Thermodynamic Stability of Zirconium(IV) Complexes with Hydroxy Ions

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A protometric study on the speciation of zirconium(IV) was performed in an aqueous solution at 25 °C in KNO_3 and four ionic strengths (0.2, 0.5, 1, and 2 mol·dm^{-3}). This study indicates the formation of the soluble species $Zr(OH)_3^+$, $Zr_2(OH)_7^+$, and $Zr(OH)_4$ in the pH range 1.5–3.5. The use of an appropriate titration technique allows the precipitation of the zirconium hydroxide to be limited. The overall stability constants β_{mlh} of these three hydroxo complexes were computed and refined, by the program PROTAF, for each ionic strength. The solubility product Ks of $Zr(OH)_4$ was calculated by taking these β_{mlh} constants into account. The thermodynamic values were determined by extrapolation at zero ionic strength (Specific ion Interaction Theory method): $\log \beta°_{10-3} = -0.52$ (0.01); $\log\beta°_{20-7} = -2.22(0.07)$; $\log\beta°_{10-4} = -4.52$ (0.07); $\log Ks° = -55.26(0.08)$.

For about fifty years zirconium has been a strategic metal. Its importance in the military and industrial nuclear fields is due to its mechanical and thermal properties and its outstanding resistance to corrosion, as well as to a low neutron capture cross-section. It is an essential constituent of the core of the nuclear power station and for confining fissile materials.

The running of nuclear installations relies on the processing of nuclear fuels and fission by-products, but also on the long-term storage, in protected sites, of confined materials which have acquired an appreciable radioactivity.

In the long-term one may expect the possibility of corrosion and fissuring of the confining containers leading to a contamination of soils and waters.

Modelling programs which take into account the whole local physical parameters as well as the physicochemical data allow the quantification of these contamination risks. The values used for these simulations, especially those relating to zirconium, have to be as reliable as possible in order to yield realistic estimations.

The chemistry of zirconium(IV) in aqueous media is dominated by the complexation of Zr^{4+} with OH^-. The data currently available on zirconium hydroxide complexes comes from studies carried out (essentially) before 1975[1][2][3][4][5][6][7][8][9]. The advanced species formulae and, above all, the values of the corresponding complexation constants, seem questionable.

Baes and Mesmer[10] have reviewed bibliographical results concerning zirconium hydrolysis in aqueous solution. When the zirconium concentration is low ($< 10^{-4}$ mol·dm^{-3}), they conclude that there is formation of mononuclear complexes $Zr(OH)_h^{(4-h)+}$ where $h = 1-5$.

According to these two authors, only the stability of the $ZrOH^{3+}$ species has been determined with a reasonable accuracy: $\log \beta_{10-1} = 0.3 \pm 0.05$ at zero ionic strength[9]. The hydrolysis constants of the more hydrolysed complexes [$Zr(OH)_2^{2+}$ through to $Zr(OH)_5^-$] are only rough estimates [for instance $\log K \leq -1.8$ for the equilibrium $ZrOH^{3+} + H_2O \rightleftharpoons Zr(OH)_2^{2+} + H^+$]. Increasing zirconium concentration induces the formation of polynuclear species $Zr_m(OH)_h^{(4m-h)+}$. In accordance with studies from Zielen and Connick[2], Johnson and Kraus[11], and Angstadt and Tyree[12], Baes and Mesmer conclude that the existence of a trimer, $Zr_3(OH)_4^{8+}$ or $Zr_3(OH)_5^{7+}$, and of the tetramer $Zr_4(OH)_8^{8+}$ is probable.

Aja et al.[13] also published a review concerning the aqueous chemistry of zirconium(IV). They principally take into account the results obtained by Russian scientists[5][6][8][14]. They consider that the values of the formation constants of the mononuclear hydroxide complexes depend little on the ionic strength and the nature of the supporting electrolyte. For these constants, they have retained average values which are very different from those given by Baes and Mesmer.

More recently, Adair et al.[15] published an article entitled "A review of the aqueous chemistry of the zirconium-water system" in which they simply give the same values of constants that Baes and Mesmer indicated for the mono- and polynuclear zirconium hydroxide complexes at 25°C.

In short, numerous studies deal with the formation of zirconium-hydrolysed complexes in aqueous solution but many discrepancies exist from one author to another concerning the major species formed and the values of the corresponding constants of formation. It must be pointed that in these studies the stoichiometry of the soluble species have not been experimentally determined.

