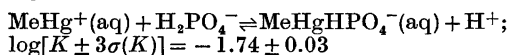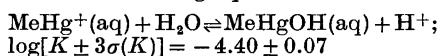# Solvent Extraction Studies on the Hydrolysis and Complex Formation of Methylmercury(II) with Phosphate Ions

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The hydrolysis of methylmercury(II) (MeHg$^+$) and its complex formation with phosphate ions have been studied by measuring the distribution of MeHg(II) in the two-phase system o-xylene/1.0 M (Na,H)(Cl,NO$_3$,PO$_4$) as a function of phosphate concentration and [H$^+$] for different constant values of chloride concentration. The distribution of MeHg(II) between the two phases has been measured by a radiometric method using MeHg(II) labelled with Hg-203 and also by the use of a spectrophotometric titration method. Graphical and computer analysis of the distribution data using the Letagrop-Distr program indicates the formation of the complexes MeHgOH(aq) and MeHgHPO$_4^-$(aq) with the following equilibrium constants:

MeHg$^+$(aq) + H$_2$O $\rightleftharpoons$ MeHgOH(aq) + H$^+$;
log[$K \pm 3\sigma(K)$] = -4.40 ± 0.07

MeHg$^+$(aq) + H$_2$PO$_4^-$ $\rightleftharpoons$ MeHgHPO$_4^-$(aq) + H$^+$;
log[$K \pm 3\sigma(K)$] = -1.74 ± 0.03

The only species in the organic phase is MeHgCl whose distribution coefficient and stability constant in the two-phase system 1 M (Na,H)(ClO$_4$,Cl)/o-xylene have been determined previously. The results are discussed in the light of studies by other authors.

The polluting effects of organomercurials in the environment which have been shown to endanger the health of man and animals [1] have focussed interest on studies of, among other things, the solution chemistry of organomercury(II) ions and, in particular, their complex formation with the inorganic ligands that are commonly found in natural waters, e.g. Cl$^-$ or SH$^-$ ions. Many studies have been reported on the ecological effects of organomercurials as well as on their metabolism in nature.[2,3] A

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search in the chemical literature, however, showed that only few studies have been published on the complex chemistry of organomercurial compounds in aqueous solution.[4-14]

In a previous work [13] we studied the complex formation between methylmercury(II) and chloride ions in the two-phase system o-xylene/1 M (Na,H)(ClO$_4$,Cl) using radiometric and spectrophotometric titration methods. The use of these experimental techniques has the advantage of enabling us to make detailed studies of the complex chemistry of methylmercury(II) ions at tracer levels of metal concentrations as often found in natural waters. In the present work we report the results of studies on the hydrolysis of CH$_3$Hg(II) and its complex formation with phosphate ions from studies of the distribution of CH$_3$Hg(II) in the two-phase system o-xylene/1.0 M (Na,H)(NO$_3$,Cl,PO$_4$). Preliminary results from this work have been reported elsewhere.[15]

Studies of the complex chemistry of organomercuric ions with several ligands have been reported previously. Maynard and Howard [9] as well as Johns et al.[10] found results of conductance measurements of MeHgOH and MeHgNO$_3$ in aqueous and ethanol solution to be consistent with the formation of the hydrolyzed species MeHgOH. Schwarzenbach and Schellenberg [4-6] studied the hydrolysis of CH$_3$Hg$^+$ and its complex formation with a series of organic and inorganic ligands. From their potentiometric data they demonstrated among other things the formation in 0.1 M KNO$_3$ medium of the hydrolysed species CH$_3$HgOH, (CH$_3$Hg)$_2$OH$^+$ and the complex CH$_3$HgHPO$_4^-$. Zanella et al.,[8] however, using potentiometric methods found only the formation of the hydrolysed species RHgOH

