Speciation of Technetium(IV) in Bicarbonate Media

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The technetium isotope ^{99}Tc is a major fission product from nuclear reactors. It will ultimately be disposed of as radioactive waste since it has few applications outside of scientific research. Geochemical modeling of the dissolution of nuclear waste and of the solubility and speciation of the dissolved radionuclides in groundwaters is an important part of the Performance Assessment of the safety of nuclear waste repositories. It relies on the availability of a critically-assessed thermodynamic database. The potential of the Tc(VII)/Tc(IV) redox couple is here measured in various chemical conditions to verify the stoichiometries of Tc complexes and determine their stabilities: (i)-$\log_{10}[H^+]$ in range 7.0 – 10.0, for 0.3, 0.6 and 0.7 M $[CO_3]_{total}$, (ii) $[CO_3]_{total}$ in range 0.01 to 0.6 M at -$\log_{10}[H^+]$ about 8.6, and (iii) [Tc(VII)]/[Tc(IV] ratios of (6.02 10^{-5} M)/(10^{-6} M) and (6.02 10^{-5} M)/(6.02 10^{-5} M) at -$\log_{10}[H^+]$ = -9.1 and $[CO_3]_{total}$ = 1 M. Assuming that Tc(VII),TcO_4^-, is the only species is in all these chemical conditions, the potentiometric results are interpreted with two hydroxide – carbonate monomeric complexes. The hydrolysis equilibrium between these two complexes is $Tc(CO_3)(OH)_2$ + H_2O ⇔ $Tc(CO_3)(OH)_3^-$ + H^+ with $-\log_{10}[H^+]_{1/2} = 8.69 \pm 0.20$; which is consistent with the -8.3 ± 0.6 corresponding hydrolysis constant of the NEA TDB review. 733 ± 44 mV/SHE and 575 ± 60 mV/SHE are measured for the standard potentials of the TcO_4^- / $Tc(CO_3)(OH)_2$,and of the TcO_4^- / $Tc(CO_3)(OH)_3^-$ redox couples respectively. The corresponding formation constants from $TcO(OH)_2$ are $\log_{10}K_{1,2}=19.8\pm0.5$ and $\log_{10}K_{1,3}=10.5\pm0.5$ to be compared with the 19.3 ± 0.3 and 11.0 ± 0.6 values proposed by the NEA TDB review. Note that these values have been converted to the formation reactions describe here, thus the given values are not those of the NEA TDB review. However, $Tc(CO_3)(OH)_2$ is predicted to predominate in a surprisingly large range of chemical conditions. The monomeric character of the Tc(IV) complexes is here checked.

Introduction

In the framework of the management of high-level radioactive wastes, safety assessments require to evaluate the radiotoxicity induced by possible releases of radionuclides into natural aquifers from typically underground repositories. Migration of radionuclides can be limited by their solubilities and interactions with inorganic materials -*i.e.*, via coprecipitation or/and sorption. Conversely it can be increased by complexation with inorganic or organic ligands present in groundwaters.

Technetium-99 (^{99}Tc) is formed with 6.13% yield from ^{235}U fission. With a half-life of 2.13×10^5 years, it is a significant component of long-lived radioactive wastes. It is therefore of concern for both intermediate and high-level waste managements. Many studies focuse both on its transmutation(1) and its disposal in deep geological repositories. In the latter case, physico-chemical conditions are expected to be anoxic, reducing (E_h < -300 mV), and bicarbonate ions impose pH values slightly higher than 7 as typically in the French underground laboratory.(2) The environmental behavior of technetium is controlled primarily by its speciation: under oxic conditions, technetium forms the pertechnetate anion (TcO_4^-), which is predicted to be one of the most mobile radionuclides in the environment. By contrast, under reducing conditions -as typically in deep geological repositories, only poorly soluble Tc(IV) species are expected to form. To validate such an assumption its aqueous speciation has to be confirmed, since Tc(IV) studies in bicarbonate media are rare: to our best knowledge, only two studies have been published.(3;4)

Paquette *et al.*(3) reporte some spectroscopic evidences for the formation of carbonate complexes for both Tc(III) and Tc(IV). They provide further experimental details and information on the behavior of the Tc(IV)/Tc(III) redox couple in bicarbonate solutions at pH = 8. The $[Tc(CO_3)_q(OH)_n]^{4-n-2q}$ and $Tc(CO_3)_q(OH)_{n+1}]^{3-(n+1)-2q}$ species are proposed with n+2q>4, but the exact values of the stoichiometric coefficients (n and q) are not determined. More recently, Eriksen *et al.*(4) have reported the results of a solubility study for $TcO_2.xH_2O(s)$ as a function of pH under various CO_2 partial pressures. They observe an increase of the solubility of $TcO_2.xH_2O(s)$ in the presence of $CO_2(g)$ at a partial pressure up to 1 bar in the pH range 6.26 – 8.56. They interpreted this effect by the formation of two hydroxide-carbonate monomeric complexes $Tc(CO_3)(OH)_2$ and $Tc(CO_3)(OH)_3^-$, and they measure associated thermodynamic data. These species are accepted by the Nuclear Energy Agency review(5) and by Rard *et al.*(6).

Recent studies suggest the formation of polynuclear Tc(IV) complexes in inorganic media,(7;8) while Eriksen's and Paquette's do not consider polymerization. On the other hand, their results are consistent; but there is only a single experimental determination of the stoichiometries and thermodynamic stabilities of such Tc(IV) carbonato-hydroxo-complexes of Tc(IV). This needs confirmation as these thermodynamic data correspond to surprisingly high stabilities for carbonate complexes: from $\log_{10}K = 1.1 \pm 0.3$ selected by the NEA TDB review for equilibrium

$$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \leftrightarrow TcCO_3(OH)_2(aq) \quad (9)$$

We calculate that the $TcCO_3(OH)_2$ carbonate complex would be the Tc(IV) predominating species in the (2.5 ± 0.3) – (10.9 ± 0.4) pH range for carbonic partial pressures (P_{CO_2}) more than $10^{-1.1\pm0.3}$ atm. This is a surprisingly high relative stability: in such chemical conditions hydroxide complexes dominate the carbonate ones for many cations.(5;6;9;10) This stabilization could originate from strong (hence covalent?) bonding of CO_3^{2-} to Tc(IV), which is not specially expected for such an hard (CO_3^{2-}) anionic ligand.

In the present study, we aim at confirming the thermodynamic stabilities of these carbonate complexes of Tc(IV) by means of an independent experimental technique. Electrochemical techniques can very well be used to determine formation constants of technetium complexes.(11-15) Therefore, we here measure the potential of the Tc(VII)/Tc(IV) redox couple in bicarbonate media as a function of the chemical composition of the aqueous solution -H^+, Tc and total carbonate concentrations. In this way, we aim at probing the number of Tc(IV) complexes, their Tc, hydroxide and carbonate stoichiometries, and the associated thermodynamic formation constants. To do this, we use the slope analysis method typically adapted for this kind of study.(10;16;17)

Experimental Section

Safety

Technetium-99 is a radioactive beta emitter (E_{max} = 293 keV). It should be handled in a properly equipped radiochemistry laboratory. The possession and use of radioactive material is subject to statutory controls.

