

Voltammetric Study on Transfer of UO_2^{2+} Across the Interface Between Aqueous and Nitrobenzene Solutions in the Presence of Octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine Oxide (CMPO)

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The characteristics of the phase transfer of UO_2^{2+} across aqueous(*w*)/nitrobenzene(*nb*) solutions interface in the presence of octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (CMPO) as an ionophore were investigated by cyclic voltammetry (VITIES) and polarography (PITIES) for ion transfer at the interface of two immiscible electrolyte solutions. The transfer of UO_2^{2+} from *w* to *nb* is remarkably facilitated by CMPO and the ion transfer reaction exhibits an irreversible nature. The rate-determining step of the UO_2^{2+} transfer is assigned to adsorption / desorption process of the UO_2^{2+} -CMPO complex at the *w/nb* interface. The ion transfer potential of UO_2^{2+} shifts more positively when the two phase system is allowed to stand stationarily for a given time before the measurement of the cyclic voltammogram. The potential shift with the standing time is attributable to a decrease in the interfacial concentration of "free" CMPO due to the protonation of CMPO followed by the accumulation of the ion pair between HCMPO^+ and TPhB^- at the *w/nb* interface.

Introduction

An ion transfer across the interface of two immiscible electrolyte solutions (ITIES) such as aqueous(*w*)/organic(*org*) solutions interface has become an increasingly attractive subject on account of its feasibility to direct utilization for the separation technology and its informative significance in not only equilibrium but kinetic studies of liquid/liquid interfacial phenomena. The first electrochemical study of ITIES was conducted on the transfer of ions in the water/phenol/water system.¹ The aim of the work was primarily to develop methods for the measurement of the transport number in the organic solvents.^{2,3} After these preliminary electrochemical investigations, interests in the ITIES has spread to physiologists who pointed out an analogy between the water/oil/water cell and biological membranes.^{4,5} The oil-water interface then became a model in studying bioelectrical potentials and currents, fascinating the scientific community.^{6,7}

Voltammetry (VITIES) and polarography (PITIES) for ITIES are very powerful methods for elucidating the ion transfer phenomena with a unique feature in that they can determine simultaneously the transfer energy (as a potential) of the ion and the amount (as a current) of the ion transferred. The VITIES and PITIES have furnished a deeper insight into the thermodynamics and kinetics of a solvent extraction reaction, a phase transfer catalysis, an ion-selective electrode and a biological membrane transport, etc.⁸⁻¹⁷

In studying the transfer of actinide ions from *w* to *org* there is an inevitable difficulty due to a strong hydrophilicity of these ions. It is hard to measure a current-potential relationship for the transfer of actinide ions between *w* and *org* by means of the conventional VITIES or PITIES. Therefore, appropriate ionophors such as multidentate phosphine oxide derivatives¹⁸ that form stable complexes with these metal ions were employed to facilitate the ion transfer from *w* to *org*. In the present study, the transfer of UO_2^{2+} has been studied using octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide

(CMPO) as the ionophore by VITIES and PITIES with aqueous/nitrobenzene (*w/nb*) solvent pair. Though CMPO has been extensively studied in the solvent extraction and has become an important extractant for the separation of actinide ions,^{19,20} interfacial phenomena involved in the extraction system, especially in the kinetic aspects, has not been fully understood.

Experimental

Chemicals. A stock solution of UO_2^{2+} was prepared by dissolving uranium metal (JAERI-U4) with nitric acid. After the addition of 0.5 M H_2SO_4 , the solution was heated to remove an excess of acid, and the residue was dissolved with 0.5 M H_2SO_4 . A working solution of UO_2^{2+} was prepared by diluting the stock solution in 0.1 M $(\text{NH}_4)_2\text{SO}_4$ (pH = 3.0).

CMPO, the product of Wako Pure Chemical Industries, Ltd., was used without further purification. Nitrobenzene as the organic solvent and crystal violet - tetraphenylborate (CV^+TPhB^-) as the organic supporting electrolyte were employed.

Other chemicals were of reagent grade.

Polarography (PITIES) and Voltammetry (VITIES) for the Ion Transfer at the Interface of Two Immiscible Electrolyte Solutions.¹¹ Polarograms were recorded with an aqueous electrolyte dropping electrode (AEDE) and cyclic voltammograms were recorded with a stationary *w/nb* interface electrode having an interfacial area (*A*) of 0.38 cm². The potential difference at the *w/nb* interface was measured using a Ag/AgCl electrode in *w* and a tetraphenylborate ion-selective electrode (TPhBE) in *nb*. The potential in the present paper is referred to the standard potential denoted as TPhE, which is equivalent to a transfer energy of zero. The potential of TPhBE referred to TPhE is 0.350 V for *w/nb* interface at 25 °C. Equipments such as an HA 501 potentiostat, an HB 105 function wave generator, an HI 203 ohmic potential drop compensator (Hokuto Denko) and an X-Y recorder were employed. The pH was measured by an HM-266 pH meter (TOA) with a GST-5311C pH combination electrode.

