Metal Complexes With Mixed Ligands. 14. A Potentiometric Study of the Systems \( \text{Zn}^{2+} - \text{Imidazole} \) and \( \text{Zn}^{2+} - \text{OH}^- - \text{Imidazole} \) in 3.0 M (Na)ClO\(_4\) and 3.0 M (Na)Cl

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Three component equilibria between zinc(II), imidazole (C\(_5\)H\(_7\)N\(_4\); L) and OH\(^-\) have been studied by means of emf titrations at 25 °C in two media 3.0 M (Na)ClO\(_4\) 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 ≤ B ≤ 0.075 M and 0.0025 ≤ C ≤ 0.295 M and the ratios C/B between 0.25 ≤ C/B ≤ 45. At the highest C/B-ratios data can be explained solely with step-wise metal complexes ZnL\(_n\)^{n+} \( n = 1, 2, 3, 4 \) and the following log \( \beta \) values could be determined:

\[
\log \beta_1 = 2.92 \quad \log \beta_2 = 4.93 \quad \log \beta_3 = 8.77 \quad \text{and} \quad \log \beta_4 = 11.41
\]

in 3.0 M (Na)ClO\(_4\) 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 hydroxoimidazoles \( \text{Zn(OH)L}_n^{n+} \) and \( \text{Zn}_2(\text{OH})_2L_2^{4+} \) in 3.0 M (NaClO\(_4\)) and (NaOH)L\(^+\) and \( \text{Zn}_2(\text{OH})_2L_2^{4+} \) in 3.0 M (Na)Cl also seem to be formed. The equilibrium constants with standard deviations (3\(\sigma\)) are given in Table 4. Data have been analyzed with the least squares computer program LETAGROPVRD.

In previous studies of zinc(II) – imidazole complexes no experimental attempts seem to have been made to find hydroximidazoles. Earlier data indicated that only ZnL\(_n\)^{n+} 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% \( \text{H}_2\text{O}\)) 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.\(^5\) The differences in concentrations analyzed and expected value were always less than 0.5%.

Apparatus. The thermostat, cell arrangement and electrodes were described earlier.\(^6,11\) 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.\(^5\) 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.
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.\(^4\) The total concentrations (initial concentrations) of B and C were varied within the limits 0.0025 ≤ B ≤ 0.043 M, 0.0025 ≤ C ≤ 0.143 M in 3.0 M (Na)Cl and 0.0025 ≤ B ≤ 0.075 M, 0.0025 ≤ 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 ZnCl₃⁻\(^7\) and perhaps even ZnCl₄⁻\(^\text{−}\). 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 pKₐ 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, 1.5, 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.\(^1\)

The mathematical analysis of data was performed with the least squares computer program LETAGROPVRID*(version ETTR).\(^2\)

On treating the emf data the error squares sum \(U = \sum(Z_{\exp} - Z_{\text{calc}})^2\) was minimized, where \(Z = (h - H)/C\). The standard deviations were defined and calculated according to Sillén.\(^1\)

The computation was performed on a CD 3300 computer.

Concerning the binary proton imidazole equilibrium

\[
HL^+ + e^- \rightleftharpoons L + H^+ 
\]

(1)

we will make use of the results obtained from separate experiments. For reaction (1) we found 
\[ \log(K_s + 3g) = -7.846 \pm 0.002 \text{ in } 3.0 \text{ M (NaCl) and } -7.814 \pm 0.002 \text{ in } 3.0 \text{ M (NaClO}_4 \text{).} \]

For the binary hydrolysis equilibria
\[ p\text{H}^+ + q\text{Zn}^{2+} = \text{Zn}_q\text{H}_p^{(p+q)+} \hspace{1cm} (2) \]

we used the results obtained by Schorsch \[ 14 \] (3.0 M (NaCl) and Biedermann \[ 18 \] (3.0 M (Li)ClO\textsubscript{4}). The investigations both of Schorsch and Biedermann clearly show that the main species in a hydrolyzed Zn\textsuperscript{2+}-solution is Zn\textsubscript{4}OH\textsuperscript{4+} and the following log \[ \beta_{11} \text{-values were reported: } -7.50 \text{ (3.0 M (NaCl)) and } -8.7 \text{ (3.0 M (Li)ClO\textsubscript{4}). In the chloride medium the complex ZnOH}^+ \text{ with log } \beta_{11} = -9.25 \text{ was also reported. These binary equilibria were assumed to be exactly known and all effects above this level will be treated as being caused by binary ZnL\textsubscript{4}^{2+} and ternary species.} \]

