

Metal Complexes With Mixed Ligands. 14. A Potentiometric Study of the Systems Zn^{2+} —Imidazole and Zn^{2+} — OH^- —Imidazole in 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl

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Three component equilibria between zinc(II), imidazole ($\text{C}_3\text{H}_4\text{N}_2$; L) and OH^- have been studied by means of emf titrations at 25 °C in two media 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl using a glass electrode. The total zinc, B , and the total imidazole, C , have been varied within the limits $0.0025 \leq B \leq 0.075$ M and $0.0025 \leq C \leq 0.295$ M and the ratios C/B between $0.25 \leq C/B \leq 45$. At the highest C/B -ratios data can be explained solely with step-wise metal complexes ZnL_n^{2+} $n=1, 2, 3, 4$ and the following $\log \beta_n$ -values could be determined: $\log \beta_1=2.92$ $\log \beta_2=4.93$, $\log \beta_3=8.77$ and $\log \beta_4=11.41$ in 3.0 M (Na)ClO₄ and $\log \beta_1=3.12$, $\log \beta_2=5.64$, $\log \beta_3=7.66$ and $\log \beta_4=9.04$ in 3.0 M (Na)Cl. At the lowest C/B -ratios ternary hydroxo-imidazoles $\text{Zn}(\text{OH})\text{L}_3^+$ and $\text{Zn}_2(\text{OH})\text{L}_3^{3+}$ in 3.0 M (Na)ClO₄ and $\text{Zn}(\text{OH})\text{L}^+$ and $\text{Zn}_2(\text{OH})\text{L}_2^{3+}$ in 3.0 M (Na)Cl also seem to be formed. The equilibrium constants with standard deviations (3σ) are given in Table 4. Data have been analyzed with the least squares computer program LETAGROPVRID.

In preceding papers of this series the three-component equilibria in the systems copper(II)–imidazole– OH^- ^{3,7,12} and nickel(II)–imidazole– OH^- ⁴ have been investigated. Besides the metal complexes ML_n^{2+} , $n=1, 2, 3, 4$, ternary complexes were also formed. In the copper system data clearly indicated the formation of $\text{Cu}_2(\text{OH})_2\text{L}_2^{3+}$, $\text{Cu}_2(\text{OH})_2\text{L}_4^{2+}$ and $\text{Cu}(\text{OH})\text{L}^+$ and in the nickel system $\text{Ni}(\text{OH})\text{L}^+$.

In the binary zinc(II)– OH^- ^{13,41} system the hydroxy complexes are $\text{Zn}_2\text{OH}^{3+}$ and ZnOH^+ . One would then expect hydroxoimidazoles of the types $\text{Zn}_2(\text{OH})\text{L}_2^{3+}$ and $\text{Zn}(\text{OH})\text{L}_y^+$. The present investigation was made to determine whether such ternary complexes exist in the zinc(II)–imidazole– OH^- system.

In previous studies of zinc(II)–imidazole complexes no experimental attempts seem to have been made to find hydroxoimidazoles. Earlier data indicated that only ZnL_n^{2+} should be formed (see Table 1).

EXPERIMENTAL

Chemicals and analysis. Stock solutions of sodium chloride and sodium perchlorate were prepared and analyzed as described earlier.⁴ The dilute hydrochloric and perchloric acids and the stock solutions of imidazolium, HL^+ , were prepared and standardized as earlier.⁴ Dilute sodium hydroxide was prepared from "oljelut" (50 % NaOH and 50 % H₂O) and standardized against acid or hydrazine sulfate. Stock solutions of zinc chloride and zinc perchlorate were prepared by dissolving carefully washed zinc pellets in hydrochloric and perchloric acids and analyzed for zinc by titration with EDTA and analyzed for $[\text{H}^+]$ by titration with a hydroxide solution using a Gran plot.² The differences in concentrations between analyzed and expected value were always less than 0.2 %.

