

ELECTROCHEMICAL CHARACTERISATION OF THE Ce(IV) LIMITING CARBONATE COMPLEX

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ABSTRACT

The stoichiometry and the thermodynamic formation constant of the limiting complex of Ce(IV) were determined at $19.3 \pm 1.0^\circ\text{C}$ by using the cyclic voltametry technique at a hanging mercury drop working electrode in concentrated bicarbonate/carbonate medium. The Ce(IV/III) redox potential was measured at pH varying from 9.3 to 10.6 and $[\text{CO}_3^{2-}]$ varying from 1.0 to 1.5 M by performing a CO_3^{2-} titration with CO_2 gas. The ionic strength and junction potential effects were taken into account for the potentiometric calibrations and measurements. Quantitative interpretation of the variations of the formal potential $E_{\text{IV/III}}$ showed that no polymerisation took place during the redox reaction, and that two CO_3^{2-} ligands, but no OH^- ligand, were exchanged. As the accepted stoichiometry for the limiting complex of Ce(III) is $\text{Ce}(\text{CO}_3)_4^{4-}$, it is therefore shown that the Ce(IV) species is $\text{Ce}(\text{CO}_3)_6^{8-}$. In a 3.06 molal Na^+ carbonate/bicarbonate medium (Ionic strength = 4.33 mol.kg^{-1}), $E_{\text{IV/III}}^0 = 0.161 \pm 0.008 \text{ V/SHE}$ (in molal units) was measured. This value, combined with the published $\text{Ce}(\text{CO}_3)_4^{4-}$ formation constant and the (reevaluated) $(\text{Ce}^{4+}/\text{Ce}^{3+})$ standard potential, is used to calculate the $\text{Ce}(\text{CO}_3)_6^{8-}$ formation constant $\log_{10}(\beta_6^{\text{IV}}) = 42.2 \pm 0.5$ (defined in molal concentration except for Ce^{4+} in activity) in the same medium. The values $E_{\text{IV/III}}^0 = 0.180 \pm 0.009 \text{ V/SHE}$ and $\log_{10}(\beta_6^{\text{IV}}) = 41.8 \pm 0.5$ in molar units are deduced in a 2.67 M NaClO_4 medium (Na^+ molality = molal ionic strength = 3.06 mol.kg^{-1}). Possible $\text{Ce}(\text{CO}_3)_5^{6-}$ formation is discussed, $\log_{10}(\beta_5^{\text{IV}}) \leq 41.8 \pm 0.5$ (in molar units) is estimated.

METHODOLOGY

Redox reaction	$\text{Ce}(\text{CO}_3)_4^{5-} + \left(\frac{j}{n} - 4\right) \text{CO}_3^{2-} + \frac{i}{n} \text{H}_2\text{O} \rightleftharpoons \frac{1}{n} \text{Ce}_n(\text{OH})_i(\text{CO}_3)_j^{4n-i} + \frac{i}{n} \text{H}^+ + e^-$
Nernst law	$E = E_{\text{IV/III}}^0 + A \log_{10} \frac{a_{\text{IV}}^{1/n} a_{\text{H}^+}^{i/n}}{a_{\text{III}} a_{\text{CO}_3^{2-}}^{j/n-4} a_{\text{H}_2\text{O}}^{i/n}}$
Stoichiometry coefficient i and j	$E_{\text{IV/III}} = E_{\text{IV/III}}^0(\text{I}) + A \left[\frac{i}{n} \log_{10} m_{\text{H}^+} - \left(\frac{j}{n} - 4\right) \log_{10} m_{\text{CO}_3^{2-}} \right]$ <p>where $E_{\text{IV/III}}^0(\text{I}) = E_{\text{IV/III}}^0 + A \log_{10} \frac{\gamma_{\text{IV}}^{1/n} \gamma_{\text{H}^+}^{i/n}}{\gamma_{\text{III}} \gamma_{\text{CO}_3^{2-}}^{j/n-4} a_{\text{H}_2\text{O}}^{i/n}}$</p> <p>☞ Plotting $E_{\text{IV/III}}$ versus pH and $m_{\text{CO}_3^{2-}}$ gives i and j</p>
Stoichiometry coefficient n	$E_{1/2} = E_{\text{IV/III}} + A \left[\left(1 - \frac{1}{n}\right) \log_{10} 2 - \frac{1}{n} \log_{10} n \right] - \left(1 - \frac{1}{n}\right) A \log_{10} m_{\text{Ce}}$ <p>☞ Plotting $E_{1/2}$ versus m_{Ce} gives n</p> <p>☞ Si n = 1, $E_{1/2} = E_{\text{IV/III}}$</p>

