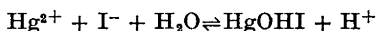


## The Mixed Complexes of Mercury(II) with Hydroxide and Iodide

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The mixed complexes formed between mercury(II), hydroxide and iodide in solutions with 0.5 M sodium perchlorate as supporting electrolyte have been studied at 25°C, by measuring the emf of the cell -GE|S|SE+, where GE is a glass electrode and SE a standard reference electrode. S had the general composition:  $B \text{ Hg(II)}$ ,  $H \text{ H}^+$ ,  $(0.5 \text{ M} - 2B - H) \text{ Na}^+$ ,  $X \text{ I}^-$ ,  $(0.5 \text{ M} - X) \text{ ClO}_4^-$ . The ratio  $X/B$  was 0.5 or 1.0. The experimental data  $Z$  (average number of  $\text{OH}^-$  bound per mercury(II)) as a function of  $\log h$  could be described by assuming one mixed complex, *viz.*  $\text{HgOHI}$ . The equilibrium constant,  $\beta_{1,1,1}$ , for the reaction



was determined as  $\log \beta_{1,1,1} = 8.9 \pm 0.1$ .

The equilibrium between mercury and iodide with 0.5 M  $\text{NaClO}_4$  as supporting electrolyte has been studied by Sillén *et al.*<sup>1-3</sup> by emf measurements and by Marcus<sup>4</sup> using distribution equilibrium methods. Their results are shown in Table 1. Sillén's values have been used in the calculations. Analogously to the hydrolysis of the mercury bromide,<sup>5</sup> it is  $K_{1,2}$ , the equilibrium constant for the reaction



that together with  $\beta_{1,1,0}$  and  $\beta_{2,1,0}$  has to be known when computing the equilibrium constant  $K_{1,1}$ , for the reaction

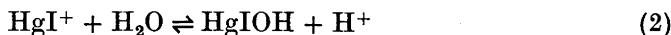
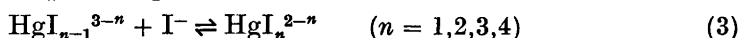
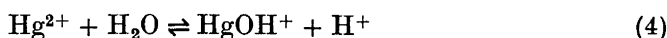


Table 1 also gives  $K_n$ , the equilibrium constant for the reaction



The equilibrium constant for the reactions



and



Table 1. Equilibrium constants for the system  $\text{Hg}^{2+} - \text{I}^-$ .

Ref.	Method	$K_{1,2}$	$\log (K_1/M)$	$\log (K_2/M)$	$\log (K_3/M)$	$\log (K_4/M)$
Sillén <i>et al</i> 1949 <sup>1,2</sup>	red, Hg	115	12.87	10.95	3.78	2.23
Sillén 1949 <sup>3</sup>						
Marcus <sup>4</sup>	distr.	81			3.67	2.37

have been taken from the work by Hietanen and Sillén,<sup>10</sup>  $\log (\beta_{1,1,0}/M) = -3.70 \pm 0.07$ ,  $\log (\beta_{2,1,0}/M^2) = -6.30 \pm 0.05$ .

### EXPERIMENTAL

*Chemicals.* Sodium perchlorate, perchloric acid, sodium hydroxide, silver perchlorate, and mercury perchlorate were prepared as described previously.<sup>5,6</sup> Sodium iodide (Malinckrodt, *p.a.*) was analysed potentiometrically.

*Details of the emf measurements.* In order to produce hydrolysed solutions of  $u = 1.0$  the following solutions were carefully mixed into the titration vessel. Since  $\text{HgI}_2$  is the least soluble species especially the additions of  $S_4$  had to be performed very slowly to avoid Tyndall effects.

- $S_1$ : 0.75 mM Hg(II), 0.08 mM  $\text{H}^+$ , 498.5 mM  $\text{Na}^+$ , 500 mM  $\text{ClO}_4^-$ .  
 $S_2$ : 0.75 mM Hg(II), 0.08 mM  $\text{H}^+$ , 498.5 mM  $\text{Na}^+$ , 496.3 mM  $\text{ClO}_4^-$ , 3.75 mM  $\text{I}^-$ .  
 $S_3$ : 1.50 mM Hg(II), 0.16 mM  $\text{H}^+$ , 496.8 mM  $\text{Na}^+$ , 500 mM  $\text{ClO}_4^-$ .  
 $S_4$ : 1.50 mM Hg(II), 0.16 mM  $\text{H}^+$ , 496.8 mM  $\text{Na}^+$ , 492.5 mM  $\text{ClO}_4^-$ , 7.5 mM  $\text{I}^-$ .  
 $S_5$ : 13.38 mM NaOH, 500 mM  $\text{ClO}_4^-$ .

