Hydrolytic Behavior of Th^{4+}, UO_2^{2+}, and Ce^{3+} Ions at Various Temperatures

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The hydrolytic behavior of Th^{4+}, UO_2^{2+}, and Ce^{3+} was investigated using the potentiometric method at elevated temperatures in KCl medium. For each metal ion, stability constants were obtained from the pH-metric data using the program HYPERQUAD2006. The formation of $[Th(OH)]^{3+}$, $[Th(OH)_2]^{2+}$, $[Th(OH)_3]^{+}$, $Th(OH)_4$, $[Th_4(OH)_8]^{8+}$, and $[Th_6(OH)_{15}]^{9+}$ for the thorium ion, $[UO_2(OH)]^{+}$, $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_3(OH)_4]^{2+}$, and $[(UO_2)_3(OH)_5]^{+}$ for the uranyl ion, and $[Ce_2(OH)]^{5+}$, $[Ce_2(OH)_2]^{4+}$, $Ce(OH)_3$, and $[Ce_2(OH)_5]^{+}$ for the cerium ion was taken into consideration. In addition, the effect of temperature on the stability constants was studied, and thermodynamic parameters were derived and discussed.

Introduction

The chemical properties of the actinide and lanthanide elements in aqueous solution, such as their oxidation states and the extent of their hydrolysis and complexation reactions, govern their behavior in complex mixtures. The hydrolysis of actinides and lanthanides has recently been a compelling subject.[1−3]

The determination of stability constants is an essential process in solution chemistry as well as for many other branches of chemistry. To compute stability constants from potentiometric and spectrophotometric data, many software programs such as BEST, LETAGROP, MINIQUAD, PKAS, SUPERQUAD, and HYPERQUAD[4] have been used to date. All of these programs use the least-squares approach. Among them, HYPERQUAD2006 is one of the most recent versions of the HYPERQUAD program to determine stability constants from potentiometric and spectrometric data. In HYPERQUAD, the calculation proceeds in two stages. First, estimates must be made of all free concentrations using the HYPERQUAD simulation and speciation program, HySS. Then, these estimates are refined by Newton−Raphson iteration. Finally, the refinement must be terminated with a suitable criterion.[5,6]

In the present study, the hydrolytic behavior of Th^{4+}, UO_2^{2+}, and Ce^{3+} has been investigated using pH titration data at elevated temperatures. The stability constants of the hydrolytic species of these metal ions were simulated using the HySS program and were computed with the aid of the HYPERQUAD2006 computer program.[5−7] Furthermore, thermodynamic data on the complexation of actinides at elevated temperatures is mandatory to gain an understanding of the coordination chemistry of actinides[8] and lanthanides. Therefore, thermodynamic parameters were derived and discussed by utilizing this data.

Experimental Section

Materials. All chemicals were supplied by the Merck Chemical Co. (Germany). Bidistilled water was obtained from the Millipore (Milli-Q Gradient A-10) water purification instrument. Solutions of Th^{4+}, UO_2^{2+}, and Ce^{3+} were prepared from their nitrate salts ($UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$). Stock solutions of 0.1 M NaOH and 0.1 M HCl were prepared in CO_2-free bidistilled water and standardized by a literature method.[9] KCl (1 M) was used to adjust the ionic strength of the media.

Apparatus and Procedure. pH-Metric titrations were performed in a 100 mL jacketed cell (Metrohm, thermostat jacket, 6.1418.250) that has two ports for electrodes, a port for titrant addition, and a port for purging with inert gas. The titrations were carried out at (25 ± 0.1) °C, (37 ± 0.1) °C, and (45 ± 0.1) °C by circulating water from a thermostat (Nüve-BM 302). Metrohm autoburets (Titroprocessor 686 and Dosimat 665) with a glass electrode (Metrohm 6.0262.100) were used for the pH measurements. To avoid any side effects that could come from oxygen, argon gas (ultrahigh purity, 99.99 %) was bubbled through the solution before and during the pH measurements in all titrations. The pH meter was calibrated with standard buffer solutions (pH 4.0 and 7.0; HC607673 and OC516474, respectively) before the pH measurements.

The results of strong acid versus alkali titrations were analyzed using a computer program called GLEE (glass electrode evaluation). The program GLEE has been developed as part of the HYPERQUAD suite of programs for stability constant determination. The values of pK_w were confirmed using GLEE[7] ($pK_w = 13.78$ at 25 °C, 13.46 at 37 °C, and 13.16 at 45 °C). The ionic strength (I) of all of the titration mixtures was adjusted to 0.1 by the addition of the requisite volume of 1 M KCl solution, and a constant volume was maintained at 100 mL. Before performing the titrations, we simulated titration conditions using the HySS 2006 computer program.[6] For the determination of stability constants, a few preliminary titrations were performed to investigate the effects of experimental variables such as the time interval between consecutive titration readings and varying concentrations of relevant metal ions at appropriate pH ranges and at desired temperatures. The pH measurements were done using the MET program of Titroprocessor 686 by recording the pH measurements at suitable time intervals for each metal ion.

