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Studies on the Hydrolysis of Methylmercury(II) and its Complex Formation with Some Aliphatic Carboxylic and Aminocarboxylic Acids

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The hydrolysis of methylmercury(II), the protonation of formic acid and acetic acid, glycine, alanine and valine (=HL) and their complex formation with methylmercury(II) ions have been studied by a potentiometric method at 25 °C and 1.0 M $(Na,H)NO_3$ ionic medium. The data were computer analyzed using the ETITR-LETAGROP program and indicate the formation of the species MeHgOH, $(MeHg)_2OH^+$ and 1:1, 1:2 and 2:1 complexes between $MeHg^+$ and the acid HL.

The following values of log K were obtained for the equilibrium reactions: $MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$, −4.686; $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$, −1.725; $MeHgOH(s) \rightleftharpoons MeHg^+ + OH^-$, −13.66 (in water); $MeHg^+ + L^- \rightleftharpoons MeHgL$, 2.681 (formic acid), 3.204 (acetic acid), 7.518 (glycine), 7.516 (α-alanine), 7.268 (DL-valine); $MeHg^+ + 2L^- \rightleftharpoons MeHgL_2^-$, 9.468 (glycine), 9.450 (α-alanine), 9.157 (DL-valine); $2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$, 5.279 (acetic acid).

Organomercurial compounds have been shown to cause hazardous environmental pollution. The harmful ecological effects of these substances and their metabolism in nature have previously been reported.[1-3] Although the use of these substances as fungicides in seed dressing has been discontinued in many countries including Sweden, because of their toxic nature, yet there is experimental evidence that inorganic and metallic mercury from the industrial waste is partially transformed into methylmercury and dimethylmercury by certain bacteriological processes.[4,5] The organic form of mercury is easily absorbed and accumulated by the living organisms and thus it may endanger the health of man and animals.

Studies on the complex formation between these compounds and the ligands that are commonly found in nature are of importance for a better understanding of their ecological behaviour. The equilibria of complex formation between methylmercury(II) and certain organic and inorganic ligands have been studied by different methods, such as ion-exchange,[6] solvent extraction,[7-10] polarography,[7] NMR,[11,12] conductance measurements[13] and potentiometry.[14-16] In our previous publications, we have reported the results of solvent extraction studies on the complex formation between methylmercury and some ligands that are commonly present in natural waters, such as chloride,[8] bromide[9] and phosphate.[10] However, only a few studies on the complex formation of methylmercury with organic ligands have been reported in the literature.[7,11]

In the present paper we report the results of the hydrolysis of methylmercury(II) and its complex formation with some model aliphatic carboxylic acids, *i.e.* formic and acetic acid and the aminocarboxylic acids glycine, alanine and valine in 1.0 M $NaNO_3$ ionic medium. These acids were chosen as model ligands, since they contain functional groups which are of analytical and biochemical interest. In preliminary experiments we also studied, in the same medium, the protonation of the acids by potentiometric titration, and the equilibrium constants evaluated by LETAGROP[17] were used in subsequent calculations where the complex formation of methylmercury(II) ions with these acids was considered.

PREVIOUS WORK

Formation of methylmercury(II) and other alkylmercury(II) hydrolysis species. Maynard and Howard[18] – as well as Johns *et al.*[19] – from conductance data of MeHgOH aqueous and ethanol solutions assumed the formation of the MeHgOH complex. Schwarzenbach and Schellenberg[15] explained their potentiometric data in 0.1 M KNO_3 medium with the formation of the species MeHgOH and $(MeHg)_2OH^+$. They were the first to report the formation of dimeric hydrolyzed species by EMF measurements of systems with varying $C_{MeHg} = 5.85 \times 10^{-4}$ to 2.19×10^{-2} M. Zanella *et al.*[16] reported the formation of only RHgOH species in 0.1 M KNO_3 for R = Me, Et, Pr and Bu. Waugh *et al.*[20] assumed the formation of RHgOH (R = Me, Et, and Ph) to explain their potentiometric titration data. Libich and Rabenstein[11] from NMR data of MeHg(II) solutions of different pH, found indications of the formation of MeHgOH and $(MeHg)_2OH^+$ species. Using NMR and Raman spectroscopy, Rabenstein *et al.*[12] reported evidence for the formation of MeHgOH and $(MeHg)_2OH^+$ species in (Na.H)ClO_4 medium. Ingman and Liem[10] explained their distribution data of MeHg(II) in the two-phase system *o*-xylene/1.0 M (Na,H)(Cl,NO_3,-PO_4) by the formation of MeHgCl in both phases and MeHgOH and $MeHgHPO_4^-$ in the aqueous phase.

Woodward *et al.*[21] studied the Raman spectra of methylmercury(II) hydroxide solution in nitrate medium and explained their data by assuming the formation of the species MeHgOH and $(MeHg)_2OH^+$ which they assigned to the bands at 577 and 511 cm^{-1}.

Formation of methylmercury(II) complexes with alkylcarboxylic acids and aminocarboxylic acids. Simpson[7] from polarographic data assumed the formation of the complex MeHgAc between methylmercury(II) and acetate ions, the species $MeHgHY^{2-}$, $MeHgY^{3-}$ and $(MeHg)_2Y^{2-}$ with EDTA (= H_4Y) and the complex MeHgSR with cysteine and glutathione (RSH) and $MeHgNH_2$(his) with histidine. Libich and Rabenstein[11] used NMR technique to study the pH dependence of the chemical shift of the methyl group of CH_3Hg(II) and that of the protons of several derivatives of alkylcarboxylic acids in aqueous solution of approximately 0.4 M ionic strength. These authors explained their experimental data assuming the formation of 1:1 complexes between methylmercury(II) and all the carboxylic acids they studied.

