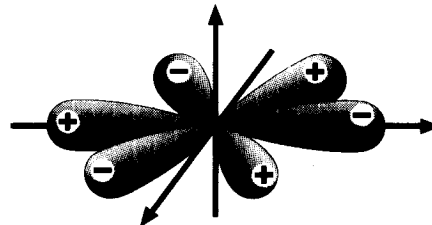


# f-Block Elements

**chemistry, technology, nuclear medicine  
and radiochemistry**



# f-Block Elements

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**Basic chemistry and processes of the lanthanide and actinide elements.** Papers will be considered for publication involving work on coordination and organometallic chemistry; nuclear medicine; radiochemistry and nuclear processes.

## Standard Potentials of the ( $\text{MO}_2^{2+}/\text{MO}_2^+$ ) Systems for Uranium and Other Actinides

Ch. RIGLET, P. VITORGE\*

CEA - DRDD/SESD, Laboratoire de Chimie (LCh), BP no 6 - 92265 Fontenay-aux-Roses Cédex, France

and I. GRENTHE

Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44, Stockholm 70, Sweden

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### Abstract

The formal potentials of the ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ) couple has been determined in media of varying ionic strength. These data have been interpreted by using the Brönsted–Guggenheim–Scatchard specific ionic interaction theory (S.I.T.) to give the standard potential  $E^\circ(\text{UO}_2^{2+}/\text{UO}_2^+) = +0.089 \pm 0.002$  V/NHE (at  $I=0$ ) and the interaction coefficient  $\epsilon(\text{UO}_2^+, \text{ClO}_4^-) = +0.28 \pm 0.04$ . The applicability of the S.I.T. and other types of virial expansion (Debye–Hückel, Davies, Baes and Mesmer, Pitzer etc.) have also been discussed.

A review of published data on the formal potentials of ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ), ( $\text{NpO}_2^{2+}/\text{NpO}_2^+$ ), ( $\text{PuO}_2^{2+}/\text{PuO}_2^+$ ) and ( $\text{AmO}_2^{2+}/\text{AmO}_2^+$ ) couples has been made using the S.I.T. We found that all of the existing experimental determinations of formal potentials could be well described by the specific interaction theory with constant interaction coefficients  $\epsilon(\text{MO}_2^{2+}, \text{ClO}_4^-) = +0.46 \pm 0.02$  and  $\epsilon(\text{MO}_2^+, \text{ClO}_4^-) = +0.28 \pm 0.04$  for all actinides.

### Introduction

Thermodynamic equilibrium modelling is an important tool for the description of complex chemical processes and systems. The technique has been used extensively in the fields of hydrogeology and environmental chemistry. A special case of great current interest is the modelling of radionuclide migration from nuclear waste repositories.

Thermodynamic models are no better than the quality of the data base used and the data always refer to a chosen standard state (for solutes, this is often the infinite dilution aqueous solution). However, data for many equilibria cannot be determined accurately, or at all in dilute solutions. This is invariably true for equilibria involving ions of high

charge, e.g. most actinide species. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of fairly high concentration, usually 0.5–4 M. The presence of an inert salt ensures that the activity factors of the reactants and products are reasonably constant and that it is possible to estimate their magnitude. We are then faced with the problem of converting data obtained in media of different ionic strengths and ionic compositions to a common reference state.

The usual procedure consists in calculating the thermodynamic constants as a function of ionic strength and extrapolating these data to  $I=0$  using either an empirical equation, e.g. the Davies equation, or semi-theoretical electrolyte models, as used by Baes and Mesmer [1], Brönsted, Guggenheim and Scatchard (abbreviated 'B.G.S. equation' or 'S.I.T.' for specific interaction theory) [2], or Pitzer [3].

The S.I.T. approach [2] assumes that the activity coefficient of a single ion,  $i$ , is the sum of two terms: the Debye–Hückel term which takes into account the long-range electrostatic interactions and a second term  $\sum \epsilon(i,j) m_j$  which accounts for short-range, non-electrostatic interactions between ions of opposite charges. The ion interaction coefficients  $\epsilon$  are mostly concentration independent for low-charged electrolytes at concentrations less than 3 M.

The Pitzer method [3] is a more developed specific interaction approach than the S.I.T. and also takes into account the interactions between ions of the same charge. It uses a more elaborate virial expansion which permits the calculation of fairly accurate activity factors over a large range of ionic strengths. The dependence of the second virial coefficients  $B_{kj}$  (equivalent to  $\epsilon$  in S.I.T.) on the ionic strength is also taken into account in this approach.

