REDOX POTENTIALS OF M(VI)/M(V) LIMITING CARBONATE COMPLEXES (M = U OR Pu) AT DIFFERENT IONIC STRENGTHS AND TEMPERATURES. ENTROPY AND HEAT CAPACITY.

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For waste disposal programs, actinide aqua ions and limiting complexes had been studied by cyclic voltametry. Measured redox potentials in non complexing media were modelled by using SIT and Taylor's series expansions to the second order for ionic strength I, and temperature T, influences. These data treatments give standard values for redox potential E°, corresponding ΔS°, ΔH° and $\Delta C_p°$ of reactions, and excess values (variations of E'°, ΔS, ΔH and ΔC_p with I) that can be deduced by using T influence on fitted SIT coefficients Δε. This methodology is used here at 5 to 70°C in 0.3 to 1.5 M Na_2CO_3 media (I = 0.9 to 4.5 M). E° = 0.191±0.015 (-0.779±0.010) V/SHE, ΔS° = -178±37 (-174±5) $J.K^{-1}.mol^{-1}$, $\Delta C_p°$ = -516±744 (-414±176) $J.K^{-1}.mol^{-1}$ and Δε = -0.17_5±0.04 + $(2.1±2.0)10^{-3}$ ΔT -$(2.4 ± 7.7)10^{-5}$ $(\Delta T)^2$ /2 (-0.91±0.10 + $(7.0±1.9)10^{-3}$ ΔT -$(5.8 ± 0.11)10^{-5}$ $(\Delta T)^2$ /2) $kg.mol^{-1}$ are obtained at 25°C and I=0 for the $MO_2(CO_3)_3^{4-} + e^- \rightarrow MO_2(CO_3)_3^{5-}$ reaction where M = Pu (and U respectively). $\lg(\beta_3^{V°}/\beta_3^{VI°})$= -12.6±0.3 (-14.65±0.17) is deduced. $\lg\beta_3^{V}$ = 3.1±1.4 (6.95±0.18) is proposed using published β_3^{VI} values.

ΔS° and E°(U-Pu(VI)/Pu(V)) limiting CO_3 complexes

1 Introduction

Redox properties, hydrolysis, carbonate complexation are studied to understand geochemical behaviour of radioelements. Their migration in groundwaters can be modelled by coupling hydrodynamics, physico-chemical interactions with rock surfaces studied in batches [1] and aqueous chemistry. We typically checked experimentally such predictions by using column experiments with Np(V) in bicarbonate media [2]. Aqueous speciation was calculated with complexation constants obtained from our measurements and critical review [3], part of OECD program [4]. This bibliographic work pointed out contradictions and lack of published data. For this, actinide aqua ions and limiting carbonate complexes have been studied in our laboratory. Cyclic voltametry technique and data treatment were first validated with well-known U redox system, and mean activity coefficients of typically HCl and NaCl electrolytes: redox potentials of actinide couples had previously been measured in non complexing media as a function of T and I, to obtain thermodynamic data, activity coefficients, γ, and T influence on γ [5]. We are now reporting this type of measurements for Pu. We shall also reinterpret previous U data [6, 7] to compare the chemistry of analogue actinide ions.

2 Notations

A(T) A(T)= R T ln(10)/ F = 0.0591597 V at 298.15 K
a_i , m_i, [i] : activity ($mol.kg^{-1}$), molality ($mol.kg^{-1}$), molarity ($mol.l^{-1}$) of ion i
z_i, γ_i charge, activity coefficient of ion i: $\gamma_i = a_i / m_i$,
Δz^2, Δε : $z^2_{Red} - z^2_{Ox}$, $\varepsilon(Red,Na^+) - \varepsilon(Ox,Na^+)$. Δε(T) = Δε value at T
ε(i,j)(T) : value of the specific interaction coefficient between ions i and j at T, ($kg.mol^{-1}$)
D(T,I) = $a(T)\sqrt{I} / (1 + a_j\, b(T)\sqrt{I})$ [8-10], a_j = 1.5/b(25°C), a(25°C) = 0.509 $kg^{0.5}mol^{-0.5}$
F = 96485.309 $C.mol^{-1}$
I, T, ΔT : ionic strength ($mol.kg^{-1}$), temperature (K), ΔT= T - T°, T° = 298.15 K
R, r = 8.314510 $J.K^{-1}.mol^{-1}$, r = R ln(10) = 19.144867 $J.K^{-1}.mol^{-1}$
X(T,I), X° : X value at T and I, where X is E, S, C_p, or D, X° = X(T°,0)

