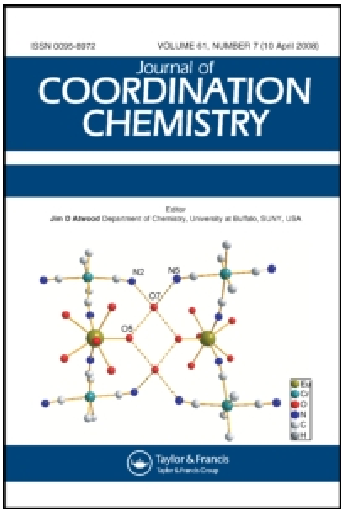

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OXIDATION OF CERIUM(III) IN AQUEOUS CARBONATE SOLUTIONS

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The stoichiometric composition of Cerium(III) and Cerium(IV) carbonato complexes in concentrated aqueous Na_2CO_3 solutions has been investigated by emf measurements based on a junctionless cell. It is found that in the range of carbonate concentration between 2.084 m and 4.00 m, the prevailing species are the tetracarbonato cerium(III) and the esacarbonato cerium(IV) complexes. There is evidence that the large negative charge on the complexes is partially neutralized by Na^+ ions. The above results rest upon an account of activity coefficients (which unavoidably vary by changing carbonate concentration) based on the Specific Interaction Theory.

Keywords: Cerium(III, IV), carbonate, complexes, activity coefficients, stability constants

INTRODUCTION

Perusal of the literature[1] shows that there is general agreement on the stabilization of the tetravalent state of cerium in concentrated aqueous carbonate solutions. For example, in ref. 2, a formal reduction potential of −0.19 V is attributed to the Ce(IV)/Ce(III) couple in 5.5 M K_2CO_3 (to be compared with ~1.8 V in perchloric acid[3]). Dolezal and Novak[4] report that the polarographic oxidation of Ce(III) in 2 M K_2CO_3 proceeds reversibly, producing a well-developed wave with half wave potential of −0.158 V *vs* SCE; they suggest the electrochemical reaction (*1*).

$$Ce(CO_3)_2^- + 3CO_3^{2-} \rightleftarrows Ce(CO_3)_5^{6-} + e \qquad (1)$$

Although there is no doubt that both Ce(III) and Ce(IV) are extensively complexed in carbonate solutions, the actual composition of the complexes is still an open problem; the postulated reaction (*1*) is for instance not consistent with solubility data for $NaCe(CO_3)_2(s)$ in carbonate[5] which show that $Ce(CO_3)_4^{5-}$ largely prevails at CO_3^{2-} concentrations less than 0.7 M. The nature of the composition of the Ce(III) and Ce(IV) carbonato complexes is a problem which challenges present equilibrium analysis methodology. The prime reason for this is that (because of the formation of a number of solid phases) appreciable amounts of cerium can be kept in solution only if the CO_3^{2-} concentration is very large ($\gg$2 m).

Under usual equilibrium analysis conditions, examination of the formal reduction potential of the Ce(IV)/Ce(III) couple at different carbonate levels would unravel the stoichiometry of the electrochemical reaction. In the present case however (because of the large CO_3^{2-} concentrations to be employed) data at different carbonate levels cannot be directly compared unless the unavoidable activity coefficient variations of all species (which arise on changing the carbonate concentration) can be accounted

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for. Changes of the liquid junction potential further complicate the analysis of data based on cells with a junction.

In the present paper the Specific Interaction Theory[6-10] is employed to select experimental conditions under which minimal activity coefficient variations take place over the range of data. Difficulties related to liquid junction potentials are avoided by employing a junctionless cell.

EXPERIMENTAL

Method

The electrochemical reaction shown in (*2*)

$$\begin{aligned}&\mathrm{Ce(IV)(CO_3)}_p\mathrm{(Na)}_x^{(2p-x-4)-} + \mathrm{e} \rightleftarrows \\ &\qquad \mathrm{Ce(III)(CO_3)}_q\mathrm{(Na)}_y^{(2q-y-3)-} + (p-q)\mathrm{CO_3^{2-}} + (x-y)\mathrm{Na^+}\end{aligned} \qquad (2)$$

has been investigated at 25°C by emf measurements based on the junctionless cell (G): $-$GENa/TS/Pt $+$. GENa represents a sodium ion-selective glass membrane electrode, and TS, the test solution, had the following general analytical composition (concentrations are in mol/Kg-water (m)):

$$\begin{aligned}\mathrm{TS} = {} & B(\mathrm{III})\,\mathrm{m\ Ce(III)},\ B(\mathrm{IV})\,\mathrm{m\ Ce(IV)},\ A\,\mathrm{m\ CO_3^{2-}}, \\ & (8.00-2A+3B(\mathrm{III})+4B(\mathrm{IV}))\mathrm{m\ ClO_4^-},\ 8.00\,\mathrm{m\ Na^+}\end{aligned}$$

