Thermodynamic Study of Ce\(^{4+}/\text{Ce}^{3+}\) Redox Reaction in Aqueous Solutions at Elevated Temperatures: 1. Reduction Potential and Hydrolysis Equilibria of Ce\(^{4+}\) in HClO\(_4\) Solutions

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The redox potential \(E\) of the couple Ce\(^{4+}/\text{Ce}^{3+}\) has been determined up to 368 K by means of cyclic voltammetric measurement in aqueous HClO\(_4\) solutions with \(c_{\text{HClO}_4}\) decreasing from 7.45 to 0.023 mol kg\(^{-1}\). A constant potential of \((1.741 \text{ V})_{298 \text{ K}}\), resp. \((1.836 \text{ V})_{368 \text{ K}}\), indicating the existence of pure unhydrolysed Ce\(^{4+}\) was obtained at \(c_{\text{HClO}_4} \geq 6.05 \text{ m}\). At lower HClO\(_4\) concentration, the potential as a function of the HClO\(_4\) molality, as well as of the pH shows 4 further distinct steps. At 298 K, for instance, the potential became nearly constant at pH values of 0.103, 0.735, 1.115, after which it drastically decreased, respectively at 1.679, just before the precipitation of Ce(OH)\(_4\) occurred. The curves indicate obviously the stepwise formation of the Ce(IV) mono-, di-, tri- and tetrahydroxo complexes. The slope of the curves \(E\) vs. pH increased gradually with increasing temperature. \(\Delta S\) and \(\Delta H\) of the redox reaction were determined as functions of \(T\) at the different HClO\(_4\) concentrations. \(\Delta S\) is positive at \(c_{\text{HClO}_4} > 1.85 \text{ m}\) and turns to be negative at lower concentrations. \(\Delta H\) is negative at all HClO\(_4\) concentrations studied. The cumulative formation constants \(\beta_i\) of the Ce(IV) hydroxo complexes and the corresponding hydrolysis constants \((K_{l_i})\) were calculated. An unusual decrease of \(\beta_i\) with increasing temperature has been discussed.

Key words: Redox potential of Ce\(^{4+}/\text{Ce}^{3+}\); Aqueous solutions; Thermodynamics of redox equilibria; Ce(IV) hydrolysis; Cyclic voltammetry.

1. Introduction

The knowledge of the redox potential of the Ce\(^{4+}/\text{Ce}^{3+}\) couple in aqueous solutions, as well as the evaluation of the hydrolysis and complex formation equilibria of Ce ions at elevated temperatures is necessary for the interpretation of the Ce anomaly in geochemical systems. Such data are also important for the investigation of some corrosion processes in technical hydrothermal systems (i.e. turbine systems of power plants). We run a program to obtain these data by means of cyclic voltammetric and potentiometric measurements at different pH, in absence of complexing agents (Perchlorate systems), as well as in systems containing the ligands SO\(_4^{2-}\) and HCO\(_3^-/\text{CO}_3^{2-}\).

In this paper we report on the reduction potential and hydrolysis of Ce(IV) in aqueous HClO\(_4\) at temperatures up to 368 K. Bilal and Langer [1] have shown that the hydrolysis of Ce\(^{3+}\) at pH \(\leq 3\) is negligible at temperatures up to \(\approx 338 \text{ K}\). Because of the higher charge and the smaller radius of Ce\(^{4+}\), its electrostatic interaction with ligands such as OH\(^-\) is much stronger than that of Ce\(^{3+}\). A significant hydrolysis must, therefore, be expected to occur at pH much lower than 3 and a precipitation of Ce(OH)\(_4\) would take place in relatively acidic solutions, if no stronger complexing agent is competing with the OH\(^-\) ligand.

The cyclic voltammetric method applied here, the thermodynamics of the (Ag/AgCl) NaCl = 0 A m \(E_{\text{Ag/AgCl}} = 0 \text{ V}\) electrode used as a reference, as well as the dependence of the redox potential on \(T\) and \(p\) in general have been described in details by Bilal in a previous paper [2].

