Metal Complexes with Mixed Ligands. 11. The Formation of Ternary Mononuclear and Polynuclear Mercury(II) Complexes in the System Hg^{2+}—Cl^-—OH^-. A Potentiometric Study in 3.0 M $(Na)ClO_4,Cl$ Media

STAFFAN SJÖBERG

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

The hydrolytic equilibria of the different $HgCl_n^{(2-n)}$ species, $n = 0$, 1, 2, 3 and 4, have been investigated within the range $-9 \leq \log [H^+] \leq -1$. The measurements have been performed as potentiometric (glass electrode) titrations in 3.0 M $(Na)ClO_4,Cl$ media at 25 °C. The measurements can be divided into series in which the ratio total chloride concentration/total mercury(II) concentration has been kept constant at values 0, 1/3, 1/2, 2/3, 1, 2. In two series the chloride excess over the $HgCl_2$ level was kept at 0.1 and 3.0 M, respectively. Data have been analysed using the least squares program LETAGROPVRID. Besides pure binary hydrolytic species, $HgOH^+$, $Hg(OH)_2$ and $Hg_2(OH)_2^{2+}$ and unhydrolyzed mercury-(II) − chloride complexes, $HgCl_n^{(2-n)+}$, $n = 1$, 2, 3 and 4, all data could be explained with the ternary complexes $HgOHCl$, $Hg_2OHCl_2^+$ and $Hg_3(OH)_2Cl^{3+}$.

In a series of investigations in progress in this department, aqueous equilibria and complex formation in metal ion systems, containing three or four reacting components, are under extensive investigations. Our main interest is focused on the formation of ternary complexes and particularly towards those containing OH^-. The systems under study are: $M - OH^- - L$, $M - OH^- - Cl^-$ and $M - OH^- - L - Cl^-$, where M stands for the metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and L for imidazole, $C_3H_4N_2$.

The aim of the present paper is to give and discuss the results obtained in the three components system $Hg^{2+} - OH^- - Cl^-$.

PREVIOUS STUDIES

The system $Hg^{2+} - OH^-$. The hydrolytic equilibria in Hg^{2+}-solutions have been extensively investigated by means of a great number of methods.[1-9] In 1952 Hietanen and Sillén[2] made accurate emf-measurements using glass and redox electrodes in 0.5 M $(Na)ClO_4$ medium. With the total mercury(II) concentration, B, ranging from 0.001 to 0.015 M, they found the hydrolytic species to be $HgOH^+$ and $Hg(OH)_2$ with $\log K_a(Hg^{2+}) = -3.70$ and $\log K_a(HgOH^+) = -2.60$. In order to find out whether polynuclear complexes exist in hydrolyzed Hg^{2+}-solutions, Ahlberg[3] (1962) extended the measurements to more concentrated solutions ($0.0025 \leq B \leq 1.3$ M). As ionic medium she used 3 M (Na) ClO_4, 3 M (Mg)ClO_4 and 3 M (Ca)ClO_4. Ahlberg concluded that in addition to the previously found mononuclear complexes $HgOH^+$ and $Hg(OH)_2$, polynuclear complexes also exist. At B-values 0.1, 0.5 and 1.0 M and within the $-\log h$ range 0.3 − 2.0 the complexes Hg_2OH^{3+}, $Hg_2(OH)_2^{2+}$ and $Hg_4(OH)_3^{5+}$ were found.

X-Ray scattering measurements on hydrolyzed mercury(II) perchlorate solution have been performed by Johansson.[8] It was concluded that polynuclear complexes are formed, and besides binuclear, trinuclear rather than tetranuclear complexes were proposed. By comparing the result of the solution X-ray measurements with the crystal structure of the solid pha-

ses $Hg_5O_2(OH)_2(ClO_4)_4(H_2O)_x$ (triclinic),[10] $Hg_7O_4(OH)_2(ClO_4)_4$ (orthorhombic)[11] and $Hg_2O(OH)ClO_4$ (monoclinic),[46] Johansson could also derive possible structures for some hydrolysis complexes of mercury(II) in solution.

The system $Hg^{2+} - Cl^-$. It is well-known that Hg^{2+} forms a series of mononuclear complexes $HgCl_n^{(2-n)+}$, with $n = 1$, 2, 3 and 4,[1] (see Table 1) and these equilibria have been investigated in water solutions using potentiometric, calorimetric, solubility and extraction methods.

The formation of polynuclear $Hg^{2+} - Cl^-$ complexes was claimed by Linhart[15] in 1915. He concluded, by measuring the distribution of $HgCl_2$ between a water and benzene phase, that the species Hg_2Cl_4, $Hg_2Cl_5^-$ and $Hg_2Cl_6^{2-}$ were formed. However, in solutions with the $HgCl_2$ concentration less than 0.2 M, Ciavatta[16] found no evidence for the formation of polynuclear complexes. Recently Sandström[17] has shown that in concentrated solutions ($B \geq 0.5$ M) with a Cl/Hg mol ratio around three, polynuclear complexes occur. His X-ray diffraction as well as Raman data were explained by assuming the dominating complex to be tri- and tetranuclear with double chlorine bridges between the mercury atoms.

The system $Hg^{2+} - Cl^- - OH^-$. Studies of the hydrolytic equilibria of the $HgCl_n^{(2-n)+}$-species seem to have been restricted to the $HgCl_2$-complex.[18-21] Recent careful work in Ciavattas[16] laboratory on the hydrolysis of $HgCl_2$ in 1.0 M $(Na)ClO_4$ medium has shown that the hydrolytic species HgOHCl and $Hg(OH)_2$ predominate in a concentration range 0.005 – 0.2 M in $HgCl_2$. This equilibrium model was also reported by Partridge et al.[22] in 1965, valid at zero ionic strength. Hydrolytic equilibria in solutions containing $HgCl^+$, $HgCl_3^-$ and $HgCl_4^{2-}$ do not seem to have been investigated.

The crystal structure of several mercury(II) oxide chlorides have been determined by the single crystal X-ray method.[23-27] In these structures, mercury and oxygen usually form endless chains or networks of different geometries. In Hg_3OCl_4, however,[24] trinuclear pyramidal ions $OHg_3Cl_3^+$ and chloride ions form the structure. Another trinuclear complex $SO_4 - Hg - OH - Hg - OH - Hg - SO_4$ (zigzag form) exists as isolated units in the compound $Hg(OH)_2 \cdot 2HgSO_4$.[28] In $HgO \cdot Hg(CN)_2$[29] dinuclear molecules $Hg_2O(CN)_2$ are the building elements.

No investigation dealing with the structure of an $Hg_q(OH)_pCl_r$ complex in water solutions has yet been reported.

EXPERIMENTAL

Chemicals and analysis. Sodium chloride (Merck p.a.) was dried at 200 °C and used without further purification. Fresh chloride solutions were always used in the measurements to avoid the contamination by bacteria.

Sodium perchlorate, perchloric acid and *sodium hydroxide* were prepared and analyzed as described earlier.[30]

Mercury(II) perchlorate was prepared by dissolving a weighed amount of HgO (Merck p.a.) in a known excess of standardized $HClO_4$. It was checked that no opalescence appeared due to the formation of Hg_2Cl_2 upon adding an excess of Cl^-.

Mercury(II) chloride (Merck p.a.) was recrystallized from water and dried over H_2SO_4

Table 1. Previously published results log K_n ($HgCl_{n-1}^{(3-n)+} + Cl^- \rightleftharpoons HgCl_n^{(2-n)+}$) valid at 25 °C.

