However, it is expected that at pH > 4 a large series of higher oligomers are evolving.

Conclusions

The present work substantiates a number of important observations:

(1) Monitoring the evolution of Cr(III) hydrolytic oligomers after the addition of base to Cr^{3+} has shown that an apparently constant pH does not necessarily indicate that equilibrium has been reached.

(2) The trimer was the predominant oligomer in all solutions studied (pH 2.3–3.2). This stable and inert[11] oligomer may be the prototype for Cr(III) polymerization. In contrast, the compact deprotonated tetramer (**3b**) is the most stable among the deprotonated oligomers.

(3) The stability constants support the structures proposed for these oligomers in our eariler work.[11,12]

(4) Core and links calculations, with one polymerization constant, cannot appropriately describe the hydrolysis of chromium(III) aqua ion.

Work aimed at the isolation and characterization of further members of the Cr(III) hydrolytic oligomer series is continuing (L.S.[3]).

Experimental Procedures

All experimental methods including the preparation and analysis of Cr^{3+} stock solutions, the procedure for chromatographic analysis of solutions of Cr(III), and the procedure for pH measurement have been described previously.[11] Where necessary, details of conditions used in the equilibration studies are given in Tables I–III.

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Contribution from the Joint Research Centre, Ispra Establishment,
Commission of the European Communities, 21020 Ispra (Va), Italy,
and Department of Inorganic Chemistry, The Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden

Use of Thermal Lensing Spectrophotometry (TLS) for the Study of Mononuclear Hydrolysis of Uranium(IV)

Ingmar Grenthe,*,† Giovanni Bidoglio,‡ and Nicolo Omenetto‡

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The possibility of using thermal lensing spectrophotometry (TLS) for the quantitative determination of chemical equilibria in very dilute ($\sim 10^{-5}$ M) aqueous solution has been explored. The hydrolysis of uranium(IV) has been used as a test case. TLS turned out to be a convenient, precise, and rapid method to obtain information about the mononuclear hydrolysis, information that is difficult to obtain with more traditional solution chemical methods. The TLS data were obtained at 25 °C in the concentration range of $0 \le -\log [H^+] \le 2.8$ by using a 3 M $(Na,H)ClO_4$ ionic medium. The data were described with the following chemical model: $U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+$, $\log {}^*\beta_1 = -1.65 \pm 0.05$; $U^{4+} + 2H_2O \rightleftharpoons U(OH)_2^{2+} + 2H^+$, $\log {}^*\beta_2 < -4.5$. Apart from its higher sensitivity, the TLS method has the same characteristics as ordinary spectrophotometric methods. The experimental results of this study and previous literature information were interpreted by using the specific ion interaction theory to give $\log {}^*\beta^\circ_1 = -0.51 \pm 0.03$ ($\log {}^*\beta^\circ_1$ is the equilibrium constant at zero ionic strength) and $\Delta\epsilon = -0.14 \pm 0.02$, where $\Delta\epsilon$ is the ion interaction term $\Delta\epsilon = \epsilon(UOH^{3+},ClO_4^-) + \epsilon(H^+,ClO_4^-) - \epsilon(U^{4+},ClO_4^-)$.

Introduction

Aquometal ions are acids, and the stoichiometry and equilibrium constants of metal hydroxide complexes

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

is a "traditional" field of solution chemistry. A recent review is given by Baes and Mesmer in ref 1. Polynuclear complexes are the predominant hydroxide complexes formed for most metal ions, particularly for those with a high oxidation state. The stoichiometry of these complexes is many times identical with the stoichiometry of polynuclear units that are found in solid "basic salts" of the metal ions; e.g. basic bismuth perchlorate $BiOClO_4 \cdot nH_2O(s)$ contains discrete hexanuclear complexes $Bi_6O_4(OH)_4^{6+}$,[2] and this complex has also been identified in solution.[3]

The polynuclear complexes are presumably formed by condensation reactions involving species of lower nuclearity, e.g. the mononuclear hydroxide species $M(OH)_p^{n-p}$. In order to explore the fundamental chemistry of these reactions, it is important to have access to thermodynamic data for the mononuclear hydrolysis reactions.