Titration of Thorium. An aqueous solution of thorium at variable concentrations ((0.5, 1.0, and 2.0) $mmol \cdot dm^{-3}$) and between (1.0 and 2.3) mL of standardized ∼ 0.1 M HCl was added to each sample. (The amount of required metal and proton concentrations was established by speciation calculations using the program HySS.)[6] We performed titrations by recording the pH measurements. A summary of the titrations used in the

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Table 1. Results of Potentiometric Measurements of Hydrolysis of Th^{4+}

t/°C	Th^{4+} hydrolytic species	metal ion range mmol·dm^{-3}	−log β	ref
25	(1, −1)	0.044 to 1.09	3.51 ± 0.03	1[a]
	(1, −3)		10.75 ± 0.14	
15	(1, −1)	0.0096 to 0.104	3.6 ± 0.1	2[b]
	(1, −2)		8.8 ± 0.1	
	(1, −3)		14.9 ± 2.8	
	(1, −4)		22.0 ± 0.4	
	(4, −8)		20.2 ± 0.3	
	(6, −15)		41.4 ± 0.2	
25	(1, −1)	0.0116 to 0.123	3.3 ± 0.1	
	(1, −2)		8.6 ± 0.1	
	(1, −3)		14.2	
	(1, −4)		19.4 ± 0.5	
	(4, −8)		19.1 ± 0.1	
	(6, −15)		39.5 ± 0.2	
35	(1, −1)	0.0104 to 0.103	3.2 ± 0.1	
	(1, −2)		8.4 ± 0.1	
	(1, −3)		12.7 ± 3.5	
	(1, −4)		17.8 ± 0.4	
	(4, −8)		18.0 ± 0.1	
	(6, −15)		36.6 ± 0.2	
25	(1, −2)	0.1	8.36 ± 0.11	12[c]
	(1, −3)		11.63 ± 0.09	
	(1, −4)		18.24 ± 0.13	
	(2, −7)		24.32 ± 0.08	
25	(1, −1)	0.5 to 2.0	3.29 ± 0.21	this work
	(1, −2)		6.86 ± 0.08	
	(1, −3)		10.85 ± 0.29	
	(1, −4)		15.81 ± 0.58	
	(4, −8)		16.89 ± 1.02	
	(6, −15)		35.03 ± 0.97	
37	(1, −1)		2.89 ± 0.42	
	(1, −2)		5.98 ± 0.19	
	(1, −3)		10.04 ± 0.44	
	(1, −4)		15.33 ± 0.45	
	(4, −8)		15.15 ± 0.79	
	(6, −15)		31.08 ± 1.09	
45	(1, −1)		3.06 ± 0.35	
	(1, −2)		5.96 ± 0.27	
	(1, −3)		9.08 ± 0.53	
	(1, −4)		15.26 ± 0.95	
	(4, −8)		14.38 ± 1.44	
	(6, −15)		29.76 ± 2.33	

[a] Medium: 1 M $NaClO_4$, titration data of experiments were analyzed by HYPERQUAD. [b] Medium: 1 M $NaClO_4$, titration data of experiments were analyzed by MINIQUAD. [c] Medium: 0.1 M $NaClO_4$ titration data of experiments were analyzed by SIRKO_P and SUPERQUAD.

Table 2. Summary of Titrations of Th^{4+} in 1.0 mol·dm^{-3} KCl

t/°C	initial total [Th^{4+}] mmol·dm^{-3}	pH range	no. of points
25	0.5	2.82 to 4.60	43
	1.0	2.55 to 4.51	106
	2.0	2.99 to 4.28	109
37	0.5	2.81 to 5.07	44
	1.0	2.50 to 4.46	131
	2.0	2.68 to 4.31	121
45	0.5	2.73 to 4.59	49
	1.0	2.50 to 4.51	124
	2.0	2.52 to 4.24	117

Table 3. Results of Potentiometric Measurements of Hydrolysis of UO_2^{2+}

t/°C	UO_2^{2+} hydrolysis species	metal ion range mmol·dm^{-3}	−log β	ref
25	(2, −2)	2.99	6.15 ± 0.05	1[a]
	(4, −6)		18.43 ± 0.09	
	(4, −7)		23.36 ± 0.07	
25	(2, −2)		5.89 ± 0.37	1[b]
	(3, −5)		16.19 ± 0.16	
25	(1, −1)	0.206 to 2.060	5.17 ± 0.03	15[c]
	(2, −2)		5.86 ± 0.04	
	(3, −4)		12.00 ± 0.06	
	(3, −5)		16.09 ± 0.06	
10	(1, −1)	0.4 to 11.0	6.1 ± 0.3	17[d]
	(2, −2)		6.30 ± 0.02	
	(3, −5)		17.52 ± 0.01	
25	(1, −1)		5.58 ± 0.24	
	(2, −2)		5.83 ± 0.02	
	(3, −5)		16.37 ± 0.02	
40	(1, −1)		5.11 ± 0.11	
	(2, −2)		5.43 ± 0.01	
	(3, −5)		15.35 ± 0.01	
55	(1, −1)		5.07 ± 0.24	
	(2, −2)		5.06 ± 0.03	
	(3, −5)		14.45 ± 0.02	
70	(1, −1)		4.51 ± 0.11	
	(2, −2)		4.73 ± 0.03	
	(3, −5)		13.61 ± 0.02	
85	(1, −1)		4.24 ± 0.15	
	(2, −2)		4.49 ± 0.03	
	(3, −5)		12.94 ± 0.02	
25	(1, −1)	0.18 to 0.74	5.54 ± 0.35	this work
	(2, −2)		5.60 ± 0.24	
	(3, −4)		11.21 ± 0.31	
	(3, −5)		16.07 ± 0.16	
37	(1, −1)		5.33 ± 0.03	
	(2, −2)		5.42 ± 0.28	
	(3, −4)		11.36 ± 0.03	
	(3, −5)		15.66 ± 0.45	
45	(1, −1)		< 0	
	(2, −2)		4.97 ± 0.42	
	(3, −4)		11.81 ± 0.40	
	(3, −5)		15.04 ± 0.85	