EXPERIMENTAL

$NaNO_3$ (*p.a.* Merck) was dried at 110 °C and used without further purification. NaOH, HNO_3 (*p.a.* Merck) stock solutions were prepared and standardized as described previously.[9] Formic acid, acetic acid (*p.a.* Merck) and glycine, alanine and DL-valine (Merck, Biopur grade) were used without further purification and assayed potentiometrically by the method described by Pehrsson and coworkers.[22] Boiled double distilled water was used to prepare all solutions.

EMF titration. The cell used for the EMF titration may be represented as follows:

Reference half cell	v ml 1.0 M Na,(OH,NO_3) / V_0 ml 1.0 M (Na,H,MeHg)(L,NO_3)	Glass electrode

where L is the ligand anion of the organic acid HL, v the volume of titrant added and V_0 the initial volume in the titration vessel. Additions of titrant were made with a pneumatically operated burette (AGA, Sweden) which can deliver any volume between 0.5 to 5.0 ml with a high degree of reproducibility.

The $[H^+]$ is measured potentiometrically using a combined glass electrode (Ingold 2293) with a built-in reference half cell of saturated KCl solution/Ag,AgCl in conjunction with a digital voltmeter (Systemteknik Type S1016H). In the Nernst relationship (1) the E'_0 and j for correction of the pH dependent parts of the liquid junction potential and the activity coefficients were determined, as a rule, before and after each titration as described elsewhere.[22] The E'_0 value found before and after each titration was constant within 0.1 mV and $j = -19$ mV/M.

$$E = E'_0 + 59.156 \log [H^+] + j[H^+] \quad (1)$$

During the experiment, the solution was protected from atmospheric CO_2 by bubbling N_2 gas that passed through "Ascarite" and 1.0 M $NaNO_3$. All experiments were carried out in a thermostated room at 25.0±0.5 °C and the titration vessel immersed in a thermostatic bath of 25±0.05 °C.

Chemical model. We assume the formation of the species $(H^+)_p(MeHg^+)_q(HL)_r$ with the equilibrium constant

$$K_{pqr} = [(H^+)_p(MeHg^+)_q(HL)_r]\text{-}[H^+]^{-p}[MeHg^+]^{-q}[HL]^{-r} \quad (2)$$

A species may thus be characterized by the set of numbers (p,q,r), *e.g.* $(MeHg)_2OH^+$ will be denoted by (−1,2,0) and MeHgL by (−1,1,1). The formation of $(MeHg)_2OH^+$ is given by (8) and that of MeHgL

by the reaction: $MeHg^+ + HL \rightleftharpoons MeHgL + H^+$; $K_{-111} = [MeHgL][H^+][MeHg^+]^{-1}[HL]^{-1}$. For the reagent components MeHg(II) and HL the following material balance equations are valid:

$$C_{MeHg} = [MeHg^+] + \Sigma q K_{pqr}[H^+]^p[MeHg^+]^q[HL]^r \quad (3)$$

$$C_L = [HL] + \Sigma r K_{pqr}[H^+]^p[MeHg^+]^q[HL]^r \quad (4)$$

$$C_H = [H^+] + \Sigma p K_{pqr}[H^+]^p[MeHg^+]^q[HL]^r \quad (5)$$

Given the values of $[H^+]$, C_{MeHg}, C_L and the set of constants K_{pqr} for the formation of the species (p,q,r), we can calculate for each point the values for $[MeHg^+]$ and $[HL]$ from (3) and (4) and $C_{H(calc)}$ from (5). In the ETITR-LETAGROP program this is calculated using the procedure BDTV.[23] In the EMF titration the following applies for the proton excess:

$$C_{H(exp)} = (C_H^* V_0 - C_{OH}^* \cdot v)/(V_0 + v) \quad (6)$$

where C_H^* = the initial molarity of acid in the titration vessel,
C_{OH}^* = the molarity of NaOH in the titrant,
V_0 = the initial volume of solution in the titration vessel,
v = the volume of titrant added.

Computer analysis of the data. The data have been computer analyzed by the ETITR-LETAGROP program. In this program for the assumed set of complexes $(H^+)_p(MeHg^+)_q(HL)_r$, the program adjusts the set of constants $K_1, K_2 \ldots K_n$ for their formation so as to minimize the error-square sum $U = \sum_1^{Np} (y_{calc} - y_{exp})^2$. Np represents the number of experimental points, y a parameter which is a function of the equilibrium constants $K_1, K_2 \ldots$ and the known experimental parameters, such as C_{MeHg}, C_L, $\log [H^+]$. In ETITR-LETAGROP with Typ = 1, we minimize the square-sum of the error $\Delta H = H_{calc} - H_{tot}$, where H_{calc} is calculated from (5) and H_{tot} from (6). The "best" model accepted, is the one which gives the least error-square sum, U_{min}, and within the limit of the experimental errors gives the simplest description of the data. Once the "best" model has been found, one can make use of the HALTAFALL program,[23] to calculate titration or distribution curves for the given reaction conditions.

RESULTS

The primary data are available on request from the authors (F.I. or D.H.L.).

