Mercury(II) Halide Mixed Complexes in Solution

II. Complexity Constants of the Binary Complexes

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Complexity constants for mercury(II) halide complexes were determined by solvent (benzene) distribution for 0.50 M NaClO₄ ionic medium and 25°. The constants found are:

Reaction	Constant	Chloride	Bromide	Iodide
$\text{Hg}^{2+} + \text{HgX}_2 \rightleftharpoons 2\text{HgX}^+$	$\log K$	0.26 ± 0.03	0.94 ± 0.06	1.91 ± 0.07
$\text{HgX}^+ + \text{X}^- \rightleftharpoons \text{HgX}_2$	$\log k_2$	6.3 ± 0.2	8.3 ± 0.3	
$\text{HgX}_2 + \text{X}^- \rightleftharpoons \text{HgX}_3^-$	$\log k_3$	0.95 ± 0.03	2.27 ± 0.02	3.67 ± 0.02
$\text{HgX}_2 + 2\text{X}^- \rightleftharpoons \text{HgX}_4^{2-}$	$\log k_3 k_4$	2.00 ± 0.05	4.02 ± 0.02	6.04 ± 0.02

These values agree with published potentiometric values, except for bromide, but the solvent distribution value of $\log K$ agrees with a redetermined potentiometric value of $\log K = 0.94 \pm 0.03$. The constants found here will be taken to apply in the solvent distribution work on the mixed complexes.

In order to study the relative stability of the mixed mercury(II) halide complexes, the complexity constants of the binary complexes were measured, using the same ionic medium and temperature, and the same method (solvent distribution), as later on for the ternary systems. The binary constants have previously² been determined by potentiometric methods for these same conditions, namely 25° and 0.50 M (perchlorate + halide) ionic medium. As a check on the assumption that benzene has no effect on the aqueous equilibria, some potentiometric measurements were made on comparable solutions with and without benzene.

Symbols. The symbols used here are defined in part I¹ p. 330.

EXPERIMENTAL

The experimental details of the solvent distribution experiments are described in part I¹ p. 331. The potentiometric measurements followed the procedure of Sillén and Infeldt³.

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The titrations consisted of adding ($\text{Hg}^{2+} + \text{Br}^-$) titrant to 100.0 ml ($\text{Hg}^{2+} + \text{Hg}_2^{2+}$) solution in the titration vessel. The 0.2 M bromide stock solution was tested for iodide, but no coloration by iodine could be detected by the nitrite-starch test, whereas adding I^- to a ratio $(\text{I}^-)/(\text{Br}^-) = 5 \times 10^{-5}$ gave an observable coloration. The titrations were performed in a thermostated bath at $25.0 \pm 0.1^\circ$ and N_2 , free from O_2 , was bubbled through the solution during the titration. The reference electrode was Ag, AgCl/10 mM Ag^+ , 10 mM H^+ 480 mM Na^+ 500 mM ClO_4^- // and two Pt electrodes, compared against it, usually agreed to within 0.05 mV. Steady potentials were obtained 5 min after the addition of titrant, and the potentials usually deviated no more than 0.03 mV from values obtained 25 min later.

DETERMINATION OF K , THE EQUILIBRIUM CONSTANT FOR $\text{Hg}^{2+} + \text{HgX}_2 \rightleftharpoons 2 \text{HgX}^+$

Derivation of equations, solvent distribution

In solutions of mercury and halide, where the stoichiometric ratio X/M is 2.00 or less, the only species occurring will be M^{++} , MX^+ and MX_2 , provided the solutions are not so dilute that X^- also appears (see below, p. 603). The pertinent equilibrium reaction will then be

The mass balances of mercury and halide will be

$$M = [\text{M}] + [\text{MX}] + [\text{MX}_2] + [\text{MX}_2]_{\text{or}} \quad \text{and} \quad (2)$$

$$X = M\bar{n} = [\text{MX}] + 2[\text{MX}_2] + 2[\text{MX}_2]_{\text{or}} \quad (3)$$

The equilibrium constant of (1) will give

$$[\text{MX}]^2 = K [\text{M}] [\text{MX}_2] \quad (4)$$

When such an aqueous solution is equilibrated with benzene,

$$[\text{MX}_2]_{\text{or}} = \lambda [\text{MX}_2] \quad (5)$$

and the distribution ratio of mercury will be

$$D = [\text{MX}_2]_{\text{or}} ([\text{M}] + [\text{MX}] + [\text{MX}_2])^{-1} \quad (6)$$

