

Studies on the Hydrolysis of Metal Ions

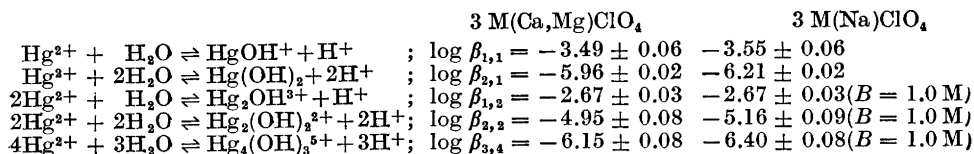
38. The Hydrolysis of Mercury(II) in Perchlorate Medium

INGRID AHLBERG

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

The hydrolysis of Hg(II) has been studied at 25.0°C with the media 3.0 M (Na)ClO₄, (Ca)ClO₄ and (Mg)ClO₄. [H⁺] was measured with a glass electrode and in the more dilute solutions [Hg²⁺] was measured with a redox electrode, Hg₂²⁺, Hg²⁺/Pt.

The data for (Mg)ClO₄ and (Ca)ClO₄ media coincide and differences for (Na)ClO₄ are attributed to variations in activity factors.



The hydrolysis of mercury(II) has been studied by Hietanen and Sillén¹ using 0.5 M (Na)ClO₄ as ionic medium and Hg concentrations between 0.015 M and 0.001 M. They found in this range two mononuclear complexes, with log β_{1,1} = -3.70 ± 0.07 and log β_{2,1} = -6.30 ± 0.05. Their rather unusual result, with a second acidity constant larger than the first (K₁/K₂ = 10^{-1.10} = 0.08), was later confirmed by Anderegg, Schwarzenbach, Padmayo and Borg², who investigated the hydrolysis in nitrate solutions. Extrapolating to ionic strength zero, they got a value of 0.04 for the ratio of the constants for the first and second protonation.

These and other earlier investigations were mostly carried out in dilute solutions and only mononuclear complexes were found. Hayek³, however, determined the solubility of HgO in concentrated mercury perchlorate and concluded that the solution contained polynuclear ions Hg(HgO)₂²⁺. He was able to isolate the solid compound, Hg₃O₂(ClO₄)₂. Crystals of corresponding composition, Hg₃O₂(NO₃)₂H₂O have been found by Bernstein, Pars and Blumenthal⁴.

The self-medium method recently used by Hietanen and Sillén⁵ in studies of Th^{4+} and UO_2^{2+} seemed to be useful in searching for polynuclear complexes in Hg(II) solutions.

When dealing with complicated equilibria in solution it is desirable to keep the activity coefficients constant, allowing the use of concentrations instead of activities in the calculations. This may be brought about through the addition of a large amount of neutral salt as in the inert medium method. If only a minor fraction of the ions in a concentrated metal salt solution is converted into complex species, one might also consider the alteration of the ionic environment to be so small that the same approximation may be made. Since in this work we found it valuable to vary the metal concentration within a very wide range, and were thus forced to substitute a large proportion of the medium ions for mercury ones, we found it advisable also to investigate the influence of the positive medium ion on the activity factors. Sodium, magnesium and calcium perchlorate were used.

The commoner symbols used in the text are the same as in earlier papers in this series (*e.g.* Refs.^{5,8}).

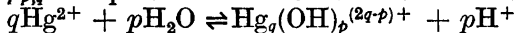
B = total Hg(II) concentration

b = concentration of Hg^{2+}

H = analytical hydrogen ion excess concentration

h = actual $[\text{H}^+]$

$\beta_{p,q}$ = equilibrium constant for the reaction



Z average number of hydrogen ions split off by one Hg(II)

$$BZ = h - H = \sum p\beta_{p,q}b^q h^{-p} \quad (1)$$

$$\eta = \log \frac{B}{b} = \log(1 + \sum q\beta_{p,q}b^{(q-1)}h^{-p}) \quad (2)$$

$y(x)_v = y$ as a function of x at constant v

Other symbols are defined where they appear in the text. All concentrations in tables and figures are expressed in M (mole/l) and equilibrium constants are given on the M scale. In the text the unit mM (millimole/l) will sometimes be used for convenience. The complexes are sometimes written as $\text{Hg}_q(\text{OH})_p$, sometimes as A_pB_q where $A = \text{OH}^-$ or $(-\text{H}^+)$ and $B = \text{Hg}^{2+}$.

EXPERIMENTAL

The experiments were carried out as potentiometric titrations. The hydrogen ion concentration, h , was measured with a glass electrode. Quinhydrone, hydrogen or mercury electrodes could not be used because of their reducing effect on mercury(II).

$$(-)\text{ref/S/glass } (+) \quad (I)$$

$$E_{\text{h}} = E_{\text{oh}} + 59.15 \log h + E_j \quad (3)$$

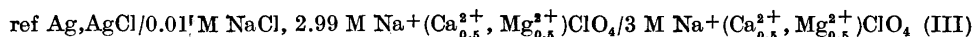
The composition of the solution, S, was for $B = 0.1 M - 1.3 M$: $B M \text{Hg(II)}$, $H M \text{H}^+$, $(3-2B-H) M \text{Na}^+(\text{Ca}_{0.5}^{2+}, \text{Mg}_{0.5}^{2+})$, $3 M \text{ClO}_4^-$ and for $B = 0.01 M - 0.0025 M$ $B M \text{Hg(II)}$, $B' M \text{Hg}_2^{2+}$, $H M \text{H}^+$, $(3-2B-2B'-H) M \text{Na}^+(\text{Ca}_{0.5}^{2+}, \text{Mg}_{0.5}^{2+})$, $3 M \text{ClO}_4^-$. The concentration of free mercury(II) ions, b , was measured with the cell

$$\text{ref/S/Pt} \quad (II)$$

$$E_x = E_{\text{or}} + 29.58 \log [\text{Hg}^{2+}]^2 / [\text{Hg}_2^{2+}] + E_j \quad (4)$$

and h as before with a glass electrode. Oxidation during the titration was prevented by bubbling CO_2 through the solution. In solutions with higher B , stirring was performed by bubbling N_2 through the solution during the titration.

The reference half cell was



Ag, AgCl electrodes were prepared according to Brown ⁶.

The emf of cell (I) was read on a Radiometer valve potentiometer PHM 4, reading accuracy ± 0.2 mV, calibrated against a Leeds and Northrup compensator type K 3. The latter instrument was used for measuring the emf of cell (II).

