TEMPERATURE AND IONIC STRENGTH INFLUENCE
ON U(VI/V) AND U(IV/III)
REDOX POTENTIALS IN AQUEOUS ACIDIC
AND CARBONATE SOLUTIONS

H. CAPDEVILA, P. VITORGE

Laboratoire de Chimie CEA IRDI/DERDCA/DRDD/SESD/SCPCS
92265 Fontenay aux Roses, Cedex (France)

Redox potentials: $E(UO_2^{2+}/UO_2^+) = 60 \pm 4$ mV/NHE, $E(U^{4+}/U^{3+}) = -630 \pm 4$ mV/NHE measured at 25 °C in acidic medium ($HClO_4$ 1M) using cyclic voltametry are in accordance with the published data. From 5 °C to 55 °C the variations of the potentials of these systems (measured against Ag/AgCl electrode) are linear. The entropies are then constant: $[\Delta S(UO_2^{2+}/UO_2^+) - \Delta S(Ag/AgCl)]/F = 0 \pm 0.3$ mV/°C, $[\Delta S(U^{4+}/U^{3+}) - \Delta S(Ag/AgCl)]/F = 1.5 \pm 0.3$ mV/°C. From 5 °C to 55 °C, in carbonate medium ($Na_2CO_3 = 0.2M$), the Specific Ionic Interaction Theory can model the experimental results up to $I = 2M$ (Na^+, ClO_4^-, CO_3^{2-}): $E(UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}) = -778 \pm 5$ mv/NHE ($I = 0$, $T = 25$ °C, $\Delta\epsilon(25$ °C$) = \epsilon(UO_2(CO_3)_3^{4-}, Na^+) - \epsilon(UO_2(CO_3)_3^{5-}, Na^+) = 0.92$ kg/mole, $\Delta S(UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}) = -1.8 \pm 0.5$ mV/°C ($I = 0$), $\Delta\epsilon = \epsilon(Cl^-, Na^+) = (1.14 - 0.007T)$ kg/mole. The U(VI/V) potential shift, between carbonate and acidic media, is used to calculate (at $I = 0$, 25 °C):

$$\log \frac{\beta_3 U(V)}{\beta_3 U(VI)} = -14.7 \pm 0.5$$

and then

$$\log \beta_3 U(V) = 6.6 \pm 0.3.$$

Introduction

In order to assess the safety of the storage of nuclear waste, it is important to know the behaviour of radioelements in the environment, and especially their redox potentials. Experimental conditions are very often different from natural ones: the ionic strength of aqueous solutions used for the electrochemical measurements is much higher than in deep groundwaters, where the temperature is also higher than 25 °C.

In acidic medium, the Specific Interaction Theory (S. I. T.) can model the activity coefficients[1-2] of cations with reasonable precision (except, perhaps, for the highly

charged tetravalent cations).[2] In carbonate medium, there is very little experimental evidence[3] that the S. I. T. can be used to determine the standard potential (at 0 ionic strength) of anions.

The objective of the present work is to measure the redox potential of the couple $UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}$ to test S. I. T. theory with the highly charged anionic limiting complexes of hexavalent and pentavalent uranium, that exist in concentrated carbonate solutions.[4,5] The poor precision of published results on the entropy of actinide ions induces uncertainties on the redox potentials at high temperature;[2] so we decided to study the variation of the redox potentials of the couples UO_2^{2+}/UO_2^{+}, U^{4+}/U^{3+} and $UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}$ versus temperature.