B(III) and B(IV), the analytical concentrations of Ce(III) and Ce(IV), respectively, assumed values between 5×10^{-4} and 2×10^{-3} m and A, the analytical carbonate concentration, ranged between 2.084 and 4.000 m. The emf, E_g (in mV), of cell (G) can be written as in (*3*) at 25°C,

$$E_g = e_g^0 + 59.16\log(B(\mathrm{IV})/B(\mathrm{III})) \qquad (3)$$

where e_g^0, under the experimental conditions is but a function of A in TS; e_g^0 values, reported in Table I in the form e_g^0 (log$A$) (and which form the basis of subsequent calculations), have been obtained by the procedure described below. An initial solution, TS$_i$, was prepared by mixing weighed amounts of $\mathrm{Ce(ClO_4)_3}$ and $\mathrm{NaClO_4}$ stock solutions (from which $\mathrm{O_2(g)}$ had been excluded by bubbling with $\mathrm{N_2(g)}$) with a suitable weight of $\mathrm{Na_2CO_3(s)}$ under an inert atmosphere. Since it proved impossible to avoid oxidation of small amounts of cerium(III) on mixing, the composition of this initial solution is

$$\begin{aligned}\mathrm{TS_i} = {} & B_i(\mathrm{III})\,\mathrm{m\ Ce(III)},\ B_i(\mathrm{IV})\,\mathrm{m\ Ce(IV)},\ A\,\mathrm{m\ CO_3^{2-}} \\ & (8.00-2A+3B_i(\mathrm{III})+4B_i(\mathrm{IV}))\,\mathrm{m\ ClO_4^-},\ 8.00\,\mathrm{m\ Na^+}\end{aligned}$$

(although the sum $B_i(\mathrm{III}) + B_i(\mathrm{IV})$ was accurately known from the preparation, neither B_i(III) nor B_i(IV) was exactly known; however $B_i(\mathrm{III}) \gg B_i(\mathrm{IV})$). A weighed amount of TS$_i$ was poured into the titration vessel of cell (G) and Ce(IV) generated stepwise in the solution by passing an accurately known current (for an accurately known time) through the circuit shown.

$$-\mathrm{Hg}/0.1\ \mathrm{m}\ \mathrm{Hg(ClO_4)_2},\ 7.8\ \mathrm{m}\ \mathrm{NaClO_4}/8.00\ \mathrm{m}\ \mathrm{NaClO_4}/\mathrm{TS}/\mathrm{Pt(net)}\ +$$

After each electrolysis step the emf of cell (G) was recorded. By indicating (ω_s) the total number of μF passed after s electrolysis steps, (*3*) can be rewritten in the abridged form (*4*)

$$e_g^\circ = E_g - 59.16\log((\omega(\mathrm{IV}) + \omega_s)/(\omega - \omega(\mathrm{IV}) - \omega_s)) \qquad (4)$$

in which ω is the number of micromoles of cerium(III + IV) and ω(IV) the number of micromoles of Ce(IV) in $\mathrm{TS_i}$. The right hand side of (*4*) is readily evaluated for an assumed value of ω(IV) as a function of s. If Ce(III) is oxidized to Ce(IV) with 100% current efficiency, then a value of ω(IV) is found which makes the right hand side of (*4*) independent of s. It was found that this is actually the case if the electrolysis current does not exceed ~0.01 mA $\mathrm{cm^{-2}}$

TABLE I

Summary of the experimental data for e_g° (see (*3*)) as a function of the analytical carbonate concentration, *A*. Uncertainty of e_g° is ±0.25 mV;