The liquid junction potential was measured with a glass electrode and a Ag, AgCl electrode. In 1.5 M $\text{Ca}(\text{ClO}_4)_2$ with $0.5 > h > 0.006$ M we found $E_j = -(16.5 \pm 0.5)h$ mV and in 1.5 M $\text{Mg}(\text{ClO}_4)_2$ with $0.2 > h > 0.006$ M $E_j = -(18.5 \pm 1)h$ mV. In 3 M NaClO_4 E_j was found to be $-16.7 h$ mV, in agreement with Biedermann and Sillén ⁷.

For each value of B , one hydrolysed $\text{Hg}(\text{ClO}_4)_2$ solution and one with excess acid were prepared. Two sets of titration were then made. In one the acid solution was added to the hydrolysed one, in the other the hydrolysed solution was in the burette. The latter type of titration was used in order to determine E_{oh} .

Materials and analysis

Sodium, magnesium and calcium perchlorate were each prepared by dissolving the carbonate in perchloric acid and recrystallizing the product twice. The concentration of free strong acid was determined as described by Olin ⁸, and ClO_4^- by ion exchange methods. *Hydrochloric acid* (Kebo p.a.) was standardized against recrystallized Ti_2CO_3 and KHCO_3 . *Sodium hydroxide* was prepared from 50 % NaOH and standardised against HClO_4 . *Calcium hydroxide*. By burning CaCO_3 in an oven at 900°C we got CaO, which was dissolved in water. The clear solution was standardized against HClO_4 . *Mercury (II) oxide* (Merck p.a.) was used without purification. *Mercury (I) perchlorate* was prepared by reducing a solution of $\text{Hg}(\text{ClO}_4)_2$ (see below) with Hg(l).

Determination of remaining Hg^{2+} . After the $\text{Hg}(\text{ClO}_4)_2$ solution had been in contact with Hg for two days it was analysed for Hg^{2+} . From the reduced solution and stock solutions of $\text{Hg}(\text{ClO}_4)_2$, NaClO_4 and HClO_4 two solutions were made up, both 3 M in ClO_4^- and with 50 mM H^+ . One, S_1 contained $(c_1 - \delta)$ mM Hg_2^{2+} and δ mM Hg^{2+} and the other, S_2 , $(c_1 - \delta)$ mM Hg_2^{2+} and $(c_2 + \delta)$ mM Hg^{2+} . c_1 and c_2 were known, δ was unknown. A potentiometric titration was then made, starting with v_0 ml of S_1 and adding gradually v ml of S_2 . The concentration of Hg^{2+} was measured with cell (II). We have ⁹

$$E_{\text{T}} = E_{\text{or}} + 59.15 \log \frac{[\text{Hg}^{2+}] = \delta + vc_2/(v_0 + v)}{[\text{Hg}_2^{2+}]^{0.5} = E'_0 + 59.15 \log [\text{Hg}^{2+}]}$$

since $[\text{Hg}_2^{2+}]$ is constant.

$$[\text{Hg}^{2+}] = 10^{(E - E'_0)/59.15} = \delta + vc_2/(v_0 + v)$$

By analogy with the method developed by Gran ¹⁰ for determination of h , $10^{(E - E'')/59.15}$ ($E'' =$ arbitrary constant) was plotted as a function of $vc_2/(v_0 + v)$ and extrapolated to zero; this gave δ as the intercept on the axis. The ratio $[\text{Hg}^{2+}]/[\text{Hg}_2^{2+}]$ was calculated and found to be close to the value of the equilibrium constant for the reaction $\text{Hg}^{2+} + \text{Hg} \rightleftharpoons \text{Hg}_2^{2+}$ given by Hietanen and Sillén ¹¹ for the actual perchlorate concentration.

Mercury (II) perchlorate. HgO was dissolved in HClO_4 . A clear solution was obtained only with an excess of acid. Since it was desirable to cover as broad a Z range as possible, we wanted a hydrolysed solution saturated with HgO. First we started by dissolving an excess of HgO in an acid 3 M ClO_4^- solution and filtered off the undissolved oxide. On analysing this solution, however, we came upon several difficulties.

Determination of $[\text{Hg}]_{\text{tot}}$. Winkler's method, in which Hg is precipitated as Hg_2Cl_2 , gave values that agreed very well with each other. To test the accuracy of the analysis we used a solution with a known amount of Hg(II) and found a difference of -0.3 %. With electrolysis, using a rotating platinum net in acid solution, the difference was even greater.

Table 1.

Values of $-\log h$, Z and η with 1.5 M $\text{Ca}(\text{ClO}_4)_2$ medium

$B = 0.0025$ M: $-\log h$, Z , η ; 3.280, 1.554, 0.7352; 3.194, 1.396, 0.6069; 3.111, 1.250, 0.5023; 3.040, 1.111, 0.4189; 2.970, 0.988, 0.3500; 2.849, 0.743, 0.2475; 2.737, 0.549, 0.1775; 2.631, 0.404, 0.1278; 2.536, 0.301, 0.0954; 2.379, 0.172, 0.0597; 2.255, 0.120, 0.0392; 2.164, 0.090, 0.0318; 2.032, 0.060, 0.0215; 1.941, 0.044, 0.0166; 1.872, 0.024, 0.0142; 1.817, 0.024, 0.0108; 1.743, 0.020, 0.0086; 1.673, —, 0.0069; 1.576, —, 0.0047; 1.498, —, 0.0034;

$B = 0.005$ M: $-\log h$, Z , η ; 2.952, 0.923, 0.3341; 2.862, 0.761, 0.2629; 2.776, 0.615, 0.2046; 2.692, 0.491, 0.1589; 2.612, 0.383, 0.1238; 2.533, 0.299, 0.0964; 2.455, 0.236, 0.0757; 2.326, 0.144, 0.0509; 2.213, 0.111, 0.0367; 2.129, 0.082, 0.0287; 2.002, 0.056, 0.0198; 1.912, 0.040, 0.0154; 1.817, 0.026, 0.0118; 1.750, 0.014, 0.0100; 1.682, 0.022, 0.0068;

Table 2.

Values of $-\log h$, Z and η with 3 M NaClO_4 medium.

