Thermodynamic Study of Ce^{4+}/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+}/Ce^{3+} has been determined up to 368 K by means of cyclic voltammetric measurement in aqueous $HClO_4$ solutions with c_{HClO_4} decreasing from 7.45 to 0.023 mol kg^{-1}. A constant potential of $(1.741\ V)_{298\ K}$, resp. $(1.836\ V)_{368\ K}$, indicating the existence of pure unhydrolysed Ce^{4+} was obtained at $c_{HClO_4} \geq 6.05$ 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. ΔS and ΔH of the redox reaction were determined as functions of *T* at the different $HClO_4$ concentrations. ΔS is positive at $c_{HClO_4} > 1.85$ m and turns to be negative at lower concentrations. ΔH is negative at all $HClO_4$ concentrations studied. The cumulative formation constants β_i of the Ce(IV) hydroxo complexes and the corresponding hydrolysis constants $(K_h)_i$ were calculated. An unusual decrease of β_i with increasing temperature has been discussed.

Key words: Redox potential of Ce^{4+}/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+}/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^-/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 ≤ 3 is negligible at temperatures up to ≈ 338 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 $(Ag/AgCl)_{NaCl = 0.1\ m}$ 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

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as $HClO_4$ 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 H^+ activity of the solutions with $HClO_4$ concentration ≤ 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 $c_{HClO_4} \leq 0.094$ 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

$$Ce^{4+} + 1/2\, H_2 \Leftrightarrow Ce^{3+} + H^+ . \qquad (1)$$

With decreasing H^+ activity, hydroxo complexes are formed:

$$Ce^{4+} + i\, H_2O \Leftrightarrow [Ce(HO)_i]^{(4-i)+} + i\, H^+ . \qquad (2)$$

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

$$[Ce(OH)_i]^{(4-i)+} + 1/2\, H_2 + (i-1)\, H^+ \Leftrightarrow Ce^{3+}\, i\, H_2O . \qquad (3)$$

Reaction (1), as well as the sum of the reaction (2) and (3) leads to an increase of the 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 H^+ activity of the solution with $c_{HClO_4} =$ 0.94 m increases by 0.016% and that of the solution with $c_{HClO_4} = 0.023$ m by 0.6%. These differences are within the limit of experimental error and can be neglected.

The pH of the solutions with $c_{HClO_4} > 0.94$ 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 laking data of the ions at the corresponding concentrations and temperatures. However, neglecting the relatively small decrease of the pH due to the formation of $Ce(OH)]^{3+}$ in these solutions, their H^+ activity can be calculated at 298 K and 313 K according to Haase, Dücker and Küppers [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 $c_{HClO_4} \geq 0.94$ 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 $c_{HClO_4} =$ 6.05 m and $c_{Ce} = 0.005$ 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 ≤ 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, $HClO_4$ molalities and pH values (resp. the corresponding pOH).