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Results and Discussion

Characteristics of UO_2^{2+} Transfer Studied by PITIES.

The transfer of UO_2^{2+} from *w* to *nb* in the presence of CMPO was investigated by PITIES. The results are shown in Figure 1. Polarogram 1 is a residual polarogram observed with *w* of 0.1 M $(\text{NH}_4)_2\text{SO}_4$ (pH = 3.0) without UO_2^{2+} and *nb* of 5×10^{-2} M $\text{CV}^+\text{TPhB}^- + 5 \times 10^{-2}$ M CMPO. The final rise of anodic current of the residual polarogram is due to the transfer of H^+ from *w* to *nb* which is facilitated by CMPO. The transfer potential of H^+ with CMPO shifted to more negative side so that the potential at which 10 μA of anodic current flows shifted from +0.18 V (without CMPO) to +0.032 V (with 5×10^{-2} M CMPO). In polarogram 2 recorded using *w* containing 1×10^{-3} M UO_2^{2+} , an anodic wave due to the transfer of UO_2^{2+} from *w* to *nb* is observed at half-wave potential $\Delta V_{1/2}$ of -0.057 V, though the wave is not a typical S-shape polarogram predicted from Nernst equation.

Polarograms were recorded under various conditions of the concentration of UO_2^{2+} in *w*, $C_{\text{U(VI)},w}$, the concentration of CMPO in *nb*, $C_{\text{CMPO},nb}$, and the flow rate of *w* to prepare AEDE, *f*. Figure 2 shows the results of logarithmic analysis, i.e., ΔV vs $\log[i / (i_l - i)]$ plot, where i_l and *i* denote a limiting current and an instantaneous current, respectively, of the polarogram for the transfer of 1×10^{-3} M UO_2^{2+} from *w* to *nb*. The plots show clear linearity. The slopes 56–81 mV, which decrease with an increase of $C_{\text{CMPO},nb}$, are larger than that expected for the reversible transfer of a divalent cation, 29 mV. The UO_2^{2+} transfer facilitated by CMPO is concluded to be not reversible.

The $\Delta V_{1/2}$ and i_l of the polarographic waves are summarized in Table 1. The $\Delta V_{1/2}$ depends strongly on $C_{\text{CMPO},nb}$ when the ratio of $C_{\text{CMPO},nb}$ to $C_{\text{U(VI)},w}$ enough high, and the $\Delta V_{1/2}$ shifts to more negative side with increasing $C_{\text{CMPO},nb}$. The dependence of $\Delta V_{1/2}$ on $C_{\text{CMPO},nb}$ was found to be -98 mV/dec. The i_l of the polarogram with *w* of 1.0×10^{-3} M UO_2^{2+} is influenced by $C_{\text{CMPO},nb}$ in the range of 5×10^{-3} to 1×10^{-2} M and approaches a constant, $42 \pm 1.5 \mu\text{A}$, when $C_{\text{CMPO},org}$ is higher than 1×10^{-2} M. This result indicates that the amount of transferring UO_2^{2+} is virtually independent of the diffusion of CMPO when the

ratio of $C_{\text{CMPO},nb}$ to $C_{\text{U(VI)},w}$ is larger than *ca.* 10. A linear relationship between i_l and $C_{\text{U(VI)},w}$ is clearly observed at $C_{\text{U(VI)},w}$ in the range of 2×10^{-4} to 2×10^{-3} M when $C_{\text{CMPO},nb} = 5 \times 10^{-2}$ M. It is also indicated in Table 1 that i_l was almost independent of *f* in the range of 0.25 to 1.5 ml/min. Both of the relationship between i_l and $C_{\text{U(VI)},w}$ and that between i_l and *f* are contradictory to each other if only a diffusion-controlled process is taken into account. Alternative reaction steps determining the limiting current other than the diffusion process need to be elucidated for interpreting these phenomena. A similar phenomenon was observed in the polarograms for the transfer of UO_2^{2+} facilitated by multi-dentate phosphine oxide derivatives,¹⁸ which was explained based on an assumption that the UO_2^{2+} transfer reaction involves the adsorption/desorption processes of the UO_2^{2+} -phosphine oxide complex as well as the phosphine oxide itself at the *w/nb* interface. In that work the