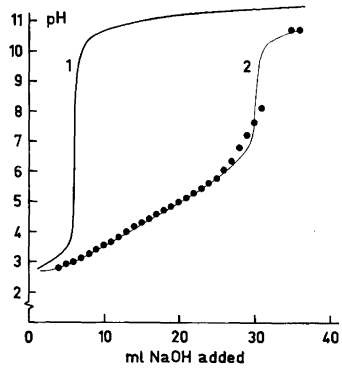

Fig. 1. Titration of 100.04 ml solution S against v ml 1.0 M $Na(OH,NO_3)$, $[OH] = 0.033294$ M. The initial composition of S is 8.002×10^{-3} M $MeHgNO_3$, 1.994×10^{-3} HNO_3, 0.990 M $NaNO_3$. The drawn curves have been calculated assuming in one case no formation of $MeHg(II) - OH^-$ species (Curve 1) and in another case the formation of MeHgOH and $(MeHg)_2OH^+$ species with the equilibrium constants given in Table 1 (Model II, Curve 2).

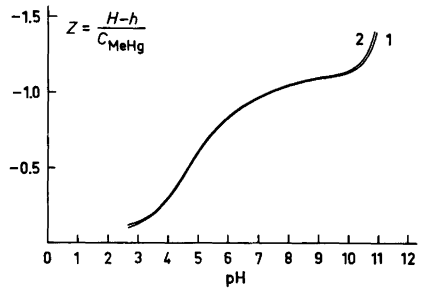

Fig. 2. Titration of 1.0 M $(H,Na,MeHg)NO_3$ against 1.0 M $Na(OH,NO_3)$ given as Z, the average number of OH bound per MeHg(II), *versus* pH. The initial concentration of $MeHgNO_3$ in the titrated solution is 8.002×10^{-3} M (Curve 1) and 4.804×10^{-3} M (Curve 2).

Formation of methylmercury(II) hydrolyzed species. EMF titration data for the hydrolysis were taken at different concentrations of methylmercury. In Fig. 1, two titration curves are shown. The curve marked 1 is a normal acid-base potentiometric titration, and the one marked 2 represents the same titration conditions, but with methylmercury(II) ions present in the solution. Comparing the two titration curves, one can clearly observe the higher buffer capacity at low pH-values of the solution containing methylmercury(II) ions, indicating the

Table 1. Equilibrium constant log K_{pq} for the formation of $(H^+)_p(MeHg^+)_q$ species in 1.0 M (Na.H)(NO_3) ionic medium at 25 ± 0.05 °C for various assumptions of chemical models which minimize the error-square sum $U = \sum_1^{89}(H_{calc} - H_{exp})^2$. The limits given correspond approximately to log $[K \pm 3\sigma(K)]$.

Model No.	Equilibrium reactions	log $(K \pm 3\sigma)$	U_{min}	σ(H)
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	-4.648 ± 0.130	29.373	0.577
II	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	-4.686 ± 0.045 -1.725 ± 0.090	2.257	0.161
III	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ $2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ $3MeHg^+ + 2H_2O \rightleftharpoons (MeHg)_3(OH)_2{}^+ + 2H^+$	-4.688 ± 0.057 -1.728 ± 0.102 -5.638 max. -4.410	2.226	0.162

formation of hydrolyzed methylmercury(II) species. In Fig. 2 the number of OH^- bound per MeHg(II), $Z = (H_{tot} - h)/C_{MeHg}$, h denoting the concentration of free hydrogen ions, is plotted as a function of *pH*. As can be seen, the Z curve levels off with increasing *pH* to a limiting value, indicating the predominant formation of the MeHgOH species. Furthermore, the Z-curves for different C_{MeHg} values (8.002×10^{-3} M and 4.801×10^{-3} M) do not fully coincide over the pH range studied, which indicates the additional formation of polynuclear methylmercury(II) hydrolyzed species. In Table 1, we summarize the results of the computer calculations for the formation of $(H^+)_p(MeHg^+)_q$ species, using $Np = 89$ points. Model No. 1, in which the formation of methylmercury(II) hydrolyzed species, MeHgOH only, is assumed, gives a large error-square sum ($U_{min} = 29.373$, $\sigma(H) = 0.577$) compared with the other models. Model No. 2, assuming the formation of MeHgOH and $(MeHg)_2OH^+$, seems to give the best description of the data with $U_{min} = 2.257$ and $\sigma(H) = 0.161$. Model No. 3, with the additional formation of $(MeHg)_3(OH)_2^+$ species, does not give a significant improvement to U or σ(H). Moreover, the standard deviation, $\sigma(K)$, found for the formation constant of $(MeHg)_3(OH)_2^+$ species is higher than the value of the constant K itself, $[\sigma(K) = 5.30K]$, thus indicating that no such species is formed under the present experimental conditions.

We may thus conclude that our data can be explained by assuming the formation of species MgHgOH and $(MeHg)_2OH^+$ with the following equilibrium constants:

$$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$$
$$\log (K \pm 3\sigma) = -4.686 \pm 0.045 \qquad (7)$$

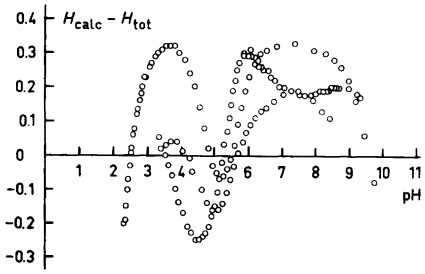

Fig. 3. The distribution of the error $(H_{calc} - H_{tot})$ in the titration of 1.0 M (H,Na,MeHg)NO_3 against 1.0 M Na(OH,NO_3) solution as a function of pH. The error $(H_{calc} - H_{tot})$ has been calculated assuming the formation of the species MeHgOH and $(MeHg)_2OH^+$ with the equilibrium constants given in Table 1 (Model II).