Method	Medium, M	log K_1	log K_2	log K_1K_2	log K_3	log K_4	Ref.
red. Hg	0.5 $(NaClO_4)$	6.74	6.48	13.22	0.85	1.00	12
dis	0.5 $(NaClO_4)$	6.74	6.48	13.22	0.95	1.05	42, 12
sp	0.5 $NaClO_4$				0.66	1.10	43
red. Hg	1.0 $(NaClO_4)$	6.72	6.51	13.23	1.00	0.97	13
red. Hg	3.0 $(Na)ClO_4$	7.07	6.91	13.98	0.75	1.38	14
		± 0.15	± 0.15		± 0.12	± 0.06	
cal	3.0 $(Na)ClO_4$				1.08	1.09	14
					± 0.21	± 0.24	
gl	3.0 $(Na)ClO_4$,Cl	7.22	6.78	14.00	1.07	1.07	This
		± 0.03	± 0.05		± 0.03	± 0.05	work

in a vacuum desiccator. Small amounts (less than 0.1 %) of insoluble products, probably Hg_2Cl_2, were filtered off before use. The mercury content was analyzed gravimetrically as HgS and was about 0.2 % less than that expected from the amount weighed. Solutions of known $HgCl_2$ concentration were prepared by dissolving the solid according to its formula weight.

Determination of H. The analytical H^+-concentration, H, (calculated over the 0-level $HgCl_2$, Cl^- and H_2O) must be known very accurately in order to obtain reliable results. Of course all test solutions have been prepared by mixing reagents with known H. As long as the quotient (total chloride concentration, Y)/(total mercury(II) concentration, B) ≥ 2, the value of H could be controlled using Gran extrapolation method.[31] At quotients $Y/B < 2$, the complex formation starts at $-1 > \log[H^+] > -3$ and no accurate determination of H can be made with this method. However, in separate experiments, NaCl was added to suppress the hydrolytic equilibria and H could be determined as above. All test solutions were analyzed and controlled in this way.

Apparatus. The thermostat, cell arrangement and experimental details of the emf measurements were fully described earlier.[30,32] The electrodes used were of the type Beckman No. 40498 and Ingold NS201. In order to check their reliability, usually two electrodes were immersed in the equilibrium solution during the titration. If a drift in the difference between the measured emf values was found to exceed 0.2 mV, these experimental points were not included in the calculations. Emf values stable to within $0.01 - 0.02$ mV were reached within $15 - 20$ min.

Method. The measurements were carried out as a series of potentiometric titrations at 25 °C. The solutions were made to contain $[ClO_4^-] + X = 3.0$ M, where X is the chloride excess over $HgCl_2$. This medium will enable us to use and compare the results obtained in previous investigations concerning the chloride complex formation (Arnek[14]) and hydrolytic equilibria of Hg^{2+} (Ahlberg[3]). The solutions had the general composition B M Hg^{2+}, H M H^+, Y M Cl^-, $([ClO_4^-] + Y - 2B - H)$ M Na^+ and 3.0 M ClO_4^-, $(X \leq 0)$ or $(3.0 - X)$ M ClO_4^- $(X \geq 0)$. In general B and Y were kept constant in each of the titrations. These can be divided into series in which the ratios Y/B have been kept constant. The free hydrogen ion concentration, h, was varied by adding H^+ or OH^- and determined by measuring the emf of the cell $- RE$ ||equilibrium solution|glass electrode $+$ The same reference half cell (RE) as before was used.[31] The emf in mV of this cell may be written

$$E = E_0 + 59.157 \log h + Ej \qquad (1)$$

where $Ej = -16.7$ h mV[33] has been used.

In the present investigation changes in E_0 were observed, especially when working with high B ($B \geq 0.04$ M). Within the concentration range $B \leq 0.320$ M, the change in E_0 was 12.0 mV M^{-1} at $[H^+] \sim 0.1$ M. To find out whether this change is dependent on $[H^+]$, additional measurements were performed in which data in the form $E(B)_{[H^+]}$ were collected. The measurements were performed at $[H^+] = 0.4$ and 0.7 M respectively with B ranging from 0 to 1.0 M. In these measurements the change in E_0 due to B was 10.4 ± 0.1 and 10.5 ± 0.1 mV M^{-1}, respectively; thus a slightly lower value compared with that obtained at $[H^+] = 0.1$ M was obtained. This may indicate that at this H^+-level, complex formation occurs to some extent at high B, however, the effects expressed in mV are less than ~ 0.2 mV for the highest B-value (0.160 M) investigated.

The dependence of E_0 due to the total concentration of Cl^- and $HgCl_2$ was also investigated. Within the ranges $0 \leq X \leq 3.0$ M (with $[ClO_4^-] + X = 3.0$ M) and $0 \leq [HgCl_2] \leq 0.100$ M the values found were 0 ± 0.1 mV M^{-1} and -3.0 ± 0.5 mV M^{-1}, respectively. Thus the concentration scale for H^+ does not seem to have changed although the amount of ClO_4^- ions has been completely changed to Cl^- ions.

We will assume the presence of 3-component equilibria of the general form

$$pH_2O + qHgCl_2 + rCl^- \rightleftharpoons (Hg)_q(OH)_pCl_r^{(2q-p-r)+} + pH^+ + 2qCl^-; \ \beta_{pqr} \qquad (2)$$
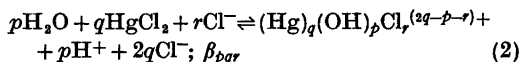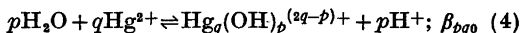
Besides the 3-component equilibria in (2) we have first to consider (i) the complex formation between Hg^{2+} and Cl^- according to

$$Hg^{2+} + rCl^- \rightleftharpoons HgCl_r^{(2-r)+}; \ \beta_{01r} \qquad (3)$$
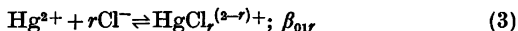
where $r = 1, 2, 3$ and 4.

(ii) the hydrolysis of Hg^{2+}

$$pH_2O + qHg^{2+} \rightleftharpoons Hg_q(OH)_p^{(2q-p)+} + pH^+; \ \beta_{pq0} \qquad (4)$$

with pq-combinations as determined in this investigation: 1,1, 2,1 and 2,2 (see below).

Data treatment. The refinement of constants and the error calculations were performed with the least squares program LETAGROPVRID,[34] version ETITR.[35] On treating the emf data the error squares sums $U = \sum (Z_{calc} - Z)^2$, where $Z = h - H/B$, were minimized. The standard deviations are defined and calculated according to Sillén.[36] The computation was performed on a CD 3300 computer.

DATA, CALCULATIONS AND RESULTS

The evaluation of the different equilibria in the system $Hg^{2+} - Cl^- - OH^-$ will be much simplified if it can be divided into smaller

systems in which the number of equilibria is reduced. The different "subsystems" chosen in the present investigation were:

(1) the hydrolysis of $HgCl_2$ at $X = 0$ M,
(2) the hydrolysis of $HgCl_4^{2-}$ at $X = 3.0$ M,
(3) the hydrolytic equilibria in solutions containing mixtures of $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$,
(4) the hydrolysis of Hg^{2+} at $Y = 0$ M,
(5) the hydrolytic equilibria in solutions containing mixtures of Hg^{2+}, $HgCl^+$ and $HgCl_2$, e.g. $0 < Y/B < 2$.

The results obtained will now be discussed in detail.

(1) *Hydrolysis of $HgCl_2$ in 3.0 M (Na)ClO_4.* When dissolving $HgCl_2$ in an acid solution, where the hydrolysis is suppressed, $HgCl_2$ becomes the dominating mercury(II)-chloride complex, while less than 1 % of B is transformed to $HgCl^+$, $HgCl_3^-$ and $HgCl_4^{2-}$ species (*cf.* Fig. 1).