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X', X'', σ : $(\frac{\partial X}{\partial T})_p$, $X'(T,I)$ is X' value at T and I. $X'' = (X')'$. σ is standard deviation.
ΔZ $= Z_{Red} + Z_{H^+} - 0.5\ Z_{H_2} - Z_{Ox}$ for reaction $Ox + 1/2\ H_2 \rightarrow Red + H^+$, Z is S, or C_p
β_3^{VI} (β_3^{V}) $= [MO_2(CO_3)_3^{z}] / ([MO_2^{2+}]\ [CO_3^{2-}]^3)$, where $z^{VI} = -4$ and $z^{V} = -5$.

3 Method

The Specific Interaction Theory (S.I.T.) was used to calculate activity coefficients γ_i,

$$\lg\gamma_i = -z_i^2\ D(T,I) + \varepsilon(i,Na^+)(T)\ m_{Na^+} \tag{1}$$

[7-11], and then to extrapolate to the standard state (I = 0)

$$E_{Ox/Red}(T,I) = E_{Ox/Red}(T,0) + A(T)\ [\Delta z^2\ D(T,I) - \Delta\varepsilon(T)\ m_{Na^+}] \tag{2}$$

$E_{Ox/Red}(T,0)$ and $\Delta\varepsilon(T)$ were obtained (Eq.2) by linear regression on $(Y(T,I), m_{Na^+})$ data, where $Y(T,I) = [E_{Ox/Red}(T,I)\ /\ A(T) - \Delta z^2\ D(T,I)]$. $E(T°,I)$, $\Delta S(T°,I)$ and $\Delta C_p(T°,I)$ were obtained (Fig.1) by fitting experimental data $E(T,I)$ (vs. T at constant I), to Eq.(3)

$$E(T,I) = E(T°,I) + [\Delta S(T°,I)\ /\ F]\ \Delta T + [\Delta C_p(T°,I)\ /\ 2T°]\ (\Delta T)^2 + ... \tag{3}$$

ΔS and ΔC_p are in first and second order terms, and the precision of the measurements is not enough to determine a third order term [5, 11]. Still ΔC_p for solutes in aqueous solutions, usually vary with T, $\Delta C_p(T°,I)$ obtained in this way, is rather a mean value slightly depending on the T° and ΔT values chosen. We obtained I influence by combining thermodynamic definitions with S.I.T. relation [11]:

$$\Delta H(T°,I) = \Delta H° + r\ T°^2\ [\Delta z^2\ D'(T°,I) - m\ \Delta\varepsilon'(T°)] \tag{4}$$

$$\Delta S(T°,I) = \Delta S° + r\ [\Delta z^2\ (D(T°,I) + T°\ D'(T°,I)) - m\ (\Delta\varepsilon(T°) + T°\ \Delta\varepsilon'(T°))] \tag{5}$$

$$\Delta C_p(T°,I) = \Delta C_p° + r\ T°\ [\Delta z^2\ (2\ D'(T°,I) + T°\ D''(T°,I)) - m\ (2\ \Delta\varepsilon'(T°) + T°\ \Delta\varepsilon''(T°))] \tag{6}$$

$D(T,I)$ was calculated analytically. $\Delta\varepsilon(T)$ and $D(T,I)$ derivatives were calculated from the first and second order terms of polynomial regressions vs. ΔT. $[2\ \Delta\varepsilon'(T°) + T°\ \Delta\varepsilon''(T°)]$ can also be determined as the slope of $[\Delta C_p(T°,I)\ /\ r - \Delta z^2\ (2\ D'(T°,I) + T°\ D''(T°,I))]$ vs. m (Eq.6). Similar linear regressions can be performed based on Eq.(4 or 5). I influence is usually small on $\Delta H(T°,I)$ because it depends only on γ' ($D'(T°,I)$ and $\Delta\varepsilon'(T°)$ in Eq.(4)) and not on γ itself.

