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Dependence on Ionic Strength of the Hydrolysis Constants for Dioxouranium(VI) in NaCl(aq) and $NaNO_3$(aq), at pH < 6 and $t = 25$ °C

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The hydrolysis of UO_2^{2+} was studied potentiometrically (H^+−glass electrode) in NaCl (0.1−4.5 mol L^{-1}) and $NaNO_3$ (0.1−1 mol L^{-1}) aqueous solution, at pH < 6 and $t = 25$ °C. Computer calculations indicate the presence of the species $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_7^-$ whose equilibrium constants are reported together with parameters for dependence on ionic strength for both ionic media. Extrapolation to infinite dilution gave ($\beta_{pq} = [(UO_2)_p(OH)_q^{(2p-q)}][H^+]^q[UO_2^{2+}]^{-p}$): $\log \beta_{11} = -5.19 \pm 0.05$, $\log \beta_{22} = -5.76 \pm 0.04$, $\log \beta_{34} = -11.82 \pm 0.08$, $\log \beta_{35} = -15.89 \pm 0.06$, and $\log \beta_{37} = -29.26 \pm 0.10$. The speciation scheme was critically examined in the light of uncertainties derived by error propagation. The significance of the species found is discussed in relation to the different experimental conditions (concentration of UO_2^{2+} and medium). A comparison with literature findings is made.

Introduction

The environmental impact of uranium and its waste products, in particular in relation to nuclear waste disposal, is a serious social problem, which interests scientists from a number of quite different research areas. Its presence in natural waters is characterized by the formation of several complex species, with variable stability, owing to the presence of several inorganic and organic ligands. Moreover, in all its oxidation states, uranium undergoes strong hydrolysis with the formation of many mono- and polynuclear species. It follows that, to fully appreciate how uranium behaves in an aquatic environment, speciation studies (i.e., the study of the distribution of a component in the different species) are of fundamental importance.

To make a contribution to the understanding of the speciation of UO_2^{2+} in natural waters, we undertook a study of this cation in aqueous solutions containing different ligands (including low and high molecular weight polycarboxylates, polyamines, amino acids, and nucleotides), at different ionic strengths and in different ionic media. Because of the strong tendency of dioxouranium(VI) to hydrolysis, we had to carry out a preliminary investigation of the formation and stability of different hydrolytic species in different ionic media.

The hydrolysis of UO_2^{2+} in aqueous solution has been studied in several laboratories. A critical overview has been reported by Grenthe et al.,[1] and many data can be found in some compilations and databases.[2−6] Comparisons with literature findings have also been reported[7−9] in a few papers dealing with the experimental determination of hydrolysis constants by different techniques. While several studies have been carried out in $NaClO_4$(aq), relatively few determinations have been made in other ionic media, particularly in NaCl(aq).

Here we report a potentiometric (H^+−glass electrode) study in NaCl, $I = 0.1$−4.5 mol L^{-1}, and in $NaNO_3$, $I = 0.1$−1 mol L^{-1}, at $t = 25$ °C.

Experimental Section

Materials. The dioxouranium(VI) cation (UO_2^{2+}) was used as nitrate salt (Fluka, ACS product). Sodium chloride and sodium nitrate were used as anhydrous salts (Fluka). The purity of dioxouranium(VI) nitrate, checked gravimetrically after precipitation as U_3O_8 by gaseous ammonia, was >99.5%. Hydrochloric and nitric acids and sodium hydroxide solutions were prepared by diluting concentrated ampules (Fluka). Solutions of acid and hydroxide were standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All the solutions were prepared using freshly prepared CO_2-free ultrapure water ($R = 18$ MΩ cm^{-1}), and grade A glassware was always employed.

Potentiometric Measurements. The measurements were carried out using potentiometric apparatus consisting of a Metrohm model 665 automatic dispenser coupled with a Metrohm model 654 potentiometer and a combination Orion-Ross 8102 glass electrode. The estimated error of this system was ±0.15 mV and ±0.003 mL within a 95% confidence interval for emf and titrant volume readings, respectively. In the titration cells, pure nitrogen was bubbled through the solutions in order to avoid O_2 and CO_2 inside, and the solutions were magnetically stirred.