		T/K							
		298	308	318	328	338	348	358	368
$-\log K_w$		13.996	13.680	13.396	13.137	12.925	12.712	12.515	12.355
c_{HClO_4}									
6.05 m	E/V	1.741	1.760	1.778	1.795	1.810	1.820	1.829	1.836
5.46 m	E/V	1.715	1.735	1.754	1.769	1.783	1.795	1.804	1.812
4.83 m	E/V	1.705	1.720	1.735	1.748	1.762	1.771	1.778	1.785
3.44 m	E/V	1.696	1.705	1.713	1.720	1.725	1.730	1.734	1.736
1.85 m	E/V	1.693	1.693	1.693	1.693	1.693	1.693	1.693	1.693
0.940 m	E/V	1.690	1.688	1.685	1.683	1.680	1.678	1.672	1.666
	pH	0.103	0.110	0.117	0.122	0.127	0.132	0.138	0.144
	pOH	13.893	13.570	13.279	13.015	12.798	12.580	12.377	12.211
0.710 m	E/V	1.663	1.661	1.658	1.654	1.650	1.646	1.642	1.634
	pH	0.251	0.255	0.260	0.265	0.269	0.273	0.279	0.285
	pOH	13.745	13.425	13.136	12.872	12.656	12.439	12.236	12.070
0.471 m	E/V	1.654	1.652	1.648	1.644	1.640	1.635	1.628	1.620
	pH	0.437	0.441	0.448	0.451	0.457	0.464	0.468	0.475
	pOH	13.559	13.239	12.948	12.686	12.468	12.248	12.047	11.880
0.283 m	E/V	1.652	1.649	1.645	1.642	1.637	1.632	1.625	1.616
	pH	0.658	0.663	0.668	0.672	0.676	0.682	0.685	0.690
	pOH	13.338	13.017	12.728	12.465	12.249	12.030	11.830	11.665
0.236 m	E/V	1.651	1.648	1.644	1.641	1.636	1.631	1.624	1.615
	pH	0.735	0.740	0.744	0.748	0.753	0.758	0.764	0.768
	pOH	13.262	12.940	12.652	12.389	12.172	11.954	11.751	11.587
0.189 m	E/V	1.634	1.629	1.624	1.618	1.609	1.600	1.589	1.575
	pH	0.829	0.833	0.837	0.840	0.845	0.850	0.855	0.862
	pOH	13.167	12.847	12.559	12.297	12.080	11.862	11.660	11.493
0.094 m	E/V	1.630	1.624	1.616	1.608	1.598	1.587	1.575	1.559
	pH	1.115	1.119	1.122	1.125	1.127	1.133	1.137	1.145
	pOH	12.882	12.561	12.274	12.012	11.798	11.579	11.378	11.210
0.071 m	E/V	1.589	1.589	1.575	1.557	1.536	1.508		
	pH	1.228	1.231	1.234	1.237	1.243	1.247		
	pOH	12.768	12.449	12.162	11.900	11.682	11.465		
0.047 m	E/V	1.592	1.579	1.564	1.545	1.521			
	pH	1.393	1.395	1.397	1.400	1.405			
	pOH	12.604	12.285	11.999	11.737	11.520			
0.023 m	E/V	1.588	1.575	1.557	1.536	1.513			
	pH	1.679	1.683	1.688	1.692	1.696			
	pOH	12.317	11.997	11.708	11.445	11.229			

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 Sweeton, Mesmer, and Baes [6] and by Marshall and Franck [7] as well.

Conley [8] measured potentiometrically $(1.7431\ \text{V})_{298\,\text{K}}$ and $(1.7615\ \text{V})_{308\,\text{K}}$ for the redox potential of the half cell

$$Ce^{4+} + e^{-} \Leftrightarrow Ce^{3+} \,. \tag{4}$$

We obtained $(1.741\ \text{V})_{298\,\text{K}}$, respectively $(1.760\ \text{V})_{308\,\text{K}}$, which deviate by $\approx 0.1\%$ from the values of Conley. He also obtained $(1.6966\ \text{V})_{298\,\text{K}}$, $(1.6941\ \text{V})_{308\,\text{K}}$, and $(1.6914\ \text{V})_{318\,\text{K}}$ in solutions having $c_{HClO_4} = 0.9964$, 1.0065, and 1.0130 m, respectively. The comparison with our values obtained in the solution with $c_{HClO_4} = 0.94$ m, yields a deviation of $\approx 0.4\%$ which is very probably due the difference of the $HClO_4$ molality.

Temperature Effect

The temperature increase leads to an increase of the redox potential in solutions where pure uncomplexed

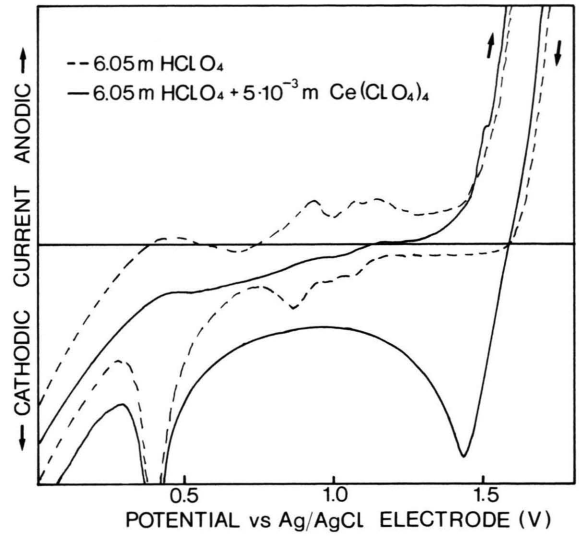

Fig. 1. Cyclic voltammogram at 298 K of the solution with $c_{HClO_4} = 6.05$ m and $c_{Ce} = 0.005$ m and of the pure $HClO_4$: Scan rate = 20 mV/s.