Values of B ranging from 0.0025 to 0.100 M were investigated. Measurements with $B > 0.1$ M could not be realized due to the limited solubility of $HgCl_2$ in 3 M $NaClO_4$ medium. The available log h range was $-7 \lesssim \log h \lesssim -4$ giving $Z \lesssim 0.6$. As is seen in Fig. 2, where $Z(\log h)_B$ curves are plotted, B increases with decreasing log h at a given Z-value. This indicates that Cl^- is set free in the hydrolysis reactions. From the different Z-curves it was found that $(\Delta \log B/\Delta \log h)_Z = -1$ for $B < 0.01$ M.
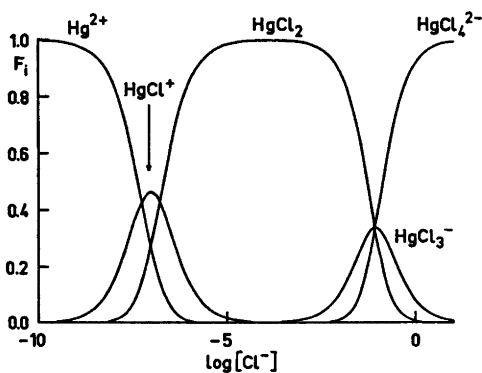

Fig. 1. Distribution diagram $F_i(\log[Cl^-])_B$. F_i is defined as the ratio between mercury(II) in a species and total mercury(II), B. The final proposed constants given in Table 5 have been used in the calculation.
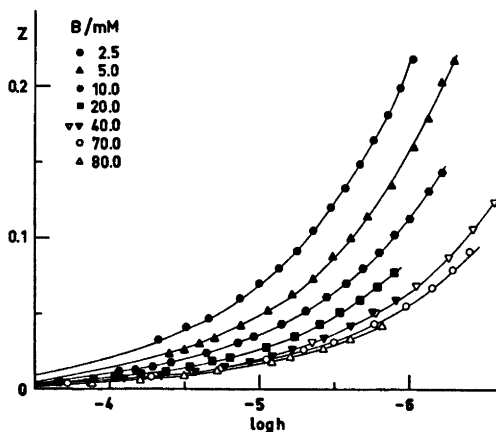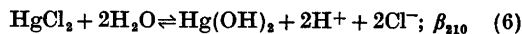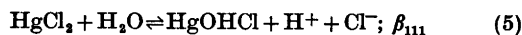

Fig. 2. A part of experimental data plotted as curves $Z(\log h)_B$ for $X = 0$ M. Open symbols are obtained in forward titrations (decreasing log h) and filled in reverse titrations. The full curves have been calculated with the set of proposed constants in Table 5.

This indicates reactions of the type:

$$HgCl_2 + H_2O \rightleftharpoons HgOHCl + H^+ + Cl^-; \ \beta_{111} \quad (5)$$

$$HgCl_2 + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+ + 2Cl^-; \ \beta_{210} \quad (6)$$

By assuming the concentrations of Hg^{2+}, $HgCl^+$, $HgCl_3^-$, $HgCl_4^{2-}$ and $HgOH^+$ to be negligible compared with the concentration of $HgCl_2$, Z is given by

$$Z = ([HgOHCl] + 2[Hg(OH)_2])/([HgCl_2] + [HgOHCl] + [Hg(OH)_2]) = (\beta_{111}h^{-1}x^{-1} + 2\beta_{210}h^{-2}x^{-2})/(1 + \beta_{111}h^{-1}x^{-1} + \beta_{210}h^{-2}x^{-2}) \quad (7)$$

i.e. Z is solely a function of h and x. As BZ is equal to the amount of Cl^- set free, x can now be calculated by using the relation

$$x = x_{Z=0} + BZ \quad (8)$$

The experimental $Z(\log h)_B$-data were now recalculated in the form $Z(-\log h - \log x)_B$. Data with $B \leq 0.01$ M were plotted in this form (see Fig. 3) giving coinciding curves, indicating that the proposed equilibria in (5) and (6) predominate. These curves were superimposed on plots of normalized functions $Z(\log v)_B$, where

$$Z = (v + 2uv^2)/(1 + v + uv^2)$$
$\log v = \log \beta_{111} - \log h - \log x$; $\log u = \log \beta_{210} - 2 \log \beta_{111}$
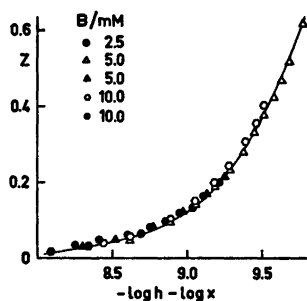
Fig. 3. Experimental data plotted as curves $Z(-\log h - \log x)_B$ for $X = 0$ M and $B \leq 0.01$ M. The full curve has been calculated with the set of proposed constants in Table 5.

The best fit was obtained with log $\beta_{111} = -9.90 \pm 0.05$ and log $\beta_{210} = -20.20 \pm 0.10$. At $B > 0.01$ M $(\Delta \log B/\Delta \log h)_Z > -1$ and the different $Z(-\log h, -\log x)_B$-curves no longer coincide, indicating that another complex(es) must be included in the equilibrium model. Assuming the potentiometrically determined equilibrium constants given by Arnek for the formation of $HgCl_3^-$ and $HgCl_4^{2-}$ to be correct, systematic deviations were found at high B. In order to determine whether ternary polynuclear complexes are present, a pqr analysis was performed. The best fit was obtained with the complex $Hg_3(OH)_3Cl^{2+}$ giving $\sigma(Z) \times 1000 = 1.3$, but the complexes Hg_2OHCl_3, $Hg_2(OH)_2Cl^+$ and $Hg_3(OH)_2Cl_3^+$ could explain data as well (all giving $\sigma(Z) \times 1000 = 1.4$). However, it was also found that a change in the equilibrium constant for $HgCl_3^-$ by 0.3 logarithmic units (log $\beta_{013} = 1.08 \pm 0.03$) gave a fit as good as with any polynuclear complex (see Table 2). This value is in good agreement with that reported by Arnek from his calorimetric measurements (log $\beta_{013} = 1.08 \pm 0.21$).

Supplementary measurements were now performed with a slight excess Cl^- ($X = 0.001 - 0.003$ M). Calculations, given in Table 2, show that at this level log $\beta_{013} = 1.07 \pm 0.04$, while a change of about 0.2 log units was found in the equilibrium constant for the polynuclear complexes mentioned above. Thus it is reasonable to assume the "polynuclear effect" to be caused by a too small value in β_{013}. Measurement at $X = 0.100$ M will also confirm this (see below).

Table 2. Results of graphical and LETAGROP calculations concerning the complexes formed and defined according to the equilibria:
$$pH_2O + qHgCl_2 + rCl^- \rightleftharpoons Hg_q(OH)_pCl_r^{(2q-p-r)+} + pH^+ + 2qCl^-; \quad \beta_{pqr}$$
The errors $3\sigma(\log \beta_{pqr})$ are given (in parentheses) when the corresponding equilibrium constant has been varied.

