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Electrochemical properties of uranium(VI) complexes with multidentate ligands in *N*,*N*-dimethylformamide

Seong-Yun Kim[a,*], Toshihide Asakura[a], Yasuji Morita[a], Yasuhisa Ikeda[b]

[a] *Department of Fuel Cycle Safely Research, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan*

[b] *Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550, Japan*

Abstract

Electrochemical behaviours of UO_2(β-diketonate)$_2$DMF, UO_2(trop)$_2$DMF and UO_2(sap)(DMF)$_2$, (DMF, *N*,*N*-dimethylformamide; β-diketonate, thenoyltrifluoroacetonate(ttfa); benzoyltrifluoroacetonate(btfa) and dibenzoylmethanate(dbm); trop, tropolonate and sap, 2-salicylidenaminophenolate) complexes in DMF solution containing tetrabutylammonium perchlorate as a supporting electrolyte have been investigated by cyclic voltammetry. These uranyl(VI) complexes were found to be quasi-reversibly reduced to U(V) species. The formal redox potentials (E^0, versus ferrocene/ferrocenium) for U(VI)/U(V) couples were determined to be −1.176 V for UO_2(ttfa)$_2$DMF, −1.183 V for UO_2(btfa)$_2$DMF, −1.461 V for UO_2(dbm)$_2$DMF, −1.456 V for UO_2(trop)$_2$DMF and −1.585 V for UO_2(sap)(DMF)$_2$ complex.

Keywords: Uranyl complexes; Electrochemistry; Cyclic voltammetry; Redox reaction; Multidentate ligands

1. Introduction

Uranium(V) species has been known to be unstable in solution, because of its disproportionation [1]. Hence, despite of many studies on U(V) formed by electrochemical and photochemical reductions of U(VI) species [2–14], its properties have not been clarified in details. We have investigated the electrochemical properties of U(VI) complex in carbonate solution [3] and U(VI) complexes in non-aqueous solution [4–9]. From results of such studies, we have proposed that uranyl complexes are reduced reversibly or quasi-reversibly to form relatively stable U(V) species, that the resulting U(V) species are yl-type, $U^VO_2{}^+$, and that uranyl complexes with multidentate ligands can produce more stable U(V) complexes than those with unidentate ligands, $[UO_2L_5]^{2+}$.

To confirm the validity of our proposal, hence, we investigated the electrochemical properties of U(VI) complexes with bidentate and tridentate ligands, i.e., UO_2(β-diketonate)$_2$DMF, UO_2(trop)$_2$DMF and UO_2(sap)(DMF)$_2$, [DMF, *N*,*N*-dimethylformamide; β-diketonate, thenoyltrifluoroacetonate (ttfa); benzoyltrifluoroacetonate (btfa) and dibenzoylmethanate (dbm); trop, tropolonate and sap, 2-salicylidenamino phenolate] complexes.

2. Experimental

2.1. Materials

The UO_2(β-diketonate)$_2$DMF and UO_2(sap)(DMF)$_2$ complexes were synthesized by using the reported methods [15–19]. The UO_2(trop)$_2$DMF complex was prepared by refluxing UO_2(trop)$_2$ in DMF at 80 °C for 3 h. The UO_2(trop)$_2$ complex was synthesized by the reported method [20]. Dry vacuum distilled *N*,*N*-dimethylformamide (Kanto Chemical Co., Ind.) was purified using sodium anthracenide to remove any traces of water and oxygen according to the method [21]. Tetrabutylammonium perchlorate (TBAP, Fluka Chemika, electrochemical grade) was used as supporting electrolytes as received.

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[*] Corresponding author. Tel.: +81 29 282 5421; fax: +81 29 282 6677.
E-mail address: skim@procsafe.tokai.jaeri.go.jp (S.-Y. Kim).

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2.2. *Measurements of cyclic voltammetry (CV)*

Cyclic voltammograms were measured at 25 ± 1 °C under N_2 atmosphere using a BAS CV-660A voltammetric analyzer. A three-electrode system was utilized, i.e., a Pt working electrode (surface area: 0.02 cm^2), a reference electrode (Ag/Ag^+ in TBAP/acetonitrile solution), and a Pt auxiliary electrode. A ferrocene/ferrocenium (Fc/Fc^+) couple was used as the reference redox system [22]. The potential of the reference electrode was determined to be −0.073 V versus Fc/Fc^+. All potentials reported here are versus Fc/Fc^+. All sample solutions were prepared by dissolving U(VI) complexes and TBAP in DMF solvent, and deoxygenated by passing N_2 gas for at least 20 min prior to measurements. All measurements were performed under N_2 gas atmosphere.

