Mercury(II) Halide Mixed Complexes in Solution

IV. Mixed Bromo-Iodo Complexes

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Independent values for the mixed complex formation constants k_{ij} for $\text{HgBr}_{i-1}\text{I}_j + \text{Br} \rightleftharpoons \text{HgBr}_i\text{I}_j$ were obtained from mercury distribution data (D , a , r), where D is the Hg distribution ratio, a is free bromide concentration and r is ratio free iodide to free bromide, using cuts $D(a)$, and $D(r)_a$, and from iodine distribution data (D , a , B , M); D is the iodine distribution ratio, and B and M are total mercury and iodine. The constants are: $\log k_{21} = 1.85 \pm 0.03$, $\log k_{12} = 1.88 \pm 0.03$, $\log k_{31} = 1.49 \pm 0.06$, $\log k_{22} = 1.49 \pm 0.05$ and $\log k_{13} = 1.10 \pm 0.10$. Also, the constants for $\text{HgBr}_2 + 2\text{I}^- \rightleftharpoons \text{HgI}_2 + 2\text{Br}^-$, $\log p = 6.94 \pm 0.03$ and for $\text{HgBr}_2 + \text{I}^- \rightleftharpoons \text{HgBrI} + \text{Br}^-$, $\log q = 4.01 \pm 0.04$, and the distribution coefficient of HgBrI between benzene and the ionic medium $\log \lambda_{11} = 0.79 \pm 0.02$ were obtained. These constants are valid for 25° and 0.5 M (perchlorate + halide) ionic medium.

The mercury(II)-bromide-iodide system was subjected to a thorough study of possible mixed species. Use was made not only of mercury solvent distribution data but also of ligand—iodine—distribution. The rather difficult problem of having two independent variables was overcome in a number of ways, and complexity constants could be assigned to all mixed species.

Symbols. For a definition of the symbols used in this paper see part I, p. 330². The constants k'_{03} and k'_{04} will here be written k_{03} and k_{04} , since no mistake is possible. In addition, the terms $p = \beta_{02}\beta_{20}^{-1}$ and $q = \beta_{11}\beta_{20}^{-1}$ will be useful. The functions c_i and f_i are defined in eqns. (1), (1a), (2) and (8).

Experimental. For experimental details see part I, p. 331². Benzene was used as the organic solvent, the temperature was 25°, the ionic medium was 0.5 M (perchlorate + halide) and the phase volumes were equal.

General equations. In solutions of MA_2 and excess A^- and B^- , assuming maximum coordination number four⁴, six mixed species might form. Introducing the ratio $r = ba^{-1}$, and selecting, for the sake of convenience, such formation reactions as either (I) are based on MA_2 for MB_j species, or (II) consist of the addition of one A^- to a precursor species for the mixed complexes, *e. g.*

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(I) $\text{MA}_2 + 3 \text{B}^- = \text{MB}_3^- + 2 \text{A}^-$; pk_{03} , or (II) $\text{MAB}_2^- + \text{A}^- = \text{MA}_2\text{B}_2^-$; k_{22} ,

the concentration of the species present may be written as:

$$\begin{array}{llll} [\text{MA}_2] & = u & [\text{MB}_2] & = upa^{-2}b^2 = upr^2 \\ [\text{MA}_3] & = uk_{30}a & [\text{MAB}_2] & = upk_{12}a^{-1}b^2 = upk_{12}ar^2 \\ [\text{MA}_4] & = uk_{30}k_{40}a^2 & [\text{MA}_2\text{B}_2] & = upk_{12}k_{22}b^2 = upk_{12}k_{22}a^2r^2 \\ [\text{MAB}] & = uqa^{-1}b = uqr & [\text{MB}_3] & = upk_{03}a^{-2}b^3 = upk_{03}ar^3 \\ [\text{MA}_2\text{B}] & = uqk_{21}b = uqk_{21}ar & [\text{MAB}_3] & = upk_{03}k_{13}a^{-1}b^3 = upk_{03}k_{13}a^2r^3 \\ [\text{MA}_3\text{B}] & = uqk_{21}k_{31}ab = uqk_{21}k_{31}a^2r & [\text{MB}_4] & = upk_{03}k_{04}a^{-2}b^4 = upk_{03}k_{04}a^2r^4 \end{array}$$

At equilibrium with a benzene phase, the additional species

$$[\text{MA}_2]_{\text{or}} = u\lambda_{20} \quad [\text{MAB}]_{\text{or}} = uqa^{-1}b\lambda_{11} = uqr\lambda_{11} \quad [\text{MB}_2]_{\text{or}} = upa^{-2}b^2\lambda_{02} = upr^2\lambda_{02}$$

will be present.

The problem is to find the six mixed complex formation constants (q and the five k_{ij}) and also p .

EQUATIONS FOR MERCURY DISTRIBUTION

Cuts at constant r

In a recent paper³ Sillén has described a way of treating data with three variables (here D , a and r), and the following derivation is based on this treatment.