$$(E(PuO_2(CO_3)_3^{4-}/PuO_2(CO_3)_3^{5-}) - E(PuO_2^{2+}/PuO_2^{+})) = A\ (\lg\beta_3^{V} - \lg\beta_3^{VI}) \tag{7}$$

equation was used for thermodynamic cycles: $\lg\beta_3^{V}$ for Pu(V) that disproportionates in carbonate media, was deduced from $\lg\beta_3^{VI}$(3 M $NaClO_4$) = 18.2 ± 0.4 we obtained from $PuO_2CO_{3(s)}$ solubility measurements and $\lg\beta_3^{VI}$(I = 0) = 17.4 ± 0.5 was proposed [12]. We pointed out small inconsistency for $\varepsilon(CO_3^{2-},Na^+)$ numerical value used for this type of extrapolation to I = 0, and this was corrected later [8]. Anyhow we recently determined I correction for the Np system is slightly different from the U one. Using for Pu, the Np correction to I = 0, we obtain $\lg\beta_3^{VI}$(I = 0) = 15.7 ± 1.3 which is much less than the previous estimation, and needs confirmation. Experimental details were described elsewhere [6, 7].

4 Results, Interpretation and Discussion

The difference between the two potential peaks of the voltammograms increased with the scanning speed, but the half sum was constant (within 1 mV). It was used as an estimate of the formal potential. This nearly reversible behaviour is often found for couples of ions of similar geometry. For potential measurements (Table 1), σ on T regressions (Eq.3) was 3 to 7 mV (Table 2). The uncertainty is set to 10 mV, it includes systematic errors and junction potential. For extrapolation to I = 0 (Eq.2), σ was less than 10 mV (Table 1); the uncertainty is set to 15 mV, and the series at T = 5°C is rejected because of the too low number of experimental points. Our data are in reasonable agreement with published ones (Table 3) considering junction potential, I effect and possible dissociation of the Pu(V) limiting complex in 0.1 M K_2CO_3 as for Np(V) [3], that were not documented in published works. We performed similar measurements on the Np(VI)/Np(V) redox system [3, 13], and our formal potential measurements are in very good agreement with Simakin's study [14] when interpreting his data with the SIT [3].

E variations with T are quite small and similar at each I (Fig.1), hence (Eqs.5 and 6), ΔS and above all the ΔC_p variations with I are small (Fig.2 and 3). ΔS variations vs. I might be compared with a line (Eq.5) of slope $[-r\ (\Delta\varepsilon(T°) + T°\ \Delta\varepsilon'(T°))]$ when $I > 0.5$ mol.kg^{-1}. The uncertainty on ΔC_p, is of the order of magnitude of the variations with I. But the ΔC_p term is maintained to determine the uncertainty of ΔS, and to perform the same treatment of data as in acidic media [5]. E decreases with T (Fig.1): Pu(VI) becomes more stable than Pu(V).

This can be attributed to increase of ionic radii with T: this steric effect should be more dramatic on Pu(VI) ion because it is smaller than Pu(V) one, hence it can also explain β_3^{VI}, β_3^{V}, and β_3^{VI}/β_3^{V} values (Table 4) decrease with atomic number (from U to Pu). I influence at high carbonate concentration is not the same for U and Pu limiting complexes. We already pointed out this type of difference between $NpO_2(CO_3)_3^{5-}$ and $UO_2(CO_3)_3^{5-}$ [15], and between $Pu(CO_3)_5^{6-}$ and $U(CO_3)_5^{6-}$[16] activity coefficients: the numerical values of $\Delta\varepsilon$ are different. Anyhow the S.I.T. might not be accurate enough in this case because I was too high or the complexes too highly charged, . In addition ion pair formation between Na^+ and $UO_2(CO_3)_3^{5-}$ are suspected [15]. To obtain complexation constants in 1 M and 3 M $NaClO_4$ media where some of them have already been measured, we calculated our data in this media with the S.I.T. coefficients measured in this work. From published [5-7, 9, 12] potential values in acidic media and $\lg\beta 3^{VI}$ value, we deduced Eq.(7) $\lg\beta 3^{V}$, using Np(VI)-Pu(VI) analogy for I corrections: our $\varepsilon(Na^+,NpO_2(CO_3)_3^{5-})$ determination [3, 4] propagates (in thermodynamic cycles) to Pu values of $\beta 3^{VI}$ and $\beta 3^{V}$, that are surprisingly low, this has to be confirmed.