Notations

log	— decimal logarithm,
ln	— natural logarithm,
z_i	— charge of ion i,
Δz^2	$= z^2{}_{Ox} - z^2{}_{Red}$,
[i]	— molarity of ion i (mol/l = M),
m_i	— molality of ion i = concentration (mol/kg),
m_R	— in carbonate medium, $m_R = m_{Na+}$ of the reference compartment, in acidic medium, $m_R = m_{ClO_4^-}$,
m_s	— in carbonate medium, $m_R = m_{Na+}$ of the working solution, in acidic medium, $m_R = m_S = m_{ClO_4^-}$,
T	— temperature solution,
I_S	— ionic strength of the working solution (mol/kg),
I_R	— ionic strength of the reference solution (mol/kg),
D(T, I)	— Debye-Hückel term[6] $D = a \dfrac{\sqrt{I}}{1+ba_j^0\sqrt{I}}$
A	$= \dfrac{RT\ln(10)}{F} = 59.16$ mV (at 25 °C),
$\epsilon(i, j)$	— specific interaction coefficient between ions i and j of opposite charge (i = Ox or Red), in acidic medium j = ClO_4^-, in carbonate medium j = Na^+,
$\Delta\epsilon(T)$	$= \epsilon(Ox, j) - \epsilon(Red, j)$,
$\epsilon_{Cl-}(T)$	$= \epsilon(Na^+, Cl^-) = 0.03$ at 25 °C[6],
$\Delta\epsilon'(T)$	$= \Delta\epsilon(T) + \epsilon_{Cl^-}(T)$,

$E_{1/2}$ (T, I)   — half-wave potential measured by cyclic voltametry against Ag/AgCl reference,

index $_{O/R}$ — for a potential measured against NHE,

$E_{O/R}$ (T, I_S)   — potential of Ox/Red when [Ox] = [Red] formal potential,

$E_{O/R}$ (25, 0)   — standard potential of Ox/Red,

E_{Ref} (T, I_R)   — Ag/AgCl potential at I_R, T and [Cl$^-$] = 0.02M,

$E_{Ag/AgCl}$ (T, 0)   — Ag/AgCl potential at I=0, T and m_{Cl^-} = 1,

$$\Delta S_a^b (T, I) = F \left(\frac{\partial E_a^b (T, I)}{\partial T} \right)_{p,ni},$$

$$\beta_3 [M(VI) \text{ or } M(V)] = \frac{[MO_2(CO_3)_3^{i-6}]}{[MO_2^{i+}][CO_3^{2-}]^3}$$ where MO_2^{i+} is an actinide of redox number

VI or V.

Experimental

Apparatus

To measure redox potentials of uranium systems we have chosen the cyclic volta-metry technique. The reasons of this choice and the circuit description have been already published.[1,2] We used a classical 3-electrode circuit. The platinum counter electrode was put directly in the working solution. In acidic medium, to stabilize the Ag/AgCl reference electrode that was directly put in the cell solution, 0.02M Cl$^-$ was added in the supporting electrolyte NaClO$_4$. In carbonate medium, the Ag/AgCl reference electrode was put in a microcapillary low leakage junction, filled with (NaClO$_4$ I_RM; NaCl 0.02M) solution. This separated compartment was used in order to avoid the precipitation of AgCO$_3$. The working electrode was a hanging Hg drop electrode.

Reagents

The uranium stock solution was prepared from uranyl nitrate [UO$_2$(NO$_3$)$_2$, 6H$_2$O]. It was dissolved in HNO$_3$ 1N Prolabo acid. Then, adding Na$_2$CO$_3$ Prolabo to the solution, we precipitated the yellow solid UO$_2$CO$_3$. This precipitate was redissolved in 1M HClO$_4$, prepared from HClO$_4$ Prolabo 70%. The stock solution was analyzed spectrophotometrically: the U(VI) concentration was 0.21 mol/l. The working solutions were millimolar uranium ones. In carbonate (or acidic) medium the stock solu-

tion was diluted in solutions of different ionic strengths ($0.2M$ Na_2CO_3, xM $NaClO_4$) (or $HClO_4$ $1M$) where $x = 2.6$, 1.4, 0.6, or $0M$.