Potentiometry

The electrochemical set-up is the same as that used for coprecipitation experiments(18) *i.e.* three electrodes set-up with pH control. The working electrode and the counter electrode are both platinum rolls with surfaces of 23.6 cm^2 and 18.9 cm^2 respectively. An Ag/AgCl wire immersed in a saturated KCl aqueous solution is used as reference electrode. This electrode is isolated from the working solution by means of a capillary extension filled with a $NaHCO_3$ aqueous solution of same ionic strength as the working solution to minimize the junction potential.

The potential of the Ag/AgCl saturated KCl electrode is 199.0 mV/SHE.(19) It is controlled with an electrochemical buffer: a hexacyanoferrate(III)/hexacyanoferrate(II) aqueous solution with the same ionic strength as the working solutions imposed by $NaHCO_3$. This electrochemical buffering reaction is

$$Fe(CN)_6^{3-} + 1e^- \leftrightarrow Fe(CN)_6^{4-} \qquad \text{Eq.(1)}$$

The potential of this redox buffer is

$$E^{0'} = E^0_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} + E_N\left(7D(I_m) + m_{NaHCO_3}\left(\varepsilon\left(Na+,Fe(CN)_6^{3-}\right) - \varepsilon\left(Na+,Fe(CN)_6^{4-}\right)\right)\right)$$

with $E_{/SHE} \bumpeq 370.4 \pm 0.5$ mV. (20) Eq.(2)

$$E_N = \frac{\ln(10)RT}{F} = 59.16mV$$

at 25℃, R is the molar gas constant, T the thermodynamic temperature and F the Faraday constant

The other terms are originated in the corrections to high ionic strength with the SIT (Specific Interaction Theory) formula, to our knowledge, no values are published for the $\varepsilon(Na^+,Fe(CN)_6^{z-})$ SIT coefficients of Na^+ with the cyanide complexes but the interaction coefficient between K^+ and $Fe(CN)_6^{4-}$ is -0.17±0.03 (5). Moreover, typical values for these coefficients are about -(0.25±0.1) and -(0.26±0.1) kg.mol.$^{-1}$ respectively(21) for anions of charges -3 and -4 respectively as typically tabulated in Ref.(22). From these values we calculate $\Delta\varepsilon = \varepsilon(Na^+,Fe(CN)_6^{3-}) - \varepsilon(Na^+,Fe(CN)_6^{4-}) = +(0.1 \pm 0.1_4)$ kg.mol.$^{-1}$ corresponding to the +(6±8) mV.kg.mol^{-1} correction. For the (0.302 and 1.028 mol.kg^{-1}) highest molal ionic strengths here used, the (+(2±3)mV and +(4±6)mV) corrections are within the uncertainty of the correction itself. For this reason, we neglect this ionic strength correction on the electrode calibration. This induced an error lower than 5 and 10 mV on the potentials given at 0.302 and 1.028 mol.kg^{-1} ionic strengths respectively. However this error cancels out on the interpretations of data at the same ionic strength.

The commercial solution used to control the reference electrode has a redox potential equal to +225mV vs Ag/AgCl system at 25℃ in dilute media corresponding to a $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ ratio equal to 8. Sodium bicarbonate is dissolved in this solution to obtain concentrations of 0.302 and 1.028 $mol.kg^{-1}$. The redox potentials of these solutions are measured giving 260 and 270 mV/Ag-AgCl saturated KCl respectively. This 10mV difference is only partly originated in the ((4±6)-(2±3))=(2±5)mV estimated above from the difference in the activity coefficients of the buffer. The remaining 3 to 8 mV can reflect junction potential or other uncertainties. The potential of the reference electrode is checked once a day. When its potential deviated by more than 5 mV, a new reference electrode is prepared. The carbonate ions are certainly at the origin of this slow alteration of the electrode.

The pH is continuously measured with a Profitrode (ref. 6.0255.100) combined glass electrode commercialized by Metrohm® and connected to a Metrohm® pH-meter. The pH combined glass electrode is calibrated in $-\log_{10}[H^+]$ unit (not in activity) with different $NaHCO_3/Na_2CO_3$ mixtures with same molar ionic strength as the studied solutions: 1 M $NaHCO_3$ ($-\log_{10}[H^+] = 8.27$), 0.2 M $NaHCO_3$ / Na_2CO_3 ($-\log_{10}[H^+] = 10.08$) and 0.25 M Na_2CO_3 ($-\log_{10}[H^+] = 11.78$). The response of the pH electrode is checked once a day.

In this paper, the different potentials are given versus the Ag/AgCl saturated KCl electrode.

Apparatus

Sodium bicarbonate ($NaHCO_3$, >99.5%) and sodium carbonate (Na_2CO_3, ACS reagent, anhydrous, 99.95-100.05% dry basis) from ALDRICH® are used as received. The sodium bicarbonate/carbonate solutions are prepared by dissolving the corresponding salts in degassed MilliQ water (Millipore, 18.2 MΩ.cm).

Technetium-99 is provided as an ammonium pertechnetate (NH_4^+, TcO_4^-) solution by CERCA LERCA AREVA.

The experiments and $-\log_{10}[H+]$ measurements are carried out under anoxic atmosphere ($p(O_2)$ inferior to 5 ppm in volume) in a argon filled glove box (MBraun®, MB-200 with an extension model MB-200 MOD 1250/1000) at room temperature. The experiments are carried out in a hermetically closed glass cell with double walls.

Experimental conditions

1.2×10^{-4} M pertechnetate stock solutions are prepared by diluting 5 mL of 1×10^{-3} M ammonium pertechnetate solution in 45 mL. The Tc(IV) solutions are obtained by reducing this same pertechnetate solution by applying a potential equal to -600 mV/Ref until the appearance of a blue solution, characteristic of Tc(III) carbonate complexes.(3) These complexes are unstable when the reducing potential is no more applied: Tc(III) is oxidized to Tc(IV) in bicarbonate solutions under anoxic conditions. The concentrations of the technetium species are determined or monitored by measuring the UV-visible spectra of the solutions (**Figure 1**) using the absorption bands at 288 nm for TcO_4^-, 512 nm for Tc(IV) and 630 nm for Tc(III).(3) From **Figure 1** and considering the molar extinction coefficients of Tc(VII) (236 $m^2.mol^{-1}$)(23) and Tc(IV) (68 [3] $m^2.mol^{-1}$), the initial Tc(IV) concentration is 1.2×10^{-4} M with less than 2.1×10^{-6} M (1.75%) of Tc(VII) impurities. Consequently, when we use this solution to prepare 0.1 mM Tc(IV) working solutions, the maximal concentration of Tc(VII) is 1.75×10^{-6} M. This concentration is negligible compared to the total aqueous concentration of Tc(VII) added from pertechnetate ammonium solution in $NaHCO_3$. Nevertheless, it is included in the uncertainty calculations.

The above Tc(VII), Tc(IV) and eventually $NaHCO_3$ solutions are used as stock solution to prepare all the working solutions.

