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Studies on Metal Carbonate Equilibria. 5. The Cerium(III) Carbonate Complexes in Aqueous Perchlorate Media

DIEGO FERRI,* INGMAR GRENTHE, SIRKKA HIETANEN and
FRANCESCO SALVATORE *

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

The complex formation equilibria were studied by solubility measurements at 25 °C in a 3 M $Na(ClO_4)$ ionic medium. Two different solid phases were used, $Ce_2(CO_3)_3 \cdot 8H_2O$ which is the thermodynamically stable phase at $[CO_3^{2-}] < 10^{-4.8}$ M, and $NaCe(CO_3)_2 \cdot 2H_2O$ which is stable at $[CO_3^{2-}] > 10^{-4.8}$ M. The solubility of $Ce_2(CO_3)_3(s)$ was measured as a function of $[H^+]$ in solutions with $[H^+] > 10^{-8}$ M saturated with CO_2 or mixtures of CO_2-H_2.

The solubility data were explained by assuming the following equilibria

$Ce_2(CO_3)_3(s) + 6H^+ \rightleftarrows 2Ce^{3+} + 3CO_2(g) + 3H_2O$
$\log K_{s,I} = 21.80 \pm 0.05$

$Ce^{3+} + H_2O + CO_2(g) \rightleftarrows CeCO_3^+ + 2H^+$
$\log \beta_{2,1} = -11.30 \pm 0.05$

$Ce^{3+} + 2H_2O + 2CO_2(g) \rightleftarrows Ce(CO_3)_2^- + 4H^+$
$\log \beta_{4,2} = -24.1 \pm 0.1$

The solubility of $NaCe(CO_3)_2 \cdot 2H_2O$ was measured in Na_2CO_3 solutions with $[H^+] < 10^{-8}$ M as a function of $[CO_3^{2-}]$.

The data were explained with the following equilibria

$NaCe(CO_3)_2(s) \rightleftarrows Ce^{3+} + Na^+ + 2CO_3^{2-}$
$\log K_{s,II} = -17.5 \pm 0.1$

$Ce^{3+} + 3CO_3^{2-} \rightleftarrows Ce(CO_3)_3^{3-}$
$\log \beta_3 = 12.6 \pm 0.2$

$Ce^{3+} + 4CO_3^{2-} \rightleftarrows Ce(CO_3)_4^{5-}$
$\log \beta_4 = 13.7 \pm 0.1$

No evidence was found for the formation of mixed species.

A short review of thermodynamic data for complex formation reactions in lanthanoid(III)$-CO_3^{2-}-H_2O$ systems was given in part 3 of this series,[1] where an emf study of the La(III)$-CO_3^{2-}-H_2O$ system in concentrated solutions of La(III) was reported. The acidity range investigated was $3.1 < -\log[H^+] < 4.1$, the upper limit was determined by the precipitation of $La_2(CO_3)_3(s)$. The stability constants for the formation of $La_2CO_3^{4+}$, $LaHCO_3^{2+}$ and $LaCO_3^+$ were determined. To extend the measurements to lower acidities, *i.e.* higher carbonate concentrations, it is necessary to use a different experimental approach. Dumonceau *et al.*[2] used an extraction technique to determine the stability constant for the limiting complex $Ln(CO_3)_4^{5-}$ for all lanthanoids except Ce and Pm. The measurements refer to a 2.5 M NH_4NO_3 medium.

A number of solid phases, *e.g.* $Ln_2(CO_3)_3(s)$, $Ln(OH)CO_3(s)$ and $MeLn(CO_3)_2(s)$ (Me=an alkali ion) [3] are formed in the Ln(III)$-CO_3^{2-}-H_2O$ system. From the solubility of these phases [4] as a function of the carbonate concentration, one can obtain information on solubility products as well as on the composition and the stability constants of the complexes formed in solution. The Ce(III)$-CO_3^{2-}-H_2O$ system was selected as a model for a solubility study in a wide carbonate concentration range. Data of this type are needed to decide whether the concentration of tervalent lanthanoids and actinoids in ground water may be limited by solubility factors or not.

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* Permanent address: Istituto Chimico dell'Università Via Mezzocannone 4, 80134 Napoli, Italy.

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This, in turn, is related to problems of radionuclide migration from nuclear waste repositories.

