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Electrolytic preparation, redox titration and stability of pentavalent state of uranyl tetraketonate in dimethyl sulfoxide

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Abstract

Uranyl(VI) complex with tetraketone ligand, *m*-bis(2,4-dioxo-l-pentyl)benzene, which possesses two monomer acetylacetone moieties was synthesized. Cyclic voltammetric study on U(VI)/U(V) couple revealed that this electrode reaction is simple reversible reaction on glassy carbon (GC) electrode in dimethyl sulfoxide (DMSO). Electrolytic preparation of DMSO solution of uranyl(V) tetraketonate was carried out starting from the corresponding uranyl(VI) complex by using a flow electrolysis system. New redox titration method using bis(cyclopentadienyl)iron(III) hexafluorophosphate ($FcPF_6$) was developed and used for quantitative analysis of uranyl(V). Titration curve of uranyl(V) tetraketonate was explained by a simple oxidation by $FcPF_6$, in contrast to the result of uranyl(V) acetylacetonate. Half-life of the uranyl(V) tetraketonate was determined by spectrophotometry as 3.7 h, which is much longer than 1.5 h of uranyl(V) acetylacetonate.

Keywords: Uranyl(V) tetraketonate; Uranyl(V) acetylacetonate; Half-life of uranyl(V); Redox titration in aprotic solvents; Uranium redox-flow battery

1. Introduction

Light actinide such as neptunium and uranium are known to show two couples of reversible or quasi-reversible electrode reactions as seen in Np(III)/Np(IV) and Np(V)/Np(VI) [1]. In the case of uranium, electrode reactions of U(III)/U(IV) and U(V)/U(VI) are regarded as reversible or quasi-reversible in the absence of proton [2,3] which promotes the disproportionation reaction degrading U(V) to U(IV) and U(VI) [4,5]. By utilizing these two couples of fast reactions suppressing overvoltage at electrodes, uranium redox-flow battery with high efficiency has been proposed [3,6]. This uranium battery requires the stability of oxidation states of U(III), U(IV), U(V) and U(VI), but very limited information is available for U(V), except for a report stating that uranyl(V) produced from $UO_2(NO_3)_2$ in dimethyl sulfoxide (DMSO) showed a stability with a half-life of about one hour [4]. Though a detection of the uranyl(V) species in solutions is known to be possible by spectroscopic method in visible, near infra-red and infra-red region [7–10], to our knowledge, only two literature reported molar absorption coefficients ε of uranyl(V) species ($87 \pm 1\ M^{-1}\ cm^{-1}$ at 1510 nm, prepared from $UO_2(dmso)_5(ClO_4)_2$ [4]; $3.6\ M^{-1}\ cm^{-1}$ at 1.88×10^3 nm, prepared from $[U^VO_2(CO_3)_3]^{5-}$ [10]; M: mol dm^{-3}).

For active materials of the uranium redox-flow battery, large solubility in aprotic solvent is required and therefore uranium β-diketonates were systematically studied [3]. These complexes showed dissociation and association of the ligands which prevent kinetics and formal potential of their electrode reactions from being suitable for the active material. In order to suppress this dissociation reaction, tetraketone ligands with two acetylacetone moieties have been studied and these ligands showed stable complexation with metal ions at III–VI valences [11].

In this study, a synthesis of new uranyl(VI) complex with a tetraketone ligand, *m*-bis(2,4-dioxo-l-pentyl)benzene, studies on mechanism and kinetics of U(VI)/U(V) reaction of this complex on glassy carbon electrode and on the half-life of the uranyl(V) in solution were reported. In order to estimate molar absorption coefficient of uranyl(V) tetraketonate in DMSO, its concentration was determined by using a redox titration method developed in this study. The stability of pentavalent state in the uranyl(V) tetraketonate was discussed

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in comparison with those in uranyl(V) acetylacetonate and uranyl(V) dimethyl sulfoxide.

