

Metal Complexes with Mixed Ligands. 12. A Potentiometric Study of the Systems Hg^{2+} —Imidazole, Hg^{2+} — OH^- —Imidazole and Hg^{2+} — Cl^- —Imidazole in 3.0 M (Na)ClO₄, Cl Media

STAFFAN SJÖBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Four component equilibria between mercury(II), imidazole ($\text{C}_3\text{H}_4\text{N}_2$; L) OH^- and Cl^- have been studied at 25 °C by means of emf titrations using a glass electrode. The measurements were performed in media consisting of mixtures of 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl with $0 \leq [\text{Cl}^-] \leq 3.0$ M. Besides pure binary species HgL^{2+} and HgL_2^{2+} , all data could be explained with the ternary complexes HgClL^+ , HgCl_2L , HgCl_3L^- and HgCl_4^{2-} . The formation of a mixed hydroxo complex $\text{Hg}(\text{OH})\text{L}^+$ has also been established. The equilibrium constants determined are collected in Table 4. Data have been analysed with the least squares computer program LETA-GROPVRID.

In a preceding publication,⁵ equilibria in hydrolyzed mercury(II) chloride solutions were reported. Besides pure binary hydrolytic complexes, HgOH^+ , $\text{Hg}(\text{OH})_2$ and $\text{Hg}_2(\text{OH})_2^{2+}$ and unhydrolyzed $\text{HgCl}_n^{(2-n)+}$ ($n = 1, 2, 3, 4$) species, experimental data were explained with the ternary complexes HgOHCl , $\text{Hg}_2\text{OHCl}_2^+$ and $\text{Hg}_3(\text{OH})_2\text{Cl}^{2+}$. The aim of the present investigation is to determine

the composition of the complexes formed in the system Hg^{2+} —imidazole (L)— OH^- — Cl^- .

PREVIOUS STUDIES

The literature concerning aqueous mercury(II) imidazoles indicates that two mononuclear species, HgL^{2+} and HgL_2^{2+} , should be formed (see Table 1). Brooks and Davidson¹ performed some potentiometric titrations (0.15 M NaClO₄, 27 °C) using both a mercury-mercury(II) and a glass electrode. They concluded that the principal complex formed is HgL_2^{2+} while HgL^{2+} , for which no stability constant was evaluated, seemed to be present only in small amounts. Recently Marsicano *et al.*² [0.5 M (Na)ClO₄, 25 °C] evaluated from titration calorimetric measurements, formation constants for both HgL^{2+} and HgL_2^{2+} . The investigation by Smith³ yielded very low values of the formation constants (*cf.* Table 1), which most certainly is due to the ionic medium consisting of 0.058 M KCl. As mercury(II) in this medium

Table 1. Earlier studies on mercury(II)—imidazoles. The constants are defined according to the equilibria: $\text{Hg}^{2+} + n\text{L} \rightleftharpoons \text{HgL}_n^{2+}$; β_n

Temp. °C	Medium	Method	$\log(\beta_1 + 3\sigma)$	$\log(\beta_2 + 3\sigma)$	Ref.
27	0.15(Na)ClO ₄	pot. (gl. Hg)	—	18.74	1
25	0.5(Na)ClO ₄	cal.	9.64(35)	18.29(21)	2
25	0.058 KCl	pot. (gl.)	3.57	6.95	3
25	3.0(Na)ClO ₄	pot. (gl.)	9.18(12)	18.19(2)	This work

exists as chloride complexes, the equilibrium constants given are not true stability constants, but rather "conditional" constants.

Any attempt to try to find $\text{Hg}^{2+} - \text{OH}^- - \text{L}$ or $\text{Hg}^{2+} - \text{Cl}^- - \text{L}$ species has not been reported.

EXPERIMENTAL

Chemicals and analysis. All solutions used were prepared and analysed as described earlier.^{4,5}

Apparatus. The thermostat, cell arrangement and experimental details for the emf measurements are fully described in Refs. 4 and 5.

Method. The measurements were carried out as potentiometric titrations at 25 °C. The titration procedures used were similar to those described earlier.

The equilibrium solutions were made to contain $[\text{ClO}_4^-] + X = 3.0 \text{ M}$. X is defined as the total chloride concentration over the HgCl_2 level. The solutions had the general composition: $B \text{ M HgCl}_2$, $C \text{ M HL}^+$, $H \text{ M H}^+$, $X \text{ M Cl}^-$, $([\text{ClO}_4^-] + X - C - H) \text{ M Na}^+$ and $3.0 - X \text{ M ClO}_4^-$. B and C are the total concentrations of mercury(II) and imidazole, and H stands for the total concentration of protons, calculated over the 0-level HgCl_2 , HL^+ , Cl^- and H_2O .

The free hydrogen ion concentration, h , was determined according to the relation

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$

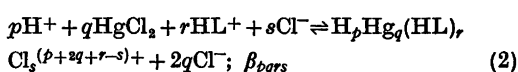
The liquid junction potential E_j was expected to be caused mainly by the presence of H^+ . In 3.0 M NaClO_4 and 3.0 M NaCl $E_j = -16.7 h \text{ mV}^{12}$ and $-17.0 h \text{ mV}$,⁸ respectively, have been used. In solutions where $3.0 < X < 0 \text{ M}$ a value of $E_j = -16.7 h \text{ mV}$ has been used.

To find out whether the replacement of ClO_4^- to Cl^- or the reverse, will change the concentration scale for H^+ , some supplementary titrations were performed. In these $B = C = 0$ and h was either kept constant or varied, while X ranged from 0 to 3.0 M. It was found that E_0 of the glass electrode did not change by more than $\pm 0.1 \text{ mV M}^{-1}$ of exchanged anion. Thus the concentration scale of H^+ does not seem to be affected by the change of chloride ions in the ionic medium.