No. of titr./No. of points	Y/mM	HgOHCl log β_{111}	Hg(OH)$_2$ log β_{210}	HgCl$_3^-$ log β_{013}	HgCl$_4^{2-}$ log β_{014}	HgCl$^+$ log β_{011}	Hg^{2+} log β_{010}	$\sigma(Z) \times 1000$	Remarks
17/337	2B	$-9.90(5)$	$-20.20(10)$	–	–	–	–	–	graphical
9/132	2B+X	$-9.91(1)$	$-20.18(2)$	1.08(3)	–	–	–	1.9	$X = 0.001 - 0.003$ M
7/118	2B+100	$-9.94(2)$	$-20.19(3)$	1.07(3)	2.14(4)	–	–	0.7	
2/30	B/3	$-9.90(1)$	$-20.22(2)$	1.07(4)	2.14	$-6.83(9)$	$-14.01(4)$	1.7	$B \leq 10$ mM
3/66	B/2	$-9.83(1)$	$-20.26(3)$	1.07	2.14	$-6.82(6)$	$-14.01(2)$	3.3	$B \leq 10$ mM
2/44	2B/3	$-9.84(1)$	$-20.26(1)$	1.07	2.14	$-6.83(3)$	$-14.01(2)$	4.5	$B \geq 10$ mM
5/97	B	$-9.94(3)$	$-20.22(2)$	1.07	2.14	$-6.78(2)$	$-13.99(2)$	2.5	$B \leq 10$ mM
	B/3·B	$-9.84(1)$	$-20.27(2)$	1.07	2.14	-6.91	-13.98	3.0	
	B/3·B	$-9.90(5)$	-20.23	1.07	2.14	$-6.78(1)$	$-14.01(11)$	–	graphical
12/237		$-9.86(1)$	$-20.24(1)$	1.07	2.14	$-6.91(5)$	$-13.98(15)$	4.6	$B \leq 10$ mM
				0.75(12)	2.13(8)				Arnek (pot.)
				1.08(21)	2.17(9)				Arnek (cal.)

(2) *Hydrolysis of $HgCl_4^{2-}$ in 3.0 M (Na)Cl.* Some measurements were performed with $X = 3.0$ M. At this chloride level $HgCl_4^{2-}$ is the predominating $Hg^{2+} - Cl^-$ complex (*cf.* Fig. 1). For $B \leq 0.010$ M, Z reached a maximum value of ~ 0.1, and the complex formation was suppressed to log $h < -10.5$. It was found that these experimental data could not be explained by assuming HgOHCl to be the main hydrolytic species. The experimental difficulties at this high pH are great. Since reliable results cannot be obtained with the glass electrode, we find it unwise to try to explain the effects as caused by complex formation.

(3) *Hydrolysis of $HgCl_2 + HgCl_3^- + HgCl_4^{2-}$ mixtures.* To attempt to evaluate the hydrolytic species formed from $HgCl_3^-$ and $HgCl_4^{2-}$, measurements were performed at a constant chloride level $X = 0.100$ M.

In the measurements, B ranged from 0.005 to 0.100 M, $-9 \leq \log h \leq -6$ giving $Z \lesssim 0.6$.

A calculation based upon the equilibrium model found at $X = 0 - 0.003$ M gave the result given in Table 2. log $\beta_{013} = 1.07 \pm 0.04$ is a value in very good agreement with that found at $X = 0$ and log $\beta_{014} = 2.14 \pm 0.04$ can be compared with Arneks 2.13 ± 0.06 (red. Hg) and 2.17 ± 0.09 (cal.). The constants log β_{111} and log β_{210} were found to be -9.90 ± 0.01 and -20.22 ± 0.02, values in good agreement with those obtained at the lower chloride level. The complexes

$HgCl_2OH^-$, $HgCl_3OH^{2-}$, $HgCl_2(OH)_2^{2-}$ and $HgCl(OH)_3^-$ were also tested, but without any significant improvement.

We may thus conclude by summarizing that in solutions of $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$, the predominating hydrolytic species within the log h range -4 to -9, are HgOHCl and $Hg(OH)_2$.

(4) *Hydrolysis of Hg^{2+} in 3.0 M (Na)ClO$_4$.* Before investigating the hydrolysis reactions in solutions containing $HgCl^+$, some titrations were performed in order to check the equilibrium model in hydrolyzed Hg^{2+}-solutions, reported by Ahlberg.[3]

The concentration ranges studied were $0.005 \leq B \leq 0.160$ M, $-5 \leq \log h \leq -1$, with $Z \leq 2.00$. With $B \leq 0.010$ M experimental data could be explained with the complexes $HgOH^+$ (log $\beta_{110} - 3.58 \pm 0.02$) and $Hg(OH)_2$ (log $\beta_{210} = 6.228 \pm 0.004$). These equilibrium constants are in good agreement with those reported by Ahlberg.

In the polynuclear range ($B > 0.01$ M) a *pq*-analysis showed that all experimental data could be explained by assuming $Hg_2(OH)_2^{2+}$ to be the only polynuclear complex. A good fit was obtained with log $\beta_{22} = -4.84 \pm 0.02$ giving $\sigma(Z) \times 1000 = 1.5$. Attempts were also made to add the complex Hg_2OH^{3+}, which has been proposed by Ahlberg (see Table 3). However, a great uncertainty in β_{12} was always obtained

Table 3. Results of LETAGROP calculations concerning the complexes formed in hydrolyzed $Hg^{2+} - ClO_4^-$ solutions. The stability constants β_{pq} are defined according to $qHg^{2+} + pH_2O \rightleftharpoons Hg_q(OH)_p^{(2q-p)+} + pH^+$; β_{pq} Ranges 1 and 2 refer to data with $0.0025 \leq B \leq 0.010$ M and $0.010 \leq B \leq 0.160$ M, respectively. In some calculations E_0 for the glass electrode was covaried with one or two stability constants. ΔE_0 is defined as $E_0(\text{exp}) - E_0(\text{calc})$. In the lower half of the table some LETAGROP calculations have been made on $Z(\log h)_B$-data (3.0 M (Na)ClO$_4$ medium) published by Ahlberg.[3]

Range	$\sigma(Z)$ $\times 1000$	log $(\beta_{11} \pm 3\sigma)$	log $(\beta_{2i} \pm 3\sigma)$	log $(\beta_{12} \pm 3\sigma)$	log $(\beta_{22} \pm 3\sigma)q$	Rem.
1 (63 points)	4.9	$-3.58(2)$	$-6.228(4)$	$-$	$-$	
2 (92 points)	4.5	-3.58	-6.228	$-2.60(5)$	$-$	
	3.2	-3.58	-6.228	$-2.51(5)$	$-$	a
	2.5	-3.58	-6.228		$-4.81(2)$	
	1.5	-3.58	-6.228		$-4.84(2)$	b
	1.5	-3.58	-6.228	$-3.38(31)$	$-4.89(7)$	c
$B = 0.1$ M	0.9	-3.55	-6.21	$-2.66(8)$	$-5.41(4)$	
	3.0	-3.55	-6.21	$-$	$-4.88(9)$	$\Delta E_0 = 0.15$ mV

^{a} $\Delta E_0 = 0.55$, 1.29, 0.01, 0.04, 0.04, 0.98 mV. ^{b} $\Delta E_0 = -0.15$, -0.36, -0.04, -0.27, -0.18, -0.08 mV. ^{c} $\Delta E_0 = -0.04$, -0.10. -0.04, -0.23, -0.14, -0.09 mV.

and the error squares sum was not significantly lowered. This seems to indicate that if Hg_2OH^{3+} is formed, it exists only in small amounts ($< 1\%$ of B), within the concentration range investigated.

As no primary $E(H)_B$ data were given by Ahlberg, it was difficult to test different assumptions concerning the complexes found. Calculations based upon her published $Z(\log h)_B$ data will always be affected by the fact that E_0 of the glass electrode was determined under the assumption that the complex Hg_2OH^{3+} was formed with $\log \beta_{12} = -2.70$. As a consequence, Z as well as $\log h$, are to some extent dependent on the refined value in E_0.

However, some calculations have been performed on her $Z(\log h)_B$ data with $B = 0.1$ M (see Table 3). As can be seen from this table, a calculation where $Hg_2(OH)_2^{2+}$ was assumed to be the only polynuclear complex, gave $\log \beta_{22} = -4.88 \pm 0.09$ (cf. the value -4.84 ± 0.02 obtained in this work) with $\sigma(Z) \times 1000 = 3.0$ and a correction in E_0 of 0.15 mV. As a fairly good explanation is obtained and the result is in accordance with that obtained in the present investigation, we will, in the following calculations, assume $Hg_2(OH)_2^{2+}$ to be the only polynuclear complex within the concentration ranges investigated.