Summing up the concentrations of the species listed above, the total concentration of mercury in the aqueous phase may be written as

$$\begin{aligned} M - M_{\text{or}} &= u(c'_0 + c'_1a + c'_2a^2) \\ c'_0 &= 1 + qr + pr^2 \quad c'_1 = k_{30} + qk_{21}r + pk_{12}r^2 + pk_{03}r^3 \\ c'_2 &= k_{30}k_{40} + qk_{21}k_{31}r + pk_{12}k_{22}r^2 + pk_{03}k_{13}r^3 + pk_{03}k_{04}r^4 \end{aligned} \quad (1)$$

where the parameters c'_i are functions of r only, and constant for a series of experiments at constant r . Similarly, for the organic phase.

$$M_{\text{or}} = uc'_0 \quad c'_0 = \lambda_{20} + q\lambda_{11}r + p\lambda_{02}r^2 \quad (1a)$$

may be written, giving for the distribution ratio D the simple expression

$$\begin{aligned} D &= \frac{M_{\text{or}}}{M - M_{\text{or}}} = \frac{c'_0}{c'_0 + c'_1a + c'_2a^2} = c_0(1 + c_1a + c_2a^2)^{-1} \\ c_0 &= c'_0c'^{-1}_0 \quad c_1 = c'_1c'^{-1}_0 \quad c_2 = c'_2c'^{-1}_0 \end{aligned} \quad (2)$$

The parameters c_i may then be obtained by curve fitting from plots $\log D$ ($\log a$). A set of (c_i) values may then be obtained for a number of discrete values of r , and the resulting functions $c_i(r)$ solved for the equilibrium constants.

A provisional value of pq^{-1} may be obtained for high r by using the definition of c_0 (eqn. (2), (1a) and (1)) and neglecting the terms for MA_2 : 1 in c'_0 (1) and λ_{20} in c'_0 (1a):

$$pq^{-1} \approx (c_0 - \lambda_{11}) (\lambda_{02} - c_0)^{-1} r^{-1} \quad (3)$$

(λ_{11} and λ_{02} being known^{1,2}). With this, an estimate of q obtained at low r

$$q = c_0 r^{-1} [pq^{-1} (\lambda_{02} - c_0)r - (c_0 - \lambda_{11})]^{-1} \quad (4)$$

or, alternatively, $q = K(pq^{-1})$, with K from part III¹, may be used in the correction term to give a refined value for pq^{-1} by plotting the left hand side of

$$c_0 (1 + q^{-1}r^{-1}) - \lambda_{11} = pq^{-1} (\lambda_{02} - c_0)r \quad (5)$$

against $(\lambda_{02} - c_0) r$.

From the definition of c_1 (eqn. (2) and (1)), the equation

$$c_1(q^{-1}r^{-1} + 1 + pq^{-1}r) - k_{30}q^{-1}r^{-1} - k_{03}pq^{-1}r^2 = k_{21} + k_{12}pq^{-1}r \quad (6)$$

is obtained. Since k_{30} and k_{03} are known⁴, a plot of the left side of (6) against r gives the constants k_{21} and k_{12} .

Similarly, for c_2 , knowing $k_{30}k_{40}$ and $k_{03}k_{04}$ ⁴, a plot of the left side of

$$c_2 (q^{-1}r^{-1} + 1 + pq^{-1}r) - k_{30}k_{40}q^{-1}r^{-1} - pq^{-1}k_{03}k_{04}r^3 = \frac{k_{21}k_{31} + pq^{-1}k_{12}k_{22}r + pq^{-1}k_{03}k_{13}r^2}{k_{21}k_{31} + pq^{-1}k_{12}k_{22}r + pq^{-1}k_{03}k_{13}r^2} \quad (7)$$

against r yields the equilibrium constants $k_{21}k_{31}$, $k_{12}k_{22}$ and $k_{03}k_{13}$.

Cuts at constant a

A slightly different approach uses cuts at constant a instead of at constant r . Eqn. (1) may be written as

$$\begin{aligned} M - M_{or} &= uqr [f_0q^{-1}r^{-1} + f_1 + pq^{-1}f_2r + (f_3 + f(r))r^2] \\ f_0 &= 1 + k_{30}a + k_{30}k_{40}a^2 \\ f_1 &= 1 + k_{21}a + k_{21}k_{31}a^2 \\ f_2 &= 1 + k_{12}a + k_{12}k_{22}a^2 \\ f_3 &= pq^{-1}k_{03}k_{13}a^2 \end{aligned} \quad f(r) = pq^{-1}k_{03}a(1 + k_{04}ar) \quad (8)$$

Eqns. (8) and (1a) — again neglecting λ_{20} — yield an expression for D , which, when rearranged, becomes

$$(\lambda_{11} + \lambda_{02} pq^{-1}r)D^{-1} - (f_0q^{-1}r^{-1} + f(r)r^2) = f_1 + pq^{-1}f_2r + f_3r^2 \quad (9)$$

Eqn. (9) may be solved graphically for f_i , and f_1 and f_2 , in turn, for the required equilibrium constants, as will be shown below.

