Hydrolysis of the Zinc(II) Ion in Sodium Nitrate, Chloride and Perchlorate Medium: the Effect of the Anionic Medium

Nikola B. Milić* and Ratomir M. Jelić
Faculty of Science, University of Kragujevac, Radoja Domanovića 12, YU-34000 Kragujevac, Yugoslavia

Hydrolysis of the zinc(II) ion in 0.5 mol dm^{-3} (Na)NO_3, (Na)Cl or (Na)ClO_4 solution was studied by the electromotive force method at 25 °C. The data cover the zinc(II) concentration range 2.5–40 mmol dm^{-3} within the pH range 2.0–6.0. The general least-squares treatment of the data indicates the formation of only mononuclear complexes. The complex $[Zn(OH)]^+$ was found in all three media, while $Zn(OH)_2(aq)$ was found only in perchlorate solution. This, as well as the differing values for the stability constant of $[Zn(OH)]^+$, demonstrate the effect of the anionic medium on both complex formation and stability of the hydrolytic species.

Although hydrolysis of the zinc(II) ion has been studied by several authors[1-5] there is still disagreement concerning the composition and stability of its hydrolytic complexes. Schorsch's[1] [3] data indicate the formation of monomeric $[Zn(OH)]^+$ and dimeric $[Zn_2(OH)]^{3+}$ in 2 and 3 mol dm^{-3} NaCl and KCl media, while Perrin[4] found only $[Zn(OH)]^+$ in KNO_3 medium. Ferri and Salvatore[5] observed two mononuclear hydrolytic complexes $Zn(OH)_2(aq)$ and $[Zn(OH)_4]^{2-}$ in alkaline 3 mol dm^{-3} $NaClO_4$ solutions. The stability constants of these complexes differ from one report to another.

Biologically zinc is one of the most important metals. Its enzymes are present in a great number of body cells and the hydrolysis of zinc(II) ions might significantly influence their activity. Hydrolytic reactions may also influence other reactions of zinc(II) ions in water solutions, particularly those which are conducted at low acidity. Therefore, some additional data on zinc hydrolysis would be useful for both inorganic- and bio-chemistry.

In our studies[6] on metal ion hydrolysis the effect of ionic medium on the composition and stability constants of hydrolytic complexes was observed. Thus, contention in the explanation of the hydrolytic behaviour of zinc might be a consequence of the various experimental conditions under which the hydrolysis was studied. Therefore, more reliable information can be obtained by investigation of the hydrolysis of zinc in various ionic media, but under the same experimental conditions. In this work, we investigate zinc hydrolysis in sodium nitrate, chloride and perchlorate media under the same experimental conditions. The hydrolysis was studied by the electromotive force (emf) method at 25 °C.

Experimental

Reagents and Analysis.—Although the chemicals used were of analytical grade, most were additionally purified by recrystallization. All solutions were prepared using freshly distilled water and handled under a nitrogen atmosphere in order to avoid the effect of CO_2 on their pH.

The zinc nitrate stock solution was prepared from $Zn(NO_3)_2 \cdot 9H_2O$, zinc chloride solution from $ZnCl_2$ and zinc perchlorate solution from $Zn(ClO_4)_2 \cdot 6H_2O$. All three salts were additionally purified by recrystallization.

In order to prevent initial hydrolysis of the zinc(II) ion in the stock solutions an appropriate amount of nitric, hydrochloric or perchloric acid was added. As a consequence, all zinc(II) solutions used for the titrations contained some free acid, referred to as the analytical excess of acid (H) to distinguish it from the hydrogen ions released in the course of the hydrolysis reaction (h). The concentration of the free acid (H) was determined potentiometrically by a Gran plot.[7] Since the concentration of H is used for the determination of E_0 for the glass electrode (and both H and E_0 for the determination of the composition and stability of the complexes) its accuracy is very important. Therefore, we have developed the computer program GEZ (GranEzeroZet, to be published), which determines both H and E_0 with high accuracy.