<p>Formation constant of the Ce(IV) limiting complex</p>	$E_{\text{IV/III}}^0(\mathbf{I}_m) - E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0(\mathbf{0}) = A [\log \beta_{m4}^{\text{III}}(\mathbf{I}_m) - \log \beta_{m6}^{\text{IV}}(\mathbf{I}_m)]$
<p>Ionic strength correction : Specific Interaction Theory</p>	<p>$\log_{10}(\gamma_i) = -z_i^2 D(\mathbf{I}_m) + \varepsilon(i, \mathbf{X}) m_X$ for an ion i of charge z_i in a \mathbf{X} medium, where \mathbf{X} is an ion of charge opposite to that of i ; $D(\mathbf{I})$ = Debye-Hückel term ; $\varepsilon(i, \mathbf{X})$ = Specific Interaction Coefficient between i and \mathbf{X}.</p>

EXPERIMENTAL

Technique : Cyclic voltametry

$$E_{IV/III} \# E_{1/2} \# [E_p(\text{Ox}) - E_p(\text{Red})]/2$$

Electrodes

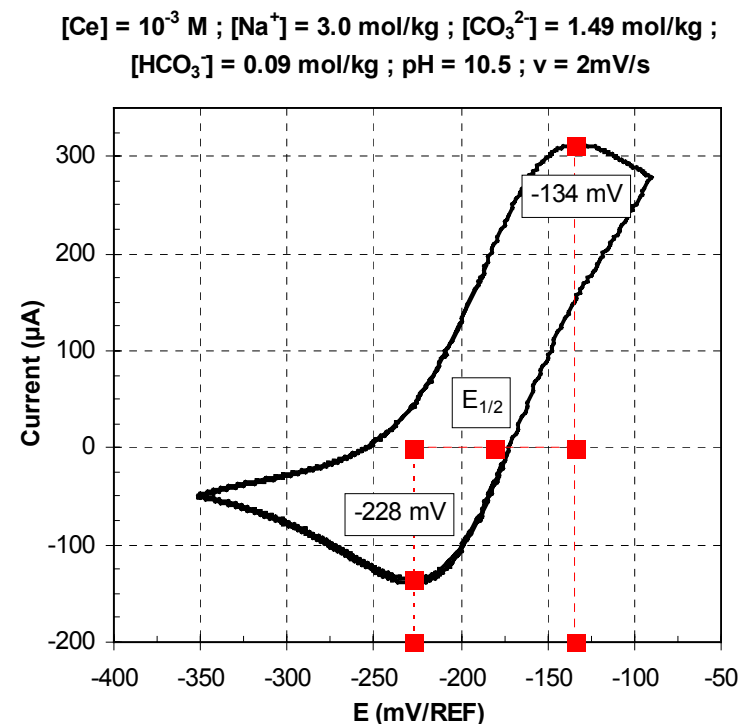
WORKING ELECTRODE : Hanging Mercury Drop Electrode (HMDE)