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(R = Me, Et, Pr, and Bu) in 0.1 M KNO$_3$. Waugh *et al.*[7] *a priori* assumed the formation of RHgOH (R = Me, Et, and Ph) and determined its formation constant by potentiometric titration of RHgOH aqueous solution with HNO$_3$ and HClO$_4$ solutions. The hydrolysis of methylmercuric ions was studied by Schwarzenbach and Schellenberg [4-6] at pH = 3.16 − 6.66 and a total concentration of methylmercury, $C_{MeHg} = 1.17 \times 10^{-2} − 5.85 \times 10^{-4}$ M and by Zanella *et al.*[8] at a range of pH and metal concentrations which are not clearly specified. Libich and Rabenstein [14] reported the formation of MeHgOH and (MeHg)$_2$OH$^+$ from studies of the *pH*-dependence of the chemical shift of the methyl protons of methylmercury in an aqueous solution containing 0.190 M MeHg(II). These authors, however, made no use of an ionic medium to control the activity factor of the species studied. The formation of a CH$_3$HgHPO$_4^-$ complex was found by Schwarzenbach and Schellenberg [4-6] from potentiometric data for a constant value of $C_{PO_4} = 1.055$ mM, $C_{MeHg} = 1.99 − 0.995$ mM and pH = 3.76 − 7.54. In the present work we have extended the concentration ranges studied ($C_{MeHg} = 4.15 \times 10^{-5} − 5.35 \times 10^{-4}$ M; $C_{PO_4} = 0 − 0.333$ M and pH = 1.26 − 9.27) in order to investigate the formation of other methylmercuric complexes. The use of the Letagrop computer program in the analysis of the data enabled us to find effectively the chemical model which gives the best fit to the experimental data.

SYMBOLS AND EQUILIBRIUM CONSTANTS

[ ]   = equilibrium concentration in the aqueous phase.

[ ]$_{org}$ = equilibrium concentration in the organic phase.

C_{Cl} = initial total concentration of chloride ion in the system referred to the aqueous phase, *i.e.* $\sum n_{Cl}/V_{aq}$, where $\sum n_{Cl}$ represents the total number of moles of Cl(−I) in the two-phase system, and V_{aq} the volume of the aqueous phase.

C_{MeHg} = initial total concentration of methylmercury(II) ion in the organic phase.

C_{PO_4} = initial total concentration of phosphate ion in the aqueous phase.

K_{pqrs}^{org} = formation constant of the complex (H$^+$)$_p$(MeHg$^+$)$_q$(Cl$^-$)$_r$(H$_2$PO$_4^-$)$_s$ in the organic phase, *cf.* (2).

K_{klmn}^{aq} = formation constant of the complex (H$^+$)$_k$(MeHg$^+$)$_l$(Cl$^-$)$_m$(H$_2$PO$_4^-$)$_n$ in the aqueous phase, *cf.* (1).

MeHg   = CH$_3$Hg, methylmercury(II).

I_{aq}, I_{org} = γ-activity of Me^{203}Hg in the aqueous and organic phases given in cpm for equal volumes of samples.

C_{aq}, C_{org} = total concentration of MeHg(II) in the equilibrated aqueous and organic phases.

D = $\sum[\text{MeHg}]_{org}/\sum[\text{MeHg}] = I_{org}/I_{aq}$ ($= C_{org}/C_{aq}$), net distribution ratio of methylmercury.

EXPERIMENTAL

Reagents. NaNO$_3$ (*p.a.* Merck-Darmstadt) was dried at 120 °C and used without further purification. Na$_2$HPO$_4$.12H$_2$O (*p.a.* Merck-Darmstadt) was recrystallized from water, air-dried and stored over silica gel. A disodium hydrogenphosphate stock solution was made from the recrystallized phosphate and the concentration of P(V) analyzed by a titrimetric method. H$_3$PO$_4$, HNO$_3$ (*p.a.* Merck) were used without further purification. NaOH solution was prepared as described in Ref. 16. o-*Xylene, chloroform, dithizone, non-radioactive CH$_3$HgOH solution* were of the same quality and were purified as described previously.[13] *Radioactive CH$_3^{203}$Hg-(II)* was purchased in the form of (CH$_3^{203}$Hg)$_2$O (Radiochemical Centre, Amersham, England) and as CH$_3^{203}$HgNO$_3$ aqueous solution (Swedish Atomic Energy, Studsvik). The CH$_3^{203}$Hg(II) was purified as described previously [13] except that instead of benzene, o-xylene was used to extract the purified CH$_3^{203}$HgCl. For the distribution experiments a stock solution of 8.2×10^{-6} M CH$_3^{203}$HgCl in o-xylene was used.

