Metal Complexes with Mixed Ligands. 15. A Potentiometric Study of the System Zn^{2+}—Cl^-—Imidazole in 3.0 M (Na)ClO$_4$,Cl Media

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Four component equilibria between zinc(II), imidazole ($C_3H_4N_2$; L), OH^- and Cl^- were studied by means of emf titrations at 25 °C in 3.0 M (Na)ClO$_4$,Cl using a glass electrode. The total zinc, B, the total imidazole, C, and the total chloride, X, were varied within the limits $0.005 \leq B \leq 0.025$ M, $0.040 \leq C \leq 0.185$ M and $0 \leq X \leq 3.0$ M and the ratios C/B between $3.4 \leq C/B \leq 36.2$. In addition to the stepwise metal complexes ZnL_n^{2+} $n = 1, 2, 3, 4$, data can be explained with the following ternary complexes: $ZnClL_n^+$ $n = 1, 2, 3, 4, 5$, $ZnCl_2L_2$ and $ZnCl_3L^-$. The equilibrium constants are given in Table 1. Data were analyzed with the least squares computer program LETAGROPVRID.

In part 14 of this series the three-component equilibria in the system zinc(II) – imidazole – OH^- in 3.0 M (Na)ClO$_4$ and 3.0 M (Na)Cl were investigated using a glass electrode at 25 °C. It was found that in both media at high quotients $(C/B > 4)$ only stepwise metal complexes ZnL_n^{2+} [2] were formed. The equilibrium 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)ClO$_4$[1] and 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)Cl.[1] Thus the complexation in the two media is different. In the chloride medium the ZnL_n^{2+} series can be well explained with a two-parameter approximation of the type $K_{n+1} = K_0 k^n$, $n = 0, 1, 2, 3$, with log $K_0 = 3.126$ and log $k = -0.57$. This is not possible in the perchlorate medium, probably due to a coordination shift at the second step. The values of K_1 and K_2 are also greater in the chloride medium in spite

of the fact that no correction for chloro complexes has been made. This behaviour can be explained by the fact that in 3.0 M (Na)Cl at least 90 % of the total zinc is obtained in the complex $ZnCl_3^{-2}$ or even $ZnCl_4^{2-}$, which already has a tetrahedral configuration. In this case the complexation with imidazole implies a stepwise exchange of the chloride ions around the zinc ion for imidazole molecules without any coordination shift.

This model for complexation signifies the existence of the ternary complexes $ZnLCl_3^-$, ZnL_2Cl_2 and ZnL_3Cl^+. Since the binary zinc(II) – chloro complexes besides $ZnCl_3^-$ are $ZnCl^+$ and $ZnCl_2$,[2] one would also expect other ternary complexes of the types ZnL_xCl^+, ZnL_yCl_2 and $ZnL_zCl_3^-$ at other chloride concentration levels.

Another interesting difference in the two media concerns the crystalline phases. In the chloride medium two different crystalline phases have been found corresponding to the formulae ZnL_2Cl_2[3] and $ZnL_6Cl_2.4H_2O$.[7] In the former crystal the configuration around zinc is tetrahedral and in the latter octahedral. In the perchlorate medium no octahedral complex is found but only the tetrahedral $ZnL_4(ClO_4)_2$.[5] Thus the chloride ions seem to make the formation of the octahedral complex ZnL_6^{2+} easier.

The purpose of the present study was to investigate the zinc(II) – imidazole – chloro system and to confirm the formation of ternary $Zn^{2+} - L - Cl^-$ complexes.