AUXILIARY ELECTRODE : Platinum wire

REFERENCE ELECTRODE : Ag/AgCl | 0.02M NaCl, (I-0.02) M NaClO₄ ||

(I = ionic strength of the initial test solution)

$$E_{\text{REF}} = E_{\text{AgCl/Ag}}^0 + A \log_{10}(a_{\text{Cl}^-})$$



Measurements

- ☑ The composition (pH, $m_{\text{CO}_3^{2-}}$) of the test solution was varied by performing an acidic titration of the CO_3^{2-} ions par CO_2 gas.
- ☑ The pH is measured with a combined glass electrode. The Ag/AgCl reference electrode compartment was filled with a 0.02 M NaCl, (I-0.02) M NaClO₄ solution of same molar ionic strength I as that of the initial NaHCO₃/Na₂CO₃ test solution. The glass electrode is calibrated in activity ($-\lg_{10}[a_{\text{H}^+}]$) with carbonate/bicarbonate buffers of same ionic strength as that of the test solutions.
- ☑ From the known Na₂CO₃ and NaHCO₃ initial concentrations and pH measurements, the speciation (m_{OH^-} , $m_{\text{CO}_3^{2-}}$, $m_{\text{HCO}_3^-}$...) was determined at each step of acidification by thermodynamic calculations.
- ☑ At each pH step, the measured $E_{IV/III} \# E_{1/2}$ potential (see figure) was corrected for the junction potential E_j , which was determined independently at the same pH by means of the cell REF || 0.02 M NaCl, $c_{\text{CO}_3^{2-}}$ M Na₂CO₃, $c_{\text{HCO}_3^-}$ M NaHCO₃ || REF', where REF' is an Ag/AgCl wire.

RESULTS

FIG. 1. GLASS ELECTRODE CALIBRATION.

The calibration was obtained by performing two titrations of a 1 M NaHCO_3 solution with a 1 M NaOH solution at $T = 19.3 \pm 1.0^\circ\text{C}$. The theoretical pH ($-\log_{10} a_{\text{H}^+}$ and not $-\log_{10} [\text{H}^+]$) values were calculated by using the equilibrium constants and SIT coefficients recommended by the NEA/TDB. The observed deviation at $\text{pH} > 10$ was taken into account in the treatment of the experimental data of the Ce(IV)/Ce(III) redox potential. No deviation (of the glass electrode slope) was observed at $\text{pH} < 8.2$ where $\text{NaHCO}_3/\text{CO}_2(\text{g})$ buffers were used for the pH calibration.

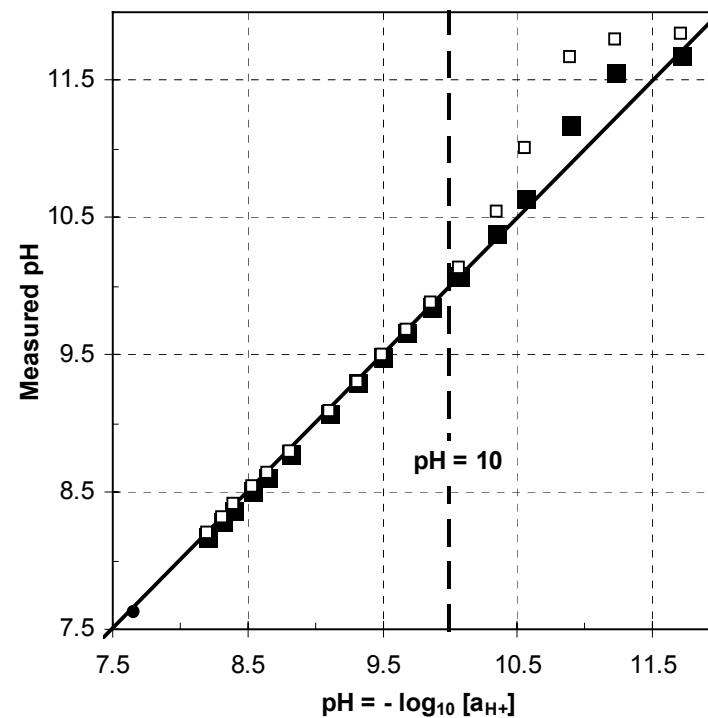


FIG. 2. INFLUENCE OF THE CERIUM TOTAL CONCENTRATION ON THE CE(IV)/CE(III) REDOX POTENTIAL IN CONCENTRATED CARBONATE /BICARBONATE MEDIA.