It is obvious that the formation of polynuclear complexes is strongly dependent on the total concentration of the metal ion; cf. eq 1. Hence, the relative importance of mononuclear species over the polynuclear ones increases with decreasing total concentration of M. This fact may be of importance for the speciation of metal ions, e.g. in natural water systems where the total metal concentrations are often very low. Such trace metals may, for example, be uranium or transuranium elements released from radioactive waste repositories of various kinds.

Potentiometry is the most precise experimental method for the study of chemical equilibria in solution. However, it requires fairly large total concentrations of the reacting species. Hence, it may be difficult to study mononuclear complex formation in systems where polynuclearity is predominant. In the following we will explore the utility of thermal lensing spectrophotometry (TLS)[4] as a quantitative tool for the study of such a system. No previous quantitative studies of the use of TLS in equilibrium analysis have been published as far as we are aware. We have selected the uranium(IV)–H_2O system because of its interest from both the fundamental and the applied points of view.

Chemistry of the U(IV)–H_2O System. The hydrolysis of uranium(IV) has previously been studied by Kraus and Nelson,[5,6] Sullivan and Hindman,[7] and Hietanen and Sillen.[8] The data can be described by the following two equilibria:

$$U^{4+} + H_2O \rightleftharpoons UOH^{3+} + H^+ \qquad \log {}^*\beta_1 = -2.1 \pm 0.15 \qquad (2)$$

$$6U^{4+} + 15H_2O \rightleftharpoons U_6(OH)_{15}^{9+} + 15H^+ \qquad \log {}^*\beta_{6,15} = -16.9 \pm 0.3 \qquad (3)$$

Both values refer to a 3 M perchlorate medium.

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[‡] Commission of the European Communities.

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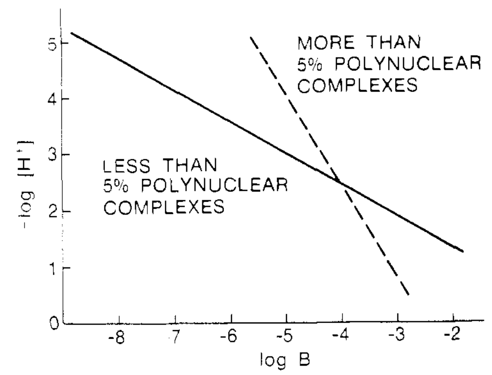

Figure 1. Diagram showing curves where the ratio $[U_6(OH)_{15}^{9+}]/6[UOH^{3+}] = 0.05$ (full-drawn curve) and $[U_6(OH)_{15}^{9+}]/6[U(OH)_2^{2+}] = 0.05$ (dashed cruve). Below the straight lines, less than 5% of UOH^{3+} and $U(OH)_2^{2+}$, respectively, are present in polynuclear form.

The experimental work is complicated by the ease of oxidation of U(IV) and also by slow hydrolytic equilibria; cf. ref 5. The amount of UOH^{3+} formed is also rather small at the comparatively high metal ion concentrations that had to be used in the previous studies. This results in a fairly large uncertainty in the value of log $^*\beta_1$. By combining eq 2 and 3, we obtain

$$6UOH^{3+} + 9H_2O \rightleftharpoons U_6(OH)_{15}^{9+} + 9H^+ \qquad \log K = -4.3$$

From this equation we can calculate the $-\log [H^+] - \log B$ range (B is the total concentration of U(IV)) where a certain fraction α of UOH^{3+} is present as polynuclear species.

Figure 1 shows the $-\log [H^+] - \log B$ range where mononuclear hydrolysis can be studied without noticeable influence of polynuclear complexes. The predominant species at $-\log [H^+] \lesssim 2$ is U^{4+}(aq). The metal concentrations studied by the previous investigators are in the range 6×10^{-4} M $< B < 3.5 \times 10^{-2}$ M. Accurate data could only be obtained at acidities larger than $\sim 10^{-2}$ M.