Most of the titrations were started with a calibration of the glass electrode using those acidic points where hydrolysis and complex formation can be neglected. This calibration thus gives E_0 and E_j , and H could be controlled by using Gran's extrapolation method.⁷ However, with $X = 0$, the complex formation starts at $\log h > -3$, and no accurate determinations of both E_0 and H can be made. Instead E_0 was estimated from the most acidic points in the titrations, and H was controlled in separate experiments by the addition of NaCl (to

suppress the complex formation between HgCl_2 and L) as described earlier.⁸

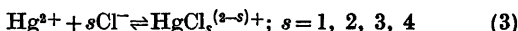
We will assume the presence of 4-component equilibria of the general form:



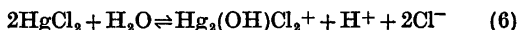
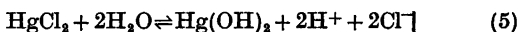
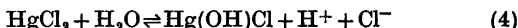
It will be convenient to write complexes where $-p=r$ as $\text{Hg}_q\text{L}_n\text{Cl}_s$ and the stability constants as β_{nqs} , which is used throughout in this paper whenever possible.

Besides the four component equilibria in (2) we have to take into account,

(i) the complex formation between Hg^{2+} and Cl^- according to



(ii) the hydrolysis of these chloride complexes which with $\log h > -9$ is explained by the following equilibria:

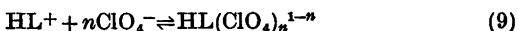


(iii) the proton imidazole equilibrium:



which has been found to be dependent on the composition of the ionic medium; e.g. $\log K_a(\text{HL}^+) = -7.913$ and -7.635 in 3.0 M $(\text{Na})\text{ClO}_4$ and 3.0 M $(\text{Na})\text{Cl}$,⁸ respectively. Equilibrium constants for reactions (3)–(7) have been determined in earlier investigations⁸ and will be assumed to be known.

$K_a(\text{HL}^+)_X$ in mixed media with $[\text{ClO}_4^-] + X = 3.0 \text{ M}$. In separate measurements this acidity constant was determined at $X = 0.1, 0.2, 0.4, 0.5, 0.75, 1.0$ and 1.5 M with the results given in Table 2. According to this table there is a steady increase in K_a with increasing X . As a hypothesis we will try to explain this tendency as caused by complex formation. Calculations on the collected experimental data showed that two alternative explanations were possible. Either by assuming the perchlorate ion to form complexes with the imidazolium ion or speciation between the imidazole molecule and chloride ions. Letagrop calculations showed that a satisfactory fit was obtained by assuming the equilibria



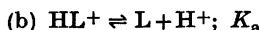
with $\log \beta(\text{HLCIO}_4) = -0.57 \pm 0.01$, $\log \beta[\text{HL}(\text{ClO}_4)_2^-] = -1.63 \pm 0.08$ and $\log K_a(\text{HL})^+ = -7.636 \pm 0.002$.

Table 2. Results of LETAGROP calculations on the system $H^+ - HL^+ - Cl^-$. The complexes formed at different levels of X were defined either according to



with $n=0, 1, 2$

or according to



In the last column under (b) a calculated value of K_a is given, in which the relation

$$K_a(\text{calc}) = \beta_{100}x^0 + \beta_{101}x^1 + \beta_{102}x^2$$

has been employed. In the calculation $x = X$ has been used, which seems reasonable as the change in x due to the complex formation with L is small.

(a)

No. of titr./ No. of points	X/M	$\sigma(Z) \times 1000$	$\log(\beta_{100} \pm 3\sigma)$	$\log(\beta_{101} \pm 3\sigma)$	$\log(\beta_{102} \pm 3\sigma)$
14/317	0.0–3.0	2.2	–7.940(2)	–8.641(16)	–9.279(26)

(b)

X/M	$\sigma(Z) \times 1000$	$-\log(K_a \pm 3\sigma)$	$-\log K_a(\text{calc.})$
0		7.913(1) ^a	7.940
0.1	2.2	7.927(4)	7.931
0.2	1.9	7.922(5)	7.921
0.4	2.0	7.907(3)	7.903
0.5	2.7	7.894(2)	7.889
0.75	2.3	7.865(3)	7.863
1.0	1.5	7.845(1)	7.844
1.5	2.6	7.794(4)	7.792
3.0		7.637(2) ^b	7.635

^a Value taken from Ref. 4. ^b Value taken from Ref. 8.

Alternatively it was found that the equilibria



with equilibrium constants given in Table 2, equally well could explain the experimental data.

Whether $HL^+ - ClO_4^-$ and/or $L - Cl^-$ complexes are formed is difficult to predict from the type of measurements performed in this work. As these complexes are very weak, we can put $x = X$ and $[ClO_4^-] = [ClO_4^-]_{\text{tot}}$ as a good approximation. This means that interpretation of the four-component equilibria as defined under (2) are independent of whether equilibria (9) or (10)–(11) are introduced in the equilibrium model. However, to restrict the number of components to four, corrections for the medium dependence of $K_a(HL^+)$ will be made by means of equilibria (10)–(11) (see below).

Data treatment. For the case when only complexes of the general type $Hg_qL_r^{2q+}$ are formed, e.g. when $-p=r$ in (1), \bar{n} is defined as the average ligand number and is given by

$$\bar{n} = (h - H - K_w h^{-1} - [L])/B \quad (12)$$

where K_w is the ionic product of water. In the present study the term $K_w h^{-1}$ can be neglected. $[L]$ can be calculated from the relation

$$[L] = K_a h^{-1} [HL^+] = K_a h^{-1} [C - (h - H)] \quad (13)$$

In cases with $-p \neq r$ it can easily be shown that

$$[HL^+] \neq C - (h - H) \quad (14)$$

and apparent values of \bar{n} and $[L]$ are obtained. These parameters are now calculated only to test how poorly a set of experimental data fits a series of complexes $Hg_qL_r^{2q+}$.