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EXPERIMENTAL

Chemicals and analysis. All solutions used were prepared and analyzed as described earlier.[1]

Apparatus. The cell arrangement and experimental details of the emf measurements are fully described earlier.[6]

Method. The titrations were performed as potentiometric titrations at 25 °C similarly to those described in earlier papers.[6,7] The equilibrium solutions were made to contain $[ClO_4^-] + X = 3.0$ M, where X is the chloride concentration. The general compositions of the solutions were: B mM Zn^{2+}, C mM $C_3H_5N_2^+$, H mM H^+, X mM Cl^- ($[ClO_4^-] + X - C - H - 2B$) mM Na^+ and $3000 - X$ mM ClO_4^-. In the titrations the total concentrations of zinc(II), B, and imidazole, C, were varied, while the ratio C/B was always held constant. The total concentration of hydrogen ions, H, was calculated over the zero level, Zn^{2+}, HL^+ and H_2O and the free hydrogen ion concentration, h, was varied by addition of OH^- and measured with a glass electrode. h was determined according to the relation

$$E = E_0 + 59.157 \log h + E_j \tag{1}$$

where E_0 is a constant determined in acid solutions where complex formation could be neglected. The liquid junction potential $E_j = -16.7 \ h$ mV was used in 3.0 M (Na)ClO_4, 3.0 M (Na)Cl as well as in mixtures of these two media. It has earlier been shown by Sjöberg[7] that within the concentration range $0 \leq X \leq 3.0$ M with $[ClO_4^-] + X = 3.0$ M the concentration scale for H^+ remains constant. No change in E_0 could be found on replacing ClO_4^- by Cl^- or *vice versa*.

We will assume the presence of four-component equilibria of the general form

$$pH^+ + qZn^{2+} + rHL^+ + sCl^- \rightleftharpoons$$
$$H_pZn_q(HL)_rCl_s^{(2q+p+r-s)+}; \quad \beta_{pqrs}' \tag{2}$$
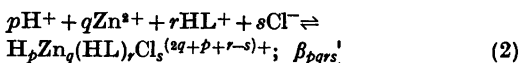
It is convenient to write complexes where $-p = r$ as $Zn_qL_nCl_s^{(2q-s)+}$ and the stability constants as β_{nqs}. This terminology is used throughout this paper.

In addition to the four-component equilibria in (2) we have

(i) the complex formation between Zn^{2+} and Cl^-

$$Zn^{2+} + sCl^- \rightleftharpoons ZnCl_s^{(2-s)+} \tag{3}$$
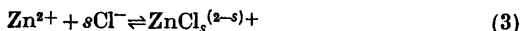
(ii) the imidazole equilibria, which within the concentration range $0 \leq X \leq 3.0$ M with $[ClO_4^-] + X = 3.0$ M are

$$HL^+ \rightleftharpoons L + H^+; \quad k_a \tag{4}$$

$$HL^+ + Cl^- \rightleftharpoons LCl^- + H^+; \quad \beta_{101} \tag{5}$$

$$HL^+ + 2Cl^- \rightleftharpoons LCl_2^{2-} + H^+; \quad \beta_{102} \tag{6}$$
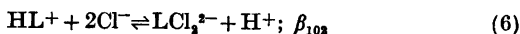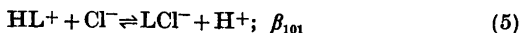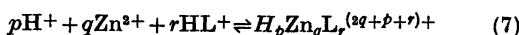
Table 1. Results of the final LETAGROP calculations giving the formation constants for the "best fitting" complexes. The Roman numerals in brackets refer to the different data sets mentioned in the text. The formation constants are related according to the reaction $pL + Zn^{2+} + rCl^- \rightleftharpoons L_pZn_qCl_r^{(2q-r)+}$, where L stands for $C_3H_4N_2$. When no 3 (log β_{pqr}) is given, the formation constant has not been varied.