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Table 1. **Experimental Results**. Pu(VI)/Pu(V) redox potential E (mV/SHE), are Eq.(2) extrapolated to I = 0. The values in parenthesis are σ's on these SIT linear regressions.

0.3 M		0.5 M		1 M		1.5 M Na$_2$CO$_3$		I = 0		
T	E	T	E	T	E	T	E	T	E	$\Delta\varepsilon$ (kg.mol^{-1})
9	325	15	327	4	360	5	389	5	196 (6)	0.41 (0.05)
16	320	20	329	10	356	10	383	10	216 (5)	0.21 (0.04)
20	314	25	318	15	350	10	383	15	207 (4)	0.20 (0.04)
21	311	25	313	20	344	15	375	20	201 (4)	0.18 (0.03)
25	297	25	315	25	340	15	376	25	188 (4)	0.18 (0.02)
25	307	30	307	25	336	20	368	30	183 (4)	0.16 (0.04)
30	299	35	298	25	337	20	369	35	171 (4)	0.20 (0.04)
31	299	35	306	25	336	25	362	40	164 (5)	0.11 (0.04)
35	294	40	290	34	326	25	356	45	151 (6)	0.11 (0.04)
35	286	45	280	35	324	25	362	50	143 (7)	0.12 (0.04)
40	285	45	280	40	315	30	353	55	124 (8)	0.15 (0.04)
40	287	55	264	43	313	35	340	60	102 (9)	0.20 (0.04)
45	279	60	256	45	307	35	345	65	112(10)	0.08 (0.05)
45	279			50	298	40	338			
50	269			50	300	45	323			
50	271			52	297	45	330			
55	259			55	290	50	322			
65	246			60	278	50	330			
				64	277	55	308			
						55	320			
						55	315			
						60	307			
						60	310			
						60	299			
						65	298			

Table 2. **Entropies and Heat Capacities.** Results of the regressions vs. T (Eq.3) from E and $\Delta\varepsilon$ data (Table 1). Values in parenthesis are σ's.

Na$_2$CO$_3$ (mol.l^{-1})	molality / molarity (l.kg^{-1}) [8]	E(T°) (mV/SHE)	ΔS(T°) / F (mV.K^{-1})	ΔC$_p$(T°) /(2 T° F) (μV °K^{-2})
0	1	191 (8)	-1.84 (0.19)	-9.0 (6.5)
0.3	1.0033	306 (3)	-1.34 (0.09)	-3.8 (3.2)
0.5	1.0043	315 (3)	-1.47 (0.13)	-7.7 (4.7)
1	1.0094	338 (2)	-1.30 (0.04)	-8.7 (1.4)
1.5	1.0170	360 (4)	-1.52 (0.07)	-0.4 (2.7)
		$\Delta\varepsilon$(T°) (kg.mol^{-1})	$\Delta\varepsilon$'(T°) (g.mol^{-1}K^{-1})	$\Delta\varepsilon$"(T°)/2 (mg.mol^{-1}K^{-2})
		0.18 (0.05)	-2.1 (1.1)	24 (38)

Table 3. **Literature redox potential for the M(VI)/M(V) couple in carbonate media**

Ref.	Medium		E (mV/SHE)	E (mV/SCE)	Ref.	Medium		E (mV/SHE)
[17]	1 M K_2CO_3	Pu	320 ± 10		[9]	I = 0	U	-752 ± 16
[17]	0.1M K_2CO_3	Pu	300 ± 10		p.w.	I = 0	U	-779 ± 15
[18]	1 M Na_2CO_3	Pu	351 ± 10	110 ± 10				
p.w.	1 M Na_2CO_3	Pu	337 ± 10					

Table 4. **Comparison of thermodynamic data for U and Pu** at 25°C. Uncertainty is 1.5σ, or calculated using propagation rules.