$B = 0.0025$ M: $-\log h$, Z , η ; 3.104, 1.005, 0.3692; 3.023, 0.845, 0.2954; 2.948, 0.699, 0.2370; 2.872, 0.576, 0.1903; 2.800, 0.472, 0.1541; 2.734, 0.382, 0.1252; 2.668, 0.315, 0.1024; 2.607, 0.259, 0.0839; 2.550, 0.223, 0.0612; 2.455, 0.167, 0.0531; 2.375, 0.135, 0.0415; 2.255, 0.096, 0.0286; 2.171, 0.065, 0.0228; 2.103, 0.062, 0.0189; 2.051, 0.055, 0.0172; 1.828, 0.028, 0.0091; 1.687, —, 0.0061; 1.505, —, 0.0046;

$B = 0.005$ M: $-\log h$, Z , η ; 2.827, 0.521, 0.1755; 2.784, 0.462, 0.1550; 2.744, 0.407, 0.1388; 2.702, 0.359, 0.1236; 2.621, 0.277, 0.0964; 2.546, 0.211, 0.0757; 2.473, 0.166, 0.0614; 2.315, 0.102, 0.0384; 2.201, 0.073, 0.0279; 2.117, 0.060, 0.0222; 2.002, 0.040, 0.0168; 1.664, 0.012, 0.0066; 1.488, 0.008, 0.0044;

$B = 0.010$ M: $-\log h$, Z , η ; 2.271, 0.092, 0.0347; 2.326, 0.114, 0.0406; 2.380, 0.137, 0.0472; 2.429, 0.163, 0.0549; 2.482, 0.202, 0.0642; 2.511, 0.224, 0.0707; 2.335, 0.126, 0.0419; 2.191, 0.075, 0.0279; 2.080, 0.049, 0.0205; 1.992, 0.035, 0.0157; 1.836, 0.016, 0.0111; 1.723, 0.012, 0.0076; 1.566, 0.002, 0.0057; 1.456, —, 0.004; 1.373, —, 0.0046; 1.307, —, 0.0041;

Table 3.

Values of $-\log h$, Z with 1.5 M $\text{Ca}(\text{ClO}_4)_2$ medium.

$B = 0.100$ M: $-\log h$, Z ; 2.032, 0.0929; 1.956, 0.0737; 1.880, 0.0587; 1.807, 0.0476; 1.741, 0.0388; 1.677, 0.0333; 1.625, 0.0283; 1.533, 0.0204; 1.454, 0.0178; 1.393, 0.0131; 1.341, 0.0095; 1.295, 0.0071; 1.217, 0.0066; 1.155, 0.0079; 1.107, 0.0032;

$B = 0.500$ M: $-\log h$, Z ; 1.697, 0.0998; 1.670, 0.0913; 1.645, 0.0838; 1.584, 0.0709; 1.523, 0.0595; 1.462, 0.0500; 1.400, 0.0427; 1.332, 0.0355; 1.290, 0.0319; 1.243, 0.0276; 1.155, 0.0227; 1.084, 0.0192; 1.025, 0.0164; 0.950, 0.0148; 0.891, 0.0134; 0.830, 0.0112; 0.783, 0.0086; 0.741, 0.0092; 0.710, 0.0056; 0.673, 0.0052; 0.644, 0.0066; 0.617, 0.0044; 0.587, 0.0040;

$B = 1.000$ M: $-\log h$, Z ; 1.474, 0.0983; 1.446, 0.0895; 1.415, 0.0815; 1.382, 0.0742; 1.346, 0.0680; 1.283, 0.0563; 1.217, 0.0474; 1.156, 0.0403; 1.099, 0.0350; 1.048, 0.0306; 0.984, 0.0254; 0.921, 0.0230; 0.872, 0.0203; 0.832, 0.0175; 0.779, 0.0181; 0.735, 0.0137; 0.700, 0.0122; 0.670, 0.0113; 0.636, 0.0104; 0.583, 0.0089; 0.546, 0.0074; 0.516, 0.0078; 0.494, 0.0067; 0.720, 0.0132; 0.690, 0.0123; 0.656, 0.0114; 0.624, 0.0104; 0.388, 0.0090; 0.551, 0.0070; 0.507, 0.0074; 0.473, 0.0069; 0.438, 0.0059; 0.387, 0.0058; 0.328, 0.0050;

Table 4.

Values of $-\log h$, Z with 1.5 M $\text{Mg}(\text{ClO}_4)_2$ medium.

$B = 0.100$ M: $-\log h$, Z ; 2.026, 0.0949; 1.966, 0.0794; 1.908, 0.0657; 1.849, 0.0552; 1.793, 0.0466; 1.741, 0.0396; 1.692, 0.0346; 1.606, 0.0269; 1.533, 0.0208; 1.471, 0.0176; 1.371, 0.0116; 1.293, 0.0097; 1.202, 0.0098; 1.134, 0.0072; 1.063, 0.0080; 1.003, 0.0042; 0.954, 0.0050;

$B = 0.200$ M: $-\log h$, Z ; 1.868, 0.0816; 1.817, 0.0700; 1.765, 0.0604; 1.714, 0.0518; 1.660, 0.0458; 1.567, 0.0355; 1.484, 0.0288; 1.415, 0.0231; 1.298, 0.0181; 1.212, 0.0136; 1.145, 0.0095; 1.084, 0.0108; 1.035, 0.0107; 0.996, 0.0080; 0.942, 0.0095; 0.888, 0.0075; 0.845, 0.0045; 0.808, 0.0055;

$B = 0.500$ M: $-\log h$, Z ; 1.701, 0.0998; 1.677, 0.0916; 1.645, 0.0845; 1.584, 0.0714; 1.525, 0.0598; 1.464, 0.0503; 1.403, 0.0426; 1.347, 0.0363; 1.295, 0.0312; 1.244, 0.0277; 1.156, 0.0227; 1.085, 0.0191; 1.030, 0.0149; 0.954, 0.0136; 0.893, 0.0132; 0.834, 0.0096; 0.783, 0.0092; 0.744, 0.0076; 0.708, 0.0062; 0.681, 0.0054; 0.631, 0.0034; 0.558, 0.0062; 0.534, 0.0050;

$B = 1.000$ M: $-\log h$, Z ; 1.488, 0.1014; 1.457, 0.0928; 1.423, 0.0848; 1.393, 0.0773; 1.359, 0.0706; 1.292, 0.0591; 1.227, 0.0497; 1.168, 0.0420; 1.112, 0.0360; 1.060, 0.0315; 0.992, 0.0263; 0.933, 0.0230; 0.884, 0.0197; 0.840, 0.0176; 0.786, 0.0153; 0.744, 0.0128; 0.707, 0.0117; 0.678, 0.0096; 0.644, 0.0081; 0.610, 0.0069; 0.573, 0.0066; 0.544, 0.0058; 0.517, 0.0083; 0.499, 0.0078; 0.451, 0.0077; 0.396, 0.0080; 0.348, 0.0067;

$B = 1.300$ M: $-\log h$, Z ; 1.446, 0.1197; 1.429, 0.1130; 1.407, 0.1070; 1.369, 0.0954; 1.331, 0.0852; 1.292, 0.0763; 1.253, 0.0685; 1.214, 0.0618; 1.178, 0.0557; 1.124, 0.0484; 1.080, 0.0418; 1.033, 0.0370; 0.992, 0.0328; 0.935, 0.0287; 0.888, 0.0255; 0.897, 0.0232; 0.815, 0.0207; 0.774, 0.0192; 0.735, 0.0176; 0.695, 0.0153; 0.663, 0.0145; 0.637, 0.0132; 0.610, 0.0127; 0.830, 0.0222; 0.800, 0.0199; 0.764, 0.0185; 0.729, 0.0165; 0.688, 0.0155; 0.647, 0.0136; 0.604, 0.0123; 0.568, 0.0109; 0.531, 0.0098; 0.504, 0.0096; 0.475, 0.0099; 0.448, 0.0087; 0.418, 0.0085; 0.387, 0.0077;

Table 5.