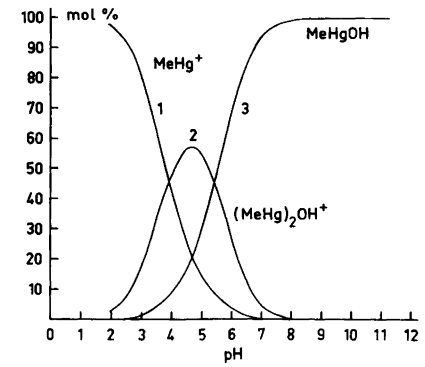

Fig. 4. The mol % of the different MeHg(II) species in 1.0 M (H,Na,MeHg)(NO_3OH) solution as a function of pH for $C_{MeHg} = 8.00 \times 10^{-3}$ M. The curves have been calculated assuming the formation of MeHgOH and $(MeHg)_2OH^+$ species with the equilibrium constants given in Table 1, Model II).

Table 2. Solubility of MeHgOH(s) in water at 25 °C.

$-\log [H^+]$	C_{MeHg^+} (mol/l)	$[MeHg^+]$ (calc. from eqn. 11)	$\log K_{so}$
8.80	0.0598	2.832×10^{-9}	−13.75
12.46	0.1142	8.562×10^{-13}	−13.61
12.69	0.1087	4.921×10^{-13}	−13.62
			$\log K_{so} \pm \sigma = -13.66 \pm 0.08$

$$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$$
$$\log (K \pm 3\sigma) = -1.725 \pm 0.090 \quad (8)$$

Assuming the ionization constant of water $K_w = [H^+][OH^-] = 10^{-13.95}$ M^2 at $I = 1.0$ (Ref. 26), the formation of these MeHg(II) species may also be described by the following equilibrium reactions:

$$MeHg^+ + OH^- \rightleftharpoons MeHgOH$$
$$\log (K \pm 3\sigma) = 9.264 \pm 0.045 \quad (9)$$

$$MeHgOH + MeHg^+ \rightleftharpoons (MeHg)_2OH^+$$
$$\log (K \pm 3\sigma) = 2.961 \pm 0.049 \quad (10)$$

In Fig. 3 the error $H_{calc} - H_{tot}$ is plotted *versus* pH for the best model assumed (*cf.* Table 1, model 2). In Fig. 4 using the HALTAFALL program[24] the distribution of the methylmercury(II) species is given as a function of pH for $C_{MeHg} = 8.002 \times 10^{-3}$ M, assuming the formation of MeHgOH and $(MeHg)_2OH^+$ with the equilibrium constants given in (7) and (8).

Solubility equilibrium of methylmercury hydroxide. The solubility of MeHgOH(s) has been studied as a function of pH and the data given in Table 2. Assuming the formation of the species MeHgOH and $(MeHg)_2OH^+$ with the constant of formation given in (7) and (8), we have the following equation for the solubility of MeHg(II):

$$C_{MeHg} = [MeHg^+] + [MeHgOH] + 2[(MeHg)_2OH] = [MeHg^+] + 10^{-4.686}[MeHg^+][H^+]^{-1} + 2 \times 10^{-1.725}[MeHg^+]^2[H^+]^{-1} \quad (11)$$

Given the values of C_{MeHg} and $[H^+]$ one can calculate $[MeHg^+]$ from (11) and hence the solubility product for MeHgOH(s). For $K_w = 10^{-14.0}$ M^2, the following value for K_{so} has been obtained:

$$MeHgOH(s) \rightleftharpoons MeHg^+ + OH^-$$
$$\log K_{so} = -13.66 \pm 0.08$$

Dissociation equilibria of the acids HL. The dissociation equilibria of the acids HL have been studied by potentiometric acid-base titration. The data have been computer analyzed using the ETITR-LETAGROP program and the results of the calculations summarized in Table 3. In Fig. 5

Table 3. Equilibrium constants $\log K_{pq}$ for the protonation of the acids, $(H^+)_p(L^-)_q$ in 1.0 M (Na,H)(NO_3,L) ionic medium at 25 ± 0.05 °C which minimize the error-square sum $U = \sum_1^{Np} (H_{calc} - H_{exp})^2$. The limits given correspond approximately to $\log [K \pm 3\sigma(K)]$.