(5) *Hydrolysis of* $Hg^{2+} + HgCl^+ + HgCl_2$ *mixtures.* For solutions, in which $Y/B < 2$, the amount of $HgCl^+$ at equilibrium is at most about 50 % of B (see Fig. 1). This means that at these ratios the hydrolysis of Hg^{2+} and $HgCl_2$ must be accounted for as well.

The ratios $Y/B = 0.5$ and 1.0 were at first investigated. However, it was later found that to obtain a full understanding of the equilibrium situation at high B, the data range had to be extended to include $Y/B = 1/3$ and 2/3 as well (see below).

The following concentration ranges were investigated: $0.0025 \leq B \leq 0.160$ M and $-8 \lesssim \log h \lesssim -1$, with $Z \lesssim 2 - Y/B$. With $B \leq 0.010$ M, the experimental $Z(\log h)_{Y/B}$-curves were found to coincide up to $Z = 2 - Y/B$. Coinciding curves indicate a complex of composition HgOHCl, which can be shown as follows. Assuming that the concentration of $HgCl_3^-$, $HgCl_4^{2-}$ and Cl^- may be neglected in the range studied, the following expression will hold taking Hg^{2+}, Cl^-, H_2O as 0-point.

$$Y/B = ([HgCl^+] + 2[HgCl_2] + [HgOHCl])/ \\ ([Hg^{2+}] + [HgOH^+] + [Hg(OH)_2] + [HgCl^+] + \\ [HgOHCl] + [HgCl_2]) \tag{9}$$

$$Z = ([HgOH^+] + 2[Hg(OH)_2] + [HgOHCl])/ \\ ([Hg^{2+}] + [HgOH^+] + [Hg(OH)_2] + [HgCl^+] + \\ [HgOHCl] + [HgCl_2]) \tag{10}$$

Taking the expression for $[HgCl_2]$ from (9), and inserting in (10), we have after rearrangement:

$$Z = ([HgOH^+] + 2[Hg(OH)_2] + [HgOHCl])(2 - \\ Y/B)/(2([Hg^{2+}] + [HgOH^+] + [Hg(OH)_2]) + \\ [HgCl^+] + [HgClOH]) = (\beta_{110}h^{-1} + 2\beta_{210}h^{-2} + \\ \beta_{111}h^{-1}x)(2 - Y/B)/(2(1 + \beta_{110}h^{-1} + \beta_{210}h^{-2}) + \\ \beta_{011}x + \beta_{111}h^{-1}x) \tag{11}$$

Thus at high pH, Z will reach a limiting value $2 - Y/B$. Furthermore, Z is a function of h, x and Y/B. From (9) it can easily be shown that x is a function of h and Y/B, i.e. Z depends only on h and Y/B. (The derivation of eqn. (11) has earlier been given by Ahlberg and Ledén in Ref. 41).

By assuming different values of β_{111}, taking β_{110}, β_{210} from $Y/B = 0$, β_{011} and β_{012} according to Arnek, one may calculate sets of Z-curves by means of the computer program HALTAFALL,[37] or SOLGASWATER.[45] Curve fitting gave the results given in Table 2. In the LETAGROP calculations β_{011} and β_{012} as well as β_{111} and β_{210} were refined and the results are given in the same table.

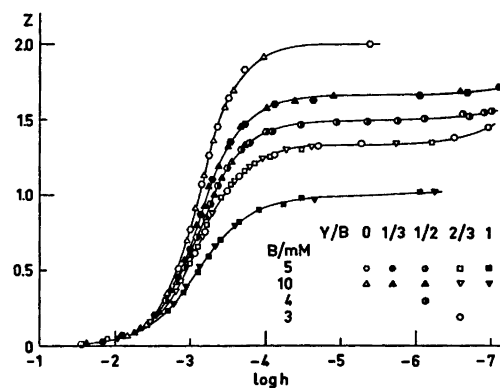As can be seen from Fig. 4, a narrow Z-range, $Z > 2 - Y/B$, is obtained at low $B (B \leq 0.005$ M).

Fig. 4. Experimental data plotted as curves $Z(\log h)_B$ for quotients $Y/B = 0$, 1/3, 1/2, 2/3 and 1.
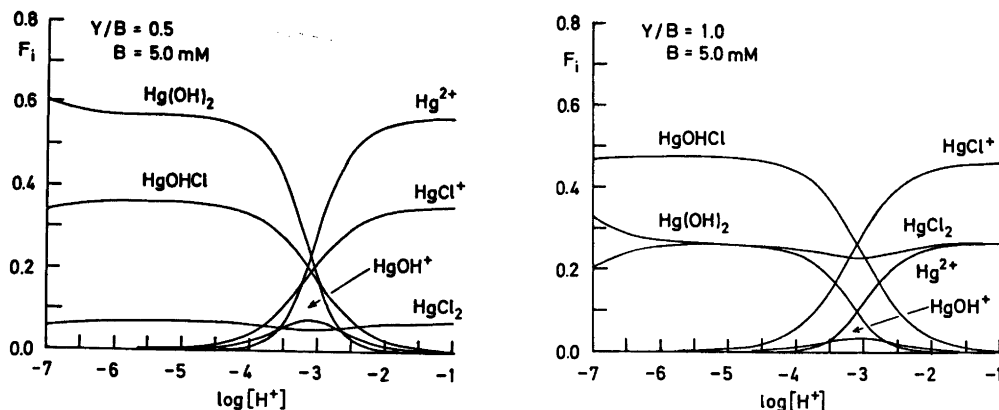
Fig. 5. Distribution diagrams $F_i(\log h)_B$ for $Y/B = 1/2$ (a) and 1 (b).

Within this range it was found that reproducible and reversible equilibria were obtained only in hydrolyzed solutions, which were allowed to stand for several weeks. Otherwise effects, probable due to slow precipitation reactions, were observed.

Distribution diagrams are given in Fig. 5.

With $B > 0.010$ M systematic deviations from the mononuclear curves were observed indicating the existence of polynuclear hydrolytic species. As the deviations could not be explained with the binary $Hg_2(OH)_2{}^{2+}$-complex, ternary polynuclear complexes $Hg_q(OH)_pCl_r$ must be formed. Experimental $Z(\log h)_{Y/B,B}$-curves are given in Fig. 6, showing the onset of the complex formation to be at $\log h \sim -1$, which means that there is no suitable range available for calibration of the glass electrode. Instead E_0 was estimated from the most acidic points in the titrations ($\log h \gtrsim -1$), and was then usually covaried with the tested equilibrium model in the LETAGROP-calculations.
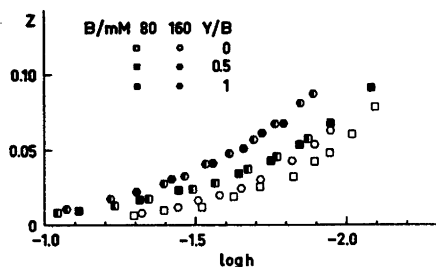
In the final equilibrium model, the difference E_0 (estimated) $- E_0$ (refined) never exceeded 0.2 mV.

With experimental data from ratios $Y/B = 0.5$ and 1.0 available, the search for the ternary polynuclear complexes was started with a pqr-
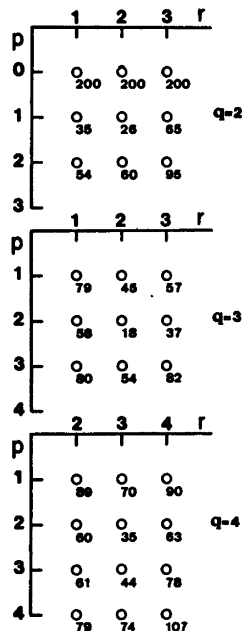

Fig. 6. A part of experimental data $Z(\log h)_B$ for quotients $Y/B = 0$, 1/2 and 1.