Values of $-\log h$, Z with 3 M NaClO_4 medium.

$B = 0.100$ M: $-\log h$, Z ; 2.088, 0.0817; 2.019, 0.0661; 1.948, 0.0541; 1.880, 0.0445; 1.814, 0.0382; 1.753, 0.0338; 1.701, 0.0296; 1.613, 0.0219; 1.533, 0.0199; 1.473, 0.0156; 1.418, 0.0131; 1.369, 0.0134; 1.292, 0.0107; 1.229, 0.0091; 1.178, 0.0067; 1.112, 0.0078; 1.016, 0.0051;

$B = 0.500$ M: $-\log h$, Z ; 1.758, 0.0945; 1.733, 0.0872; 1.699, 0.0799; 1.635, 0.0663; 1.566, 0.0550; 1.496, 0.0459; 1.429, 0.0386; 1.368, 0.0326; 1.307, 0.0289; 1.256, 0.0251; 1.165, 0.0204; 1.092, 0.0169; 1.033, 0.0137; 0.957, 0.0120; 0.898, 0.0104, 0.834, 0.0096; 0.784, 0.0080; 0.744, 0.0070;

$B = 1.000$ M: $-\log h$, Z ; 1.518, 0.0946; 1.479, 0.0864; 1.446, 0.0784; 1.408, 0.0714; 1.375, 0.0646; 1.304, 0.0535; 1.233, 0.0450; 1.168, 0.0381; 1.107, 0.0331; 1.053, 0.0293; 1.003, 0.0268; 0.923, 0.0223; 0.877, 0.0188; 0.832, 0.0173; 0.778, 0.0154; 0.734, 0.0142; 0.700, 0.0120; 0.668, 0.0120; 0.634, 0.0110; 0.683, 0.0125; 0.656, 0.0110; 0.593, 0.0098; 0.524, 0.0081; 0.456, 0.0068; 0.375, 0.0061; 0.296, 0.0060;

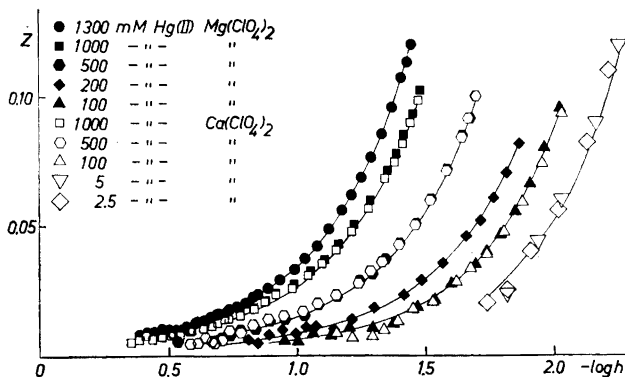


Fig. 1. Hydrolysis of Hg^{2+} in 1.5 M $\text{Ca}(\text{Mg})(\text{ClO}_4)_2$. Experimental data plotted as $Z(-\log h)_B$. The curves are calculated with the equilibrium constants given in the text.

Determination of H. Several methods are recommended in the literature for the determination of the analytical hydrogen content. Bromide¹³ forms strong complexes with mercury and diminishes the hydrolysis, but on adding strong mercury(II) solution to sodium bromide solution we got a precipitate, which it was possible to dissolve only by protracted boiling. Under these conditions there was a strong smell of Br_2 , the indicator lost its colour and the equivalence point was transitory. Adding bromide to a diluted mercury (II) solution and bubbling with nitrogen during the titration in order to get rid of carbon dioxide and prevent oxidation by atmospheric oxygen, gave values agreeing to within 0.1 %, but all 1 % lower than the correct one. Potentiometric titration with acid, using a Gran diagram¹⁰ gave a concave curve instead of a straight line, even if both $\text{Hg}(\text{II})$ and Br^- were kept constant during the experiment. The results seemed also to depend upon the time of contact between the mercury (II) and bromide solutions. Thus it did not seem likely that this method would give accurate results unless a more complicated technique could be used.

Shaking with liquid Hg and titrating the reduced solution potentiometrically with acid, using the Gran extrapolation, gave too high H -values.

Determination of total perchlorate content. Good results for the total perchlorate content ($= 2B + H$) were obtained by passing a known amount of solution of known $[\text{ClO}_4^-]$ through a H^+ saturated ion exchanger and titrating the eluate with NaOH . When mercury was removed by electrolysis and the solution afterwards titrated with NaOH we got slightly lower values for $(2B + H)$. If B is high serious errors in H might arise from the mercury analysis on using the two last methods.

Final preparation. After having tried these different methods of analysis for H with not too good results, we decided to proceed in the simplest way. We could use the approximate information given by the experiments, described above, about the highest Z -value that could be reached. We weighed out 5–25 g oxide and dissolved this in a weighed amount of standard acid by heating on a waterbath for a few days. By this method we got more reproducible results, *i.e.* with separately made solutions we got the same $Z(\log h)_B$ curve.

For each B value we prepared one acid and one hydrolysed solution. The latter frequently became turbid after addition of perchlorate and dilution to the desired volume. The precipitate was filtered off through a porcelain filter and weighed after being dried in a desiccator at room temperature. In order to avoid errors arising from changes in air humidity, a second crucible of the same kind was treated in the same way and used as a blank for weight correction. The precipitate weighed about 1 mg/100 ml solution. If it is assumed to be HgO , the correction in H may be calculated. It was never as large as 0.1 % of B .

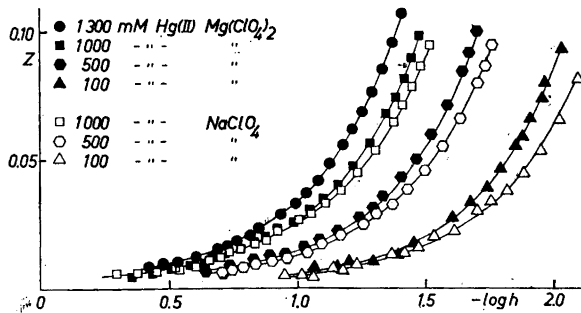


Fig. 2. Hydrolysis of Hg^{2+} in 3 M $Na(Mg)ClO_4$. Experimental data plotted as $Z(-\log h)_B$. The curves are calculated with the equilibrium constants given in the text.