2. Experimental

The cyclic voltammetric measurements (using Pt for the indicator and the counter electrode) were carried out in 10 K steps during heating the systems up to 368 K and cooling them back down to 298 K in order to deduce any irreversibility of the systems with respect to the temperature change. Ce(OH)\(_4\) was precipitated from available Ce(SO\(_4\))\(_2/\)sulfuric acid solution and dissolved in HClO\(_4\) to prepare three sets of solutions having Ce concentrations of 0.005, 0.0025, and 0.000125 mol kg\(^{-1}\), as well as

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as $\text{HClO}_4$ concentrations of 7.45, 6.05, 5.46, 4.83, 3.44, 1.85, 0.94, 0.71, 0.471, 0.283, 0.236, 0.189, 0.094, 0.071, 0.047, and 0.023 mol kg$^{-1}$ in every set. These three sets were studied in order to find out if any deviation of the redox potential with respect to the Ce concentration was obtained due to its possible polymerization. The results in this work are based on the measurements using the set with the lowest Ce concentration.

The $\text{H}^+$ activity of the solutions with $\text{HClO}_4$ concentration $\leq 0.94$ m was determined potentiometrically up to 368 K by means of Pt/H$_2$ electrodes in a concentration cell as described previously by Becker and Bilal [3]. A Glas electrode was also used up to 323 K (limit of the temperature compensation of the used pH-meter) for the pH measurement in the solutions with $c_{\text{HClO}_4} \leq 0.094$ m (where it does not yet show a negative error). No deviation beyond the limit of the experimental one was observed between the two measurements.

Due to the reduction of Ce$^{4+}$ and Ce(IV) complexes on contact with the platinized hydrogen electrode, its potential became constant first after the reduction of Ce(IV) species was completed. In strongly acidic solutions, where only Ce$^{4+}$ ions are present, they are reduced according to

$$\text{Ce}^{4+} + \frac{1}{2} \text{H}_2 \leftrightarrow \text{Ce}^{3+} + \text{H}^+.$$  \hspace{1cm} (1)

With decreasing $\text{H}^+$ activity, hydroxo complexes are formed:

$$\text{Ce}^{4+} + i \text{H}_2\text{O} \leftrightarrow [\text{Ce(OH)}]^{4-i+} + i \text{H}^+.$$  \hspace{1cm} (2)

The reduction of the complexes may be based on reaction (1), where they are dissociated prior to the reduction. Possibly they are reduced directly due to

$$[\text{Ce(OH)}]^{4-i+} + \frac{1}{2} \text{H}_2 + (i-1) \text{H}^+ \leftrightarrow \text{Ce}^{3+} + i \text{H}_2\text{O}.$$  \hspace{1cm} (3)

Reaction (1), as well as the sum of the reaction (2) and (3) leads to an increase of the $\text{H}^+$ activity in the solution by one mole for each mole Ce$^{4+}$. Due to the high partial pressure of H$_2$ used in the concentration cell, the equilibria in (1) and (3) are so far shifted to the right-hand side that Ce$^{4+}$ is practically totally reduced. Considering the set with the lowest Ce concentration, the $\text{H}^+$ activity of the solution with $c_{\text{HClO}_4} = 0.94$ m increases by 0.016% and that of the solution with $c_{\text{HClO}_4} = 0.023$ m by 0.6%. These differences are within the limit of experimental error and can be neglected.