The ratio of the volumes of  $S_1$  and  $S_2$  was 4:1 and of  $S_3$ ,  $S_4$  and  $S_5$  4:1:5.

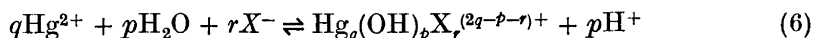
$$S_0 = S_1 + S_2 + S_3 + S_4 + S_5$$

The solutions  $S_1$  and  $S_2$  were prepared from 100 mM stock solutions of Hg(II) perchlorate.  $S_2$  and  $S_4$  originated from stock solutions of sodium iodide and mercury(II) perchlorate.

Magnetic stirring was applied and  $\text{N}_2$  was passed through the solution. This was then immediately titrated with an acid solution which had the same values of  $B$  and  $X$  as had  $S_0$ .

### LIST OF SYMBOLS

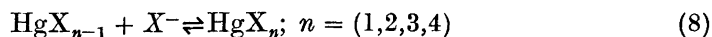
- $B$  = total Hg(II) concentration.  
 $b$  = concentration of  $\text{Hg}^{2+}$ .  
 $X$  = total halogen concentration.  
 $x$  = concentration of free halogenide.  
 $u = X/B$ .  
 $H$  = analytical hydrogen ion excess concentration.  
 $h$  = actual concentration of hydrogen ion.  
 $a = h^{-1}$ .  
 $\beta_{p,q,r}$  = equilibrium constant for the reaction



$Z$  average number of hydrogen ions split off per Hg(II)

$$BZ = h - H = p \beta_{p,q,r} b^p h^{-p} x^r \quad (7)$$

$K_n$  = equilibrium constant for the reaction



$K_{1,2}$  = equilibrium constant for the reaction



#### MEASUREMENTS AND CALCULATIONS

Potentiometric measurements were performed in the cell previously described.<sup>5</sup> The solutions S in the titration vessel had compositions analogous to those described for the bromide systems, *i.e.*  $X/B$  was maintained constant in each titration. However, the low solubility of mercury(II) iodide further complicated the study of the mercury-hydroxide-iodide system. When  $u=0.5$ ,  $B$  was 5.00 mM or 2.5 mM. The concentration of free iodide,  $x$ , increases both with  $u$  and  $-\log h$ .

When  $u=1.0$ , it was necessary to lower the total iodide concentration in order to obtain a hydrolysed solution without precipitation of red  $\text{HgI}_2$ . Therefore the value of  $B$  was chosen as 0.75 mM.

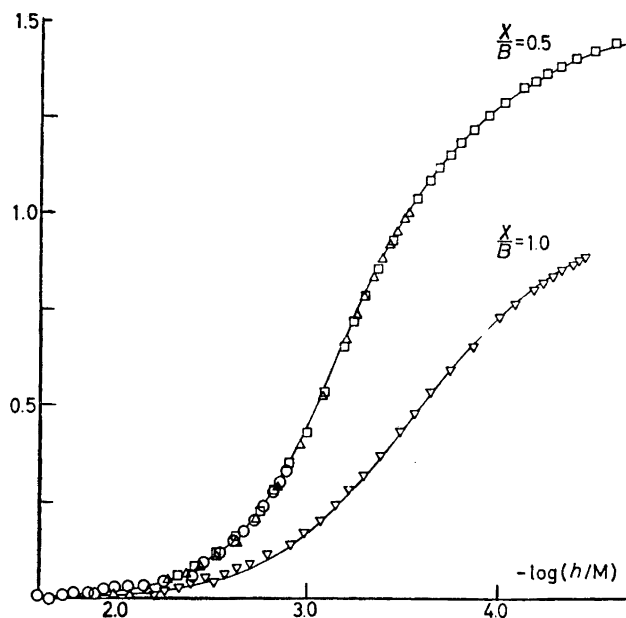


Fig. 1. The formation of hydroxo complexes in solutions containing mercury(II) and iodide. The curves have been calculated from the equilibrium constants in Table 3. The experimental points are denoted  $\circ$ ,  $\triangle$ ,  $\square$ , and  $\nabla$  for  $B=10$ , 5, 2.5, and 0.75 mM, respectively.

Table 2. Survey of titrations.