No. of titr./ No. of points	$\sigma(C-c)$ $\times 1000$	$ZnCl^+$ log(β_{011}) $\pm 3\sigma$	$ZnCl_2$ log(β_{012}) $\pm 3\sigma$	$ZnCl_3^-$ log(β_{013}) $\pm 3\sigma$	$ZnLCl^+$ log(β_{111}) $\pm 3\sigma$	ZnL_2Cl^+ log(β_{211}) $\pm 3\sigma$	ZnL_3Cl^+ log(β_{311}) $\pm 3\sigma$	ZnL_4Cl^+ log(β_{411}) $\pm 3\sigma$	ZnL_5Cl^+ log(β_{511}) $\pm 3\sigma$	$ZnLCl_3^-$ log(β_{113}) $\pm 3\sigma$	ZnL_2Cl_2 log(β_{212}) $\pm 3\sigma$
13/201 (I)	0.11	−0.19	−0.60	0.15	3.50 ±0.04	5.97 ±0.16	9.59 ±0.02			3.60 ±0.01	6.93 ±0.01
14/235 (II)	0.18	−0.19	−0.60	0.15	3.50	5.97	9.58 ±0.02	10.96 ±0.12	12.79 ±0.07	3.60	6.93
11/80 (III)	0.06	−0.19	−0.60	0.15	3.44 ±0.03	5.97				3.59 ±0.02	6.95 ±0.02
11/80 (III)	0.06	−0.25 ±0.10	−0.65 ±0.10	0.133 ±0.005	3.38 ±0.08	5.97				3.58 ±0.04	6.92 ±0.02
8/35	0.07	−0.19	−0.60	0.15	3.43 ±0.05	5.97				3.60 ±0.04	6.95 ±0.03

with log $k_a = -7.940$, log $\beta_{101} = -8.641$ and log $\beta_{102} = -9.279$.[7]

(iii) the zinc(II) imidazole equilibria

$$pH^+ + qZn^{2+} + rHL^+ \rightleftharpoons H_p Zn_q L_r^{(2q+p+r)+} \qquad (7)$$

with equilibrium constants given in Table 1. In the present study hydrolytic equilibria of the zinc(II) ion as well as formation of ternary zinc(II) $-$ OH$^-$ $-$ imidazole complexes could be neglected.

Equilibria (3) $-$ (7) were determined in separate investigations and are assumed to be known in calculations concerning the four-component equilibria.

Data treatment. It is possible to reduce the four-component system H$^+$ $-$ Zn^{2+} $-$ HL$^+$ $-$ Cl$^-$ to the three-component system L $-$ Zn^{2+} $-$ Cl$^-$ under the assumption that $-p = r$ in eqn. (2), which means that only complexes of the type $Zn_q L_n Cl_s^{(2q-s)+}$ are formed. With this assumption [L] can be calculated according to the relation

$$[L] = k_a h^{-1}[HL^+] = k_a h^{-1}[C - (h - H)] \qquad (8)$$

where k_a is the acidity constant of HL$^+$ in 3.0 M (Na)ClO$_4$. Thus as input to the computor, data in the form $(C, \log[L], B, X)$ are given instead of $(H, \log h, B, C, X)$. This was done to save computer time, which is considerably greater with four components.

The mathematical analysis were performed with the least squares computor program LETAGROPVRID[8] (version ETITR[9]). On treating the emf data the error squares sum $U = \sum(A_{calc} - A_{exp})^2$ was minimized, where A denotes C-c, *i.e.* the total imidazole concentration not obtained as HL$^+$. The standard deviations were defined and calculated according to Sillén.[10] The computation was performed on a CDC 3300 computer.

DATA, CALCULATIONS AND RESULTS

The complex formation between zinc(II) and imidazole has already been investigated in 3.0 M (Na)ClO$_4$ and 3.0 M (Na)Cl media by using the emf-titration method. Results of these measurements are found in Ref. 1.

The binary zinc(II) $-$ Cl$^-$ system in 3.0 M (Na)ClO$_4$ has been investigated by Liljeqvist and Sillén[2] by potentiometric titrations using a zinc amalgam electrode. Their data comprises the chloride concentration range $0 \leq [Cl^-] \leq 0.9$ M with the dominating species ZnCl$^+$, ZnCl$_2$ and ZnCl$_3^-$. Since in this investigation the chloride concentration range is increased to $0 \leq [Cl^-] \leq 3.0$ M, special attention must be paid to the eventual formation of ZnCl$_4^{2-}$.

