

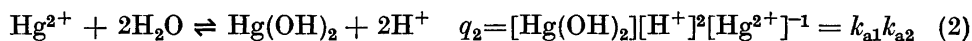
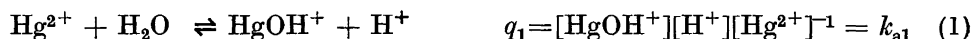
Studies on the Hydrolysis of Metal Ions

II. The Hydrolysis of the Mercury(II) Ion Hg^{2+}

SIRKKA HIETANEN and LARS GUNNAR SILLÉN

*Department of Inorganic Chemistry, Royal Institute of Technology;
Institute of Inorganic and Physical Chemistry, University, Stockholm, Sweden*

It has been known for a long time that solutions of mercury(II) salts in water have an acid reaction; this is especially strong if the anion is perchlorate or nitrate, neither of which forms strong complexes with Hg^{2+} . A possible mechanism is that the ion $\text{Hg}(\text{H}_2\text{O})_n^{2+}$ acts as an aquo acid, splitting off one or more protons. Omitting the co-ordinated water molecules we may write the formulas for the formation of the first two products as follows:



where k_{a1} and k_{a2} would be the first and second acid constants of the acid $\text{Hg}(\text{H}_2\text{O})_n^{2+}$.

There are few data recorded in literature on these equilibria, and they do not allow of reliable separate estimations of k_{a1} and k_{a2} , as will be seen below. Garrett and Hirschler¹ measured the solubility of HgO in water at 25° C and, by combining it with the previously determined solubility product $[\text{Hg}^{2+}][\text{OH}^-]^2$, calculated the "basic dissociation constant of $\text{Hg}(\text{OH})_2$ " as $1.8 \cdot 10^{-22} = 10^{-21.74}$. From this value and $\text{p}K_w = 14.00$ one may calculate $\text{p}k_{a1} + \text{p}k_{a2} = 6.26 = \text{p}q_2$.

From two pH measurements at 21.5° C, J. Bjerrum² obtained the values 2.68 and 2.88 for $\text{p}k_{a1}$, neglecting the second dissociation step. He estimated the most probable value to be $\text{p}k_{a1} = 2.8$ and concluded that $\text{p}k_{a2} = 3.5$. From Ley's conductivity measurements³ on mercury(II) perchlorate solutions at 25° C, Bjerrum estimated $\text{p}k_{a1}$ to be of the order of magnitude 2.4, in reasonable agreement with his own measurements.

Garrett and Howell ⁴ measured the solubility of HgO at 25° C in nitric acid at various concentrations and estimated the equilibrium constant for $\text{Hg}(\text{OH})_2 \rightleftharpoons \text{HgOH}^+ + \text{OH}^-$ to be $7.1 \cdot 10^{-12} = 10^{-11.15}$ and for $\text{Hg}(\text{OH})_2 \rightleftharpoons \text{Hg}^{2+} + 2\text{OH}^-$, $2.2 \cdot 10^{-23} = 10^{-22.66}$, which by the way differs from ¹. With $\text{p}K_w = 14.00$ these values would give $\text{p}k_{a1} = 2.49$, $\text{p}k_{a2} = 2.85$.

On the other hand Hayek ⁵ concluded from the great solubility of HgO in strong mercury(II) perchlorate solutions (of the order of magnitude 2–4 C) and from the existence of a solid salt $\text{Hg}_3\text{O}_2(\text{ClO}_4)_2$ that these solutions contain polynuclear ions $\text{Hg}(\text{HgO})_n^{2+}$.

If this were so, there would be a strong analogy with bismuth solutions; the hydrolysis of Bi^{3+} has been shown by Granér and Sillén ⁶ not to proceed by mononuclear reactions analogous to equation (1) and (2) but rather by the formation of polynuclear complexes such as $\text{Bi}_n\text{O}_{n-1}^{(n+2)+}$. Other ions studied in this laboratory — thorium ⁷, cerium(IV) ⁷, and iron(III) ⁸ — have also proved to hydrolyze with the formation of polynuclear complexes. It thus seemed worth while investigating whether the mercury(II) ion behaves in the same way.