Apparatus. The thermostat, cell arrangement and electrodes were described earlier.^{4,12} The potentiometric titrations were performed with an automatic system for precise emf titrations, a system constructed and built at this institute by O. Ginstrup.⁶

METHOD

Method. The titration procedures used were similar to those described in earlier papers.^{3,4} During the titrations the total concentrations of zinc, B , and imidazole, C , were kept either constant or varied. In general each titration was performed at a constant C/B -ratio. The free hydrogen ion concentration, h , was varied

Table 1. Values of the gross stability constants of zinc(II)–imidazole complexes collected for comparison from the literature. Temperature 25 °C; potentiometric method.

Ref.	Medium	pK_a	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
19	0.16 ^a NaNO ₃	7.11	2.58	4.95	7.18	9.20
20	0.16		2.57	4.93	7.15	9.16
21	0.16	7.08	2.52	4.84	7.18	9.21
22	0.15 ^b		2.6			
1	0.058 (KCl)		3.15	6.10		
23	0.2 KNO ₃	7.12	2.13			
24	0.5 NH ₄ NO ₃		2.29– 2.46	4.65– 4.72	6.87– 7.15	9.08– 9.11
18	0.25 (Na)ClO ₄	7.052	2.588	4.424		
18	0.5 (Na)ClO ₄	7.125	2.618		7.596	10.041
18	1 (Na)ClO ₄	7.287	2.663	4.451		10.292
18	2 (Na)ClO ₄	7.575	2.745		8.253	10.919
18	4 (Na)ClO ₄	8.176	3.441			
This work	3 (Na)ClO ₄	7.914	2.916	4.925	8.77	11.417
This work	3 (Na)Cl	7.646	3.123	5.641	7.66	9.04

^a 24 °C. ^b Distribution method.

by adding hydroxide ions or hydrogen ions and measured with a glass electrode. To check their reliability often two electrodes were immersed in the same equilibrium solution. The change in the differences between the emf values was not allowed to exceed 0.2 mV. A constant ionic medium of 3.0 M (Na)ClO₄ or 3.0 M (Na)Cl was used in order to avoid activity coefficient variations. The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-\log h$) and backward (decreasing $-\log h$) titrations. To check the reversibility at low C/B quotients dilution experiments were carried out. Special efforts were made to cover as great a part of the concentration range as possible. Owing to the formation of precipitates, the available $-\log h$ range was restricted to an upper limit of 6–8.5. An account of these precipitates will be published in a forthcoming paper.¹⁶ The total concentrations (initial concentrations) of B and C were varied within the limits $0.0025 \leq B \leq 0.043$ M, $0.0025 \leq C \leq 0.143$ M in 3.0 M (Na)Cl and $0.0025 \leq B \leq 0.075$ M, $0.0025 \leq C < 0.295$ M in 3.0 M (Na)ClO₄. A greater concentration range was studied in the perchlorate medium because of the fact that in the 3.0 M (Na)Cl medium much of the total zinc, B , occurs as the

complexes ZnCl₂⁻¹⁷ and perhaps even ZnCl₄²⁻. At high zinc concentrations so much chloride is bound in the complex that the medium is changed and that will influence the proton imidazole equilibrium. The change in pK_a is about 0.02 for 0.1 M change in the chloride medium. The following quotients C/B were studied: 0.5, 0.6, 0.7, 0.8, 1, 1.4, 1.6, 1.8, 2, 2.2, 2.8, 3.4, 3.9, 5.6, 7.7 and 10.5 in 3.0 M (Na)Cl, and 0.6, 0.9, 1, 1.1, 1.3, 1.35, 1.5, 1.8, 2.2, 3, 4, 5.4, 6, 11 and 44.9 in 3.0 M (Na)ClO₄.

Calibrations and assumptions in connection with the use of the glass electrode were the same as described earlier.¹³

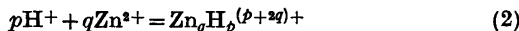
The mathematical analysis of data was performed with the least squares computer program LETAGROPVRID⁹ (version ETITR).¹⁰ On treating the emf data the error squares sum $U = \sum (Z_{\text{exp}} - Z_{\text{calc}})^2$ was minimized, where $Z = (h - H)/C$. The standard deviations were defined and calculated according to Sillén.¹¹ The computation was performed on a CD 3300 computer.