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

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

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 $c_{HClO_4} > 1.85$ m and turns to be negative at lower $HClO_4$ concentration due to the complex formation.

$$(\partial E/\partial T)_p = \Delta S(T)/zF \tag{5}$$

(ΔS = 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 ΔS is not known. However, the isobaric change of E between the $T_0 = 298$ K and T can be described to a good approximation by the empirical equation

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

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

ΔS 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:

$$\Delta S = (\partial E/\partial T)_p zF = \{a + 2b(T - T_0)\}\, zF . \tag{7}$$

ΔH is then calculated from the fundamental equation

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

ΔS and ΔH of the redox reaction at the various $HClO_4$ concentrations are shown in Figs. 3 and 4. Only ΔS and ΔH 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 ($\Delta S = -17$ J mol^{-1} K^{-1} and $\Delta H = -168.3$ kJ mol^{-1}), obtained in the solution with $c_{HClO_4} = 0.94$ m and $c_{Ce} = 0.000125$ m are between those reported in [8] for the two solutions having $c_{HClO_4} = 1$ m and $c_{Ce} = 0.005$ m, respectively $c_{HClO_4} = 1$ m and c_{Ce} extrapolated to zero m ($\Delta S = -11.29$ J mol^{-1} K^{-1}, $\Delta H = -165.9$ kJ mol^{-1}, respectively $\Delta S = -26.75$ J mol^{-1} K^{-1}, $\Delta H = -171.38$ 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