[a] Medium: 1 M $NaClO_4$, titration data of experiments were analyzed by HYPERQUAD. [b] Medium: 0.1 M $NaClO_4$. [c] Medium: 0.1 M KCl, titration data of experiments were analyzed by MINIQUAD. [d] Medium: 0.1 M tetraethylammonium perchlorate, titration data of experiments were analyzed by HYPERQUAD.

Table 4. Summary of Titrations of UO_2^{2+} in 1.0 mol·dm^{-3} KCl

t/°C	initial total [UO_2^{2+}] mmol·dm^{-3}	pH range	no. of points
25	0.18	3.64 to 6.07	49
	0.37	3.29 to 5.38	55
	0.74	3.60 to 5.16	58
37	0.18	3.68 to 5.34	50
	0.37	3.29 to 5.18	59
	0.74	3.66 to 5.32	64
45	0.18	3.63 to 5.04	49
	0.37	3.29 to 4.93	57
	0.74	3.67 to 5.39	56

numerical analysis for the three temperatures and concentrations is given in Tables 1 and 2.

Titration of Uranium. An aqueous solution of uranium at variable concentrations ((0.18, 0.37, and 0.74) mmol·dm^{-3}) and between (0.2 and 0.5) mL of standardized ∼ 0.1 M HCl was added to each sample as described above. The numerical values for hydrolytic species of UO_2^{2+} have been evaluated pH-metrically at 25 °C, 37 °C, and 45 °C and are tabulated in Tables 3 and 4.

Titration of Cerium. An aqueous solution of cerium at variable concentrations ((0.5, 1.0, and 2.0) mmol·dm^{-3}) and 0.5 mL of standardized ∼ 0.1 M HCl was added to each sample. (The amount of required metal and proton concentrations were established by speciation calculations using the program HySS.)[6] We performed titrations by recording the pH measurements. A summary of the titrations used in the numerical analysis for three different concentrations and at 25 °C, 37 °C, and 45 °C is given in Tables 5 and 6.

Each set of titrations was repeated at least three times at (25, 37, and 45) °C for different metal ion concentrations.

Calculations. The data from each titration were imported to the program HYPERQUAD2006 and treated by nonlinear least-squares refinement.[5] The β values of each metal species given in Tables 1, 3, and 5 are the average values of logarithms. The

Table 5. Results of Measurements of Hydrolysis Of Ce^3

t/°C	Ce^{3+} hydrolysis species	data type[a]	metal ion range mmol·dm^{-3}	$-\log \beta$	ref
25	(1, −1)			8.1	21[b]
	(1, −2)			16.3	
	(1, −3)			26.0	
	(3, −5)			32.8	
25	(1, −1)	pt	1.0	6.87 ± 0.08	12[c]
	(1, −3)			19.82 ± 0.05	
	(1, −4)			28.93 ± 0.06	
	(2, −3)			15.93 ± 0.09	
	(2, −7)			44.7 ± 0.1	
50	(1, −1)	volt		9.13 ± 0.03	19[d]
	(2, −1)			9.45 ± 0.09	
	(3, −5)			35.60 ± 0.03	
25	(2, −1)	pt	0.5 to 2.0	4.02 ± 0.49	this work
	(2, −2)			11.51 ± 0.36	
	(1, −3)			23.65 ± 0.82	
	(2, −5)			35.70 ± 0.80	
37	(2, −1)			3.39 ± 0.30	
	(2, −2)			< 0	
	(1, −3)			21.67 ± 1.19	
	(2, −5)			32.99 ± 1.40	
45	(2, −1)			3.20 ± 0.34	
	(2, −2)			< 0	
	(1, −3)			20.81 ± 1.66	
	(2, −5)			31.95 ± 1.61	

[a] pt: potentiometric, volt: voltametric. [b] Medium: ionic strength 1.0. [c] Medium: 0.1 M $NaClO_4$, titration data of experiments were analyzed by SIRKO_P and SUPERQUAD. [d] Medium: 3 m $LiClO_4$.

Table 6. Summary of Titrations of Ce^{3+} in 1.0 mol·dm^{-3} KCl

t/°C	initial total [Ce^{3+}] mmol·dm^{-3}	pH range	no. of points
25	0.5	3.33 to 10.91	210
	1.0	3.22 to 10.87	148
	2.0	2.29 to 11.05	149
37	0.5	3.30 to 10.79	168
	1.0	3.30 to 10.28	76
	2.0	3.28 to 10.43	142
45	0.5	3.25 to 10.18	124
	1.0	3.29 to 10.04	76
	2.0	3.05 to 11.04	153