		U[m]	Pu	U	Pu
		$MO_2(CO_3)_3^{4-} + e^- \rightarrow MO_2(CO_3)_3^{5-}$		$MO_2^{2+} + e^- \rightarrow MO_2^{+}$	
E°	(mV/SHE)	-779 ± 10[a]	191 ± 15[a]	87.9 ± 1.3[b]	938 ± 10[c]
E(1M)[d]	(mV/SHE)	-613 ± 10	311 ± 10	63.8 ± 1.4	915 ± 5
E(3M)[d]	(mV/SHE)		360 ± 10	84.9 ± 2.4	939 ± 5
$\Delta\varepsilon$	(kg.mol^{-1})	-0.91 ± 0.1[e]	-0.17$_5$ ± 0.04[e]	-0.2 ± 0.01[b]	-0.22 ± 0.05[c]
$\Delta\varepsilon'$	(g.mol^{-1}.K^{-1})	7.0 ± 1.9[e]	2.1 ± 2.0[e]		1.48 ± 0.34[c]
$\Delta\varepsilon''/2$	(mg.mol^{-1}.K^{-2})	-58.1 ± 1.1[e]	-24 ± 77[e]		-12.2 ± 13.0[c]
$\Delta S°/F$	(mV.K^{-1})	-1.80 ± 0.05[f]	-1.84 ± 0.38[f]	-0.06 ± 0.05[m]	0.34 ± 0.04[c]
$\Delta S(1M)/F$[d]	(mV.K^{-1})	-1.52 ± 0.2	-1.41 ± 0.40	-0.24 ± 0.02[m]	0.16 ± 0.04
$\Delta S(3M)/F$[d]	(mV.K^{-1})		-1.52 ± 0.55		-0.02 ± 0.02
$\Delta C_p°/2T°F$	(μV.K^{-2})	-7.2 ± 3.1[f]	-9 ± 13[f]		-6.77 ± 1.62[c]
$\Delta C_p(1M)/2T°F$[d]	(μV.K^{-2})	-3.98	-7 ± 14		-7.29 ± 1.53
$\Delta C_p(3M)/2T°F$[d]	(μV.K^{-2})		-4 ± 20		-4.86 ± 1.00
$MO_2^{2+} + MO_2(CO_3)_3^{5-} \rightarrow MO_2(CO_3)_3^{4-} + MO_2^{+}$					
$\lg(\beta_3^{VI°}/\beta_3^{V°})$[g]		-14.65 ± 0.17	-12.63 ± 0.30		
$\lg(\beta_3^{VI}(1M)/\beta_3^{V}(1M))$[g]		-11.44 ± 0.17	-10.21 ± 0.19		
$\lg(\beta_3^{VI}(3M)/\beta_3^{V}(3M))$[g]			-9.78 ± 0.19		
		$MO_2^{2+} + 3\ CO_3^{2-} \Leftrightarrow MO_2(CO_3)_3^{4-}$		$MO_2^{+} + 3\ CO_3^{2-} \Leftrightarrow MO_2(CO_3)_3^{5-}$	
$\lg\beta_3°$		21.60 ± 0.05[b]	15.7 ± 1.3[j,l]	6.95 ± 0.18[k]	3.1 ± 1.4[k,l]
$\lg\beta_3(1M)$		21.84 ± 0.07[h]	16.5 ± 1.2[j,l]	10.40 ± 0.19[k]	6.2 ± 1.2[k,l]
$\lg\beta_3(3M)$		22.41 ± 0.18[h]	18.2 ± 0.4[i]		8.4 ± 0.4[k]

[a]obtained (Eq.2) from E data (Table 1 and [6, 7]). [b][9]. [c][5]. [d]calculated (Eq.2) from other data of this table. [e]deduced (Eq.3) from $\Delta\varepsilon(T)$ obtained[a] (Eq.2) in this work. [f]deduced (Eq.3) from E° values obtained[a] (Eq.2) in this work. [g]calculated (Eq.7) from other data of this table. [h]calculated (Eq.2) from data of Ref.[9]. [i][12]. [j]calculated (Eq.2) from data of Ref.[12] and Np $\varepsilon(Na^+,NpO_2(CO_3)_3^{5-})$ value [3] for Pu. [k]β_3^V values calculated from β_3^{VI}/β_3^V and β_3^{VI} data of this table. [l]Surprisingly low value due to $\varepsilon(Na^+,PuO_2(CO_3)_3^{5-})$ estimate[j] (see text). [m]From data in 0.2 M Na_2CO_3 + 0, 0.6 and 1.4 M $NaClO_4$ [6, 7]