TABLE 1: Characteristics of Polarograms for the Transfer of UO_2^{2+} from *w* to *nb* Facilitated by CMPO

$C_{\text{U(VI)},w}$ (M)	$C_{\text{CMPO},nb}$ (M)	flow rate, <i>f</i> (ml/min)	$\Delta V_{1/2}$ (V vs TPhE)	i_l (μA)
1.0×10^{-3}	5.0×10^{-3}	0.5	0.047	31.5
1.0×10^{-3}	1.0×10^{-2}	0.5	0.012	41.5
1.0×10^{-3}	2.0×10^{-2}	0.5	-0.025	43.0
1.0×10^{-3}	5.0×10^{-2}	0.5	-0.057	43.0
1.0×10^{-3}	1.0×10^{-1}	0.5	-0.080	42.5

2.0×10^{-4}	5.0×10^{-2}	0.5	-0.059	8.5
5.0×10^{-4}	5.0×10^{-2}	0.5	-0.057	20.0
2.0×10^{-3}	5.0×10^{-2}	0.5	-0.055	88.0

1.0×10^{-3}	5.0×10^{-2}	0.25	-0.062	40.5
1.0×10^{-3}	5.0×10^{-2}	0.75	-0.054	42.0
1.0×10^{-3}	5.0×10^{-2}	1.0	-0.050	41.2
1.0×10^{-3}	5.0×10^{-2}	1.25	-0.048	40.5
1.0×10^{-3}	5.0×10^{-2}	1.5	-0.045	40.3

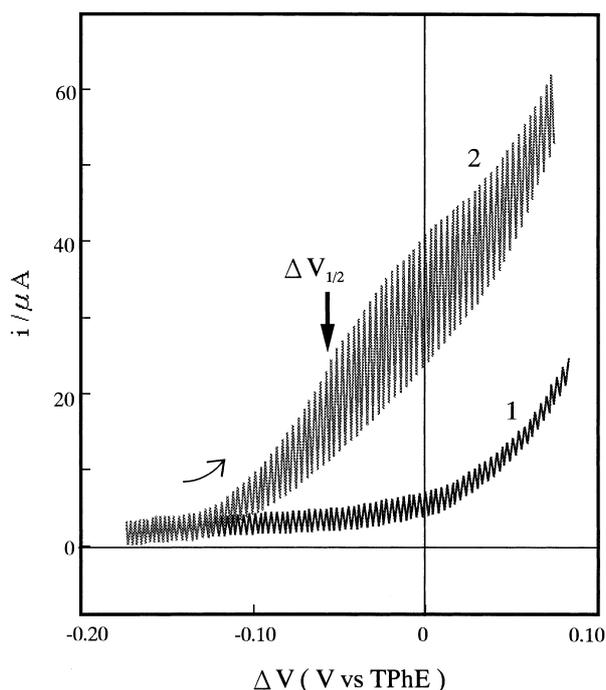


Figure 1. Polarograms recorded by PITIES for the transfer of UO_2^{2+} from *w* to *nb* facilitated by CMPO. *w*: 0.1 M $(\text{NH}_4)_2\text{SO}_4$, pH = 3.0 + (1) none (residual polarogram), (2) 1×10^{-3} M UO_2^{2+} , *nb*: 5×10^{-2} M $\text{CV}^+\text{TPhB}^- + 5 \times 10^{-2}$ M CMPO, *f* = 1.0 ml min⁻¹.