Table 7. Thermodynamic Parameters for Th^{4+} (Initial Total [Th^{4+}] = 1.0 mmol·dm^{-3}, in 1.0 mol·dm^{-3} KCl) and Literature Data

		thermodynamic parameters			
t/°C	Th^{4+} ion ($+p$, $-q$)	ΔH (kJ·mol^{-1})	ΔG (kJ·mol^{-1})	ΔS (J·mol^{-1})	ref
25	(1, −1)	40.5 ± 6.4	20.0 ± 0.2	68.8 ± 20.7	this work
	(1, −3)	86.3 ± 6.8	60.1 ± 0.8	87.9 ± 19.9	
	(1, −4)	13.0 ± 8.3	92.5 ± 2.0	−266.4 ± 21.2	
	(4, −8)	214.5 ± 1.1	102.2 ± 0.8	376.6 ± 0.8	
	(6, −15)	352.0 ± 16.7	202.8 ± 1.9	501.1 ± 49.5	
37	(1, −1)		17.7 ± 1.3	73.5 ± 16.6	
	(1, −3)		57.8 ± 0.2	92.0 ± 21.2	
	(1, −4)		93.9 ± 4.3	−260.9 ± 13.1	
	(4, −8)		95.3 ± 1.3	384.3 ± 7.8	
	(6, −15)		193.8 ± 3.9	510.8 ± 66.6	
45	(1, −1)		18.9 ± 0.4	68.0 ± 21.3	
	(1, −3)		58.6 ± 0.5	87.2 ± 19.7	
	(1, −4)		98.1 ± 1.2	−267.4 ± 22.6	
	(4, −8)		95.10 ± 1.2	375.3 ± 0.4	
	(6, −15)		193.3 ± 1.9	499.5 ± 46.7	
0	(1, −1)	24.7		3.8	13
25	(1, −2)	58.1		46	
95	(2, −2)	61.9		118.7	
	(4, −8)	241.3		445.8	
	(6, −15)	453.7		818.4	
15	(1, −1)	38 ± 6		60 ± 20	2
25	(1, −2)	36 ± 1		−44 ± 4	
35	(1, −3)	190 ± 40		300 ± 100	
	(1, −4)	360 ± 40		800 ± 100	
	(4, −8)	191 ± 3		280 ± 10	
	(6, −15)	410 ± 60		600 ± 200	

weights of the titrant were directly input into the HYPERQUAD2006 program as independent variables and the emf or pH values were directly input as the dependent variables. Whereas the log β values for the proton−ligand or metal−ligand species are calculated under acceptable conditions in the solution, others worsen the statistical parameters and are rejected as being negative or excessive by the HYPERQUAD program. Errors in fixed values are not introduced in HYPERQUAD, so that error propagation is not considered in optimizing the protonation constants. Statistical data refer to protonation constants: N = total number of experimental data points used, χ^2 = observed statistical parameter based on weighted residuals of the emf or pH readings (values < 12.6 indicate a confidence level of > 95 %), and σ = ratio of the root-mean-square of the weighted residuals to the estimated error under the actual working conditions (σ_V and σ_E).[10]

In the current study, the hydrolysis reactions of lanthanides and actinides are generally represented by the following equation

$$pM^{n+} + qH_2O \leftrightarrow M_p(OH)_q^{(np-q)} + qH^+ \qquad (1)$$

The equilibrium constants for the overall reaction are described as

$$\beta^*_{pq} = \frac{[M_p(OH)_q^{(np-q)+}][H^+]^q}{[(M^{n+})]^p} \qquad (2)$$

where; $M^{n+} = Th^{4+}$, UO_2^{2+}, or Ce^{3+} (in this study).

The thermodynamic parameters, enthalpy change ($\Delta H°$), entropy change ($\Delta S°$), and Gibbs energy change ($\Delta G°$), were determined from the stability constants using Gibbs and van't Hoff equations.

Results and Discussion

A summary of literature data and mean values of the hydrolysis constants (the log values) obtained from this study for each metal ion with the associated experimental parameters is given in Table 1, 3, and 5. The data used in the numerical analyses are summarized for each metal ion in Tables 2, 4, and 6.

Also, thermodynamic parameters and literature data for hydrolytic species of Th^{4+}, UO_2^{2+}, and Ce^{3+} have been calculated and summarized in Tables 7, 8, and 9. In addition, percent distributions of metal ions in various hydrolytic species at certain temperatures are shown in Figures 1, 2, and 3. These Figures were drawn using the IUPAC Stability Constants Database (SC-Database).[11]

Relationships among the metal concentrations and other variables were analyzed by multivariate statistics using the SPSS 10 program (Univariate Variance Analyses and (Chicago, IL) Pearson Correlation). Correlation is significant at p < 0.01 for the 99 % confidence level. Whereas log β values were chosen as dependent variables, the independent variable was temperature for each metal ion.

Hydrolysis of Thorium Ion, Th^{4+}. In aqueous solution, thorium exists only in the tetravalent state and is stable at pH 3 or less. It has several polymeric hydrolysis products such as $[Th(OH)]^{3+}$, $[Th_2(OH)_2]^{6+}$, $[Th_4(OH)_8]^{8+}$, and $[Th_6(OH)_{15}]^{9+}$ depending on the ionic strength of the medium, as indicated in Table 1. The hydrolytic species of the thorium ion include monomeric species such as $[Th(OH)]^{3+}$ and $[Th(OH)_3]^+$ and the polymeric species $[Th_4(OH)_8]^{8+}$ and $[Th_6(OH)_{15}]^{9+}$ that were reported to be stable in different pH ranges.[1,2] The data obtained in the present study showed that both monomeric and polymeric