The pH of the solutions with $c_{\text{HClO}_4} > 0.94$ m is not accurately determinable. Using HCl as a reference solution, whose mean ionic activity coefficient as a function of the ionic strength is well known at 298 K, respectively was calculated at higher temperatures by Helgeson, Kirkham and Flowers [4], the diffusion potential participates increasingly in the emf of the concentration cell. Exact calculation of the diffusion potential according to the Handerson equation is not possible because of the lacking data of the ions at the corresponding concentrations and temperatures. However, neglecting the relatively small decrease of the pH due to the formation of $\text{Ce(OH)}^{3+}$ in these solutions, their $\text{H}^+$ activity can be calculated at 298 K and 313 K according to Haase, Ducker and Kuppers [5], as well as approximated for the other temperatures according to the estimation given in [4] for HCl and taking into account that the mean ionic activity coefficients of HClO$_4$ and HCl are similar. Since the pH at $c_{\text{HClO}_4} \geq 0.94$ m is not needed for the calculation of the formation constants of the hydroxo complexes (see below), it is more accurate and meaningful to correlate the potential values in this region with the HClO$_4$ molality of the corresponding solutions.

3. Results and Discussion

Figure 1 shows, as an example, the cyclic voltammogram obtained at 298 K in the solution with $c_{\text{HClO}_4} = 6.05$ m and $c_{\text{Ce}} = 0.005$ m (solid curve), as well as in a solution with the pure HClO$_4$ (dashed curve). The scan rate was 20 mV/s. The cathodic peak was very well distinct, while the anodic one was in many cases difficult to recognize because it lies beyond the oxidation potential of water. The difference between the reduction and the oxidation peak is about 60 mV, indicating a reversible redox process. Such simple diagrams were obtained in all other solutions even at higher temperatures and higher scan rates up to 100 mV/s.

The potential values in all three sets of solutions were independent of the Ce concentration, so that a polymerization of Ce(IV) at concentration $\leq 0.005$ m was excluded.

No significant difference was also found between the potential values of the heating and those of the cooling curves, indicating no irreversibility of the systems with respect to the temperature change.

Table 1 shows (for accurate reading) the values of the redox potential and of the pH measured in the set
Table 1. The redox potential at various temperatures, HClO₄ molalities and pH values (resp. the corresponding pOH).

<table>
<thead>
<tr>
<th>T/K</th>
<th>298</th>
<th>318</th>
<th>328</th>
<th>338</th>
<th>348</th>
<th>358</th>
<th>368</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>0.103</td>
<td>0.110</td>
<td>0.117</td>
<td>0.122</td>
<td>0.127</td>
<td>0.132</td>
<td>0.138</td>
</tr>
</tbody>
</table>

containing Ce in the concentration 0.000125 m. The corresponding pOH values were calculated using the values of the ion product of water $K_w$ given by Swee- ton, Mesmer, and Baes [6] and by Marshall and Franck [7] as well.

Conley [8] measured potentiometrically (1.7431 V)₂₉₈K and (1.7615 V)₃₀₈K for the redox potential of the half cell

$$\text{Ce}^{4+} + e^- ⇌ \text{Ce}^{3+}.$$ (4)

We obtained (1.741 V)₂₉₈K, respectively (1.760 V)₃₀₈K, which deviate by ≈0.1% from the values of Conley.

He also obtained (1.6966 V)₂₉₈K, (1.6941 V)₃₀₈K, and (1.6914 V)₃₁₈K in solutions having $c_{\text{HClO}_4} = 0.9964$, 1.0065, and 1.0130 m, respectively. The comparison with our values obtained in the solution with $c_{\text{HClO}_4} = 0.94$ m, yields a deviation of ≈0.4% which is very probably due the difference of the HClO₄ molality.

**Temperature Effect**

The temperature increase leads to an increase of the redox potential in solutions where pure uncomplexed
Fig. 1. Cyclic voltammogram at 298 K of the solution with $c_{HClO_4} = 6.05 \text{ m}$ and $c_{Ce} = 0.005 \text{ m}$ and of the pure $HClO_4$; Scan rate = 20 mV/s.

Table 2. The coefficients $a$ and $b$ in (6) at 298–368 K.