NOTATIONS

Previous studies of the La(III)$-CO_3^{2-}-H_2O$ [1] and Y(III)$-CO_3^{2-}-H_2O$ [5] systems indicate that the concentration of polynuclear complexes should be negligible at the low metal ion concentrations encountered in this solubility study. The equilibria in the presence of CO_2(g) may then be written

$$Ce^{3+}+pH_2O+rCO_2(g) \rightleftarrows Ce(OH)_p(CO_2)_r^{3-p}+pH^+ \tag{1}$$

with $(OH)CO_2^- \equiv HCO_3^-$ and
$(OH)_2CO_2^{2-} \equiv CO_3^{2-}$

where B=the total concentration of Ce(III), *i.e.* the measured solubility, H=analytical proton concentration excess:

$$H \simeq [ClO_4^-]-[Na^+] = h-[HCO_3^-]-2c-\sum_n 2n[Ce(CO_3)_n^{3-2n}] \tag{2}$$

where the last term is negligible throughout this study, b,h=molar concentrations of Ce^{3+} and H^+, respectively, c=molar concentration of CO_3^{2-}, a=partial pressure of CO_2(g), $\beta_{p,r}$=the equilibrium constant for the reaction (1), $K_p=\sum_r \beta_{p,r} \cdot a^r$, a conditional equilibrium constant at constant a, β_n=the equilibrium constant for the reaction

$$Ce^{3+}+nCO_3^{2-} \rightleftarrows Ce(CO_3)_n^{3-2n}$$

$\alpha=\log(B\,a^{3/2}h^{-3})$, $\psi=\log(B[Na^+])$, $K_{a1}=10^{-7.987}$ is the equilibrium constant [1] for $CO_2(g)+H_2O \rightleftarrows H^++HCO_3^-$ $K_{a2}=10^{-9.63}$ is the constant [1] for

$$HCO_3^- \rightleftarrows H^++CO_3^{2-} \tag{3}$$

$K_{s,I}$, $K_{s,II}$ are the equilibrium constants for the reactions (4) and (5) respectively.

$$Ce_2(CO_3)_3(s)+6H^+ \rightleftarrows 2Ce^{3+}+3CO_2(g)+3H_2O \tag{4}$$

$$NaCe(CO_3)_2(s) \rightleftarrows Na^++Ce^{3+}+2CO_3^{2-} \tag{5}$$

METHOD

The solubility of two different solid phases, $Ce_2(CO_3)_3 \cdot 8H_2O$ and $NaCe(CO_3)_2 \cdot 2H_2O$ were studied at 25±1 °C in a 3 M Na(ClO_4) medium.

The solubility of the $Ce_2(CO_3)_3$ phase was measured as a function of the hydrogen ion concentration, in solutions of acidity $10^{-8}<h$ *tl*$<10^{-4}$ *M. These were saturated with* CO_2-H_2 *mixtures of known partial pressure,* a, of CO_2. Gas mixtures containing H_2 were chosen because Ce(III) in carbonate media is easily oxidized to Ce(IV) by air. The oxidation could be avoided by passing the H_2 gas mixture over a Pd sponge in the test solution of the general composition:

H M H^+, $(3.000-H)$ M Na^+, 3.000 ClO_4^- saturated with $Ce_2(CO_3)_3$(s) and CO_2(g, a atm).

At acidities lower than 10^{-8} M, $NaCe(CO_3)_2 \cdot 2H_2O$ is the stable solid phase. Its solubility was measured in solutions of the general composition:

H M H^+, 3.000 M Na^+, $(3.000+H)$ M ClO_4^- saturated with $NaCe(CO_3)_2$(s)

as a function of the carbonate ion concentration in the range $10^{-3}<c<1$ M.

H_2 was passed through these solutions in the presence of a Pd catalyst, only for the time necessary to remove O_2, every time the reaction vessel was opened for sampling. We were thus able to avoid both oxidation and significant changes of h due to removal of CO_2.

c was calculated from H and h by using eqns. (2) and (3). H is a known analytical quantity, while h was obtained by means of the cell

$$\text{Ref} \,|\, \text{test solution} \,|\, \text{glass electrode} \tag{A}$$

where Ref indicates

$$\text{Ag,AgCl}\left|\begin{array}{l}2.99\text{ M NaClO}_4,\\0.01\text{ M AgClO}_4\end{array}\right|3\text{ M NaClO}_4$$

or, for combined glass electrodes

$$\text{Ag,AgCl}\left|\begin{array}{l}2.99\text{ M NaClO}_4,\\0.01\text{ M NaCl}\end{array}\right|3\text{ M NaClO}_4$$

The emf of cell (A) is equl to

Table 1. Survey of the experimental data.