Table 8. Thermodynamic Parameters for UO_2^{2+} (Initial Total $[UO_2^{2+}] = 0.18\ mmol \cdot dm^{-3}$ in $1.0\ mol \cdot dm^{-3}$ KCl) and Literature Data

		thermodynamic parameters			
	UO_2^{2+} ion	ΔH	ΔG	ΔS	
t/°C	$(+p, -q)$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(J \cdot mol^{-1})$	ref
25	(2, −2)	85.0 ± 20.2	30.4 ± 0.2	182.9 ± 66.9	this work
	(3, −5)	171.6 ± 5.1	92.2 ± 1.0	266.4 ± 20.7	
37	(2, −2)		29.8 ± 0.4	177.8 ± 66.4	
	(3, −5)		89.7 ± 0.1	264.1 ± 16.9	
45	(2, −2)		26.5 ± 1.1	183.8 ± 67.0	
	(3, −5)		86.7 ± 1.6	266.8 ± 21.3	
10	(1, −1)		32.1		17
	(2, −2)	51.5 ± 0.9	33.0	65.3 ± 3.6	
	(3, −5)	128.0 ± 0.5	91.61	128.5 ± 2.0	
25	(1, −1)	46.5 ± 3.7	30.8	53 ± 13	
	(2, −2)	48.2 ± 1.7	32.1	54 ± 6	
	(3, −5)	120.1 ± 1.6	89.84	101.5 ± 5.7	
40	(1, −1)		29.5		
	(2, −2)	50 ± 2	31.2	60 ± 6	
	(3, −5)	119 ± 2	88.12	99 ± 6	
55	(1, −1)		30.6		
	(2, −2)	53 ± 8	30.4	69 ± 24	
	(3, −5)	113 ± 7	86.57	80 ± 21	
70	(1, −1)		28.3		
	(2, −2)	58 ± 3	29.6	83 ± 7	
	(3, −5)	112 ± 3	84.87	79 ± 9	
85	(1, −1)	58 ± 7	27.6		
	(2, −2)	61 ± 2	29.1	89 ± 6	
	(3, −5)	110 ± 2	83.78	73 ± 6	

Table 9. Thermodynamic Parameters for Ce^{3+} (Initial Total $[Ce^{3+}] = 0.5\ mmol \cdot dm^{-3}$, in $1.0\ mol \cdot dm^{-3}$ KCl)

		thermodynamic parameters		
	Ce^{3+} ion	ΔH	ΔG	ΔS
t/°C	$(+p, -q)$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(J \cdot mol^{-1})$
25	(2, −1)	128.0 ± 23.6	25.9 ± 1.3	343.9 ± 83.3
	(1, −3)	42.8 ± 24.3	137.0 ± 3.2	−316.1 ± 71.2
	(2, −5)	288.3 ± 48.2	205.4 ± 1.5	278.2 ± 166.6
37	(2, −1)		21.1 ± 0.2	346.9 ± 76.6
	(1, −3)		142.0 ± 1.1	−320.0 ± 75.2
	(2, −5)		200.8 ± 1.8	282.2 ± 149.6
45	(2, −1)		19.1 ± 3.3	343.5 ± 84.4
	(1, −3)		143.1 ± 1.9	−315.5 ± 70.5
	(2, −5)		200.2 ± 5.7	277.5 ± 169.5

species such as $[Th(OH)]^{3+}$, $[Th(OH)_2]^{2+}$, $[Th(OH)_3]^+$, $Th(OH)_4$, $[Th_4(OH)_8]^{8+}$, and $[Th_6(OH)_{15}]^{9+}$ are stable in the same pH range, time interval, and metal ion concentration. This result is in agreement with the literature data. Another study on Th(IV) hydrolysis found in the literature was carried out by Bentouhami et al. at 25 °C using potentiometry.[12] The hydrolytic $[Th_2(OH)_7]^+$ species found in the pH range between 5 and 8 differs from that of our study because of the higher pH interval.

Figure 1a shows that $[Th_6(OH)_{15}]^{9+}$ and $[Th(OH)_3]^+$ are the dominant species at lower pH, whereas $Th(OH)_4$ is the most abundant species at higher pH in $1.0\ mmol \cdot dm^{-3}$ at 25 °C. There is a good agreement with the distribution of hydrolytic species previously indicated by Ekberg et al. when the differences in thorium ion concentration are considered.[2] At 37 °C, as seen in Figure 1b, $[Th(OH)_3]^+$ becomes the dominant species at lower pH, and $Th(OH)_4$ becomes the dominant species at higher pH. Despite this discrepancy between the dominant hydrolysis species at lower pH at temperatures between (25 and 37) °C, there are no significant differences in the distribution of species at (37 and 45) °C, as seen in Figure 1b,c. $[Th_4(OH)_8]^{8+}$ and $[Th_6(OH)_{15}]^{9+}$ are found to be stable in a narrow pH range similar to the results reported by Ekberg et al. Calculated stability constants for thorium species increase with increasing temperature. Therefore, there is a reasonable agreement with literature data for the species $[Th(OH)_2]^{2+}$, $Th(OH)_4$, $[Th_4(OH)_8]^{8+}$, and $[Th_6(OH)_{15}]^{9+}$, except for $[Th(OH)]^{3+}$, in the present study.[2]