Two sets of experiments were performed: $[\text{Na}^+] = 3.0$ (or 3.1) mol.kg^{-1} , $[\text{CO}_3^{2-}] = 1.45$ (or 1.36) mol.kg^{-1} , $[\text{HCO}_3^-] = 0.13$ (or 0.38) mol.kg^{-1} and $\text{pH} = 10.36$ (or 9.86) respectively, $T = 19.3 \pm 1.0^\circ\text{C}$, $A = 58.03 \text{ mV}/\log_{10}$ unit. This figure shows that the measured redox potential $E_{\text{IV/III}}$ is independent of the Ce total concentration. Since in these conditions the Ce(III) major aqueous species are mononuclear, it is deduced that Ce(IV) species are also mononuclear. Theoretical curves are plotted for $n = 1$ (solid line) and $n = 2$ (dotted line), where n is the Ce stoichiometric coefficient in the Ce(IV) aqueous species (for $n > 2$, the deviation between the experimental data and the theoretical lines are even greater than for $n = 2$).

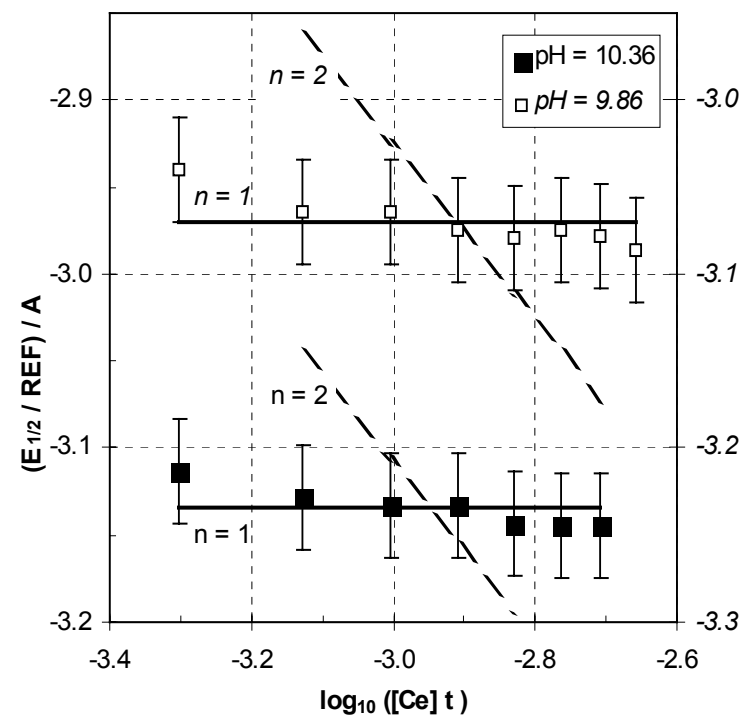


FIG. 3. INFLUENCE OF THE CO_3^{2-} CONCENTRATION ON THE CE(IV/III) FORMAL POTENTIAL IN CONCENTRATED CARBONATE/BICARBONATE MEDIA.

$T = 19.3 \pm 1.0^\circ\text{C}$, $[\text{Ce}]_t = 0.001 \text{ M}$,
 $A = 58.03 \text{ mV}/\log_{10} \text{ unit}$, $[\text{Na}^+] = 3.06 \text{ mol.kg}^{-1}$,
 $1.00 < [\text{CO}_3^{2-}] < 1.45 \text{ mol.kg}^{-1}$,
 $9.2 < \text{pH} < 10.6$.

