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The Complex Formation of Organomercury with 8-Quinolinol

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Organomercury(II)(RHg^+, R; ethyl, *n*-propyl, *n*-butyl) forms two kinds of water-soluble complexes, RHgq and $RHg(q)(OH)^-$, with 8-quinolinol(oxine Hq). These complex-formation reactions are studied by means of spectrophotometry, and the formation constants of these complexes, RHgOH, RHgOAc, and $RHg(OH)(OAc)^-$, in 4 %(v/v) ethanol at the ionic strength of 0.1 are determined. Reliable results are obtained for ethylmercury(II) and *n*-propylmercury(II) complexes.

There have been several reports and patents[1] on the reactions of alkyl- and arylmercury(II) (RHg^+) with 8-quinolinol (oxine Hq) in an aqueous solution, and in those reports the reaction product has been reported to be RHgq. However, complex-formation reactions have not yet been studied in detail.

In this study, complex-formation reactions of ethyl-, *n*-propyl-, and *n*-butyl-mercury(II) ($EtHg^+$, *n*-$PrHg^+$, *n*-$BuHg^+$) with 8-quinolinol in an aqueous solution have been investigated by means of spectrophotometry, and two kinds of water-soluble complexes, one of which is extractable into a nonpolar solvent such as benzene, have been found to be formed. Generally, 8-quinolinol forms water-insoluble complexes with all metals except alkali metals, therefore, the reactions of RHg^+ with 8-quinolinol are very interesting.

Experimental

1. Reagent. *RHg^+ Solution*: To a suspension of the desired amount of RHgBr synthesized by the Grignard reaction[2] in water 1.5 times the equivalent of Ag_2O freshly prepared from $AgNO_3$ was added, after which the solution was stirred for several days by use of a magnetic stirrer. After the complete precipitaton of the AgBr, the solution was made up to 0.1 M ($1 M = 1 mol dm^{-3}$) in OH^- by the addition of solid NaOH and then left to stand overnight to ensure the quantitative precipitation of the dissolved Ag^+. Then after the filtration of the AgBr and the excess Ag_2O (to prevent the dissolution of Ag_2O the precipitate was not washed), the filtrate was neutralized with perchloric acid and diluted to about 5×10^{-2} M in RHg^+ with a pH of about 3. The standardization of the stock solution was done by the decomposition of RHg^+ on heating with nitric acid, followed by the gravimetric determination of Hg^{2+} as HgS. The stock solution was used after a 10-fold dilution with deionized water.

8-Quinolinol Solution: Guaranteed-reagent-grade 8-quinolinol was used as the ethanolic solution. This solution could not be used for over 3 d.

In this work, commercially available guaranteed-reagent-grade acetic acid, sodium acetate, and sodium perchlorate were used without further purification. The ethanol was purified by distillation as usual.

2. Aparatus. The absorption spectrum of a solution was measured with a Shimadzu MPS-50 recording spectrophotometer and a Hitachi 124 double-beam spectrophotometer. A Hitachi-Horiba F-5 pH meter was used for the pH measurement of a solution.

3. Experimental Procedure. To a 25.00-cm^3 measuring flask, desired amounts of RHg^+, acetic acid, sodium acetate, sodium perchlorate, and 8-quinolinol solutions were added, and then deionized water was added to bring the solution to the mark. The ionic strength of the solution was maintained at 0.1. Spectrophotometric and pH measurements were made on the solution after 1.5 h. Separately, the same measurements were made on the blank solution.

Results snd Discussion

By the addition of 8-quinolinol to an aqueous solution of $EtHg^+$, yellow coloration is obtained at a pH value above 5. The solution shows absorption maxima at 340 and 395 nm, and with an increase in the pH of the solution the absorbance at 340 nm decreases and that at 395 nm increases, as shown in Fig. 1. These spectra are different from that of the free 8-quinolinol solution in this pH range. Therefore, $EtHg^+$ is considered to form two kinds of complexes with 8-quinolinol, with the sbsorption maxima at 340 and 395 nm respectively. Both *n*-$PrHg^+$ and *n*-$BuHg^+$ with 8-quinolinol show the same coloration, and the wavelength at the absorption maximum is the same as that of $EtHg^+$ complexes. Hereafter, complexes with the absorption maxima at 340 and 395 nm will be denoted as Complexes **I** and **II** respectively.