When ternary species $Hg^{2+} - Cl^- - L$ are formed \bar{n} can be calculated in two ways. When

measurements have been performed at constant levels of X , $[L]$ can be calculated either by the use of the "conditional" acidity constant of HL^+ valid at the X -level in question, or by assuming the value of K_a valid in 3.0 M $(Na)ClO_4$ to be the "true" acidity constant. In the latter case complex formation between L and Cl^- is assumed to occur and \bar{n} is now given by

$$\bar{n} = (h - H - [L] - [LCl^-] - [LCl_2^{2-}]) / B \quad (15)$$

where $[L]$ is given by (13) and $[LCl^-]$ and $[LCl_2^{2-}]$ are calculated according to

$$[LCl^-] = \beta_{101} h^{-1} x [HL^+] = \beta_{101} h^{-1} x (C + H - h) \quad (16)$$

$$[LCl_2^{2-}] = \beta_{102} h^{-1} x^2 [HL^+] = \beta_{102} h^{-1} x^2 (C + H - h) \quad (17)$$

The same \bar{n} is now obtained independently of whether the "conditional" or the "true" value of $K_a(HL^+)$ has been used. However, a difference in $\log [L]$ is obtained equal to the difference between the logarithms of the two acidity constants.

The search for the "best" model was performed by using the least squares computer program LETAGROPVRID⁹ (version ETITR¹⁰). The error squares sum $U = \sum (Z_{\text{calc}} - Z_{\text{exp}})^2$ 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.

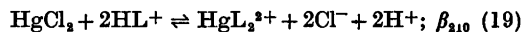
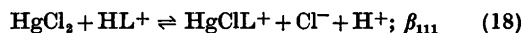
DATA, CALCULATIONS AND RESULTS

The complex formation between $HgCl_2$ and imidazole in a 3.0 M $(Na)ClO_4$ medium was at first investigated. These measurements yielded formation constants for $HgClL^+$, HgL_2^{2+} and $Hg(OH)L^+$. When $HgCl_2$ was dissolved in 3.0 M $(Na)Cl$ medium, $HgCl_4^{2-}$ becomes the dominating mercury(II)-chloride complex, and the complex formation with imidazole was strongly suppressed. It was also found that if these experimental data were to be explained assuming the same equilibrium model as was found at the $HgCl_2$ level, a change in the equilibrium constant for $HgClL^+$ by a factor ~ 500 was observed. This great difference is an indication that additional complexes must be formed upon increasing the chloride content in the ionic medium, *i.e.* when $HgCl_3^-$ and $HgCl_4^{2-}$ are formed.

Supplementary measurements were now performed at different chloride concentrations, X , with $[ClO_4^-] + X = 3.0$ M. The results ob-

tained at the different levels of X will now be discussed in detail.

$HgCl_2 + L$ in 3.0 M $(Na)ClO_4$. Complex formation between $HgCl_2$ and L was at first investigated. Experimental data have been collected covering the following concentration ranges: $0.0025 \leq B \leq 0.080$ M, $0.00125 \leq C \leq 0.320$ M, with $\bar{n} \leq 2$ and $-\log h \lesssim 7.2$. In each titration the quotients C/B were kept constant and had values 0.25, 0.5, 1, 2, 4, 8, 16, 32 and 64. A total of 30 ($B-C$) combinations were investigated. Parts of these experimental data are visualized in Figs. 1 and 3 in the form of Bjerrum plots $\bar{n}(\log [L])$. It was found (*cf.* Fig. 1) that for different quotients C/B , different curves were obtained. Furthermore, the space between the different curves was constant, giving $(\Delta \log B / \Delta \log [L]) \bar{n} = +1$ within the concentration ranges studied. This indicates reactions of the type



By assuming the amount of the species Hg^{2+} , $HgCl^+$, $HgCl_3^-$ and $HgCl_4^{2-}$ to be negligible, \bar{n} is given by

$$\bar{n} = ([HgClL^+] + 2[HgL_2^{2+}]) / ([HgCl_2] + [HgClL^+] + [HgL_2^{2+}]) = (\beta_{111} h^{-1} c x^{-1} + 2\beta_{210} h^{-2} c^2 x^{-2}) / (1 + \beta_{111} h^{-1} c x^{-1} + \beta_{210} h^{-2} c^2 x^{-2}) \quad (20)$$

Thus \bar{n} is a function of both x and $[L]$ ($= K_a h^{-1} c$). The amount of Cl^- set free according to

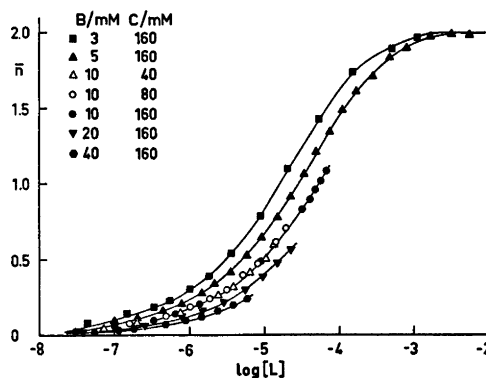


Fig. 1. A part of experimental data plotted as curves $\bar{n}(\log [L])$ for $X = 0$ M. The full curves have been calculated with the set of constants given in Table 4.