2. Experimental

2.1. Materials

The tetraketonate ligand, *m*-bis(2,4-dioxo-l-pentyl)benzene (H_2T), was synthesized as previously reported [11]. Uranyl(VI) tetraketonate was synthesized by adjusting pH of the mixture of uranyl(VI) nitrate salt and tetraketone ligand, oily coarse product obtained was purified by recrystallization from ethanol. Elemental analysis of the purified product using a CHN elemental analyzer (Flash EA1112, Thermo Quest Italia) and ICP-AES spectrophotometer (ICP-7500, Shimazu Corp., Japan) revealed that the complex was identified as $UO_2T\ (C_2H_5OH)(H_2O)_{0.5}$ (hereafter designated as UO_2T). Calcd. for: U, 35.45; C, 39.35; H, 4.95. Found: U, 35.20; C, 39.45; H, 4.70.

Uranyl(VI) bis(acetylacetonate) ($UO_2(acac)_2$), uranyl (VI) dimethyl sulfoxide ($UO_2(dmso)_5(ClO_4)_2$) [3] and bis(cyclopentadienyl)iron(III) hexafluorophosphate ($FcPF_6$) [12] were synthesized and identified by the method mentioned above. Dimethyl sulfoxide (DMSO) was purchased from Wako Pure Chemical Ind., Japan, and used after distillation under reduced pressure. Other chemicals were used as purchased.

2.2. Methods

Cyclic voltammetry measurements were conducted by using an electrochemical measurement system (HZ-3000, Hokuto Denkou Corp., Japan) and an electrochemical cell installed inside the inert gas glove box (O_2, $H_2O < 1$ ppm). A glassy carbon (GC) working electrode (1ϕ), a $Ag/AgNO_3$ reference electrode and a 10 mm × 10 mm platinum plate counter electrode were used. Each measurement was followed by the measurement of the ferrocene/ferrocenium (Fc/Fc^+) couple according to the IUPAC recommendation.

Bulk electrolysis was carried out by using a flow electrolysis system, installed inside the glove box, and composed of a flange-type cell, a piece of anion exchange membrane (Selemion APS, Asahi Glass Engineering Co., Ltd., Japan), two carbon felt electrode (XF208, 25 mm × 25 mm × 2 mm, Toyobo Co., Ltd., Japan), two electrolyte tanks and two liquid pumps. Negative electrolyte was circulated also to a flow-type optical cell (optical path length of 2 mm) installed outside the glove box which enables in situ absorption spectroscopy (UV-3100PC, Shimazu Corp., Japan).

The titration measurements were carried out by using an automatic titration system (COMTITE-900, Hiranuma Sangyo Co., Ltd., Japan) and a beaker-type cell maintained at $25 \pm 1\ ^\circ C$, from which the solution was circulated through the flow-type optical cell. A drop of $FcPF_6$ was made only when the potential fluctuation became smaller than 1 mV within 5 s.

3. Results and discussion

3.1. U(VI)/U(V) electrode reaction

Fig. 1(a) shows a cyclic voltammogram of U(VI)/U(V) reaction of UO_2T on GC electrode, which shows only a redox couple a1/c1 at $E_{1/2} = -1.460$ V versus Fc/Fc^+, which is corresponding to a redox couple a1/c1 of $UO_2(acac)_2$, i.e. $E_{1/2} = -1.440$ V versus Fc/Fc^+ (Fig. 1(b)). The complex $UO_2(acac)_2$ has known to show another couple a2/c2 at $E_{1/2} = -1.212$ V versus Fc/Fc^+ in DMSO, and this is indicative of dissociation and association of β-diketone ligand as observed for $UO_2(ba)_2$ in DMSO [3]. As a result of the dimerization of acetylacetone ligands, the redox potential of UO_2T is identical to that of $UO_2(acac)_2$ and UO_2T seems to undergo a simple reaction without ligand dissociation, described as:

$$U^{VI}O_2T + e^- \underset{a1}{\overset{c1}{\rightleftharpoons}} U^{V}O_2T^- \tag{1}$$

Fig. 2 shows cyclic voltammograms of UO_2T in DMSO solution at sweep velocities of $v = 50$–2000 mV. On the basis of the relationship between the peak current and $v^{1/2}$, diffusion constant D is determined as $5.0 \times 10^7\ cm\,s^{-2}$ [13]. Difference in peak potentials ΔE_p for a1/c1 couple are in the