Nevertheless, Pitzer's model generally contains three parameters (as compared to one in the specific interaction theory) and few data on actinides and complex ions concerning these coefficients are currently available. Hence, the S.I.T. presents a practical advantage over the inherently more precise Pitzer

\* Author to whom correspondence should be addressed.

approach: the interaction coefficients for simple ions can be obtained from tabulated data [4, 5], and those for complexes can either be estimated from the charge and the size of the ion or determined experimentally. This is of great interest for equilibria involving complexes for which direct experimental information is difficult to obtain.

The redox system ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ) has been extensively studied by several investigators in media of different ionic strengths [9–12]. However, the large difference between the formal potential values available in the literature and the extrapolated value at  $I = 0$  proposed by Fuger and Oetting [15] calls for a redetermination of the standard potential of the ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ) system. In order to compare the various results, one must convert the data to a common reference state (zero ionic strength) using the S.I.T., for instance. Some activity coefficients are available for the species  $\text{UO}_2^{2+}$  but those concerning  $\text{UO}_2^+$  are unknown. Hence, we decided to study the ionic strength dependence of an equilibrium involving the  $\text{UO}_2^+$  ion in order to determine the interaction coefficient  $\epsilon(\text{UO}_2^+, \text{ClO}_4^-)$ . We have selected the redox equilibrium  $\text{UO}_2^{2+} + e^- \rightleftharpoons \text{UO}_2^+$  in  $\text{NaClO}_4$  medium. This information might be used as a good model for other actinides.

### Notation

$i$	concentration of the ion $i$
$a_i$	activity of the ion $i$
$\gamma_i$	activity coefficient of the ion $i$ ( $a_i = \gamma_i [i]$ )
$z_i$	charge of the ion $i$
$m_i$	molality of the ion $i$ in the solution (mol $\text{kg}^{-1}$ )
$I$	ionic strength of the solution (mol $\text{kg}^{-1}$ ) $\left( I = \frac{1}{2} \sum_i m_i z_i^2 \right)$
$\epsilon(i, j, I)$	specific interaction coefficient between the ions $i$ and $j$ of opposite charges: $\epsilon_{\text{VI}} = \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$ ; $\epsilon_{\text{V}} = \epsilon(\text{UO}_2^+, \text{ClO}_4^-)$
$E^\circ$	standard potential of the system ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ) (at 0 ionic strength)
$E^{\circ\circ}$	formal potential of the system ( $\text{UO}_2^{2+}/\text{UO}_2^+$ )
$E_1$	formal potential of the $\text{Ag}/\text{AgCl}$ reference electrode
$A$	$RT/F \lg(e) = 59.16 \text{ mV}/\lg \text{ unit at } 25^\circ \text{C}$

### Method

The following treatment of the data can only be applied in the case of a reversible system. Since we verified the reversibility of the couple ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ) as will be discussed later, the Nernst equation is valid at any time during the experiment. Hence, we have for the reaction  $\text{UO}_2^{2+} + e^- \rightleftharpoons \text{UO}_2^+$ ,

$$E = E^{\circ\circ} + \frac{RT}{F} \ln \frac{[\text{UO}_2^{2+}]_{\text{el}}}{[\text{UO}_2^+]_{\text{el}}} \quad (1)$$

where  $[ ]_{\text{el}}$  = concentration of electroactive species in the diffusion layer and

$$E^{\circ\circ} = E^\circ + \frac{RT}{F} \ln \frac{\gamma_{\text{UO}_2^{2+}}}{\gamma_{\text{UO}_2^+}} \quad (2)$$

is the formal potential of the system ( $\text{UO}_2^{2+}/\text{UO}_2^+$ ). The half-wave potential value is a very good approximation of  $E^{\circ\circ}$  for a reversible system [6].