In this study, 8-quinolinol is added as an ethanolic solution. Moreover, it is observed that the absorbance of each complex decreases with an increase in the concentration of ethanol, especially in the higher concentration range. Therefore, in this work the concentration of ethanol is fixed at 4% (v/v), and the effect of the concentration of ethanol on the complex formation is not studied.

The absorbance of complex solutions of RHg^+ with 8-quinolinol at 340 and 395 nm increases with stand-

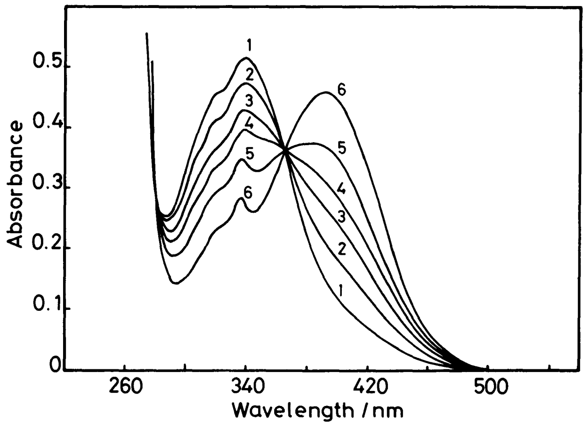

Fig. 1. pH Dependence of absorption spectrum of *n*-$PrHg^+$–8-quinolinol solution.
C_M°; 1.98×10^{-4} M, C_L°; 2.00×10^{-4} M.
pH: 1; 4.45, 2; 4.98, 3; 5.16, 4; 5.50, 5; 5.96, 6; 7.85.

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ing and shows a constant value after standing for 1.5 h when RHg^+ is added in an excess to 8-quinolinol in a molar ratio, but the absorbance of the n-$BuHg^+$ complex solution decreases upon standing for over 5 h. Therefore, the measurement of the absorbance of complex solutions is made after they have stood for 1.5 h in a dark place.

The molar ratio of RHg^+ to 8-quinolinol in Complexes **I** and **II** is found by the continuous variation method to be 1 : 1 regardless of the kind of alkyl group.

At 340 and 395 nm, Complexes **I** and **II** and free 8-quinolinol show absroption. Therefore, the concentrations of Complexes **I** and **II** formed under the various conditions necessary to obtain the formation constants of these complexes are determined from the absorbance of the complex solution measured at 340 and 395 nm and the molar absorption coefficients of both complexes and 8-quinolinol at both wavelengths (the values for 8-quinolinol are the apparent ones at various pHs). The molar absorption coefficients of both complexes at 340 and 395 nm are determined as follows.

In Fig. 2 the absorbance of the $EtHg^+$–8-quinolinol solution at 340 nm is shown to be constant at pH values from 3.2 to 4.2, while that at 395 nm begins to increase at a pH of about 4.0. Moreover, the absorbance of the solution buffered with sodium acetate and acetic acid at 340 nm is lower than that of an unbuffered sodium perchlorate and perchloric acid solution. These findings show that 8-quinolinol forms Complex **I** with $EtHg^+$ quantitatively at pH values from 3.2 to 4.0 and that the acetate ion interferes with the formation of the complex. However, the interference from OAc^- is not observed when the concentration of OAc^- is lower than 5×10^{-3} M under the present conditions. From these results the molar absorption coefficients of Complex **I** at 340 and 395 nm are determined from the absorbance at these wavelengths when the molar ratio of $EtHg^+$ to 8-quinolinol is higher than 10 and when the pH values from 3.2 to 4.0 in the buffered solution in which the concentration of OAc^- is lower than 5×10^{-3} M. The molar absorption coefficients of the n-$PrHg^+$ and n-$BuHg^+$ Complex **I** at 340 and 395 nm are determined by similar procedures.

