August, 1984] Bull. Chem. Soc. Jpn., 57, 2271—2275 (1984)

The Extraction of Organomercury with 8-Quinolinol into Benzene

Takao Sugimoto, Kunishige Naito, and Shinsuke Takei*
Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Nakanarusawa-cho, Hitachi 316

(Received May 13, 1983)

The extraction of organomercury(II)(RHg^+, R; ethyl, *n*-propyl, *n*-butyl, phenyl) with 8-quinolinol into benzene has been studied by means of spectrophotometry. This study confirmed that there was no co-extraction of electrically neutral species RHgOH by its investigation of the effect of the pH on the extraction of ethylmercury(II) chloride into benzene. Moreover, it was found that RHg^+ forms 1:1 complexes with both HPO_4^{2-} and PO_4^{3-}. The formation constants of these complexes and of hydroxo complexes have been determined.

Organomercury(II) (RHg^+) forms two kinds of water-soluble complexes with 8-quinolinol (oxine, Hq), and one of these can be extracted into an inert solvent such as benzene. The formation of water-soluble complexes of ethylmercury(II) ($EtHg^+$), *n*-propylmercury(II) (*n*-$PrHg^+$), and *n*-butylmercury(II) (*n*-$BuHg^+$) with 8-quinolinol has previously been reported.[1] In this work, the extraction of 8-quinolinates of $EtHg^+$, *n*-$PrHg^+$, *n*-$BuHg^+$, and phenylmercury(II) ($PhHg^+$) into benzene, together with the complex formation of $EtHg^+$ with Cl^- and its extraction into benzene and the complex formation of RHg^+ with OH^- and phosphate ions, has been investigated by means of spectrophotometry.

Experimental

1. Reagent and Apparatus. Organic Solvents. The benzene and carbon tetrachloride, reagent-grade, were purified by distillation.

Dithizone Solution in Carbon Tetrachloride: The purified dithizone solution in carbon tetrachloride was prepared by the usual method.[2]

RHg^+ Solution: All the RHg^+ solutions used were prepared and standardized by the method previously reported.[1]

All the other reagents used in this work were guaranteed-reagent-grade and were used without further purification.

A Shimadzu MPS-50 recording spectrophotometer and a Hitachi 124 double-beam spectrophotometer were used for the measurements of the absorption spectra and the absorbance of the solutions. A Hitachi-Horiba F-5 pH meter was used for the measurement of the pH of an aqueous solution.

2. Experimental Procedures. *a. Extraction of EtHgCl into Benzene*: The extraciton of $EtHg^+$ as dithizonate into carbon tetrachloride has been reported to be unaffected by the Cl^- and the pH under the experimental conditions applied in this work.[3] Then, after the extraction of EtHgCl from $10.00\,cm^3$ of an aqueous solution into $10.00\,cm^3$ of benzene, an aliquot amount of the aqueous solution was taken and $EtHg^+$ was extracted as dithizonate by the addition of a dithizone solution on the solution and shaking. Also, from the absorbance of dithizone in excess at 620 nm, the $EtHg^+$ was determined and the distribution ratio of $EtHg^+$ was obtained.

b. Extraction of RHg^+ 8-Quinolinate: Into a glass-stoppered test tube, desired amounts of NaH_2PO_4, Na_2HPO_4, and RHg^+ solutions were taken and deionized water was then added to make the solution up to $10.00\,cm^3$. To this solution $10.00\,cm^3$ of an 8-quinolinol solution in benzene was added, after which the solution was shaken for 30 min. After this solution had been separated into two layers, the absorbance of the organic solution at the absorption peak of the complex and the pH of the aqueous solution were measured.

Results and Discussion

The complex of RHg^+ with 8-quinolinol is extracted into benzene at a pH above about 5. In order to analyse the extraction reaction, it is necessary to ascertain whether or not the electrically neutral species RHgOH can be extracted into benzene. The extraction of methylmercury(II) and $PhHg^+$ halides from an acidic solution into nonpolar solvents has been studied;[4] then by the investigation of the effect of the pH of the extraction of EtHgCl, the extraction of EtHgOH was studied.