Measurement of hydrogen ions concentration. The [H$^+$] in the aqueous phase (for log [H$^+$] < −2) was determined with a Wilhelm-type salt bridge arrangement:
RE|1.0 M NaNO$_3$|equilibrated sample solution|GE
where RE = Ag,AgCl/1.0 M AgClO$_4$ and GE = glass electrode. A Beckman glass electrode type 40498 was used in conjunction with a Radiometer pHM4c valve potentiometer. The glass electrode was standardized with a 1.0 M (Na,H)NO$_3$ buffer solution with −log[H$^+$] = 2.000. For a 1.0 M (Na,H)NO$_3$ aqueous solution and −log [H$^+$] $\geq$ 2 the error in the measured value of pH caused by neglecting the liquid junction potential is expected to be less than 0.002 pH unit.[17]

Ionic strength and acidity constants. In the distribution experiment the aqueous solutions were adjusted such as to give a calculated constant ionic strength $I = \sum \frac{1}{2} c_i z_i^2 = 1.0$ M. The following values for the acidity constants for phosphoric acid H_3PO_4 were assumed:[18-22] $K_{a1} = [H_2PO_4^-][H^+][H_3PO_4]^{-1} = 1.99 \times 10^{-2}$ M, $K_{a2} = [HPO_4^{2-}][H^+][H_2PO_4^-]^{-1} = 3.314 \times 10^{-7}$ M, $K_{a3} = [PO_4^{3-}][H^+][HPO_4^{2-}]^{-1} = 7.936 \times 10^{-12}$ M. All experiments were carried out in thermostated rooms at 25 ± 0.3 °C according to procedures described previously.[13]

Basic assumptions for the chemical model. We assume that the chemical species of interest in the system may be represented by the general formula: $(H^+)_k(MeHg^+)_l(Cl^-)_m(H_2PO_4^-)_n(aq)$ in the aqueous phase and $(H^+)_p(MeHg^+)_q(Cl^-)_r(H_2PO_4^-)_s(org)$ in the organic phase. Complex formation with other ionic species, *e.g.* NO_3^- or Na^+, and molecules, *e.g.* H_2O or *o*-xylene, in the medium has been disregarded. Using this notation we may for example describe the species MeHgCl(org) and MeHgOH(aq) as the $(0,1,1,0)$(org) and $(-1,1,0,0)$(aq) species. The constant for the formation of the species will be given by the expressions:

$$K_{klmn}^{aq} = [(H^+)_k(MeHg^+)_l(Cl^-)_m(H_2PO_4^-)_n] \times [H^+]^{-k}[MeHg^+]^{-l}[Cl^-]^{-m}[H_2PO_4^-]^{-n} \quad (1)$$

and

$$K_{pqrs}^{org} = [(H^+)_p(MeHg^+)_q(Cl^-)_r(H_2PO_4^-)_s]_{org} \times [H^+]^{-p}[MeHg^+]^{-q}[Cl^-]^{-r}[H_2PO_4^-]^{-s} \quad (2)$$