A volume of 25 mL of solution containing dioxouranium(VI) nitrate (0.5 to 5 mmol L^{-1}) and the background salt (NaCl or $NaNO_3$), in order to adjust ionic strength values, was titrated with standard sodium hydroxide solutions. To check formal electrode potential ($E°_{int}$), a slight excess of acid (hydrochloric or nitric acid, depending on the ionic medium used) was added to the solution. Three titrations were done for each experimental condition. Independent titrations of hydrochloric or nitric acid solutions with NaOH

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were performed for each experiment, under the same experimental ionic strength conditions as the systems under study, to determine formal electrode potential ($E°_{ext}$) and acidic junction potential ($E_j = j_a[H^+]$). Following this procedure, potentiometric readings are given in the free hydrogen concentration scale.

Calculations. Calculations relative to the refinement of potentiometric titration parameters (formal potential, junction potential coefficients; NaOH, HCl, and HNO_3 standardization) were performed using the ESAB2M computer program.[10] Hydrolysis constants were refined using STACO[11] and BSTAC[12] computer programs. STACO refines formation constants by minimizing the weighted error squares sum of titrant volumes, i.e., $\sum w(v - v_{calcd})^2$, while BSTAC minimizes $\sum w(E - E_{calcd})^2$. Weights may be kept constant ($w = 1$) or proportional to the potentiometric curve gradient using error propagation. Moreover, STACO and BSTAC are able to perform calculations under nonconstant ionic strength conditions (in particular, at low ionic strength there may be significant I variations during the same titration) and to refine some titration parameters (such as $E°$ or analytical concentrations). These utilities were used mainly to check the consistency of the systems under study. Calculations relative to speciation diagrams and formation percentages, together with relative errors, were performed using the ES4EC computer program.[12]

Hydrolysis constants are expressed according to the equilibrium

$$pUO_2^{\ 2+} = (UO_2)_p(OH)_q^{\ (2p-q)} + qH^+$$

$$\beta_{pq} = [(UO_2)_p(OH)_q^{\ (2p-q)}][H^+]^q[UO_2^{\ 2+}]^{-p}$$

and are given in the molar (mol L^{-1}) concentration scale. Dependence on ionic strength was taken into account using the Debye−Hückel type equation

$$\log \beta_{pq} = \log {}^{T}\beta_{pq} - z^*DH + L(I) \tag{1}$$

with

$$z^* = 4p - q - (2p - q)^2$$

$$DH = 0.5115I^{1/2}/(1 + 1.5I^{1/2})$$

$$L(I) = CI + DI^{1.5} + EI^2$$

where C, D, and E are empirical parameters. The results of a series of investigations[13] and references therein showed that, when all interactions are taken into account, the empirical parameters of eq 1, for $I \le 1$ mol L^{-1}, are given by

$$C = 0.11p^* + 0.20z^* \tag{1a}$$

$$D = -0.075z^* \tag{1b}$$

with

$$p^* = \sum (\text{moles})_{\text{reactants}} - \sum (\text{moles})_{\text{products}}$$

In this case the activity of water was taken into account by the simple relationship log $a_w = -0.015I$, calculated from osmotic coefficients of several common electrolytes (the ratio (log a_w)/I is very constant for $I < 5$ mol L^{-1}). The values of empirical parameters of eq 1, parts a and b were used only for calculating approximate formation constants of medium weak interactions (see here after discussion on medium effect). When formation data at different ionic strengths are available, empirical parameters can be obtained by fitting these data.

Table 1. Hydrolysis Constants of UO_2^{2+} at 25 °C, in Different Ionic Media and at Different Ionic Strengths