From Figure 1 it is obvious that by working at lower values of B, one should be able to extend the mononuclear region to lower acidities. This is important in order to obtain information for the higher mononuclear hydroxide complexes $U(OH)_n^{4-n}$, $n > 1$. TLS offers the possibility to obtain spectroscopic data down to $B \sim 10^{-6}$ M, i.e. $-\log [H^+] \sim 3.6$, which possibly could be used to identify the complex $U(OH)_2^{2+}$. Baes and Mesmer (see ref 1, p 412) predicted that this complex is predominant at $-\log [H^+] \sim 3$.

Experimental Methods and Interpretation of Data

Chemicals Used. A U(VI) perchlorate solution was prepared and analyzed as described before.[9] A stock solution of uranium(IV) of the composition $[U(IV)] = 2.00 \times 10^{-3}$ M, C_H M $HClO_4$, and $(3.00 - C_H)$ M $NaClO_4$, with $C_H = 0.100$ M or 0.600 M, was prepared by reduction with H_2(g) using a platinum net covered with electroplated Pd sponge; cf. ref 10. All other chemicals used were prepared of reagents of analytical grade and analyzed by standard methods.

TLS Equipment. A double-beam arrangement for the observation of the thermal lensing effect is practically the only choice for pulsed laser excitation. Our system, which has already been described in the literature,[11] was based on an excimer-pumped tunable dye laser as excitation source. The excimer laser (Model EMG-102 Lambda Physik, Gottingen, FRG) was operated with XeCl at 308 nm with a Coumarin-460 dye dissolved in spectroscopically pure methanol. The selected wavelength was 490 nm. Typical output values for the dye laser were pulse energy = 3 mJ, pulse duration = 5 ns, and spectral bandwidth = 0.02 nm. The laser output was focused in the middle of the absorbing solution by means of a quartz lens (25-cm focal length) while a small fraction of the beam was sent to a monochromator (Model H-10, Jobin Yvon, Longjumeau, France) and detected by a photomultiplier so as to provide a continuous monitoring of its energy fluctuations during the measuring time. The effect was probed by a He–Ne laser (Model 05-LHR-151, Melles Griot, Irvine, CA), which was focused with a second lens (25-cm focal length) *after* the absorbing solution. In this way, the effect was *positive*; i.e. the intensity at the beam center increased. Such increase was monitored in the far field ($\sim$3 m away) with a photodiode located behind a 1.5-mm-diameter pinhole. All the optical components were accurately adjusted in the X–Y–Z planes so that the pumps and the probe beams could be made colinear within the absorption path.

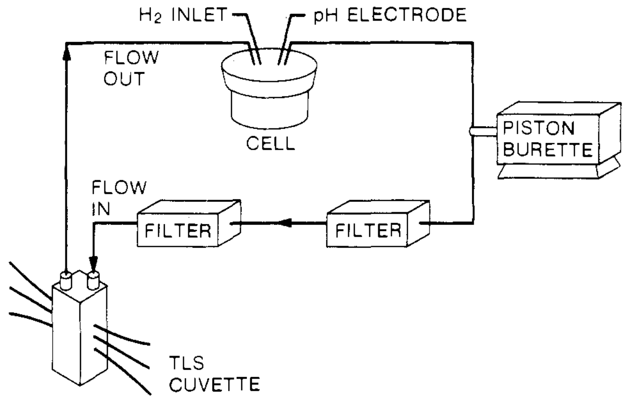

Figure 2. Schematic diagram of the experimental setup used for TLS measurements of U(IV) solutions.

The photodiode current was converted into a voltage, which was amplified and fed into a digital storage oscilloscope (Model 468, Tektronix, Beaverton, NJ) and a boxcar integrator (Model SR-250, SR-245, Stanford Research, Palo Alto, CA) and finally displayed on a strip-chart recorder. The laser system was triggered externally at a repetition frequency of 10 Hz.