Measurements

The temperature was regulated by a Haake F3 thermostat and controlled with a thermometer immersed in the working solution. Before recording the voltamperogram, the oxygen was eliminated from the solution by bubbling argon for 10 minutes. For each system and each temperature (from 5 °C to 55 °C) a voltamperogram was recorded. Between two different measurements we waited at least 15 minutes to stabilize the cell solution temperature.

In acidic medium: Both systems UO_2^{2+}/UO_2^+ and U^{4+}/U^{3+} were studied. For UO_2^{2+}/UO_2^+ the voltamperogram is recorded from $E = -100$ mV to -450 mV against the reference Ag/AgCl electrode, whose potential in this medium ($HClO_4$ $1M$, NaCl $0.02M$) is 327.8 mV at 25 °C (it was calculated using the S. I. T.) To study the system U^{4+}/U^{3+} we started with a UO_2^{2+} solution. To obtain U^{3+} species in the diffusion layer of the hanging Hg drop electrode, the solution was reduced at -1100 mV for 1 minute; then the U^{4+}/U^{3+} voltamperogram was recorded from -1100 mV to -750 mV.

In carbonate medium: The $UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}$ voltamperogram was recorded from -300 mV to -1500 mV. We studied the ionic strength and temperature influences on the redox potential.

Method and treatment of data

Ionic strength influence

The half-wave potential, $E_{1/2}$ (T, I), measured using cyclic voltametry, is a good approximation of $E_{O/R}$ (T, I), the working half-cell potential when [Ox] = [Red]:[2]

$$E_{1/2}(T, I) = E_{O/R}(T, I_S) - E_{Ref}(T, I_R) \tag{1}$$

The potentials of uranium systems are measured at varying ionic strengths. To model the results and extrapolate to I = 0 we used the Specific Interaction Theory (S. I. T.)[1,2] and NERNST law for both half cells:

$$E_{O/R}(T, I_S) = E_{O/R}(T, O) + A(T)[-\Delta z^2 D(T, I_s) + \Delta\epsilon(T)m_s] \tag{2}$$

$$E_{Ref}(T, I_R) = E_{Ag/AgCl}(T, O) - A(T)[-D(T, I_R) + \epsilon_{Cl^-}(T)m_R + \log(m_{Cl^-})] \tag{3}$$

Inserting Eqs (2) and (3) into Eq. (1), one obtains:

$$E_{1/2}(T, I) = E_{1/2}(T, O) + A(T)[-\Delta z^2 D(T, I_S) - D(T, I_R) + \Delta\epsilon'(T)m_S + \epsilon(T)(m_R - m_S)] \quad (4)$$

where

$$E_{1/2}(T, O) = E_{O/R}(T, O) - E_{Ag/AgCl}(T, O) + A \log(m_{Cl^-}) \quad (5)$$

In our experimental conditions $\Delta m = (m_R - m_S) \ll m_S$.

In carbonate medium

$$I_R = [m_R ClO_4^- + m_R Na^+]/2$$

$$I_S = [m_S ClO_4^- + m_S Na^+ + 4m_S CO_3^{2-}]/2$$

In S. I. T. approximation, Eq. (4) is used for linear regression (at $T = 25\ ^\circ C$): the plot of

$$\left(\frac{E_{1/2}(25\ ^\circ C, I)}{A(25\ ^\circ C)} + \Delta z^2 D(25\ ^\circ C, I_s) + D(25\ ^\circ C, I_R) - \epsilon(25\ ^\circ C\ \Delta m) \right)$$

versus m_S is a straight line, whose slope is $\Delta\epsilon'$ (25 °C) and the intercept $m_S = 0$ is $\dfrac{E_{1/2}(25\ ^\circ C, O)}{A(25\ ^\circ C)}$.

In Eq. (5), $E_{1/2}$ (25 °C, O) is calculated from experimental results, m_{Cl^-} is an experimental value, and $E_{Ag/AgCl}$ (25 °C, O) is published,[7] so we can deduce $E_{O/R}$ (25 °C, O) (it is the standard potential).