Concerning the binary proton imidazole equilibrium



we will make use of the results obtained from separate experiments. For reaction (1) we found $\log(K_a \pm 3\sigma)$ to be -7.646 ± 0.002 in 3.0 M (Na)Cl and -7.914 ± 0.002 in 3.0 M (Na)ClO₄.

For the binary hydrolysis equilibria



we used the results obtained by Schorsch¹⁴ (3.0 M (Na)Cl) and Biedermann¹⁵ (3.0 M (Li)ClO₄). The investigations both of Schorsch and Biedermann clearly show that the main species in a hydrolyzed Zn²⁺-solution is Zn₂OH²⁺ and the following $\log \beta_{-12}$ -values were reported: -7.50 (3.0 M (Na)Cl) and -8.7 (3.0 M (Li)ClO₄). In the chloride medium the complex ZnOH⁺ with $\log \beta_{-11} = -9.25$ was also reported. These binary equilibria were assumed to be exactly known and all effects above this level will be treated as being caused by binary ZnL_n²⁺ and ternary species.

DATA, CALCULATIONS AND RESULTS

The data were visualized by making a Bjerrum plot $\bar{n}(\log [L])$. This plot is shown in Fig 1. It is seen from the plot that for quotients $C/B \geq 4$ the function $\bar{n}(\log [L])$ seems to be independent of B and C thus indicating the formation of a series of stepwise metal complexes ZnL_n²⁺.

A Letagrop analysis showed that data in both media fulfilling these conditions could be well explained with the complexes ZnL²⁺, ZnL₂²⁺, ZnL₃²⁺ and ZnL₄²⁺. The analysis ended at a $\sigma(Z)$ of 0.002 in both media and must be considered as a very good explanation. The data included in the analysis consist of around 300 experimental points distributed over 15 BC-combinations. The best equilibrium constants with the corresponding standard deviations obtained in these analysis are given in Table 4 calculation denoted 1. The residuals $\Delta Z = Z_{\text{exp}} - Z_{\text{calc}}$ after best fit are given together with experimental data in Table 4.

Data 2. These data cover the ranges $0.0025 \leq B \leq 0.043$ M, $0.0028 \leq C \leq 0.072$ M in 3.0 M (Na)Cl and $0.0025 \leq B \leq 0.070$ M, $0.0075 \leq C \leq 0.118$ M in 3.0 M (Na)ClO₄, $1 < -\log h \leq 8$ and $0.25 \leq C/B \leq 5$. In the search for the ternary hydrolytic species it was assumed that the binary species ZnL_n²⁺ were known and that the equilibrium constants had the values given above.

The search was started with a *pqr* analysis (systematic testing of *pqr*-complexes) in the

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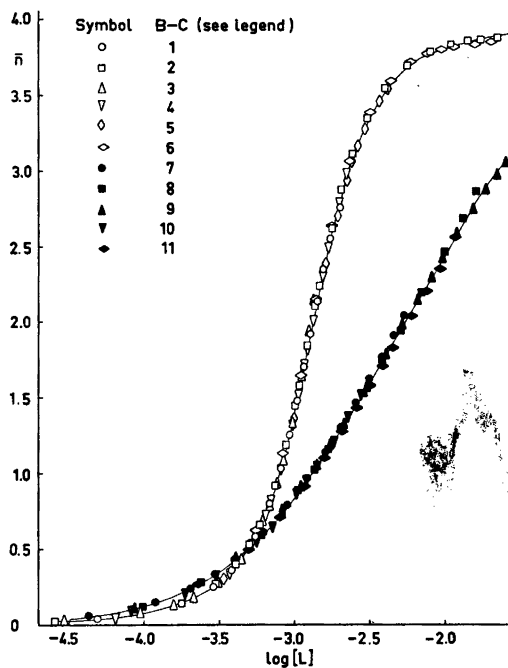


Fig. 1. Experimental data plotted as curves $\bar{n}(\log [L])$ for high C/B ratios ($3 \leq C/B < 45$) and high C concentrations. Open symbols mark titrations in 3 M (Na)ClO₄ and dark symbols 3 M (Na)Cl. The figure also gives a comparison between the strength of complexation in the two media. The symbols stand for the following B and C in mM (start concentrations). 1, 35.4–6.57; 2, 185–16.9; 3, 118–39.3; 4, 118–19.7; 5, 58.9–9.86; 6, 147–3.28; 7, 85.9–25.5; 8, 82.7–10.7; 9, 107–10.2; 10, 17.2–5.11; 11, 41.4–5.36. In order to make the figure clear only a few titrations have been plotted. The full curves have been calculated with a set of proposed constants in Table 4.