Particularly at low $\bar{n}$-values where the concentrations of the binary ZnCl$_s^{(2-s)+}$-complexes are high, appreciable amounts of ZnCl$_4^{2-}$ would influence the calculations. Thus in this region two different data sets were arranged. One data set comprises the chloride concentrations $0 \leq [Cl^-] \leq 1.0$ M and the other set $0 \leq [Cl^-] \leq 3.0$ M. No significant differences either in the model or the formation constants were obtained in the calculations. The results are given for comparison in Table 1. Furthermore the species ZnCl$_4^{2-}$ was rejected by the computor in all the calculations.

In the search for the ternary zinc(II) $-$ imidazole $-$ Cl$^-$ species it was assumed that the binary complexes were exactly known and that the equilibrium constants had the values given in Ref. 1 and Ref. 2, respectively. However, a final covariation of the binary complexes, together with the ternary complexes, was made to determine whether any ternary species would be eliminated by a small variation of the binary ones (see below).

Many titrations were performed at a constant X-level ($X = 0$, 0.5, 1, 3; $[ClO_4^-] + X = 3.0$ M; $X = [Cl^-]$). In these cases $[C_3H_4N_2]$ can be calculated either by use of the conditional acidity constant of $C_3H_5N_2^+$ valid at the actual X-level or by assuming the value of k_a valid in 3.0 M (Na)ClO$_4$ to be the genuine acidity constant. Thus the constants at the different X-levels are a result of complex formation between L and Cl$^-$ and $\bar{n}$ is given by

$$\bar{n} = (h - H - [L] - [LCl^-] - [LCl_2^{2-}])/B \qquad (9)$$

where [L] is given by (8) and [LCl$^-$] and [LCl$_2^{2-}$] are calculated according to

$$[LCl^-] = \beta_{101}h^{-1}X[HL^+] = \beta_{101}h^{-1}X(C + H - h) \qquad (10)$$

$$[LCl_2^{2-}] = \beta_{102}h^{-1}X^2[HL^+] = \beta_{102}h^{-1}X^2(C + H - h) \qquad (11)$$

The same $\bar{n}$ is now obtained independently of whether the conditional or the complex formation model above has been used.

The calculated quantities $\bar{n}$ and log [L], visualized as Bjerrum plots in Fig. 1, are calculated using the conditional acidity constant. As seen from the plot, the complexation is stronger in the mixed chloride media at low $\bar{n}$-values ($\bar{n} < 2$) in spite of the fact that no
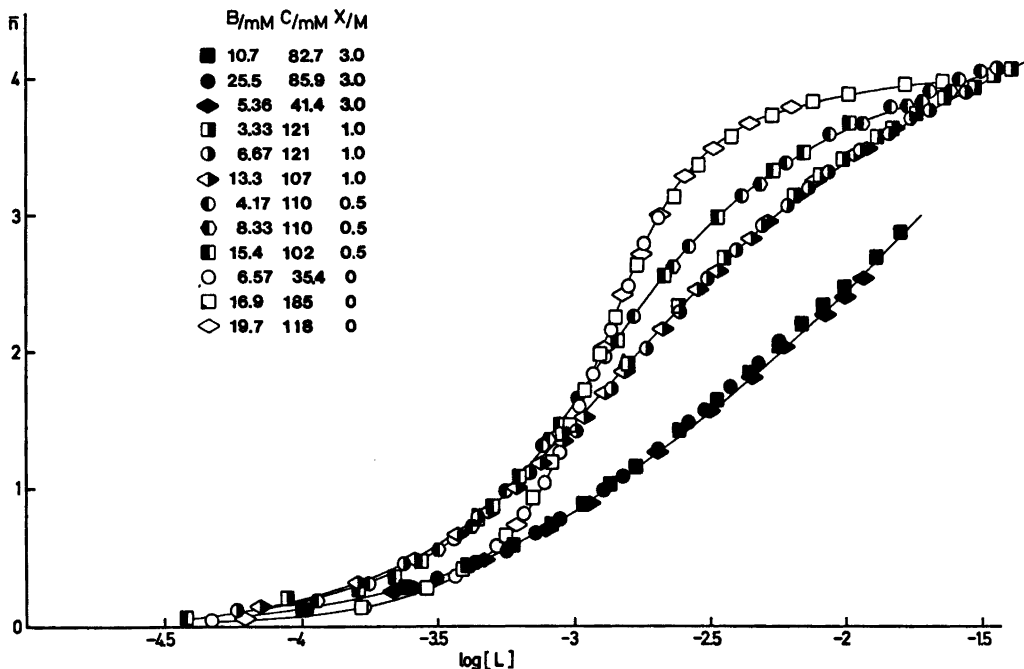
Fig. 1. Parts of experimental data plotted as curves $\bar{n}(\log[L])$ in the mixed 3.0 M (Na)ClO$_4$ Cl media. The full curves were calculated with the set of constants given in Table 1.