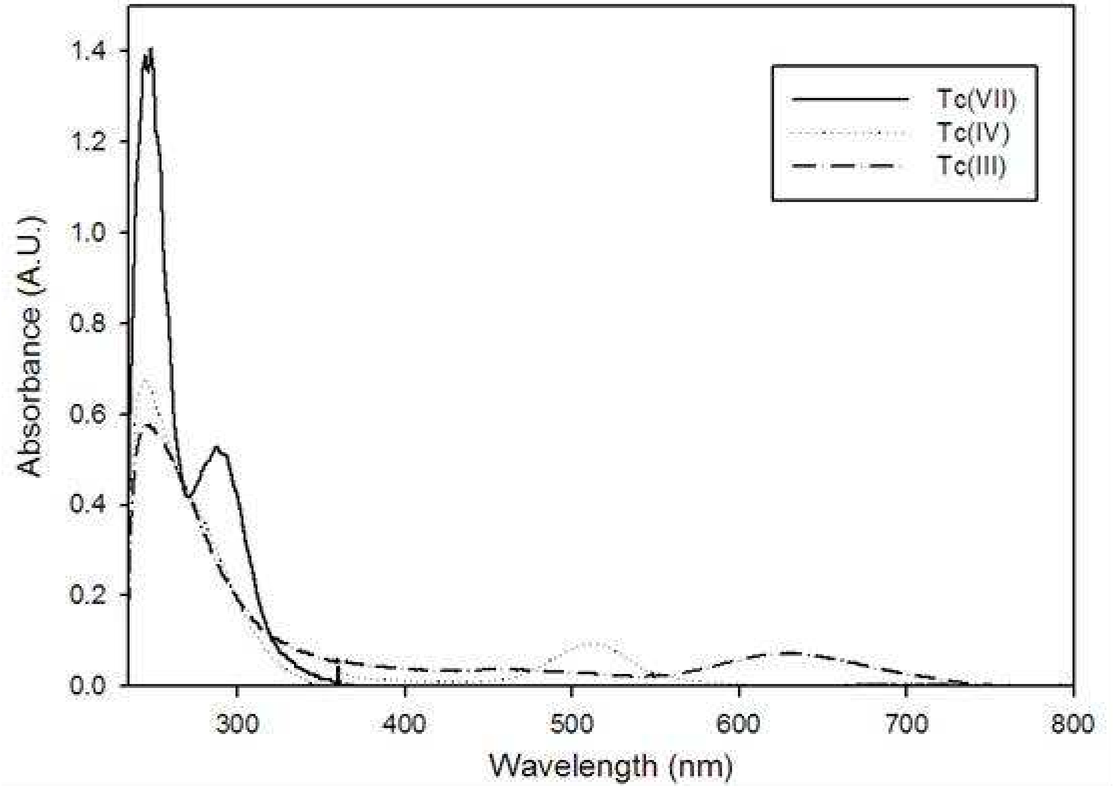

Figure 1. **Ultraviolet - visible absorption spectra**
for TcO_4^- (full line), Tc(IV) (dotted line) and Tc(III) (dashed line),
at $[Tc]_{total} = 3x10^{-4}$ M, $[CO_3]_{total} = 0.7$ M and pH 8.98.

Data Treatment.

Ionic strength corrections

The SIT formula is in molality units.(24) The conversion from molarity ($mol.dm^{-3}$) to molality ($mol.kg^{-1}$) is

$$m_B = \frac{1000c_B}{1000\rho - c_B M} \qquad \text{Eq.(3)}$$

where m_B and c_B are the molarity and the molality of species B respectively. ρ is the density of the solution and M is the molar weight of the solute. In our conditions -different concentrations of $NaHCO_3$ as major species- we deduce the values of the conversion factor from the densities given by Laliberte *et al.*(25).

Equilibria involving $H_2O(l)$ as a reactant or product require a correction for activity of water (a_{H2O}). The electrolyte used to control the ionic strength, $NaHCO_3$, is assumed to be a strong electrolyte when the water activity is calculated from its concentration.

$$\log_{10} a_{H_2O} = \frac{-2m_{NaHCO_3}\Phi}{\ln(10)\times 55.51} \qquad \text{Eq.(4)}$$

where Φ, the osmotic coefficient of the solution, is derived from the SIT formula at 25℃:

$$1-\Phi=\frac{0.5091}{m_{NaHCO_3}(1.5)^3}\left(1+1.5\sqrt{m_{NaHCO_3}}-2\log_{10}\left(1+1.5\sqrt{m_{NaHCO_3}}\right)-\frac{1}{1+1.5\sqrt{m_{NaHCO_3}}}\right)+\frac{1}{\ln(10)}\varepsilon(Na^+,HCO_3^-)m_{NaHCO_3} \quad \text{Eq.(5)}$$

with $\varepsilon(Na^+, HCO_3^-)$, the SIT coefficient obtained from (26). The osmotic coefficient and the associated water activity are extracted from experimental data published by Sarbar et al.(27). The SIT formula for activity coefficients is:

$$\log_{10}\gamma_i=-z_i^2D(I_m)+\sum_j\varepsilon(i,j)m_j \quad \text{Eq.(6)}$$

where z_i is the charge of ion i,

$$D(I_m)=\frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} \quad \text{Eq.(7)}$$

is a Debye-Hückel term at 25℃, and I_m the molal ionic strength. The SIT coefficients for the pair of species i and j are assumed to be equal to zero for neutral species or for ions of same sign. In most cases the summation in Eq.(4) can here be restricted to the major HCO_3^- and Na^+ counter-ions (= j). The values of ε_{ij} used in this work (Table 1) are extracted from the literature, or are estimated by analogy with ions of same charge and similar sizes.(10;17) In that case, the ε_{ij} uncertainties are increased by ±0.05 kg.mol^{-1}.

Table 1. ε_{ij} (kg.mol^{-1}) values used for the SIT formula Eq.(5)

ε_{ij} (kg.mol^{-1})	j=HCO_3^-	j=CO_3^{2-}	j=TcO_4^-	j=$TcCO_3(OH)_3^-$
i=Na^+	0.00±0.02[a]	-0.08±0.03[b]	-0.05±0.05[b]	-0.20[c]
i=H^+	0.07±0.05[b]			

[a]reference(26), [b]reference(5), [c]Determined in the present work (Figure 6)

Solubility of Tc(IV)

Precipitation of TcO_2(s) must be avoided in order to determine the stoichiometries and thermodynamic data of carbonate-technetium complexes. Indeed, when TcO_2(s) precipitates, the redox potential do not depend on the aqueous speciation of Tc(IV) as shown by the

$$TcO_4^- + 3e^- + 4H^+ \leftrightarrow TcO_2.2H_2O \quad \text{Eq.(8)}$$

equilibrium, from which

$$E=E^0_{TcO_4^-/TcO_2}+\frac{E_N}{3}\left(\log_{10}\left(TcO_4^-\right)+4\log_{10}\left(H^+\right)-5D+m_{NaHCO_3}\left(\varepsilon(TcO_4^-,Na^+)+4\varepsilon(HCO_3^-,H^+)\right)\right) \quad \text{Eq.(9)}$$

with E°=746±12 mV. In that case, E is constant at constant pH and ionic strength for various $[TcO_4^-]$.