Eliminating all concentrations from (2), (3), (4), (5) and (6), the following expression for K is obtained:

$$K = \frac{[\bar{n}(1 + D) \lambda - 2D(1 + \lambda)]^2}{D[(1 - \bar{n})(1 + D)\lambda + D(1 + \lambda)]} \quad (7)$$

For the special case $\bar{n} = 1.00$ this reduces to:

$$K_{\bar{n}=1.00} = [\lambda - D(2 + \lambda)]^2 D^{-2} (1 + \lambda)^{-1} \quad (7a)$$

Although eqn. (7) is valid for all values of $\bar{n}$ less than 2.00, the best accuracy is obtained with $\bar{n}$ around unity.

Experimental results, solvent distribution

Table 1 gives the results for the three halides, as $\log D(\bar{n})$. The M values are also given, although they do not enter the calculations. The values of $\log$

K were obtained by solving numerically (7) — or (7a) in the case of bromide — and are averaged at the end of each section. The values of λ , obtained from part I¹, are given at the top of each section.

Table 1. The constant K of the equilibrium $\text{Hg}^{2+} + \text{HgX}_2 \rightleftharpoons 2 \text{HgX}^+$

Chloride, $\log \lambda = -0.963$				Bromide, $\log \lambda = 0.152$				Iodide, $\log \lambda = 1.77$			
$\bar{n}$	$-\log M$	$-\log D$	$\log K$	$\bar{n}$	$-\log M$	$-\log D$	$\log K$	$\bar{n}$	$-\log M$	$-\log D$	$\log K$
0.20	3.37	1.07	0.23	1.00	3.15	0.75	0.93	0.64	3.33	0.73	1.85
0.20	3.15	1.04	0.25	1.00	3.02	0.74	0.88	0.86	3.33	0.48	1.84
0.20	3.07	1.04	0.25	1.00	2.85	0.74	0.88	0.88	4.00	0.42	1.89
0.20	2.85	1.01	0.27	1.00	2.72	0.77	1.00	1.00	4.00	0.36	1.92
0.20	2.73	0.99	0.28	1.00	2.55	0.74	0.88	1.08	3.33	0.29	2.02
0.20	2.55	1.04	0.25	1.00	2.42	0.74	0.88	1.28	3.33	0.08	1.92
0.20	2.47	1.01	0.27	1.00	2.25	0.77	1.00				
0.20	2.25	1.03	0.26	1.00	2.11	0.77	1.00				
0.20	2.17	1.05	0.24	1.00	1.95	0.76	0.97				
0.20	1.95	1.03	0.26								
0.94	1.75	1.55	0.26								
1.09	1.75	1.45	0.29								
1.17	1.75	1.39	0.24								
$\log K_{\text{av}} = 0.26 \pm 0.03$				$\log K_{\text{av}} = 0.94 \pm 0.06$				$\log K_{\text{av}} = 1.91 \pm 0.07$			
$\log K_{\text{pot}} = 0.26 \pm 0.03$				$\log K_{\text{pot}} = 0.77 \pm 0.05$				$\log K_{\text{pot}} = 1.92 \pm 0.05$			

Potentiometry

The value of K for bromide from the solvent distribution experiments differs sufficiently from the earlier potentiometric value to warrant being checked. The method of Sillén and Infeldt³ used in the earlier potentiometric work was followed. These authors showed that if v ml titrant (X M $\text{Br}^- + M$ M Hg^{2+}) is added to 100.0 ml solution (M M Hg^{2+} + some Hg_2^{2+}), the potential of a Pt electrode against a suitable reference electrode at 25° will be

$$E_v = E_0 - 29.58 \log (1 + v/100) + 59.16 \log mM^{-1} \quad (8)$$

where E_0 is the potential before the addition of any titrant. The ligand number will be

$$\bar{n} = Xv (100 + v)^{-1} M^{-1} \quad (9)$$

and combined with mM^{-1} obtained from (8) this gives

$$K = (2 - 2mM^{-1} - \bar{n})^2 (mM^{-1})^{-1} (mM^{-1} + \bar{n} - 1)^{-1} \quad (10)$$

Table 2 gives the values of K (numerical averages from the values at individual points) obtained for several experiments with solutions at different con-

Table 2. Potentiometric titrations for K for $\text{Hg}^{2+} + \text{HgBr}_2 \rightleftharpoons 2 \text{HgBr}^+$.