Fig. 7. Result of a pqr-analysis in the polynuclear range with $Y/B = 1/2$ and 1. Lowest error squares sums ($U_{min} \times 10^{-4}$) are plotted as a function of various pqr-sets with $q = 1$, 2 and 3. p, q and r stand for the number of OH^-, Hg^{2+} and Cl^- in the complexes.

analysis. In this search, the formation constants refined in the LETAGROP calculations on data from the mononuclear range, were assumed to be correct and no attempts were made to refine them further. In this analysis different pqr-combinations were systematically tested, and the results are given in Fig. 7. The two "best" complexes found were $Hg_2(OH)Cl_2^+$ with log log $\beta_{122} = -15.25 \pm 0.04$, $\sigma(Z) \times 1000 = 4.2$ and $Hg_3(OH)_2Cl_2^{2+}$ with log $\beta_{232} = -29.94 \pm 0.04$, $\sigma(Z) \times 1000 = 3.6$. However, after a closer look at the residuals $Z_{calc} - Z_{exp}$, systematic trends were found, indicating that another complex(es) must be taken into account. As in the pqr-analysis, tetranuclear species were not found to give as good improvement of data as binuclear and trinuclear ternary complexes, pairs of pqr triplets with $q = 2$ and 3 have been tested. As n species will yield $n(n-1)/2$ combinations, n had to be reduced to save computer time, and the following species were picked out from the pqr-analysis: $Hg_2(OH)Cl^{2+}$, $Hg_2(OH)Cl_2^+$, $Hg_2(OH)_2Cl^+$, $Hg_2(OH)_2Cl_2$, $Hg_3(OH)_2Cl^{3+}$, $Hg_3(OH)_2Cl_2^{2+}$ and $Hg_3(OH)_2Cl_3^+$. The "best"

combinations out of the 21 that can be formed of these 7 species, are given in Table 4. Thus the "best" explanation is given by the combination $Hg_2(OH)Cl_2^+$ and $Hg_3(OH)_2Cl^{3+}$ $(U = 330,$ $\sigma(Z) \times 1000 = 1.3)$. Another combination with a somewhat higher error squares sum $(U = 490,$ $\sigma(Z) \times 1000 = 1.6)$ is found for the combination $Hg_2(OH)Cl^{2+}$ and $Hg_3(OH)_2Cl_3^+$. In these two combinations, the nuclearity and ratio OH/Hg are the same, and thus well established, while the difference is found in the Cl/Hg ratio. To obtain a more distinct answer to what combination is the "best", the ratios $Y/B = 1/3$ and $2/3$ were investigated in addition. By comparing the residuals given in Fig. 8, the combination $Hg_2(OH)Cl_2^+ + Hg_3(OH)_2Cl^{3+}$ shows no systematic trend within the experimental uncertainty and the fit is better at each ratio studied (especially at $Y/B = 1/3$) compared with the $Hg_2(OH)Cl^{2+} + Hg_3(OH)_2Cl_3^+$-combination. Some measurements were performed at constant Z and B, where the ratio Y/B was varied between 0 and 2 in order to check whether additional effects are found in the range $1 \leq Y/B < 2$.

Table 4. Results of calculations for some different assumptions concerning the ternary polynuclear complexes formed at (a) $Y/B = 1/2$ and 1 (9 titrations 209 points) and (b) $Y/B = 1/3$, $1/2$, $2/3$ and 1 (17 titrations 359 points). In the calculations pairs of pqr triplets were tested and binary and ternary (mononuclear) constants given in Table 5 were not varied. The constants β_{pqr} are defined as in Table 2. In the calculations E_0 has been refined together with the stability constants.

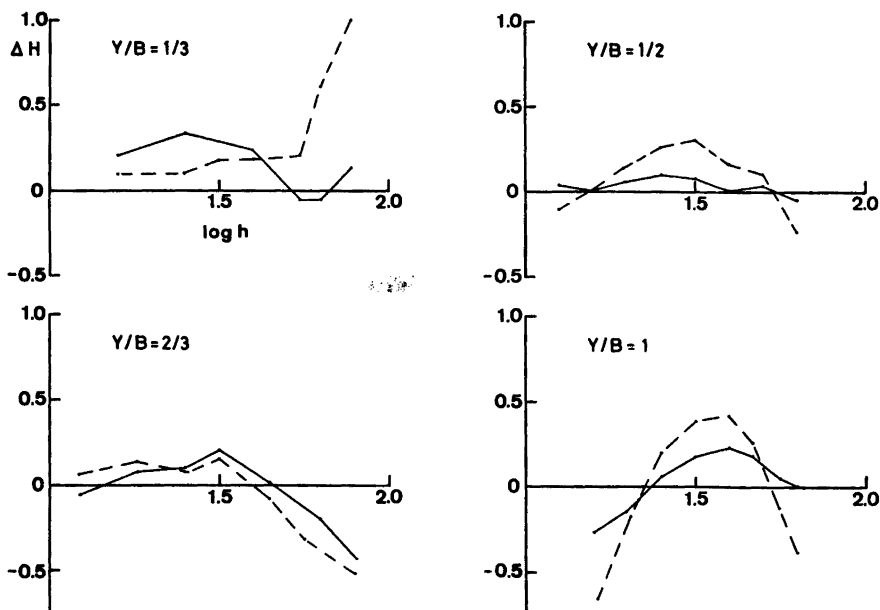| $U \times 10^{-3}$	$\sigma(Z) \times 1000$	Complex-combination	$\log(\beta_{pqr} \pm 3\sigma)$
(a)			
0.33	1.3	$Hg_2Cl_2OH^+$ $Hg_3Cl(OH)_2^{3+}$	$-15.26(2)$ $-37.78(4)$
0.49	1.6	Hg_2ClOH^{2+} $Hg_3Cl_3(OH)_2^+$	$-22.55(3)$ $-23.14(4)$
1.23	2.5	$Hg_3Cl_3(OH)_2^+$ $Hg_2Cl(OH)_2^{3+}$	$-22.94(4)$ $-37.60(5)$
1.95	3.1	$Hg_3Cl_2(OH)_2^{2+}$ $Hg_2Cl_2(OH)_2$	$-30.05(5)$ $-18.12(2)$
2.07	3.1	$Hg_3Cl(OH)_2^{3+}$ $Hg_2Cl_2OH^+$	$-37.80(4)$ $-15.29(4)$
(b)			
0.61	1.3	$Hg_2Cl_2OH^+$ $Hg_3Cl(OH)_2^{3+}$	$-15.25(1)$ $-37.79(2)$
0.81	1.6	Hg_2ClOH^+ $Hg_3Cl_3(OH)_2^{3+}$	$-22.55(2)$ $-23.15(3)$

Fig. 8. Residual plots $H = (H_{calc} - H_{exp})$ mM at Y/B ratios 1/3, 1/2, 2/3 and 1 with $B = 0.16$ M. Broken and full lines show residuals by assuming the ternary polynuclear complexes to be $Hg_2OHCl^{2+} + Hg_3(OH)_2Cl_3^+$ and $Hg_2OHCl_2^+ + Hg_3(OH)_2Cl^{3+}$, respectively. Proposed constants for binary and ternary (mononuclear) complexes given in Table 5 were used and not varied in the calculations.

As no additional species seem to be formed in this range, no separate investigations were undertaken. Thus within the range $0 < Y/B < 2$ the ternary polynuclear complexes formed, $Hg_2OHCl_2^+$ and $Hg_3(OH)_2Cl^{3+}$, are proposed with log $\beta_{123} = -15.25 \pm 0.01$ and log $\beta_{231} = 37.79 \pm 0.02$ giving $\sigma(Z) \times 1000 = 1.3$. Thus a good explanation of experimental data is obtained and if other ternary species are present

(*e.g.* $Hg_3(OH)_2Cl_3^+$) they are formed in very small amounts.