CALCULATIONS

The experimental data are presented in Tables 1–5 and Figs. 1–4. It should be observed that, on increasing B , the limiting composition will be the same for all three media, namely 1.5 M $Hg(ClO_4)_2$. One may ask how much the activity factors are affected by the change in ionic medium. It is seen that, within the experimental error, the data $Z(\log h)_B$ for 3 M $(Mg)ClO_4$ coincide with those for 3 M $(Ca)ClO_4$ in the whole B range studied.

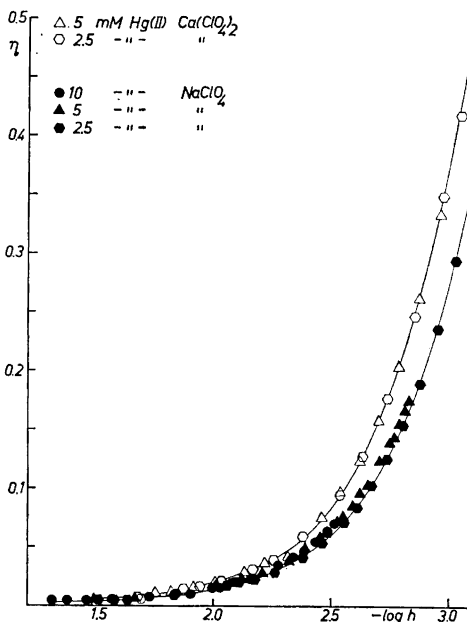


Fig. 3. Experimental data $\eta = \log(B/b)$ as a function of $-\log h$. The curves are calculated with the mononuclear constants given in the text.

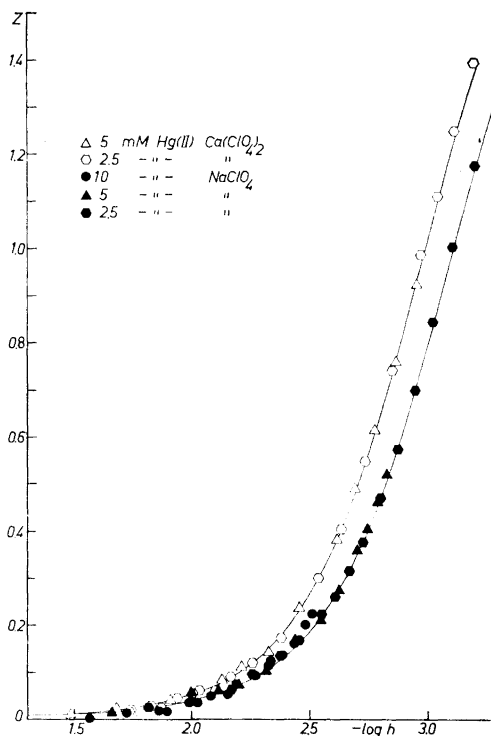


Fig. 4. Experimental data plotted as $Z(-\log h)_B$. The curves are calculated with the equilibrium constants given in the text.

The simplest explanation is that the activity factors are not perceptibly changed when Hg^{2+} is replaced by another bivalent ion, Mg^{2+} or Ca^{2+} . The data in 3 M (Ca)ClO₄ and 3 M (Mg)ClO₄ will therefore be considered together as one group and the emphasis will be laid on them.

With 3 M (Na)ClO₄ on the other hand, the curves for low B deviate considerably from those with 3 M (Ca, Mg)ClO₄. For low B we may still assume constant activity coefficients and equilibrium constants in 3 M (Na)ClO₄, but these will be different from those in 3 M (Ca, Mg)ClO₄.

When B increases, separate curves are obtained for different B values (Figs. 1 and 2). This indicates the presence of polynuclear complexes.

Treatment of data in the mononuclear range

For the lowest values of B the points fall on the same $\eta(\log h)_B$ or $Z(\log h)_B$ curve, the "mononuclear wall" (Figs. 3 and 4), *i.e.* only mononuclear complexes are found and this is in agreement with the results of Hietanen and Sillén¹.

Z-data. We have $Z = \frac{\beta_{1,1}a + 2\beta_{2,1}a^2}{1 + \beta_{1,1}a + \beta_{2,1}a^2}$ (7)

where $a = h^{-1}$.

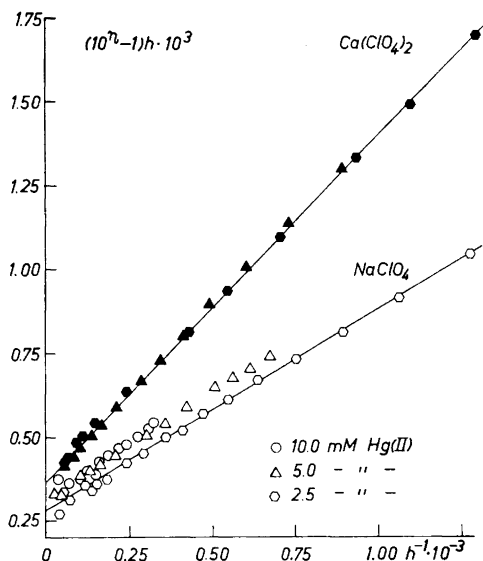


Fig. 5. $(10^\eta - 1)h$ as a function of h^{-1} . The lines give in 1.5 M $\text{Ca}(\text{ClO}_4)_2$, $\log \beta_{1,1} = -3.44$, $\log \beta_{2,1} = -5.97$ and in 3 M NaClO_4 , $\log \beta_{1,1} = -3.53$, $\log \beta_{2,1} = -6.21$.

The experimental curve $Z(\log h)_B$ was compared with normalized curves, $Z(\log u)_B$. Ref. ¹³

$$Z = \frac{u + 2ku^2}{1 + u + ku^2} \quad (8)$$

where $u = \beta_{1,1}a$ and $k = \beta_{2,1}\beta_{1,1}^{-2}$.

Redox data. Setting

$$10^\eta = B/b = 1 + \beta_{1,1}h^{-1} + \beta_{2,1}h^{-2} \quad (9)$$

and

$$(10^\eta - 1)h = \beta_{1,1} + \beta_{2,1}h^{-1}$$

$(10^\eta - 1)h$, plotted as a function of h^{-1} is shown in Fig. 5. To calculate η from E_r , a preliminary value of E_{or} was obtained from the most acid solutions, neglecting the hydrolysis. The plot $(10^\eta - 1)h$, (h^{-1}) then showed a deviation downwards from the straight line for the lowest h^{-1} values, showing that we had chosen a too low value of E_{or} . A too high value of E_{or} on the other hand caused the points to deviate upwards. The best value of E_{or} was taken as the one which gave the least deviation between the calculated line and the experimental points. In 3 M $(\text{Na})\text{ClO}_4$ the correction amounted to 0.15 mV but in 3 M $(\text{Ca})\text{ClO}_4$ where the solution was still more acid (~ 0.1 M), the preliminary E_{or} value could be used without any correction.