Acid	Equilibrium reactions	$\log(K \pm 3\sigma)$	U_{min}	σ(H)	Np (number of points)
Formic acid	$H^+ + L^- \rightleftharpoons HL$	3.472 ± 0.006	0.0033	0.011	28
Acetic acid	$H^+ + L^- \rightleftharpoons HL$	4.509 ± 0.001	0.0013	0.007	29
Glycine	$H^+ + L^- \rightleftharpoons HL$	9.642 ± 0.002	0.0766	0.031	79
	$2H^+ + L^- \rightleftharpoons H_2L^+$	12.073 ± 0.009			
α-Alanine	$H^+ + L^- \rightleftharpoons HL$	9.746 ± 0.005	0.4470	0.076	80
	$2H^+ + L^- \rightleftharpoons H_2L^+$	12.161 ± 0.022			
β-Alanine	$H^+ + L^- \rightleftharpoons HL$	10.155 ± 0.003	0.1041	0.040	66
	$2H^+ + L^- \rightleftharpoons H_2L^+$	13.838 ± 0.010			
DL-Valine	$H^+ + L^- \rightleftharpoons HL$	9.565 ± 0.007	0.7011	0.095	80
	$2H^+ + L^- \rightleftharpoons H_2L^+$	11.881 ± 0.029			

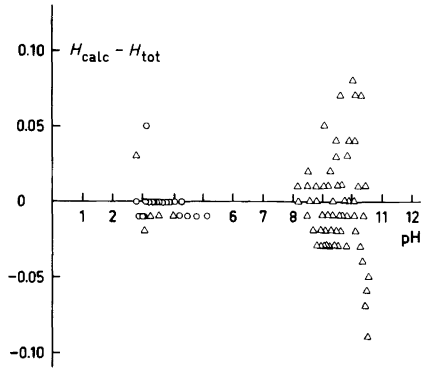

Fig. 5. The distribution of the error $(H_{calc} - H_{tot})$ *versus* pH for the titration of 1.0 M (H,Na)(L,NO_3) against 1.0 M Na(OH,NO_3) solution, where L = formate (□) and L = acetate (△). The error $(H_{calc} - H_{tot})$ has been calculated assuming the formation of HL with the equilibrium constants given in Table 3.

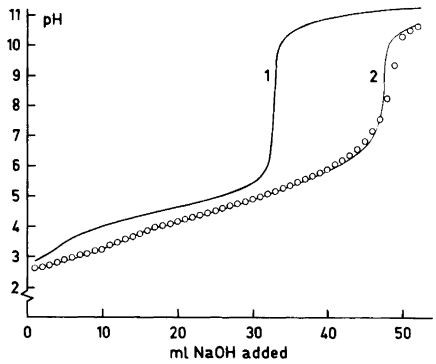

Fig. 6. Titration of 80.03 ml of solution S against v ml 1.0 M Na(OH,NO_3), [OH] = 0.0333 M, given as pH *versus* v. The initial composition of S is 6.007×10^{-3} M $MeHgNO_3$, 1.50×10^{-3} M HNO_3, 1.214×10^{-2} M HAc and 0.9804 M $NaNO_3$. Curve 1 has been calculated assuming the formation of only MeHgOH and $(MeHg)_2OH^+$ species, whereas in case of Curve 2 we assume the additional formation of the species MeHgAc and $(MeHg)_2Ac^+$ with the equilibrium constants given in Table 4 (Model IV for HAc).

the error $H_{calc} - H_{tot}$ is shown as a function of pH, assuming the set of constants which minimize the error-square sum $U = \sum_1^{Np} (H_{calc} - H_{tot})^2$. The dissociation equilibria of the different acids in 1 M (Na,H)NO_3 medium may thus be described by the reactions given in Table 5.

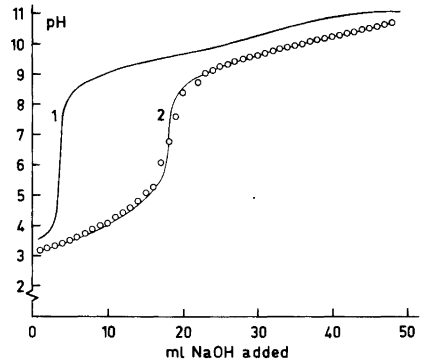

Fig. 7. Titration of 80.03 ml of solution S against v ml 1.0 M Na(OH,NO_3), [OH] = 0.0333 M. Solution S has the initial composition: 6.007×10^{-3} M $MeHgNO_3$, 1.500×10^{-3} M HNO_3, 1.247×10^{-2} M glycine, 0.9800 M $NaNO_3$. Curve 1 has been calculated assuming the formation of MeHgOH and $(MeHg)_2OH^+$ species only, while in Curve 2, we also assume the additional formation of the species MeHgGly and $MeHg(Gly)_2^-$ with the equilibrium constants given in Table 4 (Model III for glycine).

Formation of methylmercury(II) complexes with the acids HL. In Figs. 6 and 7, a part of the titration data for acetic acid and glycine, respectively, have been plotted as calculated titration curves where the curve 1, as before, depicts a normal acid-base titration. The curves marked 2 in both figures, represent the case where the titration is made in the presence of methylmercury(II) ions. These curves have been calculated taking into account the protolysis of the acids given in Table 3, and the equilibrium constants of complex formation between methylmercury and these acids given in Table 5. The experimental points from the actual titration fall essentially on curve 2, thus supporting the assumptions made in the computer analysis of the data. The results of these analyses are summarized in Table 4. In these analyses, the formation of MeHgOH and $(MeHg)_2OH^+$ species and the protolysis of the acids were taken into account and their equilibrium constants found previously were kept constant during the computer calculations. The results of these calculations indicate that formic acid forms 1:1, and acetic acid 1:1 and 2:1, whereas all the aminocarboxylic acids that is, glycine, α-alanine and DL-valine, predominantly form 1:1 and 1:2 complexes with methylmercuric ion.