The purposes of the present work are:

− The study of the complexation reactions between zirconium(IV) and hydroxy ions in aqueous solution. The stoichiometry of soluble species are determined from the position of the equivalent points on the titration curves and from the initial pH of the zirconium oxychloride solutions.

– The determination of the thermodynamical constants corresponding to the formation of the complex species by using the Specific ion Interaction Theory (SIT method).

Results

Stoichiometry of Complexes Formed

At the beginning of the titrations (pH < 2), the initial concentration of protons in $ZrOCl_2$ solutions corresponds to the liberation of one equivalent of proton per zirconium atom and to the formation of $Zr(OH)_3^+$ according to:

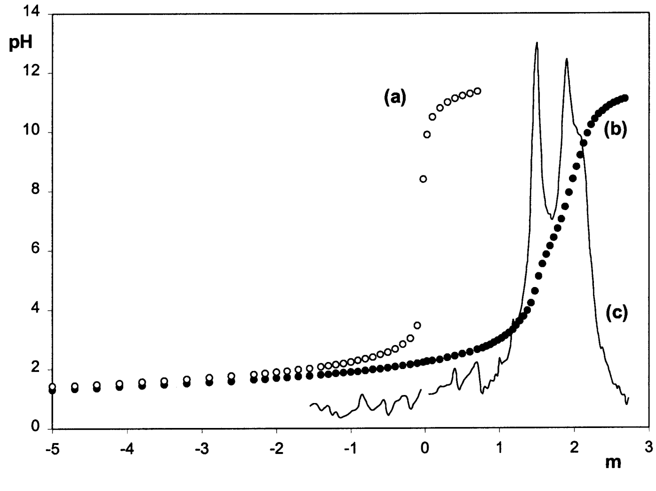
$$Zr(OH)_2^{2+} + 2\ H_2O \rightarrow Zr(OH)_3^+ + H_3O^+$$

Figure 1 shows that the potentiometric titration curve of the system $ZrOCl_2/HNO_3$ (curve b) is displaced to the right relative to the curve of nitric acid alone (curve a). In order to facilitate the interpretation of the results, the pH value is given versus the number (m) of OH^- equivalents per zirconium mol, calculated after the neutralisation of nitric acid. The derivative curve c shows two equivalent points at pH = 4 and pH = 8 which correspond to 1.5 and 2 equiv. of OH^- added, respectively. Both equivalent points correspond to the formation of species which contain 3.5 and 4 OH^- per zirconium atom according to:

$$Zr(OH)_3^+ + H_3O^+ + 1.5\ OH^- \rightarrow Zr(OH)_{3.5}^{0.5+} + 2\ H_2O$$
$$\text{and } Zr(OH)_3^+ + H_3O^+ + 2\ OH^- \rightarrow Zr(OH)_4 + 2\ H_2O$$

For the species "$Zr(OH)_{3.5}^{0.5+}$", computation led us to envisage the formation of the dimer $Zr_2(OH)_7^+$. As for the species "$Zr(OH)_4$", they are very likely to be polymeric species in which the ratio $[OH^-]/[Zr]$ is equal to four. For simplicity, these polymeric species are denoted as $[Zr(OH)_4]_n$.

Figure 1. Titration curves for (a) nitric acid ($4\cdot10^{-2}$ mol·dm^{-3}), (b) zirconium oxychloride ($8\cdot10^{-3}$ mol·dm^{-3}) in the presence of nitric acid ($4\cdot10^{-2}$ mol·dm^{-3}), (c) derivative curve of (b); the pH is given versus the number (m) of OH^- equivalents per zirconium, calculated after neutralisation of nitric acid



Precipitation occured after pH = 3.5 when the complex $Zr_2(OH)_7^+$ was still predominant. This means that the solid phase has a composition close to the composition of a ionic salt in which $Zr_2(OH)_7^+$ is associated with a counter anion, either nitrate or chloride.

To refine the composition of the solid phase several analyses were made. The precipitate was separated from the solution by centrifugation and filtration and washed with KNO_3. The solid was then dispersed in a KNO_3 solution which was titrated with KOH (0.1 mol dm^{-3}). The titration curve obtained shows that hydrolysis still occcurs at pH > 3.5, because we obtain one equivalent point at pH = 8.5 for 0.5 equiv. of OH^- added. This point corresponds to the formation of the polymeric species $[Zr(OH)_4]_n$ which confirms the previous formation of an insoluble salt at pH = 3.5. Chloride ions were titrated in the supernatant by potentiometry. The result indicates that all the chloride ions are present in solution and, consequently, that the solid phase does not contain any chloride. Infrared spectra of the solid phase were recorded and shows a band at 1380 nm which confirms the presence of nitrate anion.