The TLS experiments were made by using a reactor vessel that was connected via glass tubings and a piston buret acting as a pump to a cuvette placed in the TLS equipment. The experimental setup is shown in Figure 2. The solution was filtered on-line by using 1-μm Teflon filters (Millipore). The reactor vessel contained a Pt net covered with H_2-saturated Pd sponge, and a stream of H_2(g) was passed continuously over the net. Initially 100 mL of 3.00 M $NaClO_4$ was added to the reactor. The pump was started and the solution filtered. Then the TLS signal of the solvent (S_{solv}) was measured.

A known volume of the U(IV) stock solution was then added to the reactor and the circulation was started. By measuring the TLS signal as a function of time, we could verify if any oxidation of U(IV) or sorption on the walls of the system had occurred. At $-\log [H^+] > 3.2$ we observed a rapid oxidation of U(IV) in the reactor vessel. Once oxidized it seems as if the rate of reduction of U(VI) is slow. This might be due to the device used to bubble H_2(g) through the solution. The hydrogen gas was only in contact with a small part of the Pd/Pt net. The solution in the reactor was then titrated with a solution of 3.00 M $HClO_4$, with the same total concentration of U(IV) as in the starting solution. The hydrogen ion concentration was calculated from the additions and at the lowest acidities by measuring $-\log [H^+]$ with a glass electrode (Metrohm), calibrated in concentration units. After each addition the TLS signal was recorded, and then the TLS signal of an external standard (a dilute solution of $K_2Cr_2O_7$ in H_2O) was recorded. All experimental TLS signals were normalized to this external standard. This method was superior to the simple normalization to the output power of the dye laser.

Interpretation of Data. TLS spectroscopy is analogous to ordinary spectrophotometry, and the same methods for interpreting the data can, therefore, be used; for a review of these methods, see ref 12. A general problem with all spectroscopic methods is that one must determine the molar absorptivity or the molar TLS value, S_i, for each species present in solution. These additional parameters may make it difficult to obtain a unique chemical interpretation of the experimental data.[12]

We will use the following procedure in the data interpretation:

(i) Use the "established" chemical model and decide if the TLS data fit a model where only mononuclear complexes are formed. For the case where only U^{4+} and UOH^{3+} are formed, we have

$$S = S_0[U^{4+}] + S_1[UOH^{3+}] + S_{solv} \qquad (4)$$

$$B = [U^{4+}] + [UOH^{3+}] \qquad (5)$$

where S is the measured TLS signal, S_{solv} the TLS signal of the solvent

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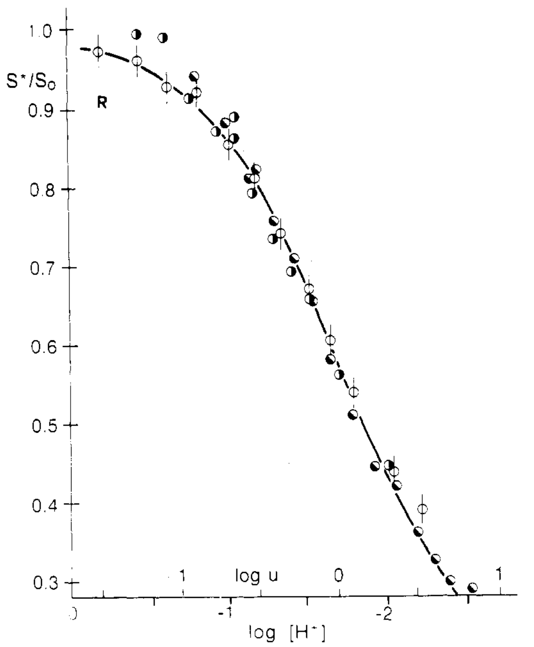

Figure 3. Experimental TLS data for the uranium(IV)–H_2O system. The symbols denote experimental S^*/s_0 values at three different total concentrations of U(IV), which have a range of a factor of approximately 2 between 1 and 2 × 10^{-5} M. The full-drawn curve, the model function $R(\log u)$, is shown in the position of best fit superimposed on the experimental data. The error bars are the estimated experimental errors. The chemical model includes the species U^{4+}, UOH^{3+}, and $U(OH)_2{}^{2+}$.

and S_0 and S_1 the molar TLS signals of U^{4+} and UOH^{3+}, respectively.