Let us state immediately that our results can be fully explained by the mechanism given in (1) and (2), although we find that Hg^{2+} differs from most other acids by having $k_{a2} > k_{a1}$. There was no evidence of polynuclear mercury ions at the low total concentrations studied by us, although they may have existed at the very high concentrations discussed by Hayek ⁵.

Another reason for studying the hydrolysis of Hg^{2+} was the fact that a large amount of work had recently been devoted to studying the complexes of Hg^{2+} with Cl^- , Br^- and I^- ⁹. In all these measurements the equilibria had been studied at 25° C for solutions with $[\text{H}^+] = 10$ mC and ionic strength as close to 0.5 C as possible, achieved by adding suitable amounts of NaClO_4 . The use of 10 mC H^+ was intended to keep the fraction of Hg^{II} present in the form of HgOH^+ etc. small and constant. It seemed of interest to know what this fraction had actually been. This was one reason for now choosing the same ionic strength as in the investigation of the mercury-halide complexes.

As will be seen in the following, for calculating the hydrolysis equilibria of Hg^{2+} it is necessary to know the magnitude of the hydrolysis of the mercury(I) ion, Hg_2^{2+} , and *vice versa* a great part of the apparent acidity of the Hg_2^{2+} ion is really due to the acidity of small amounts of Hg^{2+} present in the solution. The investigations of Hg^{2+} and Hg_2^{2+} were for this reason carried out in close co-operation. The studies on mercury(I) ions were started by Forsling even before we took up the Hg^{2+} studies, and the results will be published as Part III ¹⁰ of this series.

CHOICE OF METHOD AND EXPERIMENTAL CONDITIONS

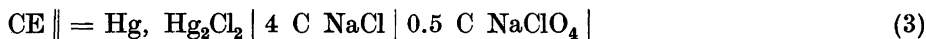
It was decided to study the hydrolysis equilibria of Hg^{2+} at 25.0°C with $[\text{ClO}_4^-] = 500\text{ mC}$ and no other anions present. As usual, by keeping the ionic strength and thus the activity factors practically constant, we could use concentrations instead of activities in the formulas for emfs and equilibrium constants. The particular choice of 0.5 C ClO_4^- facilitated a comparison with previous measurements on mercury-halide complexes.

From the analysis of our solutions we knew the amounts of Hg^{II} and hydrogen ions added per litre, $a = [\text{Hg}^{\text{II}}]_{\text{tot}}$ and H (the hydrogen ion concentration if mercury had not hydrolyzed). For studying the equilibria we thought it desirable to measure the actual concentrations both of free Hg^{2+} ions and of hydrogen ions.

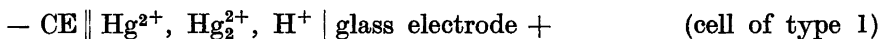
For measuring $[\text{Hg}^{2+}]$ a Hg electrode could not be used, since it would have reacted thus $\text{Hg}^{2+} + \text{Hg}(l) \rightleftharpoons \text{Hg}_2^{2+}$; the equilibrium constant $[\text{Hg}_2^{2+}] [\text{Hg}^{2+}]^{-1}$ is about 130¹¹. However, $[\text{Hg}^{2+}]$ could be determined by adding Hg_2^{2+} and measuring the redox potential of the solution. Advantage was taken of the fact, proved in Part III¹⁰, that Hg_2^{2+} is a much weaker acid than Hg^{2+} .

For measuring the hydrogen ion concentration, neither a hydrogen electrode nor a quinhydrone electrode could be used, since in both cases metallic mercury would be obtained by reduction. It was thus necessary to use glass electrodes which, although capricious, gave sufficiently accurate results.