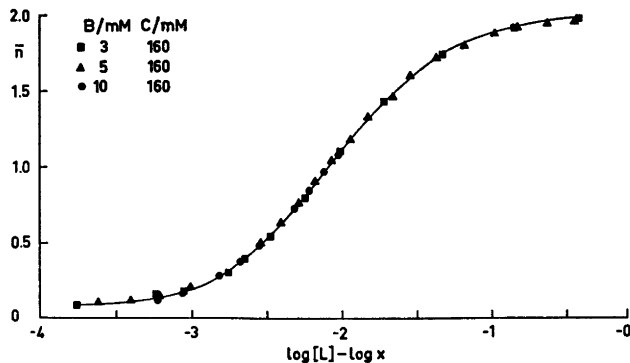


Fig. 2. A part of experimental data plotted as curves $\bar{n}(\log[L] - \log x)$ for $X = 0$ M. The full curve has been calculated with values of β_{111} and β_{210} given in Table 4.

equilibria (18) and (19) can be calculated and is equal to $B\bar{n}$, thus giving $x = [\text{Cl}^-]_{\bar{n}=0} + B\bar{n}$. This means that experimental data can now be recalculated in the form $\bar{n}(\log[L] - \log x)$. Data with $C/B > 8$ were plotted in this form (Fig. 2) giving coinciding curves, indicating that the main equilibria are given by (18) and (19). These curves could be superimposed on plots of normalized curves $\bar{n}(\log v)_u$

$$\bar{n} = (v + 2uv^2)/(1 + v + uv^2) \quad (21)$$

where $\log v = \log \beta_{111} + [\log L] - \log x - \log K_a$ and $\log u = \log \beta_{210} - 2 \log \beta_{111}$

The best fit was obtained with $\log \beta_{111} = -5.50 \pm 0.05$ and $\log \beta_{210} = -11.55 \pm 0.05$. A

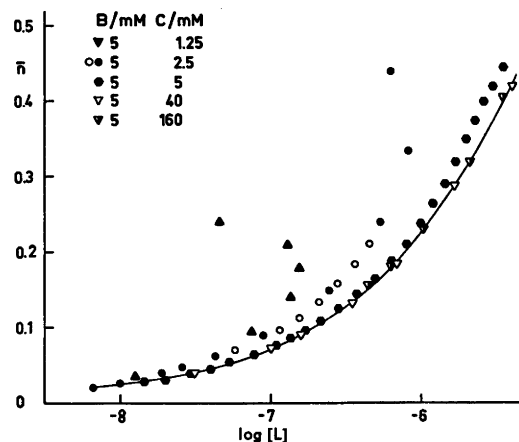


Fig. 3. A part of experimental data with $X = 0$ M plotted as curves $\bar{n}(\log[L])$ for C/B ratios 1/4, 1/2, 1, 8 and 32. The full curve has been calculated with values of β_{111} and β_{210} given in Table 4.

LETAGROP calculation yielded $\log \beta_{111} = -5.531 \pm 0.013$ and $\log \beta_{210} = -11.537 \pm 0.017$ with $\sigma(Z) \times 1000 = 0.6$.

At quotients $C/B < 4$ and $B < 0.020$ M, systematic deviations from the $\bar{n}(\log[L])_B$ curves were observed (see Fig. 3), which indicates that additional complex(es) to those previously found must be present. Among a number of species which were tested, the $\text{Hg}(\text{OH})\text{L}$ complex was found to give the "best" explanation to the experimental data with $\log \beta_{210} = -14.30 \pm 0.02$ and $\sigma(Z) \times 1000 = 3.4$ (see Table 3a).

HgCl₂ + L in 3.0 M (Na)Cl. To determine whether ternary species like $\text{HgCl}_m\text{L}^{2-m}$ ($m \geq 2$) and $\text{HgCl}_n\text{L}_2^{2-n}$ ($n \geq 1$), and eventual quaternary species $\text{Hg}^{2+} - \text{OH}^- - \text{Cl}^- - \text{L}$, exist, the chloride excess, X , was increased to 3.0 M.

At this high chloride concentration HgCl_4^{2-} is the predominating complex. The following concentration ranges have been investigated: $0.0025 \leq B \leq 0.080$ M, $0.005 \leq C \leq 0.320$ M and $-8.0 \leq \log h \leq -5.5$. The quotients C/B ranged from 0.25 to 64, yielding 53 ($B-C$) combinations.

With $C \leq 0.080$ M and $C/B \leq 8$ coinciding $\bar{n}(\log[L])$ curves were obtained independently of B and C (see Fig. 4). These data could be explained very well by assuming a mono-nuclear complex with one imidazole molecule coordinated to the mercury(II) atom. As the variation in x is very small, the number of chloride ions, coordinated in this complex, cannot be obtained.

However, an equilibrium constant for the formation of HgClL^+ , was calculated giving

Table 3a. Results of graphical and LETAGROP calculations. The errors $3\sigma(\log \beta_{pqrs})$ are given when the corresponding equilibrium constant has been varied. In the calculations constants for equilibria (3)–(8) have been taken from Ref. 5. $X=0$ M.

No. of titr./ No. of points	$\sigma(Z) \times 1000$	HgClL ⁺ $\log(\beta_{111} \pm 3\sigma)$	HgL ₂ ²⁺ $\log(\beta_{210} \pm 3\sigma)$	Hg(OH)L ⁺ $\log(\beta_{210} \pm 3\sigma)$	Rem.
15/190	0.6	-5.50(5)	-11.55(5)		graph.
7/52	3.4	-5.53(1)	-11.54(2)		
		-5.53	-11.54	-14.30(2)	

Table 3b. Calculations given in this table have been performed by assuming formation constants for the species HgClL⁺ and HgL₂²⁺ given in Table 3a, to be known. Furthermore the value of K_a taken from Table 2b has been used.

