Aqueous Chemistry of Zirconium(IV) in Carbonate Media

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The interactions between carbonate ions and zirconium oxychloride are studied by potentiometry, dialysis, and ^{13}C- and ^{17}O-NMR spectroscopy in aqueous media. The nature of the soluble carbonatohydroxo complexes depends on the proportions of hydrogencarbonate and carbonate ions in solution before the addition of zirconium oxychloride. Carbonate media lead to polynuclear entities containing no more than two complexed carbonate ions per Zr^{4+}. The presence of hydrogencarbonate favors the formation of less condensed and more carbonated complexes such as $[Zr(CO_3)_4]^{4-}$. The polycondensation degree of the species decreases when the number of carbonates linked per Zr^{4+} increases. In all complexes, the carbonate is bidentate, and the metal atoms are linked *via* hydroxo bridges. The complexation of carbonate with Zr^{4+} occurs for a total carbonate concentration higher than 0.1M. Consequently, in natural medium, the speciation of this metal is governed only by the formation of hydroxo complexes.

1. Introduction. – Aqueous chemistry of zirconium(IV) has been extensively investigated in aqueous media to predict the speciation of zirconium(IV) in natural environment. In a recent publication, we described a study of the complexation between Zr^{4+} and hydroxide ions under conditions close to those encountered in natural media [1].

The role of carbonate ions in the transport properties of Zr^{4+} is not well understood. Carbonate and hydrogencarbonate are common anions found in significant concentrations in many natural waters and are exceptionally strong complexing agents. Therefore, these anions may play an important role in migration of Zr^{4+} from a nuclear-waste repository. Most studies deal with synthesis and structural properties of solid complexes [2–5]. The analysis of solid compounds reveals that the number of carbonato ligands linked per Zr^{4+} varies from 0 to 4. Structural investigations, mainly by IR spectroscopies [2], show that the tetracarbonatozirconate has a monomeric structure with bidentate carbonato ligands [3]. When the number of carbonato ligands linked to a Zr-atom is less than four, the solid compounds have a polynuclear structure in which Zr-atoms are linked together by hydroxo, oxo, and carbonato bridges. To our knowledge, only the dinuclear structure of $[Zr_2(CO_3)_6(OH)_2]^{6-}$ has been determined by *Gorbunova et al.* [4] and *Clearfield* [5], as the potassium and ammonium salts, respectively. The Zr-atoms are each surrounded by three bidentate ions and are linked together by hydroxo bridges. Examination of the aqueous behavior of zirconium(IV) in carbonate media revealed the formation of several carbonatohydroxo complexes having the stoichiometries $[Zr(CO_3)_4]^{4-}$ (1:4:0), $[Zr(CO_3)_3(OH)]^{3-}$ (1:3:1), $[Zr(CO_3)_2(OH)_2]^{2-}$ (1:2:2), $[Zr(CO_3)(OH)_3]^{-}$ (1:1:3), and $[Zr(OH)_4]$ (1:0:4) [6]. These studies were mainly qualitative, and only the formation constant of $[Zr(CO_3)_4]^{4-}$ has been determined by *Dervin et al.* [7] by solvent extraction and solubility experiments (the value of $\log \beta_{140}$ was between 38.6 and 40.4 at ionic strength $I = 1$).

Recently, we have presented our investigation about the coordination mode of carbonate ions in $[Zr(CO_3)_4]^{4-}$ in aqueous solution and the kinetic behavior of this complex [8]. We now have determined the nature and the stoichiometry of carbonato-hydroxo complexes of Zr^{4+} by potentiometry, dialysis, and ^{13}C- and ^{17}O-NMR spectroscopy, and we suggest structures for these species.

2. Results. – 2.1. *NMR Studies. ^{17}O-NMR Data.* The ^{17}O-NMR spectra (D_2O) of potassium hydrogencarbonate and potassium carbonate are recorded separately and also as a mixture of both species. The chemical shifts of HCO_3^- and CO_3^{2-} are 173 and 191 ppm, respectively; theses values are similar to those obtained by *Banyai et al.* [9], who found 172 and 189 ppm, respectively. A mixture HCO_3^-/CO_3^{2-} displays only one peak due to the fast proton exchange between both species. The chemical shift of this latter resonance depends on the ratio HCO_3^-/CO_3^{2-} and is found between 173 and 191 ppm.

The ^{17}O-NMR spectra (D_2O) of three solutions with identical concentrations of zirconium ion (0.08M) and total carbonate (CO_3^{2-} and HCO_3^-; 0.4M), but with different ratios HCO_3^-/CO_2^{2-} each show one additional peak due to the O-atom of the complexed carbonate moiety (*Fig. 1*). The half-width $\delta\nu_{1/2}$ of this latter peak is very large and can be estimated to be close to 3500 Hz. Its chemical shift, 215 ppm, is invariant whatever the composition of the solution. Qualitative information about the extent of complexation phenomena can be deduced by simple analysis of the peak area. The latter increases when the $KHCO_3$ concentration of the initial solution increases. In fact, the peak corresponding to the coordinated carbonato ligands is hardly visible when no HCO_3^- ions are used during the preparation of the solution (*Fig. 1,c*). Thus, the extent of carbonate complexation rises with the increase of the concentration of HCO_3^- in the initial solution.

Our results can be easily compared to the behavior of $[(UO_2)_3(CO_3)_6]^{6-}$ [9], which showed only one broad peak at 215 ppm in its ^{17}O-NMR spectrum for its three bridging and three bidentate carbonato ligands. In Zr^{4+}, as well as in uranyl complexes, the broadness of the peak of coordinated carbonate ions may be due to quadrupolar relaxation and/or to a fast exchange process.

^{13}C-NMR Data. The previously determined ^{13}C-NMR chemical shifts in D_2O for potassium carbonate and potassium hydrogencarbonate alone are 168.6 and 163 ppm, respectively [8].