	I	$-\log \beta_{pq}$	
p q	mol L^{-1}	NaCl	$NaNO_3$
1 1	0.10	5.45 ± 0.03[a]	5.38 ± 0.03[a]
	0.25	5.57 ± 0.03	5.42 ± 0.03
	0.50	5.72 ± 0.02	5.41 ± 0.03
	0.75	5.84 ± 0.03	5.37 ± 0.05
	1.00	5.96 ± 0.03	5.33 ± 0.07
	2.00	6.43 ± 0.05	
	3.00	6.92 ± 0.05	
	4.50	7.73 ± 0.05	
2 2	0.10	5.98 ± 0.03	5.98 ± 0.02
	0.25	6.06 ± 0.02	6.04 ± 0.02
	0.50	6.14 ± 0.02	6.09 ± 0.03
	0.75	6.19 ± 0.02	6.12 ± 0.04
	1.00	6.24 ± 0.02	6.13 ± 0.05
	2.00	6.41 ± 0.03	
	3.00	6.60 ± 0.03	
	4.50	6.98 ± 0.04	
3 4	0.10	12.22 ± 0.05	12.29 ± 0.05
	0.25	12.33 ± 0.04	12.50 ± 0.04
	0.50	12.38 ± 0.04	12.73 ± 0.04
	0.75	12.40 ± 0.03	12.90 ± 0.04
	1.00	12.41 ± 0.04	13.06 ± 0.06
	2.00	12.44 ± 0.05	
	3.00	12.57 ± 0.05	
	4.50	13.01 ± 0.07	
3 5	0.10	16.55 ± 0.04	16.52 ± 0.03
	0.25	16.76 ± 0.03	16.70 ± 0.03
	0.50	16.93 ± 0.03	16.80 ± 0.03
	0.75	17.04 ± 0.03	16.83 ± 0.04
	1.00	17.13 ± 0.03	16.83 ± 0.06
	2.00	17.44 ± 0.05	
	3.00	17.81 ± 0.05	
	4.50	18.57 ± 0.04	
3 7	0.10	29.68 ± 0.09	29.57 ± 0.10
	0.25	29.77 ± 0.08	29.62 ± 0.07
	0.50	29.79 ± 0.07	29.58 ± 0.10
	0.75	29.79 ± 0.07	29.48 ± 0.09
	1.00	29.80 ± 0.07	29.39 ± 0.12
	2.00	29.93 ± 0.10	
	3.00	30.35 ± 0.10	
	4.50	31.58 ± 0.16	

[a] ±3 (std dev).

Throughout this paper errors in the various parameters are given as three times the estimated standard deviation.

Results and Discussion

Hydrolysis Constants. Several trials were performed to explain potentiometric data in terms of UO_2^{2+} hydrolytic species. Using literature information,[1−8] the species taken into consideration were: $(UO_2)_p(OH)_q$, p,q = (1,1), (2,1), (1,2), (2,2), (3,4), (3,5), (3,7), (4,7) (other species having higher q/p ratio were not considered since they are likely to be formed at pH ≫ 6; see, e.g., ref 8). Calculations performed with both STACO and BSTAC computer programs were consistent with the model which includes the species with p,q = (1,1), (2,2), (3,4), (3,5) and (3,7) either in $NaNO_3$(aq) or in NaCl(aq). Table 1 shows log β_{pq} values at different ionic strengths. In Figure 1, we plotted the distribution of the hydrolytic species of UO_2^{2+} vs pH at 1 mol L^{-1} in the two different NaCl and $NaNO_3$ background salts. At C_{UO_2} = 5 mmol L^{-1} the formation of the mononuclear species can be neglected (in particular in NaCl(aq)). The main species in the pH range 3.5−4.5 are the binuclear (in $NaNO_3$(aq)) and both binuclear and trinuclear (in NaCl(aq)) ones. At higher pH values trinuclear species become predominant. Only at C_{UO_2} < 1

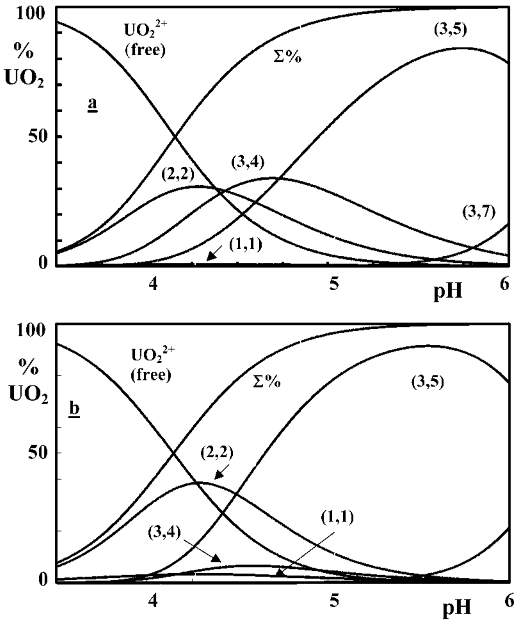

Figure 1. Speciation diagrams for the hydrolysis of UO_2^{2+} in NaCl(aq) or $NaNO_3$(aq) at 25 °C: (a) $C_{UO_2} = 5$ mmol L^{-1} $I = 1$ mol L^{-1} (NaCl); (b) $I = 1$ mol L^{-1} ($NaNO_3$).