The activity coefficient of an ion  $i$  can be calculated with the following virial expansion (here limited to the third order):

$$\log \gamma_i = -z_i^2 D + \sum_j \epsilon(i, j, I) m_j + \sum_{j, k} C(i, j, k) m_j m_k \quad (3)$$

where  $D = 0.5107(\sqrt{I}/(1 + 1.5\sqrt{I}))$  is the Debye-Hückel term (for long-range electrostatic interactions), and  $\epsilon$  and  $C$  are interaction coefficients between  $i$  and the others ions of the solution. The concentration of the ions of the ionic medium is much larger than the ones of the reacting species. Consequently, the ionic medium gives the main contribution to the value of  $\log \gamma_i$ . For a cation  $i$  in  $\text{NaClO}_4$  medium, we have:

$$\lg \gamma_i = -z_i^2 D + \epsilon(i, \text{ClO}_4^-, I) m_{\text{ClO}_4^-} + C(i, \text{ClO}_4^-) m_{\text{ClO}_4^-}^2 \quad (4)$$

From eqns. (4) and (2), we obtain:

$$E_{1/2} = E^{\circ\circ} = E^\circ + \frac{RT}{F \lg(e)} A [-3D + (\epsilon_{\text{VI}} - \epsilon_{\text{V}}) m_{\text{ClO}_4^-} + (C_{\text{VI}} - C_{\text{V}}) m_{\text{ClO}_4^-}^2] \quad (5)$$

We have tested various forms of eqn. (5) using some published expressions of activity coefficient (eqn. (4)); they are reported in Table III.

The S.I.T. is a simple case where  $C = 0$  and  $\epsilon$  is independent of the ionic strength below 3 M. Consequently, the plot  $(E_{1/2}/A) + 3D$  versus  $m_{\text{ClO}_4^-}$  is a straight line with  $E^\circ/A$  as the intercept at  $m = 0$  and  $(\epsilon_{\text{VI}} - \epsilon_{\text{V}})$  as the slope.

Curve-fitting treatments have been carried out on the other theories and the results of these interpretations compared (Table III).

All the potentials are measured against the reference

$$\parallel 0.01 \text{ M NaCl}, I \text{ M NaClO}_4 | \text{AgCl}_{(s)}, \text{Ag} \quad (\text{RE})$$

Its formal potential against NHE is:

$$E_1 = E_{\text{NHE}}^\circ - 0.05916 (\lg[\text{Cl}^-] + \lg \gamma_{\text{Cl}^-}).$$

At 25 °C,  $E_{NHE}^{\circ} = 0.2223$  V [7];  $\lg \gamma_{Cl^-}$  has been calculated with the S.I.T. using the value  $\epsilon(Na^+, Cl^-) = 0.03$  [4].

## Experimental

### Apparatus

The polarographic work was carried out with a Tacussel PRG5 potentiostat. The electromotive force values were determined with a potentiometer of type Tacussel 'ISIS 20000' and the polarograms were recorded on an X-Y plotter of type SEFRAM (TGV 164). The experimental error of the measured potentials is  $\pm 2$  mV. We have used a classical three-electrode circuit with a silver/silver chloride electrode (Tacussel) as reference. The latter was periodically controlled against another electrode of the same type, used only for this purpose.

### Reagents

Sodium perchlorate and perchloric acid solutions were prepared from the Merck p.a. products. The preparation of the U(VI) perchlorate solution has been described in ref. 8.

### Measurements

The polarograms were recorded at  $25.0 \pm 0.1$  °C. The experiments were carried out with  $10^{-3}$  M uranium(VI) perchlorate solutions of varying ionic strength (and  $NaClO_4$  as supporting electrolyte) in an acidic medium ( $10^{-2}$  M  $HClO_4$ ). A small amount of sodium chloride ( $10^{-2}$  M  $NaCl$ ) was added to the solutions to stabilize the reference electrode (the complexation of  $UO_2^{2+}$  and  $UO_2^+$  by  $Cl^-$  is then negligible). Oxygen was eliminated from the solutions by bubbling a stream of argon for 30 min. For each ionic strength, the polarogram of the background salt was first recorded, then a few microlitres of U(VI) stock solution were added. The polarogram of the resulting solution was recorded afterwards.

## Results and Treatment of the Data

The solutions investigated show two reduction waves and the limiting diffusion current of the second stage is twice as large as that of the first stage (Figs. 1 and 2).

For each ionic strength investigated, the plot  $E$  versus  $\lg i/(i_d - i)$  for the first wave is a straight line whose slope is close to  $-59.2$  mV/lg unit, which is the theoretical value at 25 °C for a reversible one-electron process [6] (Figs. 2 and 3 and Table I).

This observation, in agreement with the previous results [9–12], confirms that the wave is due to the redox reaction  $UO_2^{2+} + e^- \rightleftharpoons UO_2^+$ .