Benzene	M (in mM)	X (in mM)	$\log K$	Symbol in Fig. 1
—	2.7	24.1	0.96 ± 0.03	○
Present	2.7	24.1	0.95 ± 0.02	●
—	5.3	24.1	0.96 ± 0.03	□
Present	5.3	24.1	0.94 ± 0.04	■
—	10.7	48.3	0.93 ± 0.05	△
—	10.7	48.3	0.91 ± 0.03	△
Present	10.7	48.3	0.95 ± 0.04	▲
—	21.3	48.3	0.92 ± 0.02	×
Grand average			0.94 ± 0.03	

centrations, with benzene present in some of them. (The solutions were saturated with benzene by passing the N_2 through benzene before bubbling it through the solution in the titration vessel for a sufficient time.)

From Tables 1 and 2 the new potentiometric value of K is seen to agree very well with the solvent distribution value. Also, the presence of benzene

Fig. 1. The dilution corrected potential difference $E_v - E_0 + 29.58 \log (1 + v/100)$ as function of the ligand number $\bar{n}$, for the reaction $\text{Hg}^{2+} + \text{HgBr}_2 \rightleftharpoons 2 \text{HgBr}^+$. The symbols refer to Table 2. The curves were calculated with the indicated constants.

does not seem to affect the equilibrium in the aqueous phase. The results of the experiments are also shown in Fig. 1, where the data $E_v - E_0 + 29.58 \log (1 + v/100)$ as function of $\bar{n}$ are compared with curves calculated with various constants K . The best fit is evidently with $\log K = 0.94 \pm 0.03$, while the former potentiometric value of Sillén and Infeldt $\log K = 0.77$ does not fit the present data *.

DETERMINATION OF k_2 , THE EQUILIBRIUM CONSTANT OF $\text{HgX}^+ + \text{X}^- \rightleftharpoons \text{HgX}_2$

Derivation of equations

If a solution of MX_2 is sufficiently diluted, the dissociation $\text{MX}_2 \rightleftharpoons \text{MX}^+ + \text{X}^-$ will become appreciable, and the D values will deviate from λ . The concentration should, however, not be so low that the further dissociation of $\text{HgX}^+ \rightleftharpoons \text{Hg}^{++} + \text{X}^-$ becomes noticeable. If, then, the mass balance is $M = [\text{MX}] + [\text{MX}_2] + [\text{MX}_2]_{\text{or}}$, the charge balance is $x = [\text{MX}]$ and the ratio $\bar{n} = 2.00$, eqn. (11) may be derived:

$$k_2 = D \lambda (1 + D) (\lambda - D)^{-2} M^{-1} \quad (11)$$

The value obtained for k_2 , combined with that of K found above, yield the value of k_1 .

It may be mentioned in passing that the disproportionation $2 \text{HgX}_2 \rightleftharpoons \text{HgX}^+ + \text{HgX}_3^-$, equilibrium constant k_3/k_2 , was neglected in this work. Strictly speaking the distribution expression in HgX_2 solutions should be $\lambda = \lambda' (1 + 2\sqrt{k_3/k_2})^{-1}$, where λ' is the true distribution coefficient of the species MX_2 . Inserting the values of k_3/k_2 one finds $\log \lambda \approx \log \lambda' + 0.0008$, so that the difference between λ and λ' is much smaller than the experimental error.

Experimental results

As is seen from equation (11), the constant k_2 is inversely proportional to M , and as k_2 is of the order of 10^6 for chloride, and larger still for the other halides, this means that very low M values are necessary. If, moreover, the value of $(\lambda - D)$ should be larger than 10 % λ , in order that the values do not become too uncertain, the upper limits for $\log M$ are: chloride -4.5 , bromide -5.8 , and iodide -7.2 . The specific activity of the mercury available was, however, too low to permit a sufficient dilution of the solutions, so that no value of k_2 for iodide, and only rough estimates for chloride and bromide could be obtained. Results are shown in Table 3. The constants were calculated only from the experiments indicated, since for the others the results were too uncertain.