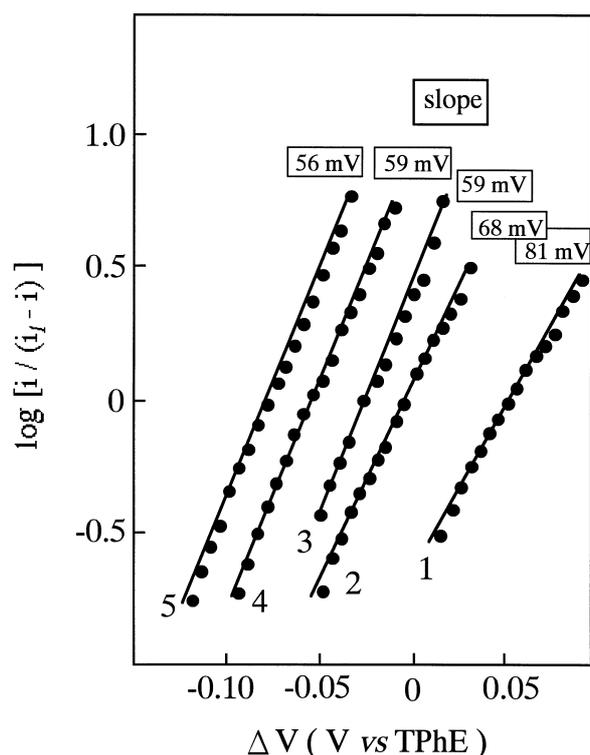


Figure 2. Logarithmic analysis of the polarographic wave for the transfer of UO_2^{2+} from *w* to *nb* facilitated by CMPO. *w*: 0.1 M $(\text{NH}_4)_2\text{SO}_4 + 1 \times 10^{-3}$ M UO_2^{2+} , pH = 3.0, *nb*: 5×10^{-2} M $\text{CV}^+\text{TPhB}^- +$ (1) 5×10^{-3} M, (2) 1×10^{-2} M, (3) 2×10^{-2} M, (4) 5×10^{-2} M, (5) 1×10^{-1} M CMPO, *f* = 1.0 ml min⁻¹.

adsorption/desorption characteristics were investigated by the measurement of the drop time, t_d , of the AEDE under the polarographic condition. The same experimental approach as above was conducted for the UO_2^{2+} transfer reaction facilitated by CMPO. The results of the t_d vs ΔV are shown in Figure 3.

The t_d decreases remarkably by the addition of CMPO into nb , indicating an adsorption of CMPO at the w/nb interface (cf. plots 1 and 2 in Figure 3). The t_d shows a further decrease but to a less extent when UO_2^{2+} is added to w (plot 3). Further decrease in t_d is attributed to an additional adsorption of the complex of UO_2^{2+} -CMPO. These results indicate that the adsorbed species of UO_2^{2+} -CMPO complex or CMPO molecule participate in the UO_2^{2+} transfer, and UO_2^{2+} transfer reaction from w to nb involves a desorption of the adsorbed species from the interface. When the $C_{\text{U(VI)}, w}$ increases, a diffusion flux of UO_2^{2+} from the bulk of w toward the interface increases. The i_l is proportional to $C_{\text{U(VI)}, w}$, if the formation of UO_2^{2+} -CMPO complex is sufficiently rapid.

A diffusion controlled limiting current, $i_{l, d}$ observed in the polarogram obtained by PITIES can be expressed by eq 1,²¹

$$i_{l, d} = (4.0 \times 10^5) n D^{1/2} C_{\text{U(VI)}, w} t_d^{1/6} m^{2/3} - (2.6 \times 10^5) n D^{1/2} C_{\text{U(VI)}, w} t_d^{-1/2} r^2, \quad (1)$$

where n , D , m and r denote a charge of the ion transferred ($n = 2$ for UO_2^{2+}), diffusion coefficient of UO_2^{2+} in w , flow mass of w to prepare the AEDE and the inner radius of the capillary to prepare AEDE, respectively. The second term of eq 1 is usually neglected, because the cross section of the capillary is much smaller than the surface area of the AEDE. The size of each drop is independent of f , and therefore, $t_d^{1/6} m^{2/3}$ becomes linear to $f^{1/2}$. When $f = 1$ ml/min and $C_{\text{U(VI)}, w} = 1 \times 10^{-3}$ M and assuming $D = 4.26 \times 10^{-6}$ cm² sec⁻¹,²² the theoretical diffusion-controlled $i_{l, d}$ is calculated to be 117 μA which is 2 to 3 times larger than the i_l observed experimentally (cf. Table 1). This result implies that the i_l of the polarogram for the transfer of UO_2^{2+} facilitated by CMPO is not fully controlled by a diffusion process but involves a kinetically controlled process. The limiting current i_l for the ion transfer voltammogram which is

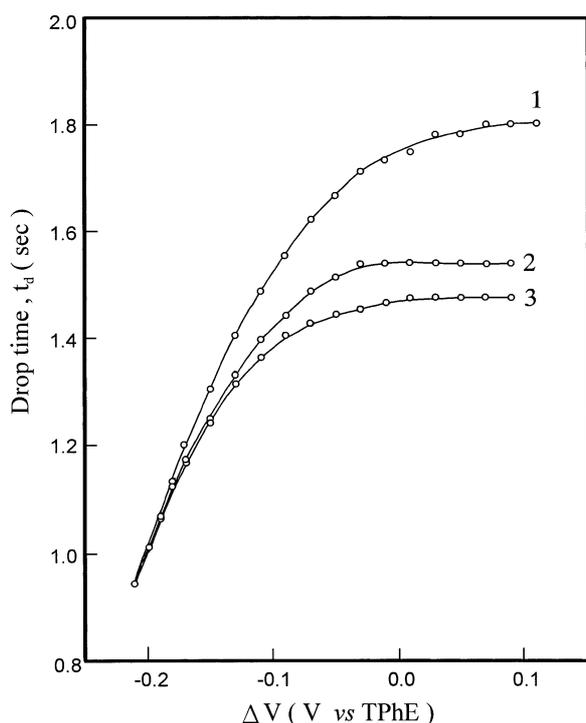


Figure 3. Drop time, t_d , of the AEDE under the condition of PITIES measurement. w ; 0.1 M $(\text{NH}_4)_2\text{SO}_4$, pH = 3.0 + (1,2) none, (3) 1×10^{-3} M UO_2^{2+} , nb ; 5×10^{-2} M CV^+ TPhB⁻ + (1) none, (2,3) 5×10^{-2} M CMPO, $f = 1.0$ ml min⁻¹.