correction for zinc(II)-chlorocomplexes has been made. These conditions must be due to the formation of ternary zinc(II)-imidazole-Cl$^-$ complexes and furthermore at least one of the species ZnCl$^+$, ZnCl$_2$ and ZnCl$_3^-$ has to be a stronger complexing agent to imidazole than the corresponding hydrated zinc(II) ion. Owing to the limited space in the data program for the number of formation constants, the LETAGROP calculations were divided into three parts, which partly overlapped each other.* The first part, Data I, comprises data where $0 \leq \bar{n} \leq 2$ and $0 \leq X \leq 3$. These data consist of 13 titrations with 201 titration points. The titrations were performed both at constant X-values ($X = 0.5, 1, 3$) and as dilution experiments at constant $\bar{n}$-values. In these experiments we titrated a solution in 3.0 M (Na)ClO$_4$ with 3.0 M (Na)Cl medium or *vice versa*. The actual $\bar{n}$-values were about 0.5, 1, 1.25 and 1.75. In this part the ternary zinc(II) $-$ L $-$ Cl$^-$ species with $\bar{n} < 4$ (less than

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* A list of experimental data is available from this Department.

four imidazole, molecules bound per zinc) were determined. The best explanation was obtained with the complexes ZnLCl$_3^-$, ZnL$_2$Cl$_2$, ZnLCl$^+$, ZnL$_2$Cl$^+$ and ZnL$_3$Cl$^+$. Other species were either rejected by the computor as ZnL$_2$Cl$_3^-$, ZnL$_3$Cl$_2$ and ZnL$_3$Cl$_3^-$ or did not lower the error squares sum to any appreciable extent as ZnLCl$_2$. In a final covariation all the "fitting" complexes were allowed to compete and the result of this computor calculations is given in Table 1. All the species except ZnL$_2$Cl$^+$ were obtained with very low standard deviations ($3\sigma \leq 0.04$). The relatively high error in the formation constant of the species ZnL$_2$Cl$^+$ ($3\sigma = 0.16$) is explained by the smaller amounts of this complex. The calculation ended at a $\sigma(A) = 0.11$. This corresponds to an error of 0.11 mM in the total imidazole concentration not obtained as HL$^+$. The second part, Data II, consists of data where $\bar{n} \geq 2$ and $0 \leq X \leq 3$. It consists of 14 titrations with 235 titration points. Similar dilution experiments as above were performed at $\bar{n}$ about 2.75, 3 and 3.75.