From the experimental data (Table I), we observe a shift of the half-wave potentials to more negative

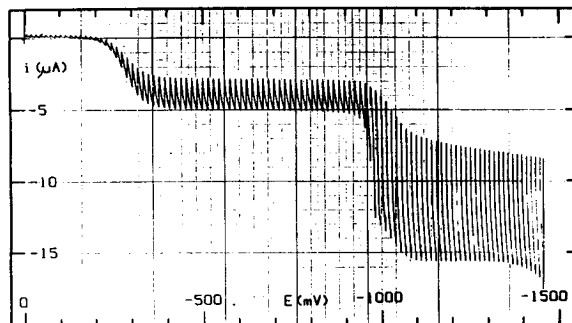


Fig. 1. Polarogram of the  $UO_2^{2+}$  ion.  $[U(VI)] = 10^{-3}$  M;  $[H^+] = 10^{-2}$  M;  $I = 1$  M  $ClO_4^-$ . The potentials refer to an Ag/AgCl electrode ( $E_{NHE}^{\circ} = +350.8$  mV).

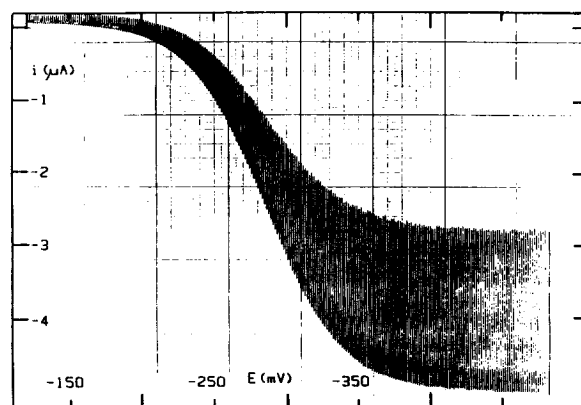


Fig. 2. First reduction wave of the  $UO_2^{2+}$  ion.  $[U(VI)] = 10^{-3}$  M;  $[H^+] = 10^{-2}$  M;  $I = 1$  M  $ClO_4^-$ . The potentials refer to an Ag/AgCl electrode ( $E_{NHE}^{\circ} = +350.8$  mV). This wave is attributed to the redox reaction  $UO_2^{2+} + e^- \rightleftharpoons UO_2^+$ .

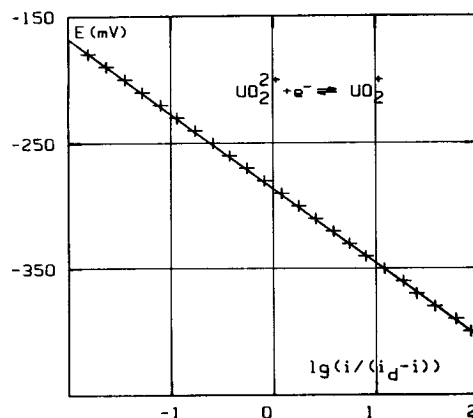


Fig. 3. Verification of the reversibility of the first reduction wave of  $UO_2^{2+}$ : analysis of the curve shown in Fig. 2. The slope of the curve  $E$  vs.  $\lg i/(i_d - i)$  is  $-60.1$  mV/lg unit.

values when the ionic strength of the solution is lowered. This means that  $UO_2^{2+}$  is stabilized at lower ionic strength. This effect stems from the term  $(\epsilon_{VI} - \epsilon_V)m_{ClO_4^-}$  whose sign is opposite to that of

TABLE I. Experimental Half-Wave Potentials for  $10^{-3}$  Uranium(VI) Perchlorate Solutions of Various Ionic Strengths in Acidic Medium ( $10^{-2}$  M HClO<sub>4</sub>) ( $E_{1/NHE}$  is the formal potential of the Ag/AgCl reference electrode:  $E_{(1/2)/NHE} = E_{(1/2)/REF} + E_{1/NHE}$ )

Medium NaClO <sub>4</sub> (mol l <sup>-1</sup> )	$m_{\text{ClO}_4^-}$ (mol kg <sup>-1</sup> )	$E_{(1/2)/REF}$ (mV)	$E_{1/NHE}$ (mV)	$E_{(1/2)/NHE}$ (mV)	Slope of $E$ vs. $\lg \frac{i}{i_d - i}$
3	3.50	-267.7	+348.8	+81.1	-61.0
2	2.21	-279.8	+350.7	+70.9	-59.7
1	1.05	-285.4	+350.8	+65.4	-60.1
0.5	0.51	-288.0	+350.5	+62.3	-60.1