MERCURY DISTRIBUTION, EXPERIMENTAL RESULTS

Data (D , a , r) were obtained in the ranges $-2.1 < \log a < -1.0$ and $-3.4 < \log r < -1.5$. For experimental convenience, not r but $R = BA^{-1}$ was kept constant in a series of experiments with varying a . As A was about 10^3 – 10^4 times M , $a \approx A$ is a very good approximation. B , however was not very large compared to M , since the specific

activity of the mercury did not permit the use of M values lower than about $10^{-5} M$, and therefore the consumption of B by M made a correction necessary. Its magnitude was relatively large, but if $\bar{n}_B$ is obtained from any provisional constants (*e. g.* statistical values), $b = B - \bar{n}_B M$ is quite a good approximation. The values of $\bar{n}_B$ were mostly between 1.5 and 2.5. As a increased, b tended towards B and r towards R . A series of experiments $\log D(a, B)_R$, where $\bar{n}_B M$ was particularly large is given in Table 1.

Table 1. Example of data $\log D(\log a, \log B)_R$ converted into $\log D(\log a)_r$.

$-\log a$	$-\log B$	$\bar{n}_B$	$-\log b$	$-\log r$	$\log D$	$\log D_{r=0.010}$
1.945	3.945	1.95	4.66	2.71	1.22 ± 0.02	1.32 ± 0.03
1.842	3.842	1.96	4.28	2.44	1.28 ± 0.03	1.23 ± 0.03
1.742	3.742	1.96	4.046	2.305	1.208 ± 0.015	1.125 ± 0.020
1.644	3.644	1.96	3.870	2.226	1.072 ± 0.015	1.025 ± 0.020
1.541	3.541	1.97	3.710	2.169	0.963 ± 0.012	0.910 ± 0.015
1.439	3.439	1.98	3.567	2.128	0.858 ± 0.012	0.790 ± 0.015
1.340	3.340	1.99	3.440	2.100	0.711 ± 0.010	0.665 ± 0.015
1.237	3.237	2.01	3.313	2.076	0.610 ± 0.010	0.580 ± 0.015
1.137	3.137	2.03	3.198	2.062	0.380 ± 0.010	0.365 ± 0.015
1.059	3.059	2.05	3.110	2.051	0.273 ± 0.010	0.255 ± 0.015

In this series $\log M = -4.330$, $\bar{n}_B$ about 2.0 and $\log R = -2.000$.

Table 2. Mercury distribution: experimental data compared with calculated values.

$-\log a$	$-\log r$	$\log D_{\text{obs}}$	$\log D_{\text{calc}}$	$-\log a$	$-\log r$	$\log D_{\text{obs}}$	$\log D_{\text{calc}}$
1.28	1.52	0.34 ± 0.01	0.38	1.39	2.35	0.83 ± 0.02	0.78
1.38	1.53	0.47 ± 0.01	0.50	1.49	2.39	0.93 ± 0.01	0.88
1.48	1.54	0.66 ± 0.01	0.69	1.59	2.44	0.96 ± 0.01	0.98
1.58	1.56	0.78 ± 0.01	0.81	1.70	1.51	1.08 ± 0.01	1.06
1.68	1.58	0.91 ± 0.01	0.92	1.80	2.63	1.12 ± 0.01	1.13
1.78	1.61	1.04 ± 0.01	1.04	1.90	2.84	1.11 ± 0.01	1.12
1.88	1.64	1.13 ± 0.02	1.14	1.07	2.76	0.13 ± 0.01	0.14
1.98	1.68	1.32 ± 0.01	1.28	1.12	2.77	0.22 ± 0.01	0.23
1.28	2.08	0.57 ± 0.01	0.87	1.22	2.78	0.38 ± 0.01	0.36
1.46	2.07	0.89 ± 0.01	0.87	1.32	2.82	0.54 ± 0.01	0.51
1.76	2.17	1.22 ± 0.02	1.18	1.42	2.86	0.64 ± 0.01	0.62
1.86	2.23	1.31 ± 0.02	1.28	1.52	2.90	0.74 ± 0.02	0.72
2.06	2.44	1.40 ± 0.03	1.36	1.62	2.98	0.82 ± 0.02	0.80
1.06	2.05	0.27 ± 0.01	0.26	1.72	3.08	0.89 ± 0.03	0.85
1.14	2.05	0.38 ± 0.01	0.38	1.82	3.33	0.80 ± 0.02	0.78
1.24	2.08	0.61 ± 0.01	0.58	1.04	3.10	-0.12 ± 0.01	-0.11
1.34	2.10	0.71 ± 0.02	0.69	1.10	3.14	-0.09 ± 0.01	-0.05
1.44	2.13	0.86 ± 0.01	0.84	1.15	3.17	0.03 ± 0.01	0.02
1.54	2.17	0.96 ± 0.01	0.93	1.20	3.20	0.05 ± 0.01	0.06
1.64	2.23	1.07 ± 0.01	1.04	1.15	3.24	0.16 ± 0.01	0.13
1.74	2.31	1.21 ± 0.01	1.18	1.31	3.28	0.21 ± 0.01	0.18
1.84	2.44	1.28 ± 0.02	1.25	1.36	3.33	0.21 ± 0.01	0.22
1.95	2.71	1.22 ± 0.02	1.21	1.41	3.40	0.25 ± 0.01	0.24
1.21	2.31	0.54 ± 0.01	0.52	1.46	3.48	0.28 ± 0.01	0.24
1.29	2.32	0.65 ± 0.01	0.63	1.51	3.60	0.33 ± 0.01	0.23

Fig. 1. The parameters c_i as function of r . ■ values obtained by "curve fitting" $\log D(\log a)$, plots, ——— calculated from the constants.