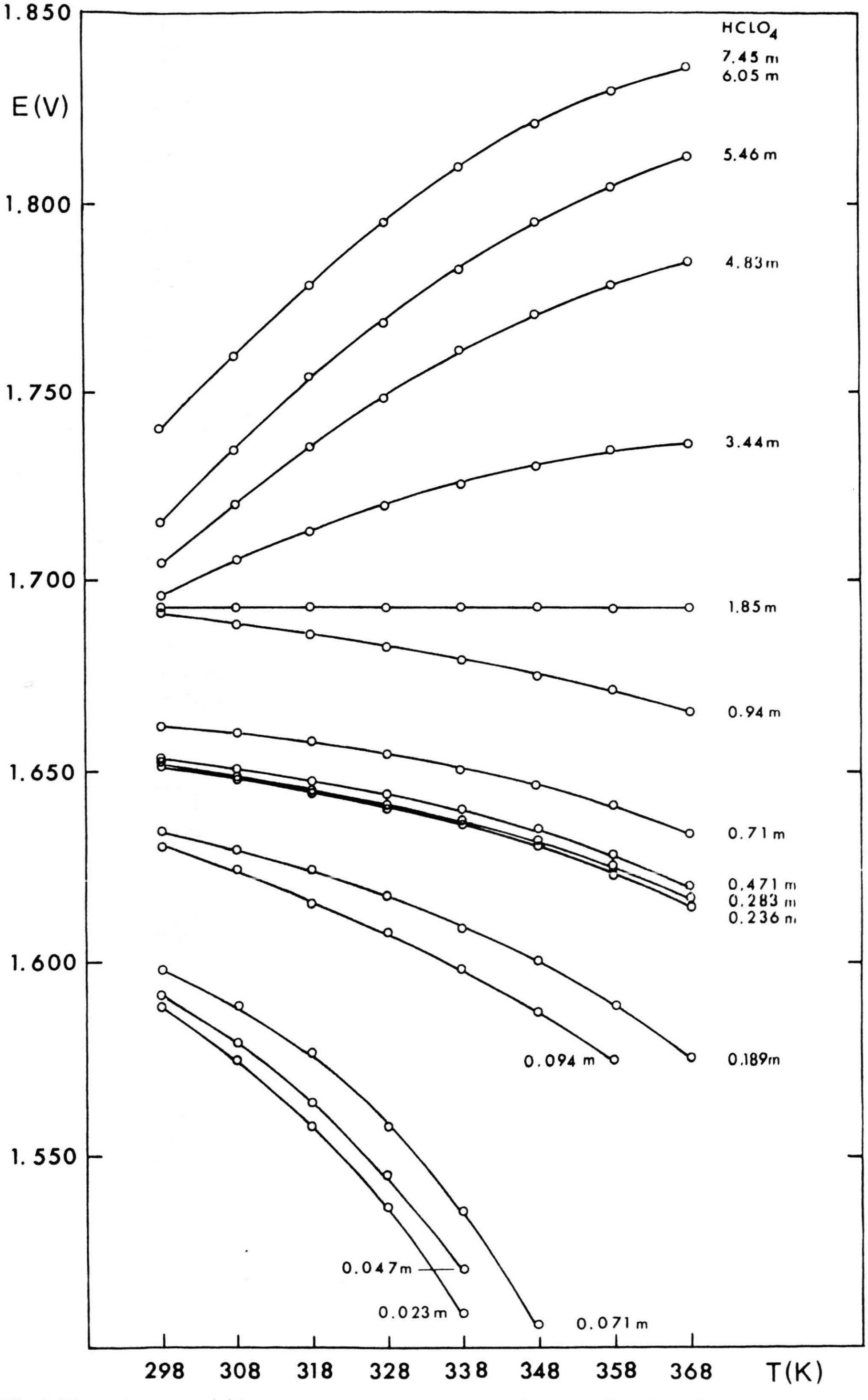

Fig. 2. The redox potential in $HClO_4$ of different concentrations as a function of temperature.