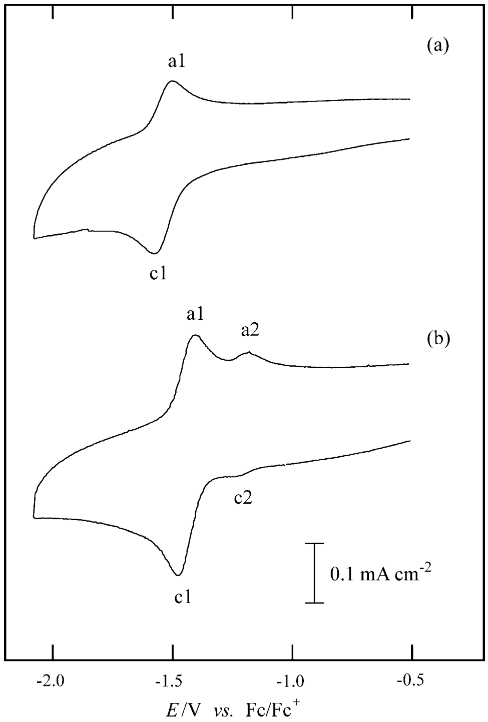

Fig. 1. Cyclic voltammograms of 1 mM UO_2T (a) and $UO_2(acac)_2$ (b) in DMSO solution containing 0.1 M $TBAPF_6$ at GC electrode. Initial sweep direction is cathodic. Sweep velocity is $0.2\ V\,s^{-1}$.

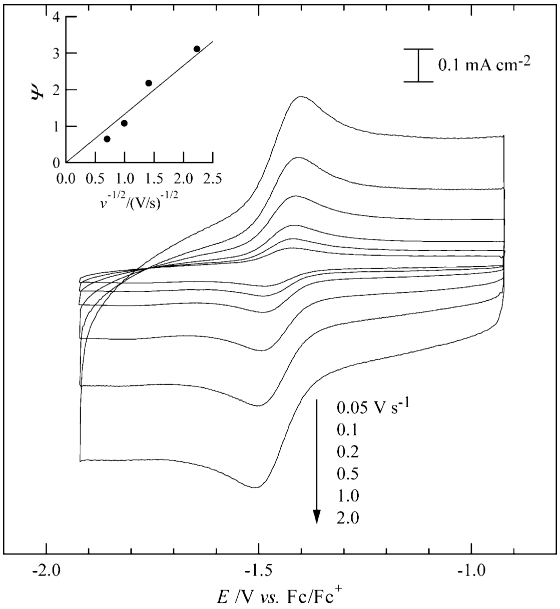

Fig. 2. Cyclic voltammograms of 1 mM UO_2T in DMSO solution containing 0.1 M $TBAPF_6$ at GC electrode. Initial sweep direction is cathodic and sweep velocities are 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 V s^{-1}. Plot of Ψ vs. $v^{1/2}$ is shown in inset (see text).

range between 50 mV and 2000 mV, which shows a character of quasi-reversible [13]. By assuming that the diffusion constants of the oxidized and the reduced species are identical, the standard rate constants k^0 (Table 1) were determined by plots of Ψ versus $v^{-1/2}$ (Fig. 2, inset) on the basis of the relationship:

$$\Psi = \left(\frac{RT}{\pi FD}\right)^{1/2} \frac{k^0}{v^{1/2}} \qquad (2)$$

where Ψ is the dimensionless parameter, F the Faraday constant, R the gas constant and T is the temperature [14]. The standard rate constant of the electrode reaction of UO_2T in DMSO is much larger than that of $UO_2(acac)_2$.

3.2. Bulk electrolysis

Three kinds of U(VI) solutions of UO_2T, $UO_2(acac)_2$ and $UO_2(dmso)_5(ClO_4)_2$ with [U] = 4 mM were electrolytically reduced by using flow cell at flow rate of 35.2 mL/min at controlled potential of −1.67, −1.67 and −1.07 V versus Fc/Fc$^+$, respectively, which are little lower than the estimated formal potentials of −1.460, −1.440 (Table 1) and −0.97 V [3] versus Fc/Fc$^+$, respectively. Fig. 3 summarizes absorption spectra obtained during these electrolysis experiments. In the solution with $UO_2(dmso)_5(ClO_4)_2$, an absorption band at around 430 nm, characteristic of dioxouranium(VI), decreased its intensity and a strong peak grew at 1512 nm, which is attributed to uranyl(V) [10]. In the electrolyzed solution obtained from $UO_2(acac)_2$, strong bands appear at 1462 and 1838 nm and also a broad band at 450–800 nm, attributed to charge transfer band from acetylacetone to uranium(VI), appeared without isosbestic point (Fig. 3(b)). A similar result was obtained for UO_2T, except for a distinct isosbestic point at 473 nm, which strongly suggests that the U(VI)/U(V) reaction of the tetraketone complex contains only a pair of species. Colors of these solutions showed remarkable changes from yellow to purple in the case of UO_2T and $UO_2(acac)_2$, whereas yellow to colorless in the case of $UO_2(dmso)_5(ClO_4)_2$.