In Table 2 all the data are presented, with the observed D as function of the actual a and r values prevailing in the individual runs. The column D_{calc} is calculated for the individual a and r values with the constants found later, and summarized in Table 5.

Cuts at constant r

Values of $\log D(\log a)$, were calculated by interpolation and were used to obtain the parameters $c_i(r)$ by curve fitting of eqn. (2). Plots of these parameters as $\log c_i(\log r)$ are given in Fig. 1.

Considering c_0 first, a provisional value $pq^{-1} = 800$ was obtained from eqn. (3), using $\lambda_{11} = 6.1 \pm 0.6$ and $\lambda_{02} = 57.5 \pm 1.2$ from parts III and I^{1,2}. From this and eqn. (4) the rough value of $\log q = 4.2 \pm 0.2$, or using $q = Kpq^{-1}$ with $\log K = 1.1 \pm 0.2$ from part III¹, $\log q = 4.0 \pm 0.2$, was obtained. A refined value $\log pq^{-1} = 2.90 \pm 0.05$ was then obtained by using eqn. (5) as shown in Fig. 2. A curve $c_0(r)$ calculated with the now known q and pq^{-1} is compared with the experimental values in Fig. 1.

Fig. 2. Plots of eqn. (5) to find pq^{-1} , the slope of the best straight line through the origin and the points.

Fig. 3. Plots of eqn. (7). ● left side of (7) calculated from experimental points, — calculated with the constants $k_{12}k_{22}$ and $k_{22}k_{31}$, - - - calculated with the additional constant k_{13} .

Fig. 4. Plot of eqn. (9) for low r values. ● ○ ▲ calculated from the experimental points, — best straight lines through the points.

The values of c_1 were inserted into eqn. (6) and the left side of it was plotted against r , and, divided by r , against r^{-1} , using $k_{30} = 185$ and $k_{03} = 4\,700^4$. From the slopes the values of the constants $\log k_{12} = 1.87 \pm 0.03$ and $\log k_{21} = 1.85 \pm 0.04$ were obtained. Inserted into a rearranged form of eqn. (6) they gave a $c_1(r)$ curve, which is compared with the experimental values in Fig. 1.

The values of c_2 were inserted into eqn. (7), and the resulting left hand term using $k_{30}k_{40} = 1.05 \times 10^4$ and $k_{03}k_{04} = 1.10 \times 10^{6(4)}$ was plotted against r in Fig. 3. Except for the last point, the plot is linear, and the constants $\log k_{12}k_{22} = 3.38 \pm 0.03$ and $\log k_{22}k_{31} = 3.35 \pm 0.04$ were obtained from it in the way outlined above for c_1 . Using these two constants the straight line in Fig. 3 was obtained, which is seen to agree well with the data, except, again, for the last point. A value of $\log k_{13} \sim 1.0$ (eqn. (7)) may bring even the last point into line (the dashed curve in Fig. 3), although the fit for some of the remaining points is then somewhat poorer. The constants were inserted into a rearranged form of eqn. (7) to give a curve which is compared with the experimental c_2 in Fig. 1.

Cuts at constant a

Using data $\log D(\log r)_a$, again calculated by interpolation, and the constants $\log pq^{-1} = 2.90$ and $\log q \sim 4.2$ found above, the left hand term of eqn. (9) was calculated, and is plotted against r (up to $r = 0.005$) in Fig. 4. The best straight lines were drawn, one for each a value, with slopes f_2pq^{-1} and intercepts f_1 . The functions $(f_1 - 1)a^{-1}$ and $(f_2 - 1)a^{-2}$ plotted against a gave straight lines of slopes $k_{21}k_{31} = 10^{3.34 \pm 0.05}$ and $k_{12}k_{22} = 10^{3.36 \pm 0.04}$,

while plots of $(f_1-1)a^{-2}$ and $(f_2-1)a^{-2}$ against a^{-1} yielded slopes $k_{21} = 10^{1.88 \pm 0.03}$ and $k_{12} = 10^{1.90 \pm 0.02}$. These constants agree very well with those obtained with cuts at constant r (see Table 5).

Using the functions f_1 and $f_2 pq^{-1}$ obtained above with eqn. (9) at $r > 0.005$, f_3 values were obtained for each a value, from which $\log k_{13} = 1.1 \pm 0.1$ was obtained. This value is a better approximation than that obtained with cuts at constant r .

The averages of the constants found for the two approaches were used to calculate the values of D_{calc} in Table 2.

EQUATIONS FOR IODINE DISTRIBUTION

The data for iodine distribution experiments will be discussed in terms of the species and complexity constants already employed above and listed on p. 812.