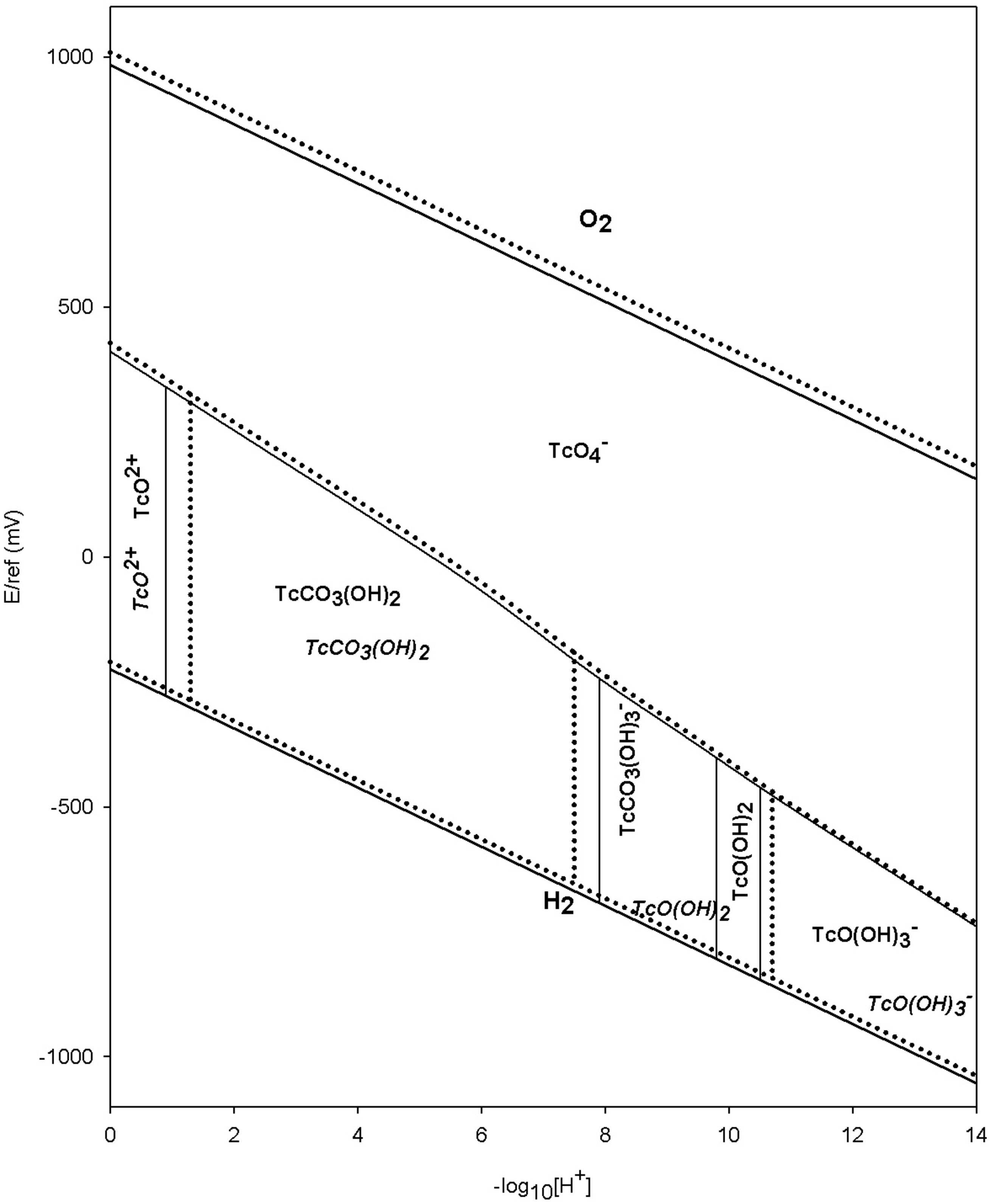

Figure 2. **Tc Pourbaix diagram**
(I = 0, 25℃) for 0.6 M (full line and the associat ed major species are bolded)
and 0.06 M (dotted line and the associated major species are italicized) total carbonate concentrations.

Table 2. Thermochemical data used in the present work (6)

$TcO_4^- + 4H^+ + 3e \leftrightarrow TcO(OH)_2 + H_2O$	$E^0_{TcO_4^-/TcO(OH)_2}$ =579±16 mV
$TcO_4^- + 4H^+ + 3e \leftrightarrow TcO_2.xH_2O + (2-x)H_2O$	$E^0_{TcO_4^-/TcO_2}$ =746±12 mV
$2H^+ + TcO(OH)_2 \leftrightarrow 2H_2O + TcO^{2+}$	$\log_{10}K_1 \lesssim 4$
$H^+ + TcO(OH)_2 \leftrightarrow H_2O + TcO(OH)^+$	$\log_{10}K_2 \cong 2.5 \pm 0.3$
$H_2O + TcO(OH)_2 \leftrightarrow H^+ + TcO(OH)_3^-$	$\log_{10}K_3 \cong -10.9 \pm 0.4$
$TcO_2.1.6H_2O \leftrightarrow TcO(OH)_2 + 0.6H_2O$	$\log_{10}K_s \cong -8.4 \pm 0.5$
$2H^+ + CO_3^{2-} + TcO(OH)_2 \leftrightarrow H_2O + TcCO_3(OH)_2$	$\log_{10}K_4 \cong 19.3 \pm 0.3$
$H^+ + CO_3^{2-} + TcO(OH)_2 \leftrightarrow TcCO_3(OH)_3^-$	$\log_{10}K_5 \cong 11.0 \pm 0.6$
$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$	$\log_{10}K_{a2} \cong -10.329 \pm 0.020$
$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$	$\log_{10}K_{a1} \cong -6.354 \pm 0.020$

Stoichiometry of Tc(IV) in bicarbonate media

The E_h-pH Pourbaix diagram of technetium is plotted (Figure 2) in experimental aqueous conditions closed to ours. This diagram is calculated from thermodynamic data(28) recommended by the OECD-NEA (Organization for Economic Cooperation and Development, Nuclear Energy Agency) review (Table 2) excepted for the TcO_2 precipitation for the reasons explained below. Accordingly, $TcO(OH)_2$ is the Tc(IV) dominating species for $-\log_{10}[H^+] < 10.5$ in aqueous solutions equilibrated at low P_{CO_2} (see Introduction), while hydroxo-carbonate complexes of Tc(IV) are predicted to predominate for $P_{CO_2} > 10^{-1.1\pm0.3}$ atm. The experiments are performed between $-\log_{10}[H^+]$ 7 and 10.

We first verify whether soluble polynuclear species of Tc(IV) can form. In this case, the potential of the solution is:

$$E = E^{0'}_{TcO_4^-/Tc_r} + \frac{E_N}{3}\left(\log_{10}\left[TcO_4^-\right] - \frac{1}{r}\log_{10}\left[Tc_r\right]\right) \qquad \text{Eq.(10)}$$

where $E^{0'}_{TcO_4^-/Tc_r}$ is the standard apparent potential of the Tc(VII)/Tc(IV) redox couple: the plot of E as a function of $\log_{10}$[Tc(IV)] is a straight line with slope $E_N/(3r)$, namely 19.71 and 9.86 mV per $\log_{10}$ unit at 25℃ for r = 1, and 2 respectively.