3. Results and discussion

3.1. *$UO_2(\beta\text{-diketonate})_2DMF$ complexes system*

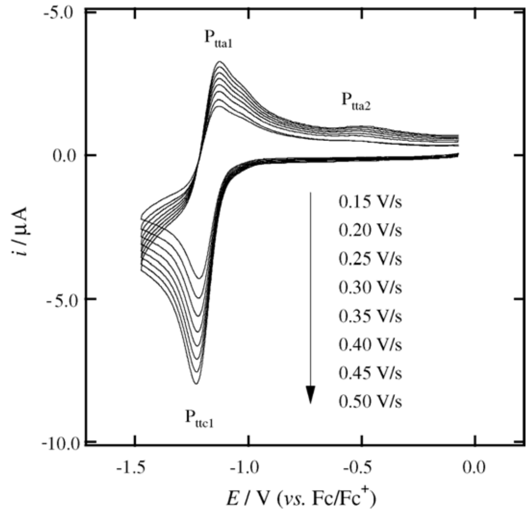

Fig. 1. Cyclic voltammograms of $UO_2(ttfa)_2DMF$ (1.05×10^{-3} M) in DMF containing 0.10 M TBAP measured in the potential range from −0.073 to −1.473 V at different scan rates (v = 0.15–0.50 V/s).

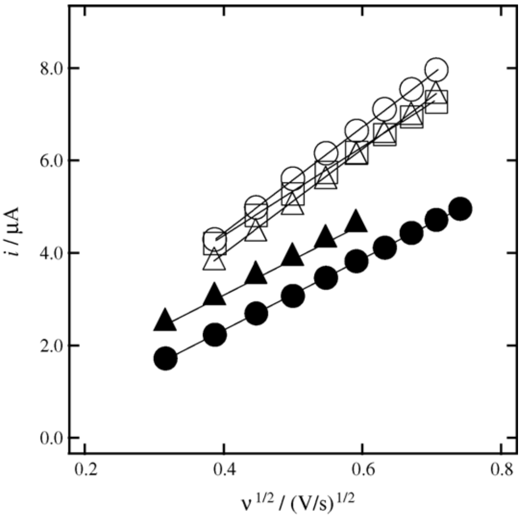

Fig. 2. Plots of cathodic peak currents (i_{pc}) vs. $v^{1/2}$ for the cyclic voltammograms of $UO_2(ttfa)_2DMF$ (○), $UO_2(btfa)_2DMF$ (△), $UO_2(dbm)_2DMF$ (□), $UO_2(trop)_2DMF$ (●) and $UO_2(sap)(DMF)_2$(▲) complexes in DMF.

The measurements of CV for DMF solution containing $UO_2(ttfa)_2DMF$ (1.05×10^{-3} M, M = mol/dm^3) and TBAP (0.10 M) were carried out in the potential range from −0.073 to −1.473 V at different scan rates (v = 0.15–0.50 V/s). The results are shown in Fig. 1. As seen from Fig. 1, peaks (P_{ttc1}, P_{tta1}) of one redox couple and weak anodic peak (P_{tta2}) are observed at around −1.22 V (E_{ttc1}), −1.13 V (E_{tta1}) and −0.51 V (E_{tta2}), respectively. The values of ΔE_{tta} (= $E_{tta1} - E_{ttc1}$) increase with increase in the scan rate, i.e, 0.088 V at v = 0.15 V/s and 0.103 V at v = 0.50 V/s, while the value of ($E_{ttc1} + E_{tta1}$)/2 (= E^0) is almost constant, −1.176 ± 0.002 V, regardless of the scan rate. Furthermore, the plot of cathodic peak currents (i_{ttc1}) versus $v^{1/2}$ gives a good linear relationship as shown in Fig. 2. These phenomena are similar to those for $UO_2(acac)_2DMF$ [7], and suggest that the $UO_2(ttfa)_2DMF$ complex is reduced to $[UO_2(ttfa)_2DMF]^-$ quasi-reversibly with successive reactions through the following mechanism proposed previously [7,9],