3.3. Redox titration

Since the acetylacetone can form stable complex with almost all metal ions, inert complex is required as oxidative titrant because free ligand usually exists in solutions of acetylacetonates. Therefore, by selecting an inert Fe(III) complex of $FcPF_6$, a calibration of this titrant was carried out with a standard reductant of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Fig. 4(a), inset) and a equivalence point is determined as 0.32 ± 0.03 mL for three titrations, which agrees excellently with 0.32 mL calculated by the amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ added.

This result indicates that $FcPF_6$ can be used as an oxidative titrant in DMSO solvent.

For the uranyl(V) dimethyl sulfoxide (Fig. 4(a)), there is a clear and typical S-shaped equivalence point at 0.544 mL and thus concentration of U(V) is estimated to be 1.55 mM. Accordingly, $\varepsilon(1512\ \text{nm}) = 82.8\ M^{-1}\ cm^{-1}$ is evaluated (Fig. 4(b)) which agrees well with 87 $M^{-1}\ cm^{-1}$ appeared in the literature [4]. Since molar ratio of uranyl(V) consumed to $FcPF_6$ added is close to unity (Fig. 4(c)), the titration reaction can be deduced as simple redox reaction as:

$$UO_2{}^{+} + Fc^{+} \rightarrow UO_2{}^{2+} + Fc \qquad (3)$$

Next, uranyl(V) acetylacetonate and uranyl(V) tetraketonate solution prepared by electrolysis were titrated (Fig. 5(a,

Table 1
Half-wave potentials, diffusion constants and standard rate constants of U(VI)/U(V) reactions of UO_2T and $UO_2(acac)_2$ at GC electrode in dimethyl sulfoxide

Complex	$E_{1/2}$ (V) vs. Fc/Fc^{+}[a]	ΔE_p (mV)[a]	D ($\times 10^7$ cm^2 s^{-1})	k^0 ($\times 10^3$ cm s^{-1})
UO_2T	−1.460	68	5.0	10.3
$UO_2(acac)_2$	−1.440[b] −1.212[c]	67[b]	13.7[b]	7.7[b]

[a] Values determined from voltammograms at v = 0.2 V s^{-1}

[b] Peaks of a1/c1.

[c] Peaks of a2/c2.

