Mercury(II) Halide Mixed Complexes in Solution

I. The Experimental Method and the Distribution of the Neutral Complex

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Experimental details are described for a study of the formation of mixed mercury(II) halide complexes. The distribution coefficients $\log \lambda^\circ$ of HgX_2 between benzene and water, obtained both directly and from the solubilities, are: HgCl_2 -1.06 ± 0.01 ; HgBr_2 0.05 ± 0.01 ; HgI_2 1.66 ± 0.01 . The coefficients for benzene — 0.5 M perchlorate ionic medium were also obtained. The solubilities of HgX_2 in benzene are: HgCl_2 $(1.92 \pm 0.01) \times 10^{-3}$ M; HgBr_2 $(1.90 \pm 0.01) \times 10^{-3}$ M; HgI_2 $(4.78 \pm 0.05) \times 10^{-3}$ M. Literature values for the solubilities and the distribution coefficients are reviewed. The salting-out effect of up to 2 M NaClO_4 on HgX_2 was studied, and the same salting-out coefficient $k_c = 0.14$ was found for all three halides. This value agrees with McDevit and Long's compression theory, although equations of other authors also fit the data.

1. INTRODUCTION

The careful study of metal complex formation in solution has mainly been confined, until recently, to systems of one metal and one ligand, which we shall call binary systems. Although practically no systematic investigation of complex systems between a metal and two ligands — which might be called ternary systems — has taken place, such cases have already been mentioned in passing, and sometimes complexity constants have been assigned to them. For instance Lister and Rivington¹ report the species FeClCNS^+ , FeBrCNS^+ , FeCl_2CNS and FeSO_4CNS , while Newman² in his recent thesis studied complexes of the type $\text{BiCl}_n\text{Br}_{5-n}^{2-}$.

It was felt that a more systematic work on ternary systems was desirable, in particular in order to find whether their formation obeys the statistical rules or is favoured or obstructed by the intra-molecular forces.

A convenient system to study was found in the mercury(II) halide complexes. These have been thoroughly studied before³, and accurate constants for the binary complexes are available. Furthermore, a convenient method of

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solvent distribution can be applied to the system, which has the advantage that the distribution of one of the mixed complexes, the neutral one, may be studied almost directly (part III).

a) Plan of work

The experimental study of mixed halide complexes of mercury included also a restudy of the binary complexes, the data for which are important in subsequent calculations. First the distribution of the neutral complex (*e. g.* HgCl_2) was studied, in the range of concentrations where it is stable, and its distribution coefficient was determined for all the halide ligands as a function of the ionic medium concentration (part I). The stepwise complexity constants of the binary complexes were then studied under the same conditions as formerly applied³, in order to check the constants against the earlier potentiometric values (part II). Later, mixed complexes were considered, where the ligand number is two, *i. e.* only the neutral species exist. Two such binary complexes (*e. g.* HgCl_2 and HgBr_2) may interact to give a ternary one (HgClBr) (part III). In the next paper the system mercury(II)-bromide-iodide is completely worked out, by both central group (Hg) and ligand (I) solvent distribution methods. The latter, incidentally, does not seem to have been used before (part IV). Finally, a literature survey of mixed complex formation is presented and commented on, and the question of ternary complex formation is discussed against the background of complex formation in general (part V).

b) Symbols

The following symbols apply in all the papers of this series:

A, B	two different ligands, for instance two halide ions, where B applies to the heavier of the two.
A, B	analytical (total) concentrations of A and B present in both the phases.
a, b	concentrations of free A and B in the aqueous phase.
D	gross distribution of M between the organic solvent and the aqueous solution, <i>i. e.</i> the ratio of concentrations, organic to aqueous, for equal volumes of the phases. (In part IV it denotes also distribution of B in the section devoted to it.)
i, j	indices, integers or zero (for mercury always $i + j \leq 4$). <i>i</i> usually applies to A, <i>j</i> to B.
K	disproportionation constant, for $\text{M} + \text{MX}_2 \rightleftharpoons 2 \text{MX}$ in part II, and for $\text{MA}_2 + \text{MB}_2 \rightleftharpoons 2 \text{MAB}$ in part III.
k_n	successive equilibrium constant for $\text{MX}_{n-1} + \text{X} \rightleftharpoons \text{MX}_n$.
$k_{i,j}$	equilibrium constant for $\text{MA}_{i-1}\text{B}_j + \text{A} \rightleftharpoons \text{MA}_i\text{B}_j$.
$k'_{i,j}$	equilibrium constant for $\text{M}_i\text{AB}_{j-1} + \text{B} \rightleftharpoons \text{MA}_i\text{B}_j$.
M	complex-forming central group, for instance Hg^{2+} .
M	analytical (total) concentration of M present in both phases.
m	concentration of free M in the aqueous phase.
$\bar{n}$	ligand number for the binary complexes $\text{M}-\text{X}$.
$\bar{n}_{\text{A,B}}$	total ligand number for the ternary system $\text{M}-\text{A}-\text{B}$ (<i>i. e.</i> the sum $\bar{n}_{\text{A}} + \bar{n}_{\text{B}}$).
) _{or}	subscript, the organic solvent phase (no subscript — the aqueous phase).
R	ratio B/A .
r	ratio b/a .
s_{solvent}	molar solubility in solvent stated.
u	concentration $[\text{MA}_2]$ in part IV.
X	general ligand, for instance halide.
X	analytical (total) concentration of X in both phases.

- x concentration of free X in the aqueous phase.
 $\beta_{i,j}$ overall complexity constant for $M + iA + jB \rightleftharpoons MA_iB_j$.
 β_n overall complexity constant for $M + nX \rightleftharpoons MX_n$.
 λ distribution coefficient of MX_n between organic solvent and aqueous solution.
 λ^0 distribution coefficient at zero ionic medium concentration (i. e. distribution benzene — pure water).
 $\lambda_{i,j}$ distribution coefficient of MA_iB_j ($i + j = 2$).
 $[\quad]$ molar concentration of the species within the brackets.
 Further symbols may be introduced and defined for occasional use in the appropriate places.

Charges are omitted in the mathematical equations and in reactions generally.

Concentrations and constants are given on the molar (moles per liter solution) scale, denoted by M.

2. EXPERIMENTAL METHOD

The description in this section applies to all the papers in this series (parts I—V).

a) Conditions of study

The complexes were studied in aqueous solutions of 0.50 M ($\text{ClO}_4^- + \text{X}^-$) ionic medium, which was made up from 0.010 M hydrogen ions, M M mercury(II) ions, 0.490—2 M M sodium ions, $A + B$ M halide and 0.500—($A + B$) M perchlorate. The function of the hydrogen ions was to repress hydrolysis, although this was actually unnecessary, since the complexing by halide is very strong. Nevertheless, this acidity was retained so that the conditions would be the same as in the earlier potentiometric study³.

The temperature of equilibration was kept fixed at $25.0 \pm 0.2^\circ\text{C}$, again the same as in the earlier study. This was achieved by equilibrating the solutions in a thermostated room.

The method of study consisted of measuring the gross distribution of the central group (mercury), or of a ligand (iodine), between an organic solvent phase (benzene) and the immiscible aqueous solution described above, by measuring the distribution of the radioactivity of ^{203}Hg or ^{131}I . The amount of benzene introduced into the ionic medium (0.036 mole %, calculated from McDevit and Long's data⁴) is quite negligible.

b) Materials

The sodium perchlorate used for the ionic medium was made by neutralizing perchloric acid with sodium carbonate to the extent of 98 %, boiling off the carbon dioxide, and making up to volume with distilled water. Sometimes a slight adjustment of acidity to exactly 0.010 ± 0.001 M was made after titration. The perchlorate concentration was checked by passing the solution through a cation exchange column in the hydrogen form and titrating the total acid. It always corresponded to 0.500 ± 0.005 M. The solution was checked from time to time for presence of halide, but always with negative results.

Stock solutions of sodium halides were prepared, about 0.49 M in halide and 0.010 M in perchloric acid, except the iodide, which was kept neutral in concentrated solutions, and was acidified only when [I] was below 0.001 M. The halide concentration was measured by Volhard titration of the stock solutions.