Table 4. The equilibrium constant log K_{pqr} for the formation of $(H)_p(MeHg)_q(HL)_r$ species in 1.0 M (Na,H)(NO_3,L) ionic medium at 25 ± 0.05 °C for various assumptions of chemical models which minimize the error-square sums $U=\sum_1^{Np}(H_{calc}-H_{exp})^2$. The limits given correspond approximately to $\log[K\pm3\sigma(K)]$. The equilibrium constants for the hydrolysis of MeHg(II) were not varied except in model I in each case. The values of the hydrolysis constants are those given in Table 1 (Model II).

Model	Equilibrium reactions	$\log(K\pm3\sigma)$	U_{min}	σ(H)
Formic acid; $Np=60$				
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−4.793 max. −4.548	20.741	0.627
	$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−0.850 max. −0.143		
II[a]	$MeHg^+ + L^- \rightleftharpoons MeHgL$	2.681±0.066	0.863	0.121
III	$MeHg^+ + L^- \rightleftharpoons MeHgL$	2.718±0.039	0.795	0.117
	$MeHg^+ + 2L^- \rightleftharpoons MeHgL_2^-$	3.973 max. 4.350		
IV	$MeHg^+ + L^- \rightleftharpoons MeHgL$	2.718±0.040	0.863	0.122
	$2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$	$K=0$		
Acetic acid; $Np=90$				
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−4.685±0.146	15.967	0.428
	$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−0.745±0.131		
II	$MeHg^+ + L^- \rightleftharpoons MeHgL$	3.231±0.045	2.072	0.152
III	$MeHg^+ + L^- \rightleftharpoons MeHgL$	3.229±0.046	2.072	0.152
	$MeHg^+ + 2L^- \rightleftharpoons MeHgL^-$	$K=0$		
IV[a]	$MeHg^+ + L^- \rightleftharpoons MeHgL$	3.204±0.044	1.453	0.128
	$2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$	5.279±0.256		
Glycine; $Np=91$				
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−4.102 max. −3.883	50.543	0.754
	$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−1.277 max. −0.870		
II	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.514±0.061	3.713	0.203
III[a]	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.518±0.050	2.316	0.161
	$MeHg^+ + 2L^- \rightleftharpoons MeHgL_2^-$	9.468±0.225		
IV	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.509±0.057	3.046	0.185
	$2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$	9.958 max. 10.231		
α-Alanine; $Np=75$				
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−4.194 max 3.979	46.686	0.708
	$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−1.377 max. −0.973		
II	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.514±0.064	3.036	0.202
III[a]	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.516±0.052	2.471	0.163
	$MeHg^+ + 2L^- \rightleftharpoons MeHgL_2^-$	9.450±0.227		
IV	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.524±0.058	3.302	0.188
	$2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$	9.952 max. 10.248		
β-Alanine; $Np=95$				
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−5.027±0.105	6.459	0.264
	$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−2.049±0.263		
II	$MeHg^+ + L^- \rightleftharpoons MeHgL$	$K=0$	12.779	0.367
III	$MeHg^+ + L^- \rightleftharpoons MeHgL$	$K=0$		
	$MeHg^+ + 2L^- \rightleftharpoons MeHgL_2^-$	$K=0$	12.970	0.367
IV	$MeHg^+ + L^- \rightleftharpoons MeHgL$	$K=0$		
	$2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$	$K=0$	12.958	0.367
DL-Valine; $Np=95$				
I	$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$	−4.284 max. −4.078	44.050	0.688
	$2MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$	−1.561 max. −1.156		
II	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.514±0.064	3.885	0.203
III[a]	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.268±0.056	2.821	0.174
	$MeHg^+ + 2L^- \rightleftharpoons MeHgL_2^-$	9.157±0.259		
IV	$MeHg^+ + L^- \rightleftharpoons MeHgL$	7.280±0.063	3.834	0.203
	$2MeHg^+ + L^- \rightleftharpoons (MeHg)_2L^+$	9.191 max. 9.967		

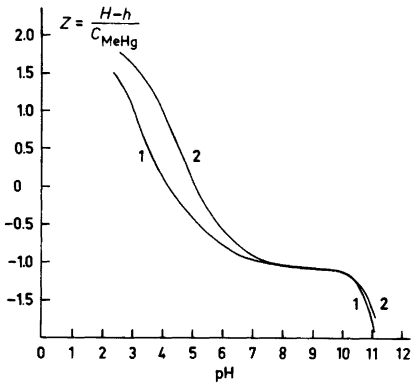

Fig. 8. Titration of 1.0 M (H,Na,MeHg)(L,NO_3) against 1.0 M Na(OH,NO_3) given as Z, the average number of OH bound per MeHg(II), *versus* pH. Curve 1 applies for L = formate, initial total concentrations $C_{MeHg} = 6.007 \times 10^{-3}$ M, $C_{HL} = 1.190 \times 10^{-2}$ M and $C_{HNO_3} = 1.52 \times 10^{-3}$ M. Curve 2 applies for L = acetate with initial total concentrations $C_{MeHg} = 6.007 \times 10^{-3}$ M, $C_{HL} = 1.214 \times 10^{-2}$ M and $C_{HNO_3} = 1.500 \times 10^{-3}$ M.