The distribution ratio for MeHg(II) between the organic and aqueous phases may be expressed by the following equation:

$$D_{calc} = \frac{\sum q[(H^+)_p(MeHg^+)_q(Cl^-)_r(H_2PO_4^-)_s]_{org}}{\sum l[(H^+)_k(MeHg^+)_l(Cl^-)_m(H_2PO_4^-)_n]} =$$

$$\frac{\sum q K_{pqrs}^{org}[H^+]^{-p}[MeHg^+]^{-q}[Cl^-]^{-r}[H_2PO_4^-]^{-s}}{\sum l K_{klmn}^{aq}[H^+]^{-k}[MeHg^+]^{-l}[Cl^-]^{-m}[H_2PO_4^-]^{-n}} \quad (3)$$

A chemical model may be assumed for the system by giving values to the sets of numbers (p,q,r,s) and (k,l,m,n). Given the values of K_{pqrs}^{org}, K_{klmn}^{aq} for the formation of the species (p,q,r,s)(org) and (k,l,m,n)(aq), the total concentration C_{MeHg}, C_{Cl}, C_{PO_4}, and $[H^+]$ for each point, we may easily calculate $[MeHg^+]$, $[Cl^-]$, $[H_2PO_4^-]$ from the mass-balances for MeHg(II), Cl($-$I) and P(V). Knowing the values of the equilibrium concentration for the component species D_{calc} may be calculated using eqn. (3). In the Letagrop-Distr [23-27] program the calculation of D_{calc} is done using the BDTV prodecure.[26] In the chemical models assumed here we make the basic assumption that only uncharged MeHg(II) species are extracted into the organic phase.

Analysis of the data. The distribution data given as log $[H^+]$, $C_{MeHg(II)}$, C_{Cl}, C_{PO_4} and

I_{aq}, I_{org}, (or C_{aq}, C_{org}), after preliminary graphical analysis, were analyzed using the computer program Letagrop-Distr.[23-27] Using a given chemical model for the system the program calculates the "best" set of values for the constants K_{pqrs}^{org} and K_{klmn}^{aq} for the formation of the species (p,q,r,s)(org) and (k,l,m,n)(aq). In principle this is done by minimizing the error-square sum $U = \sum_{1}^{Np} w(\log D_{calc} - \log D_{exp})^2$, where Np represents the number of experimental points and w the weight factor for each point. In this work we have tried to adjust the experimental conditions so that the weight factor w may be assumed to be practically equal for all points. This assumption was found to be justifiable, as will be illustrated in a latter part of this work, since for a given chemical model and minimizing the error-square sum of other types of errors, such as $U = \sum (D_{exp} D_{calc}^{-1} - 1)^2$ or $U = \sum (D_{calc} D_{exp}^{-1} - 1)^2$, which implies the assignment of somewhat different weight factor to the experimental points, it was found to give essentially the same values for the formation constants of the species assumed. In this work the weight factor has arbitrarily been given the value $w = 1$.

RESULTS

Conclusions from graphical analysis of the data. The primary distribution data in Table 1 are given as log D_{exp}, $-$log $[H^+]$ and initial total concentrations of phosphate ion, C_{PO_4}, for constant $C_{Cl} = 1.27 \times 10^{-3}$ M and constant values of $C_{MeHg(II)} = 4.15 \times 10^{-5}$, 1.816×10^{-4}, and 5.349×10^{-4} M. In Fig. 1 we plot log D as a function of log $[H_2PO_4^-]$ for some selected experimental points which have approximately constant values of $-$log $[H^+] \approx 5.14$, 5.31, 6.33, 6.81, 6.93, 7.1, 9.26. The values of $[H_2PO_4^-]$ for the experimental points given in Fig. 1 and Fig. 2 have been calculated assuming the formation of species with the equilibrium constants given in Table 2, model No. 14. However, since in the experiment MeHg(II) was at tracer levels concentrations, the fraction of phosphate bound to the methylmercury is negligible. In the range of $-$log $[H^+] = 5 - 7$ the distribution of CH_3Hg-(II) between the two phases is clearly affected by varying concentration of $H_2PO_4^-$. Log D is seen to decrease with increasing log $[H_2PO_4^-]$ with a limiting slope of -1. This relationship strongly indicates the formation of $CH_3Hg(II)$-phosphate complex in the aqueous phase with $CH_3HgH_2PO_4$, $CH_3HgHPO_4^-$ or $CH_3HgPO_4^{2-}$ as possible predominant species. These data also

