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COMPLEXES OF ORGANOMETALLIC COMPOUNDS–XX

THE ETHYLMERCURY(II)-BROMIDE SYSTEM

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Abstract—The experimental distribution of C_2H_5HgBr at 25°C between Amberlite CG-400 and aqueous LiBr(10^{-3}–8 M) was determined. The invasion of the resin by LiBr was calculated by anion exchange paper chromatography of I^- and SCN^-, using aqueous LiBr as eluent, and from the distribution of I^- between the resin and the aqueous LiBr, at 25°C. The distribution coefficients of C_2H_5HgBr were then corrected for invasion, and evidence was obtained of the presence of the neutral complex in the solution phase at [LiBr] $\leqslant$ 1 M, and of $C_2H_5HgBr_2{}^-$ and $C_2H_5HgBr_3{}^{2-}$ complexes at high ligand concentration. The anion exchange stepwise stability constants $K_2{}^* = 0{\cdot}3$ and $K_3{}^* = 1{\cdot}1$ were calculated. The results are discussed in connection with previously-investigated systems (ethylmercury-(II)-chloride, -iodide, -thiocyanate, -nitrate), and a relationship is observed between retention on resin and tendency to anionic complex formation.

PREVIOUS investigations showed that organomercury salts form the complexes $R\ HgX_n{}^{1-n}$ ($R = C_2H_5$, X = Cl, I, SCN; $R = 2\text{-}C_4H_9$, X = SCN; with n ranging from 1 to 3) [1–4]. The stability constants of the above complexes have been calculated[2–4]. Subsequent work, which is reported in this paper, was devoted to investigation of the system ethylmercury bromide-lithium bromide-water -Amberlite CG-400. The bromide ligand and the anion exchange methods have been preferred for the following reasons:

(1) $[C_2H_5Hg^{II}]^+$ is a "B" type cation[5], and the existence of anionic $C_2H_5HgBr_n^{1-n}$ species is therefore to be expected. The tendency to form bromide complexes would presumably be intermediate between those of the corresponding chloride and iodide complexes.

(2) The formation of $C_2H_5HgBr_n^{1-n}$ anionic complexes would take place at high ligand concentration[4]. For this reason it was expected that the anion exchange method would be suitable to investigate $C_2H_5HgBr_n^{1-n}$ species, particularly since the chloride complexes were studied satisfactorily by this method[2]. The results obtained agreed with expectations.

EXPERIMENTAL

Pure reagents were used throughout the work. $(C_2H_5)_2Hg$ was purchased from Light, England. C_2H_5HgBr was prepared by the reaction between $(C_2H_5)_2Hg$ and $HgBr_2$ (10 m-mole of each reagent in 30 ml of ethanol); ethylmercury bromide was precipitated and recrystallized from ethanol, m.p.

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5. R. Stuart Tobias, *Organomet. Chem. Rev.* **1**, 93 (1966), and references quoted therein.

198° C[6]. Radioactive $C_2H_5{}^*HgBr$ was prepared by the same method, except that 1 m-mole of each reagent was used in 10 ml of ethanol; 10 mc of $^{203}Hg^{II}$ (R.C.C., Amersham) were employed to label 1 m-mole of $HgBr_2$. Aqueous Na ^{131}I was purchased from R. C. C., Amersham.

The anion exchange resin Amberlite CG-400 (IRA-400), 200-mesh nominal size (B.D.H.), and the anion exchange papers SB-2 (cellulose impregnated with Amberlite IRA-400, from Rohm and Haas), were pretreated, converted to the Br^- form and dried as reported elsewhere[3] (NaBr was used instead of KSCN).

The stock aqueous LiBr(Merck) solutions were percolated before use through columns of Amberlite CG-400(Br^-) to absorb impurities strongly retained in the resin phase. The Br^- standardization was carried out argentometrically.