Types of cells used. — As in previous work, the reference calomel electrode was of the following type:



The two types of cells used in this work may be written schematically



We shall write for convenience introducing the new function φ

$$[\text{Hg}^{\text{II}}]_{\text{tot}} = a; [\text{H}^+] = h; [\text{Hg}^{2+}] = a (1 + \varphi)^{-1} \quad (4)$$

For cells of type 1 the emf E_1 will be

$$E_1 = E_{01} + E_j^* + 59.16 \log h \quad (5)$$

In (5) E_{01} is a constant *, whereas E_j^* is a function of h and comprises the

* The constants E_{01} etc. in this series are not identical with E_{10} etc. in the papers on mercury-halide complexes; however, $E_{01} \approx E_{20}$ and E_{03} (in part III) $\approx E_{10}$, the differences being the corrections for E_j and hydrolysis at $h = 10\text{ mC}$.

diffusion potential, the asymmetry potential of the glass electrode, and its deviations from the ideal slope. The sum ($E_{01} + E_j^*$) was determined as a function of h by an acid-base titration immediately preceding each titration with mercury solutions. There was no need to determine E_{01} and E_j^* separately.

For cells of type 2 we have

$$E_2 = E_{02} + E_j + 59.16 \log [\text{Hg}^{2+}] - 29.58 \log [\text{Hg}_2^{2+}] \quad (6)$$

In this equation, E_{02} is a constant (see footnote p. 749), which is at first unknown, and E_j a function of h . From the work of Biedermann and Sillén¹² we took a preliminary equation $E_j = -0.0972 h$ mV, if h is expressed in mC.

Using (4) we may transform (6) into the following equation, where the left member contains only known quantities:

$$E_2 + 0.0972 h - 59.16 \log a + 29.58 \log [\text{Hg}_2^{2+}] = E_{02} - 59.16 \log (1 + \varphi) \quad (7)$$

Denoting by E'_2 and φ' the values of E_2 and φ for a fixed value $h = h'$ we find from (7), provided a and $[\text{Hg}_2^{2+}]$ are kept constant.

$$59.16 \log [(1 + \varphi) - \log (1 + \varphi')] = E'_2 - E_2 + 0.0972 (h' - h). \quad (8)$$

EXPERIMENTAL

Reagents. — Solutions of mercury(I) perchlorate and mercury(II) perchlorate were prepared and analyzed as described previously¹³. The total perchlorate content was, however, determined by running a known amount of the perchlorate solution through an ion exchanger in its hydrogen form, and titrating for H^+ with NaOH. For some reason, the results sometimes differed by almost as much as 0.5 % from those obtained with the earlier method, electrolyzing away the mercury and then titrating with NaOH. As a check a third method was used, namely binding the mercury by adding excess of sodium bromide, and titrating the excess H^+ with NaOH. The perchlorate content was calculated from the $[\text{H}^+]$ obtained in this way and the Hg values obtained by electrolysis. This value proved to agree within 0.05 % with the $[\text{ClO}_4^-]$ values obtained by the ion exchange method. For this reason the ion exchange values were considered reliable.

The perchloric acid and sodium perchlorate were also prepared and analysed as in previous work¹³.

A stock solution of 50 % NaOH was kept in a paraffinated bottle. The NaOH solutions prepared from it by dilution were analysed by titration with HCl, which had been standardized against a weighed amount of HgO and excess of KI.

The cell was made up of a calomel electrode, a salt bridge, and a titration vessel. The first two were of a new and convenient design, and will be described in detail by Forsling, Hietanen and Sillén in part III¹⁰. The cell was kept in a paraffin oil thermostat at $25.0 \pm 0.1^\circ \text{C}$. The solutions were kept free from air by bubbling nitrogen, which was taken from a cylinder, made free from oxygen by Meyer's and Ronge's method¹⁴, saturated with water vapor by bubbling through 0.5 C NaClO_4 in the thermostat, and rinsed from droplets in a cotton-wool filter. The whole work was carried out in a thermostat room of approximately 25°C .