<table>
<thead>
<tr>
<th>$c_{HClO_4}$ (m)</th>
<th>$a \times 10^{-3}$ (mV K$^{-1}$)</th>
<th>$b \times 10^{-5}$ (mV K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.05</td>
<td>+2.100</td>
<td>-1.030</td>
</tr>
<tr>
<td>5.46</td>
<td>+2.000</td>
<td>-1.000</td>
</tr>
<tr>
<td>4.83</td>
<td>+1.720</td>
<td>-0.810</td>
</tr>
<tr>
<td>3.44</td>
<td>+0.980</td>
<td>-0.570</td>
</tr>
<tr>
<td>0.94</td>
<td>-0.190</td>
<td>-0.270</td>
</tr>
<tr>
<td>0.71</td>
<td>-0.195</td>
<td>-0.315</td>
</tr>
<tr>
<td>0.475</td>
<td>-0.200</td>
<td>-0.400</td>
</tr>
<tr>
<td>0.283</td>
<td>-0.250</td>
<td>-0.350</td>
</tr>
<tr>
<td>0.236</td>
<td>-0.260</td>
<td>-0.350</td>
</tr>
<tr>
<td>0.189</td>
<td>-0.390</td>
<td>-0.630</td>
</tr>
<tr>
<td>0.094</td>
<td>-0.550</td>
<td>-0.616</td>
</tr>
<tr>
<td>0.071</td>
<td>-0.630</td>
<td>-2.400</td>
</tr>
<tr>
<td>0.047</td>
<td>-0.105</td>
<td>-1.750</td>
</tr>
<tr>
<td>0.023</td>
<td>-0.106</td>
<td>-2.275</td>
</tr>
</tbody>
</table>

Ce$^{4+}$ is present. Due to the accompanying decrease of the dielectric constant of water and the increase of its $K_w$, the hydrolysis of Ce$^{4+}$ takes increasingly place and the redox potential is shifted to smaller values.

Figure 2 shows the redox potential ($E$) vs. $T$. The slope of the curves is positive at $c_{HClO_4} > 1.85 \text{ m}$ and turns to be negative at lower $HClO_4$ concentration due to the complex formation.

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S(T)}{zF}$$  \hspace{1cm} (5)

($\Delta S$ = the change of the partial molal entropy of the redox reaction, $z$ = number of the electrons transferred, $F$ = the Faraday constant).

The temperature dependence of $\Delta S$ is not known. However, the isobaric change of $E$ between the $T_0 = 298 \text{ K}$ and $T$ can be described to a good approximation by the empirical equation

$$E^T = E^{T_0} + a(T - T_0) + b(T - T_0)^2,$$  \hspace{1cm} (6)

where the coefficients $a$ and $b$ are determined graphically. Table 2 contains the values of $a$ and $b$ for the systems studied.

$\Delta S$ values have been determined graphically from the slope of the curves in Fig. 2, as well as obtained from the differentiation of (6) with respect to the temperature:

$$\Delta S = \left(\frac{\partial E}{\partial T}\right)_p zF = \{a + 2b(T - T_0)\} zF.$$  \hspace{1cm} (7)

$\Delta H$ is then calculated from the fundamental equation

$$\Delta H = \Delta G + T \Delta S = [T \{a + 2b(T - T_0)\} - E] zF.$$  \hspace{1cm} (8)

$\Delta S$ and $\Delta H$ of the redox reaction at the various $HClO_4$ concentrations are shown in Figs. 3 and 4. Only $\Delta S$ and $\Delta H$ at 298 K are given in [8]. A comparison with our values at this temperature is not correctly possible because of the different concentrations of Ce and $HClO_4$. However, our values ($\Delta S = -17 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H = -168.3 \text{ kJ mol}^{-1}$), obtained in the solution with $c_{HClO_4} = 0.94 \text{ m}$ and $c_{Ce} = 0.000125 \text{ m}$ are between those reported in [8] for the two solutions having $c_{HClO_4} = 1 \text{ m}$ and $c_{Ce} = 0.005 \text{ m}$, respectively $c_{HClO_4} = 1 \text{ m}$ and $c_{Ce}$ extrapolated to zero m ($\Delta S = -11.29 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H = -165.9 \text{ kJ mol}^{-1}$), respectively $\Delta S = -26.75 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H = -171.38 \text{ kJ mol}^{-1}$).