$$U^{VI}O_2(ttfa)_2DMF + e^- \underset{E_{tta1}}{\overset{E_{ttc1}}{\rightleftharpoons}} [U^{V}O_2(ttfa)_2DMF]^- \quad \text{(i)}$$

$$[U^{V}O_2(ttfa)_2DMF]^- + x\text{DMF} \xrightarrow[\text{fast}]{} [U^{V}O_2(ttfa)_2DMF_{x+1}]^- \quad \text{(ii)}$$

$$U^{V}O_2(ttfa)(\text{uni-ttfa})DMF_{x+1}]^- + DMF \xrightarrow[\text{fast}]{} U^{V}O_2(ttfa)DMF_{x+2} + ttfa^- \quad \text{(iii)}$$

$$U^{V}O_2(ttfa)DMF_{x+2} + \xrightarrow{E_{tta2}} [U^{VI}O_2(ttfa)DMF_{x+2}]^+ + e^- \quad \text{(iv)}$$

$$[U^{VI}O_2(ttfa)DMF_{x+2}]^+ + ttfa^- \xrightarrow[\text{fast}]{} U^{VI}O_2(ttfa)(\text{uni-ttfa})DMF_{x+1} + DMF \quad \text{(v)}$$

$$U^{VI}O_2(ttfa)(\text{uni-ttfa})DMF_{x+1} \xrightarrow[\text{fast}]{} U^{VI}O_2(ttfa)_2DMF \quad \text{(vi)}$$

where uni-ttfa and x symbolize ttfa coordinated to UO_2^{2+} as unidenatte ligand and any number of coordinated DMF, respectively.

However, recently, we carried out CV studies on UO_2(saloph)L [saloph, *N*,*N*′-disalicylidene-*o*-phenylenediaminate; L, dimethyl sulfoxide (DMSO) or DMF] in the mixed solvents of CH_2Cl_2 and L, and found out that the second anodic peak such as P_{tta2} becomes more distinguishable with a decrease in the concentration of L [8]. This strongly supports that the $U^{VI}O_2$(saloph)L complex is reduced to $[U^{V}O_2(saloph)L]^-$ followed by the formation of $[U^{V}O_2(saloph)]^-$ with the dissociation of coordinated L. Hence, it is likely that the subsequent reaction of $[U^{V}O_2(ttfa)_2DMF]^-$ proceeds through the dissociation of coordinated DMF, i.e., $[U^{V}O_2(ttfa)_2DMF]^- \rightarrow [U^{V}O_2(ttfa)_2]^- + DMF$. However, if the subsequent reaction is the dissociation of coordinated DMF, the second anodic peak such as P_{tta2} should be observed at the same potential regardless of L in each UO_2(β-diketonate)$_2$L complex with the same β-diketonate ligand, because the second anodic peak should correspond to the reaction, $[U^{V}O_2(\beta\text{-diketonate})_2]^- \rightarrow [U^{VI}O_2(\beta\text{-diketonate})_2] + e^-$. However, the second anodic peaks are observed at around −0.83 and −1.21 for $UO_2(acac)_2DMF$ [7] and $UO_2(acac)_2DMSO$ [5], and at around −0.83 and −1.18 V for $UO_2(ba)_2DMF$ and $UO_2(ba)_2DMSO$ (ba, benzoylacetonate) [9], respectively. This supports that the electrochemical reactions (i) is followed by chemical reactions (ii) and (iii), that is, EC mechanism.

Generally, if the reaction, $\mathrm{Oxi} + ne^- = \mathrm{Red}$, is irreversible, the peak currents (i_p) are related to $v^{1/2}$ as follows,

$$i_p = 299n(\alpha n_a)^{1/2} S C_0 D_0^{1/2} v^{1/2} \quad (\text{at } 25\,^\circ\text{C}) \tag{1}$$

where α is the transfer coefficient, n_a the number of electron transfer in the rate-determining step, C_0 (M) the concentration of species Oxi, D_0 (cm^2/s) the diffusion coefficient of species Oxi and S (cm^2) is the surface area of electrode. The αn_a value can be estimated by the following Eq. (2) [23],

$$\left|E_{p/2} - E_p\right| = \frac{0.0477}{\alpha n_a} \quad (\text{at } 25\,^\circ\text{C}) \tag{2}$$

where E_p and $E_{p/2}$ are the potentials at $i = i_p$ and $i_{p/2}$, respectively. In the present system, the $E_{ttc1/2} - E_{ttc1}$ value is 0.069 V at $v = 0.15$ V/s as seen from Fig. 1 and hence the αn_a value is evaluated to be 0.69. By using $\alpha n_a = 0.69$, $n = 1$, $C_0 = 1.05 \times 10^{-3}$ M, $S = 0.02$ cm^2, and the value of slope (1.146×10^{-5}) in Fig. 2, the diffusion coefficient (D_0) of $UO_2(ttfa)_2DMF$ at 25 °C was estimated to be 4.81×10^{-6} cm^2/s.