mmol L^{-1} does the mononuclear species show a slightly significant yield. Note that at pH = 4.5 the sum of hydrolytic species percentages is very high (>75%) and increases consistently; at pH > 5 only a small percentage of dioxouranium(VI) is present as free cation. The formation of $(UO_2)_3(OH)_7^-$ becomes significant only at pH > 5.7, just before the formation, under our experimental conditions, of insoluble species. The hydrolysis behavior of UO_2^{2+} in $NaNO_3$ is similar, with two significant differences. At I > 0.1 mol L^{-1} the formation percentages for species $(UO_2)_3(OH)_4^{2+}$ are much lower than in NaCl(aq), while those for the species $(UO_2)_3(OH)_5^+$ are higher. This is attributable to the formation of a fairly stable complex species of $(UO_2)_3(OH)_4^{2+}$ with Cl^-.[6] Hydrolysis constants for species (1,1), (2,2), and (3,5), at I > 0.5 mol L^{-1}, are considerably higher in $NaNO_3$(aq) than in NaCl(aq) because of the higher complexing ability of Cl^- toward UO_2^{2+} (see Table 1). As expected, at very low ionic strength hydrolysis constants and formation percentages increase significantly. To give some examples of these differences, in addition to the information in Figure 1, we report formation percentages for hydrolytic species in different conditions in Table 2. The speciation scheme proposed in this work is in agreement with many (but not all) literature reports (see the discussion on literature comparison below), at pH < 6. Nevertheless, some comment must be made on the effective formation of some species, and on the reliability of their formation constants. There is no doubt about the formation of species (1,1), (2,2), and (3,5); β_{pq} values are well defined for the last two, while some uncertainty persists for $UO_2(OH)^+$ owing to the low formation percentages obtained under most experimental conditions. Using error propagation (and taking into account both errors in formation constants and systematic errors in analytical concentrations) we calculated the percentage ± error under different conditions for species (1,1) (for example, at pH = 5, $C_{UO_2} = 1$ mmol L^{-1}, and $I = 1$ mol L^{-1}, we have % = 5.3 ± 1.2 in $NaNO_3$ and % = 1.4 ± 0.3 in NaCl): in all cases high relative errors and low formation percentages suggest that data for this species should be used with care. The species (3,4) is well defined in NaCl(aq) (% = 23.7 ± 2.8, under the above conditions), but in $NaNO_3$(aq) excessively low yields are observed (% = 3.5 ± 0.8). The definition of the last species, i.e. (3,7), is also critical since, under our experimental conditions, it is formed in a narrow pH range before the formation of scarcely soluble species. For this species, at pH = 6 (other conditions as above) we have % = 16.5 ± 3.2 and 26 ± 7 in NaCl and $NaNO_3$, respectively.

Dependence on Medium. Figure 2 shows dependence on ionic strength for the different species in the two salt media. The behavior of log β_{pq} vs $\sqrt{I}$ is very similar for all the species, but for $(UO_2)_3(OH)_4^{2+}$: (a) hydrolysis constants in nitrate solutions are more stable than in chloride solutions at all ionic strengths; (b) values in NaCl(aq) are ever-decreasing, while a minimum can be observed in nitrate. The opposite holds for species (3,4), further confirmation of the binding between $(UO_2)_3(OH)_4^{2+}$ and Cl^-. By suitable least squares calculation and using data at different ionic strengths, we obtained log β_{pq} values at infinite dilution (thermodynamic constants) and parameters for dependence on I/mol L^{-1}, according to eq 1; these are reported in Table 3. Owing to the limited ionic strength range, a single empirical parameter (C) is sufficient to describe the log $\beta_{pq} = f(I)$ function for data in sodium nitrate. Before analyzing the data in Table 3, we must recall some simple equations which define the effect of

Table 2. Formation Percentages of Hydrolytic Species at Different pH Values (t = 25 °C)