The absorbance of the RHg^+ Complex **II** at 340 and 395 nm are found to be constant in borate buffer solutions at pH values from 8 to 10, and the molar ratio of RHg^+ to 8-quinolinol is higher than 10. Therefore, the molar absorption coefficients of each complex at both wavelengths are determined from the absorbance measured under the conditions mentioned above.

In Table 1 the molar absorption coefficients of the RHg^+ Complexes **I** and **II** at the absorption maximum are tabulated. The variation in the value of the coefficient with the kind of alkyl group is small.

From the experimental results obtained above, the complex formation reactions may be analysed as follows.

The complex formation reactions of the **I** and **II** complexes can be written as follows:

$$RHg^+ + q^- + mY^{n-} = RHg(q)(Y)_m^{mn-}, \tag{1}$$

$$K = \frac{[RHg(q)(Y)_m^{mn-}]}{[RHg^+][q][Y^{n-}]^m}, \tag{2}$$

where Y^{n-} is an arbitrary anion in the solution which can combine with RHg^+ (hereafter, the charge of an ion will be omitted for the sake of simplicity). Moreover, the total concentration of RHg^+, C_M°, is shown as follows when the polynuclear complexes of RHg^+ are considered to be absent:

$$\begin{aligned} C_M^\circ = {} & [RHg] + \sum[RHg(q)(Y)_m] + [RHgOH] \\ & + [RHg(OH)_2] + \cdots + [RHgA] \\ & + [RHg(A)_2] + \cdots + [RHg(OH)(A)] + \cdots. \end{aligned} \tag{3}$$

TABLE 1. MOLAR ABSORPTION COEFFICIENTS OF RHg^+ COMPLEXES **I** AND **II**

RHg^+	Molar absorption coefficients $cm^{-1}\,mol^{-1}\,dm^3$	
	Complex **I** (340 nm)	Complex **II** (395 nm)
$EtHg^+$	2700	2370
n-$PrHg^+$	2690	2320
n-$BuHg^+$	2730	2400

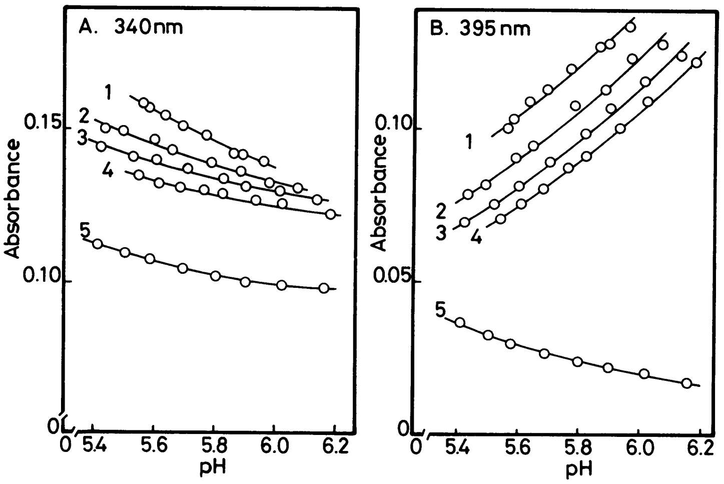

Fig. 2. pH Dependence of absorbance of $EtHg^+$–8-quinolinol complexes at 340 and 395 nm.
C_M°; 3.60×10^{-4} M, C_L°; 2.00×10^{-4} M.
[OAc]: 1; 2.00×10^{-3} M, 2; 6.00×10^{-3} M, 3; 1.00×10^{-2} M, 4; 1.40×10^{-2} M, 5; blank solution, [OAc]; 1.00×10^{-2} M.

Then:

$$C_M^\circ - \sum [RHg(q)(Y)_m] = C_M = [RHg](1+\beta_1[OH] + \beta_2[OH]^2 + \cdots + \beta_1'[A] + \beta_2'[A]^2 + \cdots + \beta_1''[OH][A] + \cdots = [RHg]\alpha, \tag{4}$$

where the β's are the formation constants of the respective complexes and where A represents the anions, except for OH^-, in the solution which can combine with RHg^+.

