Mercury(II) Halide Mixed Complexes in Solution

III.¹ The Uncharged Mixed Complexes

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The equilibrium constant K of the reaction $\text{HgA}_2 + \text{HgB}_2 \rightleftharpoons 2\text{HgAB}$ was determined by studying the distribution of mercury between benzene and an aqueous solution. The distribution coefficient λ_{11} of HgAB was obtained from the extreme parts of the log distribution ratio *vs* log total B/total A curve, while K was obtained from the middle part of the curve. The values ($\log \lambda_{11}$, $\log K$) are: HgClBr (-0.42 ± 0.04 , 2.0 ± 0.5), HgClI (0.28 ± 0.02 , 1.75 ± 0.20), HgBrI (0.79 ± 0.04 , 1.10 ± 0.20). The "stabilization constant", *i. e.* the ratio of the experimental to the statistical value ($= 4$), is larger than unity for these complexes, more so for the aqueous phase than for the organic phase.

A mixture of MA_2 and MB_2 will contain also MAB , according to the equilibrium reaction

Owing to the extraordinary stability of the uncharged mercury (II) halide complexes, all species other than MA_2 , MAB and MB_2 may be neglected. The above reaction was studied by measuring the mercury distribution between benzene and an aqueous ionic medium, for the pairs A—B: Cl—Br, Cl—I and Br—I.

Symbols. The symbols used here were defined in part I².

Experimental. The experiments were in the main carried out as described in part I². Benzene solutions of MA_2 and MB_2 were mixed and shaken at 25° with an equal volume of the aqueous ionic medium, 0.490 M NaClO_4 + 0.010 M HClO_4 , in this way ensuring that $\bar{n}_{\text{A,B}} = 2.00$ for all the solutions. The mercury concentration was about 10^{-4} to 10^{-5} M, so that no dissociation $\text{MX}_2 \rightleftharpoons \text{MX}^+ + \text{X}^-$ had to be feared (see part II¹). R , the ratio of the reactants A/B, was obtained from the volume ratio of the benzene solutions of MA_2 and MB_2 , the relative concentration of which was determined by the ratio of their radioactivities. By choosing suitable volume and activity ratios it was possible to cover and measure accurately a range of 4 to 5 powers of ten in R .

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DERIVATION OF EQUATIONS

Let a benzene solution of MA_2 be mixed with one of MB_2 and the mixture be shaken with an equal volume of the ionic medium. The general equations governing the distribution will be (in addition to (1) above):

$$[\text{MA}_2]_{\text{or}} = \lambda_{20} [\text{MA}_2]; \quad [\text{MB}_2]_{\text{or}} = \lambda_{02} [\text{MB}_2]; \quad [\text{MAB}]_{\text{or}} = \lambda_{11} [\text{MAB}] \quad (2)$$

The ratio R will be given by

$$R = \frac{2[\text{MB}_2] (1 + \lambda_{02}) + [\text{MAB}] (1 + \lambda_{11})}{2[\text{MA}_2] (1 + \lambda_{20}) + [\text{MAB}] (1 + \lambda_{11})} \quad (3)$$

and the distribution ratio D by

$$D = \frac{\lambda_{20} [\text{MA}_2] + \lambda_{11} [\text{MAB}] + \lambda_{02} [\text{MB}_2]}{[\text{MA}_2] + [\text{MAB}] + [\text{MB}_2]} \quad (4)$$

Determination of λ_{11} . Consider now the gradual addition of MB_2 to a large excess of MA_2 . As a first approximation this will result in the gradual formation of MAB by reactions (1) and (1a), while the concentration $[\text{MB}_2]$ will remain negligible, provided that R remains small. If $[\text{MA}_2]$ and $[\text{MAB}]$ are eliminated from (3) and (4) — and $[\text{MB}_2]$ neglected — the following expression is obtained

$$D = \frac{\lambda_{20} (1 + \lambda_{11}) (1-R) + 2\lambda_{11} R (1 + \lambda_{20})}{(1 + \lambda_{11}) (1-R) + 2 R (1 + \lambda_{20})} \quad (5)$$

From this the linear expression for λ_{11}

$$2(1 + \lambda_{20}) RD + (D - \lambda_{20}) (1-R) = (2(1 + \lambda_{20})R - (D - \lambda_{20}) (1-R))\lambda_{11} \quad (6)$$

is obtained, where λ_{11} is the slope when the left term is plotted *vs* the term in brackets on the right.