I	C_{UO_2}		formation percentages					
mol L^{-1}	mmol L^{-1}	pH	UO_2^{2+}	1,1	2,2	3,4	3,5	3,7
1 (NaCl)	5	4	65 ± 2[a]	<1	24 ± 2	8 ± 2	2 ± 1	0
		5	5 ± 1	<1	12 ± 2	29 ± 4	54 ± 4	<1
		6	<1	0	<1	4 ± 1	78 ± 4	17 ± 4
	0.5	4	94 ± 2	1 ± 1	5 ± 1	<1	0	0
		5	19 ± 1	2 ± 1	21 ± 2	20 ± 3	38 ± 3	0
		6	<1	<1	2 ± 1	4 ± 1	77 ± 4	16 ± 4
1 ($NaNO_3$)	5	4	62 ± 3	3 ± 1	30 ± 3	2 ± 1	3 ± 1	0
		5	4 ± 1	2 ± 1	12 ± 3	4 ± 2	78 ± 3	<1
		6	0	<1	<1	<1	72 ± 7	26 ± 7
	0.5	4	89 ± 3	4 ± 1	6 ± 1	0	0	0
		5	16 ± 1	8 ± 2	20 ± 4	3 ± 1	54 ± 5	0
		6	<1	2 ± 1	1 ± 1	<1	71 ± 7	25 ± 7
~0.001 (NO_3^-)	1	2	75 ± 2	4 ± 1	18 ± 2	2 ± 1	1 ± 1	0
		1	6 ± 2	4 ± 1	12 ± 2	9 ± 2	70 ± 3	0
		6	0	1 ± 1	<1	1 ± 1	93 ± 2	4 ± 2

[a] Uncertainties expressed as three times the standard deviation, approximated to the nearest whole number above.