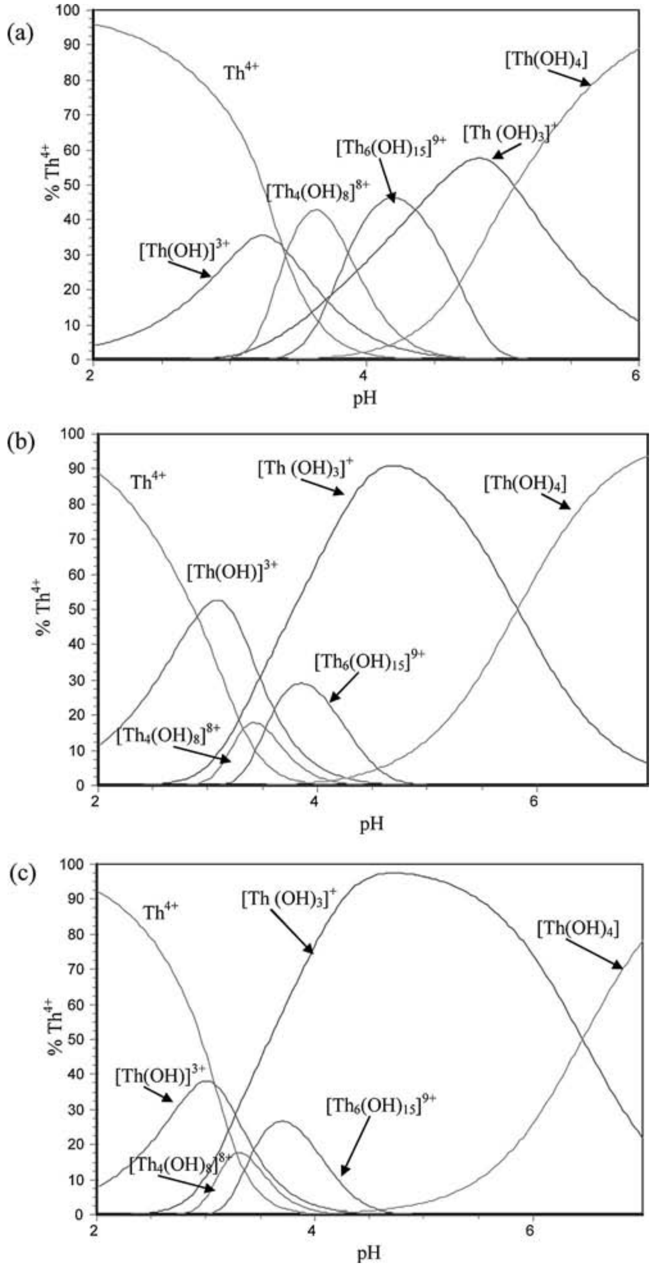

Figure 1. Percentage distribution of Th^{4+} in hydrolytic species at a total thorium concentration of $1.0\ mmol \cdot dm^{-3}$ in $1.0\ mol \cdot dm^{-3}$ KCl at (a) 25 °C, (b) 37 °C, and (c) 45 °C.

Taking into account the results of definite concentration range, there is a significant correlation between log β values and the temperature of the thorium ion, as seen in Table 1. Statistical results showed that log β values of $[Th(OH)_2]^{2+}$ ($p < 0.01$, $r^2 = 0.65$), $[Th(OH)_3]^+$ ($p < 0.01$, $r^2 = 0.74$), $[Th_4(OH)_8]^{8+}$ ($p < 0.01$, $r^2 = 0.53$), and $[Th_6(OH)_{15}]^{9+}$ ($p < 0.01$, $r^2 = 0.68$) correlated well with temperature.

The thermodynamic data calculated by Ekberg et al. and reported by Rao are also given in Table 7 for comparative purposes.[2,13] There is an agreement with the enthalpy values of the Ekberg et al. study, except for the $Th(OH)_4$ species. In the current study, all species show endothermic behavior and have a positive entropy value, except for $Th(OH)_4$, as seen in Table 7.

Hydrolysis of Uranyl Ion, UO_2^{2+}. The most extensively studied actinide is uranium. In a solution of pH less than 3, it