Furthermore, the standard rate constant (k_s, cm/s) for the reaction (i) was estimated using Eq. (3) [24],

$$\psi = \frac{k_s}{[\pi D_0 v(nF/RT)]^{1/2}} \tag{3}$$

where F and R are the Faraday constant and the gas constant, respectively. According to Nicholson's paper [24], the Ψ value is 0.87 at $\Delta E = 0.088$ V, which corresponds to ΔE_{ttfa} at $v = 0.15$ V/s. Hence, the k_s value for the reaction (i) at 25 °C was evaluated to be 8.1×10^{-3} cm/s using $n = 1$ and $D_0 = 4.81 \times 10^{-6}$ cm^2/s.

Matsuda and Ayabe have proposed the following reversibility factor (Λ) for electrode reactions [25],

$$\Lambda = \frac{k_s}{[D_0^{1-\alpha} D_R^{\alpha} (nF/RT)v]^{1/2}} \tag{4}$$

where the reversible, quasi-reversible, and irreversible systems correspond to $\Lambda > 15$, $15 > \Lambda > 10^{-2(1+\alpha)}$ and $\Lambda < 10^{-2(1+\alpha)}$, respectively. If the diffusion coefficient (D_R) of species Red is equal to D_0 (4.81×10^{-6} cm^2/s at 25 °C) and $\alpha = 0.69$ holds in the reaction (i), the Eq. (4) is expressed as $\Lambda = 7.3 \times 10^1\, k_s/v^{1/2}$. Therefore, the following relationships are derived, that is, for the reversible system: $k_s > 2.0 \times 10^{-1} v^{1/2}$, for the quasi-reversible system: $2.0 \times 10^{-1} v^{1/2} > k_s > 5.7 \times 10^{-6} v^{1/2}$, for the irreversible system: $k_s < 5.7 \times 10^{-6+} v^{1/2}$. On the basis of this classification, the reaction (i) is assigned as the quasi-reversible system, because the evaluated k_s value(= 8.1×10^{-3} cm/s) is in the range of $(7.7\text{–}14) \times 10^{-2} > k_s > (2.2\text{–}4.0) \times 10^{-6}$ at $v = 0.15$–0.50 V/s.

Similarly, the CV measurements for $UO_2(btfa)_2DMF$ (1.21×10^{-3} M) and $UO_2(dbm)_2DMF$ (1.20×10^{-3} M) in DMF were performed at different scan rates. In these cases, the peaks of one redox couple and weak anodic peak are observed at around −1.22 (E_{btc1}), −1.15 (E_{bta1}) and −0.50 V (E_{bta2}) for $UO_2(btfa)_2DMF$ in Fig. 3(c) and −1.51 (E_{dbmc1}), −1.41 (E_{dbma1}) and −0.85 V (E_{dbma2}) for $UO_2(dbm)_2DMF$ in Fig. 3(d). The values of ΔE_{bt} ($= E_{bta1} - E_{btc1}$) and ΔE_{dbm} ($= E_{dbma1} - E_{dbmc1}$) increase with increasing the scan rate, while the values of $(E_{btc1} + E_{bta1})/2$ and $(E_{dbmc1} + E_{dbma1})/2$ are constant, -1.183 ± 0.001 and -1.461 ± 0.001 V, without depending on the scan rate. Furthermore, the plots of cathodic peak currents (i_{btc1} and i_{dbmc1}) versus $v^{1/2}$ give good