The ratio R must not be decreased too much, if λ_{11} is to be obtained accurately from (6), as otherwise there will be too large a spread in the points. On the other hand, as R is increased towards unity, the assumption $[\text{MB}_2] \approx 0$ is no longer valid if $K \neq \infty$, so that a plot of (6) will be curved, and λ_{11} will be the limiting slope at $R = 0$. Actually, as will be seen below, K is large and the plot of (6) is linear, within experimental errors, up to about $R = 0.40$.

The same arguments can be applied to the opposite case, *i. e.* when MA_2 is added to a large excess of MB_2 , and R is very large. Then:

$$D = \frac{\lambda_{02} (1 + \lambda_{11}) (R-1) + 2\lambda_{11} (1 + \lambda_{02})}{(1 + \lambda_{11}) (R-1) + 2 (1 + \lambda_{02})}, \text{ and} \quad (7)$$

$$2(1 + \lambda_{02}) D + (\lambda_{02} - D) (R-1) = (2(1 + \lambda_{02}) + (\lambda_{02} - D) (R-1))\lambda_{11}, \quad (8)$$

so that λ_{11} may be obtained also from plotting eqn. (8).

The distribution coefficient of MAB, λ_{11} , is thus obtained independently from the two ranges where R is small and where it is large.

Determination of K . It remains now to consider the intermediate region where $R \sim 1$ and it is no longer permissible to neglect any of the species MA_2 , MAB and MB_2 . If, then, the concentrations of these species are eliminated from (1), (3) and (4), and the equations solved for K , the following is obtained:

$$K = 4[(\lambda_{02}-D)(1+\lambda_{20})R-(D-\lambda_{02})(1+\lambda_{02})]^2 [2(1+\lambda_{02})(D-\lambda_{11})+(1+\lambda_{11})(R-1)(D-\lambda_{02})]^{-1} [2(1+\lambda_{20})(D-\lambda_{11})R-(D-\lambda_{20})(1+\lambda_{11})(R-1)]^{-1} \quad (9)$$

which simplifies in the case of $R = 1.00$ to

$$K = \frac{((\lambda_{02}-D)(1+\lambda_{20})-(D-\lambda_{20})(1+\lambda_{02}))^2}{(1+\lambda_{20})(1+\lambda_{02})(D-\lambda_{11})^2} \quad (9a)$$

In this way K is obtained from the distribution at $R \sim 1$ combined with the value of λ_{11} obtained above. To test its validity, it is inserted into the general equations (3) and (4). Introducing the parameter $y = [\text{MB}_2]^{\frac{1}{2}}[\text{MA}_2]^{-\frac{1}{2}}$, the expressions:

$$R = \frac{2y^2(1+\lambda_{02})+K^{\frac{1}{2}}y(1+\lambda_{11})}{2(1+\lambda_{20})+K^{\frac{1}{2}}y(1+\lambda_{11})} \quad (10)$$

and

$$D = \frac{\lambda_{20} + \lambda_{11}K^{\frac{1}{2}}y + \lambda_{02}y^2}{1 + K^{\frac{1}{2}}y + y^2} \quad (11)$$

are obtained, and a plot of $\log D$ vs $\log R$, calculated with y as auxiliary variable, may then be compared with experimental values.

Table 1. Distribution data for the Hg-Br-I neutral complexes.