The zinc content of the stock solutions was determined by precipitation with ammonium hydrogen phosphate and by ethylenediaminetetraacetic acid complexometric titration, using Eriochrome Black T as indicator. Employing the gravimetric method the precipitates were ignited at 610 °C, and weighed as $Zn_2P_2O_7$. Reproducibility of the results from both methods was within ±0.2%.

Sodium nitrate, chloride and perchlorate stock solutions were prepared by dissolution of the corresponding salts. Their concentrations were determined by evaporating a known volume at 150 °C.

Sodium hydroxide stock solution was prepared in a polyethylene bottle as a 50% solution from solid NaOH. After a few days a surface film of Na_2CO_3 was removed by filtering through a G-4 Jena glass filter.

The solutions used for the titrations were freshly prepared by dilution of the sodium hydroxide and sodium nitrate (chloride or perchlorate) stock solution, and were standardized against potassium hydrogen phthalate.

Nitric and hydrochloric acid solutions were prepared by dilution of the suprapure acids (Merck), while perchloric acid solution was prepared from Analar $HClO_4$ (BDH). All solutions were standardized against NaOH.

Nitrogen gas for stirring and providing an inert atmosphere during the titrations was purified by passing it through 10% NaOH and 10% H_2SO_4. Before reaching the titrant, the gas was saturated with water vapour by bubbling it through water and the relevant medium solution (0.5 mol dm^{-3}).

Apparatus and Procedure.—The emf measurements were performed as potentiometric titrations using a Wilhelm bridge. All solutions were prepared at a constant anionic medium concentration: 0.5 mol dm^{-3} (Na)NO_3, 0.5 mol dm^{-3} (Na)Cl or 0.5 mol dm^{-3} (Na)ClO_4.† Thus, the composition of the zinc(II) solutions was: B mol dm^{-3} Zn^{2+}, H mol dm^{-3} H^+, (0.5 − 2B −

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† Designation of the medium is in accordance with ref. 8.

H) mol dm^{-3} Na$^+$, 0.5 mol dm^{-3} NO_3^- (Cl^- or ClO_4^-) where B and H denote the total concentration of the zinc(II) and hydrogen ions, respectively. Throughout the investigation of the effect of the medium concentration, the concentration of sodium nitrate varied from 0.5–3.0 mol dm^{-3}, but during each titration it was constant. During the measurements the titration vessel and the Wilhelm bridge were inserted in paraffin oil thermostatted at 25.0 ± 0.1 °C, which was placed in a room thermostatted at 25.0 ± 0.5 °C. The cell was: (−) glass electrode | zinc(II) solution, HNO_3, 0.5 mol dm^{-3} (Na)NO_3 | reference electrode (+). As reference electrode the following half cell was used: Ag–AgCl | 3.0 mol dm^{-3} $NaNO_3$, 0.01 mol dm^{-3} $AgNO_3$. During investigations of the zinc hydrolysis in sodium chloride or perchlorate media the cells contained solutions of the corresponding salts. The glass electrode was commercial (Beckman, pH 0–11), while the Ag–AgCl electrode was prepared by electrodeposition of Ag and Cl^- on Pt wire from K[Ag(CN)$_6$] and NaCl solutions.

Titrations were carried out by adding sodium hydroxide from one burette and zinc(II) solution in the same portion from a second burette. The concentration of zinc solution in the burette was twice that in the titration vessel. In this way, the total concentration of zinc(II) was kept constant throughout each titration. Since all solutions were prepared in the corresponding concentration of sodium nitrate (chloride or perchlorate), the total concentration of the anionic medium (0.5 mol dm^{-3}) was also kept constant. The concentration of free H$^+$ (h) at each point was calculated by Nernst's formula (1) where E