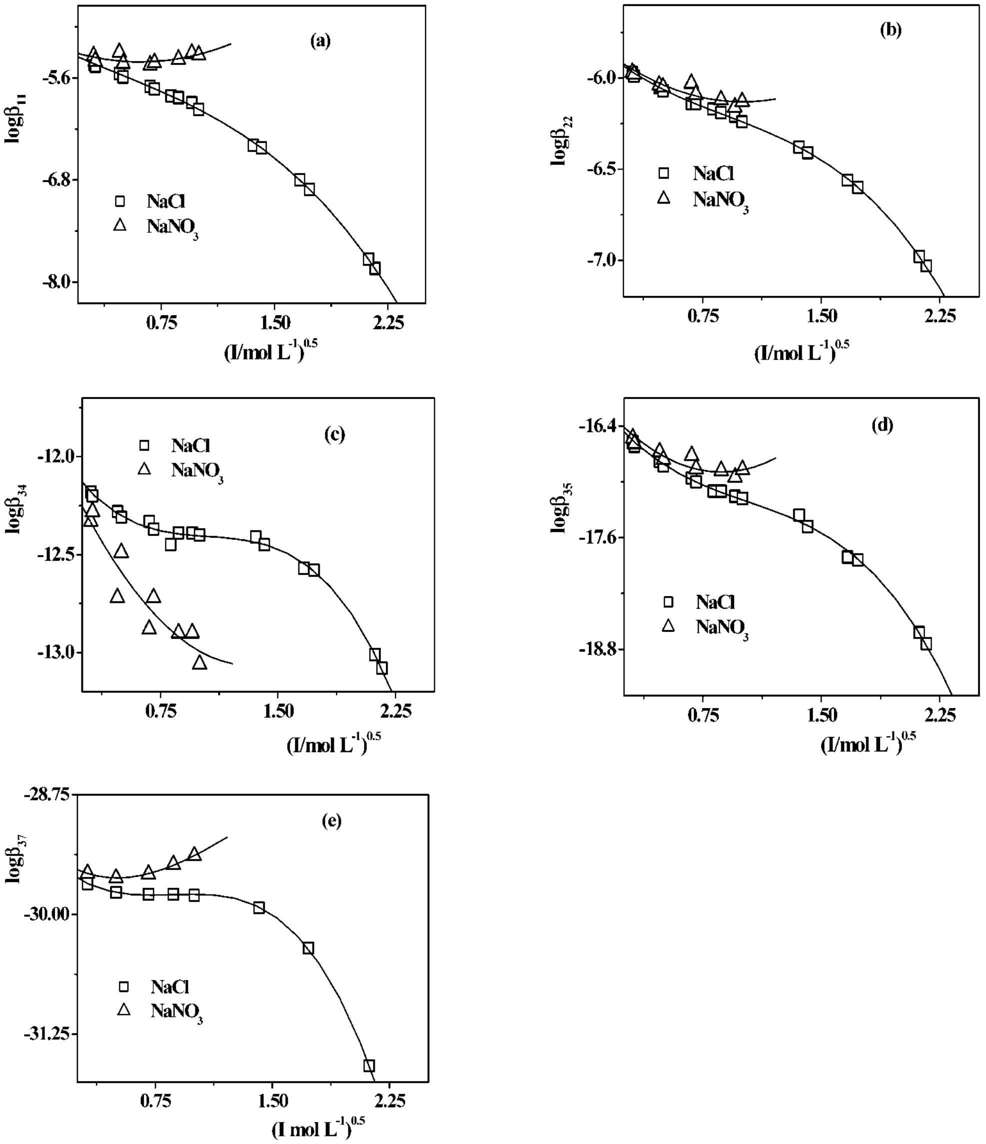

Figure 2. log β_{pq} vs (I/mol L^{-1}) in $NaCl_{aq}$ and $NaNO_3$ at 25 °C: (a) $(UO_2)(OH)^+$; (b) $(UO_2)_2(OH)_2^{2+}$; (c) $(UO_2)_3(OH)_4^{2+}$; (d) $(UO_2)_3(OH)_5^+$; (e) $(UO_2)_3(OH)_7^-$.

Table 3. Hydrolysis Constants at Infinite Dilution and Parameters[a] for Dependence on Ionic Strength in $NaNO_3$(aq) and NaCl(aq), at 25 °C

		C	C	E
p,q	$-\log^T \beta$	$NaNO_3$	NaCl	
1,1	5.19 ± 0.05[b]	0.275 ± 0.055[b]	−0.33 ± 0.045[b]	−0.025 ± 0.008[b]
2,2	5.76 ± 0.04	0.034 ± 0.032	−0.042 ± 0.028	−0.025 ± 0.005
3,4	11.82 ± 0.08	−0.42 ± 0.07	0.31 ± 0.05	−0.076 ± 0.012
3,5	15.89 ± 0.06	0.29 ± 0.05	0.063 ± 0.031	−0.070 ± 0.010
3,7	29.26 ± 0.10	0.73 ± 0.15	0.44 ± 0.11	−0.16 ± 0.03

[a] Equation 1; $D = 0$ for $NaNO_3$ and NaCl; $E = 0$ for $NaNO_3$.
[b] ±3 (std dev).

weak complexation with background salt ions on the stability of hydrolytic species. For the simple reaction

$$M^{z+} = M(OH)^{(z-1)+} + H^+$$

in the presence of an interacting X^- anion, which forms the weak complex $MX^{(z-1)+}$, we have

$$\log K = \log K^* + \log(1 + K^X C_X)$$

where K and K^* are the hydrolysis constants in the absence and in the presence of X^-, respectively, and K^X is the formation constant of the ion pair MX^0. This equation shows that $\log K > \log K^*$ and that the difference increases with C_X. Whereas, if the interaction occurs between the anionic hydrolytic species formed in the reaction

$$M(OH)_{i-1}{}^0 = M(OH)_i{}^- + H^+$$

and the Y^+ cation of the background salt, we have

$$\log K = \log K^* - \log(1 + K^Y C_Y)$$

where K^Y is the formation constant of the ion pair $(M(OH)_i{}^-)(Y^+)$. In this case $\log K < \log K^*$, i.e. we observe an increasing effect in the hydrolysis constant. Data for dependence on ionic strength (Table 3) can be explained in the light of these observations. For example, it can be seen that the value of empirical parameter C in eq 1 increases systematically, but for species (3,4) this is a function of stoichiometric coefficient q/p ratio, which is consistent with the higher interacting ability of the background salt anion toward simpler species and with the

Table 4. Literature Comparison at $t = 25$ °C and $I = 0$ mol L^{-1}

$\log\beta_{pq}$					
$UO_2(OH)^+$	$(UO_2)_2(OH)_2^{2+}$	$(UO_2)_3(OH)_4^{2+}$	$(UO_2)_3(OH)_5^+$	$(UO_2)_3(OH)_7^-$	ref
−5.2	−5.62	−11.9	−15.55	−31(±2)	1
−5.8	−5.62	−11.75	−15.63		6
−5.9	−5.58	−11.8	−15.6		4
−5.19	−5.76	−11.82	−15.89	−29.26	*d*
	−5.51		−15.33	−27.77	8
	−5.65		−15.82		*a*
	−6.04[b]		−16.50[b]		*a*
	−6.08[c]		−16.72[c]		*a*