Table 1. The distribution of methylmercury(II) in the two-phase system 1.0 M(Na,H)(NO$_3$,Cl,PO$_4$)/ *o*-xylene. Data given as log D_{exp}, log [H$^+$], C_{PO_4} M, log [H$_2$PO$_4^-$], and the error log ($D_{calc}D_{exp}^{-1}$), which has been calculated assuming the formation of the MeHg(II) species MeHgCl(org), MeHgCl-(aq), MeHgOH(aq), MeHgHPO$_4^-$(aq) with the equilibrium constants given in Table 2, model No. 14. $C_{Cl} = 1.270 \times 10^{-3}$ M, $V_{aq} = V_{org}$.

$C_{MeHg(II)} = 4.15 \times 10^{-5}$ M^a

+1.070, −1.263, 0, [H$_2$PO$_4^-$]=0, −0.000; +1.055, −4.792, 4.450 × 10^{-2}, −1.361, −0.065; +1.049, −4.684, 4.994 × 10^{-3}, −2.309, +0.011; +1.048, −5.176, 2.472 × 10^{-2}, −1.628, −0.083; +1.042, −4.366, 9.888 × 10^{-3}, −2.009, +0.019; +1.041, −5.347, 1.977 × 10-2, −1.735, −0.094; +1.040, −4.839, 1.483 × 10^{-2}, −1.839, −0.005; +1.038, −5.106, 3.461 × 10^{-2} −1.479, −0.089; +1.032, −5.145, 2.966 × 10^{-2}, −1.548, −0.077; +1.027, −2.546, 0, [H$_2$PO$_4^-$]=0, +0.043; +1.016, −4.353, 3.952 × 10^{-2}, −1.407, +0.026; +1.004, −5.330, 4.996 × 10^{-3}, −2.331, +0.023; +0.987, −5.491, 0, [H$_2$PO$_4^-$]=0, +0.063; +0.972, −5.322, 9.992 × 10^{-3}, −2.030, +0.029; +0.957, −5.316, 1.499 × 10^{-2}, −1.853, +0.020; +0.927, −5.313, 1.998 × 10^{-2}, −1.728, +0.027; +0.910, −5.305, 2.498 × 10^{-2}, −1.631, +0.024; +0.894, −5.299, 2.998 × 10^{-2}, −1.551, +0.021; +0.866, −6.308, 2.498 × 10^{-3}, −2.826, +0.018; +0.865, −5.289, 3.497 × 10^{-2}, −1.484, +0.033; +0.827, −5.257, 4.996 × 10^{-2}, −1.327, +0.030; +0.775, −6.349, 6.994 × 10^{-3}, −2.396, −0.003; +0.749, −6.459, 9.517 × 10^{-3}, −2.313, −0.068; +0.745, −6.344, 9.992 × 10^{-3}, −2.239, −0.028; +0.639, −6.478, 1.428 × 10^{-2}, −2.146, −0.046; +0.631, −6.415, 1.384 × 10^{-2}, −2.129, −0.005; +0.626, −6.340, 1.499 × 10^{-2}, −2.061, +0.014; +0.619, −6.376, 9.888 × 10^{-3}, −2.257, +0.088; +0.619, −6.381, 1.780 × 10^{-2}, −2.004, −0.036; +0.617, −6.418, 9.888 × 10^{-3}, −2.276, +0.074; +0.580, −6.386, 1.582 × 10^{-2}, −2.058, +0.029; +0.572, −6.405, 1.879 × 10^{-2}, −1.992, −0.012; +0.534, −6.364, 1.977 × 10^{-2}, −1.951, +0.032; +0.519, −6.364, 2.077 × 10^{-2}, −1.930, +0.034; +0.505, −6.327, 2.175 × 10^{-2}, −1.894, +0.053; +0.503, −6.356, 2.373 × 10^{-2}, −1.868, +0.019; +0.470, −6.334, 2.998 × 10^{-2}, −1.758, −0.003; +0.464, −6.395, 2.472 × 10^{-2}, −1.868, +0.029; +0.453, −6.384, 2.472 × 10^{-2}, −1.863, +0.046; +0.397, −6.364, 3.461 × 10^{-2}, −1.708, +0.013; +0.380, −6.325, 3.497 × 10^{-2}, −1.687, +0.046; +0.378, −6.357, 3.461 × 10^{-2}, −1.705, +0.036; +0.347, −6.779, 2.379 × 10^{-2}, −2.100, −0.002; +0.341, −6.310, 4.996 × 10^{-2}, −1.526, −0.020; +0.341, −6.325, 4.450 × 10^{-2}, −1.582, +0.010; +0.269, −6.795, 2.865 × 10^{-2}, −2.030, +0.017; +0.229, −6.784, 3.827 × 10^{-2}, −1.897, −0.028; +0.162, −6.782, 4.759 × 10^{-2}, −1.801, −0.031; −1.408, −9.266, 0.333, −3.271, −0.066; −1.493, −9.251, 0.333, −3.256, +0.031.