DATA, CALCULATIONS AND RESULTS

The data were visualized by making a Bjerrum plot \[ n(\log [L]) \]. This plot is shown in Fig 1. It is seen from the plot that for quotients \( C/B \geq 4 \) the function \[ n(\log [L]) \] seems to be independent of \( B \) and \( C \) thus indicating the formation of a series of stepwise metal complexes Zn\textsubscript{4}L\textsubscript{4}^{2+}.

A Letagrop analysis showed that data in both media fulfilling these conditions could be well explained with the complexes ZnL\textsubscript{4}^{2+}, ZnL\textsubscript{4}^{4+}, ZnL\textsubscript{4}^{6+} and ZnL\textsubscript{4}^{8+}. The analysis ended at a \( s(Z) \) 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 \text{ M}, 0.0028 \leq C \leq 0.072 \text{ M in } 3.0 \text{ M (NaCl) and } 0.0025 \leq B \leq 0.070 \text{ M, } 0.0075 \leq C \leq 0.118 \text{ M in } 3.0 \text{ M (NaClO}_4 \text{)} \text{; } 1 < -\log h \leq 8 \text{ and } 0.25 \leq C/B \leq 5 \text{. In the search for the ternary hydrolytic species it was assumed that the binary species ZnL\textsubscript{4}^{2+} were known and that the equilibrium constants had the values given above.} \]

The search was started with a \textit{pgr} analysis (systematic testing of \textit{pgr}-complexes) in the

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)ClO$_4$ medium. 1, 8.18 - 5.56; 2, 17.7 - 9.85; 3, 22.1 - 16.4; 4, 80.0 - 20.0; 5, 18.5 - 4.83; 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 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 of Zn(II) have not been varied. The constants $\beta_{pqr}$ are defined according to $p\text{H}^{+} + \text{Zn}^{2+} + q\text{HL}^{+} \rightleftharpoons (p\text{H}^{+})_p(\text{Zn}^{2+})_q(\text{HL}^{+})_r\beta_{pqr}$. 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.

<table>
<thead>
<tr>
<th>Number of titr./ number of points</th>
<th>$p_{q+r}$</th>
<th>$\log(\beta_{pqr} \pm 3\sigma)$</th>
<th>$p_{q+r}$</th>
<th>$\log(\beta_{pqr} \pm 3\sigma)$</th>
<th>$\sigma(Z)$</th>
<th>$U/10^4$</th>
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<tr>
<td>18/304</td>
<td>-2,1,1</td>
<td>-13.19(3)</td>
<td>-2,2,1</td>
<td>-10.95(3)</td>
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<td>1110</td>
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<td>-3,2,2</td>
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<td>7.2</td>
<td>158</td>
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<tr>
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<td>-3,2,2</td>
<td>-15.75(6)</td>
<td>7.1</td>
<td>151</td>
</tr>
<tr>
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<td>-4,2,2</td>
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<td>51.3</td>
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<tr>
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</table>

testing of \( pqr \)-complexes the lowest error squares sum, assuming one complex, was obtained for \( \text{Zn(OH)}_2 \text{L}^+ \). 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 \( \text{Zn(OH)}_2 \text{L}^+ \) and \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \) (see Table 3). However, nearly the same error squares sum was obtained for the combination of \( \text{Zn(OH)}_2 \text{L}^+ \) and \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \). An attempt to select one of the two combinations was made in the following way. The equilibrium constant for the complex \( \text{Zn(OH)}_2 \text{L}^+ \) 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 \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \) and \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \) were subsequently tested (see Table 3). Once more the species \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \) was obtained with the lowest error squares sum and this complex is therefore proposed to be the best complement to the mononuclear species \( \text{Zn(OH)}_2 \text{L}^+ \). 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 \( \text{Zn(OH)}_2 \text{L}^+ \), \( \text{Zn(OH)}_2 \text{L}^+ \) and \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \) together with a series of stepwise metal complexes \( \text{ZnL}^+ \), \( n = 1, 2, 3, 4 \), and it has also indicated the formation of \( \text{Zn}_2(\text{OH})_2 \text{L}^+ \). The composition of the ternary complexes seems to indicate the close connection between these species and