$$E = E_o + E_j + 59.16 \log h \qquad (1)$$

is the measured potential, E_o a constant which includes the standard potential for the glass electrode and E_j the liquid junction potential. Both E_o and E_j were determined for each titration range in a pH in which the hydrolysis did not occur. The potential was repeatedly measured after each addition of the solutions from the burettes, until a drift of $\leqslant$0.2 mV h^{-1} was reached. At the beginning of each titration a constant emf potential was obtained within 10 min. In the pH range where hydrolysis of the zinc(II) ion becomes significant, attainment of the equilibrium was rather slow. In order to check the reversibility of the hydrolytic process in each medium one back titration was carried out. After a certain hydroxide number was reached ($Z \approx 0.002$), the direction of the titration was reversed by adding acid (nitric, hydrochloric or perchloric) instead of sodium hydroxide. Good agreement between forward and back titrations indicates reversibility of the hydrolytic reaction under the conditions studied.

In this work, the hydrolysis of the following concentrations of the zinc(II) ion have been investigated: (*a*) 2.53, 5.01, 10.03, 10.26 (forward and back titration), 20.05 and 40.11 mmol dm^{-3} Zn^{2+} ion in 0.5 mol dm^{-3} (Na)NO_3; (*b*) 2.52, 5.00 (forward and back), 10.07, 20.00 and 40.26 mmol dm^{-3} Zn^{2+} in 0.5 mol dm^{-3} (Na)Cl medium; and (*c*) 2.56, 4.92, 10.03 (forward and back), 20.05 and 39.32 mmol dm^{-3} Zn^{2+} in 0.5 mol dm^{-3} (Na)ClO_4 medium.

Results and Discussion

The emf data of the hydrolysis of 2.5–40 mmol dm^{-3} Zn^{2+} ion in 0.5 mol dm^{-3} (Na)ClO_4, (Na)Cl and (Na)NO_3 are presented in Fig. 1 as a dependence of the hydroxide number of zinc(II) on the free hydrogen ion concentration, $-\log h$.* The hydroxide number Z denotes an average number of hydroxide ions reacted per zinc(II) ion and was calculated from the analytical excess of hydrogen ions, H, the measured concentration of the free hydrogen ion, h, and the total concentration of the zinc(II) ion, B, according to expression (2).

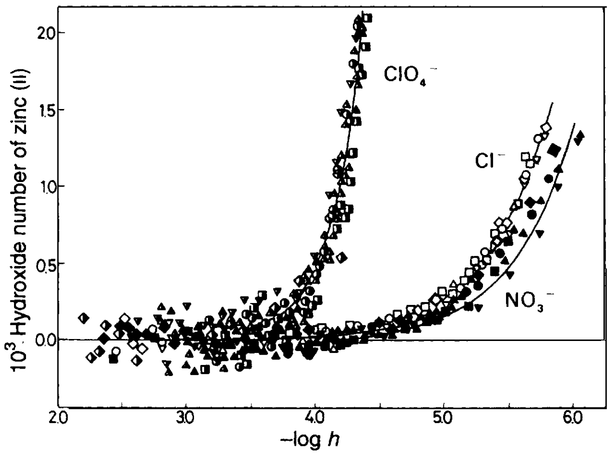

Fig. 1 Hydrolysis of the zinc(II) ion in sodium perchlorate (◑), chloride (○) and nitrate (●) medium (0.5 mol dm^{-3}): 2 (○), 5 (□), 10 (△), 20 (▽) and 40 mmol dm^{-3} Zn^{2+} (◇). Points are experimental data, while the curves have been calculated from the composition and stability of the complexes

$$Z_{Zn} = (h - H)/B \qquad (2)$$

Fig. 1 shows that in perchlorate medium the extent of hydrolysis increases more sharply than in the other two media and may be explained by the differing ability to form complexes with these anions. It is well known that the ability of the perchlorate ion to form complexes is extremely weak, and as a consequence the extent of hydrolysis is high.

In contrast to many other metal ions[6,8] the extent of zinc hydrolysis does not depend upon the concentration of the zinc(II) ions, indicating the formation of mononuclear complexes. As a consequence, zinc hydrolysis starts at a constant pH independent of the zinc concentration: in perchlorate at pH 3.0, chloride at pH 3.5 and nitrate medium at pH 4.0. Therefore, upon zinc hydrolysis only one hydrolytic curve per anionic solution was obtained, independent of the concentration of the zinc(II) ion.