A similar trend is observed in perchlorate medium; precipitation occurs at pH = 3.5, the titration curves show two inflexion points at pH = 4.4 for 1.75 equiv. of OH^- and pH = 8.5 for 2 equiv. of OH^-. These points correspond to the formation of species having the stoichiometry $Zr_3(OH)_{11}^+$ and $[Zr(OH)_4]_n$, respectively.

Determination of Stability Constants

The overall stability constants are related to the general equilibrium:

$$m\ Zr^{4+} + 2h\ H_2O \rightleftharpoons Zr_m(OH)_h^{(4m-h)+} + h\ H_3O^+$$

$$\beta^c_{m0-h} = \frac{[Zr_m(OH)_h^{(4m-h)+}][H_3O^+]^h}{[Zr^{4+}]^m}$$

The neutralisation curves were computed taking into account the species $Zr(OH)_3^+$, and $Zr_2(OH)_7^+$ and also the soluble monomeric species $Zr(OH)_4$. The concentration range of zirconium used in the calculation varies from 10^{-3} to 8×10^{-3} mol·dm^{-3}. The validity of the hypothesis was checked for lower concentrations up to 8×10^{-5} mol·dm^{-3} of Zr^{IV}. For the calculation of stability constants, data obtained in the heterogeneous phase was removed. However, further simulations were made over the whole pH range to confirm the stoichiometry of the insoluble species. Calculated curves were in good agreement with experiment over the whole pH range studied. We have included in our hypothesis the formation of polynuclear species cited in the literature[1][2][7][11][12]. After calculation, polynuclear species were not selected, and improved least square refinements were found considering only the three species previously proposed.

The precision on some log β_{10-4} values is weak because in the homogeneous phase $Zr(OH)_4$ can be considered as a very minor species. The species distribution curve shows

Table 1. Overall stability constants of $Zr(OH)_3{}^+$, $Zr(OH)_4$, and $Zr_2(OH)_7{}^{+[a]}$ (KNO_3 medium, 25 ± 0.1°C)

I [mol·dm^{-3}]	log $\beta^c{}_{10-3}$	log$\beta^c{}_{20-7}$	log$\beta^c{}_{10-4}$
0.2	−2.02 (0.01)	−5.26 (0.04)	−6.09 (0.03)
0.5	−2.18 (0.01)	−5.39 (0.04)	−6.7 (0.2)
1	−2.27 (0.01)	−5.48 (0.04)	−6.71 (0.04)
1[b]	−2.29 (0.05)	−5.56 (0.11)	−6.51 (0.08)
2	−1.77 (0.03)	−4.35 (0.05)	−6.9 (0.3)

[a] Values in parentheses represent 1 σ standard deviation. – [b] $NaClO_4$ medium, 25 ± 0.1°C.

that its proportion in solution is lower than 10% at pH = 4.0. It is also interesting to note that for $I = 1$ mol·dm^{-3}, the values of the stability constants were similar in nitrate and perchlorate media, which seems to indicate that there is no complexation between zirconium and nitrate ions.

Determination of Solubility Products

The values of the solubility product of zirconium hydroxide $Zr(OH)_4$ proposed in the literature[3][4] vary between 10^{-52} and 10^{-54}, but it is worth pointing out that most of the authors do not take into account the stability constants of soluble species in their calculations.

In our experiments, the solubility product is determined from the pH value and the free concentration of Zr^{4+} calculated for each solution from the stability constants of the soluble species $Zr(OH)_3{}^+$ and $Zr_2(OH)_7{}^+$, using the following expression where [Zr(t)] is the total concentration of zirconium:

$$\frac{2\beta_{20-7}}{[H_3O^+]^7}[Zr^{4+}]^2+\left(1+\frac{\beta_{10-3}}{[H_3O^+]^3}\right)[Zr^{4+}]-[Zr(t)]=0$$

The solubility product is then calculated using the usual expression $Ks = [Zr^{4+}][OH^-]^4$.

The mean values of the logarithms of the solubility products are reported in Table 2 for the four different ionic strengths.