From (4) and (5) and the equilibrium conditions given in (1), we obtain

$$\frac{S - S_{\mathrm{solv}}}{B} = \frac{S_0[U^{4+}] + S_1{}^*\beta_1[U^{4+}]/[H^+]}{[U^{4+}] + {}^*\beta_1[U^{4+}]/[H^+]} \tag{6}$$

Equation 6 can be transformed into

$$S^* = S - S_{\mathrm{solv}} = \frac{s_0 + s_1{}^*\beta_1/[H^+]}{1 + {}^*\beta_1/[H^+]} \tag{7}$$

where $s_n = S_n B$.

By introducing the normalized variable $u = {}^*\beta_1/[H^+]$, we obtain

$$S^* = s_0 \frac{1 + \frac{s_1}{s_0}u}{1 + u} = s_0 R \tag{8}$$

By comparing experimental plots of S^*/s_0 vs $-\log\,[H^+]$ with model functions R [where $R = (1 + (s_1/s_0)u)/(1 + u)$] vs $\log u$, we obtain at the position of best fit, $\log {}^*\beta_1 = \log\,[H^+]$ for $\log u = 0$. For further details, see ref 12 and 13.

(ii) Test the model with both UOH^{3+} and $U(OH)_2{}^{2+}$. In this case we have

$$S = S_0[U^{4+}] + S_1[UOH^{3+}] + S_2[U(OH)_2{}^{2+}]$$

$$B = [U^{4+}] + [UOH^{3+}] + [U(OH)_2{}^{2+}]$$

After introduction of the normalized variable $u = {}^*\beta_1/[H^+]$ and $L = {}^*\beta_2/{}^*\beta_1{}^2$, we obtain

$$S^* = s_0 \frac{1 + \frac{s_1}{s_0} + \frac{s_2}{s_0}Lu^2}{1 + u + Lu^2} = s_0 R \tag{9}$$

(iii) The possible influence of polynuclear complexes is identified in the plots of s^* vs $\log\,[H^+]$. If S^* at a given value of $\log\,[H^+]$ varies with B, then polynuclear complexes occur in significant amounts. No polynuclear complexes could be detected in this study.

The values of s_n pose a problem in the interpretation of the data as mentioned before. s_0 can be measured experimentally, but this is not the case for s_1 and s_2. Since the data of Kraus and Nelson[5,6] indicate that the molar absorptivity of UOH^{3+} at the chosen wavelength is much smaller than that of U^{4+}, we have assumed that this also is the case for $U(OH)_2{}^{2+}$ (see the following section).