The ^{13}C-NMR spectra for different D_2O solutions of $ZrOCl_2/K_2CO_3$ and $ZrOCl_2/KHCO_3/K_2CO_3$ exhibit two peaks which correspond to the free carbonate (*i.e.*, carbonate and hydrogenocarbonate ions) and to the complexed carbonate ion. Whatever the composition of the solution and also the nature of the ligands, the chemical shift of complexed carbonate ion is invariant and equal to 168.3 ppm. This chemical shift is not influenced by other ligands of Zr^{4+} and depends mainly on the coordination mode of the carbonato ligands.

Influence of Hydrogencarbonate Ions and of Zirconium Concentration. Since the longitudinal relaxation time can be determined, some spectra are integrated. *Figs. 2* and *3* show quantitatively the influence of experimental conditions on the extent of carbonate binding. Thus, ^{13}C-NMR spectra are recorded at constant Zr^{4+} ion (0.08M) and total carbonate (0.48M) concentrations. The increase of the initial HCO_3^- concentration from 0 to 0.30M enhances the complexation of Zr^{4+} by carbonate ions

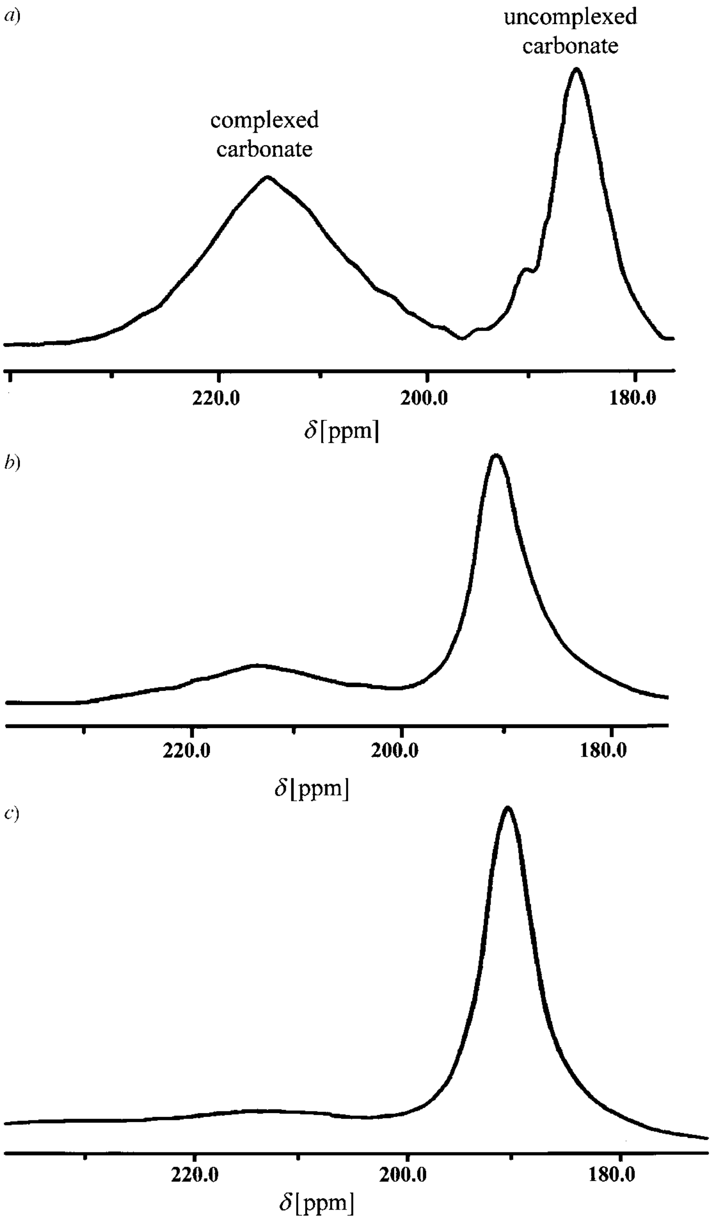

Fig. 1. *^{17}O-NMR Spectra of $ZrOCl_2/KHCO_3/K_2CO_3$ solutions in D_2O* (0.08M $ZrOCl_2$ for all solutions): a) *0.24M $KHCO_3$ and 0.16M K_2CO_3*, b) *0.16M $KHCO_3$ and 0.24M K_2CO_3, and* c) *0.4M K_2CO_3*

from 1.3 to 4 complexed carbonate ligands per Zr^{4+} (*Fig. 2*). When the average number of complexed carbonate ions per Zr-atom $\bar{n}_{CO_3}$ is equal to four, the Zr-atom is entirely present in the form of the tetracarbonatozirconate ion $[Zr(CO_3)_4]^{4-}$. Unfortunately,

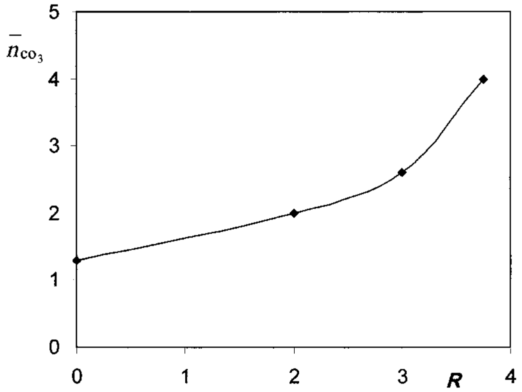

Fig. 2. *Influence of the initial hydrogencarbonate ion concentration on complexation*. Total carbonate concentration = 0.48M; $R = C_{HCO_3}/C_{Zr}$; $\bar{n}_{CO_3}$ = average number of CO_3^{2-} ions linked per Zr-atom.

when $\bar{n}_{CO_3}$ is lower than 4, the exact nature of the complexes cannot be established because certainly a mixture of complexes is present.