No significant polynuclear species are evidenced (r=1). We then determine the carbonate contents of the Tc(IV) complexes. The Tc(VII) / Tc(IV) redox equilibrium between the less hydrolyzed species proposed by OECD-NEA is:(5)

$$TcO_4^- + 4H^+ + 3e \leftrightarrow TcO(OH)_2 + H_2O \qquad \text{Eq.(11)}$$

corresponding to

$$\begin{aligned}E &= E^0_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(\log_{10}\frac{[TcO_4^-][H^+]^4}{[TcO(OH)_2]} + \log_{10}\gamma_{TcO_4^-} + 4\log_{10}\gamma_{H^+} - \log_{10} a_{H_2O}\right) \\ &= E'^0_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\log_{10}\frac{[TcO_4^-][H^+]^4}{[TcO(OH)_2]}\end{aligned} \qquad \text{Eq.(12)}$$

where the activity coefficient of neutral $TcO(OH)_2$ has been neglected, $E'^0_{TcO_4^-/TcO(OH)_2}$ is the normal potential. The chemistry of Tc(VII) is simple: pertechnetate ion predominates whatever $-\log[H^+]$ range, while Tc(IV) chemistry is more complicated. It can be hydrolyzed or complexed depending on the acidity and total carbonate concentrations of the solution, we only know [Tc(IV)], the total Tc(IV) concentration. For this, we use the Ringbom coefficients:(29)

$$\begin{aligned}\alpha_{TcO(OH)_2} = \frac{[Tc(IV)]}{[TcO(OH)_2]} &= 1 + K_1[H^+]^2 + K_2[H^+] \\ &+ \frac{K_3}{[H^+]} + \sum_{q,p} K_{p,q}[H^+]^{4-p}[CO_3^{2-}]^q\end{aligned} \qquad \text{Eq.(13)}$$

where $$K^0_{p,q} = K_{p,q}\frac{a^{3-p}_{H_2O}\gamma_{Tc(CO_3)_q(OH)_p^-}}{\gamma^{4-p}_{H^+}\gamma^q_{CO_3^{2-}}}$$

is the thermodynamic constant of equilibrium

$$(4-p)H^+ + TcO(OH)_2 + qCO_3^{2-} \leftrightarrow Tc(CO_3)_q(OH)_p^{4-2q-p} + (3-p)H_2O\,, \qquad \text{Eq.(14)}$$

See Table 2 for the K_i values and their definitions. The terms in Eq.(13) corresponding to TcO^{2+}, $TcO(OH)^+$ and $TcO(OH)_3^-$ can be neglected in our experimental condition. By substituting Eq.(12) into Eq.(13) we obtain:

$$E = E'^0_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(\log_{10}\frac{[TcO_4^-][H^+]^4}{[Tc(IV)]} + \log_{10}\alpha_{TcO(OH)_2}\right) \qquad \text{Eq.(15)}$$

$[CO_3^{2-}]$ in Eq.(13) is calculated from $[CO_3]_T$, measured $\log_{10}[H^+]$ and the Ringbom coefficient.(29)

$$\alpha_{CO_3^{2-}} = \frac{[CO_3]_T}{[CO_3^{2-}]} = 1 + \frac{[H^+]}{K_{a_2}} + \frac{[H^+]^2}{K_{a_1}K_{a_2}} \qquad \text{Eq.(16)}$$

where K_{a1} and K_{a2} are the apparent acidity constants of carbonic acid (Table 2). Our potentiometric measurements correspond to [Tc(VII)]/[Tc(IV)] = 1:

$$\begin{aligned} E &= E'^{0}_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(4\log_{10}\left[H^+\right] + \log_{10}\alpha_{TcO(OH)_2}\right) \\ &= E'^{0}_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(4\log_{10}\left[H^+\right] + \log_{10}\left(1+\sum_{r,q,p} K_{p,q}\left[H^+\right]^{4-p}\left[CO_3^{2-}\right]^{q}\right)\right) \end{aligned} \quad \text{Eq.(17)}$$

We use classical slope analysis to determine the (4-p) and q stoichiometric coefficients from Eq. 17: the idea of this study is to choose the working conditions and total aqueous concentrations of some species at constant ionic strength, in order to determine stoichiometric coefficients. Typically the plot of E as a function of $\log_{10}[i]$ is a straight line of slope directly proportional to the corresponding stoichiometric coefficient. Since there are two unknown stoichiometric coefficients (p,q), two corresponding sets of working conditions are chosen.

When the major Tc(IV) aqueous species is the $Tc(CO_3)_q(OH)_p^{4-2p-q}$ complex, Eq(17) writes:

$$E = E'^{0}_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(\log_{10} K_{r,p,q} + (8-p)\log_{10}[H^+] + q\log_{10}\left[CO_3^{2-}\right]\right) \quad \text{Eq.(18)}$$

One set of measurements aims at determining the carbonate stoichiometry (q), -number of C atoms in the complex- by varying the total aqueous carbonate concentration at constant ionic strength, [H+] and [Tc(VII)]/[Tc(IV)] ratio. For this, we use HCO_3^-/CO_3^{2-} buffer aqueous solutions prepared with weighted amounts of $NaHCO_3$ and $NaCO_3$ salts. These weighted amounts are calculated in order to obtain the target $-\log_{10}[H^+]$ values at 25℃ at the defined ionic strength. The ionic strength is adjusted with weighted amounts of $NaClO_4$ salt taking into account the contributions of the HCO_3^-, CO_3^{2-} Na^+ and ClO_4^- ions. In our experimental conditions, the initial Tc(VII) and Tc(IV) concentrations are high enough to buffer E during each measurement, we indeed obtain stable E measurements and constant [Tc(VII)]/[Tc(IV)] ratio during each measurement. Eq. 18 is rearranged as:

$$E = E_{1,p,q} + \frac{E_N}{3} q\log_{10}\left[CO_3^{2-}\right] \quad \text{Eq.(19)}$$

where $$E_{1,p,q} = E'^{0}_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(\log_{10} K_{p,q} + (8-p)\log_{10}[H^+]\right) \quad \text{Eq.(20)}$$

The plot of E as a function of $\log_{10}[CO_3^{2-}]$ is a straight line with slope $q\frac{E_N}{3}$, which is the way to determine the q parameter. Theoretical values of the $q\frac{E_N}{3}$ slope are 0, +19.72 and +39.44 mV per $\log_{10}$ unit for q = 0, 1 and 2 respectively at 25℃.

In a second set of E measurements the $-\log_{10}[H^+]$ value are varied at constant bicarbonate concentration, [Tc(VII)]/[Tc(IV)] ratio and ionic strength to determine p, the number of hydrolysis of the Tc(IV) complex. Eq. 18 is rearranged as:

$$E = E_{2,p,q} + \frac{E_N}{3}\left((8-p)\log_{10}[H^+] + q\log_{10}[CO_3^{2-}]\right) \qquad \text{Eq.(21)}$$

with

$$E_{2,p,q} = E'^0_{TcO_4^-/TcO(OH)_2} + \frac{E_N}{3}\left(\log_{10} K_{p,q}\right) \qquad \text{Eq.(22)}$$

Slope analysis (Eq. 21) gives (8-p) for $-\log_{10}[H^+] > pKa_2$ where CO_3^{2-} is the major species of carbonate and (7-p) at lower $-\log_{10}[H^+]$ where HCO_3^- predominates. Since q is previously determined (Eq.19), the influence of the -small- variations of pH are taken into account as (E - q $\log_{10}[CO_3^{2-}]$), and slope analysis provides the value of p. The $q\log_{10}[CO_3^{2-}]$ term is not included in the $E_{2,p,q}$ term, since $[CO_3^{2-}]$ is not rigorously constant for the set of measurements due to pH variations.