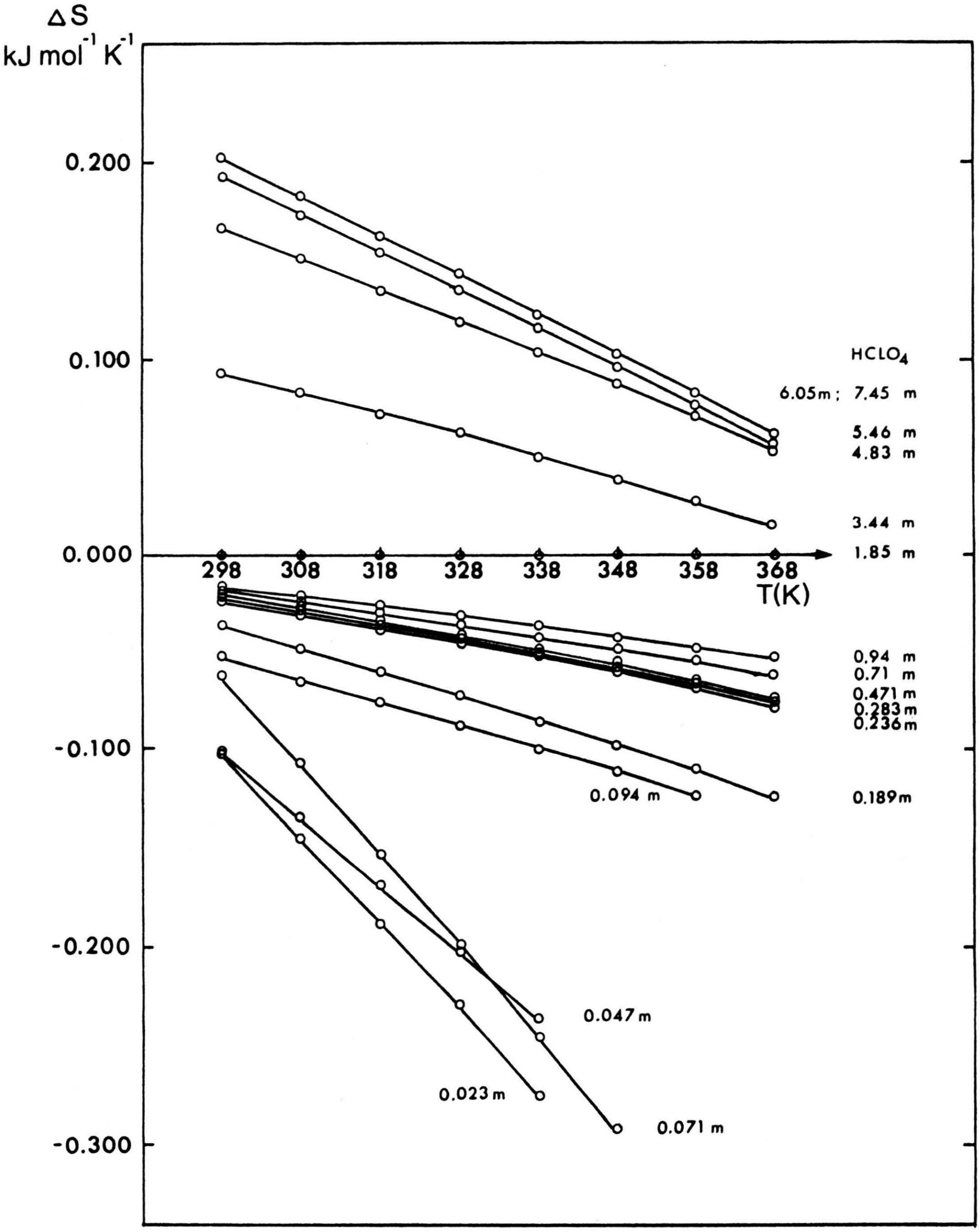

Fig. 3. ΔS of the redox reaction in $HClO_4$ of various concentrations as a function of temperature.

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.