When the total concentration of Zr^{4+} is varied from 0.1 to 0.01M, the average number of complexed carbonate ions per Zr-atom decreases from 3.2 to 1.1 (*Fig. 3*). The dilution leads to the formation of fewer carbonato complexes.

2.2. *Stoichiometry of Soluble Complexes: Protometric Study. Preamble.* The main difficulty for pH measurements in carbonate media is the possible volatilization of carbonic acid during the titration experiments. To avoid this problem, a partial pressure of carbonic acid is sometimes applied during the titration experiments [10]. Our experiments are performed under N_2 pressure. Futhermore, the global protonation constants ($\log\beta_{011}$ and $\log\beta_{012}$) of the carbonate ion are determined by titrating solutions of potassium carbonate with nitric acid between pH 11 and 6.5 at four ionic strengths and in KNO_3 media. Values of thermodynamic acidity constants are determined by extrapolation of conditional constants to zero ionic strength according to the S.I.T. theory [11]. The obtained values ($\log\beta_{011} = 10.31 \pm 0.01$ and $\log\beta_{012} =$

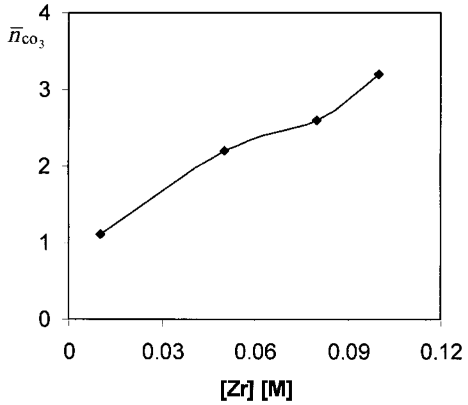

Fig. 3. *Influence of the dilution on complexation: variation of* $\bar{n}_{CO_3}$ *vs. total* Zr^{4+} *concentration.* $[ZrOCl_2]/[KHCO_3]/[K_2CO_3]$ 1:3:3 for the studied solutions.

16.70 ± 0.01) are in good agreement with those found by *Grenthe* and *Wanner* [11] and *Martell et al.* [12] ($\log\beta_{011} = 10.33 \pm 0.02$ and $\log\beta_{012} = 16.68 \pm 0.03$), which are reference values, so our titration procedure can be used with confidence.

Titrations with HNO_3. The solutions are titrated with 0.2M HNO_3 from their initial pH (which is between 9.8 and 9.2) down to pH 2. The concentration range of Zr^{4+} varied between $8 \cdot 10^{-3}$ and $4 \cdot 10^{-2}$ M.

Fig. 4 shows the neutralization curve for a solution prepared from $ZrOCl_2/KHCO_3/K_2CO_3$ in the initial ratio 1:3:3 (curve *a*) and the neutralization curve of the ligand ($KHCO_3/K_2CO_3$) at the same concentrations (curve *b*). To facilitate the interpretation of the results, the pH value is given *vs.* the number *m* of H^+ equiv. per Zr^{4+}. As shown by *Fig. 4,b*, the protonation of the two basicities of CO_3^{2-} is effective at pH 7.5 and 3.5 and requires 3 and 9 H^+ equiv. In the presence of Zr^{4+}, the protonation curve is displaced to the left, and shows also two equivalence points at the same pH, but for 1 and 7 H^+ equiv.

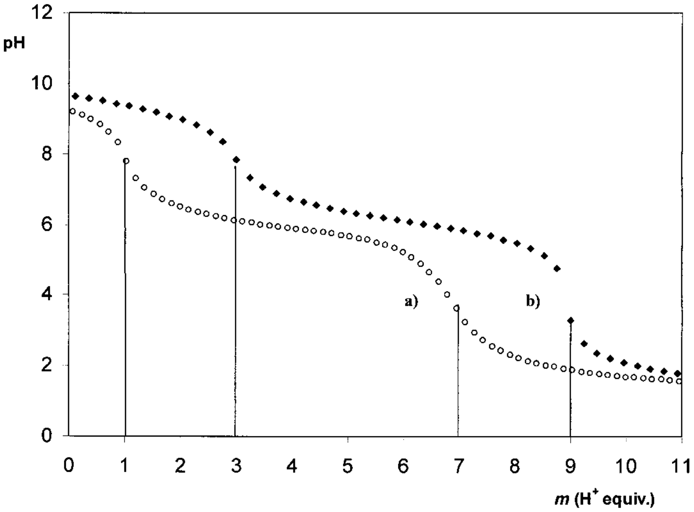

Fig. 4. *Titrations by 0.5M HNO_3:* a) *10^{-2}M $ZrOCl_2$, $3 \cdot 10^{-2}$M K_2CO_3, and $3 \cdot 10^{-2}$M $KHCO_3$*; b) *$3 \cdot 10^{-2}$M K_2CO_3 and $3 \cdot 10^{-2}$M $KHCO_3$*. pH *vs.* the number *m* of H^+ equiv. per Zr^{4+}.

When the solutions contain zirconium oxychloride, one carbonate ion is not consumed and requires 1 H^+ equiv. to be converted to the hydrogencarbonate ion. This interpretation is corroborated by the fact that upon titration, $\bar{n}_{CO_3}$ is invariant above pH 8 (see the following section for the calculation of $\bar{n}_{CO_3}$) which means that only carbonate ions are titrated below the first equivalent point. The displacement of the first equivalence point agrees satisfactorily when one assumes the formation in solution of the species of general formula $[Zr(CO_3)_{(x)}(OH)_{(4-x)}]^{x-}$ according to *Eqn. 1*; *x* values are between 0 and 4, so that the sum of complexed ligands is always equal to four. An entire value for *x* leads to the five possible stoichiometries $[Zr(CO_3)_4]^{4-}$, $[Zr(CO_3)_3(OH)]^{3-}$, $[Zr(CO_3)_2(OH)_2]^{2-}$, $[Zr(CO_3)(OH)_3]^{-}$, and $[Zr(OH)_4]$. *Eqn. 1* is valid whatever the concentration and whatever the ratio of carbonate ion to Zr^{4+}. The general reaction scheme in *Eqn. 1* shows that, for each stoichiometry, the ratio $[CO_3^{2-}]/[HCO_3^{-}]$

generated is different. For example, considering that the species $[Zr(CO_3)(OH)_3]^-$ is quantitatively formed ($x = 1$), one CO_3^{2-} and four HCO_3^- will be generated, and the pH of the solution remains at 9.06 (see *Eqn. 2*; the $pK_{a_{(HCO_3^-/CO_3^{2-})}}$ value of 9.66 is determined at $I = 2$). Thus, the mean stoichiometry of soluble species can be deduced from the simple knowledge of the initial pH of the solution.