This conclusion is based on the choice of different models tried taking into account the most probable equilibrium reactions that may take place in the solution under the present experimental conditions (see Table 4). In Fig. 8, the typical formation curves

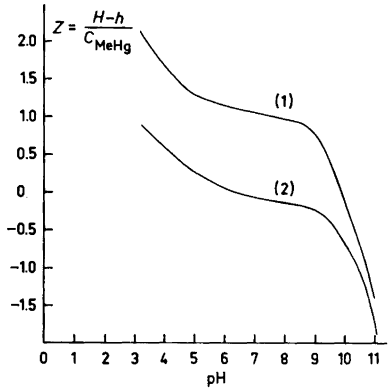

Fig. 9. Titration of 1.0 M (H,Na,MeHg)(Gly,NO_3) against 1.0 M Na(OH,NO_3) given as Z, average number of OH per MeHg(II), *versus* pH. Curve 1 applies for a solution with initial total concentrations $C_{MeHg} = 6.007 \times 10^{-3}$ M, $C_{HNO_3} = 1.490 \times 10^{-3}$ M and $C_{HGly} = 1.248 \times 10^{-2}$ M, whereas for Curve 2 $C_{MeHg} = 3.202 \times 10^{-3}$ M, $C_{HNO_3} = 3.795 \times 10^{-3}$ M and $C_{HGly} = 2.997 \times 10^{-3}$ M.

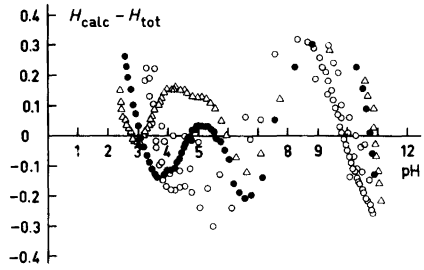

Fig. 10. The distribution of the error ($H_{calc} - H_{tot}$) in the titration of 1.0 M (H,Na,MeHg)(L,NO_3) *versus* 1.0 M Na(OH,NO_3) as a function of pH, where L = formate (△), acetate (●) and glycinate (○). The error ($H_{calc} - H_{tot}$) has been calculated assuming the formation of the MeHg(II) − HL species with the equilibrium constants given in Table 4 (Model II for formic acid; Model IV for acetic acid; Model III for glycine).

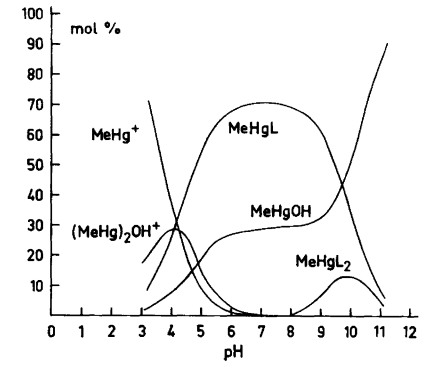

Fig. 11. The distribution of the species $(H)_p(MeHg)_q(HGly)_r$ as a function of pH. The curves have been calculated using the HALTAFALL program [24] assuming the formation of the MeHg(II) species with the equilibrium constants given in Table 4, Model III for glycine. The initial total constants given in Table 4, Model III for glycine. The initial total concentrations of $C_{MeHg} = 6.007 \times 10^{-3}$ M and $C_{HGly} = 1.247 \times 10^{-2}$ M were assumed.

for methylmercury-formate and methylmercury-acetate complexes are plotted showing $Z = (H_{tot} - h)/C_{MeHg}$ as a function of pH. Similar curves are shown in Fig. 9 for the complex formation of methylmercury with one of the amino acids, that is glycine; at two different concentrations of the acid with respect to methylmercury. The distribution of error, $H_{calc} - H_{tot}$ as a function of pH, for the accepted model assuming the formation of the

Table 5. Equilibrium constants for the formation of $(H)_p(MeHg)_q(HL)_r$ complexes in various systems.

$\log K_{MeHgOH}$	$\log K_{(MeHg)_2OH^+}$		Ref.
Hydrolysis			
-4.59^a	-2.53^a		14, 15
-4.78^a			16
-4.70^b	-2.33^b		11
-4.40 ± 0.07^c			10
-4.686 ± 0.045^d	-1.725 ± 0.090^d		This work
$\log K_{MeHgL}$	$\log K_{MeHgL_2^-}$	$\log K_{(MeHg)_2L^+}$	
Formic acid			
2.681 ± 0.066^d			This work
2.67^b			11
Acetic acid			
3.192 ± 0.034^d		5.223 ± 0.257	This work
3.18^b			11
3.55 ± 0.03^e			13
$\sim3.6^e$			7
Glycine			
7.518 ± 0.050^d	9.468 ± 0.225^d		This work
α-Alanine			
7.516 ± 0.05^{2d}	9.450 ± 0.227^d		This work
β-Alanine			
$K=0$	$K=0$	$K=0$	This work
DL-Valine			
7.268 ± 0.056^d	9.157 ± 0.259^d		This work

[a] 0.1 M $(K,H)NO_3$. [b] Aqueous. [c] 1.0 M $(Na,H)(NO_3,Cl,PO_4)$. [d] 1.0 M $(Na,H)NO_3$. [e] Undefined.

species $(H)_p(MeHg)_q(HL)_r$ with the equilibrium constants given in Table 5, is shown in Fig. 10. The error is rather small and is almost uniformly distributed over the whole pH range. In Fig. 11, the equilibrium distribution of methylmercury(II) complexes with glycine at $C_{MeHg} = 6.007\times10^{-3}$ M and $C_{HL} = 1.247\times10^{-2}$ M, is given as a function of pH. In Table 5, the available results on the hydrolysis of methylmercury(II) and its complex formation with some carboxylic and aminocarboxylic acid are summarized.