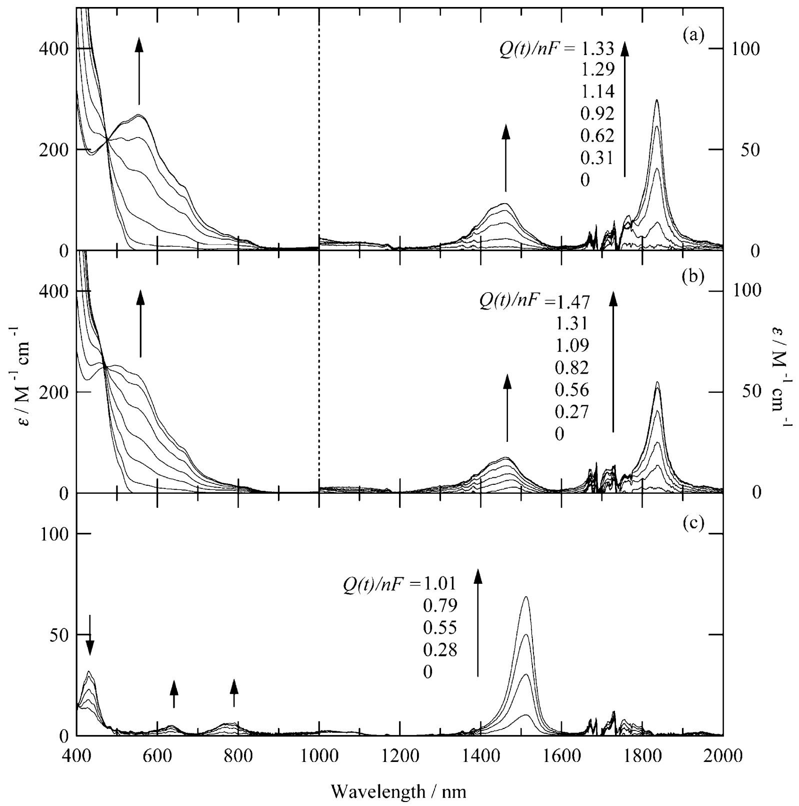

Fig. 3. Absorption spectra obtained during controlled-potential electrolysis of UO_2T (a), $UO_2(acac)_2$ (b) and $UO_2(dmso)_5(ClO_4)_2$ (c). $Q(t)$ is the amount of electricity consumed during electrolysis at time t, n molar quantity of U(VI) complex initially added in solution.

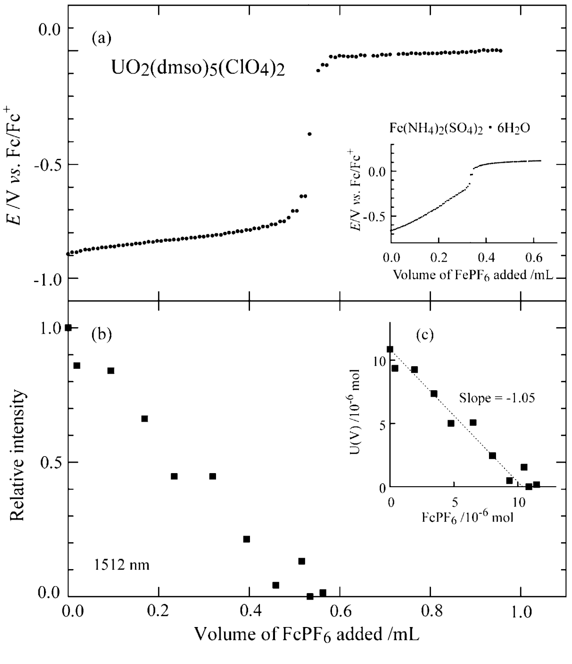

Fig. 4. Titration curve of electrolytically generated uranyl(V) dimethyl sulfoxide solution with 20.6 mM $FcPF_6$ in DMSO solution containing 0.1 M $TBAPF_6$ (a). Relative intensity of absorption band characteristic to uranyl(V) species during titration (b). Molar ratio of amount of uranyl(V) species evaluated from absorption intensity to amount of $FcPF_6$ added (c). Titration curve of 3.23 mM ammonium iron(II) sulfate hexahydrate with 19.0 mM $FcPF_6$ in DMSO solution (a, inset). Dashed lines indicate equivalence points.

b, d and e)) and clear equivalence points were observed at 0.947 and 0.591 mL, respectively (Fig. 5(a and d)). By calculating concentration of the uranyl(V) tetraketonate on the basis of this equivalence point, $\varepsilon(1462\,\text{nm}) = 18.1\,\text{M}^{-1}\,\text{cm}^{-1}$ and $\varepsilon(1838\,\text{nm}) = 56.8\,\text{M}^{-1}\,\text{cm}^{-1}$ were evaluated. From the slope of 0.99 (Fig. 5(f)), the titration reaction of tetraketonate seems to be simple, similarly to uranyl(V) dimethyl sulfoxide. In the case of the uranyl(V) acetylacetonate ($\varepsilon(1462\,\text{nm}) = 15.7\,\text{M}^{-1}\,\text{cm}^{-1}$ and $\varepsilon(1838\,\text{nm}) = 46.5\,\text{M}^{-1}\,\text{cm}^{-1}$), the above ratio of 1.56 (Fig. 5(c)) suggests that this is not a simple reaction, as supported by its relatively complex voltammograms (Fig. 1(b)) and by the lack of the isosbestic point (Fig. 3(b)).

3.4. Half-lives of uranium (V) species

Stability of pentavalent state of uranyl complexes was studied by obtaining absorption spectra with the solutions, obtained by bulk electrolysis, circulated through the flow-type optical cell. Fig. 6 shows time courses of the relative intensity of the bands at 1462, 1512 and 1838 nm, characteristic to uranyl(V) species, to their initial intensity. The half-life of pentavalent state of $UO_2(dmso)_5(ClO_4)_2$ is evaluated as 3.8 h, which is much longer than the literature value of 1 h [4], and therefore our condition seems to be more appropriate than that in the literature. The half-life of uranyl(V) tetraketonate is 3.7 and comparable to the dimethyl sulfoxide complex.