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$u = 0.500, B = 5.000 \text{ mM.}$	
$-\log(h/M), Z;$	3.548, 1.001; 3.526, 0.985; 3.485, 0.949; 3.448, 0.915; 3.441, 0.881; 3.364, 0.831; 3.318, 0.782; 3.277, 0.733; 3.219, 0.671; 3.094, 0.522; 2.976, 0.395; 2.861, 0.288; 2.746, 0.204; 2.637, 0.146; 2.541, 0.105; 2.455, 0.083; 2.384, 0.062; 2.271, 0.050; 2.180, 0.023; 2.080, 0.011; 2.002, 0.010.
$u = 0.500, B = 2.500 \text{ mM.}$	
$-\log(h/M), Z;$	4.642, 1.444; 4.527, 1.424; 4.432, 1.404; 4.349, 1.384; 4.275, 1.365; 4.215, 1.346; 4.153, 1.327; 4.051, 1.290; 3.967, 1.254; 3.893, 1.218; 3.821, 1.184; 3.762, 1.150; 3.707, 1.117; 3.656, 1.084; 3.590, 1.036; 3.532, 0.989; 3.461, 0.928; 3.385, 0.854; 3.318, 0.783; 3.257, 0.716; 3.204, 0.716; 3.101, 0.532; 3.010, 0.429; 2.919, 0.350; 2.842, 0.277; 2.768, 0.225; 2.640, 0.160; 2.540, 0.115; 2.423, 0.082; 2.337, 0.058.
$u = 1.000, B = 0.750 \text{ mM.}$	
$-\log(h/M), Z;$	4.482, 0.888; 4.448, 0.880; 4.414, 0.867; 4.357, 0.853; 4.304, 0.837; 4.255, 0.821; 4.211, 0.805; 4.105, 0.765; 4.025, 0.727; 3.886, 0.655; 3.765, 0.592; 3.663, 0.533; 3.578, 0.479; 3.499, 0.432; 3.397, 0.371; 3.308, 0.317; 3.229, 0.278; 3.161, 0.243; 3.080, 0.202; 2.995, 0.169; 2.925, 0.143; 2.804, 0.116; 2.714, 0.093; 2.640, 0.078; 2.578, 0.064; 2.539, 0.043; 2.478, 0.056; 2.403, 0.046.

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Values of  $Z$ , plotted as a function of  $\log h$ , is shown in Fig. 1. The complete data for all the titrations are given in Table 2.

For solutions having a constant  $X/B$ , the experimental  $Z(\log h)$  curves coincide for different  $B$ -values. They may be described by assuming one mixed complex,  $\text{HgIOH}$ , corresponding to that of the bromide system.<sup>5</sup> Since the mercury iodide complexes are stronger than the corresponding bromide ones,  $x$  has a lower value in the iodide solutions. The same approximations as in Ref. 5 are consequently allowed and we obtain,

$$u = \frac{X}{B} = \frac{\beta_{0,1,1}x + 2\beta_{0,1,2}x^2 + \beta_{1,1,1}ax}{1 + \beta_{1,1,0}a + \beta_{2,1,0}a^2 + \beta_{0,1,1}x + \beta_{0,1,2}x^2 + \beta_{1,1,1}ax} \quad (10)$$

$$Z = \frac{(\beta_{1,1,0}a + 2\beta_{2,1,0}a^2 + \beta_{1,1,1}ax)(2-u)}{2(1 + \beta_{1,1,0}a + \beta_{2,1,0}a^2) + \beta_{0,1,1}x + \beta_{1,1,1}ax} \quad (11)$$

$Z$  is a function of the two independent variables  $u$  and  $a$ .

Comparison of the experimental  $Z$  curves to those calculated from (14), assuming different values of  $\beta_{1,1,1}$  gives the best fit when  $\log \beta_{1,1,1} = 8.9 \pm 0.1$ .

The experimental data were treated by means of the computer program "Letagrop", designed by Sillén *et al.*<sup>7</sup> The equilibrium constants that minimized the error square sum

$$U = \sum (Z_{\text{exp}} - Z_{\text{calc}})^2 \quad (12)$$

was sought.

The values, obtained by the computer are given in Table 3. In the first row all points in Table 2 were used. When the errors in  $H_0$ ,  $H_T$  and  $E_0$  were treated

Table 3. Survey of equilibrium constants in the system Hg(II)–OH–I.

Constant	Computer			Curve-fitting
	All points	$X/B=0.5$	$X/B=1.0$	
$\beta_{0,1,1}/M^{-1}$	$7.6 \times 10^{12}$	$7.4 \times 10^{12}$	$(1.2 \pm 0.1)10^{13}$	$7.4 \times 10^{12}$
$\beta_{0,1,2}/M^{-2}$	$(8 \pm 1)10^{23}$	$(12.2 \pm 0.5)10^{23}$	$(8.2 \pm 1.6)10^{23}$	$6.6 \times 10^{23}$
$\beta_{1,1,0}/M$	$(2.21 \pm 0.04)10^{-4}$	$(2.24 \pm 0.09)10^{-4}$	$2.00 \times 10^{-4}$	$2.00 \times 10^{-4}$
$\beta_{2,1,0}/M^2$	$(5.35 \pm 0.05)10^{-7}$	$(5.52 \pm 0.03)10^{-7}$	$5.01 \times 10^{-7}$	$5.01 \times 10^{-7}$
$\beta_{1,1,1}$	$(8.4 \pm 0.5)10^8$	$(6.5 \pm 0.1)10^8$	$(18 \pm 2)10^8$	$(8 \pm 2)10^8$

as unknown constants, the computer gave high values for  $E_0$  in the last titration ( $X/B=1.0$ ), where the solutions were supersaturated with respect to  $HgI_2$ . Therefore the data from this titration were also handled separately. In this way the second and third rows of Table 3 have been obtained.