A 0.0440 M mercury(II) perchlorate stock solution was prepared by dissolving mercury(II) oxide in a calculated amount of perchloric acid, so that after dilution by sodium perchlorate solution and water the final acidity would be 0.010 M, and the final perchlorate concentration 0.50 M. The mercury(II) oxide, in its turn, was prepared by precipitation

from mercury(II) sulphate solution by sodium hydroxide, filtration and thorough washing. The mercury concentration was measured by titration with standard thiocyanate.

Benzene was equilibrated with sodium perchlorate ionic medium prior to use. The benzene then contained 0.26 mole % water⁵, but only 0.01 % material not volatile at 5° C. Apart from the water, the only species which benzene extracts from the aqueous solutions seems to be the neutral mercury halides.

Radioactive mercury(II) oxide, containing the ²⁰³Hg isotope (half-life 47.9 days, the characteristic radiation being 0.21 MeV β -rays and 0.28 MeV γ -rays) was obtained from A.E.R.E., Harwell, England, and was used after the decay of the 65 hour ¹⁹⁷Hg produced together with it. It was "specpure" and had an activity of about 26 mC/g. A weighed amount of it was dissolved in the minimum amount of 1.0 M perchloric acid and diluted with sodium perchlorate solution to a known volume. The stock solution was 0.00117 M in mercury.

A radioactive carrier-free iodide solution containing the ¹³¹I isotope (half-life 8.0 days, characteristic radiation 0.61 MeV β -rays and 0.36 MeV γ -rays) was obtained from J.E.N. E.R., Kjeller, Norway. Its activity was initially 2 mC/ml, it contained less than 1 μ g/ml iodide and less than 0.05 M reducing substances. It was added to known amounts of iodide solution before use, giving a negligible contribution to the total iodine concentration, and diluting the solutions by no more than 1 %, for which, however, no correction was made.

All the reagents used were of analytical quality grade, in particular the benzene was thiophene-free, according to the A.C.S. standard.

c) Equilibration and radioactive assay

Equilibration of the phases was effected by shaking together equal volumes (10.00 $\pm$ 0.05 ml) of aqueous solution and benzene in 40 ml glass stoppered bottles by a mechanical shaker rotating at 24 r.p.m.

The time of contact was in the large majority of cases 17 $\pm$ 1 h (overnight). In a few instances it was as short as 5 $\pm$ 1 h or as long as 43 $\pm$ 1 h. A number of experiments were made to determine the time needed for equilibrium to be reached. A small difference was sometimes found between the distribution values for 0.5 h and 1.5 h, but the latter value agreed with those for 5, 17 and 42 h, within the experimental errors.

When the shaking ended the phases separated cleanly, and were pipetted each in its turn up to a fixed height into the G.-M. tube. This was a "20th Century Electronics" M6 concentric-tubes liquid counter, containing about 9.5 ml. All measurements of radioactivity were relative, *i. e.* only ratios were obtained (usually between the activities in the two phases, in part III also between stock solutions of mercury(II) halides in benzene). Moreover, the activities making up the ratio were measured on the same day, so that no correction for decay was necessary.

Since there is a difference between the absorption of radioactive rays in the benzene and aqueous solutions, a correction must be applied. From radioactivity balance it was found that the value for the activity of Hg in benzene must be multiplied by 0.89 and that of I by 0.85 to make them comparable with those in aqueous solutions. In practice, 0.050 log units were subtracted from the log *D* values for radioactive Hg, and 0.070 log units for I.

d) Representation of results and errors

Primary data will usually appear as graphs of log *D* vs a suitable variable. Sometimes, however, they will appear in tabular form.

The experimental errors may be divided into two groups: analytical and volumetric errors on the one hand and counting errors on the other. Results of titrations are usually accurate to within ± 0.7 %. The error in the relative volumes of the phases might have come to ± 1.0 %. The errors in the counting varied, as it was necessary sometimes to count values not much above the

background. Usually the statistical error was within $\pm 1.5\%$, and thus the total error of an individual determination was about $\pm 2.5\%$ or 0.010 log units in log D . The reproducibility was quite good, even experiments made several months apart with different stock solutions usually showed results not deviating by more than the sum of the experimental errors.