The composition of the complexes was determined on the basis of the assumption that the zinc(II) ion interacts with water molecules and forms one or more hydrolytic complexes of general formula $[Zn_p(OH)_q]^{(2p-q)+}$ according to reaction (3)

$$p\,Zn^{2+} + q\,H_2O \rightleftharpoons [Zn_p(OH)_q]^{(2p-q)+} + q\,H^+ \qquad (3)$$

where the amount of H$^+$ produced is equivalent to the quantity of hydroxide ions bound to the zinc(II) ion. The general formula $[Zn_p(OH)_q]^{(2p-q)+}$ is also understood to include an unknown amount of H_2O as solvent and possibly some anions in the medium. In reaction (3) the hydration of individual ions and the complex formation of the zinc(II) ion with nitrate (chloride or perchlorate) ions are omitted. The concentration of the medium anions and water molecules is much higher than the concentration of the zinc(II) ion, and therefore, it is not possible to determine the changes in the concentration of the medium anion caused by the complex formation, nor the concentration of the water molecules involved in hydration. In order to avoid the complex formation effect, the concentration of the medium anion was kept constant (0.5 mol dm^{-3}) and much higher than the concentration of zinc(II). Under such conditions, eventual complex formation should appear as a constant effect and should not affect the number of OH$^-$ ions in the hydrolytic complexes.

The composition of the hydrolytic complexes and their

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* In order to emphasize that the concentration of hydrogen ions was determined *via* the Nernst equation instead of the pH, '$-\log h$' is used.

Table 1 Values of the stability constants for the hydrolytic complex $[Zn(OH)]^+$ in various ionic media and corresponding χ and η values

Medium/mol dm^{-3}	χ/kJ	η/mol nm^{-1}	log $\beta_{1,1}$ ± 3σ	Ref.
0.5 (Na)NO_3	353	0.81	−8.76 ± 0.03	This work
1.0 (Na)NO_3	714	1.62	−8.78 ± 0.03	This work
1.5 (Na)NO_3	1076	2.43	−8.86 ± 0.07	This work
2.0 (Na)NO_3	1438	3.24	−8.91 ± 0.05	This work
2.5 (Na)NO_3	1799	4.06	−9.01 ± 0.06	This work
3.0 (Na)NO_3	2151	4.87	−9.27 ± 0.22	This work
0.5 (Na)Cl	387	0.92	−8.57 ± 0.01	This work
0.5 (Na)ClO_4	311	0.48	−7.77 ± 0.25	This work
2 KCl	1399	3.68	−9.01	1
2 NaCl	1572	3.68	−9.12	1
3 KCl	2102	5.52	−9.26	3
3 NaCl	2362	5.52	−9.25	2
0.01 KNO_3	6	0.016	−8.96	4

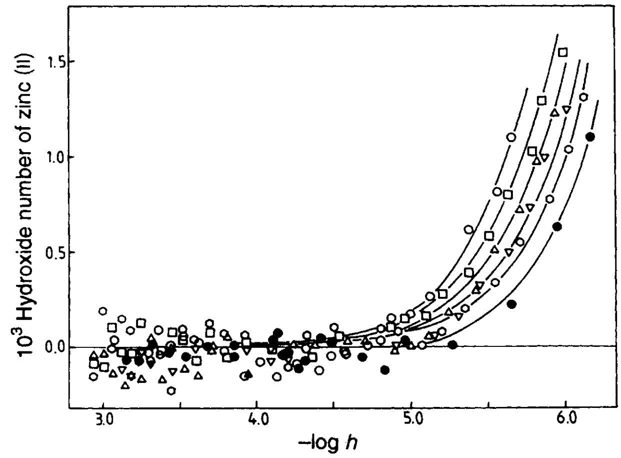

Fig. 2 Hydrolysis of 10 mmol dm^{-3} zinc(II) in sodium nitrate medium: 0.5 (○), 1.0 (□), 1.5 (△), 2.0 (▽), 2.5 (○) and 3.0 mol dm^{-3} NO_3^- (●)