Table 2. Solubility products of $Zr(OH)_4$; (KNO_3 medium, 25 ± 0.1°C)

I [mol·dm$^-$]^3	log Ks [a]
0.2	−52.71 (0.05)
0.5	−52.49 (0.06)
1	−52.72 (0.06)
2	−53.49 (0.03)

[a] Values in parentheses represent 1 σ standard deviation.

Determination of the Thermodynamical Formation Constants

The constants of formation have been determined in solution containing KNO_3 as supporting electrolyte (0.2–2 mol·dm^{-3}). The specific interaction theory[20][21][22][23] is used for the comparison of data at different ionic strengths and also for the calculation of the thermodynamic formation constants corresponding to the standard state.

The activity coefficient of a cation i of charge z is calculated from the following expression:

$$\log \gamma_i = -z_i^2\,D + \Sigma_j\,\varepsilon(i, j) \times m_j$$

where $D = \dfrac{0.5091\sqrt{I_m}}{1+1.5\sqrt{I_m}}$ is the Debye-Hückel term (for long-range electrostatic interactions); $\varepsilon(i, j)$ is the specific interaction coefficient between the cation i of charge z and the others ions j of opposite charge in the solution and m_j is the molality of the ions j.

In our study, the concentration of the nitrate ions of the supporting electrolyte KNO_3 is much larger than these of the other ionic species. Consequently, it is the main contributor to the value of log γ_i:

$$\log \gamma_i = -z_i^2\,D + \varepsilon(i, NO_3{}^-) \times I_m$$

with I_m ionic strength equal to the molal concentration of the supporting electrolyte.

For the general formation reaction,

$$m\,Zr^{4+} + 2\,h\,H_2O \rightleftharpoons Zr_m(OH)_h{}^{(4m-h)+} + h\,H_3O^+$$

$$\beta^c_{m0-h} = \frac{[Zr_m(OH)_h^{(4m-h)+}][H_3O^+]^h}{[Zr^{4+}]^m}$$

The apparent stability constant $\beta^c{}_{m0-h}$ is calculated from the molar concentrations of the reacting species. This value is then converted to molality units ($\beta^m{}_{m0-h}$ value) according to the conversion factors determined by Baes and Mesmer[10]. Finally, the thermodynamical stability constant $\beta^\circ{}_{m0-h}$ is determined from the experimental constants $\beta^m{}_{m0-h}$, by using a weighted linear extrapolation to zero ionic strength.

$$\beta^o_{m0-h} = \frac{a_{Zr_m(OH)_h^{(4m-h)+}}\,a^h_{H_3O^+}}{a^m_{Zr^{4+}}\,a^{2h}_{H_2O}}$$

The expression of the logarithm of the thermodynamical stability constant may be written as:

$$\log\beta^o_{m0-h} = \log\beta^m_{m0-h} + \log\gamma_{Zr_m(OH)_h^{(4m-h)+}} + h\cdot\log\gamma_{H_3O^+} - m\cdot\log\gamma_{Zr^{4+}} - 2h\cdot\log a_{H_2O}$$

with the logarithms activity coefficients:

$$\log\gamma_{Zr_m(OH)_h^{(4m-h)+}} = -(4m-h)^2\cdot D+\varepsilon(Zr_m(OH)_h^{4m-h)+}, NO_3^-)\cdot I_m$$
$$\log\gamma_{H_3O^+} = -D+\varepsilon(H_3O^+, NO_3^-)\cdot I_m$$
$$\log\gamma_{Zr^{4+}} = -16\,D + \varepsilon(Zr^{4+}, NO_3^-)\cdot I_m$$

Consequently:

$$\log\beta^m{}_{m0-h} + D\,[16m - h - (4m-h)^2] - 2h\log a_{H_2O} = \log\beta^o{}_{m0-h} - \Delta\varepsilon\cdot I_m$$

where $\Delta\varepsilon$ is the summation of the specific interaction terms:

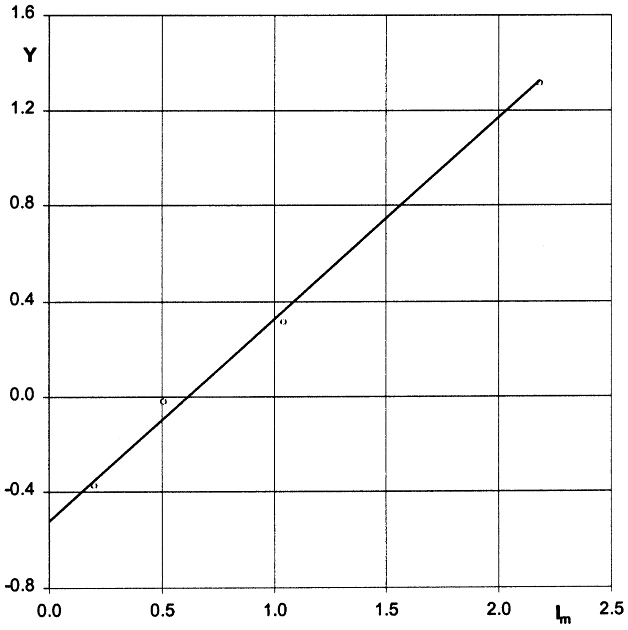
$$\Delta\varepsilon = \varepsilon[Zr_m(OH)_h^{(4m-h)+}, NO_3^-] + h\varepsilon[H_3O^+, NO_3^-] - m\varepsilon[Zr^{4+}, NO_3^-]$$

Since the solvent is a chemically reacting species, its activity must be calculated and incorporated into the expression for the thermodynamic constant.

$$\log a_{H_2O} \approx \frac{-2\cdot\Phi\cdot I_m}{55.51\cdot\ln(10)} \quad (I_m = m_{K^+} = m_{NO_3^-})$$

Φ is the osmotic coefficient which can be calculated from Stockes[24] equation.

Figure 2. Extrapolation of the logarithm of the thermodynamical formation constant of $Zr(OH)_3^+$ by weighted linear regression



The value of log $\beta°_{m0-h}$ is obtained using a weighted linear regression of the quantity Y as a function of the ionic strength[25].

$$Y = \log\beta^m{}_{m0-h} + D[16m - h - (4m - h)^2] - 2h\log a_{H_2O} = \log\beta°_{m0-h} - \Delta\varepsilon\cdot I_m$$

This procedure has been applied for the determination of log $\beta°_{10-3}$, log $\beta°_{20-7}$, log $\beta°_{10-4}$, and log $K°_s$ solubility product of $Zr(OH)_4$. For the determination of log $\beta°_{10-3}$ see, for example, Figures 2 and 3. All the results are reported in Table 3.

Discussion

The hydrolysis reactions of zirconium(IV) have been monitored by protometry, using a specific titration procedure which consist of adding the titrant very slowly (0.5 µl per 5 s) with vigorous stirring. This procedure avoids the precipitation of insoluble hydroxide at the tip of the burette and errors on the measurement of pH values.

Figure 3. Variation of the logarithm of the experimental formation constant of complex $Zr(OH)_3^+$ as a function of ionic strength (molality)

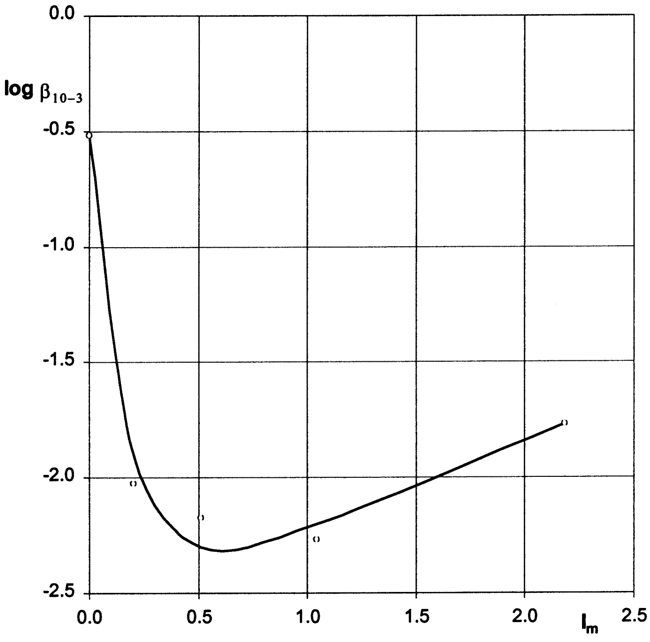


Table 3. Thermodynamic values of the logarithms of the formation constants of soluble complexes and of the solubility product of $Zr(OH)_4$; values in parentheses represent 1 σ standard deviation

$Zr(OH)_3^+$	log $\beta°_{10-3}$	−0.52 (0.01)
$Zr_2(OH)_7^+$	log $\beta°_{20-7}$	−2.22 (0.07)
$Zr(OH)_4$	log $\beta°_{10-4}$	−4.52 (0.07)
$Zr(OH)_4$	log $Ks°$	−55.26 (0.08)

In order to verify that pH measurements realised with KOH of 0.1 mol·dm^{-3} were not influenced by kinetic phenomena, we have also used KOH of 2.5·10^{-2} mol·dm^{-3}. With the same rate of KOH addition (0.5 µl per 5 s) a protometric titration lasted for about one week. The pH measurements lead to stability constants values identical with those obtained with KOH of 0.1 mol·dm^{-3}.