In the calculation of the equilibrium constants from the data, such limits of error were assigned to them, that at least 90 % of the experimental points fell between curves calculated with the extreme values of the constants.

3. THE DISTRIBUTION COEFFICIENTS

a) Experimental results

The distribution of mercury(II) halides between an organic and an aqueous phase was studied by two approaches. One was to measure the distribution directly, at very low mercury concentrations — of the order of 10^{-5} M—using radioactive mercury. The other approach was to measure the solubility of the mercury halide in each phase separately, and to take the ratio as representing the distribution coefficient, according to Nernst's law. This is permissible, provided there is only negligible intersolubility of the phases and no association, dissociation or solvation of the solute occurs. This seems to be the case with the mercury(II) halides (except for HgCl_2 , see discussion below).

The solubility of HgX_2 in water saturated benzene was measured by shaking excess HgX_2 with the benzene in a thermostated room at $25.0 \pm 0.2^\circ\text{C}$ for 42 h, allowing the solid to settle for half an hour, taking an aliquot with a calibrated pipette from the clear supernatant liquid, evaporating the benzene at room temperature in a current of air and weighing the residue. In separate experiments it was checked that no HgX_2 volatilized with the benzene by the above procedure.

The values of the benzene solubility of the mercury(II) halides $s_{\text{C}_6\text{H}_6}$ are given in Table 1 and also in Table 2.

Distribution coefficients were calculated as the ratio of the benzene solubility to the aqueous solubility, using the average of the values that are not in parenthesis in Table 2. (Column "Solubility" in Table 1).

Table 1. Experimental distribution coefficients of mercury(II) halides, log λ .

Molar Solubility $s_{\text{C}_6\text{H}_6}$	"Solubility" log λ°	Distribution coefficients		
		"Direct determination" log λ°	"Extrapolation" log λ	"Extrapolation" log λ
HgCl_2 $(1.92 \pm 0.01)10^{-2}$ $\left\{ \begin{array}{l} (-1.142) \text{ a)} \\ -1.084 \pm 0.003 \end{array} \right\}$		-1.057 ± 0.007	-0.965 ± 0.010	-0.960 ± 0.015
HgBr_2 $(1.90 \pm 0.01)10^{-2}$	0.049 ± 0.004	0.040 ± 0.007	0.150 ± 0.005	0.155 ± 0.010
HgI_2 $(4.78 \pm 0.05)10^{-3}$	1.68 ± 0.02	1.658 ± 0.010	1.782 ± 0.010	1.760 ± 0.015
$\text{Hg}(\text{CNS})_2$ $(8 \pm 2)10^{-6}$	-2.5 ± 0.1		-2.2 ± 0.1	

a) See discussion, p. 336.

Table 2. The molar solubilities in water, benzene and toluene, and the distribution coefficients of mercury(II) halides at 25°C.