i. Solutions equilibrated with $Ce_2(CO_3)_3{\cdot}8H_2O(s)$

a=0.97 atm

α, log ($h^{-2}a$): 10.81, 8.01; 10.84, 8.09; 10.90, 8.15; 10.80, 8.17; 10.88, 8.32; 10.93, 8.33; 10.83, 8.35; 10.92, 8.62; 10.85, 8.65; 10.93, 8.72; 10.86, 8.74; 10.88, 9.07; 10.90, 9.09; 10.87, 9.26; 10.91, 9.38; 10.90, 9.41; 10.80, 9.49; 10.83, 9.55; 10.96, 9.63; 10.72, 9.65; 10.92, 9.72; 10.96, 9.88; 10.94, 10.13; 10.94, 10.21; 10.97, 10.37; 11.13, 10.58; 10.98, 10.65; 11.02, 10.71; 11.05, 10.76; 10.96, 10.92; 11.07, 11.02; 11.20, 11.04; 11.23, 11.24; 11.01, 11.25; 11.23; 11.25; 11.58, 11.42; 11.45, 11.54; 11.72, 11.59; 11.67, 11.78; 12.06, 12.19; 12.26, 12.42; 12.71, 12.67; 12.97, 12.97; 13.85, 13.51; 14.20, 13.75; 14.66, 13.83; 15.05, 13.89; 14.92, 14.02; 15.01, 14.07; 15.69; 14.31; 15.71, 14.41; 15.99, 14.48; 16.85, 14.89.

a=0.097 atm

α, log ($h^{-2}a$): 10.85, 9.42; 10.88, 10.09; 10.85, 10.13; 10.86, 10.24; 11.10, 10.86; 11.20, 11.48; 11.74, 11.62; 11.92, 12.02; 12.51, 12.52; 12.66, 12.60; 13.66, 13.22; 14.17, 13.54; 14.53, 13.66; 15.56, 14.32.

ii. Solutions equilibrated with $NaCe(CO_3)_2{\cdot}2H_2O(s)$

$-\psi$, $-\log c$: 4.02, 0.16_5; 4.26, 0.29; 4.32, 0.30; 4.37, 0.30; 4.39, 0.34; 4.54, 0.42; 4.75, 0.53; 4.80, 0.58_5; 5.01, 0.68; 5.04, 0.72; 5.15, 0.77; 5.29, 0.87; 5.50, 1.04; 5.63, 1.11; 5.64, 1.18_5; 5.67, 1.20; 5.69, 1.19_5; 5.74, 1.24; 5.80, 1.31_5; 5.92, 1.50; 6.03, 1.64; 6.08, 1.66; 6.22, 1.91; 6.23, 1.98_5; 6.36, 2.35.

$$E=E_o-59.16 \log h+E_j$$

E_o is a constant which was determined in solutions of known h. E_j is the liquid junction potential between the test solutions and 3 M $NaClO_4$ which we found to be well approximated by $E_j=-7.2{\cdot}H$. We have neglected E_j for solutions with $h>10^{-11}$ M since the largest correction introduced in log h(0.04 units) hardly exceeds the present accuracy of the measurements. For solutions with $h<10^{-11}$ M, we can write eqn. (2) as

$$-H=2c \qquad (6)$$

since h is negligible and $[HCO_3^-]$ amounts to, at most, 4 % of c.

However, the value of c obtained from eqn. (6) always agreed with that obtained from eqns. (2) and (3) within 0.01 logarithmic units.

The solubility, B, was calculated by measuring the γ-activity of test solutions and by comparing it with the known specific activity of radioactive Ce(III) stock solutions. The solubility of the most acidic solutions were measured by a direct titration of Ce(III) with EDTA.

To ensure the attainment of equilibrium in the test solutions, we checked that the same value of the solubility was obtained in solutions which were initially undersaturated or supersaturated, after stirring them from one day to one week with the solid phase.

The primary data $B(h,a)$ for the $Ce_2(CO_3)_3{\cdot}8H_2O(s)$ and $B(h,H)$ for the $NaCe(CO_3)_2{\cdot}2H_2O$ phases recalculated in the form of $\alpha(\log h^{-2} a)$ and $\psi(\log c)$, respectively, are collected in Table 1 and plotted in Figs. 1 and 2. They form the basis of the following mathematical treatment.