In Fig. 1, the distribution ratio of $EtHg^+$ increases with increase in the initial concentration of Cl^-; the

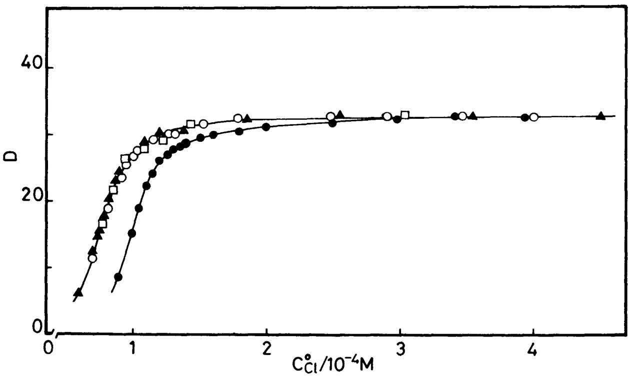

Fig. 1. Variation of distribution ratio of $EtHg^+$ with initial concentration of Cl^-.
●: pH; 1.0, C°_{M}; 1.07×10^{-4} M (1 M=1 mol dm^{-3}), ○: pH; 1.1, ▲: pH; 1.6, □: pH; 2.0, C°_{M}; 7.66×10^{-5} M.

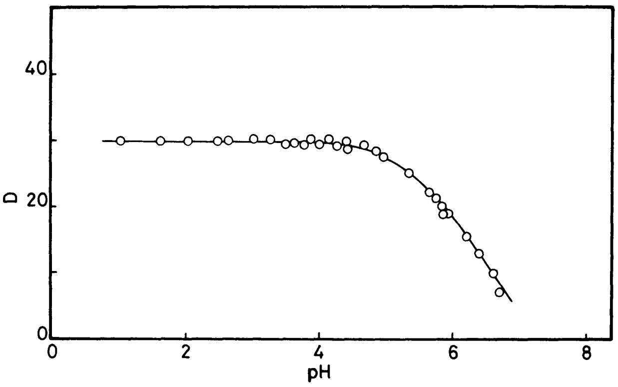

Fig. 2. Variation of distribution ratio of $EtHg^+$ with pH.
C°_{M}; 7.66×10^{-5} M, C°_{Cl}; 1.20×10^{-4} M.

higher distribution ratio is obtained when the initial concentration of RHg^+ is low. However, at higher concentrations of Cl^-, the same distibution ratio is obtained regardless of the intial concentration of $EtHg^+$.

Moreover, as is shown in Fig. 2, the distribution ratio of $EtHg^+$ decreases with the rise in the pH above 4.

These experimental results may be explained as follows. The distribution ratio D of $EtHg^+$ is written as follows;

$$D = \frac{[MCl]_o + [MOH]_o}{[M]+[MCl]+[MCl_2]+\cdots+[MOH]+[M(OH)_2]+\cdots}$$
$$= \frac{p\beta_1[Cl] + p'\beta_1'[OH]}{1+\beta_1[Cl]+\beta_2[Cl]^2+\cdots+\beta_1'[OH]+\beta_2'[OH]^2+\cdots}, \tag{1}$$

where M represents $EtHg^+$, where β's are respective complex-formation constants, and where p and p' are the distribution constants of EtHgCl and EtHgOH respectively (the charges of the ions are omitted for the sake of simplicity).

In the experimental range shown in Fig. 1 the distribution ratio of $EtHg^+$ is independent of the pH; therefore, the formation of complexes with OH^- and the distribution of EtHgOH can be neglected, and (1) becomes;

$$\frac{1}{D} = \frac{1}{p} + \frac{1}{p\beta_1[Cl]} + \frac{\beta_2}{p\beta_1}[Cl] + \cdots. \tag{2}$$

From (2) it is found that the plot of $1/D$ against 1/[Cl] gives a straight line when the main species of the $EtHg^+$ complex with Cl^- is EtHgCl, whereas the plot of $1/D$ against [Cl] gives a straight line or a quadratic curve when $EtHg^+$ forms higher complexes such as $EtHgCl_2^-$ and $EtHgCl_3^{2-}$ with Cl^-.