Similarly, the total concentration of 8-quinolinol, C_L°, can be written as follows:

$$C_L^\circ = \sum [RH(q)(Y)_m] + [H_2q] + [Hq] + [q]. \tag{5}$$

Then:

$$C_L^\circ - \sum [RHg(q)(Y)_m] = C_L = [q]\left(\frac{[H]^2}{k_1k_2} + \frac{[H]}{k_2} + 1\right) = [q]\gamma, \tag{6}$$

where k_1 and k_2 are the step-by-step acid-dissociation constants of 8-quinolinol; in this work, $pk_1=4.96$ and $pk_2=9.68$, values obtained under the present experimental conditions.

From (2), (4), and (6), (7), and (8) are introduced:

$$\frac{[RHg(q)(Y)_m]\alpha\gamma}{C_M C_L [Y]^m} = K'\frac{\alpha\gamma}{[Y]^m}, \tag{7}$$

$$K' = \frac{[RHg(q)(Y)_m]}{C_M C_L}.$$

$$\frac{[Y]^m}{K'\gamma} = \frac{\alpha}{K} = \frac{1}{K}(1+\beta_1[OH]+\beta_2[OH]^2+\cdots + \beta_1'[A] + \beta_2'[A]^2 + \cdots + \beta_1''[OH][A] + \cdots$$

$$= \frac{1}{K}(1+\beta_1[OH]+\beta_2[OH]^2+\cdots) + \frac{1}{K}(\beta_1'+\beta_1''[OH]+\cdots)[A] + \frac{\beta_2'}{K}[A]^2 + \cdots. \tag{8}$$

In (7), C_M and C_L can be obtained from the total concentrations of RHg^+ and 8-quiolinol and the experimentally determined concentrations of Complexes **I** and **II** as shown in (4) and (6). Therefore, the value of K' for each complex can be determined experimentally. Moreover, the value of γ is calculated from the pH of the solution and from k_1 and k_2 as shown in (6).

In this study, the anions in the solution are OH^-, OAc^-, and ClO_4^-, and the complex formation of RHg^+ with ClO_4^- is not observed. Judging from the results in (4) and (8) it is necesssry to consider only OAc^- as A. Therefore, (8) indicates that the $[Y]^m/K'\gamma$ values which are obtained from the experimental results at a constant pH and at various concentrations of OAc^- are linear or quardratic against [OAc] when Y and m corresponding to (1) are utilized. Moreover, as the intercepts of straight lines or quadratic curves are functions of [OH], the K and β's are determined by plotting the values of the intercepts against [OH]. Similarly, the slopes of the straight lines or the coefficients of the [OAc] of the quadratic curves are functions of [OH]; therefore, the β' and β'' constants are determined by plotting the values of the slopes or coefficients of [OAc]. By these treatments, complex-formation reactions are studied.

In the treatments described above, polynuclear complexes of RHg^+ are neglected and the K' of each complex is assumed to be independent of the concentration of RHg^+. Under the conditions where pH=5.4—6.2, $[OAc]=1.00\times10^{-2}$ M and $C_L^\circ=1.00\times10^{-4}$ M, the K' values of both Complexes, **I** and **II**, for $EtHg^+$ and n-$PrHg^+$ are found to be independent of C_M° when C_M° is 2.00×10^{-4} M or below. However, for the n-$BuHg^+$–8-quinolinol system it is necessary to maintain the total concentration of n-$BuHg^+$ at 1.3×10^{-4} M or below, even when $C_L^\circ=2.00\times10^{-4}$ M.

Figures 3 **A** and **B** show the variation in the K' values of $EtHg^+$ complexes with the pH under various concentrations of OAc^-. Both K' values decrease with