The experimental quantities studied are the independent variables a , B , and M , and the dependent variable D . Usually in solvent distribution studies, the concentration of free ligand is known, but in this case b = iodide is neither known nor negligible, and the situation is further complicated by the fact that the free ligand is a part of the material of which the distribution is studied.

The balances of mercury and iodine are:

$$M = \beta_{20}m[a^2(f_0 + \lambda_{20}) + qab(f_1 + \lambda_{11}) + pb^2(f_2 + \lambda_{02}) + pk_{03}b^3(1 + k_{13}a + k_{04}b)] \quad (10)$$

$$B = b + \beta_{20}m [qab(f_1 + \lambda_{11}) + 2pb^2(f_2 + \lambda_{02}) + 3pk_{03}b^3(1 + k_{13} + 4/3k_{04}b)] \quad (11)$$

with the f_i defined in eqn. (8), and the distribution ratio of iodine:

$$D = \beta_{20}mb (qa\lambda_{11} + 2pb\lambda_{02}) (B - \beta_{20}mb(aq\lambda_{11} + 2pb\lambda_{02}))^{-1} \quad (12)$$

At sufficiently low B , and therefore b (for M values of the order of 10^{-5} M this means B lower than $2 \cdot 10^{-4}$ M), the terms with b^3 are negligible. On the whole, it will be convenient to discuss the data in terms of three regions:

- very low B , where terms with b^2 are negligible,
- relatively high B , where terms with b (except for free B) are negligible, and
- intermediate values of B , where terms with both b and b^2 are important.

Very low B

The very low range of B is practically defined by having

$$(\partial D / \partial B)_{a,M} \approx 0 \quad (13)$$

This means that b is eliminated from the expressions for D , which requires that the only B containing species be B and MA_iB .

Since B is very low, $\Sigma[\text{MA}_i\text{B}]$ will be negligible beside $\Sigma[\text{MA}_i]$, and therefore the mercury balance is

$$M = \beta_{20}ma^2 (f_0 + \lambda_{20}) \quad (14)$$

where $a^2 (f_0 + \lambda_{20})$ is known. The iodine balance is

$$B = b (1 + \beta_{20} q m a (f_1 + \lambda_{11})) \quad (15)$$

Eliminating b and $\beta_{20} m$, the distribution of iodine will be

$$D = \lambda_{11} (f_0 + \lambda_{20}) a q^{-1} M^{-1} + f_1 \quad (16)$$

Eqn. (16) may be transformed into a linear eqn. in M^{-1}

$$D^{-1} = (f_0 + \lambda_{20}) a (q \lambda_{11})^{-1} M^{-1} + f_1 \lambda_{11}^{-1} \quad (17)$$

whence the slope of a $D^{-1} (M^{-1})_a$ plot will give the value of $q \lambda_{11}$.

If plots $D^{-1} (M^{-1})_a$ are extrapolated to $M^{-1} = 0$ (*i. e.* $M = \infty$) and the values of $\log D (\log a)_{M=\infty}$ plotted, the constants λ_{11} , k_{21} and $k_{21} k_{31}$ may be obtained by curve-fitting methods. The constant q may then be obtained from λ_{11} and the value of $q \lambda_{11}$ obtained above from the slope of (17).

Relatively high B

The range of relatively high B will be defined by having as B containing species only B and $MA_i B_2$, whence

$$(\partial \log D / \partial \log (B/M))_a = - (1 - 2 \lambda_{02} M B^{-1} (f_2 + \lambda_{02})^{-1})^{-1} \approx -1 \quad (18)$$

The mercury and iodine balances are then

$$M = \beta_{02} m b^2 (f_2 + \lambda_{02}) \quad (19)$$

$$B = b + 2 \beta_{02} m b^2 (f_2 + \lambda_{02}) = b + 2 M \quad (20)$$

Introducing the distribution ratio D and eliminating b and $\beta_{02} m$,

$$f_2 = \lambda_{02} (2 M B^{-1} (D + 1) D^{-1} - 1) \quad (21)$$

gives values for f_2 , and plots $\log f_2 (\log a)$ may be treated, *e. g.* by curve fitting methods, to yield values of k_{12} and $k_{12} k_{22}$.

Intermediate B

At intermediate values of B the species to be considered will be MA_i , $MA_i B$, $MA_i B_2$ and B. The mercury and iodine balances (10) and (11) combined, give then, neglecting terms with b^3

$$B/M = b/M + \frac{q a b (f_1 + \lambda_{11}) + 2 p b^2 (f_2 + \lambda_{02})}{a^2 (f_0 + \lambda_{20}) + q a b (f_1 + \lambda_{11}) + p b^2 (f_2 + \lambda_{02})} \quad (22)$$

Eliminating $\beta_{20} m$ from the iodine distribution ratio (12) and eqns. (10) and (11) gives

$$D = \frac{q a \lambda_{11} + 2 p b \lambda_{02}}{(M^{-1} a^2 (f_0 + \lambda_{20}) + q a f_1) + (M^{-1} q a (f_1 + \lambda_{11}) + 2 p f_2) b + (M^{-1} p (f_2 + \lambda_{02})) b^2} \quad (23)$$

Fig. 5. Plot of eqn. (17). Experimental points: ■ for $\log B = -5.9$, □ for $\log B = -6.5$, — best straight line through the points.