3.0 M (Na)Cl medium where the effects are greater. The results of the analysis with the best fitting species are given in Table 2. It is seen from these calculations that the lowest error squares sum for one complex is obtained for Zn(OH)L⁺. Assuming two species, the best combination is Zn(OH)L⁺ and Zn₂(OH)L₂²⁺. The data could also be fairly well explained with the species Zn(OH)L⁺ and Zn₂(OH)L²⁺.

In the 3.0 M (Na)ClO₄ medium the effects are not collected around $\bar{n} = 1$ as in the chloride medium, but cover $1 \leq \bar{n} < 3$. This means that probably at least two ternary complexes with different C/B -ratios exist. In the systematic

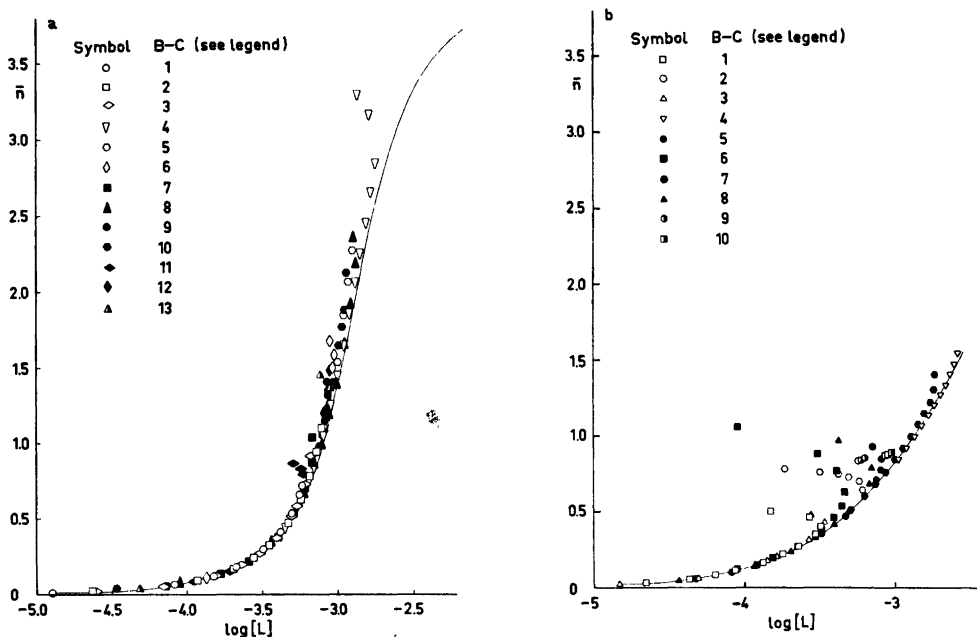


Fig. 2. Experimental data plotted as curves $\bar{n}(\log [L])$ for low C/B ratios ($0.5 \leq C/B \leq 4$). The symbols stand for the following B and C in mM (start concentrations).

a. 3 M (Na)ClO₄ medium. 1, 8.18–5.56; 2, 17.7–9.85; 3, 22.1–16.4; 4, 80.0–20.0; 5, 18.5–4.63; 6, 45.2–20.3; 7, 55.6–42.8; 8, 64.2–21.5; 9, 76.0–41.4; 10, 10.6–2.64; 11, 67.3–67.4; 12, 22.6–10.1; 13, 89.4–50.2.

b. 3 M (Na)Cl medium. 1, 9.74–18.5; 2, 23.2–29.0; 3, 18.4–34.9; 4, 14.1–5.09; 5, 11.4–10.2; 6, 2.85–2.55; 7, 11.4–5.10; 8, 5.70–5.10; 9, 24.3–25.9; 10, 42.8–39.7.