[a] Calculated by interpolating values in $NaClO_4$ at different ionic strengths ($0 < I$/mol $L^{-1} \leq 3$), reported in the literature (most of the data are taken from ref 1). [b] I = 1 mol L^{-1}. [c] I = 3 mol L^{-1}. [d] This work.

possibility of ion pair formation between the anionic hydrolytic species (3,7) and Na^+. This trend is more evident for data in NaCl. The macroscopic deviation of C value in both media accounts for the very probable formation of a fairly stable species, $(UO_2)_3(OH)_4Cl^+$. Calculations performed by considering data in $NaNO_3$ as a baseline, gave $\log K = 1.6 \pm 0.2$ for the formation of this species [$(UO_2)_3(OH)_4^{2+} + Cl^- = (UO_2)_3(OH)_4Cl^+$] and $\log K = 0.4 \pm 0.3$ for the formation of UO_2Cl^-. Analogously, for species (3,7) we calculated $\log K = 1.2 \pm 0.2$ for the reaction $(UO_2)_3(OH)_7^- + Na^+ = (UO_2)_3(OH)_7Na^0$ by considering dependence on ionic strength in the absence of significant interactions (see Calculation section), i.e., $C = 0.66$ and $D = -0.15$ (I/mol $L^{-1} < 1$). Of course, owing to the rough approximations used in deriving these values, formation constants for ion pairs must be considered only as estimates.

Literature Comparison. Some hydrolysis constants taken from literature, at $I = 0$ mol L^{-1} and $t = 25$ °C, are reported in Table 4. These are in good general agreement, in particular as concerns the species (2,2), for which the mean value is -5.65 ± 0.10. The speciation scheme proposed in this work fits those proposed in many other investigations fairly well. Nevertheless, it is worth mentioning different schemes which include species with different stoichiometries. The species $(UO_2)_2(OH)^{3+}$ has been proposed by some Scandinavian authors,[14] and its hydrolysis constant has been estimated to be $\log \beta_{pq} = -2.7 \pm 1.0$ (at $I = 0$).[1] It is likely that this species can only be formed at very high UO_2^{2+} concentration. The species $(UO_2)_4(OH)_7^+$ has been found both in 3 mol L^{-1} (NaCl)[15] and in 0.1 mol L^{-1} (KNO_3).[7] Recalculations performed by Palmer and Nguyen-Trung[8] using the experimental data of Sylva and Davidson[7] showed that this species can be replaced by the species (3,7) without significantly altering the fit. Species (3,8) and (3,10) have been found[8] at pH > 8 using $(CH_3)_4NF_3CSO_3$ (a very strong electrolyte whose cation does not form complexes with UO_2^{2+} or its cationic hydrolytic species) as the supporting electrolyte. The presence of these species was confirmed by Raman spectroscopic measurements.[9]

Final Remarks. The results of the present work can be summarized as follows.

•Hydrolytic species of UO_2^{2+} in NaCl(aq) and $NaNO_3$(aq) are $(UO_2)_p(OH)_q$, p,q = (1,1), (2,2), (3,5), and (3,7), at pH < 6, at 25 °C.

•In NaCl(aq) the species (3,4) is formed in a significant yield. The same species can also be considered in $NaNO_3$(aq), but its formation percentage is fairly negligible (Table 2).

•Hydrolysis constants are reported at each ionic strength (Table 1), and the significance of the different species is discussed in relation to formation percentages (along with relative errors) in different concentrations, ionic strengths, and medium conditions (Figure 1 and Table 2).

•Dependence on ionic strength (Figure 2) is considered for both ionic media. The relative parameters (Table 3) account for the interaction of supporting electrolyte ions with UO_2^{2+} and its hydrolytic products.

•The formation of $(UO_2)_3(OH)_4Cl^+$, UO_2Cl^-, and $(UO_2)_3(OH)_7Na^0$ complexes is hypothesized as an explanation for medium effects and approximate formation constants are given.

•Comparison with literature data (Table 4) confirms the validity of the proposed speciation model.

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