TABLE II. Experimental Points of the Curve  $E_{(1/2)/NHE}/A + 3D$  vs.  $m_{\text{ClO}_4^-}$

$m_{\text{ClO}_4^-}$ (mol kg <sup>-1</sup> )	$D$	$Y = \frac{E_{(1/2)/NHE}}{59.16} + 3D$
3.50	0.251	2.123
2.21	0.235	1.902
1.05	0.206	1.723
0.51	0.176	1.580

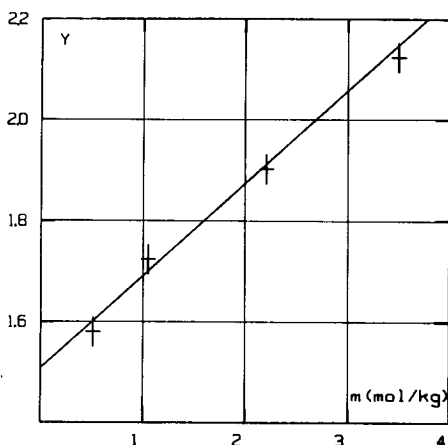


Fig. 4. Extrapolation of the potential of the (UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>+</sup>) couple to zero ionic strength. The S.I.T. predicts that the variation of  $Y = E_{(1/2)/NHE}/59.16 + 3 \times 0.5107 \sqrt{I}/(1 + 1.5\sqrt{I})$  vs. the NaClO<sub>4</sub> molality,  $m$ , is a straight line; its slope is the difference between the specific interaction coefficients [ $\epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - \epsilon(\text{UO}_2^+, \text{ClO}_4^-)$ ]. The extrapolated value of  $Y$  at  $m = 0$  gives the standard potential  $E^\circ$  of the (UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>+</sup>) couple.

the term  $-3D$  in eqn. (5); it must then be interpreted as a specific short-range interaction effect.

By plotting  $Y = E_{1/2}/A + 3D$  versus  $m_{\text{ClO}_4^-}$  (Table II and Fig. 4), one obtains a straight line within the experimental errors. Hence the specific interaction theory (S.I.T.) is able to account for our experimental data and we obtain the following results:

$$E^\circ = +0.089 \pm 0.002 \text{ V/NHE}$$

$$\epsilon_{\text{VI}} - \epsilon_{\text{V}} = +0.18 \pm 0.02$$

From the known value  $\epsilon_{\text{VI}} = +0.46 \pm 0.02$  [4, 5], the value of  $\epsilon_{\text{V}}$  is then  $+0.28 \pm 0.04$ . The uncertainties have been evaluated from the limiting straight lines which still give a good fit with the experimental points.

In Table III, we give the result of extrapolation of  $E^\circ$  to zero ionic strength, using different activity coefficient formulae. The differences between the  $E^\circ$  values thus obtained are not negligible.

The very simple Debye-Hückel and Davies theories must be excluded at once as they cannot account for our experimental results.

In the theories proposed in Table III, the Debye-Hückel term, which accounts for long-range electrostatic interactions, is the dominant term in the expression of the activity coefficients in dilute solution. The second virial term, which accounts for short-range non-electrostatic interactions, is most important at high ionic strength. We do not accept the Baes-Mesmer and Pitzer approaches in our case because the second virial term obtained by curve-fitting is not negligible at low ionic strength (*cf.* the values of the derivative of this term at  $I = 0$  in Table III). These theories, which are inherently more precise than the S.I.T. or Pitzer-Brewer approaches, require a large amount of experimental data especially at low ionic strength in order to measure the various parameters with accuracy. However, in polarography, it is absolutely necessary to work at relatively high ionic strength in order to be able to neglect the migration current. Consequently, the fitted parameters in Baes-Mesmer or Pitzer equations are very uncertain here.