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the binary hydroxo zinc complexes $\text{ZnOH}^+$ and $\text{Zn}_2\text{OH}^{2+}$. Thus it was possible to establish the following equilibria:

$$\text{ZnOH}^+ + L \rightleftharpoons \text{Zn(OH)L}^+$$ with log $K = 3.46$

and

$$\text{Zn}_2\text{OH}^{2+} + 2L \rightleftharpoons \text{Zn}_2\text{OH}_2L^2$$ with log $K = 7.04$ in 3.0 M (Na)Cl and

$$\text{Zn}_2\text{OH}^{2+} + 3L \rightleftharpoons \text{Zn}_2\text{OH}_3L^3$$ with log $K = 11.5$ in 3.0 M (Na)ClO₄.

The hydrolyzed zinc ion seems to be a stronger complexing agent than the corresponding hydrated zinc ion because $\text{Zn}^{2+} + L \rightleftharpoons \text{ZnL}^2$ 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 $\text{Zn(H}_2\text{O)}_2^{2+}$ and $\text{Zn(H}_2\text{O)}_3L^3$ 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), nickel(II), silver(I), and mercury(II) imidazole systems. An OH⁻ group together with an L molecule may equally well be interpreted as an imidazole group $\text{C}_6\text{H}_4\text{N}^-$. Thus the complexes proposed could also be $\text{ZnC}_6\text{H}_4\text{Ni}^{2+}$, $\text{Zn(C}_6\text{H}_4\text{Ni})L^2$, $\text{Zn}_2\text{C}_6\text{H}_4\text{Ni}L^3$ and $\text{Zn}_2\text{C}_6\text{H}_4\text{Ni}_2L^4$. 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 $\beta_{14} = -8.7$ in 3.0 M (Li)ClO₄]. Furthermore the species $\text{ZnOH}^+$ (e.g. for example $\text{ZnOHCl}^-$) 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, $B_t$ is obtained as the tetrahedral complex $\text{ZnCl}_4(\text{H}_2\text{O})^{17,18}$ and perhaps

even as ZnCl₂⁻, but in the perchlorate medium zinc occurs as the octahedral complex Zn(H₂O)₆²⁺. The association between zinc(II) and ClO₄⁻ 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 KZnCl₄·2H₂O,₆ Zn₄(OH)₂Cl₄·H₂O,₆ Zn₄(OH)₄(NO₃)₂·2H₂O,₇ and Zn(OH)₄Cl₂,₅ but the corresponding distance in the octahedral complex is about 2.10–2.13 Å as in Zn(NO₃)₂·6H₂O,₆ Zn₄(OH)₄(NO₃)₂·2H₂O,₇ and in the X-ray investigation of an aqueous solution of Zn(H₂O)₆²⁺.₆ 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

\[
ZnL_{n+1}^{n+} + L \rightleftharpoons ZnL_{n}^{n+} \quad n = 1, 2, 3, 4
\]

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 ZnL₄⁺ series could be well explained with a two parameter approximation of the type \( K_{n+1} = K_{n+1}^a \) with \( \log K_2 = 3.126 \) and \( \log K_4 = -0.57 \). 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.,₁⁵,₃¹,₃₂ in several other zinc(II) systems.

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

<table>
<thead>
<tr>
<th>Octahedral (Å)</th>
<th>Tetrahedral (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn–O</td>
<td>2.10–2.13</td>
</tr>
<tr>
<td>Zn–N</td>
<td>2.15–2.25</td>
</tr>
<tr>
<td>Zn–Cl</td>
<td>2.50–2.60</td>
</tr>
</tbody>
</table>

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\textsuperscript{+} in 3.0 M (Na)Cl and Zn(OH)\textsubscript{2}L\textsuperscript{+} in 3.0 M (NaClO\textsubscript{4}). An emf investigation of the four component equilibria zinc(II)—imidazole—OH\textsuperscript{-}—Cl\textsuperscript{-} in 3.0 M (NaClO\textsubscript{4}) is completed and will soon be published.

A calorimetric study of the zinc(II)—imidazole—OH\textsuperscript{-} system is planned.

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