The point of intersection with the vertical axis gave $\beta_{1,1}$ and the slope $\beta_{2,1}$. The values are tabled below. Almost the same results were obtained by curve-fitting analogous to (8).

The constants were then refined, using the experimental points and the generalized least squares treatment "Letagrop" (pit-mapping)¹⁸. The error limits given are three times the "standard" or root mean square deviation (σ).

	3 M (Ca)ClO ₄		3 M (Na)ClO ₄	
	log $\beta_{1,1}$	log $\beta_{2,1}$	log $\beta_{1,1}$	log $\beta_{2,1}$
<i>Z data</i>				
<i>B</i> = 0.005 M, 0.0025 M				
Curve-fitting	-3.50 ± 0.06	-6.00 ± 0.04	-3.55 ± 0.06	-6.21 ± 0.02
Letagrop	-3.52 ± 0.03	-5.962 ± 0.003	-3.55 ± 0.04	-6.211 ± 0.003
<i>η data</i>				
<i>B</i> = 0.005 M, 0.0025 M				
Curve-fitting	-3.48 ± 0.04	-5.96 ± 0.02	-3.53 ± 0.04	-6.20 ± 0.02
Linear plot	-3.44 ± 0.04	-5.97 ± 0.02	-3.53 ± 0.04	-6.21 ± 0.02

The larger uncertainty in log $\beta_{1,1}$ may be understood from the fact that the complex HgOH⁺ exists in a small amount (at most about 10 % of all Hg(II)) and in a narrow log *h* range.

Treatment of data in the polynuclear range

For the higher concentrations only the *Z* data were used, since the variations of η proved too small to be useful for calculations. The primary data were the measurements $E(H)_B$. To calculate *Z* and *h* one needs to know E_0 and E_j in eqn. (3). The first calculations were made using approximate values for E_{oh} , estimated from the most acidic solutions. As the calculations proceeded, E_{oh} and E_j could be refined as will be described below.

From the slope of the curves of the highest *B* values (self-media) it might be concluded⁵ that for low *Z* values the predominating complexes contain only one OH⁻ group. A comparison with the value of $\beta_{1,1}$ already determined showed that there must also be polynuclear complexes AB_{*q*} besides AB (HgOH⁺).

$$\text{Beginning from} \quad BZ = \sum p\beta_p a^p b^q \quad (1)$$

we subtracted the mononuclear terms, setting as a first approximation $b = B(1-2Z)$ or $b = B(1-Z)$, which gave the same result, since the difference is small. Assuming one polynuclear complex with one OH⁻ group and another with *p* OH⁻ groups we have

$$B_c Z_c = BZ - \beta_{1,1} ab - 2\beta_{2,1} a^2 b = \beta_{1,q} a b^{q'} + p\beta_{p,q} a^p b^q \quad (10)$$

Multiplying by $a^{-1} = h$ and extracting the first term we get, after taking logarithms,

$$\log B_c Z_c a^{-1} = \log \beta_{1,q} b^{q'} + \log (1 + p\beta_{p,q} a^{(p-1)} b^q / \beta_{1,q} b^{q'}) \quad (11)$$

Since in each titration $b \approx B = \text{constant}$ (11) may be written in the normalized form ($v = \text{const.} a^{-1}$).

$$\log B_c Z_c a^{-1} = \log k + \log(1 + v^{(1-p)}) \quad (12)$$

$$\text{where} \quad \log k = \log \beta_{1,q'} + q' \log B \quad (12a)$$

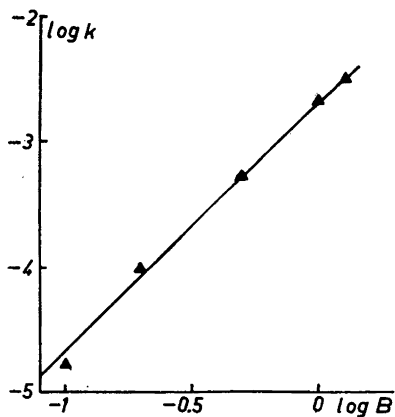


Fig. 6. $\log k$ as a function of $\log B$ according to eqn. (12 a). The slope of the line gives $q' = 2$ and the intercept on the vertical axis $\log \beta_{1,2} \sim -2.7$.

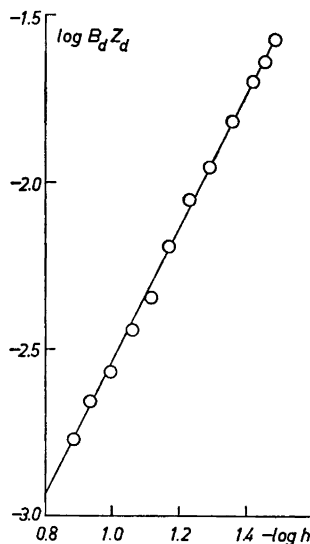


Fig. 7. $\log B_d Z_d$ as a function of $-\log h$ for $B = 1.000$ M according to eqn. (4). $B_d Z_d$; terms for HgOH^+ , $\text{Hg}(\text{OH})_2$, $\text{Hg}_2\text{OH}^{3+}$ have been subtracted. The line gives $p = 2$.

To find $\log k$ the experimental plots $(\log B_c Z_c h)(\log h)_B$ were compared with theoretical curves $\log(1 + v^{(1-p)})(\log v)$ (Ref.¹⁴), calculated for different values of p . The fit was better with $p = 2$ than with $p = 3$. The following calculation for q and $\beta_{p,q}$ was made with $p = 2$ but with another p value one would obtain a very similar result.

Plotting $\log k$ as a function of $\log B$ (Fig. 6) gave $\log \beta_{1,q}$ as intercept on the vertical axis. The slope of the line was $q' = 2$. The complex thus seems to be $\text{Hg}_2\text{OH}^{3+}$ with $\log \beta_{1,2}$ approximately $= -2.7$.

With this knowledge we could start again from the experimental data $E(H)_B$ to get a better value of E_{oh} , using a method somewhat modified from that given by Hietanen and Sillén⁵. BZ was obtained for selected values of $\log h$ from curves, calculated with the constants found above. From the relation $H = h - BZ$ we got the corresponding H values. From the experimental $E(H)_B$ diagram the corresponding values of E were interpolated. $E + 59.15 \log h$ was then plotted as a function of h , and the straight line, extrapolated to $h = 0$, gave E_{oh} and the slope E_j . The procedure had to be repeated and the results improved as one gained more knowledge about the complexes appearing; the refinement of E_{oh} and E_j of course led to corresponding small changes in H and Z .