$$[Zr(OH)_2]^{2+} + 3\,CO_3^{2-} + 3\,HCO_3^- \rightarrow [Zr(CO_3)_x(OH)_{(4-x)}]^{x-} + (3 - x + 2)\,HCO_3^- + CO_3^{2-} + (x - 2)H_2O \qquad (1)$$

$$pH = pK_{a_{(HCO_3^-/CO_3^{2-})}} + \log\frac{[CO_3^{2-}]}{[HCO_3^-]} = \log\beta_{011} + \log\frac{[CO_3^{2-}]}{[HCO_3^-]} = 9.66 + \log(1/4) = 9.06 \qquad (2)$$

The second equivalence point corresponds to six H^+ equiv. added beyond the first equivalence point, the free and complexed carbonates are also protonated. Considering the hypothesis proposed earlier, the general mechanism in *Eqn. 3* can be written, where the formation of $[Zr(OH)_4]$ is concomitant with the apparition of a solid phase.

$$[Zr(CO_3)_x(OH)_{(4-x)}]^{x-} + (4 - x + 2)\,HCO_3^- + 6\,H^+ + x\,H_2O \rightarrow [Zr(OH)_4] + 6\,H_2O + 6\,CO_2(aq) \qquad (3)$$

pH Measurement of $ZrOCl_2/K_2CO_3$ and $ZrOCl_2/KHCO_3/K_2CO_3$ Solutions. The initial pH of $ZrOCl_2/K_2CO_3$ and $ZrOCl_2/KHCO_3/K_2CO_3$ solutions (noted pH_o) depends only on the ratio $[CO_3^{2-}]/[HCO_3^-]$ and can be easily converted to $\bar{n}_{CO_3}$, the average number of CO_3^- ions fixed per Zr^{4+}. Considering the general reaction scheme of *Eqn. 4*, $\bar{n}_{CO_3}$ is calculated according to *Eqns. 5* and *6*, and the average number of $\bar{n}_{OH}$ of OH^- fixed per zirconium is deduced from *Eqn. 7*.

$$[Zr(OH)_2]^{2+} + v\,CO_3^{2-} + w\,HCO_3^- \rightarrow [Zr(CO_3)_x(OH)_{(4-x)}]^{x-} + (w - x + 2)\,HCO_3^- + (v - 2)\,CO_3^{2-} + (x - 2)\,H_2O \qquad (4)$$

$$pH_o = pK_{a_{(HCO_3^-/CO_3^{2-})}} + \log\frac{[CO_3^{2-}]}{[HCO_3^{2-}]} = pK_{a_{(HCO_3^-/CO_3^{2-})}} + \log\frac{(v - 2)}{(w - x + 2)} \qquad (5)$$

$$x = \overline{n}_{CO_3} = (2 - v)\cdot 10^{(pK_{a_{(HCO_3^-/CO_3^{2-})}} - pH_o)} + (w + 2) \qquad (6)$$

$$\bar{n}_{OH} = 4 - \bar{n}_{CO_3} \qquad (7)$$

Thus, pH measurements are made on $ZrOCl_2/KHCO_3/K_2CO_3$ 1:3:3 solutions as well as on $ZrOCl_2/K_2CO_3$ 1:5 solutions. In these experiments, the concentration range of total carbonate lies between 0.01 and 0.3M, and the ionic strength I is 2, adjusted with KNO_3. *Fig. 5* shows the variations of $\bar{n}_{CO_3}$ for solutions of variable carbonate concentrations. For the system $ZrOCl_2/KHCO_3/K_2CO_3$ 1:3:3 and for 0.3M carbonate concentration, $\bar{n}_{CO_3}$ is equal to four (*Fig. 5,a*) which means that only the tetracarbonatozirconate complex is present. The curve shows that the decrease of carbonate concentration from 0.3 to 0.03M leads to a decrease of $\bar{n}_{CO_3}$ from 4 to 1. When solutions are prepared without $KHCO_3$ (*Fig. 5,b*), the same trend is observed, except that the value of $\bar{n}_{CO_3}$ never exceeds 1.5, even for high concentrations of Zr^{4+}. The dilution of the solutions enhances the formation of hydrolyzed species.

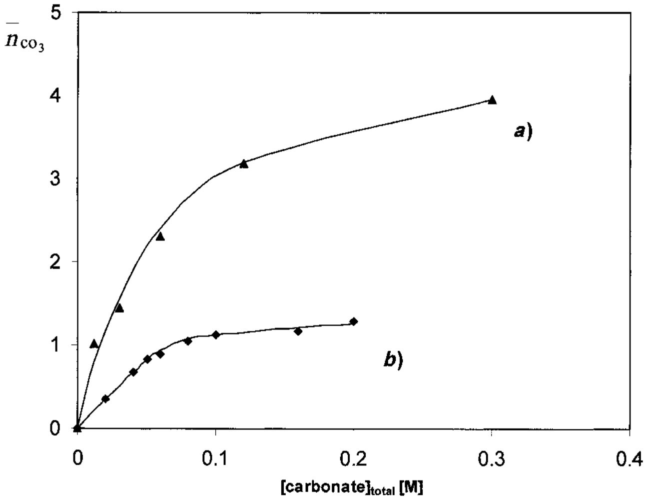

Fig. 5. *Variation of* $\bar{n}_{CO_3}$ vs. *total carbonate concentration:* a) *[$ZrOCl_2$]/[$KHCO_3$]/[K_2CO_3] 1:3:3 and* b) *[$ZrOCl_2$]/[K_2CO_3] 1:5*