Only a few titrations have been plotted. The full curves have been calculated with the set of proposed constants for the series ZnL_n^{2+} given in Table 4.

Table 2. Data 2. Results of LETAGROP calculations for some different assumptions concerning the ternary complexes formed in 3 M (Na)Cl medium. In the calculations the binary constants for the species ZnL_n^{2+} given in Table 4 and the hydrolysis constants given by Schorsch have not been varied. The constants β_{pqr} are defined according to $pH^+ + Zn^{2+} + rHL^+ \rightleftharpoons (H^+)_p(Zn^{2+})_q(HL^+)_r/\beta_{pqr}$. The errors given are $3\sigma(\log \beta_{pqr})$. The results under the line refer to titrations where $C/B < 1$ and the amounts of the ternary species are especially high.

Number of titr./ number of points	p, q, r	$\log(\beta_{pqr} \pm 3\sigma)$	p, q, r	$\log(\beta_{pqr} \pm 3\sigma)$	$\sigma(Z)$ $\times 1000$	$U/10^3$
18/304						1110
18/304	–2,1,1	–13.19(3)			6.8	140
18/304	–3,1,2	–17.85(6)			11.2	377
18/304			–2,2,1	–10.95(3)	7.2	158
18/304			–3,2,2	–15.47(3)	7.1	151
18/304	–2,1,1	–13.44(5)	–2,2,1	–11.24(6)	4.1	51.3
18/304	–2,1,1	–13.43(5)	–3,2,2	–15.75(6)	3.9	46.9
18/304	–2,1,1	–13.45(9)	–4,2,2	–23.57(10)	5.3	83.8
9/154	–2,1,1	–13.44	–2,2,1	–11.23(4)	3.7	20.6
9/154	–2,1,1	–13.44	–3,2,2	–15.71(3)	3.4	17.5

Table 3. Data 2. Results of LETAGROP calculations in 3 M (Na)ClO₄. No variation of the constants of the binary species ZnL_n²⁺ given in Table 4 and the hydrolysis constants given by Biedermann have been made. The constants β_{pqr} are refined in Table 2. The errors are 3σ(log β_{pqr}). The results under the line correspond to the calculations where the amounts of the binuclear ternary complexes are expected to be as high as possible.

Number of titr./ number of points	<i>p,q,r</i>	log(β _{pqr} ± 3σ)	<i>p,q,r</i>	log(β _{pqr} ± 3σ)	σ(Z) × 1000	U/10
21/385						4270
21/385	-2,1,1	-13.07(4)			5.1	1010
21/385	-3,1,2	-17.90(3)			4.1	629
21/385	-4,1,3	-22.81(3)			4.6	813
21/385			-4,2,3	-20.67(5)	5.8	1273
21/385			-5,2,4	-25.45(4)	5.2	1006
21/385			-6,2,5	-30.33(4)	5.3	1036
21/385	-3,1,2	-18.06(5)	-5,2,4	-25.82(9)	3.0	356
21/385	-3,1,2	-18.06(5)	-6,2,5	-30.67(8)	3.0	342
21/385	-3,1,2	-18.03(5)	-4,2,3	-21.06(9)	3.3	406
21/385	-3,1,2	-18.00(4)	-7,2,6	-35.70(9)	3.2	388
21/385	-4,1,3	-23.01(5)	-5,2,4	-25.73(6)	3.0	333
21/385	-4,1,3	-22.97(4)	-4,2,3	-20.94(5)	2.8	294
21/385	-4,1,3	-22.94(3)	-3,2,2	-16.18(5)	2.8	310
21/385	-4,1,3	-23.03(9)	-2,1,1	-13.38(10)	3.9	573
21/385	-2,1,1	-13.22(4)	-7,2,6	-35.55(6)	3.3	420
21/385	-3,2,2	-16.11(8)	-7,2,6	-35.50(8)	4.9	907
21/385	-3,2,2	-16.33(16)	-6,2,5	-30.47(8)	5.0	928
21/385	-4,2,3	-21.04(17)	-6,2,5	-30.51(11)	5.0	934
21/385	-4,2,3	-20.84(8)	-7,2,6	-35.57(11)	4.8	893
2/33	-4,1,3	-22.90(2)			2.7	
10/198	-4,1,3	-22.90	-3,2,2	-16.22(5)	2.6	130
10/198	-4,1,3	-22.90	-4,2,3	-20.99(4)	2.3	102