$-e_g^\circ$(logA):	413.9(0.602)	414.5(0.595)	415.5(0.581)
416.3(0.568)	417.0(0.555)	417.6(0.542)	418.1(0.530)
418.8(0.512)	419.3(0.495)	419.8(0.479)	420.1(0.463)
420.4(0.448)	420.7(0.433)	420.9(0.419)	421.0(0.405)
421.1(0.391)	421.2(0.378)	421.3(0.366)	421.3(0.354)
421.3(0.354)	421.3(0.342)	421.3(0.330)	421.4(0.319)

This procedure also verifies the accuracy of ω. e_g° values resulted constant to within ±0.25 mv. The ratio ω(IV)/ω was typically ~0.06 indicating that ~6% of the total cerium was oxidized on mixing. It is well known that the internal potential of the sodium-selective glass electrode may change with time, particularly if the electrode is exposed to temperature, mechanical or chemical shock. Changes in internal potential of the glass electrode would make the data in Table I inconsistent. It proved however possible by careful handling to keep the internal potential constant within the uncertainty of e_g° (the electrode was kept in a thermostatted 4.00 m $\mathrm{Na_2CO_3}$ solution between experiments). This was verified by measuring the emf of cell (H) after each titration.

$$-\mathrm{Ag,AgBr(s)}/4.00\ \mathrm{m}\ \mathrm{Na_2CO_3},\ 0.100\ \mathrm{m}\ \mathrm{NaBr}/\mathrm{GENa}+ \qquad \mathrm{(H)}$$

Materials and analysis

Sodium perchlorate stock solutions were prepared and analyzed as described elsewhere.[11] $\mathrm{Ce(ClO_4)_3}$ stock solutions were prepared and analyzed according to ref. 12. $\mathrm{Na_2CO_3(s)}$ (Merck p.a.) was recrystallized from water.

Measurements

All experiments were performed in a thermostatted oil bath (25 ± 0.05°C). Emf measurements were carried out with a precision of 0.01 mV by using a computerized data acquisition apparatus based on Hewlett-Packard components. Metrohm $\mathrm{Na^+}$-selective glass membrane electrodes have been employed. A nitrogen stream was passed through the TS during the coulometric titration in order to avoid Ce(III) oxidation by atmospheric oxygen; the N_2(g) stream was freed from oxidizing impurities by passing it through a chromium(II) solution and saturated with water vapour using A m $Na_2CO_3-(8.0-2A)$ m $NaClO_4$ solution.

RESULTS AND DISCUSSION

It is true that activity coefficients of all species in the TS vary while the analytical composition of the solution is changed as can be deduced (for instance) from the Specific Interaction Theory.[6-10] Equation (*5*) gives the activity coefficient of j,γ_j° (molal scale, infinite dilution reference state), as a function of the ionic environment, where

$$\log \gamma_j^\circ = -z_j^2 D(I) + \sum_k \varepsilon(\mathrm{j,k},I)\mathrm{m_k} \qquad (5)$$

z_j represents the arithmetic charge on ion j, I(mol/Kg) is the ionic strength (in TS the ionic strength is variable: $I = 8.00 + A$), $D(I)$ is the Debye term $0.5107\sqrt{I}/(1 + 1.5\sqrt{I})$ at 25°C, and $\varepsilon(\mathrm{j,k},I)$ is the interaction coefficient between ion j and ion k present in the solution at molality $\mathrm{m_k}$ (notice that ε is in general a function of I and the summation extends only over species k bearing charges of opposite sign to j since interaction coefficients between ions of the same charge sign are postulated to be equal to zero). By applying (*5*) to the TS it is seen that activity coefficients of all ions change because of variation of the Debye term. In addition, activity coefficients of negatively charged species may be affected by variations of their interaction coefficient with Na^+ (in this case only $\mathrm{m_k} = \mathrm{m_{Na^+}}$ appears under the summation). This effect should however not be dramatic because ε is in general a slowly varying function of I. The largest variations are expected for the activity coefficients of positive ions (*i.e.* Na^+) because of the large changes in $\mathrm{m_{CO_3^{2-}}}$ and $\mathrm{m_{ClO_4^-}}$ appearing under the summation. The immediate outcome of the drastic variation of the Na^+ activity coefficient is that the potential of the sodium ion-selective glass electrode (which is used as an internal reference in cell (G)) is not constant despite the constant Na^+ concentration in TS; e_g° values must then be recomputed to the same reference potential before interpretation is attempted. Furthermore, it is not correct in the present case to ignore the fact (as is common practice under usual equilibrium analysis conditions) that medium ions (*i.e.* Na^+, ClO_4^-) may participate in the complex formation. This is the reason for sodium ions appearing in the general electrochemical reaction (*2*). In principle one should also consider perchlorate ions in the general complex formation reaction. This has however been excluded *a priori.* It is also assumed that no appreciable amounts of mixed OH^-–CO_3^{2-} species are formed. The above assumptions can be justified under the present experimental conditions on the basis of the strength of the cerium-carbonate bond, the large excess of CO_3^{2-} over OH^- and the presumably negative charge of the prevailing complexes.