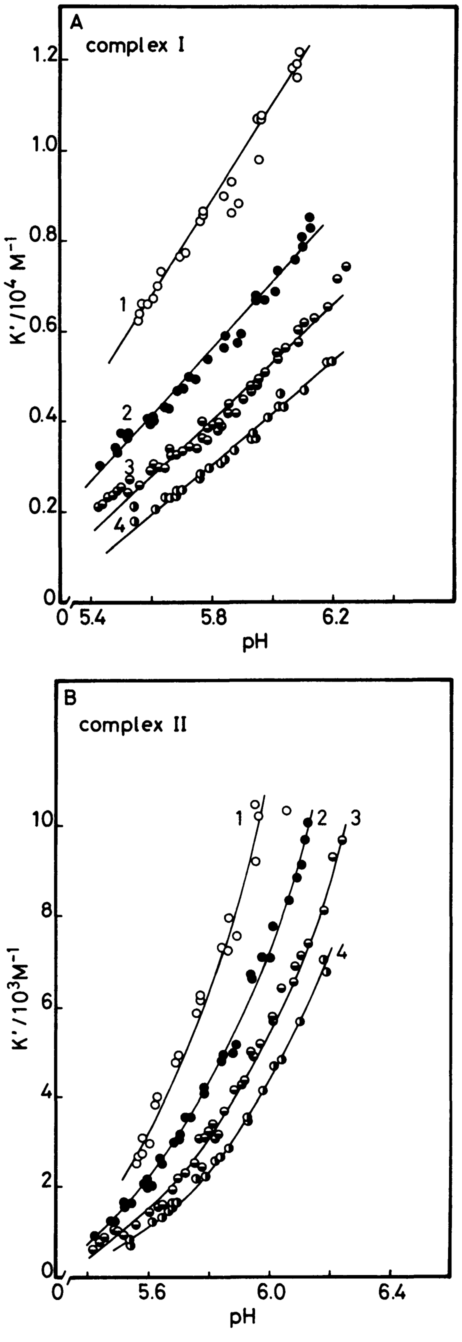

Fig. 3. pH Dependence of K' values of $EtHg^+$ complexes **I** and **II** under various concentrations of OAc^-.

[OAc]: 1; 2.00×10^{-3} M, 2; 6.00×10^{-3} M, 3; 1.00×10^{-2} M, 4; 1.40×10^{-2} M.

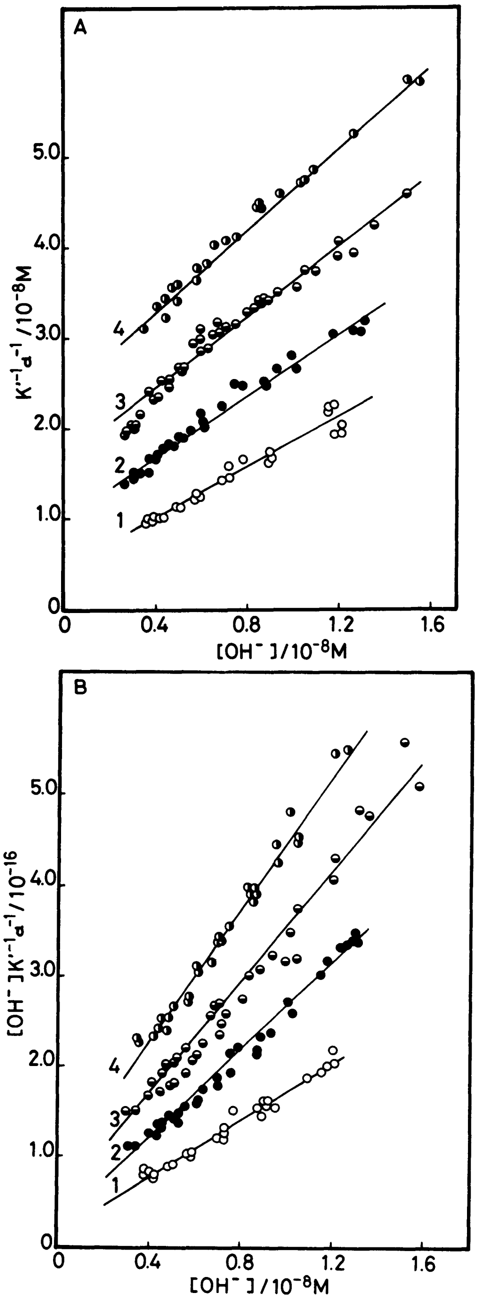

Fig. 4. **A**: Plot of $1/K'a$ of $EtHg^+$ complex **I** against [OH].
B: Plot of $[OH]/K'a$ of $EtHg^+$ complex **II** against [OH].
[OAc]: 1; 2.00×10^{-3} M, 2; 6.00×10^{-3} M, 3; 1.00×10^{-2} M, 4; 1.40×10^{-2} M.