controlled both by a kinetic and diffusion process can be expressed by eq 2 in a manner similar to an expression for a redox voltammogram observed at a rotating disk electrode.²³

$$1/i_l = 1/i_k + 1/i_d. \quad (2)$$

Here $k_f(E)$ is a rate constant of the rate-determining step, and i_k and i_d are the partial currents controlled by a kinetic and a diffusion process, respectively. When a transfer process is slow enough, $1/i_k$ is much larger than $1/i_d$, and the i_l equals approximately to i_k . The theoretical treatment of i_l for the kinetically controlled transfer of UO_2^{2+} studied presently has not yet been completed.

Characteristics of UO_2^{2+} Transfer Studied by VITIES.

Cyclic voltammograms recorded by VITIES at a stationary w/nb interface electrode are shown in Figure 4. Residual voltammogram as curve 1 was recorded with w without UO_2^{2+} and nb containing 5×10^{-2} M CMPO. The final rise of the anodic current is due to the transfer of H^+ from w to nb , which is facilitated by CMPO as mentioned above, and the final descent of the cathodic current is due to the transfer of SO_4^{2-} from w to nb or the transfer of CV^+ from nb to w .

The anodic and cathodic peaks observed in voltammogram 2 correspond to the transfer of UO_2^{2+} from w to nb and from nb to w , respectively. The characteristics of cyclic voltammograms observed under various conditions of $C_{\text{U(VI)}, w}$, $C_{\text{CMPO}, nb}$, and the potential scanning rate, v , are summarized in Table 2. The peak potential, ΔV_p , for both anodic and cathodic waves at a given v does not depend on $C_{\text{U(VI)}, w}$ in the range examined and depends on $C_{\text{CMPO}, nb}$, when $C_{\text{CMPO}, nb}$ is sufficiently higher than $C_{\text{U(VI)}, w}$. The ΔV_p vs $\log C_{\text{CMPO}, nb}$ plot shows a clear linearity and the slopes of the plots for the anodic and cathodic waves were determined to be -108 and -110 mV/dec, respectively. The ΔV_p also depends on v . The difference in ΔV_p between the anodic and cathodic waves of a cyclic voltammogram increases with an increase of v which is manifesting a typical characteristic of an irreversible electrode process.

Both of the peak currents, i_p , of the anodic and cathodic waves are proportional to $C_{\text{U(VI)}, w}$, if $C_{\text{CMPO}, nb}$ is sufficiently higher than $C_{\text{U(VI)}, w}$. The i_p of the cathodic wave increases with

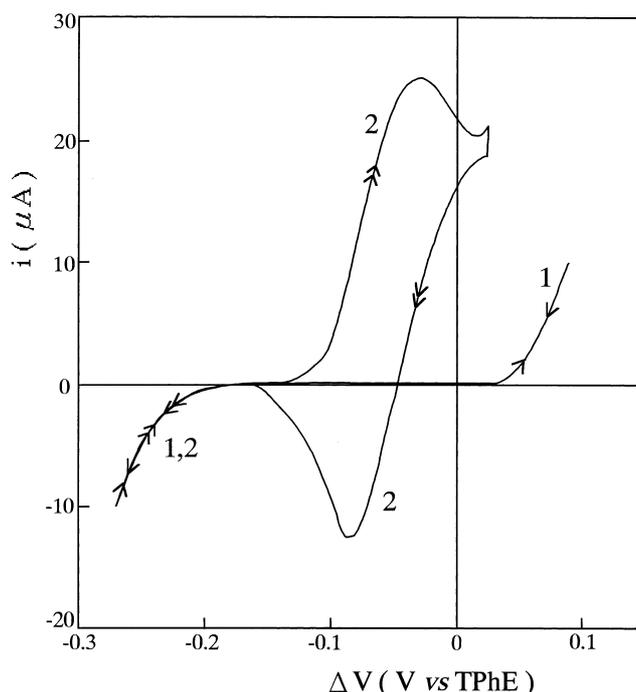


Figure 4. Cyclic voltammograms recorded by VITIES for the transfer of UO_2^{2+} between w and nb in the presence of CMPO. w ; 0.1 M $(\text{NH}_4)_2\text{SO}_4$, pH = 3.0 + (1) none (residual voltammogram), (2) 2×10^{-3} M UO_2^{2+} , nb ; 5×10^{-2} M CV^+ TPhB⁻ + 5×10^{-2} M CMPO, interfacial area A ; 0.38 cm², potential scanning rate v ; 1 mV sec⁻¹.