Author	Ref.	$\log s_{H_2O}$	$\log s_{C_6H_6}$	$\log \lambda^{\circ}_{C_6H_6}$	$\log s_{C_7H_8}$	$\log \lambda^{\circ}_{C_7H_8}$
<i>a) Mercury (II) chloride, $HgCl_2$</i>						
Linhart	6		-1.680	-1.08 ^a		-1.02 ^a
Sherrill	7	(-0.580)	-1.705	(-1.12 ^b)		
Laszcynski	8		{ -1.74 ^c			
Dukelski	9					
Marden	10		-1.674			
Flöttmann	11	-0.577				
Herz	12	-0.577				
Eddy	13	-0.577				
Thomas	14	-0.573				
Moles	15	(-0.61) ^d				
Morse	16	(-0.582)				-1.00
Brown &	17	(-0.61)			-1.71	-1.10
Drucker	18					-1.04
Hanzsch	19					-1.03
Krishtalik	20		-1.739			
This work			-1.717 ± 0.007	-1.057 ± 0.007		
<i>b) Mercury (II) bromide, $HgBr_2$</i>						
Krishtalik	20		-1.740			
Sherrill	7	-1.770	-1.712	0.050 ± 0.005		
Herz	12	-1.77				
Moles	15	-1.770				
Garrett	21	-1.770				
Morse	16					0.01
Tyrrell	22	-1.768				
This work			-1.721 ± 0.002	0.047 ± 0.007		
<i>c) Mercury (II) iodide, HgI_2</i> $\log \lambda_{0.5 M NaClO_4}$						
Sherrill	7		-2.307	(1.58) ^b		
Laszcynski	8		{ -2.31 ^c			
Gautier	23					
Beckmann	24					
Morse	16	(-3.89)				
Tananaev	25	(-4.12) ^j				
DeBruijn	26	-4.01				
Sillén	27	-3.98				1.81 ± 0.03 ^k
This work			-2.321 ± 0.005	1.66 ± 0.01		1.77 ± 0.01
<i>d) Mercury (II) thiocyanate, $Hg(CNS)_2$</i>						
Grossmann	28	-2.661 ^h				
Mason	29	-2.7 ⁱ				
Sherrill	30	-2.66				
This work		-2.658 ± 0.006	-5.1 ± 0.1	-2.5 ± 0.1		-2.2 ± 0.1

Table 2 (Contd.)

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- a) Extrapolated to zero concentration.
 - b) From ratio of solubilities.
 - c) Interpolated, though with little accuracy, from values at several temperatures between 6.5° and 54°.
 - d) Additional, less reliable, values are: Benrath ³¹ -0.59, and Benrath and Ammer ³² -0.58.
 - e) Extrapolated linearly from values at 15°: -2.37 and at 23°: -2.32.
 - f) The authors give a critical discussion on the solubility of HgI₂ in water, and also a value for the solubility in the 0.50 M NaClO₄ ionic medium: -4.13 ± 0.02.
 - g) Brown's values apply to 24°.
 - h) Author gives solubility as 0.00218 n, but, apparently this should read M.
 - i) A misquotation, *via* Comey and Hahn's "Dictionary" ³³ value of 0.0063 g/100 g solution, which is Grossmann's value.
 - j) This is the value obtained experimentally by Tananaev and Pilipenko, but with only 10 minutes' shaking. Garrett ³¹ misquoted them, the value he reports in their name is what they think is Sherrill's figure, and actually is Morse's.
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The column "Direct determination" in Table 1 gives the values found by determination of the distribution of HgX₂ between benzene and water (λ^0), and between benzene and 0.50 M sodium perchlorate ionic medium λ , starting with a benzene solution of HgX₂ to ensure having only the neutral complex.

Finally, the column "Extrapolation" gives the values found by extrapolation of distribution data of HgX₂ between benzene and excess halide X⁻ in the ionic medium (described in detail in part II) to zero excess halide.

In addition, a few experiments were made to see if Hg(CNS)₂ could also be extracted by benzene. Owing to the extremely small solubility in benzene, the distribution coefficient between benzene and the ionic medium could be obtained only very roughly. The best estimates are $\log \lambda = -2.2 \pm 0.1$. The values for solutions where excess thiocyanate was present also extrapolate roughly to the same value:

[CNS ⁻] M:	0.015	0.019	0.027
$\log D$:	-2.4 ± 0.2	-2.4 ± 0.2	-2.5 ± 0.3

The aqueous solubility of Hg(CNS)₂ does not seem to have been determined since 1905 (see Table 2), and no experimental details were given for the reported figures. The solubility was therefore determined anew. Mercury(II) thiocyanate was precipitated from a solution of radioactive mercury, and the precipitate washed well with water and dried. A portion of 0.360 g was weighed out and dissolved in 25.00 ml 0.1 M NaCNS solution, which became thus 0.00454 M in mercury, and its activity α_0 was counted. Water and 0.50 M NaClO₄ ionic medium were then shaken for 72 h at 25° with excess radioactive mercury(II) thiocyanate, and the activities α_w and α_m of the filtered solutions determined. The concentrations (*i. e.* solubilities) are then $\alpha_w \alpha_0^{-1}$ 0.00454 and $\alpha_m \alpha_0^{-1}$ 0.00454 M, respectively. The averages of two determinations are:

water solubility:	(2.20 ± 0.03)10 ⁻³ M	and
ionic medium solubility:	(1.34 ± 0.03)10 ⁻³ M.	