The glass electrode was a commercial shielded one, of Radiometer's make. The platinum electrode was of the type shown in Fig. 3, ref. 13. The emf:s for cells of type 1 were measured with a valve potentiometer (type Radiometer pHM3), those for cells of type 2 with a Jensen compensator type 10A, and a Multiflex galvanometer.

Procedure. — Our calculations are based on seven titrations, the data on which are given in Table 1. Three solutions were prepared for each titration, and are denoted as S_1 , S_2 and T. The solutions were made to contain 500 mC ClO_4^- ; for each solution Table 1 gives the concentrations of the other ions present, except for Na^+ which was the balance. The concentrations given for S_2 are the analytical ones, calculated as if no hydrolysis had occurred. The last columns of Table 1 give the order and amounts in which the solutions were added; the principle was the same in all titrations, so we shall only discuss titration 1.

Table 1. Survey of titrations.

No.	Sym- bol	a mC	S_1 mC H ⁺	T mC OH ⁻	S_2			ml added				
					mC H ⁺	mC Hg ²⁺	mC Hg ₂ ²⁺	S_1	T	S_2	$S_2 + T$	
1	△	10.00	10.00	37.00	18.64	30.00	3.00	41	9	25	18	+ 36
2	▲	10.00	10.00	39.93	30.31	30.00	15.00	41	9	25	20	+ 40
3	◆	3.00	10.00	40.00	4.00	6.00	3.00	41	9	50	13.5	+ 13.5
4	■	10.00	20.06	40.00	19.53	20.00	4.00	41	19	60	64	+ 64
5	●	3.00	20.04	49.68	10.07	6.00	3.00	60	23.5 *	30	28.5	+ 28.5
6	□	1.00	20.04	49.68	33.53	3.00	6.00	60	22	41	25.5	+ 51
7	○	1.00	20.04	49.68	33.53	3.00	6.00	60	22	41	25	+ 50

The first part of the titration was an acid-base titration, with only the glass electrode inserted in the titration vessel. The vessel originally contained 41.00 ml of the acid solution S_1 . The emf of the cell (type 1) was measured, and the alkaline solution T was added in portions and E_1 measured after each new addition. From these measurements, a diagram was made giving $(E_{01} + E_j^*)$ as a function of the hydrogen ion concentration h . This diagram was used for calculating h from E_1 in the latter part of the titration; the plot was usually roughly linear but varied slightly from day to day, the constancy of glass electrodes being what it is.

When 9.00 ml of T had been added, and the total volume was 50.00 ml, mercury ions were introduced into the solution by adding 25.00 ml of S_2 . The platinum electrode was introduced, and from now on both the CE-glass electrode emf (E_1) and the CE-platinum electrode emf (E_2) were measured.

In the latter part of the titration, for each new addition of T, half as much of S_2 was also added. In this way the concentrations of mercury(I) and mercury(II) in the solution were kept constant and equal to one third of the concentrations in S_2 . In the second half of titration 1, a total of 18 ml S_2 and 36 ml T was added. The experiment was interrupted when a lasting precipitate appeared in the solution.

* In expt. 5, the solution in the titration vessel was removed and replaced by 30.00 ml S_1 after the acid-base titration.

Table 2.

Data from titration no. 6.

Table 2 a. Acid-base titration, Initially 60.00 ml S_1 (20.04 mC H^+). T (49.68 mC OH^-) was added.

T ml	$H = h$ mC	E_1 mV	$E_{01} + E_j^*$ mV
0.00	20.04	+ 1.8	- 75.2
2.00	17.79	- 0.5	- 74.4
5.00	14.68	- 5.2	- 74.2
10.00	10.08	- 14.3	- 73.7
15.00	6.10	- 26.6	- 73.1
20.00	2.61	- 48.5	- 73.1
22.00	1.33	- 66.0	- 73.3

Table 2 b. Mercury titration. Initially 41.00 ml S_2 (33.53 mC H^+ , 3.00 mC Hg^{2+} , 6.00 mC Hg_2^{2+}) was added to the last solution from Table 2 a. Then for each addition of T , half as much S_2 was added.