Temperature influence

To compare our results with published entropy values, we used the GIBBS-HELMOTZ relation

$$\left(\frac{\partial G}{\partial T} \right)_{p, ni} = -S \quad (6)$$

and

$$\Delta G = -nFE \tag{7}$$

Substitution of (6) into (7) leads to

$$F\left(\frac{\partial E}{\partial T}\right)_{p,ni} = \Delta S \tag{8}$$

where E, ΔS and ΔG refer to the same equilibrium:

$$Ox + ne^- \rightleftharpoons Red \tag{9}$$

All the potentials were measured against a Ag/AgCl reference electrode. Since both $E_{O/R}$ and $E_{Ag/AgCl}$ depend on temperature, reporting Eq. (8) into Eq. (1), one obtained the following relation:

$$\Delta S_{1/2}(T, I) = \Delta S_{O/R}(T, I_s) - \Delta S_{Ref}(T, I_R). \tag{10}$$

In carbonate medium: to extrapolate to I = 0 using the S. I. T., we had to make an approximation. $\epsilon(Na^+, Cl^-)$ is only known at 25 °C. So, at T $\neq$ 25 °C we supposed that:

$$\epsilon_{Cl^-}(T) = \epsilon_{Cl^-}(25\ °C) + \frac{\partial \epsilon}{\partial T}(25\ °C)\ (T - 25) \tag{11}$$

Reporting Eq. (11) into Eq. (4), we then neglected the second order term $\frac{\partial \epsilon}{\partial T}(25\ °C)(T-25$

· Δm. Using the above linear regression, we determined for each temperature $E_{1/2}(T, O)$ and $\Delta \epsilon'$ (T). $E_{Ag/AgCl}(T, O)$ is published for any temperature from 5 to 55 °C, so we deduced $E_{O/R}(T, O)$ values. Since

$$\frac{\Delta S_{O/R}(T, O)}{F} = \frac{\partial E_{O/R}(T.O)}{\partial T},$$

the variation of $E_{O/R}(T, O)$ versus T allowed to determine $\Delta S_{O/R}(T, O)$.

Results

In acidic medium

The UO_2^{2+}/UO_2^+ and U^{4+}/U^{3+} couples have been studied at varying potential scanning speeds. From 5 to 800 mV/s, neither the voltamperogram shape nor the value of the half-wave potential changed. So, we considered that both systems are reversible on hanging Hg drop electrode, and that half-wave potential are good approximation of formal potential.[1,2]

We used a scanning speed of 60 mV/s (or 200 mV/s) for UO_2^{2+}/UO_2^+ (or U^{4+}/U^{3+}) system. The formal potential that we measured in $HClO_4$ 1M using cyclic voltametry is in agreement with the one obtained by polarography.[1,2] The temperature has no influence on UO_2^{2+}/UO_2^+ system. For U^{4+}/U^{3+}, the plot of E(T, 1) versus T is a straight line whose slope is ΔS (T, 1)/F (*cf. Method section*). All the results in acidic medium are compiled in Table 1.

In carbonate medium

For the system $UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-}$, the scanning speed changes the voltamperogram shape, but the half-wave potential remains constant. The system is not reversible on this working electrode but it is possible to measure formal potential of this couple by this technique. For all measurements we used a scanning speed of 300 mV/s. For each temperature, the S. I. T. (*cf. Method section*) was used to extrapolate to I = 0. So, we determined the potentials $E_{1/2}(T, 0)$, $\Delta \epsilon'$ (T) and then $E_{O/R}(T, 0)$. In these conditions, the S. I. T. fit correctly the data up to only I = 2M, and this is the same for all temperatures. For each ionic strength we plotted $E_{1/2}(T, I)$ versus T. We obtained straight lines, as in acidic medium, whose slopes are $\Delta S_{1/2}$ (T, I)/F. It is also possible to determine $\Delta S_{O/R}(T, 0)$, plotting $E_{O/R}(T, 0)$ versus T. For each temperature we obtained with the S. I. T. a value of $\Delta \epsilon'(T)$. The variation of these experimental values with temperature is linear from 5 up to 55 °C. All these results in carbonate medium are in Table 2.