an increase in the concentration of OAc^-; this result indicates that OAc^- interferes with the formation of complexes and that these complexes do not contain OAc^-. From this finding, OH^- is found to be Y in (1). In the following study, the K' values of each complex at various pHs are obtained by the treatment of the results shown in Fig. 3 as straight lines and quadratic curves and by interpolation. Then, from the results shown in Fig. 3, $[OH]^m/K'r$ is plotted against [OAc] by the use of the K' values of each complex and γ at various pHs; as shown in Figs. 4 **A** and **B**, straight lines are obtained for Complexes **I** and **II** when $m=0$ and 1 are utilized respectively. These results indicate that the Complexes of $EtHg^+$ **I** and **II** are EtHgq and $EtHg(q)(OH)^-$ respectively.

Moreover, the values of the intercept and slope of the straight lines shown in Figs. 4 **A** and **B** at various [OH] values are found to be linear against [OH]. The linear relations of the intercept and slope to [OH] indicate that $EtHg^+$ forms EtHgOH, EtHgOAc, and $EtHg(OH)(OAc)^-$ respectively. The formation constants of EtHgq, $EtHg(q)(OH)^-$, EtHgOH, EtHgOAc, and $EtHg(OH)(OAc)^-$ are determined from (8). Similar results are obtained for n-$PrHg^+$ and n-$BuHg^+$–8-quinolinol systems. The results obtained are tabulated in Table 2.

In Table 2, the formation constants of $EtHg^+$ and n-$PrHg^+$ complexes obtained separately by the method described above show a good agreement. Also the formation constant of EtHgOH, β_1, obtained in this work shows a good agreement with that previously reported by Waugh *et al.* These results indicate that the analytical method of complex-formation reactions presented here is reasonable and that the formation constants of $EtHg^+$ and n-$PrHg^+$ here estsblished are reliable. However, the formation constants of n-$BuHg^+$ with OH^- and OAc^- obtained separately show less agreement. Those results suggest that the formation of polynuclear complexes of n-$BuHg^+$ with OH^- affects the complex-formation reactions with 8-quinolinol. Therefore, in order to determine reliable formation constants of n-$BuHg^+$ complexes with 8-quinolinol, the OH^- and OAc^- setting of the experimental conditions is important to prevent polynuclear hydroxo complexes.

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TABLE 2. FORMATION CONSTANTS OF RHg^+ COMPLEXES

		$EtHg^+$	n-$PrHg^+$	n-$BuHg^+$
K_{RHgq}		$7.0\pm1.4\times10^8$	$5.2\pm1.0\times10^8$	$1.3\pm0.3\times10^9$
$K_{RHg(q)(OH)}$		$4.4\pm0.9\times10^{17}$	$7.5\pm1.5\times10^{16}$	$4.4\pm0.9\times10^{16}$
β_1	**A***	$8.0\pm1.6\times10^8$	$8.0\pm1.6\times10^8$	$1.4\pm0.3\times10^9$
	B**	$5.5\pm1.4\times10^9$	$2.3\pm0.6\times10^8$	$4.1\pm1.0\times10^8$
β_1'	**A***	$1.1\pm0.2\times10^3$	$6.7\pm1.3\times10^2$	$2.1\pm0.6\times10^3$
	B**	$2.0\pm0.3\times10^3$	$4.6\pm1.2\times10^2$	$7.1\pm2.0\times10^1$
β_1''	**A***	$5.3\pm1.1\times10^{10}$	$6.7\pm1.3\times10^9$	$4.3\pm1.0\times10^{10}$
	B**	$8.3\pm2.1\times10^{11}$	$5.3\pm1.3\times10^{10}$	$9.3\pm2.5\times10^{10}$

A*: Obtained from the analysis of the formation reaction of Complex **I**. **B****: Obtained from the analysis of the formation reaction of Complex **II**. Previous work: β_1 of EtHgOH. 1.3×10^9. T. Waugh, H.F. Walton, and J.A.Laswick, *J.Phys.Chem.*, **59**, 395(1955).

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