As will become apparent later, it is convenient to set the reference state of all species in TS in such a way that activities approach molar concentrations when the composition of the solution approaches 4.00 m in Na_2CO_3. The molal activity coefficient of j on this activity scale is γ_j. Equations (*6*)–(*9*), derived from (*5*), then apply, where

$$\log \gamma_{Na^+} = -\Delta D - [2\varepsilon(Na^+, ClO_4^-, I) - \varepsilon(Na^+, CO_3^{2-}, I)]A \\ + [2\varepsilon(Na^+, ClO_4^-, 12) - \varepsilon(Na^+, CO_3^{2-}, 12)]4 \qquad (6)$$

$$\log \gamma_A = -4\Delta D + [\varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-}, I) - \varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-}, 12)]8 \tag{7}$$

$$\log \gamma_{px} \simeq -(2p - x - 4)^2 \Delta D \tag{8}$$

$$\log \gamma_{qy} \simeq -(2q - y - 3)^2 \Delta D \tag{9}$$

$\Delta D = D(I) - D(12)$, γ_A is the activity coefficient of CO_3^{2-}, and γ_{px} and γ_{qy} represent the activity coefficients of $\mathrm{Ce(IV)(CO_3)}_p\mathrm{(Na)}_x$ and $\mathrm{Ce(III)(CO_3)}_q\mathrm{(Na)}_y$ whose charges are $(2p - x - 4)-$ and $(2q - y - 3)-$ respectively. Expressions (*8*) and (*9*) are only approximate, but not in a measure that changes the following discussion. The interaction coefficients appearing in (*6*) and (*7*) have been evaluated, in a separate set of experiments, by measuring the emf of the cell (L)

$$-\mathrm{Ag, AgBr(s)/T/GENa} + \tag{L}$$

in which T had the analytical composition

$$\mathrm{T} = 0.100\,\mathrm{m\,Br}^-,\ A_t\,\mathrm{m\,CO}_3^{2-},\ (8.00 - 2A_t)\,\mathrm{m\,ClO}_4^-,\ 8.10\,\mathrm{m\,Na}^+$$

and A_t spanned the range 2.00–4.00 m. The emf (E_l in mV) of cell (L) can be expressed by equation (*10*).

$$E_l = e_l^\circ + 59.16 \log \gamma_{\mathrm{Na}^+} + 59.16 \log \gamma_{\mathrm{Br}^-} \tag{10}$$

By developing γ_{Na^+} and γ_{Br^-} according to the SIT, (*11*) is obtained,

$$\begin{aligned}(E_l - E_l^\circ)/59.16 + 2(D(I) - D(12)) &= 2\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4^-, 12) - \varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-}, 12) \\ &\quad - [2\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4^-, I) - \varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-}, I)]A_t\end{aligned} \tag{11}$$

in which $E_l^\circ = e_l^\circ + 59.16 \cdot 2\,\varepsilon(\mathrm{Na}^+, \mathrm{Br}^-)m_{\mathrm{Br}^-}$ (notice that $\varepsilon(\mathrm{Na}^+, \mathrm{Br}^-)$ has been taken to be independent of I (see ref. 10)). E_l° is determined by taking $E_l^\circ = E_l + 2 \cdot 59.16(D(I) - D(12))$ when $A_t = 4.00$ m. The left hand side member of (*11*) is plotted *vs* A_t in Figure 1. It is apparent that $[2\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4^-, I) - \varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-}, I)]$ is, to a very good approximation, independent of I under the present conditions. From the slope of the line we obtain (*12*).

$$2\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4^-, I) - \varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-}, I) = 0.083 \pm 0.01\ \mathrm{Kg/mol} \tag{12}$$

It could be argued[10] that interaction coefficients between non-associating ions are independent of the ionic strength (*i.e.*, $\varepsilon(\mathrm{Na}^+, \mathrm{ClO}_4^-)$ is constant); (*12*) then implies that $\varepsilon(\mathrm{Na}^+, \mathrm{CO}_3^{2-})$ may be regarded as independent of I under the experimental conditions prevailing in this study. The above result makes the last term in (7) negligible (*i.e.*, variations of γ_A are readily evaluated from the variation of the Debye term). The expression (*13*) allow data in Table I to be recalculated to a common reference.

$$E_g^\circ = e_g^\circ + 59.16 \log \gamma_{\mathrm{Na}^+} = e_g^\circ + 59.16[-\Delta D + 0.083(4 - A)] \tag{13}$$

Figure 2 shows E_g° *vs* the carbonate concentration profile.