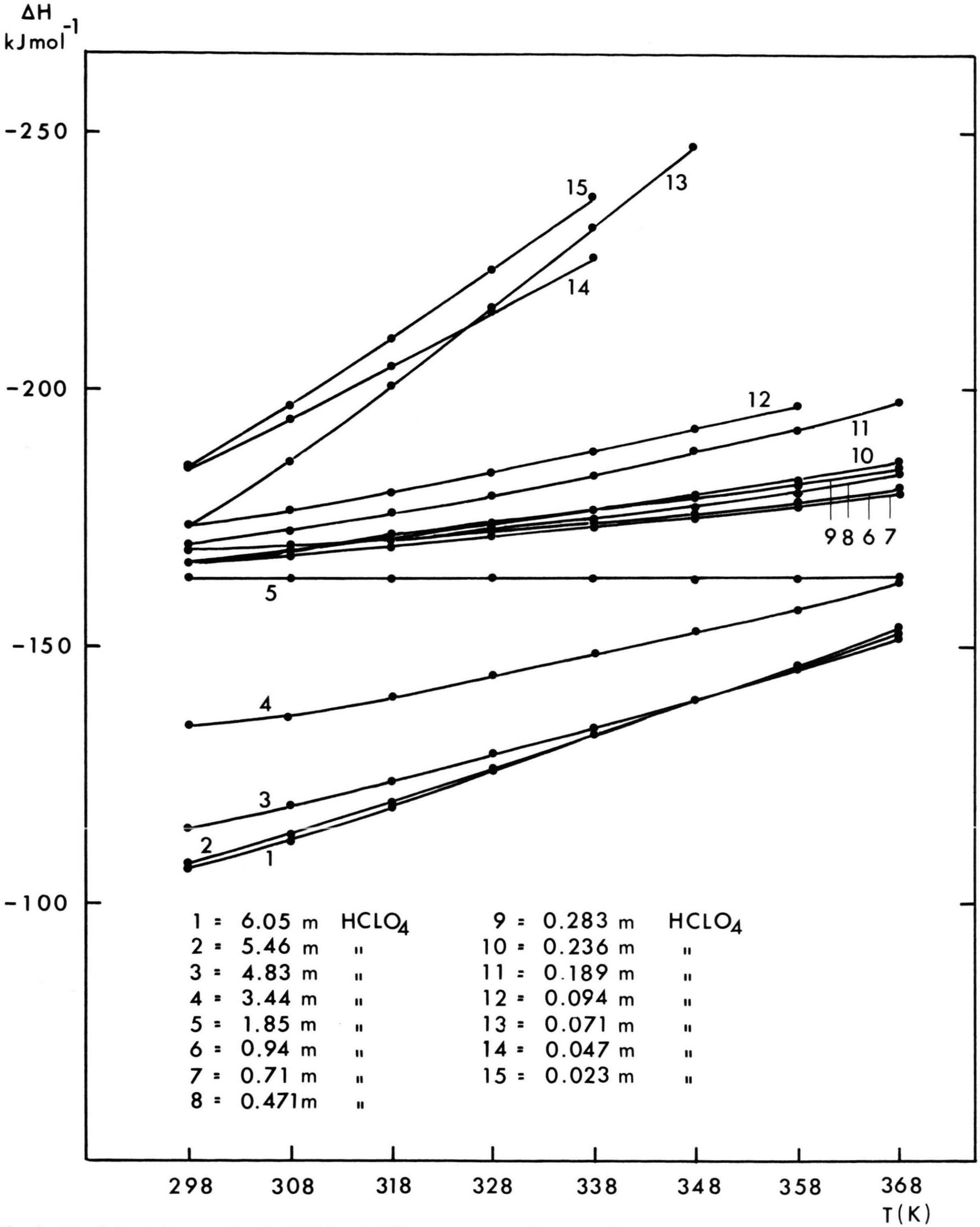

Fig. 4. *ΔH* of the redox reaction in $HClO_4$ of different concentrations as a function of temperature.