Reversibility of Acid-Base Titrations. To study the kinetics and the reversibility of complex-formation reactions, a $ZrOCl_2/KHCO_3/K_2CO_3$ 1:2.5:5 solution is titrated with 0.2M KOH up to pH 10.6, just until the appearance of a precipitate, and then back titrated with 0.2M HNO_3. Experimental data are then converted to express $\bar{n}_{CO_3}$ as a function of pH. *Fig. 6,a*, shows the direct titrations with KOH. The initial stagnation at $\bar{n}_{CO_3} = 4$ indicates that the tetracarbonato complex $[Zr(CO_3)_4]^{4-}$ is the major species present below pH 9.5. Above pH 9.5, $\bar{n}_{CO_3}$ decreases sharply, which corresponds to the formation of mixed carbonatohydroxo species. *Fig. 6,b*, shows the variation of $\bar{n}_{CO_3}$ during the back titration. The most noticeable feature is the large hysteresis effect when comparing curves *a*) and *b*). The $\bar{n}_{CO_3}$ values are higher in the forward than in the backward titrations. The hysteresis effect may indicate the formation of stable binding between Zr^{4+} and hydroxo ligands that would prevent the formation of carbonato complexes.

2.3. *Dialysis. Preamble.* To investigate the polymeric behavior of zirconium(IV) in carbonate media, we employed a dialysis-membrane technique. A dialysis membrane can be used to separate species of different relative molecular masses and has provided valuable informations about hydrolysis products of ferric and zirconium ions [13][14]. The fraction F of Zr^{4+} undialyzed can be calculated from *Eqn. 8*, where C_{ext} refers to the Zr^{4+} concentration of the external solution after dialysis, and C_o to the mean initial Zr^{4+} concentration in external and internal compartments. Two kinds of dialysis experiments are carried out, one to determine the influence of the Zr^{4+} dilution and the

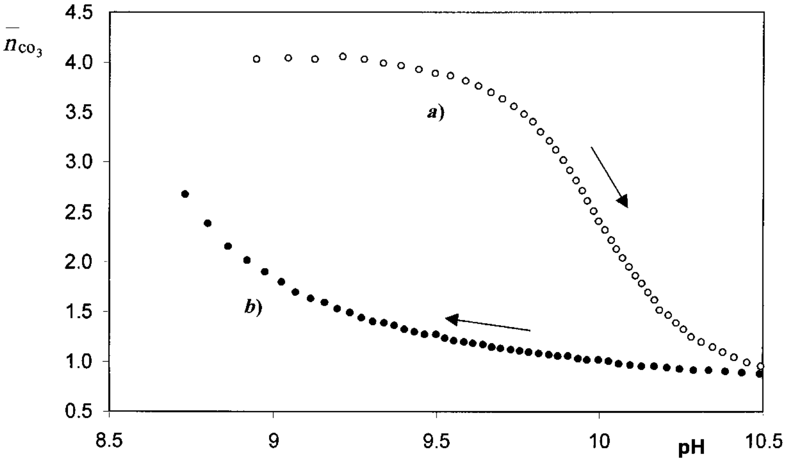

Fig. 6. *Variation of* $\bar{n}_{CO_3}$ *vs. pH in direct and back titrations:* a) *direct titration by 0.2*M *KOH and* b) *back titration by 0.2*M *HNO$_3$*. Initial concentrations: $2.5 \cdot 10^{-2}$M K_2CO_3, $5 \cdot 10^{-2}$M $KHCO_3$, and 10^{-2}M $ZrOCl_2$.

other to elucidate the role of HCO_3^- ions in the polycondensation process of Zr^{4+} species.

$$F = \frac{(C_o - C_{ext})}{C_o} \tag{8}$$

Influence of Dilution. The diffusion of Zr^{4+} from $ZrOCl_2/KHCO_3/K_2CO_3$ 1:4:3 solutions is investigated with a dialysis membrane having a low-molecular-weight cut-off (MWCO 500 Da). Initially, the external solution is constituted by solvent only. The Zr^{4+} concentration on both sides of the membrane (external and internal) is determined after 24 h of dialysis. The results are listed in *Table 1*. The dialysis of the more concentrated solutions, which contain mainly the tetracarbonatozirconate, shows that, at equilibrium, Zr^{4+} is nearly equally distributed on both sides of the membrane. The resulting value of F is close to zero. The decrease of the initial Zr^{4+} concentration from 0.1 to 0.01M increases the fraction of undialyzed Zr^{4+} from 1 to 88%. Species which are formed upon dilution have a higher polycondensation degree than the tetracarbonatozirconate. The increase of the extent of polymerization of Zr^{4+} complexes can be easily correlated with the formation of more hydrolyzed species. Condensation can also be attributed to the formation of hydroxo bridges Zr-(OH)-Zr.

Table 1. *Influence of Dilution on the Diffusion of the Carbonatozirconium Complexes: Dialysis Experiments* (MWCO 500 Da; internal volume $v_i = 2.5$ ml; external volume $v_e = 8$ ml)

Initial concentrations of internal solution [M]			Mean initial concentration [M]	Concentration after dialysis [M]	F[b])
$[Zr^{4+}]_o$	$[HCO_3^-]_o$	$[CO_3^{2-}]_o$	C_o[a])	C_{ext}	
0.1	0.4	0.3	$2.38 \cdot 10^{-2}$	$2.35 \cdot 10^{-2}$	0.01
0.02	0.08	0.06	$4.76 \cdot 10^{-3}$	$2.65 \cdot 10^{-3}$	0.44
0.01	0.04	0.03	$2.38 \cdot 10^{-3}$	$2.74 \cdot 10^{-4}$	0.88

[a]) $C_o = [Zr^{4+}]_o \frac{v_i}{v_i + v_e}$. [b]) See *Eqn. 8*.