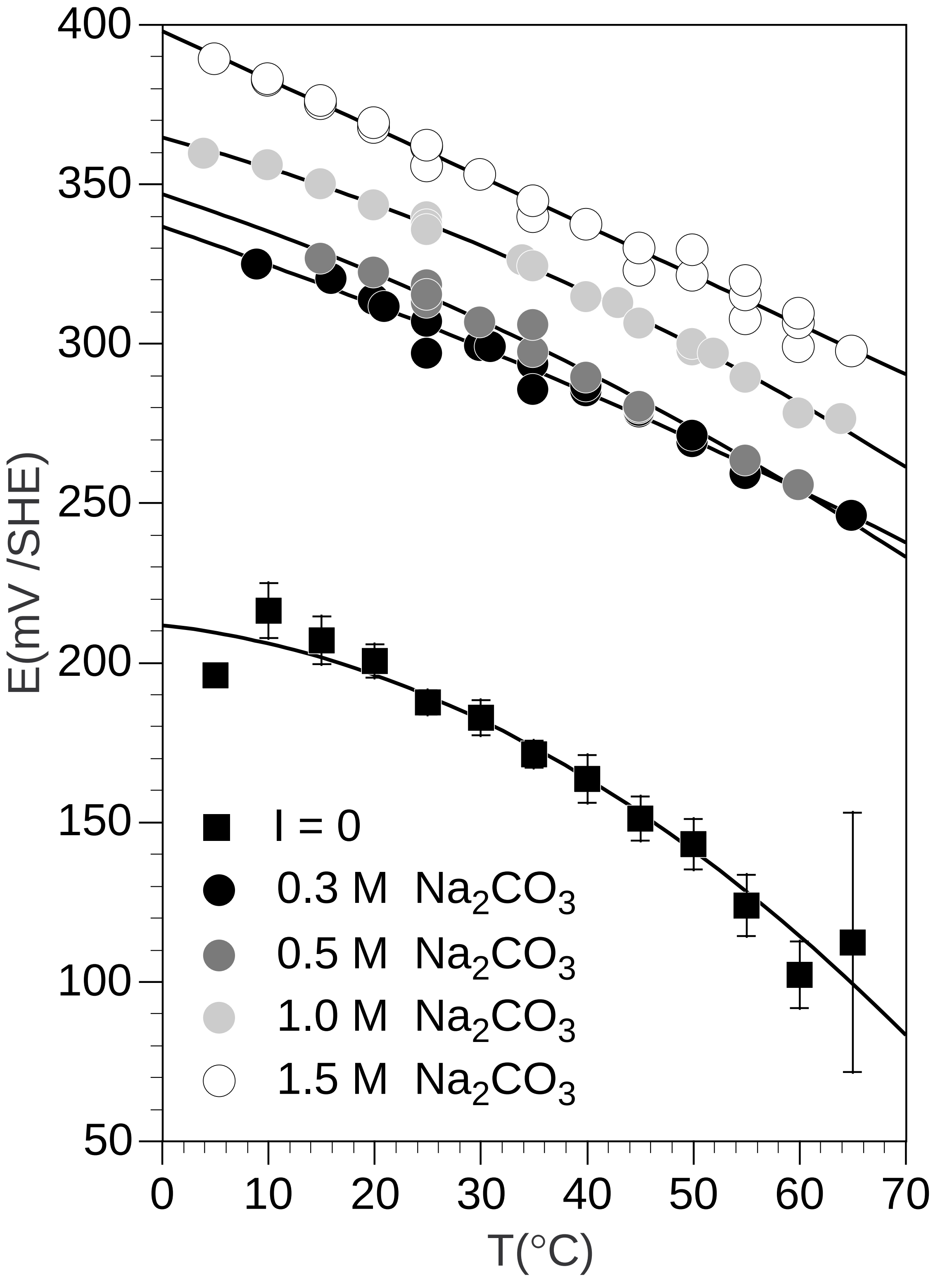

Fig. 1. **Temperature influence on the formal potential of the $PuO_2(CO_3)_3^{4-}/PuO_2(CO_3)_3^{5-}$ redox couple.** Table 1 data are plotted. Curves are calculated by using (Eq.3) with E°(T,) ΔS(T°) and $\Delta C_p(T°)$ fitted values (Table 2).