DISCUSSION

In the present investigation equilibrium constants for the formation of binary $Hg^{2+} - Cl^-$, $Hg^{2+} - OH^-$ as well as ternary $Hg^{2+} - Cl^- - OH^-$ complexes have been determined,

Table 5. Proposed complexes with formation constants defined according to the equilibria given in the table.

Equilibria	log $(\beta \pm 3\sigma)$
$Hg^{2+} + H_2O \rightleftharpoons HgOH^+ + H^+$	$-3.58(2)$
$2Hg^{2+} + 2H_2O \rightleftharpoons Hg_2(OH)_2^{2+} + 2H^+$	$-4.84(2)$
$HgCl_2 + H_2O \rightleftharpoons HgClOH + H^+ + Cl^-$	$-9.87(2)$
$HgCl_2 + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+ + 2Cl^-$	$-20.24(2)$
$2HgCl_2 + H_2O \rightleftharpoons Hg_2Cl_2OH^+ + 2Cl^- + H^+$	$-15.25(1)$
$3HgCl_2 + 2H_2O \rightleftharpoons Hg_3Cl(OH)_2^{3+} + 2H^+ + 5Cl^-$	$-37.79(2)$
$HgCl_2 \rightleftharpoons HgCl^+ + Cl^-$	$-6.78(5)$
$HgCl_2 \rightleftharpoons Hg^{2+} + 2Cl^-$	$-14.00(3)$
$HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-$	$1.07(3)$
$HgCl_2 + 2Cl^- \rightleftharpoons HgCl_4^{2-}$	$2.14(5)$

and in all 10 different equilibrium constants have been evaluated. As the free H^+-concentration was the only measured quantity, it was found necessary to investigate as wide concentration ranges as possible in B and Y and at the same time to cover the most interesting ratios Y/B. A total of approximately 150 titrations were performed including $\sim$3000 experimental points. (In this estimate, data for controls of reversibility and reproducibility have been included). A complete list of experimental data is available from this department.

As can be seen from Table 5, the standard deviations of the proposed complexes are low $(3\sigma(\log \beta_{pqr}) \leq 0.05)$ and the complexes may thus be considered as well determined.

The formation constants of the binary $HgCl_n^{(2-n)+}$-species were determined indirectly in hydrolyzed $Hg^{2+} - Cl^-$ solutions using solely a glass-electrode. As can be seen from Table 2, where results from each ratio Y/B investigated are summarized, no systematic trend in these constants is found and they all fall within its limits of error. By comparing these constants with those reported by Arnek (see Table 1), the agreement is very good in $K_1 K_2$, K_3 and K_4 (cal.), while a difference of 0.1 logarithmic unit in $\log K_1$ and $\log K_2$ is found. However, the difference lies within the limits of error given by Arnek. In $Y/B > 0$ ratios studied, both HgOHCl and $Hg(OH)_2$ have been identified with equilibrium constants given in Table 2. There seems to be a small difference in the formation constant for HgOHCl, depending on whether Y/B is greater than 2 or not. At $Y/B \geq 2$, $\log \beta_{HgOHCl} = -9.91 \pm 0.01$, while at $Y/B < 2$ a higher value -9.86 ± 0.01 is found. A corresponding difference in $\log \beta_{Hg(OH)_2}$ can be seen with values -20.20 ± 0.02 $(Y/B \geq 2)$ and -20.24 ± 0.01 $(Y/B < 2)$. Although this difference is slightly greater than the error limits, it probably is not significant, especially when the number of constants that have been determined is taken into account. Furthermore, by comparing $\beta_{Hg(OH)_2}$ determined in a pure Hg^{2+}-solution where $Y/B = 0$ with solution where $Y/B > 0$, the agreement is very satisfactory and is consistent with a value reported by Ahlberg.[3]

The formation of polynuclear hydrolytic species must be taken into consideration in solutions with ratios $Y/B < 2$. In Fig. 9 a distribution diagram $(Y/B)_{\log h,B}$ is given. According
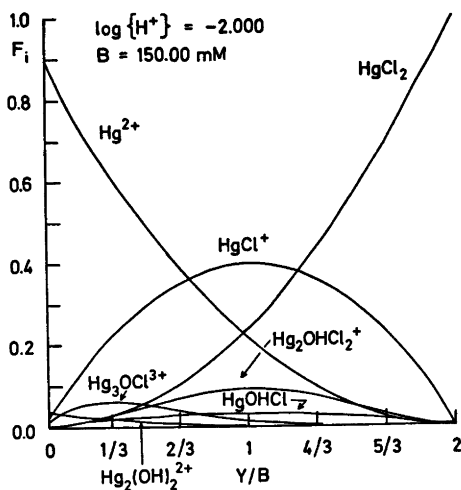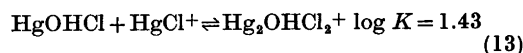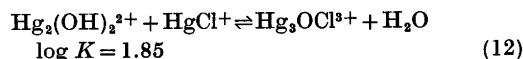
Fig. 9. Distribution diagrams $F_i(Y/B)_{\log h,B}$.

to this diagram, it seems reasonable to assume $Hg_3(OH)_2Cl^{3+}$ and $Hg_2OHCl_2^+$ to be formed according to the reactions

$$Hg_2(OH)_2^{2+} + HgCl^+ \rightleftharpoons Hg_3OCl^{3+} + H_2O$$
$$\log K = 1.85 \tag{12}$$

$$HgOHCl + HgCl^+ \rightleftharpoons Hg_2OHCl_2^+ \quad \log K = 1.43 \tag{13}$$

As mentioned earlier, isolated units $Hg_3OCl_3^+$ have been found in the solid state. Detectable amounts of this complex in solution with $1 \leq Y/B \leq 2$ have not been found. However, a possible mechanism for its formation could be

$$HgOHCl + Hg_2OHCl_2^+ \rightleftharpoons Hg_3OCl_3^+ + H_2O \tag{14}$$

It is interesting to note that in aqueous solutions of methylmercury, the hydrolytic species CH_3HgOH and $(CH_3Hg)_2OH^+$ have been identified from pH-titration data (Schwarzenbach and Schellenberg [38]), from Raman measurements (Woodward et al.[39]) and from proton magnetic resonance (^{1}H NMR) studies by Rabenstein and coworkers.[40] In a recent investigation Rabenstein et al.[42] have extended the concentration range of CH_3Hg^+ up to 0.51 M and from both Raman and ^{1}H NMR measurements they found that in a supersaturated solution with respect to $[(CH_3Hg)_3O]ClO_4$, the $(CH_3Hg)_3O^+$-cation is detectable in small amounts. They found
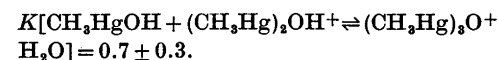
$$K[CH_3HgOH + (CH_3Hg)_2OH^+ \rightleftharpoons (CH_3Hg)_3O^+ + H_2O] = 0.7 \pm 0.3.$$

Table 6. Acidity constants of some mercury(II)-species.

Complex	$-\log K_a$	Ref.
Hg^{2+}	3.6	This work, 2, 3
$HgOH^+$	2.7	This work, 2, 2
$HgCl^+$	3.1	This work, 16, 41
$HgBr^+$	3.5	41
HgI^+	4.0	41

In Table 6 acidity constants are given for some mercury(II) complexes with ligand H_2O, OH^-, Cl^-, Br^- and I^-. It can be seen that $pK_a(HgCl^+) = 3.09$ is in good agreement with the value 3.05 obtained by Ciavatta in 1.0 M $NaClO_4$-medium. Furthermore, both $HgOH^+$ and $HgCl^+$ are stronger acids than Hg^{2+}. The higher chloride species $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ are found not to give rise to appreciable amounts of hydrolysis products in the $\log h$ range investigated ($\log h > -9$). Although one water molecule around the mercury ion is replaced by a hydroxide or a chloride ion, the tendency to hydrolyze is still appreciable. However, when the species $Hg(OH)_2$, $HgOHCl$, $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ are formed, water molecules far from the Hg^{2+}-ion are available to split off protons and the acidity constants diminish greatly (*cf.* $pK_a[Hg(OH)_2] \sim 15$ according to Garrett and Hirschler [5]).