From the ionic medium solubility and the coefficient $\log \lambda = -2.2 \pm 0.1$, the benzene solubility $\log s_{\text{C}_6\text{H}_6} = -5.1 \pm 0.1$ was calculated, and from the latter and the water solubility, the coefficient $\log \lambda^\circ = -2.5 \pm 0.1$ was obtained.

b) Previous results

Literature values, which are mostly rather old and sometimes conflicting, are summarized in Table 2.

c) Discussion

Table 1 shows very good agreement between $\log \lambda$ and $\log \lambda^\circ$ values found by two different methods. Of the two values of $\log \lambda^\circ$ reported for HgCl_2 in column 3, -1.142 is the value obtained directly from the solubilities. This value must be corrected for dimerization. According to Linhart²⁶ $[\text{Hg}_2\text{Cl}_4] = 0.3 [\text{HgCl}_2]^2$. If this is correct, then in a saturated solution (total concentration of mercury chloride 0.265 M), there is 0.233 M free HgCl_2 and 0.016 M Hg_2Cl_4 . The same equilibrium constant applies also to the benzene phase, according to Linhart, but because of the low solubility the necessary correction is negligible. If now the corrected water solubility of HgCl_2 is used, the value $\log \lambda^\circ = -1.084$ is obtained, which is nearer to the value obtained from the distribution. Moreover, as will be shown below, the salting out effect on the distribution is independent of the particular halide used, so that there is a constant difference of (approximately) $0.11 \log$ units between $\log \lambda$ for 0.50 M NaClO_4 ionic medium and $\log \lambda^\circ$ (this may be seen also in Table 1). If 0.11 is subtracted from the average $\log \lambda$ for HgCl_2 in Table 1, the value -1.07 is obtained, agreeing with the value obtained from the distribution and the corrected solubility.

The values found in this work may now be compared with those reported in literature (Table 2). Regarding the aqueous solubility of HgCl_2 , an average value of the more modern figures, $\log s_{\text{H}_2\text{O}} = -0.575 \pm 0.002$ might be a fair approximation to the truth. Very good agreement is observed among the various determinations of the aqueous solubility of HgBr_2 . Of the two groups of values for the aqueous solubility of HgI_2 , the more recent one (DeBruijn and Sillén and Biedermann), combined with the benzene solubility gives a distribution coefficient $\log \lambda^\circ$ about 1.68 , in agreement with the directly determined value 1.66 , and therefore seems to be better than the older one, yielding a coefficient of only 1.58 . The aqueous solubility of $\text{Hg}(\text{CNS})_2$ is seen to be in very good agreement with the previously reported values.

Considering the benzene solubilities, there seems to be good agreement with the few reported values, apart from HgCl_2 , where the reported data are conflicting. The directly determined distribution coefficients of HgCl_2 (Linhart²⁶) and HgBr_2 (Sherrill⁷) are quite near those obtained in this work. The salting-out of HgI_2 by 0.50 M NaClO_4 observed by Sillén and Biedermann²⁷ — a difference of $0.15 \pm 0.03 \log$ units in the solubilities — is quite near the value obtained here, $0.11 \pm 0.01 \log$ units.

4. EFFECT OF IONIC MEDIUM CONCENTRATION

a) Experimental results

The effect of the sodium perchlorate ionic medium on the distribution was studied further. Experiments were made where the distribution was measured as function of the ionic medium concentration, called C below, up to 2 M. All solutions more concentrated than 0.01 M contained 0.01 M perchloric acid, the remainder being sodium perchlorate, while more dilute solutions contained only perchloric acid. The data are summarized in Fig. 1 as plots of $\log \lambda - \log \lambda^\circ$ vs C .