Of course, we do not obtain the exact theoretical integer values for the stoichiometric coefficients, but straight lines with slopes consistent with these stoichiometric coefficients within the experimental uncertainties. To refine the interpretations we have further fitted the E experimental values with several values for q and p (Eq.17).

Finally, the fitted equilibrium constant and normal potentials are extrapolated to zero ionic strength with the SIT formula in order to compare them with literature data.

Results and discussion

Influence of the concentration of Tc

We first measure E, the redox potential of a series of aqueous solutions varying only [Tc(IV)], the total Tc(IV) concentration: pH, total aqueous carbonate concentration and ($6.02\ 10^{-5}$ M) $[TcO_4^-]$ are kept constant. Plotting E as a function of $\log_{10}[Tc(IV)]_T$ (Figure 2), a straight line is obtained with a slope of -20.3±0.9 mV per $\log_{10}$ unit, which is consistent with the theoretical value of 19.7 mV per $\log_{10}$ unit corresponding to the exchange of 3 electrons between monomeric Tc(VII) and Tc(IV) species at 25℃. It precludes Tc(IV) polymerization –theoretical slope of 9.9 mV per $\log_{10}$ unit for dimerization and less for higher degree of polymerization- and precipitation –theoretical slope of 0 mV per $\log_{10}$ unit. This interpretation of our experimental results is in agreement with the observations of Paquette et *al.*(3), who did not observe any precipitation in their electrochemical studies in bicarbonate media for a Tc(IV) concentration of about 10^{-4} M. Rard et al.(5) explain this behavior of technetium(IV) by the hydration number of $TcO_2.xH_2O$, which modifies technetium(IV) solubility.

This evidences that Tc(IV) is mainly present as monomers under our experimental conditions: 6.02×10^{-5} M TcO_4^-, 1 M carbonate aqueous solutions of pH = 9.07 for [Tc(IV)]t < 10^{-5} M. This corresponds to a technetium stoichiometry r = 1.03±0.09 (Eq.10), where uncertainty is 1.96σ. Therefore, we can conclude that under these experimental conditions, Tc(IV) does not form polynuclear species in significant quantities, which is in agreement with the literature.(3;4) The E value for [Tc(VII)]/[Tc(IV)] = 1 is extrapolated to be $E_{1/2} = -339._6 \pm 5._0$ mV corresponding to the normal potential of the Tc(VII)/Tc(IV) redox couple in these conditions.

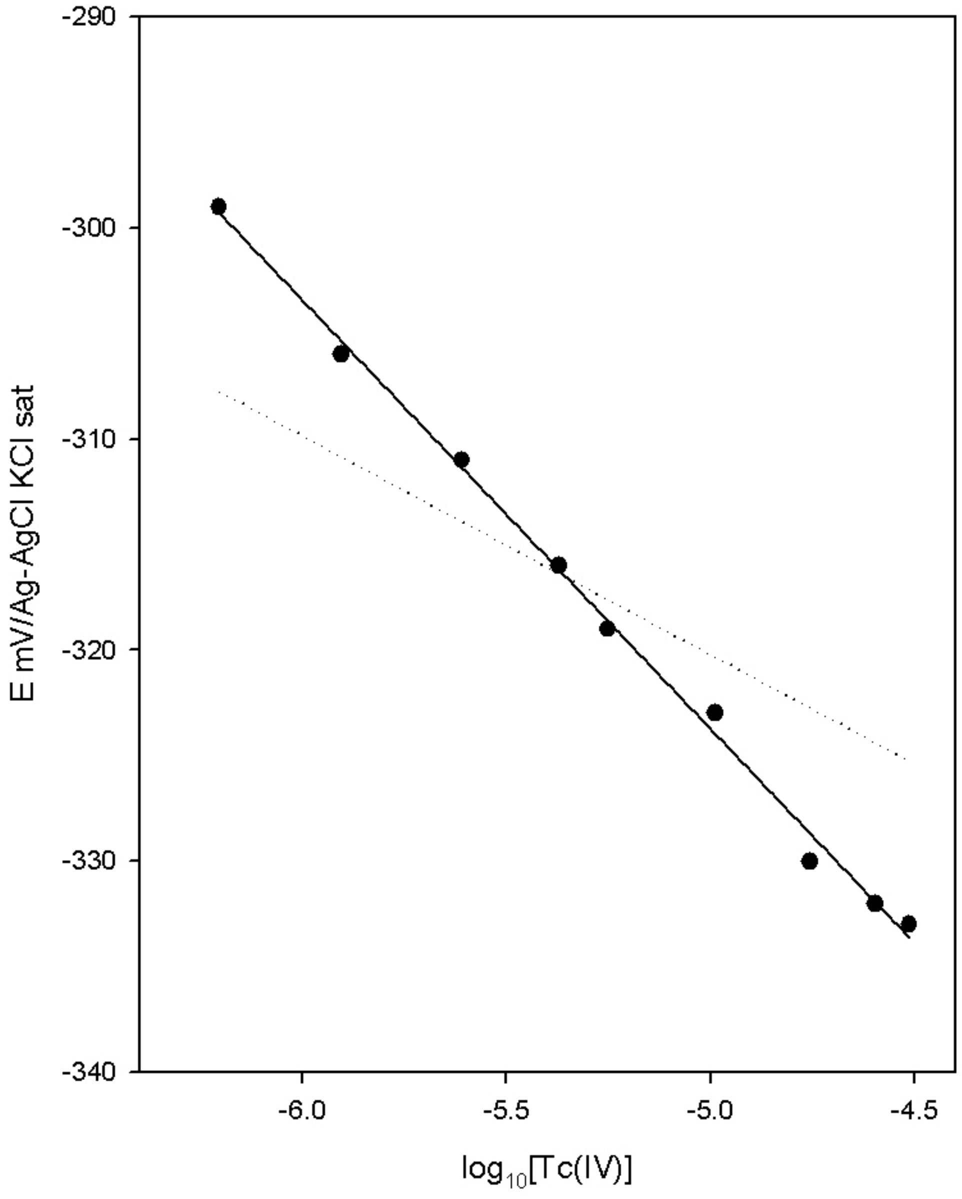

Figure 3. **Influence of the Tc(IV) concentration on the potential of the Tc(VII)/Tc(IV) redox potential** in 6.02×10^{-5} M TcO_4^-, 1 M carbonate aqueous solutions of pH = 9.07 at 25℃.
Theoretical lines are plotted for monomers (solid line) and dimers of Tc(IV) (dotted line).

Stoichiometry of Tc(IV) in bicarbonate media

In another set of measurements, we measure E, the electrochemical potential at $-\log_{10}[H^+]$ = 8.57 with a constant Tc(VII)/Tc(IV) concentration ratio, varying the bicarbonate concentration at constant ionic strength controlled by $NaClO_4$ (Figure 4) to determine q, the stoichiometric coefficient of CO_3^{2-} in the Tc(IV) complex. The plot of E as a function of $\log_{10}[CO_3^{2-}]$ does not give a straight line. This can be explained by changes in the stoichiometries of the Tc(IV) predominating species. As expected from thermochemical data selected by the TDB-NEA review(6) carbonate complexes dissociate into $TcO(OH)_2$ at the lowest carbonate concentrations used in this set of measurements. This is taken into account by considering several $Tc(CO_3)_q(OH)_p^{4-2q-p}$ stoichiometries with q=0-2 The numerical values are in agreement with data selected by Rard *et al.*(5); they are presented as Pourbaix diagram in Figure 2. The carbonate complexes of Tc(IV) dissociate into $TcO(OH)_2$ for a total carbonate concentration

0.06M at pH>7.7. In the Pourbaix diagram, one can notice that a study as a function of $-\log_{10}[H+]$ does not allow to evidence this dissociation. Only a study as a function of total aqueous carbonate evidences this dissociation.