The S.I.T. and Pitzer-Brewer approaches are equivalent and differ only in the form of the denominator in the Debye-Hückel term. The factor 1.5 used in the B.G.S. equation is empirical and has been chosen so as to minimize the variation of  $\epsilon(i, j)$  with  $I$ . Hence, the Pitzer-Brewer equation, with a concentration independent value of  $B(i, j)$ ,

TABLE III. Various Forms of Eqn. (5):  $E_{1/2} = E^\circ - 3AD + AB(I)I$ , where  $D = D(x, y)$  or  $D_p$  and  $B(I) = B_1$  or  $B_1 + B_2 + B_2F(I)$ : Results of Curve-fitting<sup>a</sup>

Models	Debye-Hückel term $-3AD(x, y)$	2nd Virial $AB(I)I$	Results $E^\circ$ (mV) $B_1$ $B_2$	$\left(\frac{dIB(I)}{dI}\right)$ at $I = 0$
Debye-Hückel	$-3AD(0.5107, 1.5)$	0		
Davies	$-3AD(0.5102, 1)$	$0.9 AI$		
Scatchard			+89.54	
Guggenheim	$-3AD(0.5107, 1.5)$	$AB_1I$	+0.18	0.18
Bronsted (S.I.T.)			0	
Pitzer-Brewer	$-3AD(0.5107, 1)$	$AB_1I$	+95.52 +0.22 0	0.82
Baes-Mesmer	$-3AD(0.511, 1)$	$AB_1I + AB_2F(I)I$	+80.67 +0.18 +1.47	4.57
Pitzer	$-3AD_p$	$AB_1I + AB_2F(I)I$	+78.39 +0.23 +2.04	6.36

$${}^a D(x, y) = \frac{x\sqrt{I}}{1+y\sqrt{I}}; \quad D_p = \frac{0.392}{\ln 10} \frac{\sqrt{I}}{1+1.2\sqrt{I}} + \frac{2}{1.2} \ln(1+1.2\sqrt{I}); \quad F(I) = \frac{1 - (1+2\sqrt{I} - 2I)e^{-2\sqrt{I}}}{4I};$$

$A = RT/F \lg(e) = 59.16 \text{ mV/lg unit at } 25^\circ\text{C. } I = \text{ionic strength of the solution} \approx \text{molality of } ClO_4^- \text{ (mol kg}^{-1}\text{)}.$

may give a less accurate estimate of the activity coefficients and then of the normal potential  $E^\circ$  than the B.G.S. equation.

Therefore, the S.I.T. probably gives the more accurate value of the standard potential of the  $(UO_2^{2+}/UO_2^+)$  couple at  $I = 0$ .

## Discussion

In the literature, there are three precise experimental studies of the standard potential of the  $(UO_2^{2+}/UO_2^+)$  couple, all using a polarographic technique. All experimental precautions have been taken to assure reversibility and to control the diffusion potentials. Kraus *et al.* [9, 10] reported a formal potential *versus* NHE equal to  $+0.062 \pm 0.002 \text{ V}$  in a 0.1 M KCl medium. A recalculation to  $I = 0$  using the interaction coefficients  $\epsilon(UO_2^{2+}, Cl^-) = 0.21$  [5] and  $\epsilon(UO_2^+, Cl^-) = 0.13$  gives the standard potential  $+0.081 \text{ V/NHE}$ . The value of  $\epsilon(UO_2^+, Cl^-)$  has been estimated with the empirical relation:

$$\frac{\epsilon(UO_2^+, Cl^-)}{\epsilon(UO_2^{2+}, Cl^-)} = \frac{\epsilon(UO_2^+, ClO_4^-)}{\epsilon(UO_2^{2+}, ClO_4^-)}$$

Anyhow, this parameter is not very sensitive, because  $\epsilon(UO_2^+, Cl^-) = 0$  gives only a 1 mV difference.

Kritchevsky and Hindman [11] measured the formal potential of the  $(UO_2^{2+}/UO_2^+)$  couple in 0.05–3.0 M perchlorate solutions. The formal potentials were found to be independent of ionic strength in perchlorate solutions between 0.05 and 1.0 M, and were shifted to a more positive value in 3.0 M perchlorate. The reported formal potentials *versus* NHE in 0.1 M  $ClO_4^-$  and 1.0 M  $ClO_4^-$  are  $+0.067 \pm 0.004 \text{ V}$  and  $+0.063 \pm 0.004 \text{ V}$ , respectively. The authors have used an SCE reference electrode and we are not convinced that this will eliminate the diffusion potentials entirely.

Kern and Orlemann [12] have also made a polarographic study of the  $(UO_2^{2+}/UO_2^+)$  couple. The authors have used a cell arrangement which eliminates liquid junction potentials. The formal potential *versus* NHE in 0.5 M  $ClO_4^-$  is  $+0.062 \pm 0.002 \text{ V}$ .