Figure 3 shows that the plot of $1/D$ against 1/[Cl], in which [Cl] is the equilibrium concentration of Cl^- corrected to the distribution of Cl^- into benzene as EtHgCl, gives a straight line. On the other hand, the plot of $1/D$ against [Cl] gives a quadratic curve with negative coefficients. These results indicate that the main species formed in the aqueous layer in the experimental range is EtHgCl. From the reciprocal of the intercept and the slope of the straight line shown in Fig. 3 the distribution constant and the formation constant of EtHgCl are obtained as 33±1 and $(2.7\pm0.5)\times10^5$ respectively. The formation constant of EtHgCl is almost the same as those of methylmercury(II) and $PhHg^+$ chlorides reported previously,[4] and no large variation with the R combined with Hg can be observed. The results shown in Fig. 2 seem to indicate that the distribution of EtHgOH in benzene is negligible. Then, from (1) the following relation is introduced;

$$\frac{1}{D} = \frac{1}{p} + \frac{1}{p\beta_1[Cl]} + \frac{\beta_1'[OH]}{p\beta_1[Cl]} + \frac{\beta_2'[OH]^2}{p\beta_1[Cl]} + \cdots. \tag{3}$$

By using the values of p and β_1 obtained above and the assumption that, in this experimental range, $EtHg^+$ forms a 1:1 complex only with OH^-, the value of β_1' is calculated from the experimental results shown in Fig. 2 and (3). By this treatment $\beta_1'=(1.7\pm0.1)\times10^9$ is obtained; this value shows fairly good agreement with that reported by Waugh *et al.*[5]

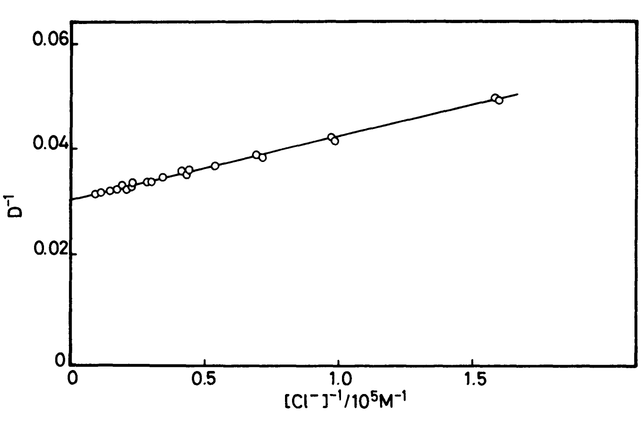

Fig. 3. Plot of 1/D of $EtHg^+$ against 1/[Cl].

Therefore, it may be concluded that the distribution of EtHgOH in benzene is negligible and that, in this experiemntal range, $EtHg^+$ forms a 1:1 complex predominantly with OH^-. From these results, the extraction of the RHg^+ complex with 8-quinolinol into benzene is analysed on the assumption that the distribution of RHgOH in benzene is negligible, regardless of the R.

The absorption maxima of benzene solutions of the $EtHg^+$, n-$PrHg^+$, and n-$BuHg^+$ complexes and that of the $PhHg^+$ complex are observed at 378 nm and 375 nm respectively; therefore, the variation in the wavelength at the absorption peak with R is vary small. The absorption of free 8-quinolinol in benzene at the absorption maxima of the complexes is negligible.

The molar ratio of RHg^+ to 8-quinolinol in the complex is found by the continuous-variation method to be 1:1, regardless of the R.

At the peak wavelength, the absorbance of the extract of the RHg^+ complex from borate buffer solutions of pH values from 9.0 to 10.0 in the presence of an excess of 8-quinolinol shows constant value. Therefore, from the absorbance measured under the conditions shown above, the molar absorption coefficient of the complex solution at the peak wavelength is determined and the following results are obtained; $EtHg^+$ complex: 3.00×10^3; n-$PrHg^+$ complex: 3.04×10^3; n-

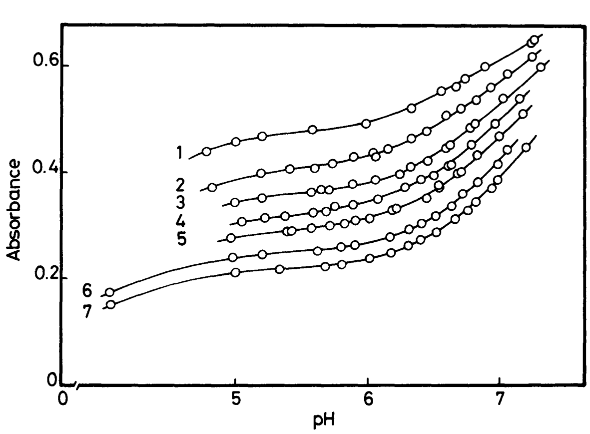

Fig. 4. Variation of the absorbance of $EtHg^+$–8-quinolinol complex in benzene with pH under various concentrations of phosphate.
C_M°; 2.55×10^{-4} M, C_L°; 4.00×10^{-3} M.
Total concentration of phosphate: 1; 0.02 M, 2; 0.03 M, 3; 0.04 M, 4; 0.05 M, 5; 0.06 M, 6; 0.08 M, 7; 0.10 M.