T ml	E_1 mV	h mC	$h-H$ mC	E_2 mV	$\frac{1 + \varphi}{1 + \varphi'}$	φ	$h^2\varphi$ mC ²	$h\varphi$ mC
0.00	- 9.4	12.26	* 0.20	552.22	1.000	0.0200	2.909	0.241
2.00	- 11.2	11.38	0.13	552.11	1.0074	0.0276	3.493	0.310
10.00	- 18.4	8.47	0.10	552.33	1.0097	0.0300	2.102	0.251
20.00	- 29.1	5.50	0.11	552.22	1.0252	0.0461	1.394	0.275
30.00	- 43.1	3.15	0.20	551.11	1.0797	0.1014	1.006	0.319
32.00	- 46.8	2.73	0.21	550.56	1.1051	0.1273	0.949	0.347
36.00	- 54.6	2.00	0.31	548.73	1.1899	0.2137	0.855	0.427
40.00	- 63.3	1.42	0.51	545.55	1.3493	0.3763	0.759	0.534
41.00	- 65.7	1.29	0.56	544.21	1.4228	0.4512	0.751	0.582
43.00	- 70.6	1.07	0.71	541.55	1.579	0.611	0.699	0.653
44.00	- 73.1	0.96	0.77	539.80	1.691	0.725	0.668	0.696
46.00	- 78.2	0.79	0.95	535.40	2.009	1.049	0.655	0.829
48.00	- 83.7	0.64	1.13	529.57	2.521	1.572	0.644	1.006
49.00	- 86.8	0.57	1.23	526.26	2.869	1.927	0.626	1.098
50.00	- 89.6	0.51	1.33	522.69	3.297	2.364	0.615	1.205
51.00	- 92.6	0.45	1.43	518.99	3.809	2.887	0.584	1.299

* For the first three points, H was used instead of h in the calculations. — To avoid rounding-off errors, an ample number of digits is sometimes given.

In titrations 3–5, the solutions S_2 and T were added in the ratio 1 : 1, making the mercury concentrations in the latter part of the experiment equal to half those in S_2 .

After each addition, the emfs attained almost immediately their new values; it was checked that they remained constant for about 10 minutes, before a new addition was made.

Data from titration no 6 are given in Table 2. In this experiment, the linearity of $E_{01} + E_j^*$ was unusually poor for low h ; in the calculations we used a straight line extrapolated from higher h values.

FORMULAS FOR MONONUCLEAR MECHANISM

For each point of any of our titrations, the experimental data gave the analytical concentrations of hydrogen ions ($= H$), mercury(II) ions ($= a$), and mercury(I) ions. Moreover, from E_1 and the preceding acid-base titration, the real hydrogen ion concentration h could be found.

From E_2 by means of equation (8) we could get the quantity $(1 + \varphi)(1 + \varphi')^{-1}$, where φ' (and h') are the values for the first point of the latter (mercury) part of the titration. Since h' was generally large, φ' was small, and could be corrected for by successive approximations as described below. Even at the lowest acidities, the correction for the hydrolysis of Hg_2^{2+} was within the limits of experimental error; its approximate magnitude was known from the work of Forsling, Hietanen and Sillén (part III)¹⁰.

In Fig. 1 and 2, the quantities $(h-H)a^{-1}$ and $[Hg^{2+}]a^{-1} = (1 + \varphi)^{-1}$ are given as functions of $\log h$. Within the limits of experimental error, the points for different total mercury(II) concentrations a are seen to fall on the same curve. This is as would be expected with a mononuclear mechanism, as is seen from formulas (9) and (15) below. However, if polynuclear complexes were formed in appreciable amounts, one would expect a relatively stronger hydrolysis, thus a higher curve in Fig. 1 and a lower curve in Fig. 2, for the highest a values.