As mentioned above the curve $\log(1 + v^{(1-p)})(\log v)$ for $p = 2$ gave a better fit with the experimental points than that with $p = 3$, which indicates a complex with two OH^- groups. In order to remove any doubt, the term for the new complex with one OH^- was subtracted.

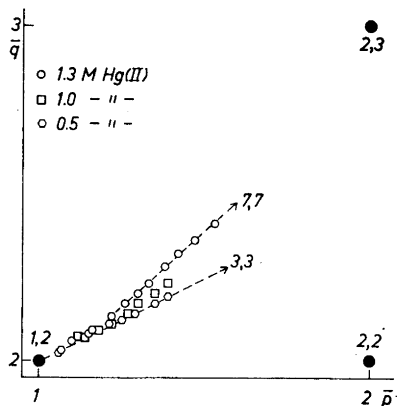


Fig. 8. \bar{q} versus \bar{p} . The main complex is AB_2 . Points for different B values lie on separate lines. The arrows marked 7,7 and 3,3 point to complexes A_7B_7 and A_3B_3 .

$$B_d Z_d = BZ - \beta_{1,1} ab - 2\beta_{2,1} a^2 b - kh^{-1} = p\beta_{p,q} a^p b^q \quad (13)$$

where $kh^{-1} = \beta_{1,q} ab^q$

$$\log B_d Z_d = p \log a + \log p\beta_{p,q} b^q \quad (14)$$

In Fig. 7, for $B = 1.0$ M, $\log B_d Z_d (\log a)_B$ gave a straight line with slope $p = 2$. From the intersection with the vertical axis $\beta_{p,q}$ was obtained. Plotting

$$\log B_d Z_d - 2 \log a = q \log B + \log \beta_{2,q} + \log 2 \quad (15)$$

versus $\log B$, the slope ($= q$) was intermediate between 2 and 3.

To distinguish between $q = 2$ and 3 several ways were tried. By integration from experimental curves, $Z(\log h)_B$ using general expressions given by Sillén¹⁵, b could be calculated. Starting the integration at $Z = Z_0 = 0.01$ and assuming the dominating complex there to be AB_2 , we have

$$B = b_0 + 2\beta_{1,2} a_0 b_0^2 \quad (16)$$

$$BZ_0 = \beta_{1,2} a_0 b_0^2 \quad (17)$$

$$BR_0 = b_0 + \beta_{1,2} a_0 b_0^2 \quad (18)$$

$$\text{and } \ln \frac{b}{B} = \ln (1 - 2Z_0) + \int_{Z_0}^Z \left(\frac{\log a}{\log B} \right)_Z dZ - \int_{Z_0}^Z Z d \ln a \quad (19)$$

As the function for the mononuclear species is known, one could subtract it and calculate the average composition of the polynuclear complexes.

$$\bar{q} = \frac{B - B_1}{BR - B_1} \quad (20) \quad \bar{p} = \frac{BZ - B_1 Z_1}{BR - B_1} \quad (21)$$

where $B_1 Z_1 = b(\beta_{1,1} a + \beta_{2,1} a^2)$ and $B_1 = b(1 + \beta_{1,1} a + \beta_{2,1} a^2)$

The plot \bar{q} against \bar{p} for $B = 1.3, 1.0$ and 0.5 M is shown in Fig. 8. Since the points for different B values lie on diverging lines, we must have at least

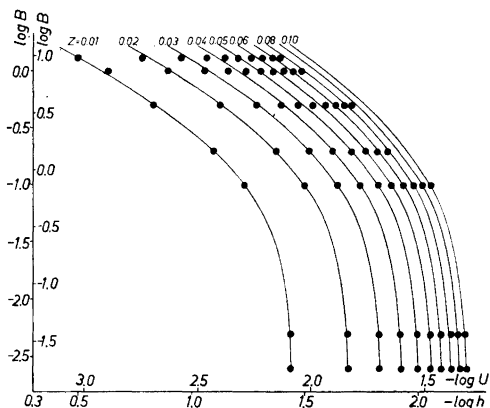


Fig. 9. Projection map: experimental data $\log B(-\log h)_Z$ and normalized curves $\log B^*(\log u)_Z$, calculated for AB, A_2B , AB_2 , A_2B_2 , assuming $\log \beta_{1,1}^{-1}\beta_{2,1} = 1.1$ and $\log \beta_{1,1}^{-1}\beta_{1,2}^{-1}\beta_{2,2} = 1.3$.

two complexes besides the ones found above. As the Z range which it is possible to integrate is very small, definite values of the p and q values cannot be determined from the plot.

The experimental data $\log B(\log h)_Z$ were compared with normalized projection maps, $\log B^*(\log h)_Z$ (Ref.¹⁶).

$$B = b + \beta_{1,1}ab + \beta_{2,1}a^2b + 2\beta_{1,2}ab^2 + q\beta_{2,q}a^2b^q \tag{22}$$

$$B^* = v + uv + ku^2v + 2uv^2 + lqu^2v^q \tag{23}$$

where

$$B^* = \beta_{1,1}^{-1}\beta_{1,2}B; \quad v = \beta_{1,1}^{-1}\beta_{1,2}b; \quad u = \beta_{1,1}a \tag{24, 24a, 24b}$$

$$k = \beta_{1,1}^{-2}\beta_{2,1}; \quad l = \beta_{1,1}^{(q-3)}\beta_{1,2}^{(1-q)}\beta_{2,q} \tag{24c, 24d}$$

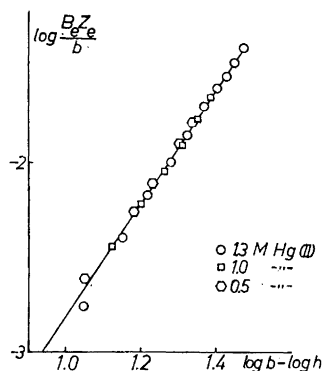


Fig. 10. $\log B_e Z_e / b$ as a function of $\log b - \log h$, according to (26). $B_e Z_e$; terms for $HgOH^+$, $Hg(OH)_2$, Hg_2OH^{3+} , $Hg_2(OH)_2^{2+}$ have been subtracted. The line gives $p=3$.

The best fit for lower B and Z values was obtained with the assumption $q = 2$, i.e. a complex A_2B_2 together with those found earlier (Fig. 9). For higher values of B and Z the experimental points lay on lines more curved towards higher $\log h$ values than the normalized ones, thus indicating another complex with higher values of p and q .