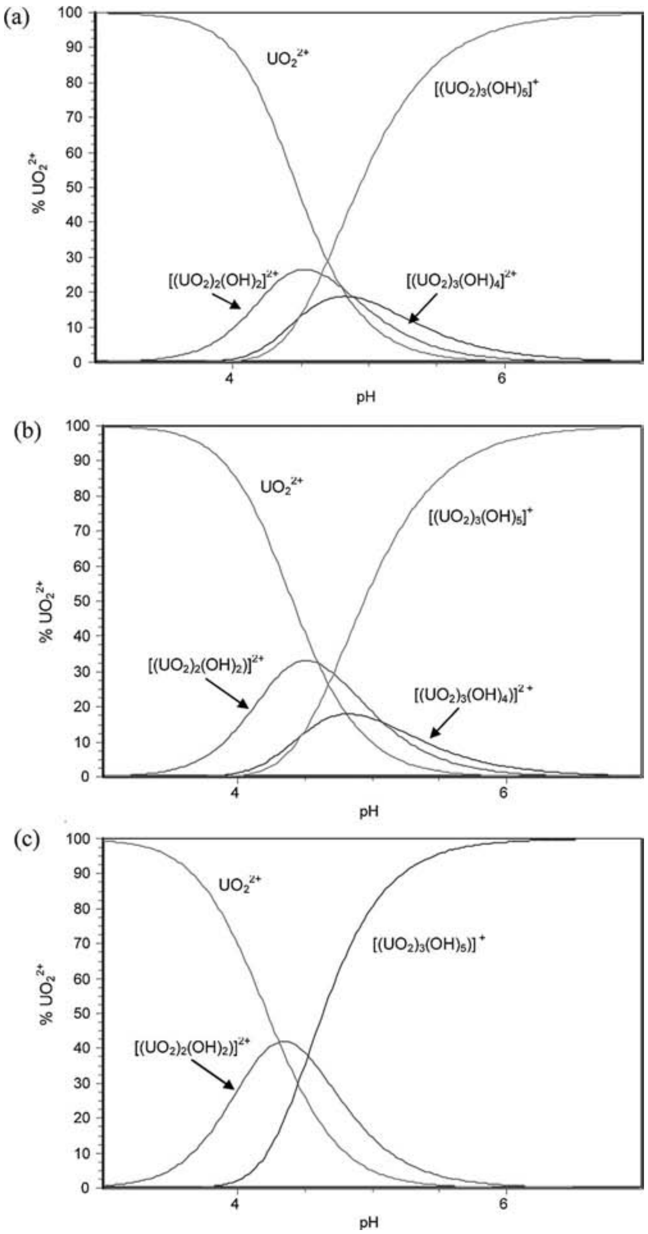

Figure 2. Percentage distribution of UO_2^{2+} in hydrolytic species at a total uranium concentration of 0.37 mmol·dm^{-3} in 1.0 mol·dm^{-3} KCl at (a) 25 °C, (b) 37 °C, and (c) 45 °C.

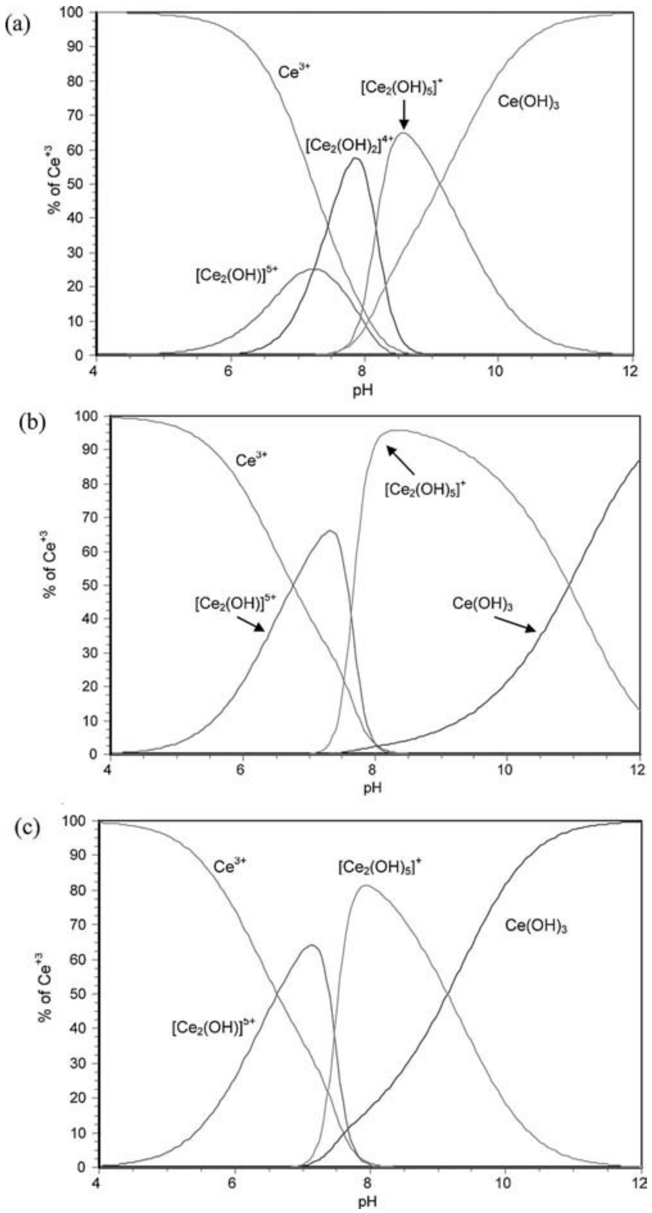

Figure 3. Percentage distribution of Ce^{3+} in hydrolytic species at a total cerium concentration of 0.5 mmol·dm^{-3} in 1.0 mol·dm^{-3} KCl at (a) 25 °C, (b) 37 °C, and (c) 45 °C.

exists as the uranyl (UO_2^{2+}) ion; formation of hydroxide complexes is important in a broad pH range starting at about pH 3. OH^- is a good bridging ligand; hence, the hydrolysis of UO_2^{2+} results almost exclusively in polynuclear species, even in very dilute solutions. Predominant species are $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$. The last one is observed at pH greater than 3.[14−16] In this study, whereas the $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_3(OH)_4]^{2+}$, and $[(UO_2)_3(OH)_5]^+$ species are present at all three temperatures, $[UO_2(OH)]^+$ is not observed at 45 °C. Figure 2a shows that $[(UO_2)_3(OH)_5]^+$ is the dominant species at pH > 4, whereas the other species are observed in a narrow pH range between 4 and 6. This is in good agreement with the findings of Sawant et al. and Brown for the corresponding species when differences in uranyl ion concentrations are considered.[1,15] Figure 2b,c shows that $[(UO_2)_3(OH)_5]^+$ continues to be the dominant species at pH greater than 4 at both (37 and 45) °C.