We thus find it justifiable to assume that the hydrolysis of the Hg^{2+} ion leads chiefly to the mononuclear products $HgOH^+$ and $Hg(OH)_2$. If this is so, we find from (1) and (2)

$$a = [Hg^{II}]_{\text{tot}} = [Hg^{2+}] + [HgOH^+] + [Hg(OH)_2] = [Hg^{2+}](1 + q_1h^{-1} + q_2h^{-2}) \quad (9)$$

From (9) and the last equation in (4) we see immediately that

$$\varphi = q_1h^{-1} + q_2h^{-2} \quad (10)$$

By multiplication of (10) by h^2 , and h , we obtain the equations

$$h^2\varphi = q_1h + q_2 \quad (11)$$

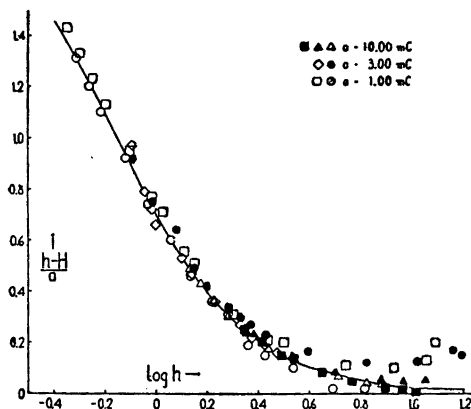


Fig. 1. $(h-H)a^{-1}$, number of protons split off per mercury (II) ion, as a function of $\log h$ (in mC). Curve calculated with $q_1 = 0.20$ mC, $q_2 = 0.50$ mC². Experimental points: symbols as in Table 1.

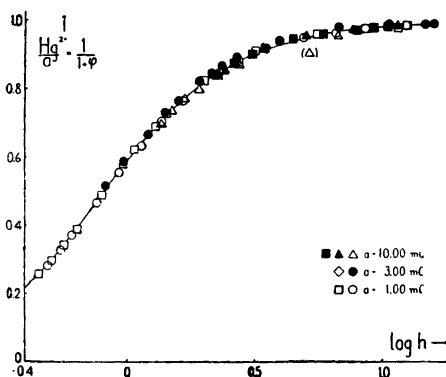


Fig. 2. $(1 + \varphi)^{-1}$, fraction of Hg^{II} present as free Hg^{2+} , as a function of $\log h$ (h in mC). Experimental points: symbols as in Table 1. Curve calculated with $q_1 = 0.20$ mC, $q_2 = 0.50$ mC².

$$h\varphi = q_1 + q_2h^{-1} \quad (12)$$

By plotting $h^2\varphi$ as a function of h , and $h\varphi$ as a function of h^{-1} one should thus obtain two straight lines, each of which would give the values for q_1 and q_2 . The real hydrogen ion concentration h should be the sum of the analytical one H , and the amount of hydrogen ions set free by the hydrolysis processes (1) and (2):

$$h = H + [HgOH^+] + 2 [Hg(OH)_2] \quad (13)$$

With (13), (1) and (2) we obtain

$$h-H = [Hg^{2+}] (q_1h^{-1} + 2 q_2h^{-2}) \quad (14)$$

and with (14), (4) and (9)

$$(h-H)a^{-1} = (\varphi + q_2h^{-2}) (1 + \varphi)^{-1} \quad (15)$$

RESULTS

Plots of (11) and (12) were constructed, neglecting φ' at the first point of the titration. From these plots rough values for q_1 and q_2 were obtained. With them an approximate value for φ' was calculated for each titration, by means of which better values for $h^2\varphi$ and $h\varphi$ were obtained. When these were plotted against h and h^{-1} , better values for q_1 and q_2 resulted and so on. By four successive approximations we obtained the values