DISCUSSION

Our results show that the predominant methylmercury(II) hydrolyzed species formed are MeHgOH and $(MeHg)_2OH^+$. This supports the results reported by other authors that are summarized in Table 5.

The structure of $(MeHg)_2OH^+$ may be expected to be similar to that of Hg(II) hydrolyzed species, as given by Johansson.[25] From the liquid X-ray diffraction studies, Johansson has reported that the structure of polynuclear complexes of hydrolyzed Hg(II) is expected to contain predominantly the linear building elements O–Hg–O, where the oxygen atoms from both OH^- and H_2O may contribute to the bonding. The only possible structure for a dinuclear $Hg_2OH(H_2O)_2^{3+}$ complex was concluded to consist of two linear O–Hg–O groups, having an oxygen in common. The author found from scattering data distances of 3.64 Å for Hg–Hg and 2.10 Å for Hg–O. This will give an angle of ~120° for HgOHg. The stability constants of the 1:1 complexes of methylmercury(II) with formate and acetate ions are in good agreement with those reported by Libich and Rabenstein[11] from NMR studies. Simpson[7] has also studied the com-

plex formation of methylmercury(II) with acetate-ions polarographically. However, the present results show that the value of the stability constant, log $K = 3.6$ that he has reported is definitely too high. The formation of a 1:2 acetate complex with methylmercury(II) is rather surprising from structural considerations, especially under the present experimental conditions where even a two-fold excess of acetate with respect to methylmercury(II) has been used. The calculations indicate that it is present in very small amounts compared with the 1:1 complex. Further studies, such as NMR or infrared spectroscopy, are therefore required to verify the existence of such a species.

The complexing ability of α-aminocarboxylic acids with methylmercury(II) is considerably higher than that of simple carboxylic acids. This is not unexpected, because with a chelating agent like $NH_2CH_2COO^-$, both metal – nitrogen and metal – oxygen bonds are involved in the complexation.

Our experiments with β-alanine indicate that it does not seem to form any complex with methylmercury(II) although its complexes with most of the metals including Hg(II) are known.[26] In the computer calculations, the stability constant of its complex formation with methylmercury(II) is invariably reduced to zero (*cf.* Table 4) meaning that no detectable complexation takes place under the present experimental conditions. This may be explained considering the steric effects partly due to the β-position of the amino group and partly due to the presence of a methyl group on Hg(II).

Several investigators,[11,27,28] have reported that approximate linear relationships exist between the

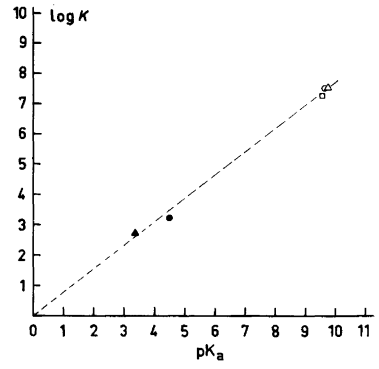

Fig. 12. The formation constant K for MeHgL as a function of the acid constant K_a of HL, for formic acid (▲), acetic acid (□), glycine (□), α-alanine (△) and DL-valine (○).

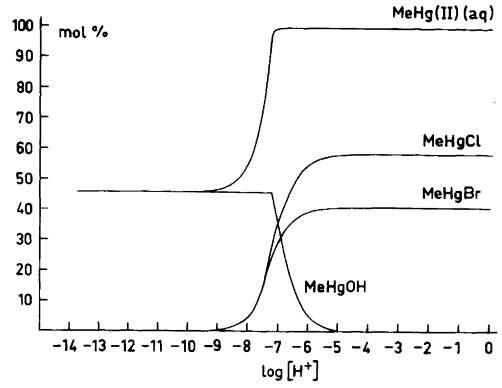

Fig. 13. The distribution of MeHg(II) species as a function of $\log[H^+]$ for initial total concentrations $C_{MeHg} = 1.00 \times 10^{-4}$ M, $C_{Cl} = 1.00 \times 10^{-3}$ M, $C_{Br} = 1.00 \times 10^{-4}$ M and $C_{NO_3} = 1.00$ M. The curves have been calculated using the HALTAFALL program,[24] assuming the formation of MeHgCl(aq), MeHgCl(s), MeHgOH(aq), MeHgOH(s), $(MeHg)_2OH^+$(aq), MeHgBr(aq), MeHgBr(s) and $MeHgBr_2^-$(aq) with equilibrium constants given in the present work and in others.[9]

stability constants of first 1:1 metal-ligand complex and the corresponding proton-ligand complex, formed by a given metal with a series of closely-related ligands. Such a relationship is important and can provide a basis for predicting the stability constants of other complexes in the series, if the stability constant of a closely related complex has been measured. The theoretical background and the conditions under which such a relationship holds, as well as its analytical significance, have been discussed by Irving and Rossotti.[29] A similar relationship has been found to exist between the pK_a values of the acids that we have studied and the stability constants of their corresponding complexes with methylmercury(II) ions (Fig. 12). In Fig. 13 we use the HALTAFALL program to simulate the equilibria of a lake that has been contaminated with methylmercury(II). The calculations are based on the formation of $(H^+)_p(MeHg^+)_q(Br^-)_r(Cl^-)_s$ species with equilibrium constants determined in the present and previous works. Moreover, the formation of solid phases of MeHgCl(s), MeHgBr(s) and MeHgOH(s) has also been considered in these calculations. This indicates that the equilibrium analysis may contribute to a better understanding of our ecological problems.

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