No. of titr./ No. of points	X/M	$\sigma(Z) \times 1000$	HgCl ₂ L $\log(\beta_{112} \pm 3\sigma)$	HgCl ₃ L ⁻ $\log(\beta_{113} \pm 3\sigma)$
7/75	0.1	1.0	-4.46(3)	-
	0.1	1.0		-3.45(3)
	0.1	0.3 ^a	-4.81(3)	-3.81 ^b
4/39	0.2	0.6	-4.38(3)	
	0.2	0.6		-3.67(2)
	0.2	0.5	-4.85(7)	-3.81
7/68	0.4	0.5	-4.15(1)	
	0.4	0.5		-3.74(1)
	0.75	0.3	-3.96(1)	
3/27	0.75	0.3		-3.83(1)
	0.75	0.3		
4/44	1.5	0.9	-3.65(2)	
	1.5	0.9		-3.82(2)
9/42	3.0	1.1	-3.30(1)	
	3.0	1.1		-3.77(1)

^a A calculation based upon data with $\bar{n} \lesssim 0.2$. ^b An average value of $\log \beta_{113}$ taken from data with $X \geq 0.75$ M.

Table 3c. In the calculations presented in this table, equilibria (8)–(10), with equilibrium constants given in Table 2a, have been included. R denotes a rejected complex.

X/M	$\sigma(Z) \times 1000$	HgCl ₂ L $\log(\beta_{112} \pm 3\sigma)$	HgCl ₃ L ⁻ $\log(\beta_{113} \pm 3\sigma)$	HgClL ₂ ⁺ $\log(\beta_{211} \pm 3\sigma)$	HgCl ₂ L ₂ $\log(\beta_{212} \pm 3\sigma)$	Points
0.75, 1.5, 3.0	1.4	-	-3.79(1)	-	-	113
0.1, 0.2, 0.4 ^a	0.9	-4.81(4)	-3.79	-	-	139
0.1, 0.2, 0.4 ^b	1.0	-4.81	-3.79	-10.84(10)	R	191
	1.3	-4.81	-3.79	-	10.26(19)	

^a $\bar{n} \lesssim 0.3$. ^b In these calculations data ($X, \log h$), have been included.

$\log \beta_{111} = -2.84 \pm 0.01$ and $\sigma(Z) \times 1000 = 1.7$, which can be compared with $\log \beta_{111} = -5.53 \pm 0.01$ obtained at $X=0$ M. The great difference, which is about 2.7 logarithmic units, cannot be due to so called "medium effects". Instead it seems more likely that the difference is

caused by an incorrect assumption concerning the equilibrium model at $X=3.0$ M. This indicates that formation of species like HgCl₂L and/or HgCl₃L⁻ are possible.

Although low values in B with $C/B=0.25$, 0.5, 1 and 2 were investigated, no indications

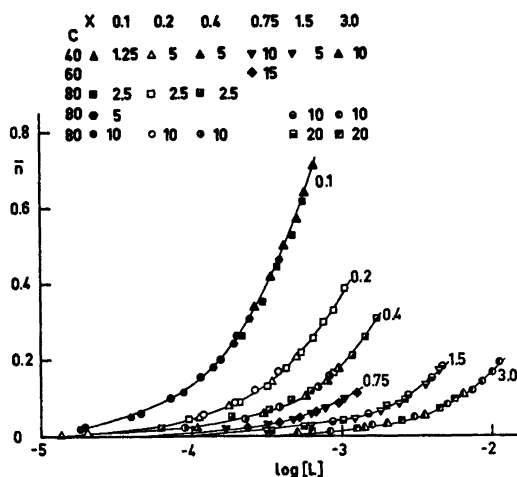


Fig. 4. "Mononuclear" $\bar{n}(\log[L])$ curves at constant levels of X ($=0.1, 0.2, 0.4, 0.75, 1.5$ and 3.0 M). The full curves have been calculated with constants for the binary $\text{Hg}^{2+} - \text{Cl}^-$ species from Ref. 5, the acidity constant of imidazolium from Table 2b and the set of constants proposed in Table 4. The concentrations are given in M (X), mM (C and B). B -values are given to the right of each symbol.

of any quaternary complex $\text{Hg}^{2+} - \text{OH}^- - \text{L} - \text{Cl}^-$ were found. At high ratios C/B , $8 \leq C/B \leq 64$, \bar{n} seems to be dependent on B and C . An analysis of these data indicates formation of acidic complexes of the type $\text{HgCl}_x\text{L}_y(\text{HL})_z^{2-x+z}$. The results and discussions of these complexes will be given in a forthcoming paper.

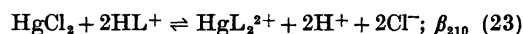
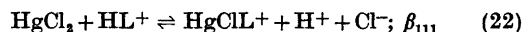
HgCl₂ + L in mixed media, with $[\text{ClO}_4^-] + X = 3.0$ M. To attempt to explain the great differences in the formation constants for HgClL^+ found at levels with $X=0$ and 3.0 , respectively, supplementary measurements were performed. These can be divided into series in which X has been kept constant at levels with $X=0.1, 0.2, 0.4, 0.75$ and 1.5 M. In another series X was varied by adding chloride ions to solutions where $Z=0.7$ and 1.2 , respectively. The concentration ranges investigated were $0.00125 \leq B \leq 0.040$ M, $0.040 \leq C \leq 0.160$ M with $4 \leq C/B \leq 32$ and $3 < -\log h < 8$.

The average ligand number \bar{n} was calculated according to eqn. (12) by using the "conditional" constant for $K_a(\text{HL}^+)$, valid at the X -level in question (cf. eqn. (13)).

Plots $\bar{n}(\log[L])_x$ are given in Fig. 4. This figure clearly shows that the complex formation is systematically suppressed with increasing X . As the curves coincide at each level of X , mononuclear complexes HgCl_xL_y are formed. Furthermore, the amount of soluble complexes seems to decrease with increasing X .

These experimental data have been treated in two ways: (i) separate calculations at each level of X , and the "conditional" acidity constant of imidazolium (see Table 2) was used; (ii) calculations where all X -levels are treated together, including data in the form $(X, \log h)_x$. In these calculations the binary $\text{L} - \text{Cl}^-$ equilibria were included in the equilibrium models.