TABLE 2: Characteristics of Cyclic Voltammograms for the Transfer of UO_2^{2+} at a Stationary w/nb Interface in the Presence of CMPO in nb

$C_{\text{U(VI), } w}$ (M)	$C_{\text{CMPO, } nb}$ (M)	potential scanning rate ν (mV/sec)	ΔV_p (V vs TPhE)		i_p (μA)	
			anodic wave	cathodic wave	anodic wave	cathodic wave
5.0×10^{-4}	2.5×10^{-2}	1	-0.007	-0.043	5.1	4.5
1.0×10^{-3}	2.5×10^{-2}	1	-0.007	-0.044	10.4	8.5
2.0×10^{-3}	2.5×10^{-2}	1	-0.007	-0.044	21	17
2.0×10^{-3}	1.0×10^{-2}	1	0.034	-0.011	19.5	12
2.0×10^{-3}	5.0×10^{-2}	1	-0.045	-0.082	21	18
2.0×10^{-3}	1.0×10^{-1}	1	-0.073	-0.12	22	18.5
2.0×10^{-3}	2.5×10^{-2}	2	0.002	-0.058	23	24
2.0×10^{-3}	2.5×10^{-2}	3	0.010	-0.068	25	30.5
2.0×10^{-3}	2.5×10^{-2}	4	no wave ^{a)}	-0.078	no wave ^{a)}	36
2.0×10^{-3}	2.5×10^{-2}	6	no wave ^{a)}	-0.088	no wave ^{a)}	39

^{a)}No clear wave was observed in the voltammogram.

an increase of ν . The dependence of the i_p of the anodic wave on ν could not be clarified, because no clear anodic current peak was observed in the voltammogram recorded with ν larger than 4 mV/sec.

For the estimation of the irreversibility of the UO_2^{2+} transfer reaction, the experimentally determined i_p is compared with the peak current predicted for a diffusion controlled reversible reaction, $i_{p,d}$, by eq 3:

$$i_{p,d} = 2.69 \times 10^5 n^{3/2} A C_{\text{U(VI), } w} D^{1/2} \nu^{1/2}. \quad (3)$$

With $A = 0.38 \text{ cm}^2$, $C_{\text{U(VI), } w} = 2 \times 10^{-3} \text{ M}$, and $\nu = 1 \text{ mV/sec}$, $i_{p,d}$ is calculated to be $38 \mu\text{A}$. The i_p experimentally measured is $21 \mu\text{A}$. The UO_2^{2+} transfer facilitated by CMPO is irreversible, and the transfer coefficient, α_a , of the anodic process is calculated to be 0.25 from the above results of $i_{p,d}$ and i_p according to eq 4:

$$i_p = 2.99 \times 10^5 n (\alpha_a n)^{1/2} A C_{\text{U(VI), } w} D^{1/2} \nu^{1/2}. \quad (4)$$

For the cathodic wave, the ΔV_p vs $\log \nu$ plot was found to be linear with a slope of -57.3 mV/dec . The slope corresponds to $30/\alpha_c n \text{ mV}$ where α_c denotes the transfer coefficient of the cathodic process, and the α_c for the electrode process of the UO_2^{2+} transfer from nb to w is thus estimated to be 0.26.

Change of the Voltammetric Behavior of UO_2^{2+} Transfer on Standing. The cyclic voltammogram was recorded after the stationary w/nb interface electrode system was allowed to stand for a given time before the VITIES measurement. The results obtained with standing time t_s in the range of 5 to 120 min are illustrated in Figure 5. The anodic and cathodic waves shifted positively with an increase of t_s . The i_p of both waves decrease slightly with an increase of t_s . The most remarkable feature of this standing time effect is that the situation having changed on standing is restored to the original state by disturbing the w/nb interfacial region. For example, the voltammogram essentially identical to voltammogram 1 in Figure 5 was observed when the w/nb interface was stirred gently for 1 min using Pyrex glass stick after the measurement of voltammogram 3. This result gives an idea that an interfacial reaction such as adsorption or accumulation of relatively slow kinetics takes place during the standing.