* It is very remarkable that such a large difference has been found between the potentiometric values of K determined in 1943 and now. Gunnar Infeldt was a very careful worker and a good analyst, and in general his values have been well confirmed, when they have later on been checked by others. One possible explanation is that there was some impurity in the bromide used by Infeldt, although it is hard to see what this could have been. Since Gunnar Infeldt has passed away in the meantime, and no samples of the old solutions are left, it is impossible to make sure.

Lars Gunnar Sillén

Table 3. The constants k_3 , k_1 and β_2 for chloride and bromide.

	$\log M$	$\log D$	$\log k_1$	$\log k_2$	$\log \beta_2$
Chloride	-4.83 ± 0.03	-1.05 ± 0.05			
	-5.13 ± 0.03	-1.09 ± 0.06			
	-5.43 ± 0.03	-1.13 ± 0.06	6.3 ± 0.2	6.6 ± 0.2	12.9 ± 0.3
Bromide	-5.46 ± 0.02	0.126 ± 0.010	8.3 ± 0.3	9.2 ± 0.3	17.5 ± 0.5
	-5.76 ± 0.05	0.09 ± 0.06			
	-6.06 ± 0.08	-0.17 ± 0.12			

DETERMINATION OF k_3 AND k_3k_4 , THE EQUILIBRIUM CONSTANTS OF
 $\text{HgX}_2 + \text{X}^- \rightleftharpoons \text{HgX}_3^-$ AND $\text{HgX}_2 + 2\text{X}^- \rightleftharpoons \text{HgX}_4^{2-}$

When there is an excess of free halide, *i. e.* when $\bar{n} > 2.00$, the complexes HgX_3^- and HgX_4^{2-} are gradually formed, whereas species with $\bar{n} < 2$ may be completely neglected. The solvent distribution will then follow the expression:

$$D = [\text{MX}_2]_{\text{or}} ([\text{MX}_2] + [\text{MX}_3] + [\text{MX}_4])^{-1} = \lambda (1 + k_3x + k_3k_4x^2)^{-1} \quad (12)$$

The constants k_3 and k_3k_4 may be found by the following methods.

Curve fitting

For applying the curve fitting method ⁴, the normalized variables Y and Z are introduced:

$$\begin{aligned} Y &= \log \lambda - \log D = \log (1 + v + pv^2) & Z &= \log v \\ v &= k_3x \text{ and } p = k_4/k_3 \end{aligned} \quad (13a)$$

or, alternatively:

$$\begin{aligned} Y' &= \log \lambda - \log D = \log (1 + p'v' + v'^2) & Z' &= \log v' \\ v' &= (k_3k_4)^{1/2} x \text{ and } p' = (k_3/k_4)^{1/2}. \end{aligned} \quad (13b)$$

The data in the form $\log D$ ($\log x$) are plotted, and compared with families of curves $Y(Z)_p$ or $Y'(Z')_{p'}$, whence the values of:

$$\begin{aligned} \log D (Y = 0) &= \log D (Y' = 0) = \log \lambda \\ \log x (Z = 0) &= -\log k_3 \\ \log p &= \log k_4 - \log k_3 \\ \log x (Z' = 0) &= -1/2 \log k_3k_4 \\ \log p' &= 1/2 \log k_3/k_4 \end{aligned}$$

are obtained. In practice, the best values of $\log k_3$ are obtained from the Y, Z, v, p family, while those of $\log k_3k_4$ are best obtained from the Y', Z', v', p' family.

Linear plots

An alternative method is to transform eqn. (12) so that its plot will be a straight line from which k_3 and k_3k_4 are obtained as intercept and slope:

$$(\lambda D^{-1} - 1) x^{-1} = k_3 + k_3k_4x \quad (14a)$$

or, alternatively:

$$(\lambda D^{-1} - 1) x^{-2} = k_3x^{-1} + k_3k_4. \quad (14b)$$

In practice it is found that k_3 is best obtained as the slope when the left term of (14b) is plotted *vs* x^{-1} , and k_3k_4 is best obtained when the left term of (14a) is plotted *vs* x .

Experimental results

Experimental data $\log D(\log x)$ were obtained in the following ranges of concentrations:

$$-4.1 < \log [\text{Cl}^-] < -0.7; \quad -4.0 < \log [\text{Br}^-] < -1.0; \quad -5.3 < \log [\text{I}^-] < -2.1$$

In every case $X > 100 M$ (except for the lowest $[\text{I}]$, where $X > 10 M$), so that x may be safely put equal to X . Plots of the data are shown in Figs. 2, 3 and 4 for chloride, bromide and iodide. The data for bromide are also given in Table 4.