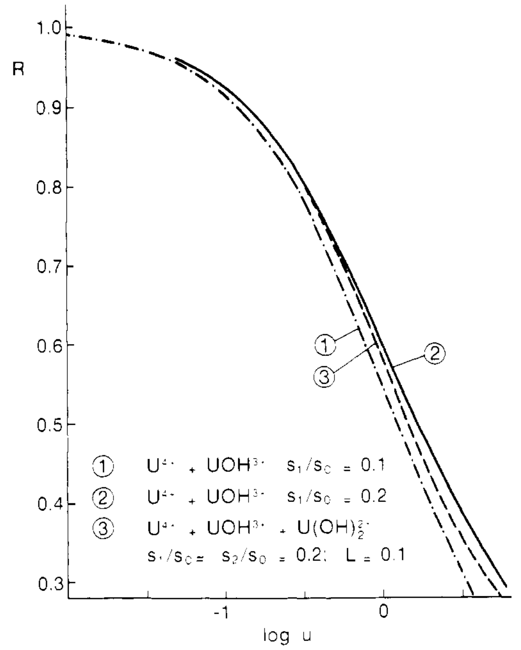

Figure 4. Model function $R(\log u)$ calculated by using two different chemical models where the first includes the species U^{4+} and UOH^{3+} and the second includes U^{4+}, UOH^{3+}, and $U(OH)_2{}^{2+}$. The first model has been tested by using two different values of s_1/s_0. The equilibrium constant is determined by moving the normalized $R(\log u)$ curves over the experimental S^*/s_0 vs ($-\log H^+$) data plotted on a diagram with the same scale as the normalized curve.

Results and Discussion

The experimental data are displayed in Figure 3 where the different symbols denote different total concentrations of U(IV). S^*/s_0 is independent of B in the concentration range studied, and we can, therefore, rule out the formation of larger amounts of polynuclear species. This is in agreement with the observations of Kraus and Nelson.[5]

The experimental data can be described with a chemical model containing only U^{4+}(aq) and $U(OH)^{3+}$. Normalized curves were calculated for various values of s_1/s_0. The best fit was obtained with $s_1/s_0 = 0.10$ and $\log {}^*\beta_1 = -1.75 \pm 0.05$. However, from the spectrophotometric data of Kraus and Nelson,[5,6] one finds that the ratio between the molar absorptivities of $U(OH)^{3+}$ and U^{4+} is closer to 0.2 at 490 nm; assuming that s_1/s_0 has the same value, we find $\log {}^*\beta_1 = -1.70 \pm 0.05$, but with a somewhat poorer fit at the higher values of $\log u$.

We then investigated if it was possible to identify a second hydroxide complex $U(OH)_2{}^{2+}$ by using the model function (9). By assuming $s_2/s_0 \approx 0.2$ and $L = 0.1$, we obtained the theoretical curve 3 (Figure 4) shown in the position of best fit in Figure 3. From this we obtain $\log {}^*\beta_1 = -1.65 \pm 0.05$.

It is obvious that one cannot distinguish between the various models using the experimental data alone. However, we may use additional chemical information from the chemistry of U(IV) to obtain some ideas about the speciation.

It is quite clear from the data that $\log {}^*\beta_1$ can be well determined and that the value is not strongly dependent on the value of s_1/s_0 or on the presence of $U(OH)_2{}^{2+}$. If $\log {}^*\beta_1 = -1.70$, we have about 87% UOH^{3+} and 13% U^{4+} at the lowest acidity ($-\log\,[H^+] = 2.50$) studied, but no appreciable amounts of polynuclear complexes (see Figure 1). If this model is correct, it implies an unusually large stability of UOH^{3+} as compared to that of the higher complexes. Such features have not been found in other U(IV) complexes, e.g. the fluorides.[13,14] We, therefore, prefer

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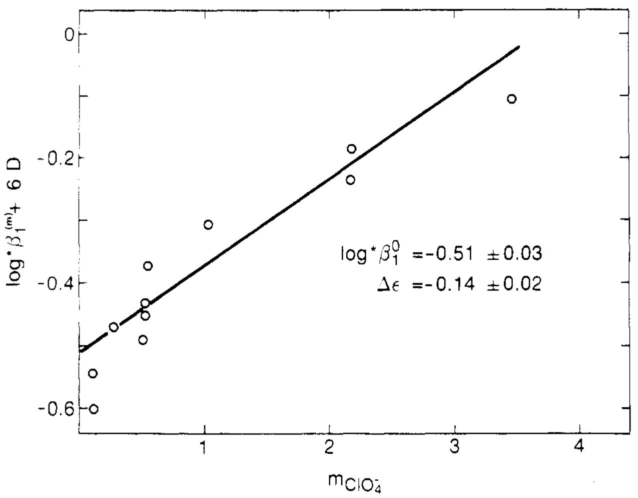