Eqs. (22) and (23) are functions of b , known constants and the as yet unknown constant p (it is assumed that a and M are kept constant). The function $\log D(\log p)_{a,b,M}$ is now plotted, calculated from (23) for discrete values of b . An approximate value for B/M may be obtained from

$$B/M \approx b/M + (1 + a(f_0 + \lambda_{20})q^{-1} b^{-1} (f_1 + \lambda_{11})^{-1})^{-1} \quad (22a)$$

Values of $\log D(\log B/M)_{a,M}$ are now obtained experimentally, and the value of $\log D$, corresponding to the B/M calculated for some value of b , gives then a provisional p value on the $\log D(\log p)$ plot for this b value. The provisional values are used in conjunction with (22) to calculate a better value of B/M , the corresponding $\log D$ found from experiment is then used to give refined values of p , this process being repeated as much as necessary.

IODINE DISTRIBUTION, EXPERIMENTAL RESULTS

Very low B

One series of experiments was made at constant $a = 0.100$ M and at two $\log B$ values, -5.9 and -6.5 , while $\log M$ changed from -4.0 to -2.0 . At the highest M values, A was varied, so as to keep a constant, and was calculated from $A = a + n_A M$, n_A being calculated using the constants k_{10} and a . The results, $\log D(\log M)_{a,B}$, are given in Table 3 and were transformed to plots of eqn. (17), $D^{-1}(M^{-1})_{a,B}$, shown in Fig. 5.

As is seen the points for the two B values fall on the same straight line, so that eqn. (13) is fulfilled, and the slope is $(2.00 \pm 0.05) \times 10^{-4}$. Since $(f_0 + \lambda_{20})a = 12.6 \pm 1.1$ (part II⁴), the value found for $\log q\lambda_{11}$ is 4.80 ± 0.04 .

A second series of experiments, presented in Table 3, was made at constant $\log B = -5.9$, and at two $\log M$ values: -4.00 and -3.00 , for each a value, while $\log a$ varied from -3.5 to -1.0 . The value of a was obtained by successive approximations from $a = A - n_A M$, when $A < 100$ M. Two points were obtained for each a in plots $D^{-1}(M^{-1})$ and the best straight line with the known slope $a(f_0 + \lambda_{20})q^{-1}\lambda_{11}^{-1}$ was drawn through them, the points falling very neatly on the line. The intercept at $M^{-1} = 0$ gives $\log D = \log \lambda_{11} - \log(1 + k_{21}a + k_{21}k_{31}a^2)$, which is plotted against $\log a$ in Fig. 6. The figure shows also the points $\log D(M)_{a,B}$. At $\log a < -2.3$, the points for the two M values coincide with that for $M^{-1} = 0$.

Fig. 6. Log D as function of $\log a$ for M^{-1} values extrapolated to zero: O, and for experimental values $M^{-1} = 10^3$: ●, and $M^{-1} = 10^4$: ▲, ——— calculated with the constants λ_{11} , k_{21} and $k_{21}k_{31}$.

The plot of $\log D(\log a)_{M=\infty}$ was "curve fitted" and yielded the constants: $\log \lambda_{11} = 0.79 \pm 0.01$, $\log k_{21} = 1.84 \pm 0.02$ and $\log k_{21}k_{31} = 3.34 \pm 0.04$. The value of λ_{11} gave with the slope of eqn. (17) the value $\log q = 4.01 \pm 0.04$. A curve calculated with the constants is compared with the data in Fig. 6.

Relatively high B

Three series of experiments were made at constant $\log B = -3.70$, one having $\log M = -5.29$, the second having $\log M = -4.90$, and the third having $\log M$ varying between -4.70 and -5.28 . In the first two series $\log a$ varied between -3.0 and -0.6 , while in the third it was constant, $\log a = -1.00$ (see Table 4). The third series illustrates the validity of eqn. (18), since $(\Delta \log D / \Delta \log M)_a \approx 1$. The data were used to calculate f_2 by eqn. (21), and the values so found are plotted as $\log f_2(\log a)$ in Fig. 7.

As may be seen from the figure, points for different M values fall on the same curve, showing that the assumptions underlying eqn. (21) — in particular the species to be considered — are valid. The curve was "curve fitted" and

Table 3. Distribution of iodine at low B values.

Constant $a = 0.100$ M			Constant $\log B = -5.9$		
$-\log M$	$-\log D$		$-\log a$	$\log D$	
	$\log B = -5.9$	$\log B = -6.5$		$\log M = -4.0$	$\log M = -3.0$
2.00	0.700	0.700	1.00	-0.845	-0.720
2.34		0.705	1.27	-0.355	-0.310
2.52	0.705		1.55	0.045	0.075
2.82		0.715	1.73	0.250	0.270
3.00	0.720		2.06	0.525	0.535
3.34		0.740	2.32	0.630	0.630
3.52	0.750		2.55	0.710	0.705
3.82	0.805		2.88	0.750	0.750
4.00	0.845	0.850	3.09	0.765	0.770
			3.52	0.780	0.780

Values of $\log D$ for $\log B = -6.5$ are ± 0.012 , all other $\log D$ values are ± 0.007 .