$\log R$	$\log M$	$\log D$	$\log R$	$\log M$	$\log D$
-2.40	-4.6	0.160 ± 0.010	0.30	-4.5	0.900 ± 0.010
-1.90	-4.1	0.170 ± 0.008	0.40	-4.3	0.975 ± 0.010
-1.70	-4.8	0.175 ± 0.015	0.46	-5.0	1.020 ± 0.015
-1.50	-4.6	0.180 ± 0.010	0.52	-4.5	1.050 ± 0.010
-1.39	-4.6	0.195 ± 0.010	0.70	-4.5	1.185 ± 0.010
-1.10	-5.1	0.225 ± 0.015	0.73	-4.3	1.230 ± 0.008
-0.90	-4.1	0.270 ± 0.008	0.90	-4.3	1.290 ± 0.010
-0.70	-4.3	0.330 ± 0.008	0.92	-5.0	1.335 ± 0.015
-0.50	-4.1	0.420 ± 0.008	1.20	-4.3	1.485 ± 0.008
-0.30	-4.9	0.480 ± 0.015	1.30	-4.9	1.515 ± 0.015
-0.20	-4.6	0.555 ± 0.010	1.35	-4.5	1.545 ± 0.010
-0.10	-4.1	0.600 ± 0.008	1.36	-4.5	1.530 ± 0.010
0.00	-4.3	0.675 ± 0.008	1.60	-5.0	1.590 ± 0.015
0.05	-5.0	0.720 ± 0.015	2.00	-4.5	1.665 ± 0.010
0.20	-5.1	0.795 ± 0.015	2.70	-5.0	1.740 ± 0.015

All values of $\log R$ are ± 0.01 , all values of $\log M$ are ± 0.1 . Symbols in Fig. 3 are: $\log M$ -4.1 to -4.3 $\bullet$, $\log M$ -4.5 to -4.6 $\blacksquare$, and $\log M$ -4.8 to -5.1 $\blacktriangle$.

EXPERIMENTAL RESULTS

The distribution values obtained for the pair of ligands Br—I are given in Table 1, while for all three pairs Cl—Br, Cl—I and Br—I the data are given as $\log D$ ($\log R$) curves in Figs. 1, 2 and 3.

In order to obtain λ_{11} , plots were made (Fig. 4) of eqns. (6) — squares — and (8) — circles — for the ranges of low R and high R , for the above three pairs of ligands, using the values of λ_{20} and λ_{02} found previously (part I²): $\log \lambda(\text{HgCl}_2) = -0.963$, $\log \lambda(\text{HgBr}_2) = 0.152$, $\log \lambda(\text{HgI}_2) = 1.77$, in conjunction with the present data.

Fig. 4 shows that the plots are linear in the regions used, $R < 0.40$ and $R > 2.5$, and shows also very good agreement of the slopes in these regions with each other, so that the value of λ_{11} obtained expresses the data well.

Fig. 1. The distribution ratio D of mercury between benzene and aqueous solutions in system Hg-Cl-Br, as function of the ratio R of $\text{HgBr}_2 \text{ tot} / \text{HgCl}_2 \text{ tot}$ ● experimental points, — calculated with $\log \lambda_{11} = -0.42$ and $\log K = 2.0$, calculated with $K = 0$.

Fig. 2. The distribution ratio D of mercury between benzene and aqueous solutions in system Hg-Cl-I, as function of the ratio R of $\text{HgI}_2 \text{ tot} / \text{HgCl}_2 \text{ tot}$ ● experimental points, — calculated with $\log \lambda_{11} = 0.28$ and $\log K = 1.75$, calculated with $K = 0$, - - - - calculated with $K = \infty$.

Fig. 3. The distribution ratio D of mercury between benzene and aqueous solutions in system Hg-Br-I, as function of ratio R of $\text{HgI}_2 \text{ tot} / \text{HgBr}_2 \text{ tot}$. ●, ■, and ▲ experimental points explained in Table 1, — calculated with $\log \lambda_{11} = 0.79$ and $\log K = 1.10$, calculated with $K = 0$, --- calculated with $K = \infty$.

Fig. 4. Plots of eqns. (6) and (8) (□ and ●, respectively), where both sides of the equations were multiplied by the same arbitrary constant to bring them down to the same scale. The best straight lines drawn have slopes equal to the λ_{11} values given in the text.