BuHg$^+$ complex: 3.03×10^3; PhHg$^+$ complex: 3.20×10^3. The variation in the molar absorption coefficient of the complexes with the R is very small except for the PhHg$^+$ complex, which shows a higher value.

Figure 4 shows the variation in the absorbance of the EtHg$^+$ complex extracts from phosphate buffer solutions in various concentrations with the pH. Similar results are obtained in other RHg$^+$ systems. In this work, the initial concentration of RHg$^+$ is made as high as possible in order to minimise the effect of the co-extraction of the RHg$^+$ complexes with, *e.g.*, the Cl$^-$ contained as an impurity in the reagents used. However, in the present experimental range the distribution ratio of RHg$^+$ is independent of the initial concentration of RHg$^+$; therefore, the formation of polynuclear complexes of RHg$^+$ is considered to be negligible.

The experimental results shown in Fig. 4 may be analysed as follows.

The extraction of RHg$^+$ with 8-quinolinol can be written as;

$$\mathrm{RHg^+ + q^- = RHgq_{(o)}}, \tag{4}$$

$$K_{ex} = \frac{[\mathrm{RHgq}]_o}{[\mathrm{RHg}][\mathrm{q}]}. \tag{5}$$

As has been mentioned above, RHgOH is not distributed into benzene, and the distribution of complexes of RHg$^+$ with phosphate ions are found to be negligible, therefore, the distribution ratio D of RHg$^+$ can be written as;

$$D = \frac{[\mathrm{RHgq}]_o}{C_M^\circ - [\mathrm{RHgq}]_o}, \tag{6}$$

$$\begin{aligned} C_M^\circ - [\mathrm{RHgq}]_o = C_M &= [\mathrm{RHg}] + [\mathrm{RHgOH}] \\ &+ [\mathrm{RHg(OH)_2}] + \cdots + [\mathrm{RHgH_2PO_4}] + \cdots \\ &+ [\mathrm{RHgHPO_4}] + \cdots + [\mathrm{RHgPO_4}] + \cdots \\ &+ [\mathrm{RHgq}] + [\mathrm{RHg(q)(OH)}] + \cdots \\ &= [\mathrm{RHg}](1 + \beta_1'[\mathrm{OH}] + \beta_2'[\mathrm{OH}]^2 + \cdots \\ &+ K_1[\mathrm{H_2PO_4}] + \cdots + K_1'[\mathrm{HPO_4}] + \cdots \\ &+ K_1''[\mathrm{PO_4}] + \cdots + K_f[\mathrm{q}] + K_c[\mathrm{q}][\mathrm{OH}] + \cdots) \\ &= [\mathrm{RHg}]\,\gamma, \end{aligned} \tag{7}$$

where C_M° is the initial concentration of RHg$^+$ in the aqueous solution and where the β's and K's are the formation constants of the respective complexes. From the measurement of the absorbance of the aqueous layer after extraction, RHg(q)(OH)$^-$ is found to be absent[1] and [RHgq] is considered to be negligible; therefore, in (7), the terms corresponding to [RHg(q)(OH)] and [RHgq] are omitted. The total concentration of 8-quinolinol, C_L°, can be written as follows;

$$\begin{aligned} C_L^\circ = {}& [\mathrm{H_2q}] + [\mathrm{Hq}] + [\mathrm{q}] + [\mathrm{RHgq}] \\ &+ [\mathrm{RHg(q)(OH)}] + [\mathrm{Hq}]_o + [\mathrm{RHgq}]_o. \end{aligned}$$