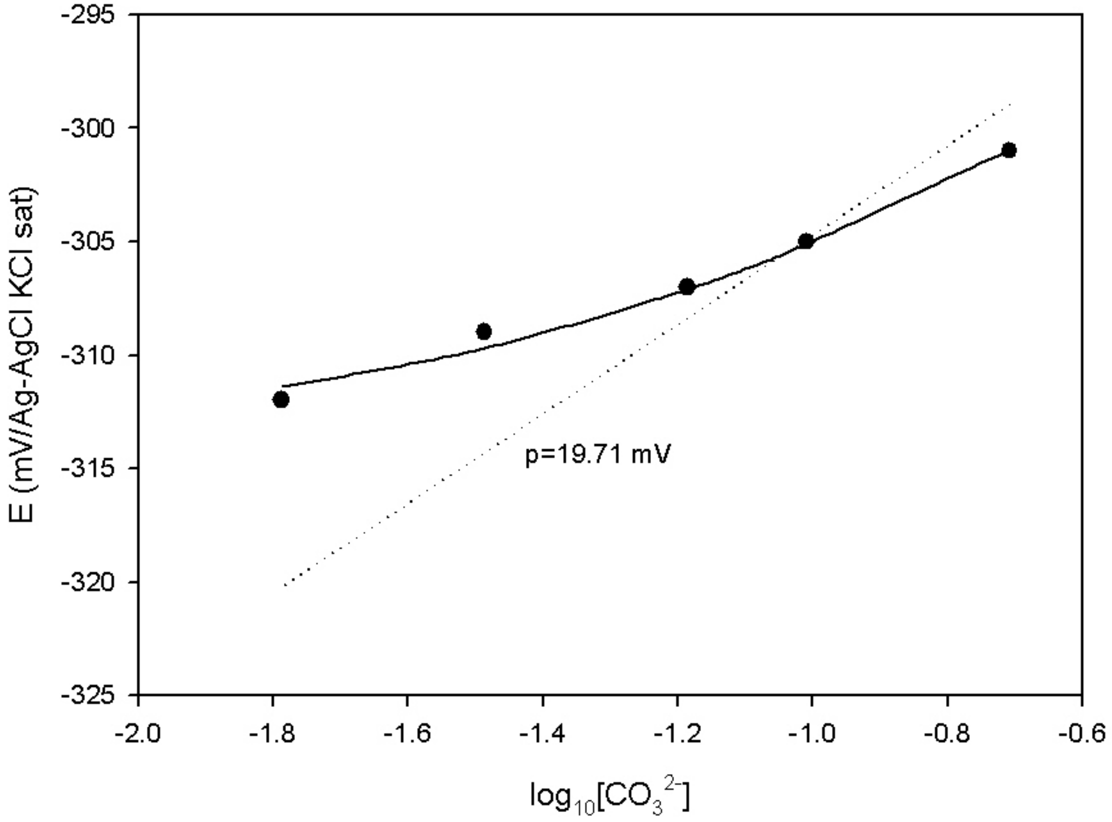

Figure 4. **Influence of the CO_3^{2-} concentration on the potential of the Tc(VII)/Tc(IV) redox potential**

in $1x10^{-4}$ M TcO_4^-, $1x10^{-4}$ M Tc(IV), $NaHCO_3$, Na_2CO_3 buffer solutions ($-\log_{10}[H^+]$ = 8.57±0.10) at 25°C I=1.2M $NaClO_4$: fit considering $TcO(OH)_2$, $TcCO_3(OH)_2$ and $TcCO_3(OH)_3^-$ (solid line), or only the $TcCO_3(OH)_2$ major carbonate species (dashed line) for Tc(IV).

In a last set of measurements, we measure E as a function of $-\log_{10}[H^+]$ to determine p, the stoichiometric coefficient associated with the hydrolysis of Tc(IV). Plotting E as a function of $-\log_{10}[H^+]$ a curve is obtained, which is not exactly a straight line (Figure 5): to model it we introduce two straight lines with the theoretical slopes of 98.6 and 78.8 mV per $-\log_{10}$ unit as a function of pH, corresponding to p = 2 and 3. This evidences that two hydroxo-carbonate complexes of Tc(IV) are formed in the 6.5 to 10.0 $-\log_{10}[H^+]$ range in our experimental conditions: $1x10^{-4}$ M TcO_4^-, $1x10^{-4}$ M Tc(IV) and various total aqueous carbonate aqueous concentrations. We fit $E_{2,1,2/Ref}'^{\circ}=516.6\pm2.3$ mV and $E_{2,1,3/Ref}'^{\circ}=414.5\pm3.6$ mV for the corresponding formal potentials in 0.6 M carbonate aqueous solutions (Eq.22). From these values and from the formal potential of the (337.5 mV/Ref.(5)) $TcO_4^-/TcO(OH)_2$ redox couple we calculate $\log_{10}K_{2,1}=17.7\pm0.5$ and $\log_{10}K_{3,1}=9.1\pm0.5$ for equilibria

$$2H^+ + CO_3^{2-} + TcO(OH)_2 \leftrightarrow H_2O + TcCO_3(OH)_2$$

$$H^+ + CO_3^{2-} + TcO(OH)_2 \leftrightarrow TcCO_3(OH)_3^-$$

in 0.6 M $NaHCO_3$ aqueous solutions. $K_{1,2}$ is extrapolated to zero ionic strength to obtain $\log_{10}K°_{2,1}=19.8\pm0.5$ by using the SIT formula (Eq.6) with estimated SIT coefficients (Table 1), we also deduce the formation constant of $TcCO_3(OH)_3^-$ from our experimental data in 0.3 and 0.7 M $NaHCO_3$ aqueous solutions: $\log_{10}K_{3,1}=9.2\pm0.5$ and 8.8 ± 0.5 respectively. The determinations of $K_{3,1}$ at these three ionic strengths are used for their extrapolation to zero ionic strength: $\log_{10}K°_{1,3}=10.5\pm0.5$ and $\varepsilon(TcCO_3(OH)_3^-,Na^+) = -0.20\pm0.15)$ are obtained. These results are in good agreement with the previous determinations by Eriksen *et al.*(4).