Ordinate: □ $\text{const}_1(2(1 + \lambda_{20}) R D + (D - \lambda_{20})(1 - R))$
 ● $\text{const}_2(2(1 + \lambda_{02}) D + (\lambda_{02} - D)(R - 1))$

Abseissa: □ $\text{const}_1(2(1 + \lambda_{20}) R - (D - \lambda_{20})(1 - R))$
 ● $\text{const}_2(2(1 + \lambda_{02}) + (\lambda_{02} - D)(R - 1))$

The values of λ_{11} obtained are:

$$\begin{aligned}\log \lambda(\text{HgClBr}) &= -0.42 \pm 0.04 & \log \lambda(\text{HgClI}) &= 0.28 \pm 0.02 \\ \log \lambda(\text{HgBrI}) &= 0.79 \pm 0.04\end{aligned}$$

For the range $-0.4 < \log R < 0.4$, the experimental values of R and D , together with the binary and ternary distribution coefficients listed above, were inserted into eqn. (9) to calculate K . The values obtained (numerical averages) are:

$$\begin{aligned}\log K(\text{HgClBr}) &= 2.0 \pm 0.5 & \log K(\text{HgClI}) &= 1.75 \pm 0.20 \\ \log K(\text{HgBrI}) &= 1.10 \pm 0.20\end{aligned}$$

The values of λ_{11} and K were inserted into eqns. (5), (7) and (11) and the calculated distribution plotted in Figs. 1, 2 and 3 (dashed curves for (5) and (7) in the range $-0.4 < \log R < 0.4$, otherwise solid curves), agreeing well with the data.

Had no mixed complexes been formed, *i. e.* $K = 0$, the dotted curves in Figs. 1, 2 and 3 would have been obtained. These, however, do not agree with the experimental data, so that the formation of the ternary complexes in solution might be considered proved.

DISCUSSION

The equilibrium in the aqueous phase. The significance of the constants obtained above may be seen in Fig. 5. In it is plotted the mole percentage of the three species MA_2 , MAB and MB_2 as function of $\log R$. The continuous curves were calculated with the experimental value $K = 56$ for Hg—Cl—I , but they express also approximately the cases of Hg—Cl—Br and Hg—Br—I , since the K values possess wide limits of error, and since the curves are not too sensitive to the exact value of K , provided it is "large". It is seen that MAB is an important species in the range of about $-1.2 < \log R < 1.2$. Moreover, it is seen that $[\text{MB}_2]$ is negligibly small up to $\log R = -0.4$ and that $[\text{MA}_2]$ is so above $\log R = 0.4$ as assumed in the calculations.

If K were equal to infinity, MAB would be completely stable at $R = 1$, and $[\text{MA}_2]$ and $[\text{MB}_2]$ would remain negligible respectively right up to and above $R = 1$. This is shown by the long-dashed curves in Fig. 5.

Had the mixed complex formation proceeded statistically, there would have been at equilibrium 25 mole % MA_2 , 25 mole % MB_2 and 50 mole % MAB when $R = 1$. The equilibrium constant would then have been $(0.50)^2 (0.25)^{-1} (0.25)^{-1} = 4$. Fig. 5 shows this case by a pair of short-dashed curves. The area enclosed between them is smaller than that corresponding to the observed K , or in other words, the mixed complexes are more stable than statistically expected. The difference $\log K - \log K_{\text{stat.}} = \log K - 0.60$ may be called the stabilization constant, $\log K_{\text{stab.}}$:

$$\begin{aligned}\log K_{\text{stab.}} (\text{HgClBr}) &= 1.4 \pm 0.5 & \log K_{\text{stab.}} (\text{HgClI}) &= 1.15 \pm 0.20 \\ \log K_{\text{stab.}} (\text{HgBrI}) &= 0.5 \pm 0.2\end{aligned}$$

More will be said about this in part V of this series.

Fig. 5. The mole percentage of the species MA_2 , MAB and MB_2 as function of the ratio R of MB_2 tot / MA_2 tot. — calculated with observed value of K (for $HgClI$), — — — calculated with $K = \infty$, - - - - - calculated with $K_{stat.} = 4$, calculated with $K = 0$.

Finally, had there been no mixed-complex formation, $K = 0$, then, of course, the area of MAB would have vanished, and the single dotted curve in Fig. 5 would have described the system MA_2 — MB_2 .