(i) *Data at constant X.* The equilibria



were established from data with $X=0$ and the calculated values of β_{111} and β_{210} were assumed to be correct. As the curves $\bar{n}(\log[L])_x$ coincide, mononuclear complexes are formed. For data with $\bar{n} \lesssim 0.2$, the species HgCl_2L and HgCl_3L^- were tested one at a time. The results of these calculations are given in Table 3b.

We will now compare the equilibrium constants β_{112} and β_{113} obtained at each level of X . As can be seen from Table 3b, $\log \beta_{112}$ increases from -4.46 ($X=0.1$ M) to -3.30 ($X=3.0$ M). On the other hand $\log \beta_{113}$ yields a nearly constant value with $X=0.4, 0.75, 1.5$ and 3.0 M ($-3.74, -3.83, -3.82, -3.77$). This seems to indicate that HgCl_3L^- is the predominating ternary complex within this concentration range.

With $X < 0.4$ M, β_{113} increases with decreasing X , which could be explained by assuming the calculated constant to represent a sum of two constants, i.e. β_{112} and β_{113} . To test this hypothesis, some additional calculations were performed at $X=0.1$ and 0.2 M. In these HgCl_3L^- with $\log \beta_{113} = -3.81$ (average value from $X=0.75, 1.5$ and 3.0) was included in the equilibrium model. The values of $\log(\beta_{112} \pm 3\sigma)$ found were -4.81 ± 0.03 and -4.85 ± 0.07 , respectively. Thus these calculations showed that experimental data $(Z, \log h)_x, X=0.1,$

0.2, 0.4, 0.75, 1.5 and 3.0 M, can fully be explained by assuming the ternary species HgCl_2L and HgCl_2L^- to exist in addition to HgClL^+ . Data with $\bar{n} > 0.5$ was reached within a rather limited range in X (see Fig. 4). However, within this range there were indications of species $\text{HgCl}_n\text{L}_2^{2-n}$, $n > 0$. Evaluation of formation constants for these complexes will be described below.

(ii) *Data with $0 < X < 3.0$ M.* As pointed out earlier, the concentration scale for protons does not seem to change within this concentration range in X . Therefore data $(Z, \log h)_x$ and $(X, \log h)_z$ were treated together. The same equilibrium model as was found under (i) was tested. The question now is whether the same model and the same equilibrium constants are obtained upon treating the experimental data in this way. All calculations are given in Table 3c.

At first β_{111} was determined from data with $X \geq 0.75$ M, where HgCl_2^{2-} is the predominating binary $\text{Hg}^{2+} - \text{Cl}^-$ complex. This calculation yielded $\log \beta_{111} = -3.79 \pm 0.01$ with $\sigma(Z) \times 1000 = 1.4$. This value is in very good accordance with the average value -3.81 ± 0.04 obtained under (i). The calculated value of $\log \beta_{112}$, derived from data with $X \leq 0.4$ M, was -4.81 ± 0.04 (cf. -4.83 ± 0.04 from (i)). Thus the agreement is good between the formation constants as determined under (i) and (ii).

Concerning eventual complexes $\text{HgCl}_n\text{L}_2^{2-n}$, with $n \geq 0$, data with $\bar{n} > 0.5$ were included. In addition to HgL_2^{2+} , the species HgClL_2^+ and HgCl_2L_2 were tested, with the results given in Table 3c. It was found that each of these complexes could explain data equally well, however in a covariation of β_{211} and β_{212} , β_{212} came out as zero. Thus it seems as if the concentration range in X , within which high \bar{n} values are obtained, should be too small to favour the formation of HgCl_2L_2 .

Hg²⁺ + L in 3.0 M (Na)ClO₄. Attempts have been made to determine the formation constant of HgL^{2+} . Since low ratios C/B must favour the formation of this complex, the titrations were performed in such a way as to increase C/B within each titration, yielding $0 \leq C/B \leq 5$. B was varied within the limits $0.003 \leq B \leq 0.010$ M and to avoid precipitation the available $\log h$ range was restricted to $\log h > -3.1$. In the calculations the formation

constant for HgL_2^{2+} was assumed to be known, as it is well determined from data with $X = 0$. Within the concentration ranges investigated HgOH^+ and $\text{Hg}(\text{OH})_2$ are formed to some extent, as imidazole was added to partly hydrolyzed solutions ($Z \lesssim 0.10$). Thus, besides the eventual formation of HgL^{2+} , there is reason to believe that the complex $\text{Hg}(\text{OH})\text{L}^+$ should be formed too. A good fit to experimental data was obtained ($\sigma(H) \times 1000 = 0.09$) with

$$\log \beta(\text{Hg}^{2+} + \text{HL}^+ \rightleftharpoons \text{HgL}^{2+} + \text{H}^+) = 1.24 \pm 0.12 \text{ and}$$

$$\log \beta(\text{Hg}^{2+} + \text{HL}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Hg}(\text{OH})\text{L}^+ + 2\text{H}^+) = -0.10 \pm 0.07,$$

a value which can be compared with -0.30 obtained from data with $X = 0$.

DISCUSSION

In all, approximately 150 potentiometric titrations (including ~ 4000 experimental points) have been performed in this investigation.* However, as the calculations on this four-component system were very time consuming, the number of experimental data in the calculations have been reduced. It has been shown that when imidazole is added successively to mercury(II) chloride solutions, binary $\text{Hg}^{2+} - \text{L}$ as well as ternary $\text{Hg}^{2+} - \text{Cl}^- - \text{L}$ and $\text{Hg}^{2+} - \text{OH}^- - \text{L}$ complexes are formed. As can be seen from Table 4, the three standard deviations of the formation constants are low and the complexes may thus be considered as well determined.

The results obtained seem to indicate that each of the species Hg^{2+} , HgCl^+ , HgCl_2 and HgCl_3^- form complexes with an imidazole molecule in the solution and the following equilibria could be established



with $\log K = 9.18, 9.18, 3.15$ and 3.08 , respectively. Thus each of the species Hg^{2+} , HgCl^+ ,

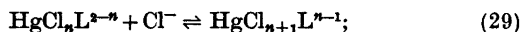
* A complete list of the experimental data is available from this Department.