Brand and Cobble [13] have determined the standard potential of the  $(NpO_2^{2+}/NpO_2^+)$  couple. They observed a difference between the standard potential and the formal potential of Sullivan *et al.* [14] which is 0.1 V. They proposed that all reported potentials for the (actinide(VI)/actinide(V)) couples should be corrected by this amount. Fuger and Oetting [15] followed this suggestion and proposed the value  $+0.163 \pm 0.05 \text{ V}$  for the standard potential of the  $(UO_2^{2+}/UO_2^+)$  couple.

TABLE IV. Survey of Interaction Coefficients  $\epsilon(i, j)$ 

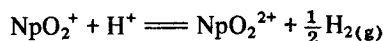
$i$	$j$	$\epsilon$ (kg mol <sup>-1</sup> )	Reference
UO <sub>2</sub> <sup>2+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.46 ± 0.02	4, 5
UO <sub>2</sub> <sup>2+</sup>	Cl <sup>-</sup>	0.21	4
UO <sub>2</sub> <sup>+</sup>	ClO <sub>4</sub> <sup>-</sup>	0.28 ± 0.04	this work
UO <sub>2</sub> <sup>+</sup>	Cl <sup>-</sup>	0.13	estimation
Na <sup>+</sup>	Cl <sup>-</sup>	0.03	4

In order to be able to compare our results with the information previously published, we used the specific interaction theory [2] to recalculate these thermodynamic data to a common reference state. Then, all data have been referred to a zero ionic strength using the interaction coefficients listed in Table IV. The results are listed in Table V.

The 8 mV shift between our  $E^\circ$  value and the one calculated from the measurements in 0.1 M Cl<sup>-</sup> medium would correspond to a change of the  $\epsilon(\text{UO}_2^+, \text{Cl}^-)$  value to 1.1. This  $\epsilon$  value seems too large for a monovalent ion: the uncertainty in the estimation of  $\epsilon(\text{UO}_2^+, \text{Cl}^-)$  cannot explain the observed 8 mV difference between the  $E^\circ$  values.

However, in perchlorate medium, the agreement between our results and those from the literature is very good: therefore, we propose the value  $+0.089 \pm 0.002$  V for the standard potential of the (UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>+</sup>) couple at zero ionic strength and the value  $+0.28 \pm 0.04$  for the interaction coefficient  $\epsilon(\text{UO}_2^+, \text{ClO}_4^-)$ .

The value of  $E^\circ(\text{UO}_2^{2+}/\text{UO}_2^+) = +163 \pm 50$  mV proposed by Fuger and Oetting [15] and Brand and Cobble [13] from their results on the (NpO<sub>2</sub><sup>2+</sup>/NpO<sub>2</sub><sup>+</sup>) system is in disagreement with our value. In their paper, Brand and Cobble write the Nernst equation corresponding to the redox reaction as:



by using the mean activities of the pure electrolytes NpO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>, NpO<sub>2</sub>ClO<sub>4</sub> and HClO<sub>4</sub> and not their

values in the mixture. Therefore, we have made a reinterpretation of Brand and Cobble's data by extrapolating to zero ionic strength using the S.I.T.: then, the plot  $Y = \frac{E}{A} + 2D - \lg[\text{NpO}_2^{2+}]/([\text{H}^+][\text{NpO}_2^+])$  versus the molality of the solutions should be a straight line with  $E^\circ/A$  as the intercept at  $I = 0$  and  $\Delta\epsilon = \epsilon_{\text{VI}} - \epsilon_{\text{V}} - \epsilon_{\text{H}}$  as the slope. Using  $\epsilon_{\text{H}} = 0.14$  [5] and the same value  $\epsilon_{\text{VI}} - \epsilon_{\text{V}} = 0.18$  for the Np and U (found in this work), we obtain a good fit with the experimental results (Fig. 5) and  $E^\circ(\text{NpO}_2^{2+}/\text{NpO}_2^+) = +1161 \pm 8$  mV.