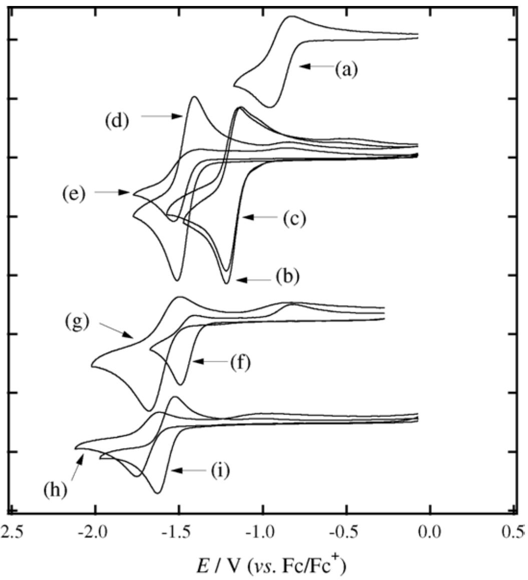

Fig. 3. Cyclic voltammograms of $UO_2(DMF)_5^{2+}$ (a), $UO_2(ttfa)_2DMF$ (b), $UO_2(btfa)_2DMF$ (c), $UO_2(dbm)_2DMF$ (d), $UO_2(acac)_2DMF$ (e), $UO_2(trop)_2DMF$ (f), $UO_2(sap)(DMF)_2$ (g), $UO_2(salen)DMF$ (h) and $UO_2(saloph)DMF$ (i) complexes in DMF.

linear relationships as shown in Fig. 2. These results suggest that the electrochemical reactions of $UO_2(btfa)_2DMF$ and $UO_2(dbm)_2DMF$ at Pt electrode occur quasi-reversibly as follows:

$$\mathrm{U^{VI}O_2(btfa)_2DMF + e^- \underset{E_{btal}}{\overset{E_{btcl}}{\rightleftharpoons}} [U^{V}O_2(btfa)_2DMF]^-} \qquad \text{(i-btfa)}$$

$$\mathrm{U^{VI}O_2(dbm)_2DMF + e^- \underset{E_{dbmal}}{\overset{E_{dbmcl}}{\rightleftharpoons}} [U^{V}O_2(dbm)_2DMF]^-} \qquad \text{(i-dbm)}$$

In order to confirm the quasi-reversibility of reactions (i-btfa) and (i-dbm), their D_0 and k_s values were estimated in a similar manner as mentioned above. The resulting D_0 and k_s values at 25 °C are 3.68×10^{-6} and 1.38×10^{-3} cm/s for $UO_2(btfa)_2DMF$ and 2.67×10^{-6} and 3.68×10^{-3} cm/s for $UO_2(dbm)_2DMF$. These results support that the reactions (i-btfa) and (i-dbm) are quasi-reversible, because the estimated k_s values are compatible with "quasi-reversible system" derived from Eq. (4), i.e., $(2.2–8.7) \times 10^{-2} > k_s > (1.3–4.2) \times 10^{-6}$ for $UO_2(btfa)_2DMF$ and $(2.3–7.6) \times 10^{-2} > k_s > (1.2–3.9) \times 10^{-6}$ for $UO_2(dbm)_2DMF$ at $v = 0.15–0.50$ V/s.

3.2. $UO_2(trop)_2DMF$ complex system

The cyclic voltammograms of $UO_2(trop)_2DMF$ (1.45×10^{-3} M) and TBAP(0.10 M) were measured at different scan rates ($v = 0.10–0.55$ V/s) to compare with the electrochemical properties of $UO_2(\beta\text{-diketonate})_2DMF$ complexes. As seen from Fig. 3(f), one cathodic peak (P_{tropc1}) coupled with anodic peak (P_{tropa1}) and uncoupled anodic peak (P_{tropa2}) are observed at around −1.49 V (E_{tropc1}), −1.41 V (E_{tropa1}) and −0.83 V (E_{tropa2}), respectively. The values of ΔE_{trop} (= $E_{tropa1} - E_{tropc1}$) increase with increasing v, while the values of $(E_{tropc1} + E_{tropa1})/2$ is constant, -1.456 ± 0.001 V, regardless of the scan rate. Furthermore, the plot of cathodic peak current (i_{tropc1}) versus $v^{1/2}$ is linear as shown in Fig. 2. These results indicate that the electrochemical reduction of $UO_2(trop)_2DMF$ is a quasi-reversible reaction accompanied by the succeeding chemical reaction as well as $UO_2(ttfa)_2DMF$, $UO_2(btfa)_2DMF$, $UO_2(dbm)_2DMF$ and $UO_2(trop)_2DMSO$ [9].