With the help of the Ferranti Mercury Computer and the program "KUSKA"¹⁷, several curves $Z(\log h)_B$ were calculated for different values of $\beta_{1,2}$ and $\beta_{2,2}$. From these the one giving the best fit for $B = 0.1$ M, was chosen. The same set of constants could also explain the experimental points for $B = 0.2$ M. When B increased, deviations appeared for high Z -values. Subtracting all four complexes one obtains

$$B_e Z_e = BZ - \beta_{1,1}ab - 2\beta_{2,1}a^2b - \beta_{1,2}ab^2 - 2\beta_{2,2}a^2b^2 = p\beta_{p,q}a^p b^q \quad (25)$$

In these calculations b was taken from the integration (19).

Setting $q = p + x$

$$\log B_e Z_e / b^x = p \log ab + \log p\beta_{p,q} \quad (26)$$

Fig. 10 shows $\log B_e Z_e / b^x$ as a function of $\log ab$ for $x = 1$. It is seen that for this value of x the points from different B values fall on the same line. The slope, p , is 3. For all other values of x points for different B values fell on different lines. The complex thus ought to be $Hg_4(OH)_3^{5+}$. The point of intersection with the vertical axis gives an approximate value of $\beta_{p,q}$.

In order to find more accurate values of the five complex constants the generalized least square treatment "LETAGROP"¹⁸ was used.

The deviation given is 3σ as above.

3 M (Ca,Mg)ClO ₄	$\log \beta_{1,1}$	$\log \beta_{2,1}$	$\log \beta_{1,2}$	$\log \beta_{2,2}$	$\log \beta_{3,4}$
Letagrop					
($B = 1.3 - 0.0025$ M)	-3.52 ± 0.03	-5.962 ± 0.003	-2.66 ± 0.06	-4.91 ± 0.12	-6.18 ± 0.12
($B = 1.3 - 0.1$ M)	-3.49 ± 0.02	(-5.96)	-2.67 ± 0.02	-4.95 ± 0.05	-6.15 ± 0.05
Proposed values	-3.49 ± 0.06	-5.96 ± 0.02	-2.67 ± 0.03	-4.95 ± 0.08	-6.15 ± 0.08

In 3 M (Na)ClO₄ the activity coefficients may have a bigger influence, so with help of the same treatment as above the constants were calculated separately for different B values.

3 M (Na)ClO ₄	$\log \beta_{1,1}$	$\log \beta_{2,1}$	$\log \beta_{1,2}$	$\log \beta_{2,2}$	$\log \beta_{3,4}$
Letagrop					
($B = 1.0$ M)	-3.55 ± 0.06	(-6.21)	-2.65 ± 0.02	-5.16 ± 0.09	-6.40 ± 0.02
($B = 0.5$ M)	-3.55 ± 0.09	»	-2.70 ± 0.03	-5.10 ± 0.09	-6.4 ± 0.1
($B = 0.1$ M)	-3.56 ± 0.08	»	-2.7 ± 0.1	-5.2 ± 0.1	-

The values given within brackets have not been varied.

CONCLUSION

From the data presented in this paper one may conclude that in Hg(II) perchlorate solutions there are polynuclear species with 1 OH, 2 OH and 3 OH, besides the mononuclear ones found previously by several investigators. The formulas ascribed above have been AB_2 , A_2B_2 and A_3B_4 , thus Hg_2OH^{3+} ,

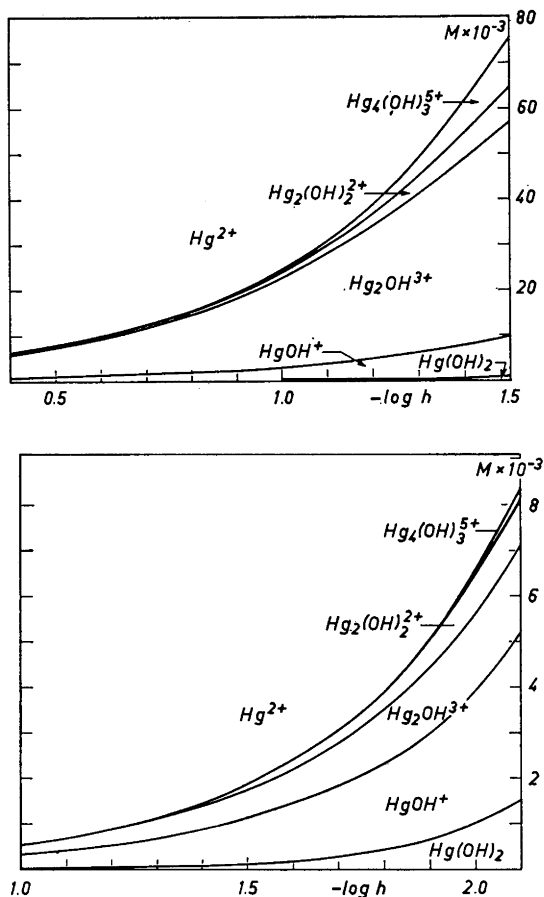


Fig. 11. Distribution of complexes as a function of $-\log h$ for the total mercury concentrations $B = 1.000$ M and $B = 0.100$ M.

$\text{Hg}_2(\text{OH})_2^{2+}$ and $\text{Hg}_4(\text{OH})_3^{5+}$ as usual with unknown amounts of H_2O and ClO_4^- . A complex AB_2 has also been found in solutions of other divalent metals for instance Pb^{2+} (Ref.¹⁹) and Cd^{2+} (Ref.²⁰), Be^{2+} (Ref.²²) and Cu^{2+} (Ref.²³). A_2B_2 was found in Fe^{3+} (Ref.²⁴), UO_2^{2+} (Ref.²¹) and Th^{4+} (Ref.⁵) among others.

As may be seen from Fig. 11, which shows the distribution of the various species as a function of $\log h$ for the two limiting concentrations $B = 1.0$ M and 0.1 M, the complexes $\text{Hg}_2\text{OH}^{3+}$ and $\text{Hg}_2(\text{OH})_2^{2+}$ are the most important polynuclear products of hydrolysis, while $[\text{Hg}_4(\text{OH})_3^{5+}]$ becomes appreciable only for the higher concentration before precipitation. For this reason the composition of the last complex is somewhat more uncertain than those of $\text{Hg}_2\text{OH}^{3+}$ and $\text{Hg}_2(\text{OH})_2^{2+}$.

It is remarkable that no differences were found if one divalent medium ion Mg^{2+} was substituted with another of the same valency, Ca^{2+} . Even if the positive medium-ion was changed to an univalent one (Na^+) the equilibrium constants were not very much affected.

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