Figure 5. SIT plot of $\log {}^*\beta_1^{(m)}$ vs $m_{ClO_4^-}$ for the reaction $U^{4+} + H_2O \rightleftharpoons UOH^{3+}$ 3 H^+. The straight line is a least-squares fit of the function $\log {}^*\beta_1 + 6D = \log {}^*\beta^\circ_1 - (\Delta\epsilon)\, m_{ClO_4^-}$ where D is the Debye–Hückel term and $\Delta\epsilon = \epsilon(UOH^{3+},ClO_4^-) + \epsilon(H^+,ClO_4^-) - \epsilon(U^{4+},ClO_4^-)$. The various ϵ's are specific ion interaction coefficients.[14] ${}^*\beta_1^{(m)}$ denotes the equilibrium constant on the molal scale.

a model that includes $U(OH)_2^{2+}$. If we make the reasonable assumption that $s_2/s_0 \approx 0.2$, we can determine an upper value of the parameter $L = {}^*\beta_2/{}^*\beta_1^2$ which gives an acceptable fit; see eq 9. This requires that $L < 0.3$, which places an upper limit on $\log {}^*\beta_2$ of 3×10^{-5}. This value is of the order of magnitude expected for a statistical distribution of the stepwise mononuclear complexes; cf. ref 1, p 412. Values of L in the range $0.03 < L < 0.3$ give an acceptable fit of the experimental data.

It is interesting to observe that the amount of $U_6(OH)_{15}^{9+}$ is also negligible in comparison with the amount $U(OH)_2^{2+}$ in the concentration range studied.

Some of the experimental values around $R = 1$ in Figure 3 deviate noticeably from the theoretical curve. These points have been obtained by adding very large volumes of the titrant to the original U(IV) solution. The U(IV) in the 3 M $HClO_4$ titrant is oxidized very slowly, while the oxidation is much more rapid in the initial test solution. The high values of R indicate, indeed, that there has been a slight oxidation of the starting solution. However, this will not influence the values of S^*/s_0 at $-\log [H^+] > 1$ because of the very small amount of titrant added (less than 2% of the total volume).

The precision of the TLS method depends strongly on the magnitude of the spectral changes caused by the complex formation. If the molar absorptivity of the complexes is much smaller than that of the aquo ion, one cannot expect to obtain accurate values for the equilibrium constant beyond the first. Low molar absorptivity also makes it necessary to use higher total concentrations of the absorbing species. We doubt that it is possible to obtain information on equilibrium data for complexes beyond $U(OH)_2^{2+}$. However, it should be noted that this system is complicated by the ease of oxidation of U(IV) at higher pH.

The value of $\log {}^*\beta_1$ is in good agreement with other literature data.[5-7] This indicates that the TLS method is both a convenient method and a precise method to study mononuclear complex formations in systems where polynuclear complexes are predominating at higher metal ion concentrations. By using the specific ion interaction theory (SIT) (see ref 15 and references cited therein), we obtain $\log {}^*\beta_1$ at $I = 0$. From the SIT we have

$$\log {}^*\beta_1 + 6D = \log {}^*\beta^\circ_1 - (\Delta\epsilon) m_{ClO_4^-}$$

where the notation is given in ref 15. The experimental data of $\log {}^*\beta_1$ vs $m_{ClO_4^-}$ are shown in Figure 5. From a least-squares fit we obtain

$$\log {}^*\beta^\circ_1 = -0.51 \pm 0.03$$

$$\Delta\epsilon = -0.14 \pm 0.02$$

The value of $\Delta\epsilon = -0.14$ is similar to the value $\Delta\epsilon = -0.12 \pm 0.03$ obtained for the reaction $U^{4+} + HF \rightleftharpoons UF^3 + H^+$[16] and is in close agreement with that calculated from estimated values of $\epsilon(U^{4+},ClO_4^-) \approx 0.8$ and $\epsilon(UOH^{3+},ClO_4^-) \approx 0.5$ and the experimental value of $\epsilon(H^+,ClO_4^-) = 0.14$.[15]

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