Influence of HCO_3^- Ions. In $ZrOCl_2/K_2CO_3$ solutions, soluble complexes are highly hydrolyzed ($\bar{n}_{CO_3}$ in these solutions does not exceed 2) so that, as seen in the preceding section, high condensation degrees are expected. Such solutions can be equilibrated with external $KHCO_3$ solutions. In these experiments, a dialysis membrane with a relatively higher molecular weight cut-off (MWCO 6000–8000 Da) than above (see *Table 1*) is used, and the concentration of Zr^{4+} moving across the membrane is determined as a function of time within one week. The results of several runs with different initial concentration of hydrogencarbonate in the external solution (see *Table 2*) are summarized in *Fig. 7*. In all cases, a rapid decrease of the fraction *F* within the first 24 h, corresponding to a rapid increase of Zr^{4+} concentration in the external solution, is observed. Comparison of the three curves shows that hydrogencarbonate ions play a predominant role in the dissociation of polynuclear species. Indeed, the increase of the HCO_3^- concentration in the external solution leads to a decrease of the fraction *F* of undialyzed Zr^{4+}. For example, after 168 h (seven days) of dialysis, more than 50% of Zr^{4+} remain undialyzed when the internal $ZrOCl_2/K_2CO_3$ solution is equilibrated with 0.10M $KHCO_3$, whereas *F* is close to 20% when 0.25M $KHCO_3$ is used. Nevertheless, dissociation is a slow process, the high fraction of undialyzed polynuclear species shows that equilibrium is not achieved after one week. Another indication that $KHCO_3$ can prevent polycondensation is obtained from another experiment: A

Table 2. *Influence of HCO_3^- Ion Concentration on the Diffusion of the Carbonatozirconium Complexes: Dialysis Experiments* vs. *Time* (see *Fig. 7*; MWCO 6000–8000 Da; internal volume v_i 10 ml; external volume v_e 20 ml)

Solution	Initial concentrations of internal solution [M]			Initial concentrations of external solution [M]
	$[Zr^{4+}]$	$[HCO_3^-]$	$[CO_3^{2-}]$	$[HCO_3^-]$
1	0.05	–	0.2	0.1
2	0.05	–	0.2	0.15
3	0.05	–	0.2	0.25
2'	0.05	0.3	0.2	–

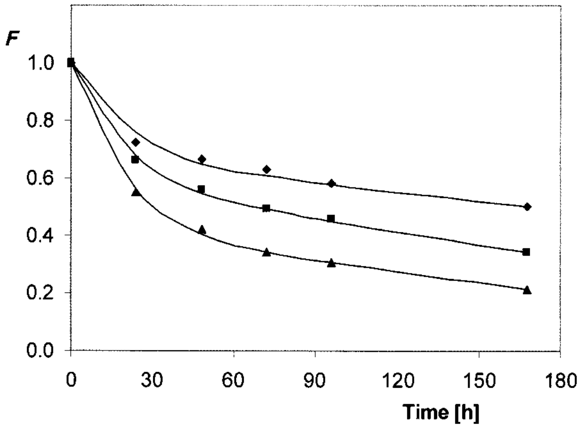

Fig. 7. *Fraction* F *of undialyzed Zr* vs. *time*. Conditions: MWCO 6000–8000 Da; solutions *1* (0.1M HCO_3^-; ◆), *2* (0.15M HCO_3^-; ■), and *3* (0.25M HCO_3^-; ▲) according to *Table 2*.

$ZrOCl_2/KHCO_3/K_2CO_3$ 1:6:4 solution with 0.05M Zr^{4+} (see *Table 2*, solution *2′*) is equilibrated with external H_2O ($v_e = 20$ ml). Analysis of the internal and external solution after 24 h of dialysis reveals that the fraction of undialyzed Zr^{4+} is equal to zero. This result can be compared to the one obtained with solution *2* since the composition in the overall system is identical in both cases (10 ml of 0.3M HCO_3^- in solution *2′* equivalent to 20 ml of 0.15M HCO_3^- in solution *2*).

3. Discussion. – This study continues our earlier investigation on the coordination mode of carbonate ions in the tetracarbonatozirconate complex by ^{13}C-NMR and *Raman* spectroscopies [8]. We showed that structural informations can be directly deduced from the knowledge of the coordination mode. The aim of this survey is to extent our earlier analysis to the mixed carbonatohydroxo complexes. The major difficulty encountered is the formation of polynuclear species.

In very acidic medium and for concentrations up to 10^{-2}M, zirconium(IV) is known to form soluble hydroxo complexes of variable polycondensation degree. In a recent paper, *Zhang* and *Glasser* [15] have shown that polycondensation occurs by olation leading to the formation of doubly bridged Zr-$(OH)_2$-Zr moieties. The polycondensation degree of soluble complexes is also strongly dependent on the number of hydroxo ligands attached to the Zr-atoms. Several surveys [16–18] have shown that condensation can be reduced by anionic ligands that undergo bidentate binding with Zr^{4+} and thus prevent the formation of hydroxo bridges. To our knowledge, only one study deals with soluble species that are formed at basic pH ($7 < pH < 11$), but no characterization has been made [6].