(I) *Determination of resin invasion by LiBr*

This was carried out at 25°C by anion exchange paper chromatography of $^*I^-$ and SCN^- on SB-2(Br^-) with aqueous LiBr as eluent, and by measuring the distribution of $^*I^-$ between Amberlite CG-400(Br^-) and aqueous LiBr. The ascending anion exchange paper chromatographic trials were carried out as described elsewhere[3]. $^*I^-$ was located on the strips either by scanning or by autoradiography, and SCN^- by spraying with aqueous Fe^{III}. R_f values are reported in Table 1.

Table 1. Anion exchange distribution of $^{131}I^-$ and SCN^- between SB-2 paper and aqueous LiBr (T = 25°C)

Molarity of LiBr	R_f I^-	R_f SCN^-
0·515	0·08	0·06
1·02	0·16	0·09
1·45	0·19	0·11
2·13	0·25	0·14
2·42	0·26	0·15
3·08	0·27	0·18
3·40	0·28	0·19
4·06	0·31	0·21
5·04	0·33	0·23

The distribution coefficients of $^*I^-$ were obtained by batch equilibration. The equilibrium was reached by shaking for 2 days at 25°C, in a water thermostat, tightly-closed glass bottles containing known amounts of dry resin(w) and Na* I solution(v); vw^{-1} ranged from 12 to 50. The initially introduced activity (A_0) and the final one (A) were measured on 10 ml samples of the solution by a scintillation detector. The distribution coefficient D was calculated as follows:

$$D = (A_0 - A)vA^{-1}w^{-1}(\text{ml g}^{-1})$$

The swelling factor was neglected in Eq. (1) since its value was determined to be 0·98–1·00 for all *the* values of [LiBr] used and for the values of vw^{-1} given above.

Experimental values of D are reported in Table 2.

(II) *Anion exchange of* C_2H_5HgBr

The distribution coefficients of C_2H_5HgBr between Amberlite CG-400(Br^-) and aqueous LiBr were determined by batch equilibration. Twenty-five ml of ~ 0·5 mM C_2H_5HgBr, containing LiBr at the appropriate concentration and known weights of dry resin (of the order of 80 mg), were brought to equilibrium with two days' shaking at 25°C. In the trials conducted with the labelled or-

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6. K. H. Slotta and K. R. Jacobi, *J. prakt. Chem.* **120**, 249 (1929).

Table 2. Anion exchange distribution of $^{131}I^-$ between Amberlite CG-400 and aqueous LiBr (T = 25°C)

Molarity of LiBr	Distribution coefficient (D)
0·009	2000
0·094	229
0·396	58·0
1·19	22·6
2·68	12·6
3·96	10·5
5·45	9·4
7·18	11·5
8·43	20·0

ganomercurial, the concentration of $C_2H_5{}^*$ HgBr was measured in 10 ml liquid samples by means of a G.M. counter, and D was calculated from Equation(1). When inactive C_2H_5HgBr was used, the organomercurial concentration was determined polarographically with an AMEL (Milano) Mod.462 polarograph. Polarographic analyses were carried out as reported previously[4], the only difference being that three final LiBr concentrations were used (0·5, 2·5 and 5·0 M LiBr instead of 1 M NaBr + 1 M $NaClO_4$). This was done in order to bring samples of organomercurial solutions in aqueous LiBr at varying concentrations to a given constant LiBr composition. Values of D(Table 3) were determined by measuring the initial limiting diffusion current ($i_d{}^\circ$) and the final one (i_d) in 20 ml samples of solution:

$$D = (i_d{}^\circ - i_d) v i_d{}^{-1} w^{-1} (\text{ml g}^{-1}). \qquad (2)$$

It is noteworthy that these investigations have been carried out at neutral pH. By taking into account the value of K_{11} for the association of CH_3Hg^+ with OH^- and Br^-[5], and assuming that the replacement of CH_3 by C_2H_5 has little effect upon K_{11}, we find that ~ 10 per cent of the organomercurial undergoes hydrolysis at pH 7 and $[LiBr] = 10^{-3}$, while hydrolysis is negligible for $[LiBr] \geq 10^{-2}$. On the other hand, distribution coefficients in 10^{-3}–10^{-2} M HBr did not significantly differ from the corresponding values in LiBr.