A growth of an interfacial layer of the adsorbed species that blocks the ion transfer is a possible origin of the standing time effect that UO_2^{2+} becomes harder to transfer from w to nb as the system stands longer. This "blocking layer" hypothesis, however, is unlikely from the following experimental result of

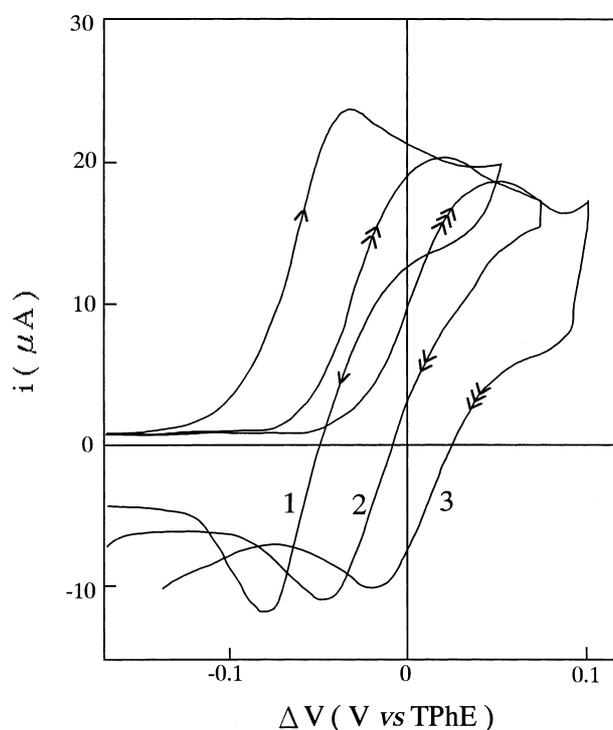


Figure 5. Effect of standing time, t_s , of a stationary w/nb interface electrode system on the cyclic voltammogram for the transfer of UO_2^{2+} in the presence of CMPO.

w ; $0.1 \text{ M } (\text{NH}_4)_2\text{SO}_4 + 2 \times 10^{-3} \text{ M } \text{UO}_2^{2+}$, $\text{pH} = 3.0$, nb ; $5 \times 10^{-2} \text{ M } \text{CV}^+\text{TPhB}^- + 5 \times 10^{-2} \text{ M } \text{CMPO}$, standing time, t_s , before the VITIES measurement; (1) 5 min, (2) 45 min, (3) 120 min, ν ; 1 mV sec^{-1} .

the transfer of tetrapropylammonium ion, TPrA^+ as a reference ion. The standing time effect was not observed for the transfer of TPrA^+ from w to nb recorded with w of $0.1 \text{ M } (\text{NH}_4)_2\text{SO}_4 + 1 \times 10^{-3} \text{ M } \text{TPrA}^+$ ($\text{pH} = 3.0$) and nb of $5 \times 10^{-2} \text{ M } \text{CV}^+\text{TPhB}^- + 5 \times 10^{-2} \text{ M } \text{CMPO}$. Here, the "blocking effect" is expected to be observed irrespective of the kind of transferring ion. In addition, the "blocking layer" hypothesis does not explain the result that the cathodic wave due to the facilitated transfer of UO_2^{2+} from nb to w shifted also to positive side with standing.

Alternative reason for the standing time effect must be investigated. A potential shift of both anodic and cathodic waves of the cyclic voltammogram is observed generally when $C_{\text{CMPO, } nb}$ is varied as shown in Table 2. The standing time effect resulting the positive shift of ΔV_p shown in Figure 5 is attributable to a decrease of the concentration of CMPO at the interfacial region, $C_{\text{CMPO, int}}$. Its decrease can be attributed to a

protonation of CMPO and successive ion-pair formation between the protonated CMPO (HCMPO^+) and TPhB^- at the w/nb interface. The ion pair $\text{HCMPO}^+\text{TPhB}^-$ accumulates at the interfacial region with increasing the standing time. If the interface is disturbed mechanically, the interfacial layer of $\text{HCMPO}^+\text{TPhB}^-$ is decomposed restoring to the original state of a "fresh" w/nb interface.