Protometric and ^{17}O- and ^{13}C-NMR results show that, in the presence of carbonate ions, soluble carbonatohydroxo complexes are formed between pH 7 and 11. The bidentate coordination of the carbonate ion in the species $[Zr(CO_3)_4]^{4-}$ was clearly established in our previous publication [8]. We are also able to propose for this species a structural model similar to those proposed for solid species [2] consisting of a central Zr-atom surrounded by four carbonato ligands in a dodecahedral disposition. Our ^{13}C-NMR results establish the bidentate coordination of carbonate ions, which can be generalized to all the soluble carbonatohydroxo species. Our investigations show that the bridging carbonato coordination envisaged by *Pospelova* and *Zaitsev* [3] is unlikely to occur.

Protometric and ^{13}C-NMR results indicate that the number of carbonate ions which can coordinate to Zr^{4+} varies from 0 to 4 and is strongly dependent on pH as well as on the ratio of carbonate ions per Zr^{4+}. The tetracarbonatozirconate complex $[Zr(CO_3)_4]^{4-}$ is formed under conditions that prevent hydrolysis, in the presence of an excess of hydrogencarbonate ions in solution, where the pH does not exceed 10. Decreasing the ratio of HCO_3^- ions in the initial solutions leads to the formation of mixed carbonatohydroxo complexes.

Polycondensation and also the structure of carbonatohydroxo complexes are highly correlated with the number of carbonate ions bound to Zr^{4+}. As shown by dialysis and protometric results, high $\bar{n}_{CO_3}$ values can be related to species that have a low degree of polycondensation, such as the monomer $[Zr(CO_3)_4]^{4-}$ [3][8] and the dinuclear species $[Zr_2(CO_3)_6(OH)_2]^{6-}$ [4][5]. Decreasing $\bar{n}_{CO_3}$ to below 3, either by dilution or by addition of alkaline reagents, leads to the formation of more condensed species. This singular trend can be easily understood when one considers the bidentate chelating coordination of carbonate ions. Substitution of hydroxide ions by carbonate ions is concomitant with the breaking of the double hydroxo bridge. The degree of condensation of soluble carbonatohydroxo species increases with the decrease of $\bar{n}_{CO_3}$.

The role of the HCO_3^- ion appears essential. We suppose that, in the presence of HCO_3^- ions, the tetrameric structure of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (*Fig. 8*, **A**) is broken to form highly carbonated species like $[Zr(CO_3)_6(OH)_2]^{6-}$ and $[Zr(CO_3)_4]^{4-}$ (**B** and **C**). Dialysis results show that the rate of diffusion of carbonatohydroxo species is strongly dependent on the HCO_3^- concentration in the external solution. The role of HCO_3^- is somewhat specific and not only limited to a buffering effect. A possible explanation is that the proton of HCO_3^- may react with hydroxo bridges *via* a mechanism analogous to the one proposed by *Devia* and *Sykes* [19] for the dissociation of the tetrameric ion $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ induced by mineral acids.

In the system $ZrOCl_2/K_2CO_3$, carbonate complexation still occurs, but $\bar{n}_{CO_3}$ values are between 1 and 1.5. One may expect that the more carbonated species contains two

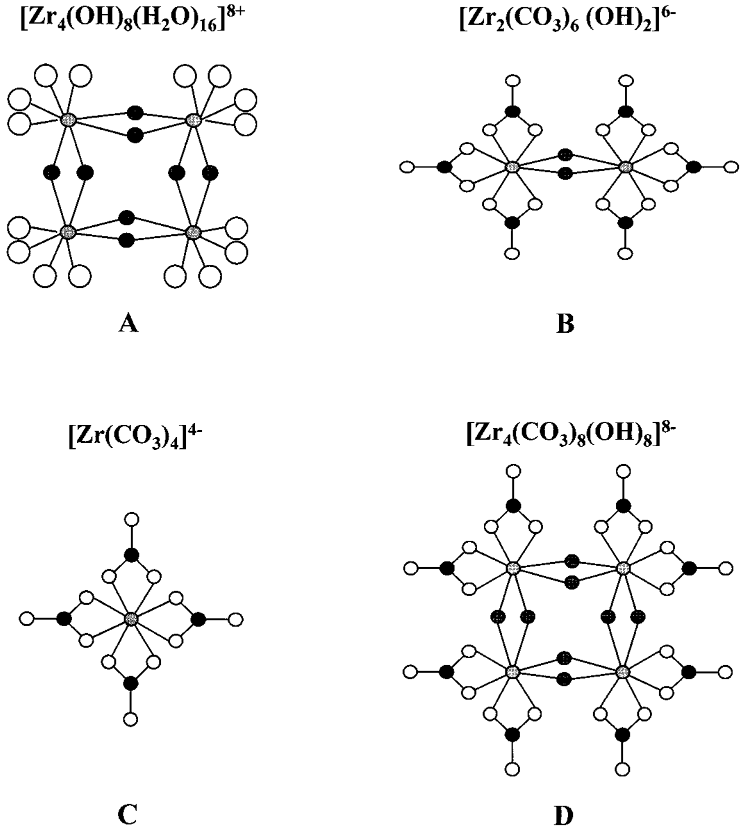

Fig. 8. *Proposed structures of carbonatohydroxo complexes of* Zr^{4+}. H_2O ○, Zr ○, OH ◍, $C(CO_3^{2-})$ ●, $O(Cl_3^{2-})$ ○

bidentate carbonate ions and two hydroxy ions per Zr^{4+}. The high stability of the $ZrOCl_2/K_2CO_3$ solutions for which $\bar{n}_{CO_3}$ is equal to 1.5 suggests that the formed complexes have a low degree of condensation. The most probable structure of $[Zr(CO_3)_2(OH)_2]_n$ is close to the one of the tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ [20]. In the $[Zr(CO_3)_2(OH)_2]_n$ unit, carbonate ions replace H_2O in the coordination sphere of Zr^{4+}, and so we propose for this species the formula $[Zr_4(CO_3)_8(OH)_8]^{8-}$, which seems more appropriate (see *Fig. 8*, **D**). The *Clearfield* tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is an entity that is present in many Zr^{4+} complexes, for example in formato- and acetozirconium complexes [21]. One may suppose that in $[Zr(CO_3)(OH)_3]_n$ units, tetramer species are still present but linked together by hydroxo bridges to form more condensed species. Condensation is favored by an increase of the degree of hydrolysis of Zr^{4+} complexes. The size of soluble species increases as $\bar{n}_{CO_3}$ decreases, leading to the formation of an insoluble phase when $\bar{n}_{CO_3}$ is below 1. Hydrolysis ultimately leads to the formation of the neutral species $[Zr(OH)_4]_n$.