Sawant et al. reported that the percentage of formation of $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_4(OH)_6]^{2+}$, and $[(UO_2)_4(OH)_7]^+$ species changes depending on the absence or presence of the fluoride ion in solution. In addition, Brown has investigated the effect of ionic strength and the type of salt used on the hydrolysis of the uranyl ion. As indicated in Table 3, the species $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$, $[(UO_2)_3(OH)_4]^{2+}$, and $[(UO_2)_3(OH)_5]^+$ were reported to be present in different media such as 0.1 M KCl, 0.1 M $NaClO_4$, and 1 M KNO_3, whereas the formation of $[(UO_2)_4(OH)_7]^+$ was reported only in nitrate media at 25 °C.[1,15] The other study about UO_2^{2+} hydrolysis was found in the literature, which was carried out by Zanonato et al. at (10 to 85) °C using potentiometry.[17] There is a good agreement with their values, especially at 25 °C for $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$, and $[(UO_2)_3(OH)_5]^+$ species.

When we discussed the effect of temperature, there was meaningful agreement between temperature and log β values. According to multiple linear regression results, log β values of $[(UO_2)_2(OH)_2]^{2+}$ ($p < 0.01$, $r^2 = 0.35$) and $[(UO_2)_3(OH)_5]^+$ ($p < 0.01$, $r^2 = 0.34$) correlated well with temperature.

In Table 8, the calculated enthalpy, entropy, and Gibbs energy for the hydrolysis of the uranyl ion are given. Enthalpy values show that the formation of all uranyl species is endothermic. According to the positive entropy values, it is proved that the formation of $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$ complexes is favorable. The results of the Zanonato et al. study performed by calorimetry[17] have different enthalpy and entropy values from our calculated values using the van't Hoff equations. Such discrepancy could be due to the accuracy of the respective methods. Direct measurements of the reaction enthalpy by calorimetry could generate more reliable data.

Hydrolysis of Cerium Ion, Ce^{3+}. Several studies have been carried out to determine the hydrolytic behavior of the lanthanide ions, such as La, Pr, Eu, Er, Lu, and Ce, in various media at different temperatures.[12,18,19] Among the metals studied, cerium is the subject of increasing interest in bioinorganic and coordination chemistry.[20]

The results of the present study show that the hydrolysis occurs at pH greater than 6 in 0.5 $\text{mmol}\cdot\text{dm}^{-3}$ at 25 °C. Therefore, when the temperature is increased, hydrolysis starts to occur at a lower pH (Figure 3). Whereas $[Ce_2(OH)]^{5+}$, $Ce(OH)_3$, and $[Ce_2(OH)_5]^+$ are present at all three experimental temperatures, $[Ce_2(OH)_2]^{4+}$ is observed only at 25 °C, as seen in Table 5.

Although the formation of M_2OH is difficult in the hydrolysis of lanthanide ions, $[Ce_2(OH)]^{5+}$ is observed under our experimental conditions. This result agrees with Ciavatta's study. In addition to the species reported by Ciavatta et al.,[19] $[Ce_2(OH)_2]^{4+}$ is also observed at 25 °C but not at (37 or 45) °C. Also the literature summary for cerium is given in Table 5. Monomeric and polymeric species for Ce^{3+} were found at 25 °C in the studies of Bentouhami et al. and Kragten et al., and among the hydrolytic species, only $[Ce(OH)_3]$ is in agreement with our result.[12,20,21] According to multiple linear regression results, log β values of $[Ce_2(OH)]^{5+}$ ($p < 0.01$, $r^2 = 0.44$), $Ce(OH)_3$ ($p < 0.01$, $r^2 = 0.37$), and $[Ce_2(OH)_5]^+$ ($p < 0.01$, $r^2 = 0.61$) correlated well with temperature.

In view of the thermodynamic data, hydrolysis of all cerium species is endothermic and all species have positive entropy values at all temperatures, except for $Ce(OH)_3$, as given in Table 9. There are few studies on the hydrolysis of Ce^{3+}. That is why it is difficult to come across studies that have measured the enthalpy of hydrolysis reactions. Therefore, there is no detailed data to compare with our calculated thermodynamic data.

Conclusions

It is concluded that experimental conditions alter the hydrolytic behavior of lanthanides and actinides, as reported by many other researchers. In the concentration range selected for each metal ion, log β values are not considerably affected in the same ionic medium, although the data obtained in this study about Th^{4+}, UO_2^{2+}, and Ce^{3+} at various temperatures significantly contribute to the understanding of the hydrolytic behavior of these ions. Multiple regression equations and adjusted r^2 coefficients show that a partial proportion of the variation in log β values of metal ions is explained by temperature. With all of these considerations, knowledge of hydrolysis constants of the lanthanides and the actinides appears to be primordial, and the present work may also contribute to the data collection.

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Supporting Information Available:

Experimental titration curves of 0.37 $\text{mmol}\cdot\text{dm}^{-3}$ U(VI), 1.0 $\text{mmol}\cdot\text{dm}^{-3}$ Th(IV), and 0.5 $\text{mmol}\cdot\text{dm}^{-3}$ Ce(III) solutions fitted with monomeric and polymeric models at (25, 37, and 45) °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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