The $U^{V}O_2(trop)DMF_{x+2}$ formed by the reactions (ii) and (iii) or $[U^{V}O_2(trop)_2]^-$ can be proposed as candidates of U(V) species. As mentioned above, it has been proposed that the $U^{VI}O_2(saloph)L$ complex is reduced to $[U^{V}O_2(saloph)L]^-$ followed by the formation of $[U^{V}O_2(saloph)]^-$ with the dissociation of coordinated L. Hence, it is likely that $[U^{V}O_2(trop)_2]^-$ species is formed as the product in the reaction, $[U^{V}O_2(trop)_2DMF]^- \rightarrow$ U(V) species. The potential of second anodic peak (P_{tropa2}, −0.83 V) is different from that (−0.51 V) in $UO_2(ttfa)_2DMF$. This suggests that the property of reaction product in ($[U^{V}O_2(trop)_2DMF]^- \rightarrow$ U(V) species) is fairly different from that in $UO_2(ttfa)_2DMF$. Unfortunately, it is difficult to judge from the present results whether the product of subsequent reaction, $[U^{V}O_2(trop)_2DMF]^- \rightarrow$ U(V) species, is $U^{V}O_2(trop)DMF_{x+2}$ or $[U^{V}O_2(trop)_2]^-$. Furthermore, the kinetic parameters (D_0 and k_s) for electrochemical reduction of $UO_2(trop)_2DMF$ were obtained from the slope in Fig. 2 (7.68×10^{-6}) and Ψ value (1.68 at $\Delta E_{trop} = 0.075$ V) by the same method as mentioned above, and are 1.09×10^{-6} and 6.12×10^{-3} cm/s at 25 °C, respectively. From Eq. (4), the following relationship can be derived as "Quasi-reversible system" $(2.5–5.6) \times 10^{-2} > k_s > (1.3–2.7) \times 10^{-6}$ at $v = 0.10–0.55$ V/s. The k_s value for the present system is in the this range and supports that the electrochemical reaction of $UO_2(trop)_2DMF$ is quasi-reversible.

3.3. $UO_2(sap)(DMF)_2$ complex system

The cyclic voltammograms of DMF solution containing $UO_2(sap)(DMF)_2$ (1.12×10^{-3} M) and TBAP (0.10 M) were also measured at different scan rates($v = 0.10–0.35$ V/s). As seen from Fig. 3(g), the coupled peaks and a weak anodic peak are observed at around −1.68 (E_{sapc1}), −1.50 (E_{sapa1}) and −0.84 V (E_{sapa2}). The values of ΔE_{sap} (=$E_{sapa1} - E_{sapc1}$) increase with increasing v, while the values of $(E_{sapc1} + E_{sapa1})/2$ are constant, -1.585 ± 0.001 V, without depending on the scan rate. Furthermore, the plot of cathodic peak current (i_{sapc1}) versus $v^{1/2}$ gives a straight line with a slope of 7.73×10^{-6}. These results indicate that the electrochemical reduction of $UO_2(sap)(DMF)_2$ occurs quasi-reversibly with the subsequent chemical reaction as well as $UO_2(\beta\text{-diketonate})_2DMF$ and $UO_2(trop)_2DMF$ systems. In this system, the most probable product of subsequent reaction is supposed to be $UO_2(sap)DMF$ or $UO_2(bi\text{-}sap)(DMF)x$, in which bi-sap means the bidentate sap. The values of D_0 and k_s for electrochemical reduction of $UO_2(sap)(DMF)_2$ were estimated as 2.50×10^{-6} and 1.04×10^{-3} cm/s at 25 °C, respectively, using the slope in Fig. 2 (7.73×10^{-6}) and the Ψ value (0.15 at $\Delta E_{sap} = 0.178$ V). Furthermore, the relationship for "quasi-reversible system" is derived as $(1.1–3.8) \times 10^{-2} > k_s > (0.4–1.3) \times 10^{-6}$ at $v = 0.10–0.35$ V/s from Eq. (4). The estimated k_s value (= 1.04×10^{-3} cm/s) is in the range of $(1.1–3.8) \times 10^{-2} > k_s > (0.4–1.3) \times 10^{-6}$. This supports that the electrochemical reaction of $UO_2(sap)(DMF)_2$ is quasi-reversible.