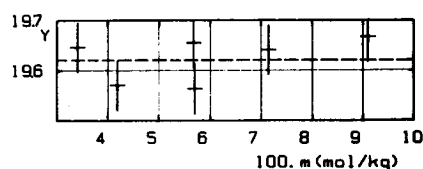


Fig. 5. Extrapolation of the potential of the (NpO<sub>2</sub><sup>2+</sup>/NpO<sub>2</sub><sup>+</sup>) couple to 0 ionic strength from the Brand and Cobble data [13]. The S.I.T. predicts that the variation of  $Y = E/59.16 + 2D - \lg[\text{NpO}_2^{2+}]/([\text{NpO}_2^+][\text{H}^+])$  versus the NaClO<sub>4</sub> molality,  $m$ , is a straight line of slope 0.04. The extrapolated value of  $Y$  at  $m = 0$  gives the standard potential  $E^\circ$  of the (NpO<sub>2</sub><sup>2+</sup>/NpO<sub>2</sub><sup>+</sup>) couple.

The difference between the obtained  $E^\circ(\text{NpO}_2^{2+}, \text{NpO}_2^+)$  value and the value of the formal potential in 1 M ClO<sub>4</sub><sup>-</sup> medium reported by Sullivan *et al.* [14] or Cohen and Hindman [17] is  $+25 \pm 8$  mV. We observed a difference of  $+24 \pm 4$  mV for the (UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>+</sup>) system. Therefore, it seems reasonable to assume that a constant correction of  $+24$  mV should be made on the formal potentials of the actinides (in 1 M ClO<sub>4</sub><sup>-</sup> medium) to reach their standard potentials (Table VI). This corresponds to the usual approximation: the  $\epsilon$  values of all actinides of the same valency are identical in a given medium.

For U, Np and Pu, the  $E^\circ$  values found in the present work are consistent with those proposed by Ahrland *et al.* [20]. For the (AmO<sub>2</sub><sup>2+</sup>/AmO<sub>2</sub><sup>+</sup>) sys-

TABLE V. Formal Potentials and Standard Potentials ( $I = 0$ ) for the (UO<sub>2</sub><sup>2+</sup>/UO<sub>2</sub><sup>+</sup>) Couple

Experimental details			Formal potential (V/NHE)	Standard potential (V/NHE)	Reference
Method	Medium	Temperature (°C)			
Pol	0.1 M Cl <sup>-</sup> pH = 3	25	$+0.062 \pm 0.002$	+0.081	9
Pol	0.1 M Cl <sup>-</sup> pH = 2	25	$+0.061 \pm 0.001$	+0.081	10
Pol	0.1 M ClO <sub>4</sub> <sup>-</sup>	25	$+0.067 \pm 0.004$	+0.085	11
	1.0 M ClO <sub>4</sub> <sup>-</sup>	25	$+0.063 \pm 0.004$	+0.088	11
	3.0 M ClO <sub>4</sub> <sup>-</sup>	25	$+0.074 \pm 0.004$	+0.081	11
Pol	0.5 M ClO <sub>4</sub> <sup>-</sup>	25	$+0.062 \pm 0.002$	+0.088	12



TABLE VI. Estimated  $E^\circ$  Values of the Redox Systems ( $\text{MO}_2^{2+}/\text{MO}_2^+$ ) for Actinides

Couple ( $\text{MO}_2^{2+}/\text{MO}_2^+$ )	Formal potential in 1 M $\text{ClO}_4^-$ medium		Standard potential (V/NHE)			
	(V/NHE)	Reference	[13]	[20]	[16]	This work
U	+0.065 ± 0.002	This work	+0.16 ± 0.05	+0.080		+0.089 ± 0.002
Np	+1.136 ± 0.001	17	+1.24 ± 0.01	+1.153		+1.160 ± 0.005
Pu	+0.9164 ± 0.0002	18	+1.02 ± 0.05	+0.933		+0.940 ± 0.004
Am	+1.600 ± 0.005	19	+1.70 ± 0.05	+1.62	+1.59 ± 0.06	+1.624 ± 0.009

tem, our  $E^\circ$  value is consistent with the one calculated (Table VI) by Bard *et al.* [16] from enthalpy and entropy data: this independent way of obtaining the  $E^\circ$  values also indicates that a 24 mV correction should be used to convert the  $E'^\circ(\text{MO}_2^{2+}/\text{MO}_2^+)$  values for actinides from 1 M  $\text{ClO}_4^-$  medium to zero ionic strength, rather than the 0.1 V suggested by Brand and Cobble. Therefore, the value of  $\epsilon(\text{MO}_2^{2+}, \text{ClO}_4^-) - \epsilon(\text{MO}_2^+, \text{ClO}_4^-)$  is equal to  $+0.18 \pm 0.02$  for all actinides.

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