METHODS OF TREATMENT OF RESULTS

The invasion of Amberlite CG-400(Br^-) by aqueous LiBr is a function ($_rF_a$) of the I^- distribution coefficient (D) and of the LiBr activity in the solution phage ($a = m\gamma\pm, m =$ molality)[7]:

$$_rF_a = \log D - \log D_1 + \log a \qquad (3)$$

D_1 is the value of D at a = 1. $_rF_a$ is also a function of $R_M = \log(R_f{}^{-1} - 1)$[3]:

$$_rF_a = R_M - R_{M1} + \log a \qquad (4)$$

where R_M refers to the distribution of a uni-univalent electrolyte between SB-2 and aqueous LiBr and R_{M1} is the R_M value at $a = 1$. Actually, at $a = 1$, LiBr invades the resin phase to a low, but nevertheless significant, extent (Fig. 1), so that the function $_rF_a$, calculated from equation(3) and (4), would assume constant negative values in the absence of invasion. In fact, no invasion occurs in the range of log a for which the slopes of plots log D and $R_M$vs. log a are − 1[7], while log D_1 and R_{M1} lie in a region where the distribution curve begins to flatten,

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7. Y. Marcus and C. D. Coryell, *Bull. Res. Coun. Israel* **A8**, 1 (1959).

Table 3. Anion exchange distribution of C_2H_5HgBr between Amberlite CG-400 and aqueous LiBr (T = 25°C)

Molarity of LiBr	Distribution coefficient (D)	Molarity of LiBr	Distribution coefficient (D)
0·001	131	3·50	107
0·003	122	4·00	105
0·010	122	4·50	89
0·035	117	4·54	87
0·10	123	5·01	93
0·35	118	6·00	107
1·00	116	7·00	145
2·00	109	8·00	140
3·00	84		

i.e., invasion begins to take place (Fig. 1). The distribution coefficient D°, corrected for resin invasion, is defined as follows [7]:

$$\log D^\circ = \log D - p_r F_a \qquad (5)$$

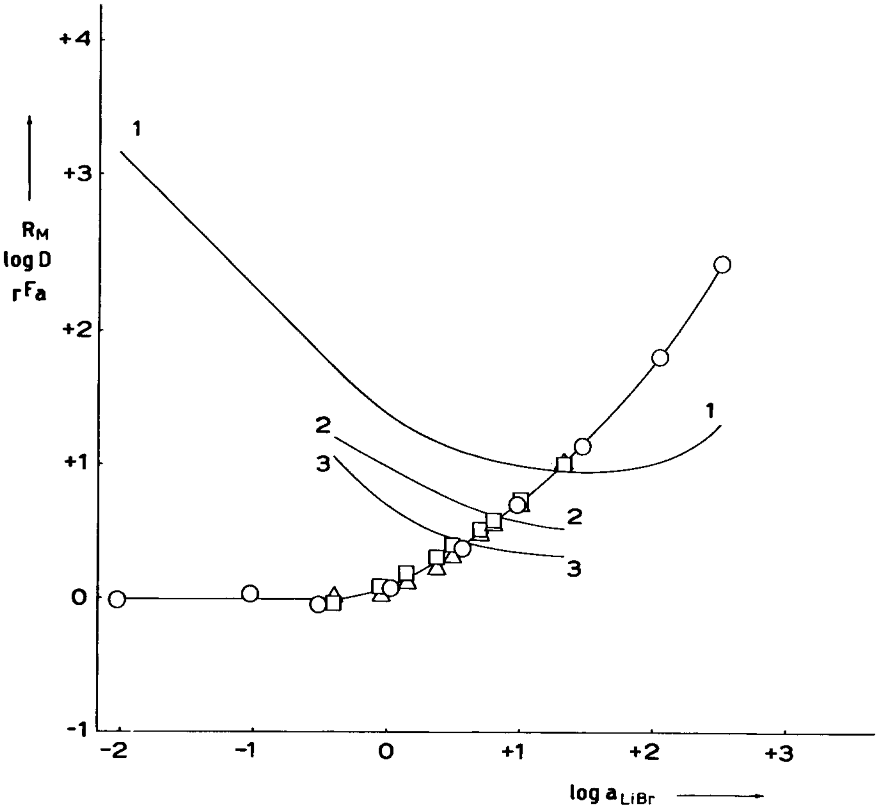

Fig. 1. The invasion of Amberlite CG-400 by aqueous LiBr at 25°C. Curve 1: log D for*I^-. Curve 2: R_M for SCN^-. Curve 3: R_M for *I^-. Data for $_rF_a$ (□, ○, △) are calculated from D for I^-(○), R_f for SCN^- (□) and R_f for *I^- (△).

where p is a parameter which is related to the charge on the anionic species exchanging in the resin sites[7]. The negative value of ${}_r\mathrm{F}_a$ then causes the corrected distribution curve to be raised artificially in the absence of invasion. Chemical intuition leads us to define ${}_r\mathrm{F}_a = \log {}_r a - \log {}_r a^\circ = 0$[7] when invasion does not occur. We then use the standard activity in the resin phase, ${}_r a^\circ$, corresponding to $a = 0{\cdot}1$ in the LiBr solution at equilibrium conditions, and calculate ${}_r\mathrm{F}_a$ as follows:

$$\begin{aligned} {}_r\mathrm{F}_a &= \log \mathrm{D} - \log \mathrm{D}_{0\cdot 1} + 1 + \log a \\ &= \mathrm{R_M} - \mathrm{R_{M0\cdot 1}} + 1 + \log a \end{aligned} \tag{6}$$

where $\mathrm{D}_{0\cdot 1}$ and $\mathrm{R}_{\mathrm{M}0\cdot 1}$ refer to values at $a = 0{\cdot}1$.

The invasion function, calculated from the data for $\mathrm{R_f}$ and D in Tables 1 and 2, is shown in Fig. 1. Data for $a = m\gamma\pm$ at 25°C were obtained by using values of $\gamma\pm$ from the literature[8]. It is noteworthy that the function ${}_r\mathrm{F}_a$ for the system LiBr-Dowex 1, determined by Andersen and Knutsen[9, 10], fits quite well that of Amberlite CG-400 if the data at low [LiBr] from Refs. 9 and 10 are corrected for retention by Freeman's procedure[11].

The experimental and corrected distribution curves for $\mathrm{C_2H_5HgBr}$ are given in Fig. 2. The ordinates $\log \mathrm{D}_1^\circ$ and $\log \mathrm{D}_2^\circ$ were taken from the data for D in Table 3 and the values of ${}_r\mathrm{F}_a$ in Fig. 1, using Equation(5) and $p = 1$, $p = 2$, respectively. The two values of p correspond to assuming that $\mathrm{C_2H_5HgBr_2}^-$ and $\mathrm{C_2H_5HgBr_3}^{2-}$ are the probable species present in the resin phase. The corrected plots show zero slope for $\log a \leqslant 0$, and limiting slopes -1 and -2 respectively. It then follows[7] that the neutral complex is present in the solution phase for $\log a \leqslant 0$, irrespective of the mercury-containing species absorbed in the resin phase, while the saturated complexes $\mathrm{C_2H_5HgBr_2}^-$ or $\mathrm{C_2H_5HgBr_3}^{2-}$, which correspond to the species respectively assumed to be retained in the resin phase, are present in concentrated LiBr solutions. The two distribution curves should follow the expressions[7]:

$$\log \mathrm{D}_1^\circ = \log \mathrm{K}_r' - \log(1 + \mathrm{K}_2^* a) \tag{7}$$

$$\log \mathrm{D}_2^\circ = \log \mathrm{K}_r' - \log(1 + \mathrm{K}_2^* a + \mathrm{K}_2^* \mathrm{K}_3^* a^2) \tag{8}$$

where K_r' refers to the exchange equilibrium and the K_i^* terms are stepwise anion exchange stability constants of organomercury-bromide complexes[7, 2, 3]†. Values of K_i^* were calculated by curve-fitting the data for $\log \mathrm{D}_1^\circ$ and $\log \mathrm{D}_2^\circ$ vs. $\log a$, following the procedure given elsewhere[12, 3]. The values obtained are:

(a) from the $\log \mathrm{D}_1^\circ$ function: $\mathrm{K}_2^* = 0{\cdot}6$
(b) from the $\log \mathrm{D}_2^\circ$ function: $\mathrm{K}_2^* = 0{\cdot}3$; $\mathrm{K}_3^* = 1{\cdot}1$.

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†Quotients K_i are "concentration constants" measured at constant total ionic concentrations using added inert salt ($\mathrm{NaNO_3}$ or $\mathrm{NaClO_4}$), while K_i^* is a "mixed" constant in which the complexes are represented by concentrations and the free ligand by its activity[7]. Qualitative comparison between the different quotients, obtained by different techniques, can be achieved[3, 4].

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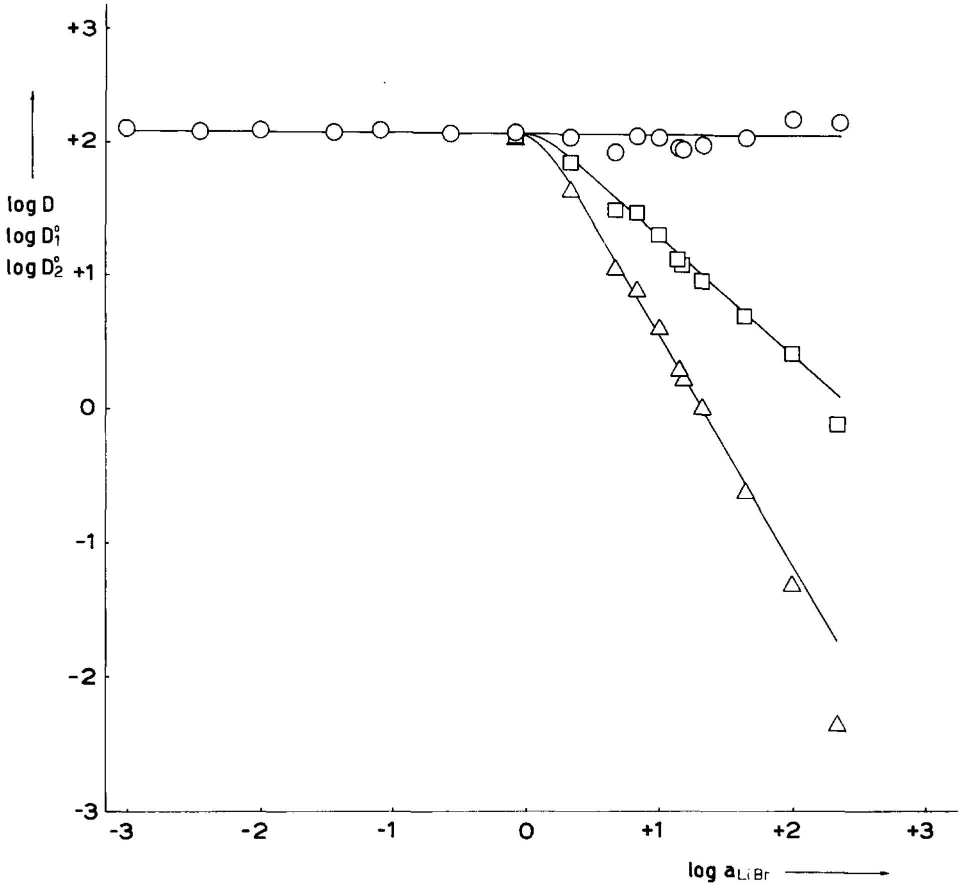

Fig. 2. Distribution of C_2H_5HgBr between Amberlite CG-400 and aqueous LiBr at 25°C.
○:log D; □:log $D_1^\circ = \log D - {}_rF_a$; △:log $D_2^\circ = \log D - 2{}_rF_a$.