4. Conclusion

The results of the present study are summarized in Table 1 and Fig. 3 with previous ones [7,8]. As seen from this table, the E^0 values become negative in order of uranyl(VI) complexes with unidentate(DMF), bidentate(ttfa, btfa, dbm, acac and trop), tridentate(sap) and tetradentate(salen, saloph) ligands. Fig. 4 shows a plot of E^0 values against pK_a values of the bidentate ligands. The E^0 values for U(VI)/(V) are similarly

Table 1
Electrochemical data for uranyl(VI) complexes with ligands in DMF

Redox reactions	E_{pc1}/V	E_{pa1}/V	E_{pa2}/V	E^0/V	D_0 ($cm^2 s^{-1}$)	k_s ($cm s^{-1}$)	References
$[UO_2(DMF)_5]^{2+} + e^- = [UO_2(DMF)_5]^-$	−0.94	−0.80	–	−0.889	2.64	3.00	[7]
$UO_2(ttfa)_2DMF + e^- = [UO_2(ttfa)_2DMF]^-$	−1.22	−1.13	−0.51	−1.176	4.81	8.12	This work
$UO_2(btfa)_2DMF + e^- = [UO_2(btfa)_2DMF]^-$	−1.22	−1.15	−0.50	−1.183	3.68	1.38	This work
$UO_2(dbm)_2DMF + e^- = [UO_2(dbm)_2DMF]^-$	−1.51	−1.41	−0.85	−1.461	2.67	3.68	This work
$UO_2(acac)_2DMF + e^- = [UO_2(acac)_2DMF]^-$	−1.54	−1.40	−0.83	−1.469	3.14	0.65	[7]
$UO_2(trop)_2DMF + e^- = [UO_2(trop)_2DMF]^-$	−1.49	−1.41	−0.83	−1.456	1.09	6.12	This work
$UO_2(sap)(DMF)_2 + e^- = [UO_2(sap)DMF]^-$	−1.68	−1.50	−0.84	−1.585	2.50	1.04	This work
$UO_2(salen)DMF + e^- = [UO_2(salen)DMF]^-$	−1.71	−1.63	−1.12	−1.672	3.08	4.80	[7]
$UO_2(saloph)DMF + e^- = [UO_2(saloph)DMF]^-$	−1.67	−1.57	−1.06	−1.626	3.40	2.50	[8]

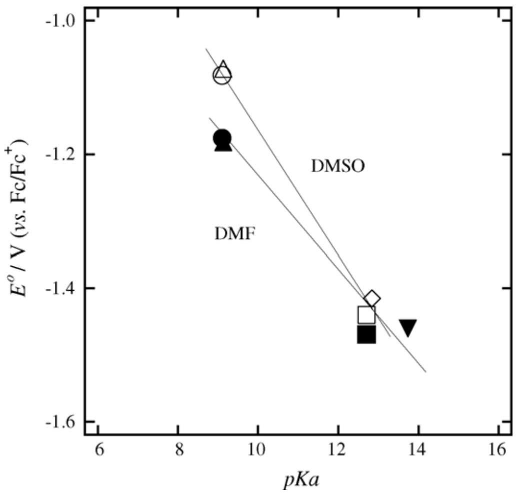

Fig. 4. Plots of the E^0 values vs. pK_a of $UO_2(ttfa)_2DMF$ (●), $UO_2(btfa)_2DMF$ (▲), $UO_2(acac)_2DMF$ (■), $UO_2(dbm)_2DMF$ (▼), $UO_2(ttfa)_2DMSO$ (○), $UO_2(btfa)_2DMSO$ (△), $UO_2(acac)_2DMSO$ (□) and $UO_2(ba)_2DMSO$ (◇) complexes determined by cyclic voltammetry.

shifted negative with increasing the ligand basicity pK_a. This indicates that the uranyl complexes with strong donor ligands are not reduced to U(V) easily. Furthermore, such U(VI) complexes with difficulty in the electrochemical reduction were found to from stable U(V) complexes, i.e., the U(V) species generated in the reduction of UO_2(β-diketonate)$_2$DMF, $UO_2(trop)_2DMF$, $UO_2(sap)$ $(DMF)_2$, $UO_2(salen)DMF$ and $UO_2(saloph)DMF$ are not reduced to U(IV), while that formed in the reduction of $[UO_2(DMF)_5]^{2+}$ is not stable and further reduced to UO_2.