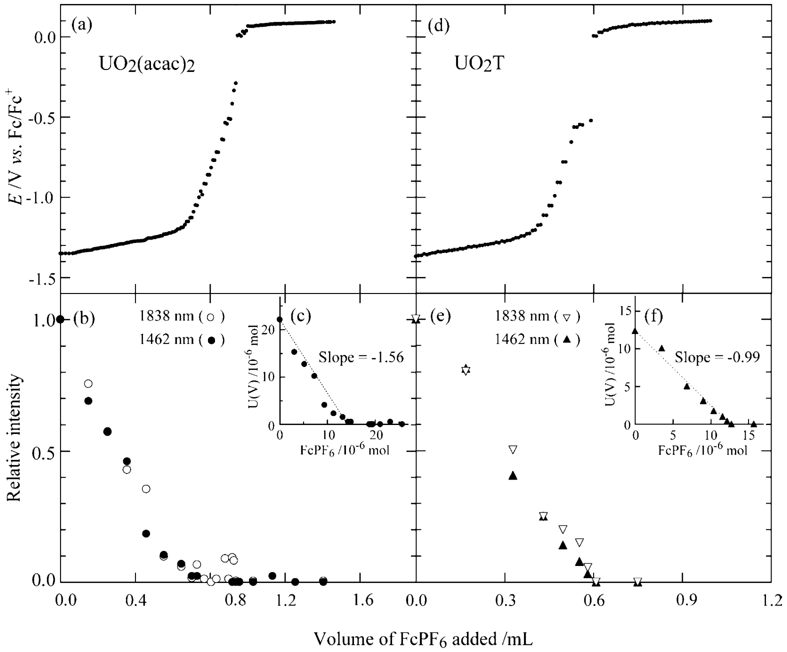

Fig. 5. Titration curve of electrolytically generated uranyl(V) acetylacetonate solution with 20.4 mM $FcPF_6$ (a) and uranyl(V) tetraketonate solution with 20.9 mM $FcPF_6$ (d) in DMSO solution containing 0.1 M $TBAPF_6$; (b and e) correspond to Fig. 4(b) and (c and f) correspond to Fig. 4(c). Dashed lines indicate equivalence points.

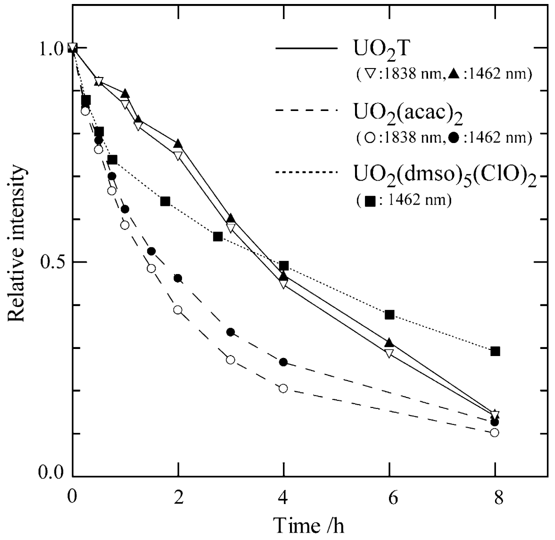

Fig. 6. Time dependence of relative intensity of absorption bands characteristic to uranyl(V) species in solution.

That of $UO_2(acac)_2$ complex is much shorter as 1.5 h. Considering the existence of water molecule in the identified UO_2T, the half-life may be shortened by this impurity.

4. Conclusion

A new tetraketone complexes of uranyl(VI) was synthesized and its electrode reaction of the UO_2T was found to be simple and include only a pair of species, contrary to the $UO_2(acac)_2$. The standard rate constant of the electrode reaction of UO_2T in DMSO is much larger than that of $UO_2(acac)_2$. The stability of pentavalent state in the tetraketone complex (half-life of 3.7 h) can be emphasized by comparison with the half-lives of 1.5 h for acetylacetone complex.

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