Studying the influence of both ionic strength and temperature allows us to correlate all measurements made in different experimental conditions and to predict by extrapolation the redox potentials in groundwaters.

Table 1

Results in acidic medium ($HClO_4$ 1M; I = 1.05 mol/kg)

Table 1a: Potentials measured against Ag/AgCl E_{Ref} (25 °C, 1.05) = 327.8 mV (calculated using the S.I.T)

T, °C	E (UO_2^{2+}/UO_2^+), mV	E (U^{4+}/U^{3+}), mV
5	−268	−990
15	−269	−974
25	−268	−960
35	−268	−944
45	−267	−928
55	−266	−912

Table 1b:

	UO_2^{2+}/UO_2^+	U^{4+}/U^{3+}
$E_{o/R}$ (25 °C, 1.05) (mV)	60 ± 4	−630 ± 4
$\Delta S_{1/2}$ (T, 1.05)/F(mV/°C)	0.0 ± 0.3	1.5 ± 0.3

$E_{o/R}$ (25 °C, 1.05) are calculated from table 1a values and E_{Ref} (25 °C, 1.05).

$$\Delta S_{1/2} \ (T, 1.05)/F = \frac{\Delta E(T, 1.05)}{\Delta T} \quad \text{where E(T, 1.05) and}$$

T are Table 1a values.

Discussion

The shift of redox potentials observed between carbonate and acidic media are due to

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \tag{13}$$

and

$$UO_2^+ + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{5-} \tag{14}$$
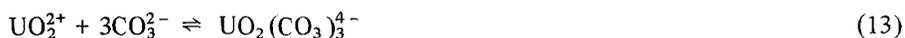
whose equilibrium costants are $\beta_3 U(VI)$ and $\beta_3 U(V)$. We calculated the expression $\log \dfrac{\beta_3 U(VI)}{\beta_3 U(V)}$ using the equation:

Table 2
Results in carbonate medium [0.2M Na_2CO_3, X M $NaClO_4$]

Table 2a: Potentials measured against Ag/AgCl $E_{1/2}$ (T, I) (mV)

I, mol/kg	5 °C	15 °C	25 °C	35 °C	45 °C	55 °C
3.66	−799	−820	−840	−861	−882	−902
2.15	−854	−868	−882	−895	−909	−921
1.24	−919	−932	−944	−956	−966	−980
0.6	−971	−981	−992	−1003	−1015	−1027

Table 2b: Results of the extrapolation to I = 0

T, °C	A, mV	$E_{1/2}$ (T, 0), mV	$(\Delta\epsilon + \epsilon)$ (T), kg/mol	$E_{Ag/AgCl}$ (T, 0), mV	E_{Ref} (T, 0) mV	$E_{o/R}$ (T, 0), mV
05	55.19	−1073	1.12	232.1	325.9	−747.1
15	57.17	−1090	1.05	228.9	326.0	−764.0
25	59.16	−1102	0.95	222.6	323.1	−778.9
35	61.15	−1119	0.90	215.2	319.1	−799.9
45	63.13	−1131	0.82	207.6	314.9	−816.1
55	65.12	−1149	0.79	198.4	309.0	−840.0

$$A = \frac{RT\ln 10}{F} .$$

$E_{1/2}$ (T, 0) and $(\Delta\epsilon + \epsilon)$ (T) are obtained from linear regression (using the S.I.T.) on Table 2a data.

$E_{Ag/AgCl}$ (T, 0) are published.[7]

E_{Ref} (T, 0) = $E_{Ag/AgCl}$ (T, 0) − A log (0.02).