Complex Formation

The simple reversible voltammograms, showing only one redox peak pair and obtained not only in the solutions containing pure uncomplexed Ce$^{4+}$ ions but also in those, where hydrolysed Ce(IV) species are present, indicate that Ce$^{3+}$ and only one Ce(IV) species are the electroactive species which participate in the potential determining electrode process and that the coupled successive equilibria between Ce$^{4+}$ ion and its complexed species are instantly established. Otherwise one would have observed at least two redox peak pairs in the voltammograms of the solutions containing more than one Ce(IV) species. These
Fig. 2. The redox potential in HClO₄ of different concentrations as a function of temperature.
The premises and the fact that only Ce$^{4+}$ exists in the highly acidic region, lead to the conclusion that this ion is the one participating in the electron exchange reaction at the electrode. This statement is underlined by the results obtained by Vetter [9] from the study of the dependence of the exchange current densities at equilibrium potential on the Ce(IV) concentration, as well as from the study of the current density vs. potential curves of the Ce$^{4+}$/Ce$^{3+}$ couple in nitric and sulfuric acid solutions.

Fig. 3. $\Delta S$ of the redox reaction in HClO$_4$ of various concentrations as a function of temperature.
Fig. 4. $\Delta H$ of the redox reaction in HClO$_4$ of different concentrations as a function of temperature.
Fig. 5. The redox potential at different temperatures as a function of the HClO$_4$ molality, as well as of the pH.
Table 3. Cumulative formation constants $\beta_i$ at 298–368 K. $(\log \beta_d)^*$ values at $T > 338$ K are extrapolated from Figure 6.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\log \beta_1$</th>
<th>$\log \beta_2$</th>
<th>$\log \beta_3$</th>
<th>$\log \beta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>14.76</td>
<td>28.04</td>
<td>40.53</td>
<td>51.86</td>
</tr>
<tr>
<td>308</td>
<td>14.75</td>
<td>27.72</td>
<td>39.91</td>
<td>51.02</td>
</tr>
<tr>
<td>318</td>
<td>14.74</td>
<td>27.45</td>
<td>39.40</td>
<td>50.34</td>
</tr>
<tr>
<td>328</td>
<td>14.73</td>
<td>27.17</td>
<td>38.93</td>
<td>49.78</td>
</tr>
<tr>
<td>338</td>
<td>14.71</td>
<td>26.92</td>
<td>38.55</td>
<td>49.35</td>
</tr>
<tr>
<td>348</td>
<td>14.67</td>
<td>26.65</td>
<td>38.11</td>
<td>48.90*</td>
</tr>
<tr>
<td>358</td>
<td>14.60</td>
<td>26.40</td>
<td>37.74</td>
<td>48.54*</td>
</tr>
<tr>
<td>368</td>
<td>14.54</td>
<td>26.20</td>
<td>37.43</td>
<td>48.25*</td>
</tr>
</tbody>
</table>

At $c_{\text{HClO}_4} \geq 6.05$ m, the potential of the half cell (4) is given by

$$E = E^0 - (RT/F) \log (a_{\text{Ce}^{3+}}/a_{\text{Ce}^{4+}}). \quad (9)$$

At equal activities $a_{\text{Ce}^{4+}}$ and $a_{\text{Ce}^{3+}}$, the redox potential is

$$E_{1/2} = E^0. \quad (10)$$

With decreasing $H^+$ activity, $\text{Ce}^{4+}$ is successively complexed by the hydroxyl ligand according to

$$\text{Ce}^{4+} + \text{iOH}^- \leftrightarrow [\text{Ce(OH)}]^i \text{Ce}^{4-i+}, \quad (11)$$

$$K_i = a_{[\text{Ce(OH)}]^i} / a_{\text{Ce}^{4-i+}} a_{\text{OH}^-}, \quad (11a)$$

$$\beta_i = \prod K_i = a_{[\text{Ce(OH)}]^i} / a_{\text{Ce}^{4-i+}} a_{\text{OH}^-}^i \quad (11b)$$

with $i = 1, 2, 3, 4$.