testing of *pqr*-complexes the lowest error squares sum, assuming one complex, was obtained for Zn(OH)L₂⁺. However, the remaining effects indicated that this species must be considered as an average of two or more other species. Assuming two complexes the best fit was obtained for Zn(OH)L₃⁺ and Zn₂(OH)L₃²⁺ (see Table 3). However, nearly the same error squares sum was obtained for the combination of Zn(OH)L₃⁺ and Zn₂(OH)L₂³⁺. An attempt to select one of the two combinations was made in the following way. The equilibrium constant for the complex Zn(OH)L₃⁺ was determined in titrations where *C/B*=4 and the amounts of other ternary complexes are low (about 1 %). In a titration set where the amounts of the binuclear ternary species are expected to be as high as possible the two complexes Zn₂(OH)L₂³⁺ and Zn₃(OH)L₃³⁺ were subsequently tested (see Table 3). Once more the species Zn₂(OH)L₃²⁺ was obtained with the lowest error squares sum and this complex is therefore proposed to be the best complement

to the mononuclear species Zn(OH)L₃⁺. However, the amounts of the binuclear species are low (5–6 %) and more information would perhaps be obtained in a less concentrated ionic medium, where the solubility is probably greater.

In order to visualize the amounts of the ternary species at some typical concentrations and *C/B*-ratios, we have collected a set of distribution diagrams which are shown in Fig. 3.

DISCUSSION

The present emf investigation has given evidence for the existence of the hydrolyzed zinc imidazole complexes Zn(OH)L⁺, Zn(OH)L₃⁺ and Zn₂(OH)L₂³⁺ together with a series of stepwise metal complexes ZnL_n²⁺, *n*=1, 2, 3, 4, and it has also indicated the formation of Zn₂(OH)L₃²⁺. The composition of the ternary complexes seems to indicate the close connection between these species and

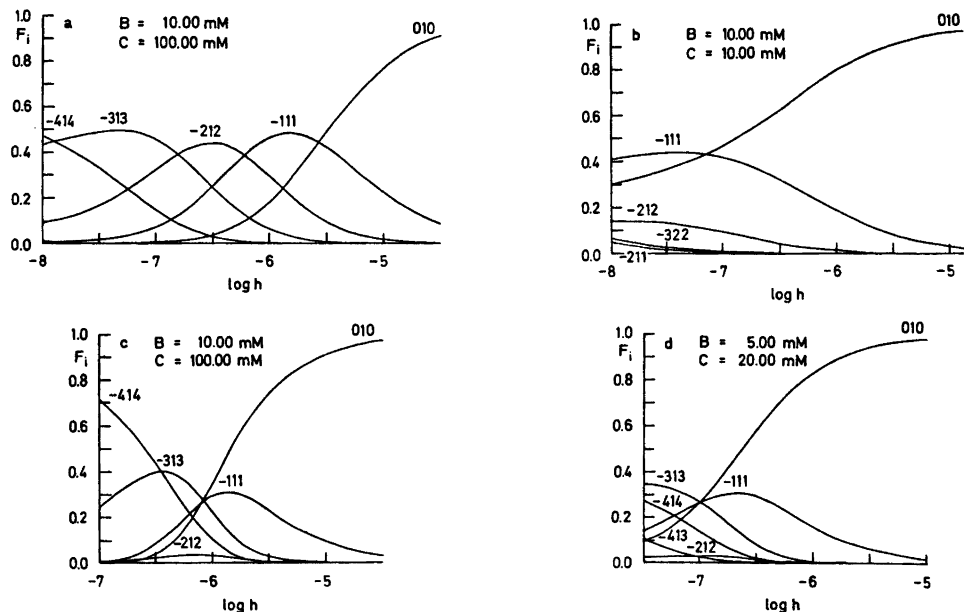
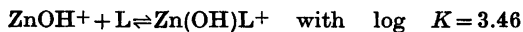
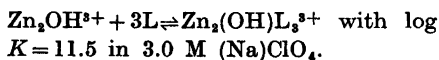
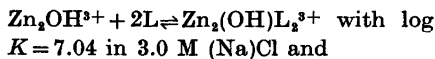