The stability constants values of Zr hydrolysed complexes, reported by Baes and Mesmer[10] and Aja et al.[13], have been estimated from results contained in several publications. Different methods have been used in these works for studying Zr hydrolysis (e.g.: solvent extraction, spectroscopy, complexometry, solubility measurements). It must be noted that the values of Aja et al. take no account of the ionic strength variation. For calculating the thermodynamic constants values, Baes and Mesmer admit that the ionic strength dependence of β_{mlh} is similar to that found in the case of other cations, e.g. U^{4+}.

In this work, the protometric titrations of zirconium oxychloride solutions by KOH allow verification of the consistency between our obtained values and those reported by Baes and Mesmer and Aja et al. In the pH range where the solutions are homogeneous (pH ≤ 3.5), the experimental pH values were compared to those calculated from the stability constants. For example, in the Figure 4 the experimental titration curve of zirconium oxychloride solution ($4 \cdot 10^{-3}$ mol·dm^{-3}) in the presence of nitric acid ($2 \cdot 10^{-2}$ mol·dm^{-3}) is represented. The calculated curves obtained by using Baes and Mesmer or Aja et al. constants are represented by dashed lines. The stability constants given at zero ionic strength by Baes and Mesmer were calculated for $I = 1$ by using the relation between β_{mlh} and I they indicate in their paper[10] ($\log \beta_{10-1} = -0.6$; $\log \beta_{10-2} = -2.3$; $\log \beta_{10-3} = -6.3$; $\log \beta_{10-4} = -11.0$; $\log \beta_{10-5} = -17.1$; $\log \beta_{30-4} = 4.5$ or $\log \beta_{30-5} = 5.2$; $\log \beta_{40-8} = 8.0$).

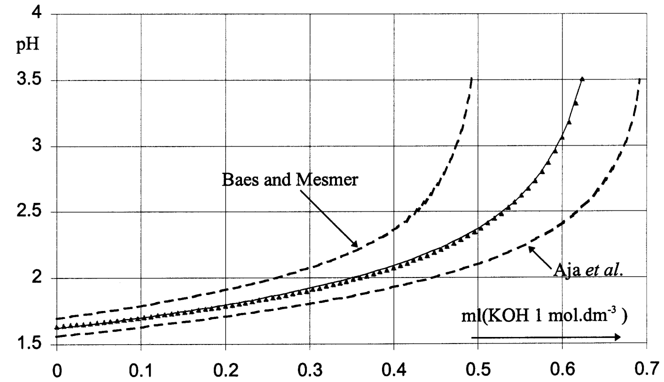


Figure 4. Titration curves of zirconium oxychloride solution ($4 \cdot 10^{-3}$ mol·dm^{-3}) in the presence of nitric acid ($2 \cdot 10^{-2}$ mol·dm^{-3}); ionic strength = 1; KOH = 1 mol·dm^{-3}; ▲ experimental curve, (—) calculated curve with our results, (-----) calculated curves with results of Baes and Mesmer[10] or Aja et al.[13]

There is a large discrepancy between the experimental curve and the two calculated curves. By using the results of Baes and Mesmer, the plot of the distribution curves of the different mono- and polynuclear hydroxo complexes shows that $Zr_4(OH)_8^{8+}$ is practically the only species formed. This tetrameric ion is that encountered in the solid zirconium oxychloride, so the dissolution of this solid compound should not modify the pH solution, which disagrees with our observations and with those of Larsen and Gammill[1]. On the other hand, the constants values reported by Aja et al. lead to the predominance of $Zr(OH)_4$ at pH = 1.5−3.5. Under these conditions, the studied solutions would not be homogeneous because of the precipitation of $[Zr(OH)_4]_n$.