Table 4. The distribution of HgBr_2 as function of excess bromide concentration.

$-\log x$	$-\log M$	$\log D$	$-\log x$	$-\log M$	$\log D$
4.01 $\pm$ 0.03	5.0	0.150 $\pm$ 0.030	2.01	4.6	-0.400 $\pm$ 0.007
3.71 $\pm$ 0.02	5.0	0.145 $\pm$ 0.015	1.86	4.6	-0.590 $\pm$ 0.010
3.41 $\pm$ 0.02	5.0	0.135 $\pm$ 0.015	1.71	4.6	-0.775 $\pm$ 0.010
3.23 $\pm$ 0.01	5.0	0.115 $\pm$ 0.015	1.63	4.6	-0.850 $\pm$ 0.010
3.01	4.6	0.060 $\pm$ 0.010	1.53	4.6	-1.055 $\pm$ 0.010
2.86	4.6	0.030 $\pm$ 0.010	1.41	4.6	-1.230 $\pm$ 0.015
2.71	4.6	0.005 $\pm$ 0.015	1.23	4.6	-1.540 $\pm$ 0.035
2.60	4.6	-0.020 $\pm$ 0.010	1.11	4.6	-1.740 $\pm$ 0.045
2.50	4.6	-0.060 $\pm$ 0.010	1.10	4.0	-1.830 $\pm$ 0.010
2.41	4.6	-0.120 $\pm$ 0.007	1.01	4.0	-1.930 $\pm$ 0.010
2.23	4.6	-0.230 $\pm$ 0.007			

Values of $\log x$ are ± 0.005 when not otherwise indicated. Values of $\log M$ are ± 0.05 .

The curve fitting technique outlined above was applied to the data, as also was the alternative method of linear plots, first transforming the data to the forms of eqns. (14a) and (14b). The results are shown in Table 5. Curves calculated from the average constants of Table 5 appear as solid lines in Figs. 2, 3 and 4. The less accurately obtained constants (in parenthesis) were not included in the average.

Fig. 2. Log D for HgCl_2 -benzene-ionic medium as function of $\log x$, excess chloride concentration. $\bullet$ $M = 5.10^{-4}$ M, $\blacksquare$ $M = 2.10^{-5}$ M, — calculated with $\log k_3 = 0.95$ and $\log k_3 k_4 = 2.00$.

Fig. 3. Log D for HgBr_2 -benzene-ionic medium as function of $\log x$, excess bromide concentration. $\bullet$ $M = 1.10^{-4}$ M, $\blacksquare$ $M = 2.5 \cdot 10^{-5}$ M, $\square$ $M = 1.10^{-5}$ M, — calculated with $\log k_3 = 2.27$ and $\log k_3 k_4 = 4.02$, - - - calculated with $\log k_3 = 2.41$ and $\log k_3 k_4 = 3.67$.

Fig. 4. Log D for HgI_2 -benzene-ionic medium as function of $\log x$, excess iodide concentration. $\bullet$ $M = 8.10^{-5}$ M, $\blacksquare$ $M = 4.10^{-5}$ M, $\square$ $M = 2.10^{-5}$ M, — calculated with $\log k_3 = 3.67$ and $\log k_3 k_4 = 6.04$.

It may also be stated in passing that experiments with various M 's showed no formation of polynuclear complexes, as all points were on the same curve (see Figs. 2, 3 and 4). This is not surprising at the low concentrations of mercury(II) employed.

PREVIOUS WORK

The constants obtained in this work are compared with those obtained in the careful and systematic potentiometric study of Sillén *et al.* (Ref.² summarizing their results) at the bottom of Tables 1 and 5. Agreement between the two sets of constants is quite good for the chloride and the iodide, within the stated limits of error, but much less so for the bromide. In the latter case, curves calculated with the earlier constants do not fit the present data (Figs. 1 and 3).

Table 5. The constants k_3 and k_3k_4 for the equilibria $\text{HgX}_2 + \text{X}^- \rightleftharpoons \text{HgX}_3^-$ and $\text{HgX}_2 + 2\text{X}^- \rightleftharpoons \text{HgX}_4^{2-}$ respectively.