$a_{\text{Ce}^{4+}}$ then results from

$$a_{\text{Ce}^{4+}} = A_{\text{Ce(IV)}} / [1 + \sum \beta_i (a_{\text{OH}^-}^i)], \quad (12)$$

where $A_{\text{Ce(IV)}}$ is the total $\text{Ce(IV)}$ activity in the system. The substitution of $a_{\text{Ce}^{4+}}$ from (12) in (9) leads to

$$E = E^0 - (RT/F) \log [1 + \sum \beta_i (a_{\text{OH}^-}^i)] a_{\text{Ce}^{4+i}} / A_{\text{Ce(IV)}}], \quad (13)$$

and the redox potential results at equal activities of $\text{Ce}^{3+}$ and $\text{Ce}(\text{IV})$. In accord with the degree of complexation, it is shifted in comparison to that of the half cell (4) to smaller values,

$$E_{1/2} = E_{1/2} - (RT/F) \log [1 + \sum \beta_i (a_{\text{OH}^-}^i)]. \quad (14)$$

Equation (14) is rearranged to

$$\exp (-\Delta E_{1/2} F/RT) = 1 + \sum \beta_i (a_{\text{OH}^-}^i). \quad (14a)$$

The left-hand side of (14a) is, therefore, determined by the mean ligand number $\tilde{n}$, which is a function of $a_{\text{OH}^-}$:

$$\tilde{n} = \sum i \beta_i (a_{\text{OH}^-}^i) / 1 + \sum \beta_i (a_{\text{OH}^-}^i). \quad (15)$$

The shape, as well as the slope of the complex formation function (15) depends on the ratios of the individual formation constants $K_i$ of the species to each other. If the $K_i$ values are not very different, an s-shaped curve is obtained. Otherwise, a stepped form results, and the slope of the formation curve becomes minimal at $\tilde{n} = 1, 2, 3, \ldots$ and maximal at $\tilde{n} = 0.5, 1.5, 2.5, \ldots$ and so on. In extreme cases, the decrease, respectively the increase of the slope around the inflection points having $\tilde{n} = $ integral numbers is so small that nearly horizontal parts are there observed.

Figure 5 shows the redox potential at different temperatures as a function of the pH in the region where $c_{\text{HClO}_4}$ is $\leq 0.94$ m, respectively as a function of the $\text{HClO}_4$ molality at higher concentrations. In the whole temperature region studied, a constant potential which indicates the existence of the pure uncomplexed $\text{Ce}^{4+}$, was first obtained at $c_{\text{HClO}_4} \geq 6.05$ m. At lower $\text{HClO}_4$ concentrations, the potential curves show further 4 distinct steps. At 298 K, for instance, the potential became nearly constant at pH values of 0.103, 0.735, and 1.115, after which it drastically decreased, respectively at 1.679, where the reduction peak could last be observed, just before the precipitation of $\text{Ce(OH)}_4$ occurred. Possibly the curves could have taken a smooth form around the observed spikes if the potential would have been measured at pH values just close to them. The curves in Fig. 5 correspond to a complex formation function of the last discussed type, where $\tilde{n} = 1, 2, 3$ and 4 are obtained at the slope minima of the 4 observed steps.

With increasing temperature, the slope of the curves in Fig. 5 increased and their stepped form became less distinct. It seems that at higher temperature, a smooth curve might probably be obtained, indicating a gradual decrease of the difference between the individual formation constants. The investigation of this aspect up to 473 K and 1 kbar is still going on in our laboratory.