For all these reasons, we have envisaged the existence of other soluble species under our experimental conditions ($1.5 \leq \text{pH} \leq 3.5$, and $8 \cdot 10^{-5}$ mol·dm^{-3} $\leq$ [Zr] $\leq$ $8 \cdot 10^{-3}$ mol·dm^{-3}). Our hypotheses are based on the following experimental results:

− The pH value at the beginning of the titrations corresponds to the liberation of one equivalent of proton per zirconium and therefore to the formation of the $Zr(OH)_3^+$ species.

− The positions of the equivalent points of the titration curves at 1.5 (in nitrate medium), 1.75 (in perchlorate medium) and 2 equiv. of OH^- per zirconium. These positions are independent of the zirconium concentration which indicates that the stoichiometry of the formed species is well defined: $Zr_2(OH)_7^+$ in nitrate medium and $Zr_3(OH)_{11}^+$ in perchlorate medium.

− The existence of $Zr_2(OH)_7^+$ is confirmed by the precipitation of the ionic salt $[Zr_2(OH)_7]NO_3$ at pH ≈ 3.5.

In short, at the beginning of the titrations, one may expect the formation of the $Zr(OH)_3^+$ species. The hydrolysis of this species leads to the formation of soluble $Zr(OH)_4$ which is always a very minor species in solution because, when its concentration increases, $Zr(OH)_4$ bonds to $Zr(OH)_3^+$ by hydroxo bridges leading to $Zr_2(OH)_7^+$. Then, in KNO_3 medium, at pH > 3.5, there is a precipitation and the probable formation of polymeric species such as $Zr_3(OH)_{11}^+$ $[Zr_2(OH)_7^+ + Zr(OH)_4]$ or $Zr_4(OH)_{15}^+$ $[Zr_3(OH)_{11}^+ + Zr(OH)_4]$. When the acidity of the solution decreases the existence of the $Zr_4(OH)_{15}^+$ species has also been suggested by Gimblett and Massey[26]. Then, according to these authors, the complex ion $Zr_4(OH)_{15}^+$ hydrolyses to a neutral tetrameric hydroxide which polymerises slowly to form colloidal particles and ultimately a solid hydroxide precipitate. Finally, at the second equivalence point of the titration curves (pH ≈ 6), the precipitated species is very likely to be a polymer of the formula $[Zr(OH)_4]_n$ because this precipitate does not dissolve in solution, even in very acidic medium.

Conclusion

The aqueous chemistry of zirconium(IV) can be explained by the formation of the soluble species $Zr(OH)_3^+$, $Zr_2(OH)_7^+$, and $Zr(OH)_4$ in KNO_3 media, in the pH range of 1.5−3.5 and for zirconium concentrations varying from $8 \cdot 10^{-5}$ to $8 \cdot 10^{-3}$ mol·dm^{-3}.

The formation constants of the species $Zr(OH)_3^+$, $Zr_2(OH)_7^+$, and $Zr(OH)_4$ as well as the solubility product of zirconium hydroxide have been determined in KNO_3 media at four ionic strengths. The values of these β_{mlh} constants were extrapolated to the standard state in order to determine the thermodynamic constants β°_{mlh}. The β°_{mlh} constants were determined at zero ionic strength by putting the Specific ion Interaction Theory (SIT method) into practice.

We have also obtained some results in heterogeneous medium, at pH > 10, which lead us to consider the formation of the $Zr(OH)_5^-$ species. Unfortunately, these results cannot be used in this case to determine the formation constant of $Zr(OH)_5^-$. A useful evaluation of the solubility of zirconium(IV) in aqueous medium is obtained by plotting the total zirconium concentration (on a logarithmic scale) as a function of pH (Figure 5).

Such a plot shows that the insoluble species $Zr(OH)_4$ is predominant between pH = 5 and pH = 12. This species distribution diagram was established at pH > 8 by using the result of Sheka et al.[3] for the formation constant of $Zr(OH)_5^-$ ($\log \beta^\circ_{10-5} \approx -19.3$).