4. Conclusion. – The carbonatohydroxo complexes formed with zirconium(IV) are studied by protometric titration, dialysis, and ^{17}O- and ^{13}C-NMR spectroscopy. Their nature depends on the proportions of the HCO_3^- and CO_3^{2-} ions in the solutions before the addition of zirconium oxychloride ($ZrOCl_2$). For instance, at pH 9.5, the hydrogencarbonate ion HCO_3^- is the major form in solution and, surprisingly, the species formed is the mononuclear and most carbonated complex $[Zr(CO_3)_4]^{4-}$. On the other hand, at pH 12, the species formed in the presence of ions CO_3^{2-} are polynuclear and contain at the most two complexed CO_3^{2-} per Zr^{4+}. In these polynuclear complexes, neither hydrogencarbonate ions nor carbonate ions can break the hydroxo bridges, which are not labile.

In all the studied carbonatohydroxo complexes, the carbonate ion CO_3^{2-} behaves as a bidentate ligand towards Zr^{4+}. These complexes contain bidentate carbonato ligands and hydroxo bridges between metallic cations. Their polycondensation degree decreases when the number of CO_3^{2-} linked per Zr^{4+} increases. These species exist only when the Zr^{4+} and the total carbonate (HCO_3^- and CO_3^{2-}) concentrations are high, greater than 0.1M.

Consequently, in natural medium like soils or waters ($5 < pH < 9$), where the concentration of free total carbonate is low (less than 0.01M), the speciation of Zr^{4+} is governed by the formation of hydroxo complexes and, especially, by the complex $[Zr(OH)_4]$ which is very little soluble.

Experimental Part

Preparation of Solutions. All chemicals used were of analytical grade. Zirconium oxychloride and potassium carbonate, nitrate, and hydrogencarbonate were purchased from *Fluka*. Nitric acid and potassium hydroxide were from *Merck*. Potassium nitrate stock solns. were filtered through *Millipore* filters (pore size 1.2 µm) before use and storage. Protometric solns. were prepared by adding drop by drop a $ZrOCl_2$ soln. to a soln. containing K_2CO_3 and $KHCO_3$ or K_2CO_3 only. The total ratio of CO_3^{2-} ions per Zr^{4+} varied from 4 to 10. Solns. were prepared at an ionic strength I of 2M, adjusted with KNO_3. Solns. were prepared 24 h before use. Solns. for ^{17}O- and ^{13}C-NMR measurements contained respectively 100 and 30% of D_2O and were prepared as above without addition of KNO_3. Solns. for ^{13}C-NMR spectra were obtained by using ^{13}C-enriched (99%) $NaHCO_3$ of reagent grade (*Sigma Chemical Product*).

Protometric Measurements. All experiments were performed at 25 ± 0.1°. The procedure and apparatus used for protometric measurements have been previously described [1]. For titration with nitric acid, a N_2 stream was maintained over the soln. 15 min before the first addition of titrant, to prevent dissolution of CO_2. The stream was stopped during the titration, to limit the release of carbonic acid (CO_2) below pH 6. To study the reversibility of complex-formation reactions, titrations were made under vigorous stirring and very slow addition of titrant (0.5 µl per 5 s) to avoid the formation of a local precipitate in consequence of the addition of the alkaline reagent. The N_2 stream was maintained throughout the titration. This procedure has been effectively used in earlier studies to determine the formation constant of hydroxo Zr complexes in acidic media [1]. Both titrations by HNO_3 and KOH were made according to the same experimental protocol.

Dialysis Technique. The solns. were prepared in the same manner as for titration experiments, except that the ionic strength was not adjusted. A known amount of zirconium/carbonate soln. was introduced inside a cellulose-acetate membrane bag (*Spectra-Por 6*) and equilibrated with a known volume of external soln. The lack of interference between soluble Zr^{4+} species and cellulose acetate has been checked elsewhere by protometric titrations of $ZrOCl_2/KHCO_3/K_2CO_3$ solns. in the presence, as well as in the absence, of cellulose acetate. In both cases, titrations were perfectly superimposable. The composition of the external soln. was chosen such that the pH value in the system did not exceed 9.5 (maximal pH value required for an optimal use of the membrane, especially for long-term experiments). Concentration of Zr^{4+} in both external and internal solns. was determined by ICP-AES after time equilibration (at least 12 h). The differences in Zr^{4+} concentration on either side of the membrane was attributed to the fraction of polymeric species that cannot move across the dialysis membrane.

NMR Measurements. ^{13}C-NMR Measurements: Bruker-DRX-500 spectrometer; at 125.77 MHz and 27°; parameters chosen to obtain quantitative data for the measured signals; *i.e.* simple delay(30 s)-pulse(6 µs, 60 degrees)-acquisition(406 ms, 4 K points)-pulse program (zg); determination of the longitudinal relaxation time T_1 according to [8] (15 s for both species HCO_3^- and CO_3^{2-}); 8 scans to provide a convenient signal-to-noise ratio; δ(C) in ppm rel. to the central line, calibrated to 49.02 ppm of external CD_3OD.

^{17}O-NMR Measurements: Bruker-DRX-300 spectrometer; at 40.68 MHz and 27°; δ(O) in ppm rel. to the central line, calibrated to 0 ppm, of D_2O; recording with the simple delay(200 ms)-pulse(17 ms, 90°)-acquisition (13 s).

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