$E_{o/R}$ (T, 0) = $E_{1/2}$ (T, 0) + E_{Ref} (T, 0).

Table 2c: Results of temperature study

I, mol/kg	3.66	2.15	1.24	0.6	0
$\Delta S/F$, mV	−2 ± 0.3	−1.3 ± 0.3	−1.2 ± 0.3	−1.1 ± 0.3	−1.8 ± 0.5

For I ≠ 0, $\Delta S/F$ means $\Delta S_{1/2}$ (T, I) [Eq (11)].

For I = 0, $\Delta S/F$ means $\Delta S_{o/R}$ (T, 0) [Eq (12)].

T, °C	5	15	25	35	45	55
$\Delta\epsilon'$, kg/mol	1.12	1.05	0.95	0.9	0.82	0.79

$\Delta\epsilon'$ (T) = 1.14 + 0.007 T.

ϵ_{Cl^-} (25 °C) = 0.03 [6], so $\Delta\epsilon$ (25 °C) = 0.92 kg/mol.

411

Table 3

Table 3a: Selected literature data in carbonate medium (redox potentials and complexation constants)

	U	Np	Pu	Am
$\beta_3 M(V)$		8.53 (1M) (a)		
$\beta_3 M(VI)$	22.6 (3M) (b)		18.2 (3M) (c)	
	21.3 (0M) (b)			
E(VI/V)	−523.6 (3M) (d)	450 (1M) (e)	350 (1M) (a)	964 (2M) (f)
	779 (0M) (g)			

(a): [8−9]; (b): [4]; (c): [3]; (d): [10]; (e): [8, 11, 12] (f): [3]; (g): this work.
(xM): ionic strength (mol/l).
From these data (Table 3a) and the following interaction coefficients:
$\epsilon(MO_2(CO_3)_3^{4-}, Na^+) = 0.09$ kg/mol [6];
$\epsilon(MO_2(CO_3)_3^{5-}, Na^+) = -0.62$ kg/mol for Np [8] and −0.83 kg/mol for U [this work];
$\epsilon(CO_3^{2-}, Na^+) = -0.05$ kg/mol [6];
$\epsilon(MO_2^{2+}, Na^+) = 0.46$ kg/mol [6]
we calculated the thermodynamic constants at I = 0M (Table 3b).

Table 3b:

	U	Np	Pu	Am
$\Delta E/59.16$	14.7	14.6	12.8	(11.6)
$\log \beta_3 M(V)$	6.6	5.4	4.6	(3.6)
$\log \beta_3 M(VI)$	21.3	19.0	17.4	(15.2)

$\Delta E = E(MO_2^{2+}/MO_2^+) - E(MO_2(CO_3)_3^{4-}/MO_2(CO_3)_3^{5-})$ (mV),
$E(MO_2^{2+}/MO_2^+)$ [8],
A = 59.16 mV (25 °C).

$$\log\frac{\beta_3 U(VI)}{\beta_3 U(V)} = [E_{(UO_2^{2+}/UO_2^+)}(T, I) - E_{(UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-})}(T, I)]/A \quad (15)$$

We deduced the constant $\beta_3 U(V)$ from published $\beta_3 U(VI)$:[4] from the potentials measured, we obtained $\beta_3 U(V)$ values at different I, and from the standard potentials

$$\log \beta_3 U(V) = 6.6 \pm 0.3 \quad \text{(at I = 0)}. \quad (16)$$

We have then compared the published results in carbonate medium for the actinides U, Np, Pu, Am (Table 3). To correlate the values and to determine the constants at