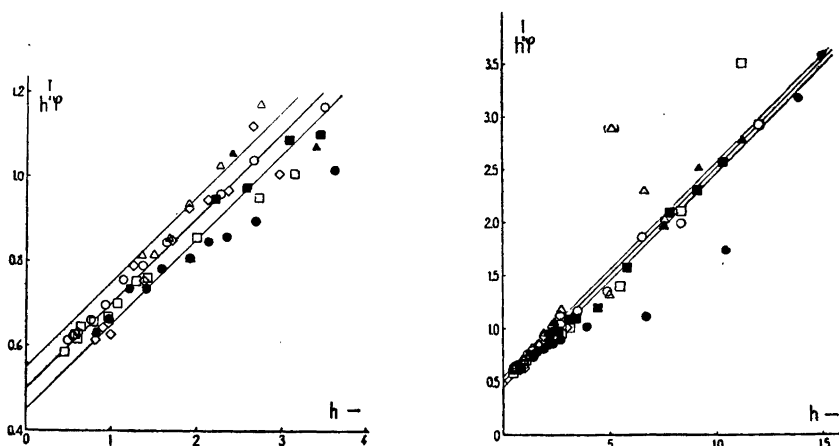


Fig. 3a. $h^2\phi$ (mC^2) as a function of h (mC). Fig 3b. Left part of Fig. 3a on larger scale. Lines calculated for $q_1 = 0.20$ mC and $q_2 = 0.50$ mC^2 (thick line), 0.45 or 0.55 mC^2 (thin lines).

$$q_1 = 0.20 \pm 0.03 \text{ mC} = (2.0 \pm 0.3) \cdot 10^{-4} \text{ C} = 10^{-3.70 \pm 0.07} \text{ C} = k_{a1} \quad (16)$$

$$q_2 = 0.50 \pm 0.05 \text{ mC}^2 = (5.0 \pm 0.5) \cdot 10^{-7} \text{ C}^2 = 10^{-6.30 \pm 0.05} \text{ C}^2 \quad (17)$$

$$k_{a2} = q_2 q_1^{-1} = 10^{-2.60 \pm 0.09} \text{ C}. \quad (18)$$

In Figs. 1, 2, 3, and 4, the agreement is shown between the experimental points and the curves or lines calculated assuming these values for the constants. In Figs. 3 and 4, thin lines show how much the line would be shifted by the maximum estimated deviation in q_1 or q_2 . Most experimental points are seen to be in the neighbourhood of the calculated curves although some deviate especially in the diagrams in Fig. 3 and Fig. 4 where the points are very sensitive to small errors.

The agreement in Fig. 1 is especially encouraging, since the experimental values for $h-H$ and (15), were not used for calculating q_1 and q_2 .

DISCUSSION

In comparison with the values estimated by J. Bjerrum², $pk_{a1} = 2.8$ and $pk_{a2} = 3.5$, ours are practically reversed. Strangely enough Hg^{2+} with $pk_{a1} = 3.7$ and $pk_{a2} = 2.6$ seems to have a second dissociation constant larger than the first. This behavior Bjerrum could hardly have guessed at; we do not know of any other example previously recorded in literature.

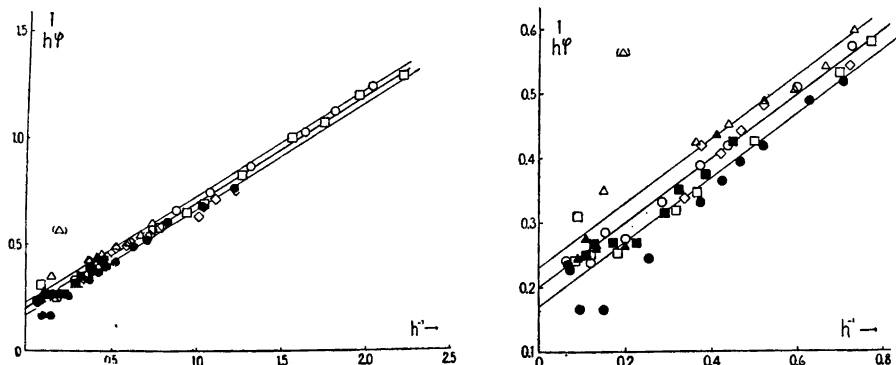
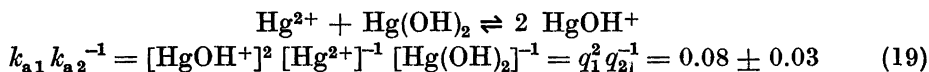


Fig. 4a. $h\phi$ (mC) as a function of h^{-1} (mC^{-1}). Fig. 4b. Left part of Fig. 4a on larger scale. Experimental points: symbols as in Table 1. Lines calculated for $q_2 = 0.50$ mC² and $q_1 = 0.20$ mC (thick line), 0.17 or 0.23 mC (thin lines).