In the following section the analytical carbonate concentration, A, is used in place

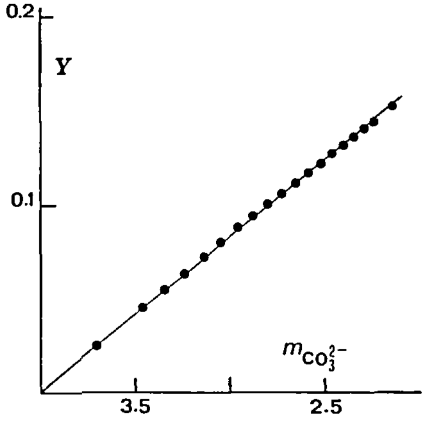

FIGURE 1 Y (the left hand side of (*11*)) *vs* the carbonate concentration profile. The slope of the line is $[2\varepsilon(Na^+,ClO_4^-) - \varepsilon(Na^+,CO_3^{2-})] = 0.083$ Kg/mol.

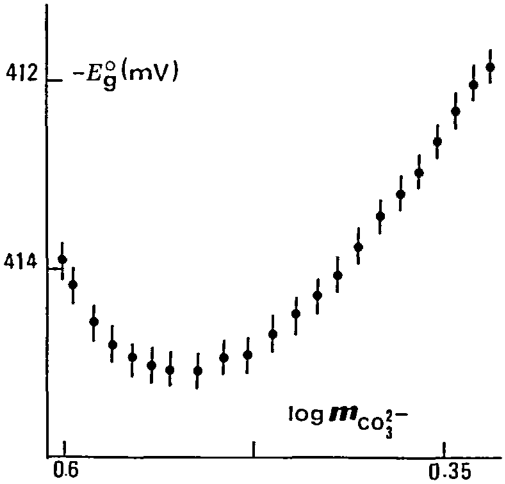

FIGURE 2 E_g^o (calculated from data in Table I via (*13*)) *vs* carbonate concentration.

of its equilibrium concentration; due to the large excess of CO_3^{2-} over other species in the TS, no appreciable error is introduced by this procedure.

Evaluation of the prevailing $(p-q)$ and $(x-y)$ values

The Nernst equation for the cell (G) can be written in the form (*14*)

$$E_g = \bar{E}_g^o + 59.16\log(B(IV)/B(III)) + 59.16\log(m_{px}/B(IV)) - 59.16\log(m_{qy}/B(III)) + 59.16\log(\gamma_{px}/\gamma_{qy}) - 59.16(p-q)\log(A\gamma_A) - 59.16(x-y+1)\log\gamma_{Na^+} \qquad (14)$$

in which $\bar{E}_g^o$ is a constant (independent of A) which also includes the constant sodium concentration term, and m_{px} and m_{qy} stand for the molal concentrations of Ce(IV)-

$(CO_3)_p(Na)_x$ and $Ce(III)(CO_3)_q(Na)_y$. By comparing (*14*) with (*13*) and (*3*), (*15*) results,

$$E_g^o = \bar{E}_g^o + 59.16\log(m_{px}/B(IV)) - 59.16\log(m_{qy}/B(III)) - 59.16(p-q)\,[\log(A\gamma_A) + (x-y)(p-q)^{-1}\log\gamma_{Na^+}] + 59.16[(2q-y-3)^2 - (2p-x-4)^2]\Delta D \qquad (15)$$