Fig. 7. $\log f_2$ obtained by eqn. (21) as function of $\log a$. Experimental points ● $\log M = -5.29$, ▲ $\log M = -4.90$, ○ $\log M$ varying between -4.69 and -5.28 , ——— calculated with the constants k_{12} and $k_{12}k_{22}$.

yielded the constants $\log k_{12} = 1.87 \pm 0.03$ and $\log k_{12}k_{22} = 3.37 \pm 0.05$. A curve calculated with these constants is compared with the data in Fig. 7.

Intermediate B

A series of experiments at constant $\log M = -4.00$ and at constant $a = 0.100$ M was made, with $\log B/M$ varying between -1.5 and $+1.6$. The results are plotted as $\log D(\log B/M)_{a,M}$ in Fig. 8. In the range of low B/M , D is independent of B/M as expected (eqn. (12)). At high B/M the slope of the curve is -1 as expected from eqn. (18). At intermediate values of B/M the curve rises slowly towards a maximum.

Curves $\log D(\log p)_{a,b,M}$ were calculated, using the constants q , λ_{11} and k_{ij} previously found, and the constant values of a and M , for the nine values of b : $\log b = -5.52 + 0.15i$, $i = 0, 1, 2 \dots 8$. The curves are shown in Fig. 9. Values of B/M corresponding to the above b were obtained, first from (22a)

Table 4. Distribution of iodine at high B/M values.

$\log M = -5.29$		$\log M = -4.90$		$\log a = -1.00$	
$-\log a$	$-\log D$	$-\log a$	$-\log D$	$-\log M$	$-\log D$
0.71	1.64	0.81	1.21	4.69	0.82
0.81	1.53	1.11	0.99	4.70	0.83
1.01	1.37	1.41	0.90	4.85	1.00
1.24	1.26	1.71	0.86	4.93	1.09
1.41	1.23	1.01	0.85	5.10	1.23
1.60	1.20			5.28	1.45
1.81	1.19				
2.23	1.18				
2.54	1.18				
3.00	1.18

Fig. 8. Log D as function of $\log B/M$ for $\log a = -1.00$ and $\log M = -4.00$. ● experimental points, ——— calculated (eqns. (22), (23)) from the constants.

and then by successive approximations, using provisional values of p , from (22). Log D values for these B/M were obtained from the experimental plot in Fig. 8, and the corresponding $\log p$ values were read off from the $\log D(\log p)$ plots, until $\log p$ proved constant $= 6.94 \pm 0.03$, and this value was accepted. The values so obtained are shown in Fig. 9.

A calculated curve, using all the constants, is compared with the data in Fig. 8.

REPRESENTATION OF RESULTS

The constants obtained from the various experimental and calculation methods are compared in Table 5.

The significance of the constants may be better understood when presented in graphical form.

One way of doing this is to show predominance areas, in a diagram with $\log a$ and $\log b$ as independent variables. Areas in it are marked with the indices ij of the complexes MA_iB_j , and correspond to a predominance of a single species (inside the shaded contour the concentration is $>50\%$). Lines mean equal concentrations of the complexes of the adjacent areas, and at triple points, three complexes are present at equal concentrations. This way gives at a

Fig. 9. Log D as function of $\log p$, with b as parameter. ——— the calculated function (eqn. (23)), ■ experimental D corresponding to B/M calculated from b and p by eqn. (22).

Table 5. Complexity constants for ternary Hg-Br-I complexes.

Reaction	Constant	Hg distribution		Iodine distribution	Final values
		$D(a)_r$	$D(r)_a$		
$MA_2 + 2B^- \rightleftharpoons MB_2 + 2A^-$	$\log p$	(7.1 ± 0.2)		6.94 ± 0.03	6.94 ± 0.03
$MA_2 + B^- \rightleftharpoons MAB + A^-$	$\log q$	4.2 ± 0.2		4.01 ± 0.04	4.01 ± 0.04
$MAB + B^- \rightleftharpoons MB_2 + A^-$	$\log q^{-1}p$	2.90 ± 0.05		(2.91 ± 0.05)	2.91 ± 0.05
$MA_2 + MB_2 \rightleftharpoons 2 MAB$	$\log K$	(1.3 ± 0.2)		(1.10 ± 0.07)	1.10 ± 0.07
$MAB \rightleftharpoons MAB_{or}$	$\log \lambda_{11}$	(0.79 ± 0.04)		0.79 ± 0.02	0.79 ± 0.02
$MAB + A^- \rightleftharpoons MA_2B^-$	$\log k_{21}$	1.85 ± 0.04	1.88 ± 0.03	1.84 ± 0.02	1.85 ± 0.03
$MB_2 + A^- \rightleftharpoons MAB_2^-$	$\log k_{12}$	1.87 ± 0.03	1.90 ± 0.02	1.87 ± 0.03	1.88 ± 0.03
$MA_2B^- + A^- \rightleftharpoons MA_3B^{2-}$	$\log k_{31}$	1.50 ± 0.06	1.46 ± 0.06	1.50 ± 0.05	1.49 ± 0.06
$MAB_2^- + A^- \rightleftharpoons MA_2B_3^{2-}$	$\log k_{22}$	1.51 ± 0.04	1.46 ± 0.04	1.50 ± 0.06	1.49 ± 0.05
$MB_3^{2-} + A^- \rightleftharpoons MAB_3^{2-}$	$\log k_{13}$	~ 1.0	1.10 ± 0.10		1.10 ± 0.10

The constants in parenthesis were calculated from others, directly obtained from the data, or were obtained from part III¹.

glance qualitative information as to the species important at given concentrations of both free A and free B. This diagram is shown in Fig. 10.