For a polyprotic acid, say H_2A , the ratio between two subsequent acidity constants is $k_{a1}k_{a2}^{-1} = [HA^-]^2 [H_2A]^{-1} [A^{2-}]^{-1}$. For oxy acids with several OH groups on the same central atom, this ratio is usually of the order of magnitude 10^5 . Even for oxalic acid, where the two protons are split off from OH-groups on different C atoms, the ratio is about 1 000. If the ratio were determined by statistical factors only, its value would be 4. The large values ordinarily found are ascribed to the electrostatic forces making it more difficult for the second proton to leave the molecule than it was for the first one.

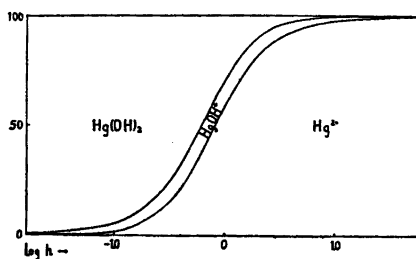
The corresponding constant for the equilibrium



is extraordinarily low, and one may calculate that the fraction of the total Hg^{II} content present in the form of $HgOH^+$ will never exceed about 12 %. In a diagram (Fig. 5) giving the relative amounts of Hg^{2+} , $HgOH^+$ and $Hg(OH)_2$ at various $\log h$, the range for $HgOH^+$ will thus be rather narrow. An unusually narrow range has also been found for $HgCl^+$; at 25° C and with 0.5 C ClO_4^- , the equilibrium constant for $Hg^{2+} + HgCl_2^+ \rightleftharpoons 2 HgCl^+$ is 1.80. The corresponding constants for $HgBr^+$ and HgI^+ , 5.8 and about 100, exceed the statistical value but are still low^{15), 16)}.

The third acidity constant of Hg^{2+} is very much lower than the first two; Garrett and Hirschler¹ have estimated $pK_{a3} = 14.85$. This is also in line with the halide complexes⁹; the linear complex HgX_2 is easily formed, but it takes a much higher $[X^-]$ to obtain the higher complexes HgX_3^- and HgX_4^{2-} .

Fig. 5. Distribution of Hg^{II} (in percent) over Hg^{2+} , HgOH^+ and $\text{Hg}(\text{OH})_2$, as a function of $\log h$ (h in mC). Note the narrow range of HgOH^+ .



Later on, Biedermann¹⁷ has found that the ion TlOH^{2+} , which is iso-electronic with HgOH^+ , has a low constant of formation from Tl^{3+} and $\text{Tl}(\text{OH})_2^+$.

A comparison of our data with the solubility of HgO given by Garrett and Howell⁴, 0.24 mC, shows that at the end of our titrations the solutions must have been supersaturated with respect to HgO .

SUMMARY

The hydrolysis of the Hg^{2+} ion has been studied at 25.0°C and $[\text{ClO}_4^-] = 0.5$ C, using emf methods. In the concentration range studied, the data could be explained by assuming a mononuclear mechanism with the formation of HgOH^+ and $\text{Hg}(\text{OH})_2$. (Equ. (1) and (2)). For the aquo acid $\text{Hg}(\text{H}_2\text{O})_n^{2+}$, $\text{p}k_{a1} = 3.70 \pm 0.07$, and $\text{p}k_{a1} + \text{p}k_{a2} = 6.30 \pm 0.05$, thus $\text{p}k_{a2} = 2.60 \pm 0.09$. For this acid the second dissociation constant is greater than the first, which means that the equilibrium amount of HgOH^+ is always rather small (Fig. 5).

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