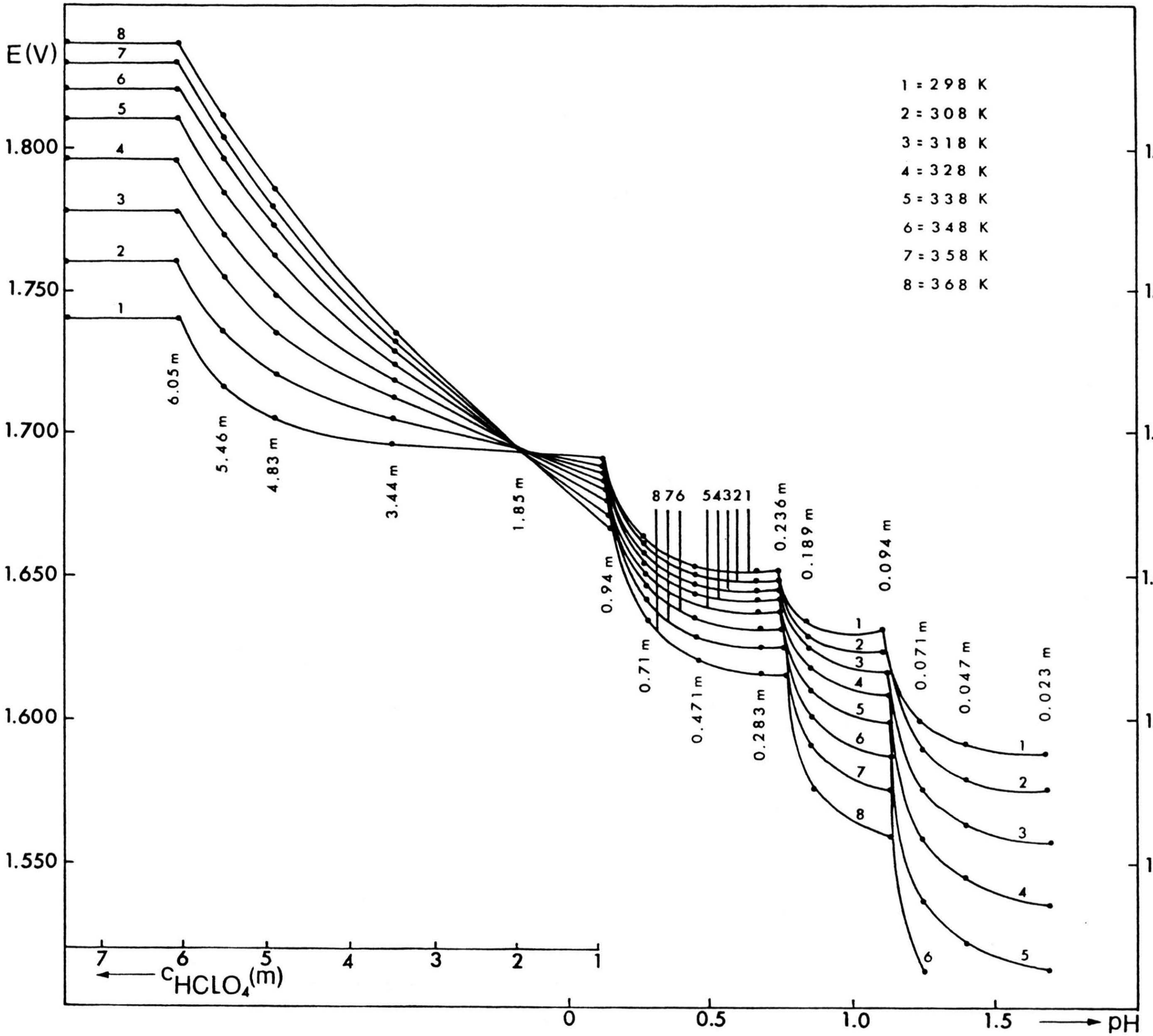

Fig. 5. The redox potential at different temperatures as a function of the $HClO_4$ molality, as well as of the pH.

Table 3. Cumulative formation constants β_i at 298–368 K. $(\log \beta_4)^*$ values at $T > 338$ K are extrapolated from Figure 6.

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

At $c_{HClO_4} \geq 6.05$ m, the potential of the half cell (4) is given by

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

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

$$E_{1/2} = E^0 . \tag{10}$$

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

$$Ce^{4+} + i\,OH^- \Leftrightarrow [Ce(OH)_i]^{(4-i)+} , \tag{11}$$

$$K_i = a_{[Ce(OH)_i]^{(4-i)+}} / a_{[\{Ce(OH)_{i-1}\}^{(4-i-1)+}]} (a_{OH^-}) , \tag{11 a}$$

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

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

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

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

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

$$E = E^0 - (RT/F) \ln \{[1 + \sum \beta_i (a_{OH^-})^i] \, a_{Ce^{3+}} / A_{Ce(IV)}\} , \tag{13}$$

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

$$E'_{1/2} = E_{1/2} - (RT/F) [\ln [1 + \sum \beta_i (a_{OH^-})^i] . \tag{14}$$

Equation (14) is rearranged to

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

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

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

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_{HClO_4} is ≤ 0.94 m, respectively as a function of the $HClO_4$ molality at higher concentrations. In the whole temperature region studied, a constant potential which indicates the existence of the pure uncomplexed Ce^{4+} ions, was first obtained at $c_{HClO_4} \geq 6.05$ m. At lower $HClO_4$ 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 $Ce(OH)_4$ 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 β_i from (14a), taking all measured values into account, leads to no convergence due to the nearly independence of the potential of a_{OH^-} in the practically horizontal parts of the curves. However, in our case β_i