A fit of $\beta_i$ from (14a), taking all measured values into account, leads to no convergence due to the nearly independence of the potential of $a_{\text{OH}^-}$ in the practically horizontal parts of the curves. However, in our case $\beta_i$
can be calculated to a good approximation using the \( a_{\text{OH}^-} \) values corresponding to the pH at which the potential became nearly constant. Equation (14a) then applies for one species and is simplified to

\[
\frac{\exp(-\Delta E_{1/2} F/RT)}{a_{\text{OH}^-}} = \beta_1.
\]

(16)

The so obtained log \( \beta_i \) values are listed in Table 3. Figure 6 shows \( \beta_i \) as a function of \( T \), where a decrease with increasing \( T \) is observed. Between 298 and 368 K, \( \beta_1 \) decreases slightly within the same order of magnitude, whereas \( \beta_2, \beta_3, \) and \( \beta_4 \) decrease drastically over 2 to 4 orders of magnitude. This behaviour contradicts the (mainly) electrostatic nature of the bond between the central ion and ligands in the lanthanide complexes. One would expect that the formation constants of the Ce(IV) hydroxo complexes (like those of the lanthanide complexes with other ligands) increase with temperature, due to the decreasing dielectric constant of water. Bilal and Langer [1] have also found that the stability constants of the fluoro-hydroxo complexes of Ce\(^{3+}\),

![Graph showing the dependence of \( \beta_i \) on temperature.](image-url)
Table 4. Hydrolysis constants ($K_h$) at 298 – 368 K.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>298</th>
<th>308</th>
<th>318</th>
<th>328</th>
<th>338</th>
<th>348</th>
<th>358</th>
<th>368</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(K_h)_1$</td>
<td>5.8</td>
<td>11.7</td>
<td>22.1</td>
<td>39.2</td>
<td>60.9</td>
<td>90.8</td>
<td>121.6</td>
<td>153.1</td>
</tr>
<tr>
<td>$(K_h)_2$</td>
<td>1.1</td>
<td>2.3</td>
<td>4.5</td>
<td>7.9</td>
<td>11.7</td>
<td>16.8</td>
<td>23.4</td>
<td>30.9</td>
</tr>
<tr>
<td>$(K_h)_3$</td>
<td>0.03</td>
<td>0.07</td>
<td>0.16</td>
<td>0.33</td>
<td>0.59</td>
<td>0.94</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>$(K_h)_4$</td>
<td>0.00007</td>
<td>0.0002</td>
<td>0.0006</td>
<td>0.002</td>
<td>0.004</td>
<td>0.01</td>
<td>0.03</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Nd$^{3+}$, Tb$^{3+}$, Er$^{3+}$, and Lu$^{3+}$ decrease with increasing temperature.

We, therefore, believe that the hydroxo complexes of the lanthanides are formed according to a mechanism which is different from that of the formation of their other complexes. Hydroxo complexes are very probably formed in such a way that protons are transferred from coordinated H$_2$O molecules to the approaching OH~ ligands. The probability of such proton transfer is the higher, the stronger the O–H bond of the coordinated water dipoles is polarized in the electric field of the central ion. Such polarization is relatively strong in the case of Ce$^{4+}$ due to its high charge/radius ratio.

With increasing temperature, the coordinated water dipoles become less oriented in the electric field of Ce$^{4+}$, so that a decrease of the polarization of the O–H bond and a lower probability of the (assumed) proton transfer takes place. The conversion of the first water molecule in the coordination sphere into OH~ leads, on one hand, to a further decrease of the polarization of the O–H bond of the remaining water molecules and, on the other hand, to a weaker electrostatic interaction with approaching OH~ due to the lower electric field of the ion as a whole. This effect becomes more drastic, the higher the number of OH~ in the coordination sphere.

The hydrolysis constants ($K_h$) of reaction (2) are calculated according to

$$K_h = \frac{[a_{(Ce(OH)_{n}H^{-})}]^{+} \cdot (a_{H^{+}})^{n}}{a_{Ce^{4+}}} = \beta_i K_w^i$$

and listed in Table 4. The $(K_h)_1$ values reported in [8] for 298 and 308 K (5.2, respectively 11.8 m) are in good agreement with ours.