As may be seen in Fig. 1, the values for all three halides lie on a single curve, with only slight random deviations.

b) Discussion

Many approaches have been proposed to describe and explain the salting-out effect, but none has found complete quantitative success. (See Ref.³⁴ for a modern review.) Empirically, salting-out data may be described by the Setchenov equation:

$$\log \lambda - \log \lambda^\circ = \log f_c = k_c C \quad (1)$$

where f_c is the activity coefficient of the non-electrolyte in the ionic medium of concentration C and k_c is the salting-out constant, and where all the symbols refer to a very dilute solution of the non-electrolyte.

When eqn. (1) is applied to the data in Fig. 1, it is seen that it described them well at the lower concentrations, with the parameter $k_c = 0.14$. However, at concentrations C above about 1.5 M a curvature upwards occurs.

Various non-linear equations have been proposed to account for this. The simplest empirical one is due to Morrison³⁵:

$$\log \lambda - \log \lambda^\circ = \log f_c = k_c C^{k_p} \quad (2)$$

Fig. 1. Salting-out mercury(II) halides as function of ionic medium concentration. $\circ$ Hg(II) chloride, $\square$ Hg(II) bromide, $\triangle$ Hg(II) iodide. — equation (1), $k_c = 0.14$, equations (2), (3) and (4).

where k_p is an empirical constant. A curve with $k_c = 0.14$ and $k_p = 1.3$ expresses the data fairly well.

Of the more fundamental approaches, Debye's electrostatic theory³⁶ has won recognition as being able to explain the effects at least qualitatively for an electrolyte of the type of sodium perchlorate. It should be possible, in principle, to calculate the parameter J in eqn. (3) below for any pair of electrolyte-non-electrolyte, provided the ionic radii of the ions and the dielectric decrement of the non-electrolyte solutions are known.

$$\log \lambda - \log \lambda^\circ = \log f_c = -\log (1-JC) \quad (3)$$

Eqn. (3) fits the data quite well with the parameter $J = 0.27$.

Finally, a recent equation proposed by Nakajima³⁷ can be rewritten in the form:

$$\log \lambda - \log \lambda^\circ = \log f_c = -\log (1-\mu C(1+\nu\sqrt{C}) (1+0.707\sqrt{C})^{-1}) \quad (4)$$

which is, again, a two parameter equation, and gives with $\mu = 0.18$ and $\nu = 1/2$ a very good fit with the data.

Eqns. (2), (3) and (4) give such similar results that they are incorporated into one curve in Fig. 1.

Although the one-parameter eqn. (1) fails at higher concentrations, it is possible to calculate the expected k_c from compressibility and volume data. According to McDevit and Long⁴ k_c is given by:

$$k_c = \lim_{C \rightarrow 0} d(\log \lambda - \log \lambda^\circ) / dC = \bar{V}_n^\circ (V_c - \bar{V}_c^\circ) (2.3\beta_0 RT)^{-1} \quad (5)$$

where $\bar{V}_n^\circ$ is the partial molar volume of the non-electrolyte, $\bar{V}_c^\circ$ that of the electrolyte — both at infinite dilution — and β_0 is the compressibility of water. Inserting the values $\beta_0 = 4.56 \cdot 10^{-5} \text{ bar}^{-1}$, $R = \text{gas constant} = 83.11 \text{ ml bar deg}^{-1} \text{ mole}^{-1}$, $T = 298 \text{ deg}$, $\bar{V}_n^\circ = 49 \text{ ml mole}^{-1}$ (given by Linhart³⁸, p. 273) for HgCl_2 , $(V_c - \bar{V}_c^\circ) = 7.5 \text{ ml}^{-1} \text{ mole}$ (Mc Devit and Long⁴), the value $k_c = 0.141$ is obtained, in very good agreement with the observed value.

This good agreement might, however, be only fortuitous. For instance, the theory assumes that the radius of the non-electrolyte molecules is much smaller than the radii of the ions, whereas they are really comparable. Moreover, the variability of $\bar{V}_n^\circ$ with the various halides was neglected here.

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