Another way to present two-dimensionally the three-dimensional diagram (% formation, a , b), is to present cuts at constant a (Fig. 11) or b (Fig. 12). This well known type of presentation shows the gradual addition of ligands, *e. g.* A in Fig. 12, while the ratios of the complexes with different numbers of the other ligand (*e. g.* B) remain constant (for cuts at constant b). Again, the complexes MA_iB_j are represented by their indices ij only.

DISCUSSION

A full discussion of the significance of the ternary complexity constants will be given in part V.

Previous work found on anionic mixed complexes of Hg(II) with halides is the Raman effect study of Delwaulle⁵. The mixed complexes HgA_nB_{4-n}

Fig. 10. Predominance area diagram. Areas correspond to predominance of the complexes MA_iB_j indicated by their indices ij (*e. g.* $HgBr_2I$ is (21)) (within shaded areas more than 50 %), as function of free bromide and free iodide concentrations.

Fig. 11. Mole % of complexes as function of free iodide concentration, at constant bromide concentrations $\log a = -1.7$ (a) and $\log a = -2.8$ (b).

Fig. 12. Mole % of complexes as function of free bromide concentration, at constant iodide concentrations $\log b = -3.6$ (a) and $\log b = -6.0$ (b).

could all be identified for A and B being any two of Cl^- , Br^- and I^- , except that lines for HgBrI_3^- could not be observed. This is in agreement with the rather weak formation of this complex found here, as is shown by its formation constant k_{13} . No complexity constants were, however, given by Delwaulle. A similar study, limited to the Br—I mixed complexes, is reported by Rolfe, Sheppard and Woodward⁹.

The treatment of mercury distribution data is essentially similar to well known examples, like that mentioned in Ref.³. On the other hand, ligand distribution does not seem to have been used similarly to central-group distribution. In the present study, the system M—A—B has been studied by measuring the distribution of total B between two liquid phases, the relevant reactions being $\text{M} + i\text{A} + j\text{B} \rightleftharpoons \text{MA}_i\text{B}_j$ and $(\text{MAB} + \text{MB}_2)_{\text{aq}} \rightleftharpoons (\text{MAB} + \text{MB}_2)_{\text{or}}$. Of course, solvent distribution is but one example of employing a two-phase system where not all the components of the complex system are soluble in both phases. The following examples show in what ways the present method is similar to or different from other methods.

Consider, for instance, that the second phase is a gas, and J. Bjerrum's measurements of the ammonia vapour tension above metal-ammonia solutions⁶ as an example of determining free A in a M—A system by two-phase distribution. The relevant reactions are then: $\text{M} + n\text{A} \rightleftharpoons \text{MA}_n$ and $\text{A}_{\text{aq}} \rightleftharpoons \text{A}_{\text{vap}}$ where M is the metal and A is ammonia.

If the second phase is a liquid, then the solvent distribution determination of free ligand may be illustrated by Dawson's study of the Hg—I system⁷. He determined the free iodide content of the solutions by measuring the iodine distribution between CS₂ or CCl₄ and the aqueous solutions, and, knowing the equilibrium constant for $I_2 + I^- \rightleftharpoons I_3^-$, he calculated [I⁻]. In this case the relevant reactions are: $M + n A \rightleftharpoons MA_n$, $A + B \rightleftharpoons AB$ and $B_{aq} \rightleftharpoons B_{or}$, where M is again the metal, A is iodide, B is iodine and AB is triiodide.

For the second phase being a solid, Leden and Parck's work may be mentioned⁸. There the distribution of radioactive iodine between solid AgI and its solution in AgClO₄ was measured. The distributing species AgI is then a member of the series of complexes studied $Ag_n I^{(n-1)+}$. The relevant reactions are then: $MA + (n-1) M \rightleftharpoons M_n A$ and $MA_{aq} \rightleftharpoons MA_{solid}$.

The first two examples belong to a group where the concentration of free ligand is measured, and as such are analogous, for instance, to measuring the concentration of a free ligand that is the anion of a weak acid by measuring the pH (potentiometrically or otherwise), where the reaction $H^+ + Anion^- \rightleftharpoons H\ Anion$ is utilized.

The present work is similar to the third example in that the total distribution of an element is measured, the distributing species being members of the complex series to be studied. There is little real difference between measuring the distribution of the central group and of the ligand, and the polynuclear system of silver iodide complexes may be considered as "silvero" complexes of the central-group iodine.

Measurements of ligand distribution may be of wide applicability, particularly in cases where there is no convenient isotope of the metal, but there is of the ligand.

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