This figure shows that, within experimental uncertainties, the measured data falls into a single straight line (dotted line), with a slope corresponding to the theoretical one assuming that two CO_3^{2-} ions are exchanged during the redox reaction. Since in these conditions the Ce(III) major species is $\text{Ce}(\text{CO}_3)_4^{5-}$, it is deduced that the Ce(IV) one is $\text{Ce}(\text{OH})_i(\text{CO}_3)_6^{8-i}$; As the pH influence plot (figure 4) confirms that $i=0$, the major Ce(IV) complex is then $\text{Ce}(\text{CO}_3)_6^{8-}$. That species is possibly partially dissociated into $\text{Ce}(\text{CO}_3)_5^{6-}$ (bolded curve).

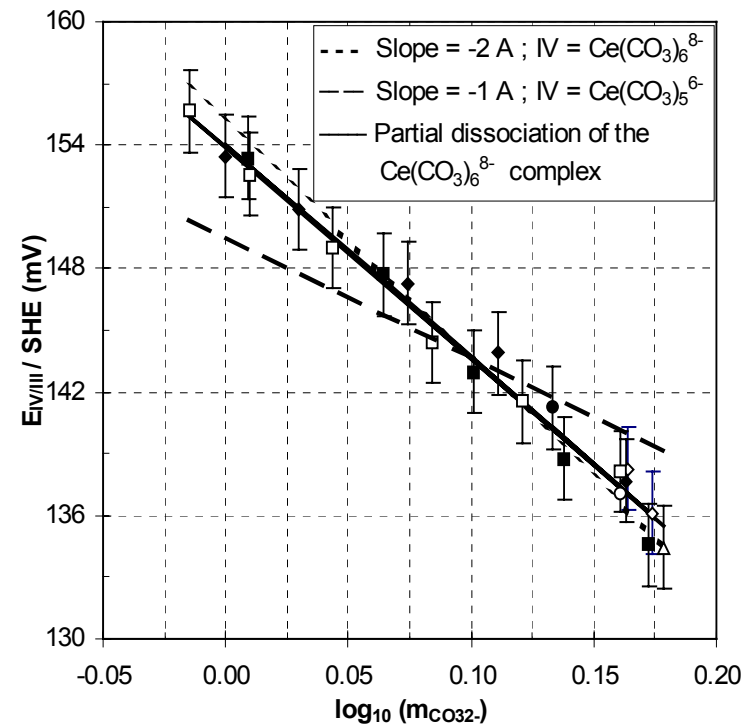


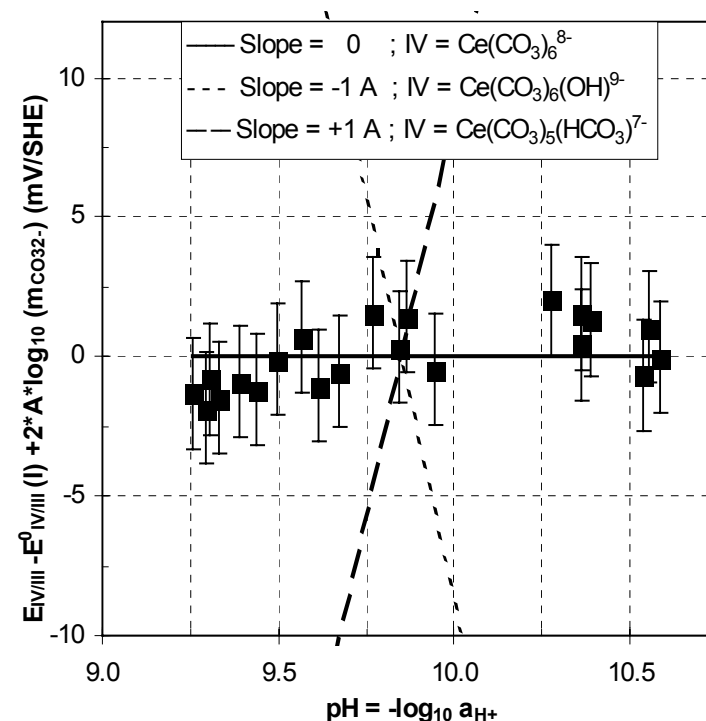
FIG. 4. pH INFLUENCE ON THE CE(IV/III) FORMAL POTENTIAL IN CONCENTRATED CARBONATE / BICARBONATE MEDIA.