If statistical reasons alone determine the formation of the complex MAB, the equilibrium constant of the reaction

$$MA_2 + MB_2 \rightleftharpoons 2MAB; \quad K = 4 \quad (15)$$
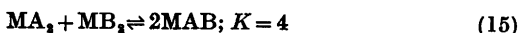
should have the value 4. However, it has been found convenient to define the equilibria

$$M + A + B \rightleftharpoons MAB; \quad \beta_{MAB} \quad (16)$$

for which the statistical value of the stability constants is easily calculated by using the equation

$$\beta_{MAB} = 2(\beta_{MA_2}\beta_{MB_2})^{1/2} \quad (17)$$

This equation can be derived from (15) and (16). Using $\log \beta_{HgCl_2} = 14.00$, $\log \beta_{Hg(OH)_2} = 22.21$ and $\log K_W = -14.22$, a statistical value of the stability constants β_{HgClOH} has been calculated. The calculated value 10 exp (18.40)
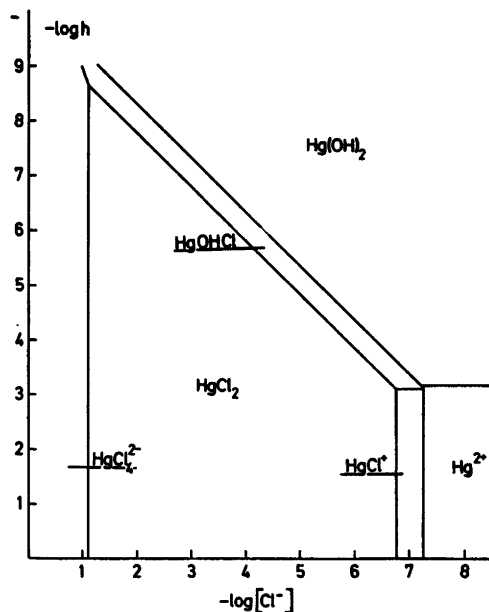

Fig. 10. Predominance area diagram. The composition of the mononuclear species predominating in a certain $\log h - \log[Cl^-]$ area is shown. The lines have been calculated by using the constants of Table 5.

M^{-2} is close to the experimental value 10 exp (18.53) M^{-2}, indicating that HgOHCl is formed almost statistically. The same has been found by Ahlberg,[41,44] concerning the formation of Hg(OH)Br and Hg(OH)I.

In Fig. 10 an attempt is made to illustrate the various equilibria by showing the ($\log h - \log[Cl^-]$) areas in which a given species predominates.

REFERENCES

1. Sillén, L. G. and Martell, A. E. (compilers) *Stability Constants, Chem. Soc. London, Spec. Publ.* No. 17 (1964) and No. 25 (1971).
2. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 6 (1952) 747.

3. Ahlberg, I. *Acta Chem. Scand. 16* (1962) 887.
4. Hayek, E. *Monatsh. Chem. 85* (1954) 472.
5. Garrett, A. B. and Howell, W. W. *J. Am. Chem. Soc. 61* (1939) 1730.
6. Garrett, A. B. and Hirschler, A. E. *J. Am. Chem. Soc. 60* (1938) 299.
7. Dyrssen, D. and Tyrrell, V. *Acta Chem. Scand. 15* (1961) 393; 1622.
8. Johansson, G. *Acta Chem. Scand. 25* (1971) 2787.
9. Panthaleon van Eck, C. L., Wolter, H. B. M. and Jaspers, W. J. M. *Recl. Trav. Chim. Pays-Bas 75* (1956) 802.
10. Johansson, G. *Acta Chem. Scand. 25* (1971) 1905.
11. Johansson, G. *Acta Chem. Scand. 25* (1971) 2799.
12. Sillén, L. G. *Acta Chem. Scand. 3* (1949) 539.
13. Ciavatta, L. and Grimaldi, M. *J. Inorg. Nucl. Chem. Lett. 30* (1968) 197.
14. Arnek, R. *Ark. Kemi 24* (1965) 531.
15. Linhart, G. A. *J. Am. Chem. Soc. 37* (1915) 259; 38 (1916) 1272.
16. Ciavatta, L. and Grimaldi, M. *J. Inorg. Nucl. Chem. Lett. 30* (1968) 563.
17. Sandström, M. *Acta Chem. Scand. A 31* (1977) 141.
18. Luther, R. *Z. Phys. Chem. 47* (1904) 107.
19. Carriere, E. and Lafitte, M. *Bull. Soc. Chim. Fr. 12* (1945) 833.
20. Carrière, E., Guiter, H. and Lafitte, M. *Bull. Soc. Chim. Fr. 15* (1945) 23.
21. Damm, K. and Weiss, A. *Z. Naturforsch. 10b* (1955) 534.
22. Partridge, J. A., Izatt, R. M. and Christensen, J. J. *J. Chem. Soc.* (1965) 4231.
23. Gmelin-Kraut, *Handbuch der anorganischen Chemie*, Heidelberg 1914, 679.
24. Aurivillius, K. *Ark. Kemi 22* (1964) 537.
25. Aurivillius, K. and Stålhandske, C. *Acta Crystallogr. B 30* (1974) 1907.
26. Aurivillius, K. *Acta Chem. Scand. 8* (1954) 523.
27. Aurivillius, K. and Stålhandske, C. *To be published.*
28. Björnlund, G. *Acta Chem. Scand. A 28* (1974) 169.
29. Šćavničar, S. *Z. Kristallogr. 118* (1963) 248.
30. Sjöberg, S. *Acta Chem. Scand. 25* (1971) 2149.
31. Gran, G. *Acta Chem. Scand. 4* (1950) 559.
32. Sjöberg, S. *Acta Chem. Scand. 27* (1973) 3721.
33. Biedermann, G. and Sillén, L. G. *Ark. Kemi 5* (1953) 425.
34. Ingri, N. and Sillén, L. G. *Ark. Kemi 23* (1964) 97.
35. 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.
36. Sillén, L. G. *Acta Chem. Scand. 16* (1962) 159; Sillén, L. G. and Warnqvist, B. *Ark. Kemi 31* (1969) 341.
37. Ingri, N., Kakolowicz, W., Sillén, L. G. and Warnqvist, B. *Talanta 14* (1967) 1261.
38. Schwarzenbach, G. and Schellenberg, M. *Helv. Chim. Acta 48* (1965) 28.
39. Clarke, J. H. R. and Woodward, L. A. *Trans. Faraday Soc. 62* (1966) 3022; Goggin, P. L. and Woodward, L. A. *Trans. Faraday Soc. 56* (1960) 1591; Goggin, P. L. and Woodward, L. A. *Trans. Faraday Soc. 58* (1962) 1495.
40. Rabenstein, D. L., Evans, C. A., Tourangeau, M. C. and Fairhurst, M. *Anal. Chem. 47* (1975) 338.
41. Ahlberg, I. and Leden, I. *Trans. R. Inst. Technol. Stockholm 249* (1972) 17.
42. Marcus, Y. *Acta Chem. Scand. 11* (1957) 599.
43. Panthaleon van Eck, C. L. *Thesis.* Leiden 1958.
44. Ahlberg, I. *Acta Chem. Scand. 27* (1973) 3003.
45. Eriksson, G. *To be published.*
46. Johansson, G. and Hansen, E. *Acta Chem. Scand. 26* (1972) 796.