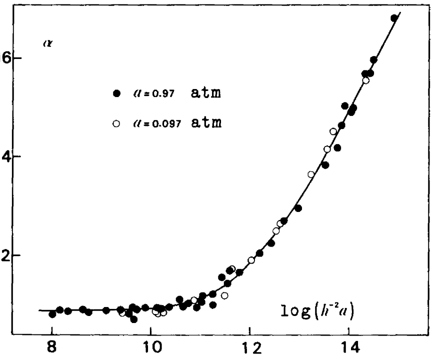

Fig. 1. The $\alpha(\log h^{-2}a)$ data at two different a, the partial pressure of CO_2. For clarity every second experimental point has been reported in the horizontal part of the plot. The curve has been calculated using the values of $\beta_{2,1}$, $\beta_{4,2}$ and $K_{s,I}$ given in Table 2.

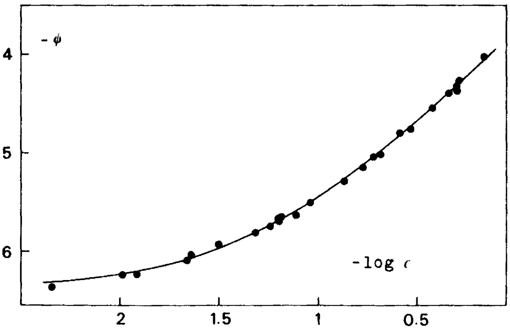

Fig. 2. The $\psi(\log c)$ data. The curve has been calculated using the values of β_2, β_3, β_4 and $K_{s,II}$ given in Table 2.

EXPERIMENTAL

A stock solution of $Ce(ClO_4)_3$ was prepared from $Ce(NO_3)_3$ (BDH, analytical grade) and perchloric acid (Merck, *p.a.*) by repeated evaporations under a heating lamp. The cerium and hydrogen ion concentrations were determined as described previously.[1] An active stock solution, used for the preparation of the solid phases, was obtained by adding a small known amount of cerium tracer to the Ce(III) stock solution. All other reagents were analyzed by standard methods.

$Ce_2(CO_3)_3 \cdot 8H_2O$ was prepared by adding $NaHCO_3$ to 0.1 M active Ce(III) stock solution. CO_2 was bubbled through the resulting slurry for 1–2 days. The precipitate was filtered, washed with water and finally dried with acetone. Analyses of Ce and carbonate confirmed the composition given above.

$NaCe(CO_3)_2 \cdot 2H_2O$ was prepared by shaking $Ce_2(CO_3)_3 \cdot 8H_2O$ with a 0.5–1 M Na_2CO_3 solution for 2 days. In order to avoid the oxidation of Ce(III) to Ce(IV), H_2(g) was bubbled through the slurry in the presence of a Pd-catalyst. Analyses of Na, Ce and CO_3^{2-} confirmed the formula. Both solids were also characterized by their X-ray powder patterns.

Ce(III) stock solutions containing tracer amounts of Ce-144, Ce-141 or Ce-139 were used for the solubility measurements. These were made either by preparing individual test solutions in glass-stoppered flasks or by using a vessel where the composition of the test solution was varied in a titration procedure. Clear samples of known volume were withdrawn from these solutions with a pipette on which a G3 filter had been fitted. Contact between solution and air was prevented before separation from the solid phase. We found the titration technique to be superior and most of the experimental data were collected by using this method.

A Tracerlab scintillation counter, model Compumatic V or Scaler Sc-57 was used. E was measured by using a Radiometer Phm 4 with Beckman, Jena or Metrohm glass electrodes.

All the glass electrodes were calibrated against the hydrogen electrode in separate experiments in the acidity range $10^{-12} < h < 10^{-3}$ M. Correction for the sodium error was negligible, down to $h = 10^{-10}$ M.

TREATMENT OF THE DATA AND RESULTS

The solubility data for the two solid phases were treated separately.

In our treatment, we assumed that only mononuclear complexes are formed.

Solubility data do not in general[4] provide information as to the nuclearity of the species formed. However, the results of previous studies on lanthanum[1] and yttrium[5] indicate that this assumption is valid at the metal concentrations encountered in this study.

I. The solubility of $Ce_2(CO_3)_3$(s) can be written

$$B = [Ce^{3+}] + \sum_p \sum_r [Ce(OH)_p(CO_2)_r] =$$
$$b(1 + \sum_p \sum_r \beta_{p,r} h^{-p} a^r) \quad (7)$$

with p and r integer.