stability constants were determined by minimization of the error-squares sum given by equation (4) where Z_{exp} is the

$$U_{min} = \Sigma(Z_{calc} - Z_{exp})^2 \qquad (4)$$

experimental value of the hydroxide number [equation (2)] and Z_{calc} the calculated one through the tested (p,q) values and stability constants β_{pq}. In equation (5) b and h are the free

$$Z_{calc} = (\Sigma q\beta_{pq}h^{-q}b^p)/(b + \Sigma p\beta_{pq}h^{-q}b^p) \qquad (5)$$

concentrations of the zinc and hydrogen ion, respectively. The minimization [equation (4)] which has been obtained from the generalized least-squares program LETAGROP,[9] indicates the formation of only mononuclear complexes. The complex $[Zn(OH)]^+$ was found in all three media, while complex $Zn(OH)_2(aq)$ (log $\beta_{1,2}$ = −11.84 ± 0.07) was found only in perchlorate medium. The values of the stability constants (log $\beta_{1,1}$) for the complex $[Zn(OH)]^+$ in these three media decreases in the order: perchlorate (−7.77) > chloride (−8.57) > nitrate (−8.76) (Table 1). Many other mononuclear and polynuclear models including $[Zn_2(OH)]^{3+}$ were also tested, but all of them were rejected, either due to negative values of β_{pq} or larger values of U_{min}. Separate calculations conducted for each medium include the following number of experimental points: nitrate, seven titrations with total 171 points; chloride, six titrations with 141 points; and perchlorate, eight titrations with 159 points.

Distribution of the complexes $[Zn(OH)]^+$ and $Zn(OH)_2(aq)$ has been calculated by the Haltafall program.[10] The formation of $[Zn(OH)]^+$ in perchlorate medium starts at pH 3.0, while $Zn(OH)_2(aq)$ formation begins at pH 3.30 and increases sharply above pH 3.75. The formation of $[Zn(OH)]^+$ in the other two media starts at pH 3.5 (Cl^-) and 4.0 (NO_3^-).

The hydrolysis of 10 mmol dm^{-3} zinc(II) in 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol dm^{-3} (Na)NO_3 media are represented in Fig. 2, also as a dependence of the hydroxide number of the zinc(II) ion *versus* −log h. The data show that the hydroxide number of the zinc(II) ion at a definite pH decreases with increasing concentration of the medium ions indicating the concentration effect. It was interesting to see if this effect, as well as the anion effect, follows the linear free energy relationship (6) established

$$\log K_w - \log K_m = \chi\eta \qquad (6)$$

by our previous work.[6] In equation (6), K_w and K_m are the equilibrium constants of the hydrolytic reaction in pure water and an ionic medium, respectively. The medium constant, χ, is a characteristic of the medium concerning interactions of its ions with water molecules, whereas the complex formation constant η is determined by reaction of the metal ions with the medium anion A [equation (7)].

$$\begin{array}{l}
[\mathrm{Na(H_2O)}]^+ + [\mathrm{A(H_2O)}]^- \\
\qquad\qquad\qquad \chi \upharpoonleft\!\downharpoonright \\
p\,\mathrm{Zn}^{2+} + q\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Zn}_p(\mathrm{OH})_q]^{(2p-q)+} + q\,\mathrm{H}^+ \qquad (7) \\
\eta \upharpoonleft\!\downharpoonright \\
\mathrm{A} \longrightarrow \mathrm{Zn}_p(\mathrm{OH})_q\mathrm{A}_r
\end{array}$$

The correlation between parameters which determine the medium constant is given by expression (8) where c is

$$\chi = c_{(a)}E_{h(a)}z_{(a)} + c_{(c)}E_{h(c)}z_{(c)}^{-1} \qquad (8)$$

concentration, E_h the hydration energy, and z the charge of the medium anion (a) and cation (c). For the calculation of χ we used the following values[11] for E_h: Na^+ 409, NO_3^- 314, K^+ 322, Cl^- 381 and ClO_4^- 229 kJ mol^{-1}.