As [RHgq] and [RHg(q)(OH)] can be neglected;

$$\begin{aligned} C_L^\circ - [\mathrm{RHgq}]_o = C_L &= [\mathrm{H_2q}] + [\mathrm{Hq}] + [\mathrm{q}] + [\mathrm{Hq}]_o \\ &= [\mathrm{q}]\left(\frac{[\mathrm{H}]^2}{k_1k_2} + \frac{[\mathrm{H}]}{k_2} + 1 + \frac{p''[\mathrm{H}]}{k_2}\right) = [\mathrm{q}]\,\alpha. \end{aligned} \tag{8}$$

From (5), (7), and (8), (9) is obtained;

$$K_{ex} = \frac{[\mathrm{RHgq}]_o\,\alpha\,\gamma}{C_M C_L} = K'_{ex}\,\alpha\,\gamma \qquad \frac{1}{K'_{ex}\,\alpha} = \frac{\gamma}{K_{ex}}. \tag{9}$$

In (9). K'_{ex} can be determined experimentally and the value of γ can be obtained from the step-by-step acid-dissociation constants of 8-quinolinol (pk_1=5.13, pk_2=9.66[6]), the distribution constant of 8-quinolinol between aqueous and benzene layers p'' ($p''=10^{2.44}$[7]), and the pH of the aqueous layer measured. From (7), the right-hand side of (9) becomes;

$$\begin{aligned} \frac{\gamma}{K_{ex}} &= \frac{1}{K_{ex}}(1 + \beta_1'[\mathrm{OH}] + \beta_2'[\mathrm{CH}]^2 + \cdots) \\ &\quad + \frac{1}{K_{ex}}(K_1[\mathrm{H_2PO_4}] + K_1'[\mathrm{HPO_4}] + K_1''[\mathrm{PO_4}] + \cdots \\ &= \frac{1}{K_{ex}}\mathrm{f[OH]} + \frac{[\mathrm{PO_4}]}{K_{ex}}\left(\frac{K_1[\mathrm{H}]^2}{k_2'k_3'} + \frac{K_1'[\mathrm{H}]}{k_3'} + K_1'' + \cdots\right) \end{aligned} \tag{10}$$

$$= \frac{1}{K_{ex}}\mathrm{f[OH]} + \frac{[\mathrm{HPO_4}]}{k_{ex}}\left(\frac{K_1[\mathrm{H}]}{k_2'} + K_1' + \frac{K_1''k_3'}{[\mathrm{H}]} + \cdots\right), \tag{11}$$

where f[OH] represents the coefficient of $1/K_{ex}$ of the first term on the right-hand side and where k_2' and k_3' are the respective acid-dissociation constants of phosphoric acid (pk_2'=6.71, pk_3'=11.8[8]).

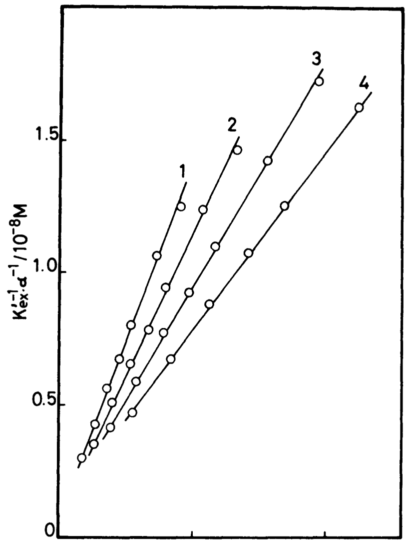

Fig. 5. Plot of $1/K'_{ex}$ a of EtHg$^+$–8-quinolinol complex against [PO$_4$].

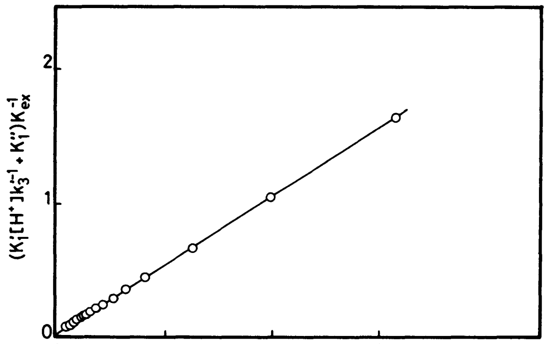

Fig. 6. Plot of Values of the slope of straight lines shown in Fig. 5 against [H].