The equilibrium in the organic phase. Equilibrium and stabilization constants may also be calculated for the organic phase according to eqn. (1a):

$HgClBr$	$\log K_{or} = 2.0 \pm 0.5$	$\log K_{or \text{ stab.}} = 1.4 \pm 0.5$
$HgClI$	$= 1.51 \pm 0.20$	$= 0.91 \pm 0.20$
$HgBrI$	$= 0.76 \pm 0.20$	$= 0.16 \pm 0.20$

The statistical value for the distribution coefficient of the ternary complexes is the geometrical mean of the coefficients of the binary complexes, and is compared below with the observed values:

$HgClBr$	$\log \lambda_{11} \text{ observed} = -0.42 \pm 0.04$	$\log \lambda_{11} \text{ statis.} = -0.40 \pm 0.02$
$HgClI$	$= 0.28 \pm 0.02$	$= 0.40 \pm 0.02$
$HgBrI$	$= 0.79 \pm 0.04$	$= 0.96 \pm 0.02$

It is seen that the distribution coefficient is significantly smaller, at least for $HgClI$ and $HgBrI$, than the statistically calculated value. This means that the ternary complex is more favoured in the aqueous than in the benzene phase, as may also be seen by comparing the respective stabilization constants in the two phases.

Previous work. Previous reports of mercury(II) mixed halides are quite numerous. Although Pelt and Boes³ could not find an indication for $HgClBr$ formation from solubility measurements on mixtures of $HgCl_2$ and $HgBr_2$,

Losana ⁵ and later Scholter and Bijvoet ⁴ found a solid, so called B-phase, made up of linear HgClBr molecules. However, with solids, mixed compound formation might be confused with mixed crystal (solid solution) formation. Mixed Hg(Cl₂, Br₂) crystals have thus been found formed from melts ⁶ or solutions ⁷. Oppenheim ⁸ claimed almost 90 years ago that HgBrI precipitates (and may be sublimed unchanged) if an alkyl iodide is added to an acetone solution of HgBr₂. Köhler ⁹ ten years later gave a method to prepare what he stated to be HgClI. Vournazos ¹⁰ concluded that a mixed bromide-iodide compound of mercury, which he claimed contains the ion Hg₂Br₄I⁻, is formed when water insoluble iodides dissolve in acetone solutions of HgBr₂.

All the above is evidence (though sometimes disputed) for the formation of solid ternary complexes, but there is also evidence for their formation in solution. Delwaulle and Francois, in a number of papers ¹¹, reported that ethanolic, methanolic and aqueous solutions of mixtures of mercury(II) halides show Raman lines which could not be ascribed to either of the binary components, but must be due to a ternary compound. Moreover, they state ^{11a} that the intensity of the Raman lines is proportional to the concentration, so that in principle it should have been possible to calculate the equilibrium constants. Unfortunately, the authors generally neither calculated the constants, nor reported their primary data, so that their results are only qualitative.

The one exception to this is the constant $K = 2,0 \pm 0,2$ reported for the reaction $\text{HgCl}_2 + \text{HgBr}_2 = 2 \text{HgClBr}$ in methanol ^{11c}. This constant is smaller than the statistical value, but the reliability of the constant seems to be less than its reported precision indicates, because of larger possible errors in the quantities entering its calculation.

Even in the vapour phase the ternary compounds seem to be rather stable. Although Hintz and Jellinek ¹² found that the vapour phase above a HgCl₂—HgBr₂ mixture is an ideal mixture, Wehrli and Milazzo ¹³ found stable HgClBr and HgBrI vapours that dissociate only under UV radiation. Müller ¹⁴ measured the spectra of MAB vapours already at temperatures as low as 50° C. He prepared HgBrI according to Oppenheim's procedure ⁸ and HgClI and HgClBr according to Köhler's ⁹. The special "mixed" bands he observed in the spectra were most intense for HgClI. He explained this effect by pointing out that HgClI has the most unsymmetrical weight distribution among the three ternary compounds.

Although the authors cited above indicate qualitatively the formation of mixed halide compounds HgAB, no values of the equilibrium constants for aqueous solutions seem to have been hitherto reported.

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