When treating these data all formation constants from the first part except for the

Table 2. Some stepwise reactions with constants calculated by means of formation constants given in Ref. 1 and Table 1. The different reactions define the stepwise uptake of ligands. (a) $C_3H_4N_2$ (L) and (b) Cl^-, are¦ to be read horizontally (ZnL$_2$Cl+ 3.61 ZnL$_3$Cl+ stands for ZnL$_2$Cl+ $+ L \rightleftharpoons$ ZnL$_3$Cl+ with log $K = 3.61$).

	log K		log K		log K		log K		log K	
(a)										
Zn^{2+}	2.93	ZnL^{2+}	2.00	ZnL$_2$$^{2+}$	3.79	ZnL$_3$$^{2+}$	2.82	ZnL$_4$$^{2+}$		
ZnCl+	3.64	ZnLCl+	2.52	ZnL$_2$Cl+	3.61	ZnL$_3$Cl+	1.38	ZnL$_4$Cl+	1.83	ZnL$_5$Cl+
ZnCl$_3$$^-$	3.45	ZnLCl$_3$$^-$								
(b)										
Zn^{2+}	−0.19	ZnCl+	−0.41	ZnCl$_2$	0.75	ZnCl$_3$$^-$				
ZnL^{2+}	0.56	ZnLCl+								
ZnL$_2$$^{2+}$	1.01	ZnL$_2$Cl+	0.96	ZnL$_2$Cl$_2$						
ZnL$_3$$^{2+}$	0.84	ZnL$_3$Cl+								
ZnL$_4$$^{2+}$	−0.61	ZnL$_4$Cl+								

species ZnL$_3$Cl+ were kept constant. Once more the complexes ZnL$_3$Cl$_2$ and ZnL$_3$Cl$_3$$^-$ were rejected by the computor. The species ZnL$_4$Cl$_2$ was rejected by a covariation with the species ZnL$_4$$^{2+}$ and ZnL$_4$Cl+.

Thus the "best fit" was obtained with the ternary species ZnL$_3$Cl+, ZnL$_4$Cl+, ZnL$_5$Cl+ together with the binary species ZnL$_4$$^{2+}$. The result of the final covariation is shown in Table 2. The calculation ended at $\sigma(A) = 0.18$. In Data III, which consists of 11 titrations and 80 titration points where $\bar{n} < 0.7$, the formation constants of the binary species ZnCl+, ZnCl₂ and ZnCl$_3$$^-$ were varied together with the ternary ones. This calculation confirmed the results from the other parts and also gave values of the binary constants in an indirect way. These values were in a very good agreement with those determined by Sillén. The results are given in Table 1. In order to visualize the amounts of the ternary species at some typical X-levels, we have collected a set of distribution diagrams, which are shown in Fig. 2. These diagrams show that the ternary zinc(II) − chloro − imidazole species are generally obtained in great amounts even at proportionally low total chloride concentration levels. For instance, at the chloride concentration level of sea water (~ 0.5 M Cl$^-$, even if, in this investigation, the total ionic medium is 3.0 M by addition of NaClO$_4$) the ternary species ZnLCl+, ZnL$_2$Cl$_2$ and ZnL$_3$Cl+ together

with the binary ZnL$_4$$^{2+}$ are dominating in spite of the fact that the amounts of the binary zinc(II) − chloro complexes are rather low.

As mentioned earlier, special calculations with $[Cl^-] \leq 1.0$ M were performed in the range $\bar{n} < 0.7$ to estimate the importance of small amounts of the complex ZnCl$_4$$^{2-}$. These data consist of 8 titrations with 35 titration points and the results are given in Table 1.

DISCUSSION

The present emf investigation has strongly confirmed the existence of ternary zinc(II) − imidazole − Cl$^-$ complexes. The dominating species besides the series ZnL$_n$Cl+, $n = 1...5$, are the complexes ZnLCl$_3$$^-$ and ZnL$_2$Cl$_2$.