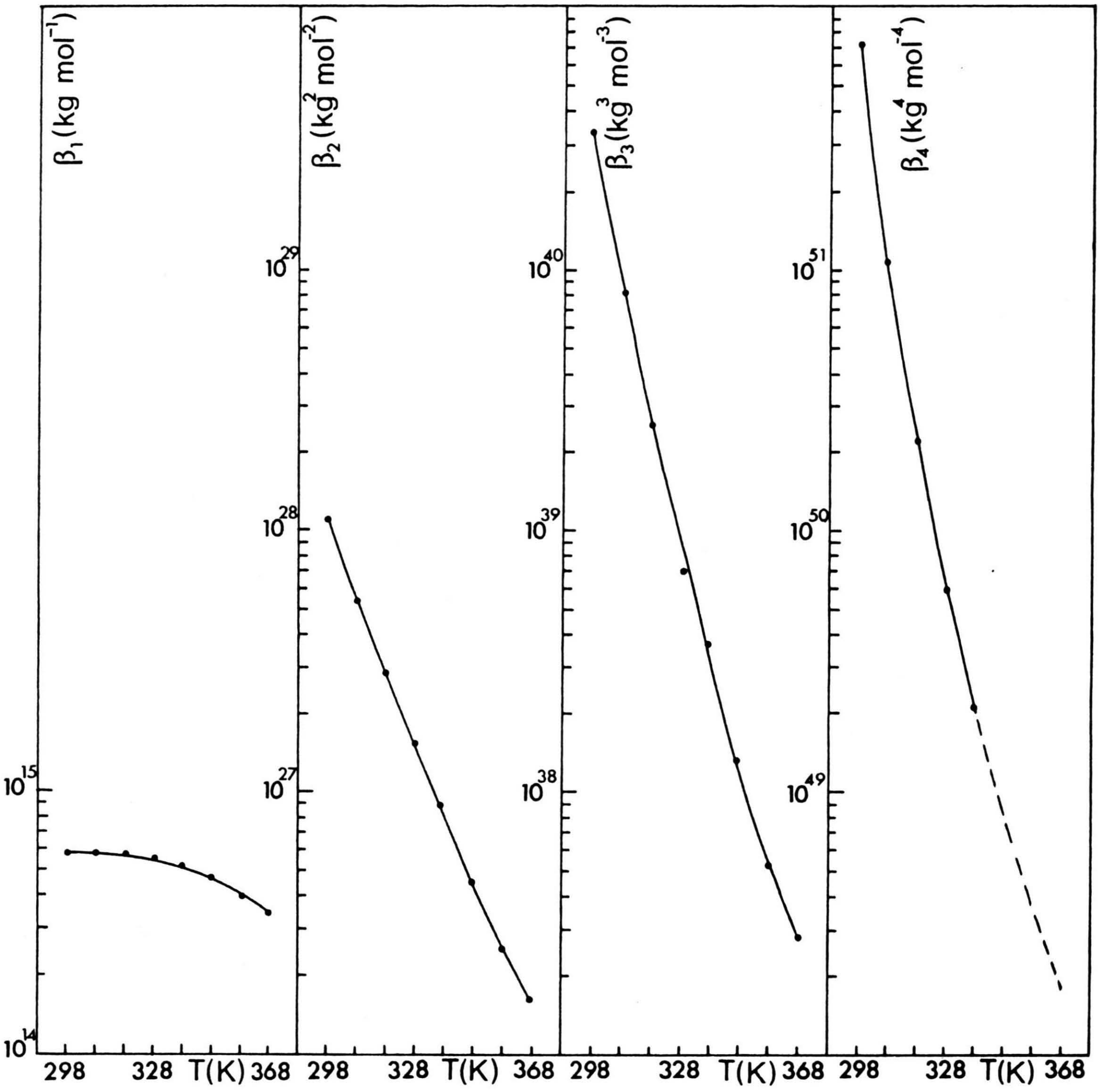

Fig. 6. The dependence of β_i on temperature.

can be calculated to a good approximation using the a_{OH^-} values corresponding to the pH at which the potential became nearly constant. Equation (14a) then applies for one species and is simplified to

$$[\exp(-\Delta E_{1/2}\,F/RT)]/a_{(OH^-)^i} = \beta_i\,. \qquad (16)$$

The so obtained log β_i values are listed in Table 3. Figure 6 shows β_i as a function of T, where a decrease with increasing T is observed. Between 298 and 368 K, β_1 decreases slightly within the same order of magnitude, whereas β_2, β_3, and β_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+},

Table 4. Hydrolysis constants $(K_h)_i$ (m^i) at 298–368 K.

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

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_2O 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 $(K_h)_i$ of reaction (2) are calculated according to

$$(K_h)_i = \{a_{[Ce(OH)_i]^{(4-i)+}} (a_{H^+})^i\} / a_{Ce^{4+}} = \beta_i K_w^i \qquad (17)$$

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.

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