$C_{MeHg(II)} = 5.15 \times 10^{-5}$ M^a

+1.040, −1.522, 0, [H$_2$PO$_4^-$]=0, +0.030.

$C_{MeHg(II)} = 1.816 \times 10^{-4}$ M^a

+1.050, −1.491, 0, [H$_2$PO$_4^-$]=0, +0.019; +0.546, −6.905, 4.579 × 10^{-3}, −2.904, +0.022; +0.394, −6.839, 1.482 × 10^{-2}, −2.363, +0.023; +0.341, −6.834, 1.913 × 10^{-2}, −2.232, +0.009; +0.279, −6.831, 2.379 × 10^{-2}, −2.136, +0.015; +0.244, −6.821, 2.865 × 10^{-2}, −2.048, +0.003; +0.208, −6.812, 3.323 × 10^{-2}, −1.977, −0.001; +0.173, −6.811, 3.827 × 10^{-2}, −1.915, −0.009; +0.162, −6.801, 4.759 × 10^{-2}, −1.814, −0.064.

$C_{MeHg(II)} = 5.349 \times 10^{-4}$ M^b

+1.184, −1.462, 0, [H$_2$PO$_4^-$]=0, −0.116; +1.039, −2.150, 0, [H$_2$PO$_4^-$]=0, +0.029; +1.037, −1.514, 0, [H$_2$PO$_4^-$]=0, +0.031; +1.027, −1.490, 0, [H$_2$PO$_4^-$]=0, +0.042; +0.845, −5.973, 4.996 × 10^{-3}, −2.421, +0.008; +0.813, −5.725, 9.992 × 10^{-3}, −2.072, +0.038; +0.798, −5.610, 1.499 × 10^{-2}, −1.880, +0.036; +0.774, −5.535, 1.998 × 10^{-2}, −1.747, +0.043; +0.763, −5.496, 2.498 × 10^{-2}, −1.646, +0.031; +0.756, −5.458, 2.998 × 10^{-2}, −1.563, +0.021; +0.732, −5.420, 3.497 × 10^{-2}, −1.493, +0.032; +0.715, −5.390, 3.997 × 10^{-2}, −1.433, +0.036; +0.691, −5.356, 4.996 × 10^{-2}, −1.333, +0.029; +0.579, −6.654, 4.996 × 10^{-3}, −2.701, +0.008; +0.534, −6.492, 9.992 × 10^{-3}, −2.310, +0.010; +0.476, −6.431, 1.499 × 10^{-2}, −2.104, +0.008; +0.410, −6.402, 1.998 × 10^{-2}, −1.965, +0.017; +0.388, −6.948, 9.517 × 10^{-3}, −2.620, −0.028; +0.376, −6.380, 2.498 × 10^{-2}, −1.858, +0.002; +0.345, −6.370, 2.998 × 10^{-2}, −1.775, −0.012; +0.322, −7.089, 1.047 × 10^{-2}, −2.688, −0.041; +0.320, −7.220, 6.662 × 10^{-3}, −2.993, −0.046; +0.298, −6.352, 3.497 × 10^{-2}, −1.700, −0.001; +0.292, −6.941, 1.428 × 