Introducing into eqn. (7) the equilibrium constant for reaction (4)

$$k_{s,I} = b^2 a^3 h^{-6}$$

and

$$K_p = \sum_r \beta_{p,r} a^r$$

valid for a series of measurements at constant a, we recalculated the experimental data in the form (8).

$$\alpha_a = \log (B a^{3/2} h^{-3})_a =$$
$$\frac{1}{2} \log K_{s,I} + \log(1 + \sum_p K_p h^{-p}) \quad (8)$$

The $\alpha(-\log h)_a$ curves proved to be parallel, with the spacing

$$((\Delta \log a)/(\Delta \log h))_a = 2.0$$

This indicates[6,7] that the complexes contain 2OH groups per CO_2, *i.e.* $r=p/2$. Thus, eqn. (8) may be written as

$$\alpha = \tfrac{1}{2} \log K_{s,I} + \log (1+\sum_p \beta_{p,p/2}(h^{-2}a)^{p/2}) \qquad (9)$$

Fig. 1 shows, as eqn. (9) suggests, that the $\alpha[\log (h^{-2}a)]$ data yield a single curve.

From its slope at the lowest h values, we deduce that the upper limit of p is 4. This means that the most probable values of p are 2 and 4, since $r(=p/2)$ must be an integer.

This hypothesis was tested by comparing the data with normalized model functions.

Assuming $p=2$ and 4, eqn. (9) takes the form

$$\alpha = \tfrac{1}{2} \log K_s I + \log (1+\beta_{2,1}h^{-2}a+\beta_{4,2}h^{-4}a^2) \qquad (10)$$

Introducing in eqn. (10) the normalized variable

$$u = \beta_{2,1}\, h^{-2}a \qquad (11)$$

the theoretical $Y(\log u)$ curves

$$Y = \log (1+u+Lu^2) \qquad (12)$$

with $L=\beta_{4,2}\beta_{2,1}^{-2}$

were calculated for various L values and compared to the experimental $\alpha[\log (h^{-2}a)]$ data.

In the position of best fit, shown in Fig. 1, $\log K_{s,I}$ was obtained from the difference of the ordinates, $\log \beta_{2,1}$ as the difference of the abscissas and $\beta_{4,2}$ from the value of L (=0.03) which gave the best fit.

The results are collected in Table 2. The errors are maximum deviations from the average.

II. At lower acidities, $[Ce^{3+}]$ is negligible and the solubility of $NaCe(CO_3)_2(s)$ can be expressed as

$$B = \sum_p \sum_n [Ce(OH)_p(CO_3)_n] = \sum_p \sum_n \beta_{p,n}\, b h^{-p} c^n \qquad (13)$$

where $\beta_{p,n}$ is the equilibrium constant of the reaction

$$Ce^{3+} + pH_2O + nCO_3^{2-} \rightleftarrows Ce(OH)_p(CO_3)_n^{3-p-2n} + pH^+ \qquad (14)$$

Introducing into eqn. (13) the equilibrium constant for reaction (5)

$$K_{s,II} = [Na^+]b\, c^2$$

and rearranging, we obtain

$$\psi = \log (B[Na^+]) = \log K_{s,II} + \log (\sum_p \sum_n \beta_{p,n} h^{-p} c^{(n-2)}) \qquad (15)$$

In Fig. 2, the $\psi(\log c)$ data are seen to fall on a single curve, although h was varied independently of c. This indicates that p, in eqns. (13)−(15), is equal to zero.

Eqn. (15) can then be more simply written as

$$\psi = \log K_{s,II} + \log (\sum_n \beta_n c^{(n-2)}) \qquad (16)$$

From the limiting slopes of the $\psi(\log c)$ function, we deduced that $2 \le n \le 4$.

Assuming the formation of three complexes with $n=2$, 3, 4, eqn. (16) takes the form

$$\psi = \log K_{s,II} + \log \beta_2 + \log (1+\frac{\beta_3}{\beta_2}c+\frac{\beta_4}{\beta_2}c^2) \qquad (17)$$

The $\psi(\log c)$ data were compared to the normalized model function $X(\log v)$

$$X = \log (1+\rho v+v^2),\ v^2=\beta_4\beta_2^{-1}c^2 \text{ and } \rho=\beta_3(\beta_2\beta_4)^{-1/2} \qquad (18)$$

Table 2. Survey of the equilibrium constants.

$-\log \beta_{p,p/2}$	$p=2$	$p=4$		
	11.30±0.05	24.1±0.1		
	$n=1$	$n=2$	$n=3$	$n=4$
$\log \beta_n$	6.32±0.08	11.1±0.1	12.6±0.2	13.7±0.1
$\log K_{s,I}$	21.80±0.05			
$-\log K_{s,II}$	17.5±0.1			

constructed for various values of ρ.