	Chloride	Bromide	Iodide
<i>Curve fitting</i>			
$\log \lambda$	-0.960 ± 0.015	0.155 ± 0.010	1.760 ± 0.015
$\log p$	0.20 ± 0.10	-0.52 ± 0.07	-1.30 ± 0.06
$\log x$ ($Z = \text{O}$)	-0.95 ± 0.02	-2.27 ± 0.02	-3.67 ± 0.02
$\log p'$	-0.1 ± 0.1	0.23 ± 0.07	0.65 ± 0.06
$\log x$ ($Z' = \text{O}$)	-1.00 ± 0.02	-2.01 ± 0.02	-3.02 ± 0.02
$\log k_3$ (from p, Z)	0.95 ± 0.02	2.27 ± 0.02	3.67 ± 0.02
$\log k_4$ (from p, Z)	(1.15 ± 0.10)	(1.75 ± 0.07)	(2.37 ± 0.06)
$\log k_3k_4$ (from p', Z')	2.00 ± 0.04	4.02 ± 0.04	6.04 ± 0.04
$\log k_3$ (from p', Z')	(0.90 ± 0.10)	(2.24 ± 0.07)	(3.67 ± 0.06)
<i>Linear plots</i>			
$\log k_3$ (eqn. 14a)	(1.00 ± 0.12)	(2.28 ± 0.06)	(3.68 ± 0.04)
$\log k_3k_4$ (eqn. 14a)	2.02 ± 0.06	4.02 ± 0.02	6.05 ± 0.02
$\log k_3$ (eqn. 14b)	0.95 ± 0.06	2.26 ± 0.03	3.66 ± 0.03
$\log k_3k_4$ (eqn. 14b)	(2.00 ± 0.12)	(4.04 ± 0.05)	(6.02 ± 0.05)
<i>Average constants</i>			
$\log k_3$	0.95 ± 0.03	2.27 ± 0.02	3.67 ± 0.02
$\log k_3k_4$	2.00 ± 0.05	4.02 ± 0.04	6.04 ± 0.04
$\log k_4$ (difference)	1.05 ± 0.06	1.75 ± 0.05	2.37 ± 0.05
<i>Previous results</i> ²			
$\log k_3$	0.85 ± 0.15	2.41 ± 0.11	3.78 ± 0.14
$\log k_3k_4$	1.85 ± 0.06	3.67 ± 0.05	6.01 ± 0.04

The values of K were obtained by the solvent distribution and the potentiometric methods with about the same accuracy, and agreement for chloride and iodide is excellent, but although the solvent distribution value for bromide agrees well with the new potentiometric value, both are 0.17 ± 0.08 log units higher than the previous potentiometric value. The solvent distribution method gives much more accurate values of k_3 than the potentiometric method, and the values obtained here all lie within the (wide) limits of error given for the potentiometric constants. The values of k_3k_4 are of comparable accuracy, agreeing very well for iodide, fairly well for chloride but not at all for bromide.

One reason for the discrepancy may, perhaps, be the fact that the potentiometric value of k_3k_4 was obtained in a region of concentration (0.15–0.40 M) where the bromide is a very high fraction of the total ionic medium, so that the assumption of constant activity factors may no longer be valid. In the present study, concentrations ranged at most to 20 % exchange of bromide for perchlorate.

Moreover, it is felt that the potentiometric values of k_3 and k_3k_4 were obtained in rather a round-about way, by directly determining β_3 and β_4 , while β_2 was obtained by a method depending on the experimentally difficult "maximum potential titration". The difference in β_2 which would bring k_3k_4 into agreement with the present value corresponds to a difference of about 9 mV in the potential. Of this, 3 mV is due to the different K values used.

The remaining 6 mV and the difference in K are difficult to explain; perhaps they are due to an impurity in the bromide solutions used previously (see foot-note p. 603).