Concerning the ZnL$_n$Cl+ series, the results can be interpreted as stepwise reactions in which imidazole molecules are successively coordinated to a ZnCl+ core or alternatively as chloride ions coordinated to ZnL$_n$$^{2+}$ core with $n = 0, 1, 2, 3, 4, 5$. Stepwise constants of these reactions are given in Table 2. As for the ZnL$_n$$^{2+}$ series it is not possible to explain ZnL$_n$Cl+ series by a two parameter approximation of the type $K_{n+1} = K_0 k^n$. The log K_n-values are given in Table 2 and the low values for the quotients $K_2/K_3 = 0.07$ and $K_4/K_5 = 0.35$ indicate coordination shifts at the second and fourth step. The first shift is probably obtained from octahedral to tetrahedral coordination
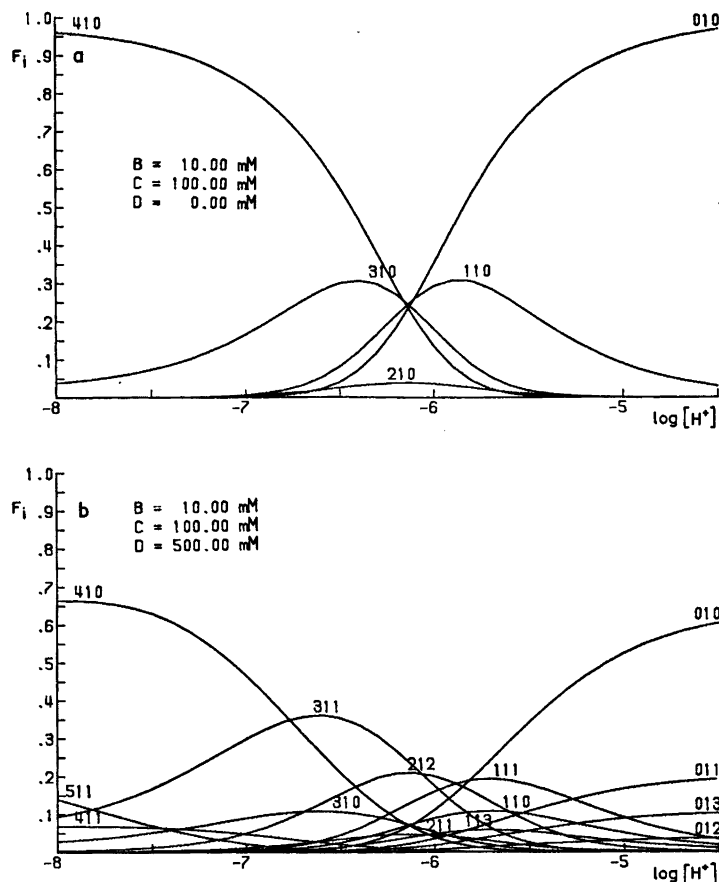
Fig. 2. Distribution diagrams $F_i(\log h)_{B,C,X}$ for the different zinc(II)−imidazole complexes. The computer program SOLGAS-WATER[12] was used in the calculations. The figures denote the number of $C_3H_4N_2$, Zn^{2+} and Cl^- in the complexes.

and the second in the reverse direction. Thus the chloride ions seem to take part in the co-ordination shift back to octahedral coordination at the fourth step. A tetrahedral series is built up from the $ZnCl_3^-$ core according to

$$ZnLCl_3^- + nL \rightleftharpoons ZnL_{n+1}Cl_{3-n}^{(n-1)+} + nCl^-$$
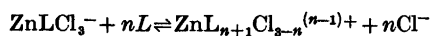
$n = 1$, 2, 3, with values of $\log K = 3.33$, 2.66 and 1.98. This series is very well explained with a two parameter approximation of the type $K_{n+1} = K_0 k^n$ with $\log K_0 = 3.33$ and $\log k = -0.67$.

Comparing the reactions $Zn^{2+} + L \rightleftharpoons ZnL^{2+}$ with $\log K_1 = 2.93$ and $ZnCl^+ + L \rightleftharpoons ZnLCl^+$ with $\log K = 3.64$ it is obvious that $ZnCl^+$,

as $ZnOH^+$, is a stronger complexing agent to imidazole than the hydrated zinc(II)-ion. The same properties have been found in the corresponding investigations of the copper(II) −[7] and nickel(II) −[11] imidazole − Cl^- systems with $\log K(M^{2+} + L \rightleftharpoons ML^{2+}) = 4.65$ (Cu^{2+}) and 3.37 (Ni^{2+}), respectively compared to $\log K(MCl^+ + L \rightleftharpoons MLCl^+) = 4.75$ (Cu^{2+}) and 3.65 (Ni^{2+}).