Table 1. Formation constants of RHg^+ complexes

RHg^+	K_{ex}	β_1'	K_1'	K_1''
$EtHg^+$	$2.9\pm0.5\times10^{10}$	$1.7\pm0.3\times10^{9}$	$1.2\pm0.2\times10^{4}$	$2.8\pm0.7\times10^{8}$
n-$PrHg^+$	$1.4\pm0.5\times10^{11}$	$1.6\pm0.5\times10^{9}$	$1.4\pm0.3\times10^{4}$	$1.1\pm0.4\times10^{8}$
n-$BuHg^+$	$7.6\pm1.1\times10^{11}$	$1.1\pm0.1\times10^{9}$	$1.8\pm0.2\times10^{4}$	$2.7\pm0.6\times10^{8}$
$PhHg^+$	$2.0\pm0.7\times10^{13}$	$9.6\pm3.6\times10^{9}$	$1.8\pm0.4\times10^{5}$	$3.1\pm1.1\times10^{9}$

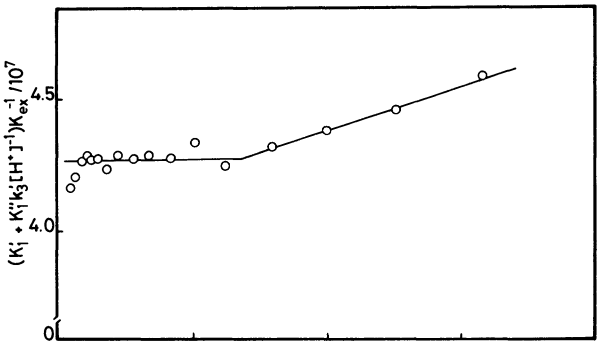

Fig. 7. Plot of values of the slope of straight lines obtained by plot of $1/K'_{ex}$ a of $EtHg^+$ complex *vs.* $[HPO_4]$ against $1/[H]$.

Equations (9), (10), and (11) indicate that $1/K'_{ex}\,\alpha$ at a constant pH is linear against $[PO_4]$ and $[HPO_4]$ and that the values of the intercept of both straight lines obtained at the same pH are equal. Moreover, intercepts of both straight lines are functions of [OH]; then, by plots of the value of the intercept against [OH], the hydroxo complexes of RHg^+ formed in the experimental range and the three constants K_{ex}, k_1' and k_2' are determined. On the other hand, the β values of the slopes of the straight lines obtained by the plot of $1/K'_{ex}\,\alpha$ against $[HPO_4]$ and $[PO_4]$ are functions of [H]; then, by plots of the values of the slope against [H] or $1/[H]$ complexes of RHg^+ with $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} and the formation constants of these complexes are determined on the bases of (10) and (11).

By these considerations, the experimental results shown in Fig. 4 are analysed. First, Fig. 5 shows the plot of $1/K'_{ex}\,\alpha$ of $EtHg^+$ against $[PO_4]$. A similar good linearity is obtained by the plot of $1/K'_{ex}\,\alpha$ against $[HPO_4]$, and the values of the intercept of both straight lines at the same [OH] show a good agreement with in a probable error of ±10%.

Moreover, the values of the intercept obtained from Fig. 5 are found to be linear against [OH]. This indicates that, in this experimental range, $EtHg^+$ forms a 1:1 complex with OH^- predominantly. In Table 1, the values of K_{ex} and β_1' obtained from this result on the basis of (10) are tabulated.

Figure 6 shows the plot of the value of the slope of the straight line shown in Fig. 5 against [H]. The good linearity indicates that there is no formation of a complex of $EtHg^+$ with $H_2PO_4^-$. The absence of the $EtHg^+$-$H_2PO_4^-$ complex is confirmed by the result that the values of the slopes of the straight lines obtained by a plot of $1/K'_{ex}\,\alpha$ against $[HPO_4]$ are linear against $1/[H]$ on the basis of (11), as shown in Fig. 7.

In Fig. 7, the slope of the straight line is zero below pH 6.8; therefore, below this pH the formation of $EtHgPO_4^{2-}$ is considered to be negligible. Figures 6 and 7 indicate that, in order to determine more precise values of the intercept and the slope of the straight line, the plot of $1/K'_{ex}\,\alpha$ against $[PO_4]$ is more suitable than that of $1/K'_{ex}\,\alpha$ against $[HPO_4]$. Therefore, in Table 1 the values of K_1' and K_1'' obtained by the treatment of the results shown in Fig. 6 by the least-squares method and by the use of the value of K_{ex} determined above are tabulated.