I = 0 we had to extrapolate using the S. I. T. (Table 3b). $\beta_3 U(V)$ values at I = 1M[8],[9] and $E(UO_2(CO_3)_3^{4-}/UO_2(CO_3)_3^{5-})$ at I = 3M [10 and this work] determined using two different experimental methods are in agreement. For all the actinides the carbonate complex of the oxidant is more stable than that of the reductant. Both $\beta_3 U(VI)$ and $\beta_3 U(V)$ constants decrease when atomic number increases. These values are only known up to Pu; we extrapolated $\beta_3 U(VI)$ and $\beta_3 U(V)$ variations versus Z, to Am (Table 3b). Using Eqs (15) and [3], we calculated the AmO_2^{2+}/AmO_2^{+} redox potential (at I = 0), which is experimentally difficult to measure

$$E(AmO_2^{2+}/AmO_2^{+}) \ (25 \ ^{\circ}C, 0) = 1443 \ mV \tag{17}$$

This work allows us to support the S. I. T. and measure $\Delta\epsilon'$ (T) between 5 and 55 °C. We have to point out that the S. I. T. fit correctly our uranium data in carbonate medium only up to I = 2M. This results has already been noticed in neptunium study;[8] this might be due to the formation of an ion pair such as $(UO_2(CO_3)_3^{5-}, Na^+)$.

Temperature influence on interaction coefficients is small and linear (Table 2c).

In acidic medium for VI/V or IV/III system, our ΔS values are in agreement with published ones (Table 4). The VI/V systems (for U, Np or Pu) are less sensitive to temperature than IV/III systems. In carbonate medium (extrapolated values at I = 0):

$$\frac{\Delta S_{O/R}}{F} = -1.8 \pm 0.5 \ mV/^{\circ}C. \tag{18}$$

Table 4
Entropy values. Comparison between our data and published ones
Acidic medium (HClO$_4$ = 1M)

	VI/V Systems			IV/III Systems			Source
	U	Np	Pu	U	Np	Pu	
$\Delta S/F$ mV/°C	0.0 ± 0.3			1.5 ± 0.3			(a)
			1.2 ± 0.4				(b)
						2.2 ± 0.4	(c)
		0.215	0.655		1.867	1.526	(d)

(a): This work; (b): Ref. 13; (c): Ref. 14; (d): Ref. 15.

References

1. Ch. RIGLET, P. VITORGE, I. GRENTHE, Inorg. Chim. Acta, 133 (1987) 323.
2. Ch. RIGLET, P. ROBOUCH, P. VITORGE, Radiochim. Acta, 46 (1989) 85.
3. P. ROBOUCH, Report CEA 5473, 1988.
4. I. GRENTHE, D. FERRI, F. SALVATORE, G. RICCIO, J. Chem. Soc. Dalton Trans., 2439 (1984).
5. I. GRENTHE, P. ROBOUCH, P. VITORGE, J. Less Common Met. 127 (1986) 225.
6. I. GRENTHE, H. WANNER, Chemical Thermodynamics of Uranium, OCDE NEA TDB, to be published.
7. J. BARD, R. PARSONS, J. JORDAN, Standard potentials in Aqueous Solution, M. Dekker, Inc., New York, NY10016, 1986, p. 304.
8. Ch. RIGLET, Chimie du Neptunium et autres Actinides en Milieu Carbonate, Thesis, March 17, 1989, Paris VI University, France.
9. L. MAYA, Inorg. Chem., 22 (1983) 2093.
10. D. FERRI, I. GRENTHE, F. SALVATORE, Inorg. Chem. 22 (1983) 3162.
11. G. A. SIMAKIN, Elektrokhimiya, 11 (1975) 1026.
12. T. W. NEWTON, J. C. SULLIVAN, Handbook of the Physics and Chemistry of the Actinides, Vol. 3, Ch. 10. A. J. FREEMAN, C. KELLER (Eds), 1985.
13. S. W. RABIDEAU, J. Am. Chem. Soc., 78 (1956) 2705.
14. R. E. CONNICK, W. H. M. VEY, J. Am. Chem. Soc., 73 (1951) 1798.
15. P. BLANC, Report CEA 5406, 1987.