Fig. 3. Distribution diagrams $F_i(\log h)_{BC}$ in 3 M (Na)ClO₄ (a and b) and 3 M (Na)Cl (c and d). F_i is defined as the ratio between zinc(II) in the species and total zinc(II). The calculations have been performed using a version of the computer program SOLGAS³⁸ valid for equilibria in solution and equipped with a plotting procedure (Gunnar Eriksson, to be published).

the binary hydroxo zinc complexes ZnOH⁺ and Zn₂OH³⁺. Thus it was possible to establish the following equilibria:



and



The hydrolyzed zinc ion seems to be a stronger complexing agent than the corresponding hydrated zinc ion because $\text{Zn}^{2+} + \text{L} \rightleftharpoons \text{ZnL}^{2+}$ with $\log K = 3.12$ in 3.0 M (Na)Cl.

It is also possible to compare the acidities (tendency to hydrolyze) of the species $\text{Zn}(\text{H}_2\text{O})_x^{2+}$ and $\text{Zn}(\text{H}_2\text{O})_y\text{L}^{2+}$ in the chloride medium. It is found that $\log K_a(\text{ZnL}^{2+}) > \log K_a(\text{Zn}^{2+})$. The actual values of $\log K_a$ are -8.92 and -9.25 , respectively. It seems that the introduction of an imidazole ligand increases the acidity of the zinc ion. The same effect

is observed in the copper(II),⁷ nickel(II),⁴ silver(I)³⁷ and mercury(II)₄³⁸ imidazole systems. An OH⁻ group together with an L molecule may equally well be interpreted as an imidazolate group $\text{C}_3\text{H}_3\text{N}_2^-$. Thus the complexes proposed could also be $\text{ZnC}_3\text{H}_3\text{N}_2^+$, $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)\text{L}_2^+$, $\text{Zn}_2(\text{C}_3\text{H}_3\text{N}_2)\text{L}^{3+}$ and $\text{Zn}_2(\text{C}_3\text{H}_3\text{N}_2)\text{L}_2^{3+}$. However, the close connection between the binary hydrolysis and the ternary complexes in this and other metal imidazole systems makes the presence of a hydroxide group in the complexes more probable.

A comparison of the behavior of the zinc system in the two media 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl is interesting. Concerning the binary zinc(II)–OH⁻ system the complexation is much stronger in the chloride medium [$\log \beta_{-12} = -7.50$ in 3.0 M (Na)Cl and $\log \beta_{-12} = -8.7$ in 3.0 M (Li)ClO₄]. Furthermore the species ZnOH⁺ (e.g. for example ZnOHCl₂²⁻) is found only in the chloride medium. This is probably due to the fact that in 3.0 M (Na)Cl at least 88 % of total zinc, B, is obtained as the tetrahedral complex $\text{ZnCl}_3(\text{H}_2\text{O})^{-17,35}$ and perhaps

Table 4. Results of the final covariations of binary and ternary constants in the two media investigated. When no $3\sigma(\log\beta_{pqr})$, is given, the formation constant has not been varied. The constants β_{pqr} are defined in Table 2.