Only one mixed complex,  $Hg(OH)I$ , was found. Its stability constant  $\beta_{1,1,1}$  was  $(8 \pm 2) \times 10^8$ .

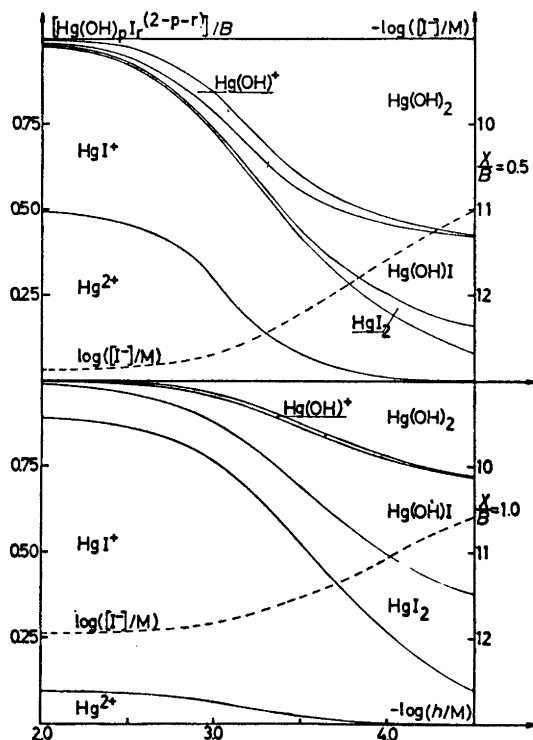


Fig. 2. The distribution of the complexes  $Hg(OH)_p I_r^{2-p-r}$  as a function of  $-\log h$ .

## RESULTS AND COMMENTS

The distributions of the various species as functions of  $-\log h$  at  $X/B = 0.5$  and 1.0 is shown in Fig. 2.

The hydrolysed solutions were supersaturated with respect to  $\text{HgI}_2$ , as is seen from the following values which correspond to some of the highest points of the  $Z$  curves:

$u$	$-\log(h/M)$	$B/M$	$[\text{HgI}_2]/M$	$[\text{Hg}(\text{OH})_2]/M$
0.5	4.6	0.0025	$2 \times 10^{-4}$	$1.4 \times 10^{-3}$
0.5	3.5	0.005	$0.9 \times 10^{-4}$	$1.6 \times 10^{-3}$
1.0	4.5	0.00075	$2 \times 10^{-4}$	$0.20 \times 10^{-3}$

From Biedermann and Sillén's<sup>8</sup> determination of the solubility of  $\text{HgI}_2$  it follows that  $[\text{HgI}_2] = 7 \times 10^{-5}$  M in a saturated solution of mercury(II) iodide. A comparison with the value of  $[\text{Hg}(\text{OH})_2] = 0.2 \times 10^{-3}$  M in solutions saturated with mercury(II) oxide, which can be deduced from Garrett's work,<sup>9</sup> indicates that the two first solutions are also supersaturated with respect to  $\text{Hg}(\text{OH})_2$ .

In a previous publication<sup>5</sup> the acidity of some species  $\text{HgX}^+$  are given and discussed. For the iodide one gets  $K_{1,1} = \beta_{1,1,1}/\beta_{0,1,1} = 1.0 \times 10^{-4}$  M, *i.e.*  $\text{HgI}^+$  is a weaker acid than the other mercury monohalide ions studied.

If statistical reasons alone determined the equilibrium constants,  $\beta_{1,1,1}$  could be calculated from the relation  $\beta_{1,1,1} = 2(\beta_{0,1,2}\beta_{2,1,0})^{\frac{1}{2}}$ , which gives  $\beta_{1,1,1} = 11 \times 10^8$ , close to the experimental value  $(8 \pm 2) \times 10^8$ .

The value of  $\beta_{1,1,1}$  depends on many different constants taken from literature. Systematic errors may also be present because it was rather difficult to prepare a clear  $S_0$ -solution. Therefore the real error in  $\beta_{1,1,1}$  might be much larger than that calculated by the computer.

My thanks are due to Professor Nils Ingri and Professor Ido Leden for valuable discussions.

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