where (*8*) and (*9*) have been employed. Use of (*15*) to deduce the relevant $(p-q)$ and $(x-y)$ values requires some strategy. The last term in (*15*) cannot at present be evaluated since the charges on the complexes are unknown. Note that $59.16\,\Delta D$ spans the range 0– ~0.25 mV in this investigation so that depending on the charges of the complexes the last term of (*15*) may become fairly large; nevertheless, as a first approach (to be verified), we assume it to be negligible. The ratios $m_{px}/B(IV)$ and $m_{qy}/B(III)$ may depend on the composition of the solution; this would be the case if more than one Ce(III) and one Ce(IV) species is formed. However, the large CO_3^{2-} and Na^+ concentrations employed here (which are troublesome from a number of points of view) are in fact favourable since high ligand concentrations (with large ligand to metal ratios) are expected to reduce the number of coexisting species. This is especially true for strong complexes since one can confidently assume that the limiting species largely prevails. According to this principle we predict that $m_{px} \simeq B(IV)$ and $m_{qy} \simeq B(III)$. Plots of E_g^o *vs* $(\log A + \log\gamma_A + (x-y)(p-q)^{-1}\log\gamma_{Na^+})$ are now constructed for assumed values of the $(x-y)/(p-q)$ ratio (note that possible values of this ratio are limited); if the above conjectures are not too much in error, one of these plots (the one constructed with the prevailing $(x-y)/(p-q)$ ratio) should approach a straight line of slope $-59.16(p-q)$. It is found that the plot constructed using $(x-y)/(p-q) = 1.5$ (Fig. 3) closely approaches a straight line of slope -2×59.16 mV, while other plots exhibit strong curvatures. Figure 2 is in fact the plot for $(x-y)/(p-q) = 0$. The above analysis indicates that $(p-q) = 2$ and $(x-y) = 3$ in the prevailing electrochemical reaction; this result also implies that the Ce(III) and Ce(IV) carbonato complexes have the same charge so that the last term in (*15*) equals zero and thus no further elaboration of the data is needed.

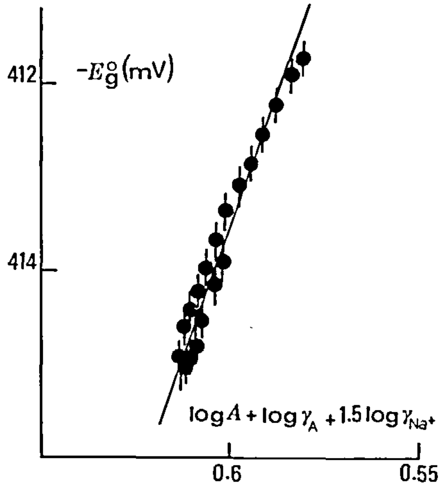

FIGURE 3 E_g^o (as in Fig. 2) as a function of $[\log A + \log\gamma_A + 1.5\log\gamma_{Na^+}]$. The drawn line has slope -2×59.16 mV. *A* represents the carbonate concentration (see (*15*)).

Evaluation of the prevailing p and q values

The equilibrium constant (K_5) for reaction (*16*)

$$\mathrm{Ce(III)(CO_3)_4^{5-} + CO_3^{2-} \rightleftarrows Ce(III)(CO_3)_5^{7-}} \qquad (16)$$

does not exceed ~0.2 m^{-1} in 3 M $NaClO_4$. This is deduced from a previous investigation of the solubility of $NaCe(CO_3)_2(s)$ in carbonate.[5] No appreciable amounts of $Ce(III)(CO_3)_5^{7-}$ were formed although $[CO_3^{2-}]$ reached about 0.7 M. If one now assumes that the pentacarbonato species is formed over the range of carbonate concentrations spanned in this investigation, then it is easily seen (on the basis of the above upper limit of K_5) that comparable concentrations of the tetracarbonato complex should be simultaneously present. This contrasts with the evidence here produced of a single Ce(III) complex being largely present. To a high degree of confidence, one can conclude that under the conditions of the present investigation the species with $q = 4$ prevails. Finally, we propose the following stoichiometry, (*17*), for the general electrochemical reaction (*2*).

$$\mathrm{Ce(IV)(CO_3)_6(Na)_x^{(8-x)} + e \rightleftarrows Ce(III)(CO_3)_4(Na)_{x-3}^{(8-x)-} + 2CO_3^{2-} + 3Na^+} \qquad (17)$$