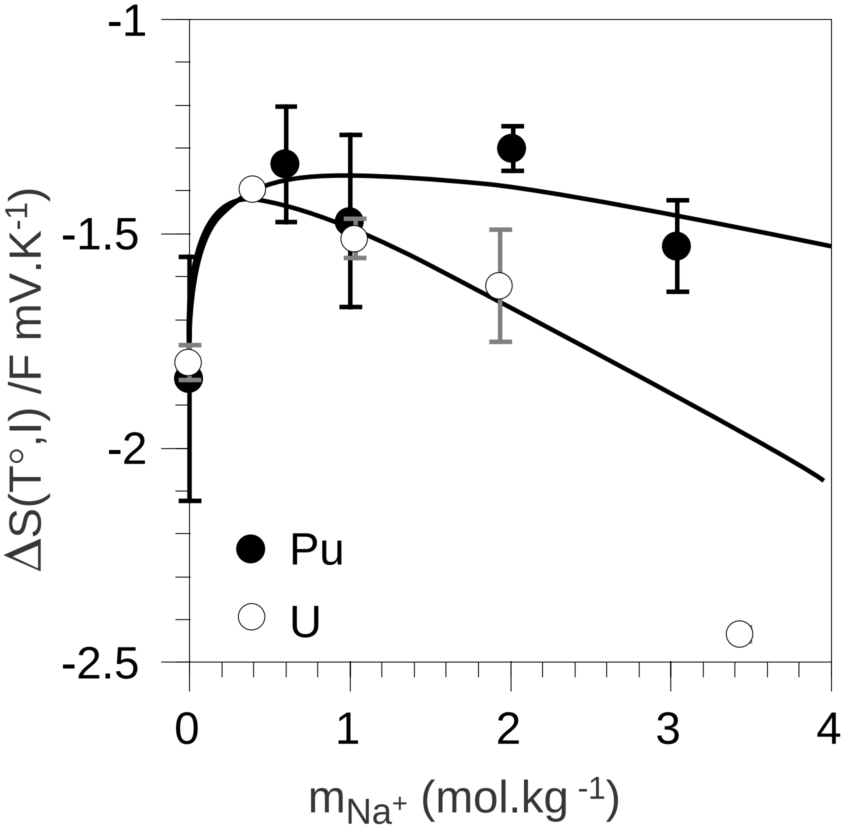

Fig. 2. **Ionic strength influence on the entropy of the $MO_2(CO_3)_3^{4-} + e^- \rightarrow MO_2(CO_3)_3^{5-}$ reaction.** For M = Pu, Table 2 data are plotted, for M = U, similar treatment was used on data published in Ref.[6, 7] where only a first order approximation (Eq.3) had been used. Curves are calculated by using (Eq.5) with ΔS°, Δε(T°) and Δε'(T°) fitted values (Table 2).