A satisfactory fit (Fig. 2) was obtained with $\rho=1.8$. Since

$$\log \beta_2 = \log \beta_{4,2} - 2 \log(K_{a1}K_{a2})$$

where $\beta_{4,2}$ refers to $Ce(OH)_4(CO_2)_2^-$, $K_{s,II}$, β_3 and β_4 were calculated as shown previously in this section.

The values of the equilibrium constants and their maximum deviations are reported in Table 2.

DISCUSSION

From the magnitude of the stability constants given in Table 2, one finds that the $Ce(CO_3)_2^-$ complex is predominant over a very wide $[CO_3^{2-}]$ range ($2\cdot10^{-5}$ M$<c<3\cdot10^{-2}$ M). Experimental measurements must be made outside this range in order to provide information on the formation of lower and higher carbonato complexes. This has not always been done in previous studies.

Lundqvist [8] studied the Eu^{3+} and Am^{3+} systems at $c<10^{-2}$ M. Hence, he only obtained information about the formation of $M(CO_3)^+$ and $M(CO_3)_2^-$. His data are in agreement with ours.

Bidoglio [9] studied a more limited c range, where $Am(CO_3)_2^-$ is predominant. He also reports the formation of hydrogen carbonato and mixed hydroxide, carbonate species. Taking the experimental errors into account, it seems possible to describe the largest part of his data with only one complex, $Am(CO_3)_2^-$.

Dumonceau *et al.*[2] find that the limiting complex in the $Ln^{3+}-CO_3^{2-}$ system is the presumably 8-coordinate $Ln(CO_3)_4^{5-}$ which is in agreement with our findings.

Polynuclear complexes seem to form only at rather high total metal ion concentrations in the lanthanoid(III) and actinoid(III) carbonate systems.[1] Weak hydrogen carbonate complexes are formed at $h\simeq10^{-3}$ M.[1]

$Ce_2(CO_3)_3(s)$ transforms into $NaCe(CO_3)_2(s)$ according to $Ce_2(CO_3)_3(s)+2Na^+ + CO_3^{2-} \rightleftarrows 2NaCe(CO_3)_2(s)$.

We were not able to make a direct experimental determination of the carbonate concentration, when the two solids are in equilibrium with one another. This is probably due to slow equilibria as observed previously in some lanthanoid–oxalate systems.[10] The equilibrium concentration, $[CO_3^{2-}]=10^{-4.8}$ M, was instead calculated from the solubility products of the two phases.

Some solubility data (at $\log(h^{-2}a)>12.97$) for the $Ce_2(CO_3)_3$-phase have been collected at $[CO_3^{2-}]>10^{-4.8}$ M. Because of the slow rate of phase transformation, these data still represent (metastable) equilibria with $Ce_2(CO_3)_3(s)$.

Most deep ground waters have $10^{-9}<h<10^{-6}$ M and total carbonate concentrations in the range 10–200 ppm.[11] Hence, tervalent lanthanoids and actinoids should occur mainly as $Me(CO_3)^+$ and $Me(CO_3)_2^-$ with $Me_2(CO_3)_3(s)$ as the most stable solid carbonate phase.

The equilibrium data obtained in a medium of high and constant ionic strength must be recalculated in order to be useful for the description of a ground water. We have previously utilized the specific ion interaction theory for this purpose.[12] Many ground waters have a low content of dissolved electrolytes and equilibrium constants valid for $I=0$ can then be used. From the following values for the interaction parameters

$$\varepsilon(Ce^{3+},HCO_3^-) \simeq \varepsilon(Ce^{3+},ClO_4^-) \simeq \varepsilon(La^{3+},ClO_4^-) = 0.47^{1}$$

$$\varepsilon(CeCO_3^+,ClO_4^-) \simeq \varepsilon(YCO_3^+,ClO_4^-) = 0.17^{11}$$

$\varepsilon(Ce(CO_3)_2^-,Na^+)\simeq0$ (taken as the average of $\varepsilon(A^-,Na^+)$ in Table 5 of Ref. 13.

$$\varepsilon(Na^+,CO_3^{2-}) = -0.05^{13}$$

we obtain

$\log K_{s,I}\ (I=0)=18.9\pm0.4$

$\log \beta_1(I=0)=8.4\pm0.4$

$\log \beta_2(I=0)=13.7\pm0.4$

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