$T = 19.3 \pm 1.0^\circ\text{C}$, $A = 58.03 \text{ mV}/\log_{10} \text{ unit}$, $[\text{Ce}]_t = 0.001 \text{ M}$,
 $[\text{Na}^+] = 3.06 \text{ mol.kg}^{-1}$, $1.00 < [\text{CO}_3^{2-}] < 1.45 \text{ mol.kg}^{-1}$,
 $9.2 < \text{pH} < 10.6$.

The experimental data are the same as in figure 3. This figure shows that the corrected redox potential

$$E_{\text{IV/III}} - E_{\text{IV/III}}^0 + A \cdot 2 \log_{10} m_{\text{CO}_3^{2-}}$$

is independent of pH. The Ce(IV) and Ce(III) aqueous species have then the same OH^- stoichiometric coefficient ($i = 0$): since the Ce(III) and Ce(IV) major species are $\text{Ce}(\text{CO}_3)_4^{5-}$ and $\text{Ce}(\text{OH})_i(\text{CO}_3)_6^{8-i}$ (Figure 3), it is deduced that the formula of the the Ce(IV) complex is finally $\text{Ce}(\text{CO}_3)_6^{8-}$, which is in agreement with the interpretation of the figure 3.



CONCLUSIONS

- ☞ **Limiting carbonate complex of Ce(IV) of stoichiometry $\text{Ce}(\text{CO}_3)_6^{8-}$**
- ☞ **No evidence of any mixed $\text{OH}-\text{CO}_3^{2-}$ or polynuclear complex**
- ☞ **Chemical difference with Actinide(IV) which rather forms $\text{An}(\text{CO}_3)_5^{6-}$**
- ☞ **Cyclic voltametry is a good tool for actinide speciation**
- ☞ **Thermodynamic constants determined in this work :**

Medium : 3.06 molal Na^+ carbonate / bicarbonate solution ($I_m = 4.33 \text{ mol/kg-1}$)	
Definition	Numerical value
$E_{\text{IV/III}}^0(I_m) \approx E_{1/2} + 2 A \lg m_{\text{CO}_3^{2-}}$	$E_{\text{IV/III}}^0(I_m) = 0.161 \pm 0.008$
$\beta_{m6}^{\text{IV}}(I_m) = \frac{m_{\text{Ce}(\text{CO}_3)_6^{8-}}}{a_{\text{Ce}^{4+}} m_{\text{CO}_3^{2-}}^6}$	$\lg \beta_6^{\text{IV}}(I_m) = 42.2 \pm 0.5$
$k_{m6}^{\text{IV}}(I_m) = \frac{m_{\text{Ce}(\text{CO}_3)_6^{8-}}}{m_{\text{Ce}(\text{CO}_3)_5^{6-}} m_{\text{CO}_3^{2-}}}$	$\lg k_6^{\text{IV}}(I_m) \leq 0.03 \pm 0.19$
$\beta_{m5}^{\text{IV}}(I_m) = \frac{m_{\text{Ce}(\text{CO}_3)_5^{6-}}}{a_{\text{Ce}^{4+}} m_{\text{CO}_3^{2-}}^5}$	$\lg \beta_5^{\text{IV}}(I_m) \leq 41.8 \pm 0.4$

FURTHER WORK

☞ **Dissociation of the $\text{Ce}(\text{CO}_3)_6^{8-}$ complex into $\text{Ce}(\text{CO}_3)_5^{6-}$ - by spectrophotometry**

➤ **Stability constant of $\text{Ce}(\text{CO}_3)_5^{6-}$**

☞ **Electrochemical study of the**

➤ **Am(IV/III) redox couple (reversible)**

➤ **Np(IV/III) and Pu(IV/III) redox couple (non reversible)**

➤ **Stability constants of the An(IV) carbonate limiting complexes**