Although the constant η reflects the complex interaction more than χ, we propose that the ionic potential of the ligand $z_{(a)}/r_{(a)}$ and the electronegativity of the donor atom (ε_{DA}) are the main parameters which determine the complex-formation ability of the ligand. Their correlation is given by expression (9)

$$\eta = \frac{c_{(a)}z_{(a)}}{r_{(a)}\varepsilon_{DA}} \qquad (9)$$

where $c_{(a)}$ is the concentration of the medium anion. For the calculation of η the following values are used: ionic radius (nm)

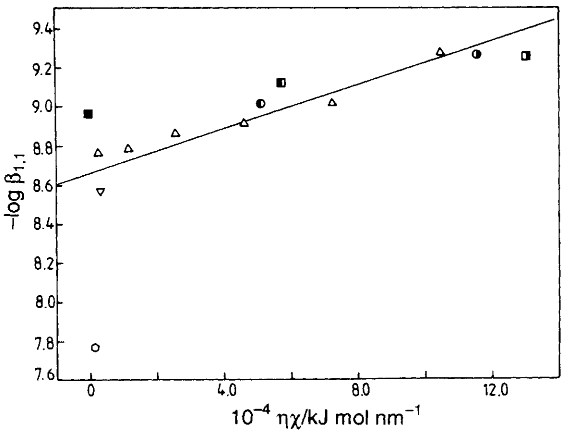

Fig. 3 Dependence of log $\beta_{1,1}$ of the complex $[Zn(OH)]^+$ on the medium parameters [correlation coefficient (R) = 0.978, standard deviation = 0.043]: 0.5–3.0 $NaNO_3$ (△), 0.5 NaCl (▽), 0.5 $NaClO_4$ (○), 2 KCl[1] (◐), 3 KCl[3] (◑), 2 NaCl[1] (◧), 3 NaCl[2] (◨) and 0.01 mol dm^{-3} KNO_3[4] (■)

NO_3^- 0.176, Cl^- 0.181, ClO_4^- 0.298; relative electronegativity O 3.5, Cl 3.0.

If the zinc hydrolysis follows the relationship (6), and if the constants χ and η include the most important parameters of the ionic medium, the representation of the stability constant of the complex $[Zn(OH)]^+$ as function (10) should give a straight line.

$$\log \beta_{pq} = f(\chi\eta) \qquad (10)$$

Fig. 3 shows that values of log $\beta_{1,1}$ for $[Zn(OH)]^+$ obtained in 0.5 mol dm^{-3} sodium chloride and at six different concentrations of sodium nitrate show a linear dependence on $\chi\eta$. [Dependencies of log $\beta_{1,1} = f(\chi)$ and log $\beta_{1,1} = f(\eta)$ are also linear, but with lower correlation coefficients (R_χ = 0.70, R_η = 0.72).] However, the value of log $\beta_{1,1}$ obtained in sodium perchlorate medium deviates significantly from linearity. The general good agreement of these data confirms the linear correlation between hydrolysis and the medium properties.

Deviation of the stability constant obtained in perchlorate medium indicates that the ionic potential and the relative electronegativity are not sufficient to describe the complex interaction between the metal ion and the medium anion. Therefore, it is necessary to have more data with various anions, as well as some additional parameters which will better describe the complexing ability of the perchlorate ligand.

Since in all three media the experimental conditions were the same, the data obtained show that the nature (perchlorate, chloride and nitrate) and concentration [0.5–3.0 mol dm^{-3} $(Na)NO_3$] of the ionic medium influence both the composition and stability of the hydrolytic complexes based on the values of the stability constants.

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