The work done previously to 1946–1948, was fully discussed by Sillén *et al.* (Refs.³ p. 61; ⁵ p. 52; ⁶ p. 482; 487; ⁷ p. 505; ⁸ p. 828) and since then, few determinations of the pertinent equilibrium constants have been undertaken. The authors not mentioned in the above references usually did not use a constant ionic medium, so that their results are not comparable with the above. Tourneux's⁹ values obtained from the solubility of KCl in HgCl_2 solutions extrapolate to $\log k_3 k_4 = 2.0$ at 25°, while Grinberg and Nikol'skaya¹⁰ quote a similar value. They also give $\log \beta_4$ as 16.23 21.64 and 30.28 for HgCl_4^{2-} , HgBr_4^{2-} and HgI_4^{2-} . Peschanski¹¹ found for HgCl_2 , $\log k_3 = 0.52$ at 18° and ionic strength 0.5, while for $\text{Hg}^{2+} + \text{HgCl}_2 \rightleftharpoons 2 \text{HgCl}^+$ she found $\log K = 0.40$ at 17°, the first being lower, the second higher than the present values for 25°. The method she employed — continuous variation for UV light absorption — is, however, open to much criticism. Strocchi¹² states that species MX_3^- and MX_4^- are formed, without giving formation constants, Yatsimirskii¹³ gives $\log k_1 = 12.36$ for HgI^+ , while a year later Yatsimirskii and Shutov¹⁴ revised this to $\log k_1 = 13.15$. Finally, Golub¹⁵ gives $\log \beta_4 = 30.18$ for HgI_4^{2-} at "constant ionic strength", and Damm and Weiss¹⁶ give for unspecified conditions $\log k_1 = 6.80$, $\log \beta_2 = 13.60$, $\log k_3 = 0.57$ and $\log k_3 k_4 = 2.03$.

DISCUSSION

The constants k_3 and $k_3 k_4$ together with the distribution coefficient are adequate for describing the behaviour of mercury halide complexes at $n \geq 2$, i. e. the region important to mixed-complex formation. The values of λ for the 0.5 M perchlorate ionic medium obtained here (Table 5) have already been compared with values obtained otherwise in part I¹. To complete the picture, values of β_2 are also necessary. The values found here for k_2 give only the orders of magnitude of the constants (see p. 603):

Chloride, solvent distribution	$\log \beta_1 \sim 6.6 \pm 0.2$	$\log \beta_2 \sim 12.9 \pm 0.3$
potentiometry	$= 6.74 \pm 0.02$	$= 13.22 \pm 0.02$
Bromide, solvent distribution	$\sim 9.2 \pm 0.3$	$\sim 17.5 \pm 0.5$
potentiometry	$= 9.05 \pm 0.03$	$= 17.33 \pm 0.04$

Work on mixed bromide-iodide complexes, to be described in part IV, led to a value for $\log \beta_2(\text{HgI}_2) - \log \beta_2(\text{HgBr}_2) = 6.94 \pm 0.03$. Accepting the potentiometric value of $\log \beta_2(\text{HgI}_2) = 23.82 \pm 0.04$, this yields a value for $\log \beta_2(\text{HgBr}_2) = 16.88 \pm 0.06$, in closer agreement with 16.98 ± 0.04 , the value obtained from the directly determined $\log \beta_4(\text{HgBr}_4^{2-}) = 21.00 \pm 0.03$ ⁸ and the solvent distribution value $\log k_3 k_4 = 4.02 \pm 0.02$, than is 17.33, the potentiometric value of β_2 . To have a consistent set of equilibrium constants, the values $\log \beta_2$ 13.22 ± 0.02 for HgCl_2 and 23.82 ± 0.04 for HgI_2 are borrowed from the potentiometric investigation, 16.88 ± 0.06 for HgBr_2 is obtained from part IV, and the values of K , k_3 and $k_3 k_4$ are taken from the solvent distribution work described above. The resulting constants are tabulated in Table 6.

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Table 6. Equilibrium constants for 0.5 M NaClO₄ ionic medium and 25°, applicable to the solvent distribution study of mercury(II) halide complexes.

Reaction	Constant	Chloride	Bromide	Iodide
$\text{Hg}^{2+} + \text{X}^- \rightleftharpoons \text{HgX}^+$	$\log \beta_1$	6.74 ± 0.03	8.94 ± 0.07	12.87 ± 0.06
$\text{Hg}^{2+} + 2\text{X}^- \rightleftharpoons \text{HgX}_2$	$\log \beta_2$	13.22 ± 0.02	16.88 ± 0.06	23.82 ± 0.04
$\text{Hg}^{2+} + 3\text{X}^- \rightleftharpoons \text{HgX}_3^-$	$\log \beta_3$	14.17 ± 0.04	19.15 ± 0.06	27.49 ± 0.04
$\text{Hg}^{2+} + 4\text{X}^- \rightleftharpoons \text{HgX}_4^{2-}$	$\log \beta_4$	15.22 ± 0.05	20.90 ± 0.06	29.86 ± 0.04

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