There is experimental evidence supporting the formation of the interfacial layer of $\text{HCMPO}^+\text{TPhB}^-$ ion pair, which is the result of the measurement of pH of w after contacted with nb for a given time. The w (50 ml) of 0.1 M $(\text{NH}_4)_2\text{SO}_4$, pH = 3.02 ± 0.01 , was allowed to contact stationarily with nb (50 ml) of various compositions for 24 h and then the pH of the w was determined. With nb containing either 5×10^{-2} M CV^+TPhB^- or 5×10^{-2} M CMPO, the pH of w after the contact were 3.04 ± 0.01 or 3.02 ± 0.01 , respectively, indicating that an appreciable amount of H^+ was not consumed in these systems. With nb containing both 5×10^{-2} M CV^+TPhB^- and 5×10^{-2} M CMPO, the pH of w was 3.12 ± 0.01 , which implied that approximately 2×10^{-4} M H^+ in the aqueous phase was consumed by contacting with the nb phase. These results suggest that H^+ reacts only with the simultaneous presence of CMPO and TPhB^- to form the ion pair $\text{HCMPO}^+\text{TPhB}^-$ at the w/nb interface. The accumulation of the ion pair at the interfacial region is assumed to be very slow.

Based on the correlation between ΔV_p and $C_{\text{CMPO}, nb}$ as shown in Table 2, the $C_{\text{CMPO}, \text{int}}$ was calculated from the results of ΔV_p of the voltammograms in Figure 5. The results of $C_{\text{CMPO}, \text{int}}$ calculated are plotted against t_s in Figure 6, plot (1). The positive shift of ΔV_p with standing corresponds to a gradual decrease of $C_{\text{CMPO}, \text{int}}$ with an increase of t_s . The reciprocal of $C_{\text{CMPO}, \text{int}}$ was found to be linear with t_s as shown by plot (2), which suggests that a bimolecular process between HCMPO^+ and TPhB^- to form ion-pair takes place at the w/nb interface.

The facilitated transfer of UO_2^{2+} by CMPO studied in the present work can be utilized as a basic reaction for the electrolytic ion-transfer separation of uranium.¹⁸ The formation of the interfacial layer of $\text{HCMPO}^+\text{TPhB}^-$ ion pair inhibits the

facilitated transfer of UO_2^{2+} from the aqueous phase to the organic phase. The interfacial layer, however, is not mechanically stable and can be removed from the interface simply by stirring the interface.

Conclusion

The transfer of UO_2^{2+} between aqueous and nitrobenzene phases in the presence of CMPO was studied by VITIES and PITIES. It is concluded that the UO_2^{2+} transfer from the aqueous to the organic phases is facilitated by CMPO dissolved in the organic phase. The mechanism of UO_2^{2+} transfer with CMPO is found to be a kinetically controlled process including the adsorption and/or desorption of UO_2^{2+} - CMPO complex. The irreversibility of UO_2^{2+} transfer is determined to be 0.25 to 0.26 of the transfer coefficients for both anodic and cathodic processes, respectively. The origin of a standing time effect on the transfer potential at a stationary w/nb interface is attributed to the gradual decrease in the interfacial concentration of free CMPO caused by the ion-pair formation of protonated CMPO with TPhB^- at the interface. The reaction mechanism elucidated in the present work may provide useful information of relevance to the solvent extraction reaction of actinide ions using CMPO as an extractant.

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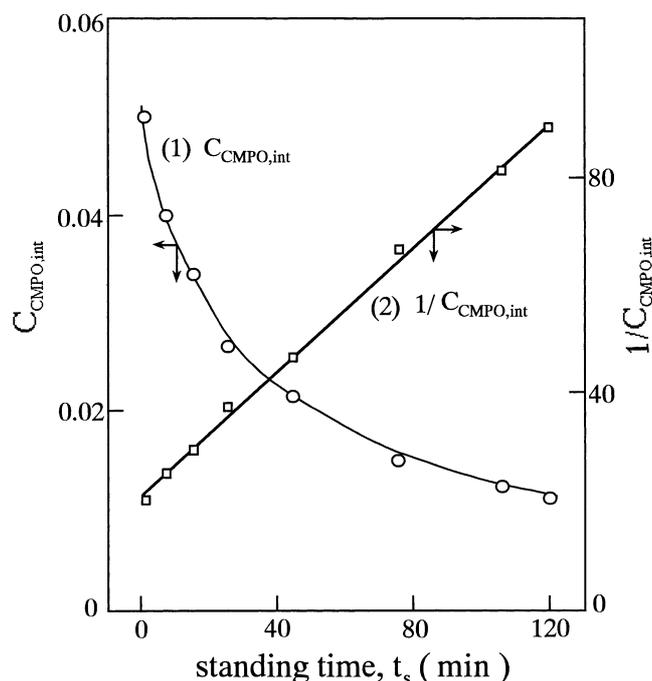


Figure 6. Decrease of the interfacial concentration of CMPO, $C_{\text{CMPO}, \text{int}}$, with standing time, t_s . (1) $C_{\text{CMPO}, \text{int}}$ vs t_s plot, (2) $1/C_{\text{CMPO}, \text{int}}$ vs t_s plot, VITIES measurement; identical condition as shown in figure caption of Figure 5.