Similar results are obtained from the n-$PrHg^+$, n-$BuHg^+$, and $PhHg^+$ 8-quinolinate extraction systems. The results of the determinations are tabulated in Table 1. However, as shown in Fig. 8, plots corresponding to Fig. 6 in the $PhHg^+$ system give a curve; therefore, possibility of the formation of higher complexes of $PhHg^+$ with OH^- can not be neglected. It is found though, that the treatment of the whole curve as a quadratic curve does not give reasonable values of K_{ex}, β_1', and β_2'. Therefore, by the treatment of the region from *a* to *b* in Fig. 8 as a straight line, K_{ex} and β_2' are determined from the intercept and slope of this straight line.

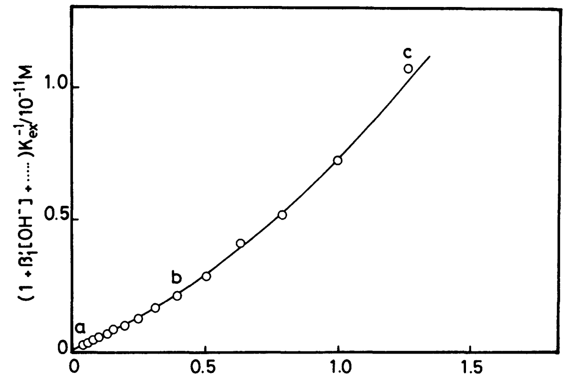

Fig. 8. Plot of values of the intercept of straight lines obtained by plot of $1/K'_{ex}$ a of $PhHg^+$ complex *vs.* $[PO_4]$ against [OH].

The formation of a 1:1 complex of methylmercury(II) with HPO_4^{2-} has been studied by Schwarzenbach *et al.*[9] and by Ingman *et al.*[10], but the formation of a complex of RHg^+ with PO_4^{3-} has not been reported previously. However, the formation constant of EtHgOH obtained here shows a good agreement with that reported previously[5] and that obtained by the study of the extraction of EtHgCl reported in this article. These results indicate that the method of analyzing a reaction presented here is reasonable. Therefore, it seems certain that RHg^+ forms complexes with both HPO_4^{2-} and PO_4^{3-}.

As has been mentioned above, $PhHg^+$ is considered to form higher complexes with OH^- in the present experimental range, but those higher hydroxo-complex-formation reactions can not be studied in detail. However, the formation constant of PhHgOH obtained here agrees well with that obtained by Waugh *et al.*⁵⁾, 1.0×10^{10}. This indicates that $PhHg^+$ forms a 1 : 1 complex with OH^- predominantly in the region from *a* to *b*, that is at pH values from 4.8 to 5.8.

References

1) J. Kuniya, N. Naito, and S. Takei, *Bull. Chem. Soc. Jpn.*, **57**, 2266 (1984).

2) E. B. Sandell, "Colorimetric Determination of Traces Metals," 2nd ed., Interscience Publishers, New York (1950), p. 107.

3) V. L. Miller, D. Polley, and C. J. Gould, *Anal.Chem.*, **23**, 1286 (1951).

4) R. B. Simpson, *J. Am. Chem. Soc.*, **83**, 4711 (1961); O. Budevsky, F. Ingman, and D. H. Liem, *Acta Chem. Scand.*, **27**, 1277 (1973) ; J. Stray and K. Kratzer, *Radiochem. Radioanal. Lett.*, **28**, 53 (1977).

5) T. D. Waugh, H. F. Walton, and J. A. Laswick, *J. Phys. Chem.*, **59**, 395 (1955).

6) A. Albert and A. Hampton, *J. Chem. Soc.*, 505 (1954); D. Dyrssen, *Svenk. Kem. Tidskr.*, **66**, 234 (1954).

7) J. Mason and I. Lipschtz, *Talanta*, **18**, 1111 (1971).

8) G. Schwarzenbach and G. Geier, *Helv. Chem. Acta*, **46**, 906 (1963).

9) G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, **48**, 28 (1950).

10) F. Ingman and D. H. Liem, *Acta Chem. Scand.*, **28**, 947 (1974).