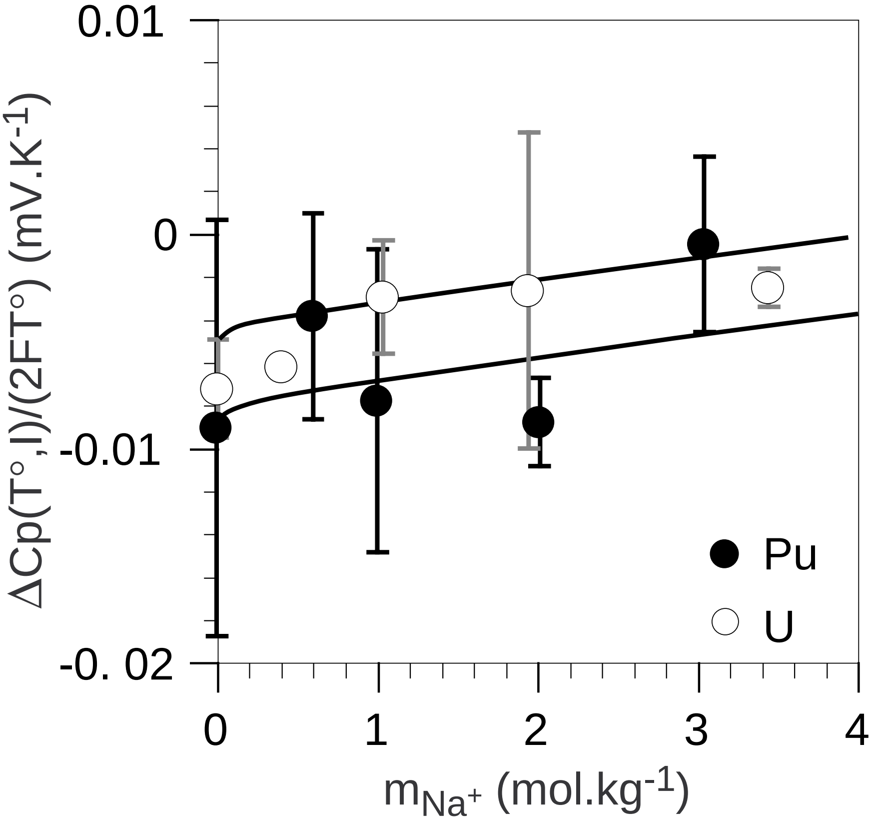

Fig. 3. **Ionic strength influence on the heat capacity of the $MO_2(CO_3)_3^{4-}$ + $e^- \rightarrow$ $MO_2(CO_3)_3^{5-}$ reaction.** For M = Pu, Table 2 data are plotted, for M = U, similar treatment was used on data published in Ref.[6, 7] where only E'° and ΔS (not ΔC_p) were estimated. Curves are calculated by using (Eq.6) with $\Delta C_p°$, Δε'(T°) and Δε"(T°) fitted values (Table 2).

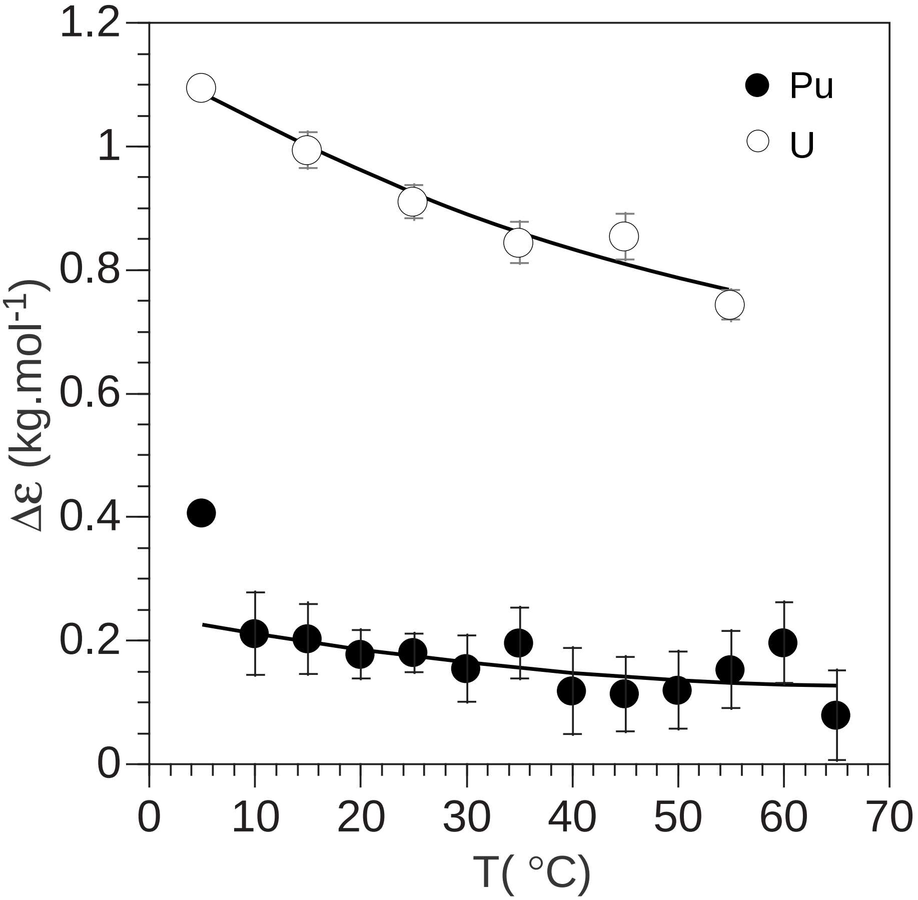

Fig. 4. **Temperature influence on ε($MO_2(CO_3)_3^{4-}$,Na^+) - ε($MO_2(CO_3)_3^{5-}$,Na^+)** = Δε (points) values (Table 1) obtained (Eq.2) at each T from I influence on the formal potential of the Pu(VI)/Pu(V) redox couple in carbonate media. Curves are second order polynomial regressions using Δε(T°), Δε'(T°) and Δε''(T°) fitted values (Table 2).