Table 4. Proposed complexes with formation constants defined according to the equilibria given in the table.

Equilibria	$\log(\beta \pm 3\sigma)$
$\text{Hg}^{2+} + \text{HL}^+ \rightleftharpoons \text{HgL}^{3+} + \text{H}^+$	1.24(12)
$\text{HgCl}_2 + \text{HL}^+ \rightleftharpoons \text{HgClL}^+ + \text{H}^+ + \text{Cl}^-$	-5.53(1)
$\text{HgCl}_2 + 2\text{HL}^+ \rightleftharpoons \text{HgL}_2^{3+} + 2\text{H}^+ + 2\text{Cl}^-$	-11.54(2)
$\text{HgCl}_2 + \text{HL}^+ \rightleftharpoons \text{Hg}(\text{OH})\text{L}^+ + 2\text{H}^+ + 2\text{Cl}^-$	-14.30(2)
$\text{HgCl}_2 + \text{HL}^+ \rightleftharpoons \text{HgCl}_2\text{L}^+ + \text{H}^+$	-4.81(4)
$\text{HgCl}_2 + \text{HL}^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2\text{L}^- + \text{H}^+$	-3.79(1)
$\text{HgCl}_2 + 2\text{HL}^+ \rightleftharpoons \text{HgClL}_2^+ + 2\text{H}^+ + \text{Cl}^-$	-10.84(10)

HgCl_2 and HgCl_2^- forms stronger complexes with the imidazole molecule than with the chloride ion, for which the corresponding values are 7.22, 6.78, 1.07 and 1.07.⁵

Alternatively the results may be interpreted as a series of stepwise reactions according to



with $n=0, 1$ and 2 . The stability constants for these reactions are given in Table 5. In this table other stepwise reactions, found in the different binary as well as ternary systems, are also given.

In addition to mono- and dicoordinated species Hg^{2+} forms with Cl^- and L ternary species which are 3- and 4-coordinated. According to Table 5 a sharp decrease in the stepwise constants is observed upon increasing the coordination number above 2. This effect is assumed to be due to a change in configuration, from linear 2-coordinated to tetrahedral or square planar 4-coordinated species. Furthermore, the stepwise constants defining the uptake of a chloride ion to form 3- and 4-coordinated complexes, is of the same mag-

nitude independently of whether the reactant is a binary $\text{Hg}^{2+} - \text{Cl}^-$, $\text{Hg}^{2+} - \text{L}$ or a ternary $\text{Hg}^{2+} - \text{L} - \text{Cl}^-$ complex.

Thus it seems plausible to estimate

$$\log K(\text{HgClL}_2^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2\text{L}_2) \sim 1.0$$

according to this finding.

As an attempt to illustrate the stability of the various $\text{Hg}^{2+} - \text{Cl}^- - \text{L}$ complexes, a predominance area diagram is given in Fig. 5.

At low ratios $0 < C/B < 4$ a mixed hydroxo complex $\text{Hg}(\text{OH})\text{L}^+$ is formed. It was found that with $X=0$, the maximum amount of $\text{Hg}(\text{OH})\text{L}^+$ is about 10 % of B , while in a perchlorate solution of Hg^{2+} this complex predominates within certain C/B ranges (cf. Fig. 6) and is formed to about 60 % of B .

Although it is impossible from potentiometric data to decide whether this complex really is a $\text{Hg}(\text{OH})\text{L}^+$ or a $\text{HgC}_3\text{H}_3\text{N}_3^+$ complex, we find the first alternative more probable. This is because

(i) in the equilibrium solutions, where effects due to this complex were observed, the hydrolytic species HgOH^+ and $\text{Hg}(\text{OH})_2$ are formed in significant amounts.

Table 5. Some stepwise reactions with constants calculated by means of formation constants proposed in Table 4 (this work), Table 5 (Ref. 5) and $-\log K_w = 14.22$.¹⁷ The different reactions are defining the stepwise uptake of ligands Cl^- , OH^- and L and should be read horizontally. (Example: $\text{HgCl}^+ 6.78 \text{ HgCl}_2$ stands for $\text{HgCl}^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2$ with $\log K = 6.78$).

Hg^{2+}	7.22	HgCl^+	6.78	HgCl_2	1.07	HgCl_2^-	1.07	HgCl_4^{2-}
Hg^{2+}	9.18	HgL^{3+}	7.23	HgClL	0.72	HgCl_2L	1.02	HgCl_2L^-
Hg^{2+}	9.18	HgL^{2+}	9.01	HgL_2	0.70	HgClL_2^+	1.0 ^a	HgCl_2L_2
Hg^{2+}	9.18	HgL^{2+}	12.68	$\text{Hg}(\text{OH})\text{L}^+$				
Hg^{2+}	10.64	HgOH^+	11.56	$\text{Hg}(\text{OH})_2$				
Hg^{2+}	7.22	HgCl^+	11.17	$\text{Hg}(\text{OH})\text{Cl}$				
Hg^{2+}	10.64	HgOH^+	7.71	$\text{Hg}(\text{OH})\text{Cl}$				

^a Estimated value.