Number of sets/ number of points	Medium	$\log\beta_{-01}$	$\log\beta_{-111}$ $\pm 3\sigma$	$\log\beta_{-212}$ $\pm 3\sigma$	$\log\beta_{-313}$ $\pm 3\sigma$	$\log\beta_{-414}$ $\pm 3\sigma$	$\log\beta_{-515}$ $\pm 3\sigma$	$\log\beta_{-616}$ $\pm 3\sigma$	$\log\beta_{-717}$ $\pm 3\sigma$	$\log\beta_{-818}$ $\pm 3\sigma$	$\log\beta_{-919}$ $\pm 3\sigma$	$\log\beta_{-1020}$ $\pm 3\sigma$	(Z)
16/268	3.0 M (Na)Cl	-7.646	-4.523(4)	-9.651(7)	-15.28(2)	-21.55(5)							0.002
18/304	3.0 M (Na)Cl	-7.646	-4.523	-9.651	-15.28	-21.55	-13.44(5)	-15.75(6)					0.004
13/294	3.0 M (Na)ClO ₄	-7.914	-4.998(6)	-10.90(6)	-14.969(8)	-20.25(1)							0.002
21/385	3.0 M (Na)ClO ₄	-7.914	-4.998	-10.90	-14.969	-20.25						-22.97(4)	-20.94(5) 0.003

even as $ZnCl_4^{2-}$, but in the perchlorate medium zinc occurs as the octahedral complex $Zn(H_2O)_6^{2+}$. The association between zinc(II) and ClO_4^- is supposed to be negligible. The distance Zn-O in the tetrahedral complexes is about 1.96 Å as for example in the structures of $KZnCl_3 \cdot 2H_2O$,²⁵ $Zn_5(OH)_3Cl_2 \cdot H_2O$,²⁶ $Zn_5(OH)_3(NO_3)_2 \cdot 2H_2O$ ²⁷ and $Zn(OH)_2$,²⁸ but the corresponding distance in the octahedral complexes is about 2.10–2.13 Å as in $Zn(NO_3)_2 \cdot 6H_2O$,²⁹ $Zn_5(OH)_3(NO_3)_2 \cdot 2H_2O$ ²⁷ and in the X-ray investigation of an aqueous solution of $Zn(H_2O)_6^{2+}$.³⁰ The shorter distance Zn-O in the tetrahedral configuration makes the water protons more acidic and thus the complexation of zinc(II)-OH⁻ stronger.

The complexation of zinc(II)-L is also different in the two media. In 3.0 M (Na)Cl the stepwise stability constants $ZnL_{n-1}^{2+} + L \rightleftharpoons ZnL_n^{2+}$ $n = 1, 2, 3, 4$ are $\log K_1 = 3.12$, $\log K_2 = 2.52$, $\log K_3 = 2.02$ and $\log K_4 = 1.37$.

In 3.0 M (Na)ClO₄ the corresponding constants are $\log K_1 = 2.92$, $\log K_2 = 2.01$, $\log K_3 = 3.84$ and $\log K_4 = 2.64$.

In 3.0 M (Na)Cl the ZnL_n^{2+} series could be well explained with a two parameter approximation of the type $K_{n+1} = K_0 k^n$ with $\log K_0 = 3.126$ and $\log k = -0.57$. In the 3.0 M (Na)ClO₄ medium this is not possible probably due to a shift from octahedral to tetrahedral configuration at the second step. This configuration shift is also proposed by Ahrland *et al.*^{15,34,35} in several other zinc(II) systems.

The configuration shift in the perchlorate medium with the corresponding changes of the differences

	Octahedral (Å)	Tetrahedral (Å)
Zn-O	2.10–2.13	1.95–1.96
Zn-N	2.15–2.25	2.00–2.01 ^{31,32}
Zn-Cl	2.50–2.60	2.25–2.30 ^{33,32}

will of course influence the occurrence of the ternary zinc(II)-imidazole-OH⁻ complexes.

This investigation indicated that the ternary complexes mainly occur in the tetrahedral form. In 3.0 M (Na)ClO₄ medium the ternary complexes are obtained at higher \bar{n} -values than in the 3.0 M (Na)Cl medium, corresponding to a higher C/B ratio in the species. This is in good agreement with the statement above.

[Compare the species $Zn(OH)L^+$ in 3.0 M (Na)Cl and $Zn(OH)L_3^+$ in 3.0 M (Na)ClO₄]. An emf investigation of the four component equilibria zinc(II)–imidazole–OH⁻–Cl⁻ in 3.0 M (NaClO₄) is completed and will soon be published.

A calorimetric study of the zinc(II)–imidazole–OH⁻ system is planned.

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