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References

[1] (a) H.G. Heal, Trans. Faraday Soc. 45 (1949) 1;
(b) H.G. Heal, J.G.N. Thomas, Trans. Faraday Soc. 45 (1949) 11;
(c) T.W. Newton, F.B. Baker, Inorg. Chem. 4 (1965) 1166;
(d) A. Ekstrom, Inorg. Chem. 13 (1974) 2237.
[2] (a) G. Folcher, J. Lambard, G.C. de Villardi, Inorg. Chim. Acta 45 (1980) L59;
(b) P. Zanello, A. Cinquantini, G.A. Mazzocchin, J. Electroanal. Chem. 131 (1982) 215;
(c) P.G. Eller, P.J. Vergamini, Inorg. Chem. 22 (1983) 3184;
(d) T. Harazono, H. Fukutomi, Bull. Chem. Soc. Jpn. 59 (1986) 2129;
(e) P.B. Hitchcock, T.J. Mohammed, K.R. Seddon, J.A. Zora, Inorg. Chim. Acta 113 (1986) L25;
(f) K.R. Howes, A. Bakac, J.H. Espenson, Inorg. Chem. 27 (1988) 791;
(g) S.S. Sandhu, R.J. Singh, S.K. Chawla, J. Photochem. Photobiol. A52 (1990) 65;
(h) A. Bakac, J.H. Espenson, Inorg. Chem. 34 (1995) 1730.
[3] K. Mizuguchi, Y.-Y. Park, H. Tomiyasu, Y. Ikeda, J. Nucl. Sci. Technol. 30 (1993) 542.
[4] S.H. Lee, K. Mizuguchi, H. Tomiyasu, Y. Ikeda, J. Nucl. Sci. Technol. 33 (1996) 190.
[5] K. Mizuguchi, S.H. Lee, Y. Ikeda, H. Tomiyasu, J. Alloys Compd. 271–272 (1998) 163.
[6] S.-Y. Kim, K. Mizuoka, K. Mizuguchi, T. Yamamura, Y. Shiokawa, H. Tomiyasu, Y. Ikeda, Proc. Actinide 2001 Int. Conf., J. Nucl. Sci. Technol. (Suppl. 3) (2002) 441.
[7] S.-Y. Kim, H. Tomiyasu, Y. Ikeda, J. Nucl. Sci. Technol. 39 (2002) 160.
[8] K. Mizuoka, S.-Y. Kim, M. Hasegawa, T. Hoshi, G. Uchiyama, Y. Ikeda, Inorg. Chem. 42 (2003) 1031.
[9] S.-Y. Kim, T. Asakura, G. Uchiyama, Y. Morita, Y. Ikeda, Radiochim. Acta 93 (2005) 75.
[10] D. Cohen, J. Inorg. Nucl. Chem. 32 (1970) 3525.
[11] J.T. Bell, H.A. Friedman, M.R. Billings, J. Inorg. Nucl. Chem. 36 (1974) 2563.
[12] G. Gritzner, J. Selbin, J. Inorg. Nucl. Chem. 30 (1968) 1799.
[13] C. Miyake, Y. Yamana, S. Imoto, Inorg. Chim. Acta 95 (1984) 17.
[14] H. Fukutomi, T. Harazono, Bull. Chem. Soc. Jpn. 59 (1986) 3678.
[15] G.M. Kramer, M.B. Dines, R.B. Hall, A. Kaldor, A.J. Jacobon, J.C. Scanlon, Inorg. Chem. 19 (1980) 1340.
[16] G.M. Kramer, E.T. Maas, Inorg. Chem. 20 (1981) 3514.
[17] Y. Ikeda, H. Tomiyasu, H. Fukutomi, Bull. Chem. Soc. Jpn. 56 (1983) 1060.
[18] Y. Ikeda, H. Tomiyasu, H. Fukutomi, Inorg. Chem. 23 (1984) 3197.
[19] O.A. Rajan, A. Chakravorty, Inorg. Chim. Acta 50 (1981) 79.
[20] D.L. Plymale, W.H. Smith, J. Inorg. Nucl. Chem. 30 (1968) 2267.
[21] T. Saji, T. Yamada, S. Aoyagni, J. Electroanal. Chem. 61 (1975) 147.
[22] G. Gritzner, J. Kuta, Pure Appl. Chem. 56 (1984) 461.
[23] R.S. Nicholson, I. Shain, Anal. Chem. 36 (1964) 706.
[24] R.S. Nicholson, Anal. Chem. 37 (1965) 1351.
[25] H. Matsuda, Y. Ayabe, Z. Elektrochem. 59 (1955) 494.