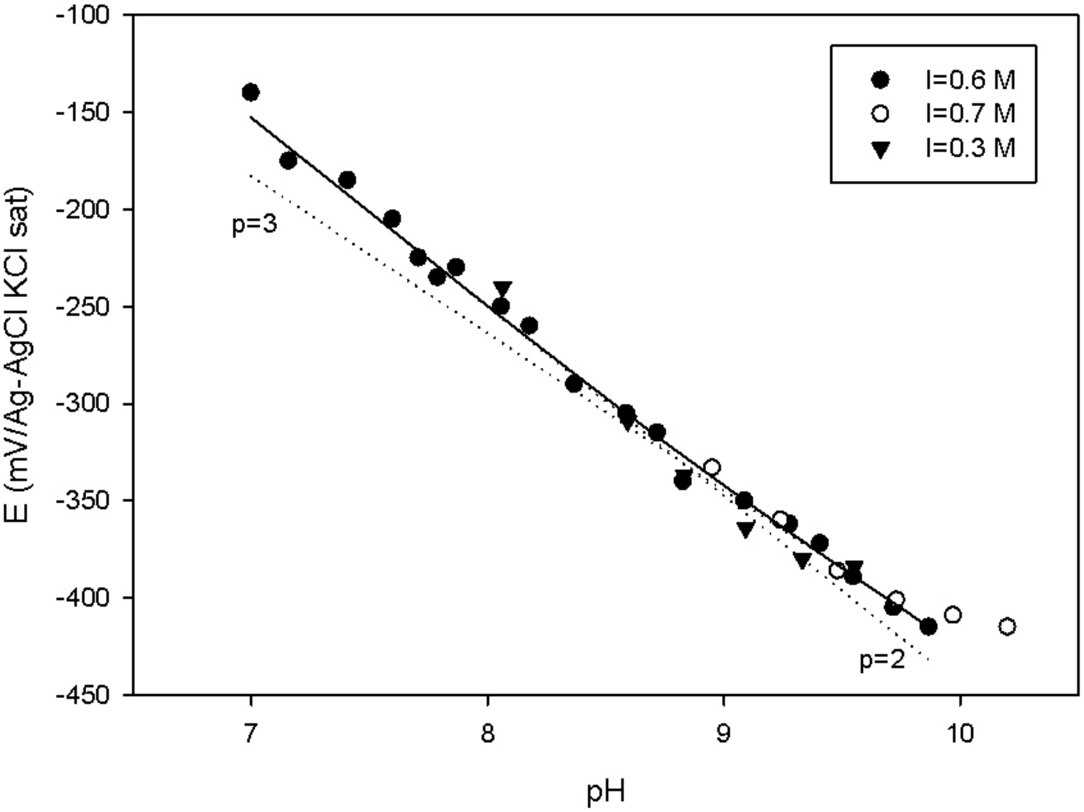

Figure 5. **Influence of the acidity on the potential of Tc(VII)/Tc(IV) redox potential**
at 25℃ for the total aqueous carbonate concentrations written on the figure, 1.10^{-4} M TcO_4^- and 1.10^{-4} M Tc(IV).
The teoreticul E value (full lline, Eq.21) and the contributions of the two $TcCO_3(OH)_p$ Tc(IV) species (doted lines, p=2 and 3) are plotted.

This study is consistent with the formation of the two Tc(IV) complexes already proposed in the literature: $Tc(OH)_2(CO_3)$ and $Tc(OH)_3(CO_3)^-$. Their thermodynamic stabilities are also consistent with previously published results. We conclude that the electrochemical method used here is reliable. We demonstrated that the $Tc(OH)_3(CO_3)^-$ complex is indeed monomeric. This complex predominates at $8 < pH < 10$ in 0.6 M total carbonate aqueous solutions (Figure 1). Tc(IV) is stabilized on acidification, and this stabilization is the same whatever the total carbonate concentration in the chemical conditions used in this studies : all the experimental points fall on a single line for $7 < pH < 10$ and a total carbonate concentration in the 0.3 to 0.7 M range (Figure 5). This result is reproduced by modelling the partial acidifying dissociation of the $Tc(OH)_3(CO_3)^-$ complex into the $Tc(OH)_2(CO_3)$ less hydrolysed complex with the same CO_3/Tc stoichiometry. Quantitative interpretation provided the value of the corresponding equilibrium constant: it confirms the value of 8.3±0.6 (4) selected by the NEA TDB review (5). This confirms the large domain of pH conditions were $Tc(OH)_2(CO_3)$ would predominate as pointed out in Introduction and illustrated Figure 1. Not all this pH domain have been experimentally investigated in the present study: further measurements in such new experimental conditions are required to confirm the proposed $Tc(OH)_2(CO_3)$ stoichiometry, especially its monomeric character.

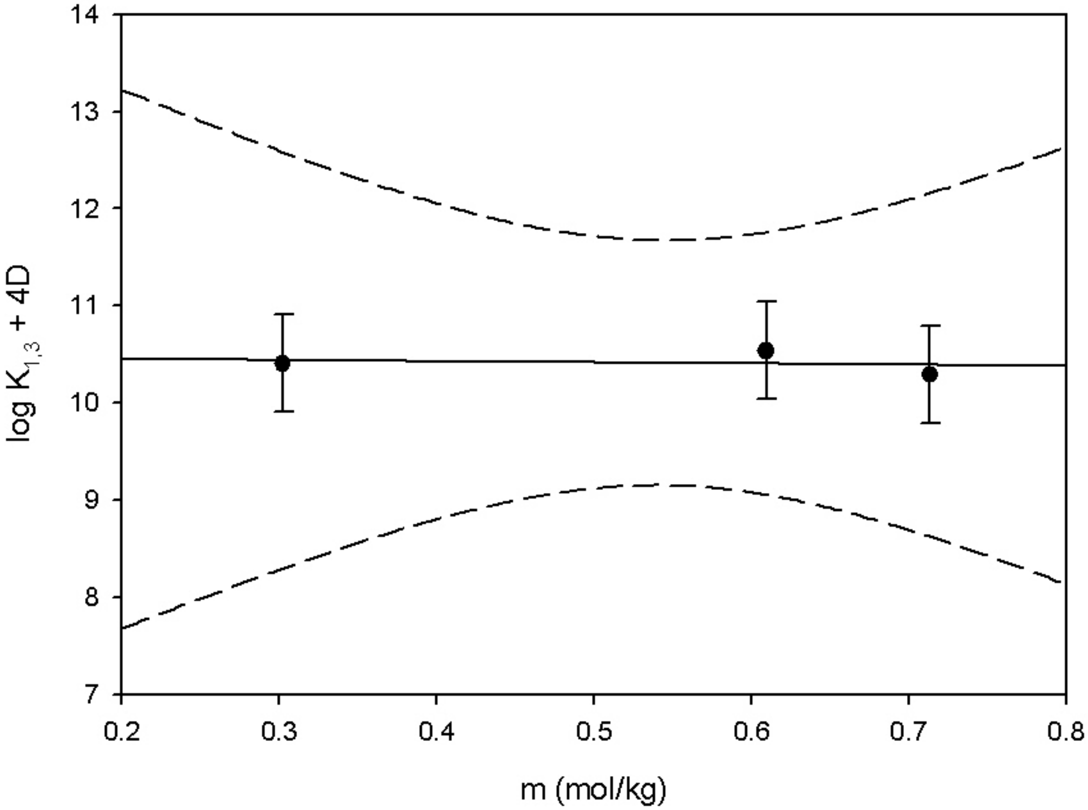

Figure 6. **Extraplation of $\log_{10} K_{1,3}$ to zero ionic strength.**
The dashed lines correspond to the hyperbolic confidence regression.

Tc(IV) carbonate complexes are predicted to predominate in reducing conditions at P_{CO_2} more than about 0.1 atm, which is one order of magnitude higher than usual chemical conditions for deep geological formation studied for the storage of nuclear wastes. Thus Tc(IV) carbonate complexes would not predominate, hence would not significantly increase it solubility (close to 10^{-8} M at these pH values).

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