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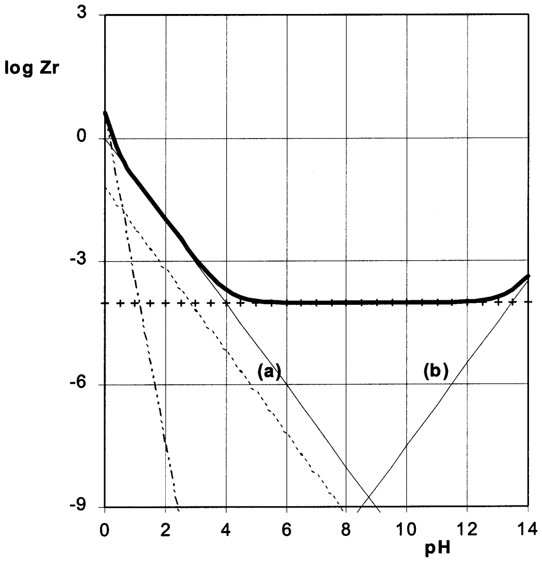
Figure 5. Speciation of hydroxy zirconium complexes in equilibrium with solid $Zr(OH)_4$ (25°C, $I = 0$); the thick line represents the total zirconium concentration in solution; Zr^{4+} (---); $Zr(OH)_4$ (+ +); $Zr_2(OH)_7^+$ (− − −); $Zr(OH)_3^+$ (a); $Zr(OH)_5^-$ (b)



Experimental Section

Reagents: All chemicals used were of analytical grade. Zirconium oxychloride and potassium nitrate were purchased from Fluka. Nitric acid and potassium hydroxide were purchased from Merck. Solutions of zirconium oxychloride were prepared with an excess of nitric acid ($[H_3O^+]/[Zr] = 5$) to prevent the formation of less reactive polymers[16]. These solutions were standardised by edta titration using an excess of Fe^{III} ions, and salicylic acid as an indicator following the procedure described by Kragten et al.[16] and Milner et al.[17]. Potassium nitrate stock solutions were filtered on Millipore filters (pore size 1.2 μm) before use and storage.

Protometric Measurements: All measurements were performed at 25 ± 0.1°C. Experiments were made at different ionic strengths ($I = 0.2$, 0.5, 1, and 2 $mol \cdot dm^{-3}$) and adjusted with potassium nitrate. A few experiments were carried out in sodium perchlorate medium to ensure that there is no complexation reaction with nitrate ions.

The protometric measurements were carried out in a thermoregularized cell with a nitrogen stream over the solution to avoid dissolution of carbon dioxide. The glass electrode Metrohm type "U" has a very low alkaline error. The reference element Hg/Hg_2Cl_2 was in contact with a solution containing KCl of a concentration of 0.1 $mol \cdot dm^{-3}$ and a variable concentration of KNO_3 to adjust ionic strength to the required value. The procedures and apparatus used for protometric measurements have been previously described[18]. For pH values below 2, a polynomial correction was used.

Because of the slow kinetics of the hydrolysis reactions, and also because of the formation of local precipitate as a consequence of the addition of the alkaline reagent, experimental procedures have been refined in order to obtain accurate and reproducible pH measurements. Titrations were made under the conditions of vigorous stirring and very slow addition of the titrant (0.5 μl per 5 s), so for high concentrations of zirconium, a titration can last several days.

Solutions of zirconium oxychloride in the concentration range of $8 \cdot 10^{-5}$ to $8 \cdot 10^{-3}$ $mol \cdot dm^{-3}$ were titrated by KOH (0.1 $mol \cdot dm^{-3}$) up to pH = 12. Further titrations with a less concentrated reagent (KOH of 0.04 $mol \cdot dm^{-3}$) were performed to ensure that the equilibrium is effectively reached throughout the experiments. The results were similar in both cases and so validate the titration procedure.

Solubility Measurements: The solubility of zirconium hydroxide $Zr(OH)_4$ was measured as a function of pH at four ionic strengths in order to evaluate its solubility product. Zirconium hydroxide was prepared by the precipitation of zirconyl chloride with ammonia. An amount of solid was introduced in zirconyl chloride solutions of variable concentration and ionic strength. After the equilibrium was reached (up to 15 d), the solutions were centrifuged and filtered using a Sartorius filter (pore size 0.45 μm). The pH value and the total concentration of zirconium for the supernatant were determined. The pH ranged from 1 to 3.5 and the zirconium concentration varied from 0.1 to 0.001 mol dm^{-3}. For each ionic strength a series of ten solutions was prepared.

Computations: The protometric data were processed by the computer program Protaf[19] in order to obtain the best-fit chemical model and refined stability constants β_{mlh} (β_{mlh} refers to the species $M_mL_lH_h$; a negative h value refers to the hydroxy ion). The program Protaf, which is based on the weighted least squares of the residues of the experimental variables (volume of titrant, pH), allows a simultaneous processing of ten titrations, each including 150 pairs of data (volume, pH).

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