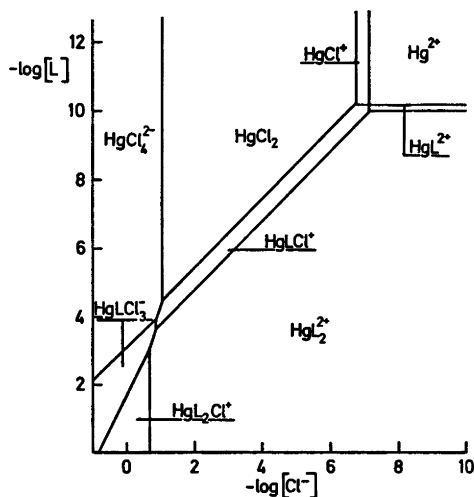
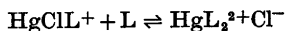
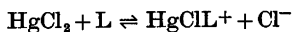
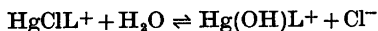


Fig. 5. Predominance area diagram. The composition of the different $Hg^{2+}-Cl-L$ species predominating in a certain $\log[L] - \log[Cl^-]$ area is shown. Along the lines the concentrations of the two adjacent species are equal. In the corner points three species prevail to the same extent. The lines have been calculated by using the constants of Table 5.

(ii) the stepwise equilibria



are well determined and it seems reasonable to assume a similar mechanism



(iii) two coordinated mercury(II) species as a rule are very stable, which favours the hydroxo complex.

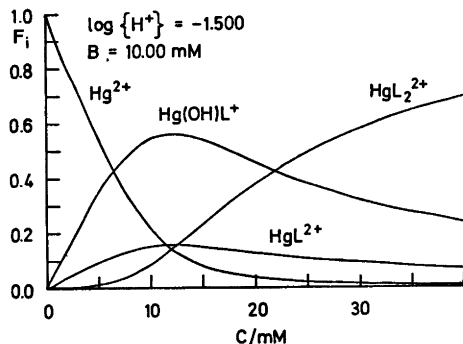


Fig. 6. Distribution diagrams $F_i(C)_{\log A, B}$.

The acidity constant of HgL^{2+} has been calculated to amount to $\log K_a(HgL^{2+}) = -1.54$. Thus this complex is an acid of appreciable strength, stronger than $HgOH^+$, $HgCl^+$ and Hg^{2+} as well, for which the acidity constants are -2.65 , -3.05 and -3.58 , respectively. Thus the introduction of a ligand Cl^- , OH^- or L will increase the acidity of the mercury(II) ion. This is in accordance with earlier findings in the systems $M-L-OH^-$. With $M = Cu^{2+}$,⁹ Ni^{2+} ¹³ and Zn^{2+} ¹⁴ the values found were: $\log K_a(ML^{2+})$, $\log K_a(M^{2+})$; -7.18 , -8.0 ; -9.19 , ≤ -10.5 ; -8.92 , -9.25 , respectively.

Assuming that statistical reasons alone determine the formation of $HgClL^+$ and $Hg(OH)L^+$, equilibrium constants have been calculated according to the formula

$$\beta_{HgL} = 2(\beta_{HgL^{2+}} \cdot \beta_{HgL})^{1/2}$$

Using $\log \beta_{HgL^{2+}} = 18.19$, $\log \beta_{HgL} = 14.00$, $\log \beta_{Hg(OH)} = 22.21$

and $-\log K_w = 14.22$,¹⁷ the calculated values were $\log \beta_{HgL^+} = 16.41$, which is very close to the experimental value of 16.38.

For $Hg(OH)L^+$ the calculated statistical value of $\log \beta_{Hg(OH)L^+}$ is 20.42 compared with 21.90 found experimentally. This great difference between the experimental and statistical value indicates, that the probability of forming $Hg(OH)L^+$ is determined by an entropy as well as by an enthalpy change.

It is interesting to note that the ternary species $Hg(OH)Cl$, $Hg(OH)Br$ ¹⁵ and $Hg(OH)I$ ¹⁶ are formed almost statistically. This seems to indicate that eventual species $HgLBr^+$ and $HgLI^+$ should be formed statistically as in the case with $HgClL^+$.

By comparing the few literature values reported concerning stability constants in the mercury(II)-imidazole system, (see Table 1) great discrepancies are found. However, the formation constants for both HgL^{2+} and HgL_2^{2+} as reported by Marsicano *et al.*² are in rather good accordance with the values deduced in this work.

Acknowledgements. I wish to thank Professor Nils Ingri for much valuable advice, for his great interest, and for all the facilities placed at my disposal. Thanks are also due to Lab.ing. Agneta Nordin for valuable help with some of the measurements. The English of the present paper has been corrected by Dr. Michael

Sharp. The work forms part of a program financially supported by the Swedish Natural Science Research Council.

REFERENCES

1. Brooks, P. and Davidson, N. *J. Am. Chem. Soc.* **82** (1960) 2118.
2. Marsicano, F., Hancock, R. D. and Finkelstein, N. P. *Private communications*.
3. Smith, J. C. *Diss.*, Kansas State Univ., Lawrence 1961.
4. Sjöberg, S. *Acta Chem. Scand.* **25** (1971) 2149.
5. Sjöberg, S. *Acta Chem. Scand. A* **31** (1977) 705.
6. Biedermann, G. and Sillén, L. G. *Ark. Kemi* **5** (1953) 425.
7. Gran, G. *Acta Chem. Scand.* **4** (1950) 559.
8. Sjöberg, S. *Acta Chem. Scand.* **27** (1973) 3721.
9. Ingri, N. and Sillén, L. G. *Ark. Kemi* **23** (1964) 97.
10. Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi* **31** (1969) 353; Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* **31** (1969) 365.
11. Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159; Sillén, L. G. and Warnqvist, B. *Ark. Kemi* **31** (1969) 341.
12. Biedermann, G. and Sillén, L. G. *Ark. Kemi* **5** (1953) 425.
13. Forsling, W. and Sjöberg, S. *Acta Chem. Scand. A* **29** (1975) 569.
14. Forsling, W. *Private communications*.
15. Ahlberg, I. and Leden, I. *Trans. R. Inst. Technol. Stockholm* **249** (1972) 17.
16. Ahlberg, I. *Acta Chem. Scand.* **27** (1973) 3003.
17. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. *Acta Chem. Scand.* **11** (1957) 1034.

Received March 8, 1977.