution–membrane interface should be depolarized by the transfer of the analyte ions. The potential at zero current in the composite polarogram observed with the analyte ions in both aqueous and organic phases, *i.e.* the equilibrium ion transfer potential of the ion corresponds to the ISE potential for the ion. Anodic and cathodic waves were observed for the transfer of $UO_2^{2+}$ from aqueous to DCE phases and from DCE to aqueous phases respectively, which implied the possibility for the preparation of a $UO_2^{2+}$ ISE on the basis of the facilitated transfer of $UO_2^{2+}$ by BDPPM.

The cell configuration for the measurement of the ISE potential is

$$\begin{array}{l|l|l|} \text{Ag/AgCl} & 0.1\ \text{M}\ H_2SO_4 + & UO_2BDPPM_3^{2+} \\ (0.1\ \text{M NaCl}) & 10^{-3}\ \text{M}\ UO_2^{2+} & +2TPhB^-\ (\text{DCE}) \\ & & \\ \text{SSE 1} & \text{inner solution} & \text{membrane} \end{array}$$

$$\begin{array}{|l|l} 0.1\ \text{M}\ H_2SO_4 & \text{Ag/AgCl} \\ +UO_2^{2+} & (0.1\ \text{M NaCl}) \\ & \\ \text{test solution} & \text{SSE 2} \end{array} \qquad (5)$$

The relations between the logarithmic concentration of $UO_2^{2+}$ in the aqueous test solution and the ISE potential measured between SSE 1 and SSE 2 in eqn. (5) are given in Fig. 3. A nernstian response with a slope of 28±2 mV was obtained. The detection limit is affected by the concentration of $UO_2BDPPM_3^{2+}$ as well as the presence of free BDPPM in excess in the membrane. When the concentrations of $UO_2BDPPM_3^{2+}$ in the membrane were $1\times10^{-4}$ M and $1\times10^{-3}$ M, the lower detection limits of the $UO_2^{2+}$ in the test solutions were $5\times10^{-6}$ M and $2\times10^{-5}$ M respectively.

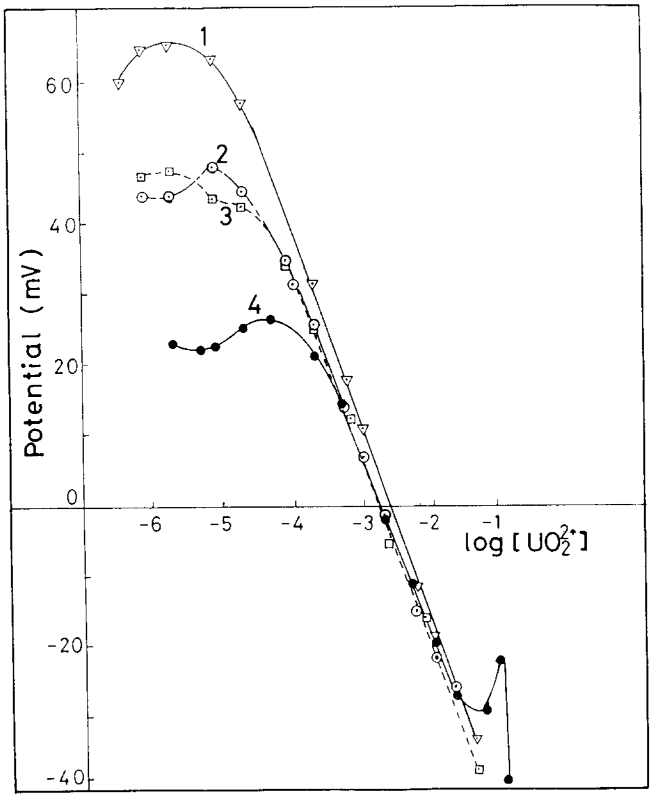

Fig. 3. Potential measured at the DCE membrane ISE for $UO_2^{2+}$ on the basis of the cell configuration of eqn. (5). The concentration of $UO_2BDPPM_3^{2+}$ was $1\times10^{-4}$ (curve 1), $1\times10^{-3}$ (curves 2 and 3) or $3\times10^{-3}$ (curve 4) M; curves 1 and 2, with free BDPPM in the membrane ($1\times10^{-2}$ M); curves 3 and 4, without BDPPM in the membrane.

## 4. Conclusion

The transfer of U, Np and Pu ions of various oxidation states from aqueous to organic phases was facilitated by bidentate phosphine oxide. On the basis of the ion transfer reaction, methods for the electrolytic separation of the ion and for the preparation of ion selective electrode were developed. Further investigations on the phase transfer of actinide ions with various neutral carrier type extractants are now in progress.

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