Formal reduction potentials of the Ce(IV)/Ce(III) couple

E_g° values evaluated from Table I *via* (*13*) and plotted in Figure 2 are formal reduction potentials of the Ce(IV)/Ce(III) couple in the TS expressed on an arbitrary scale for which the potential of our sodium ion-selective glass electrode, immersed in 4.00 m Na_2CO_3, has been taken to be equal to zero. In order to derive formal reduction potentials ($E^f_{\mathrm{Ce(IV)/Ce(III)}}$) on the standard NHE scale, the potential of our arbitrary reference *vs* NHE has been evaluated. This has been done by combining the emf of cell (H) with an estimated value of 97.4 mV (*vs* NHE) for the potential of the AgBr(s)/Ag couple in 4.00 m Na_2CO_3 – 0.100 m NaBr. Equation (*18*) then applies.

$$(18) \qquad E^f_{\mathrm{Ce(IV)/Ce(III)}} = E_g^\circ + 391.4\,\mathrm{mV}$$

The following relation holds between the formal potential in 4.00 m Na_2CO_3 (−22.5 mV) and the standard reduction potential of the Ce^{4+}/Ce^{3+} couple ($E^\circ_{\mathrm{standard}}$), (*19*),

$$E^f_{\mathrm{Ce(IV)/Ce(III)}} = -230.7 + E^\circ_{\mathrm{standard}} - 59.16\log(\beta_6/\beta_4) + 59.16\log(\gamma_4^\circ/\gamma_3^\circ) \qquad (19)$$

in which γ_4° and γ_3° represent the molal activity coefficients of Ce^{4+} and Ce^{3+} ions, respectively (infinite dilution activity scale), and β_6 and β_4 are the molal formation constants of $Ce(IV)(CO_3)_6(Na)_x$ and $Ce(III)(CO_3)_4(Na)_{x-3}$ in 4.00 m Na_2CO_3. We also have taken $59.16(2\log A + 3\log m_{\mathrm{Na^+}}) = 230.7$ mV. Equation (*19*) can be employed to obtain an estimate of the β_6/β_4 ratio. The activity coefficients in (*19*) can be expressed, according to the SIT, by (*20*) and (*21*). We have not been able to

$$\log\gamma_4^\circ = -16D(12) + \varepsilon(\mathrm{Ce}^{4+},\mathrm{CO}_3^{2-},12)4.00 \qquad (20)$$

$$\log\gamma_3^\circ = -9D(12) + \varepsilon(\mathrm{Ce}^{3+},\mathrm{CO}_3^{2-},12)4.00 \qquad (21)$$

evaluate the interaction coefficients of Ce^{4+} and Ce^{3+} with carbonate. However, for the present discussion, $\varepsilon(\mathrm{Ce}^{3+},\mathrm{CO}_3^{2-},12) \simeq \varepsilon(\mathrm{Ce}^{4+},\mathrm{CO}_3^{2-},12)$ should be a fair approximation, thus $59.16\log(\gamma_4^\circ/\gamma_3^\circ) \simeq -7\cdot 59.16D(12) = -118$ mV. $E^\circ_{\mathrm{standard}}$ should not be far from 1.81 V.[3] Finally, we obtain $\log(\beta_6/\beta_4) \simeq 25$. There is little doubt that in $\mathrm{Ce(III)(CO_3)_4^{5-}}$ two carbonates are bidentate and two are monodentate (see ref. 5); in fact the first two stepwise formation constants are $\sim 10^6$ M^{-1} while the other two drop to about 10 M^{-1}. On the other hand, Golovnya *et al.*[13] have prepared a number of solid Ce(IV) carbonato complexes including $\mathrm{(NH_4)_2[Co(NH_3)_6]_2[Ce(IV)(CO_3)_6]\cdot 4H_2O)}$, and maintain that their syntheses are explained by assuming a coordination number of eight for Ce(IV) in its carbonato complexes. An obvious corollary is that only two carbonates are bidentate in the esacarbonato Ce(IV) complex. The enormous β_6/β_4 ratio can only be explained by postulating a very great difference in the stability of the Ce(IV)–CO_3^{2-} (bidentate) and Ce(III)–CO_3^{2-} (bidentate) bonds. This is in substantial agreement with the fact (as we have often observed) that the strength of the metal–CO_3^{2-}(bidentate) bond increases in a measure comparable to the increase in the strength of the metal–OH^- bond. Application of this rule-of-thumb predicts a Ce(IV)–CO_3^{2-} (bidentate) bond $\sim 10^{11}$ times stronger than the Ce(III)–CO_3^{2-} (bidentate) bond, and this factor is large enough to justify the above conjecture.

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