DISCUSSION

Two points appear to merit discussion in connection with this work. The first concerns the formation of anionic $C_2H_5HgBr_n^{1-n}$ complexes in both resin and solution phase, and the orders of the stability constants in aqueous solution. There is no doubt that the anion exchange retentions of organomercury salts are due to complex formation, and cannot be attributed to the ethyl group bound to the mercury and the hydrophobic nature of the neutral organomercury salt. In fact, the ionic $C_2H_5HgNO_3$ shows a low retention on $SB-2(NO_3^-)$[2]; moreover, the experimental distribution curve of ethylmercury thiocyanate has a negative slope in rather dilute aqueous KSCN[3]; finally, the C_2H_5HgCl distribution curve shows a very marked acid effect (the limiting slope becomes negative when aqueous HCl is used as solution phase[13], i.e. it is opposite to that observed when employing LiCl[1, 2]). It follows that the retentions must be interpreted by assuming the formation of anionic organomercury complexes in both phases.

[13] G. C. Stocco and R. Barbieri, Unpublished results.

As to the nature of the saturated complex present in resin and solution, we are inclined to assume it to be $C_2H_5HgBr_3^{2-}$, considering also our previous work on the corresponding chloride, iodide and thiocyanate complexes[2–4]. The actual values of the stability constants would then be: $K_2^* = 0{\cdot}3$, $K_3^* = 1{\cdot}1$. A similar trend ($K_3 > K_2$) was observed for ethylmercury (II)-iodide and -thiocyanate systems in aqueous solution[4]. The average tendency of Hg^{II} in $C_2H_5HgBr_n^{1-n}$ complexes to bind Br^- in the third and fourth coordination places, as measured by $(K_2^*K_3^*)^{1/2} = 0{\cdot}57$, seems to be intermediate between those of the chloride $((K_2^*K_3^*)^{1/2} = 0{\cdot}50)$ and iodide $((K_2K_3)^{1/2} = 1{\cdot}10)$ complexes[2, 4]. On the other hand, 4-co-ordination is more pronounced in the Hg^{II}–Br^- system $((K_3K_4)^{1/2} = 10^{2{\cdot}01})$[14], and consequently the presence of a carbon-mercury bond increases the tendency to form the neutral linear organomercury bromide complex[4] $(K_1 = 10^{6{\cdot}62})$[5].

The second point concerns the relationship between the degree of retention on the anion exchange resin and the values of the stability constants. By examining the lines with zero slope for the experimental distribution coefficients of ethylmercury chloride[1, 2], bromide (this work, Fig. 2) and thiocyanate[3], it is clearly seen that the increase in retention corresponds to the increasing tendency to coordinate ligands. In fact, the zero slope corresponds to the absence of electrolyte invasion and to the presence in the solution phase of the neutral species only, so that at zero slope $D = D^\circ = K_r'$; now, the values of $D = K_r'$ and $(K_2^*K_3^*)^{1/2}$ increase in the systems

$$C_2H_5Hg^{II}\text{–}Cl^- < C_2H_5Hg^{II}\text{–}Br^- < C_2H_5Hg^{II}\text{–}SCN^-((K_2^*K_3^*)^{1/2} = 1{\cdot}8 \\ \text{for} \quad C_2H_5HgSCN_n{}^{1-n}).$$

The mechanism of absorption of the organomercurials seems to consist in the transfer of neutral species from solution to resin, followed by anionic complex formation in the resin phase. In this connection the organomercury(II) and mercury(II) derivatives seem to behave in a very similar way[15].

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