In the distribution diagrams it is easily seen that the even coordination numbers 2, 4, 6 are usually favoured compared to the odd numbers 1, 3 and 5. At chloride concentration levels less than 1.0 M many coexisting complexes make the distribution diagrams rather complicated,
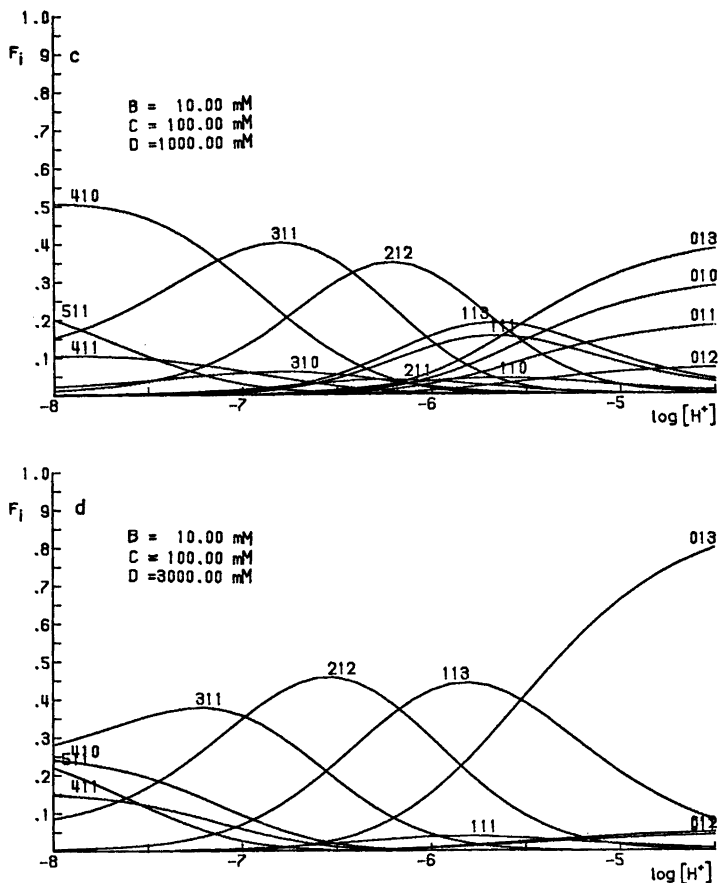
Fig. 2. c and *d*.

but in 3.0 M (Na)Cl medium the diagram is again quite simple with a few strongly dominating species. Thus the main complexes are $Zn(H_2O)Cl_3^-$, $ZnLCl_3^-$, ZnL_2Cl_2 and ZnL_3Cl^+, which accounts for the good explanation of data with the two-parameter approximation model in this medium. As seen from the plot $\bar{n}(\log[L])$ the complexation starts at $\log[L] \sim -4.5$. That leads to the fact that at the natural concentrations of sea water ($[Zn^{2+}]_{tot} \leq 10^{-7}$ M, $[NH_4^+]_{tot} \sim [\text{Amino acids}]_{tot} \leq 10^{-5.4}$ M) the amounts of the ternary species are very low. The dominating complexes in this case seem to be the hydrated zinc(II)-ion and the binary $ZnCl_s^{(2-s)+}$

Concerning the crystalline phases, powder X-ray investigations of the precipitates from the different mixed media were made. In the 3.0 M (Na)Cl medium no phases other than

those earlier X-ray investigated, ZnL_2Cl_2 and $ZnL_6Cl_2.4H_2O$, were found. In the 3.0 M (Na)ClO_4 medium ([Cl] = 0) the phase $ZnL_4(ClO_4)_2$ was identified together with a new phase not yet examined. This new phase was also found in some of the mixed media with low chloride concentrations.

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