10^{-2}, −2.439, −0.003; +0.287, −7.133, 8.565 × 10^{-3}, −2.811, +0.003; +0.275, −7.031, 1.428 × 10^{-2}, −2.507, −0.022; +0.274, −6.927, 1.913 × 10^{-2}, −2.301, −0.042; +0.272, −7.201, 4.579 × 10^{-3}, −3.140, +0.047; +0.245, −6.336, 3.997 × 10^{-2}, −1.635, +0.019; +0.242, −6.974, 2.379 × 10^{-2}, −2.241, −0.079; +0.239, −7.319, 4.759 × 10^{-3}, −3.224, +0.006; +0.233, −6.997, 1.903 × 10^{-2}, −2.356, −0.026; +0.223, −6.323, 4.996 × 10^{-2}, −1.533, −0.020; +0.199, −6.890, 2.865 × 10^{-2}, −2.098, −0.055; +0.198, −6.912, 2.379 × 10^{-2}, −2.195, −0.013; +0.114, −6.865, 3.827 × 10^{-2}, −1.954, −0.041; +0.049, −6.855, 4.759 × 10^{-2}, −1.853, −0.038; +0.018, −7.597, 2.855 × 10^{-3}, −3.697, +0.064.

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^{a} Distribution of MeHg(II) measured by a radiometric method. Initial total concentration of radioactive Me^{203}HgCl in the organic phase was 8.2 × 10^{-6} M.

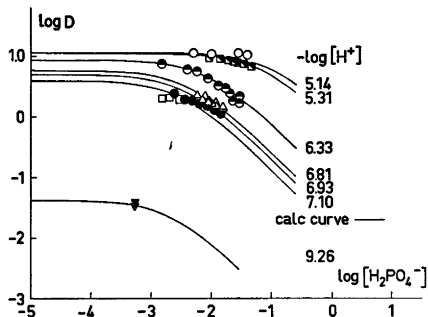^{b} Distribution of MeHg(II) measured by a spectrophotometric method.[31]

Fig. 1. The distribution of methylmercury(II) between o-xylene and 1.0 $M(Na,H)(Cl,NO_3,PO_4)$ aqueous solution as a function of log $[H_2PO_4^-]$ for selected data with $C_{MeHg(II)} = 4.15 \times 10^{-5}$ M, $C_{Cl} = 1.27 \times 10^{-3}$ M and approximately constant values of $-\log[H^+] = 5.14$ (O), 5.31 (◣), 6.33 (◓), 6.81 (△), 6.93 (●), 7.10 (□), and 9.26 (▼). The lines drawn have been calculated assuming the formation of the MeHg(II) species with the equilibrium constants given in Table 2, model 14. The distribution data are given in Table 1.
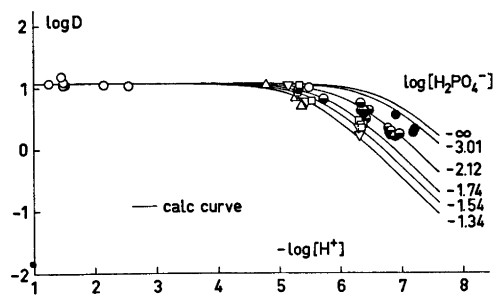
Fig. 2. Distribution of MeHg(II) in the two-phase system 1.0 M $(Na,H)(NO_3,Cl,PO_4)$/o-xylene as a function of $-\log[H^+]$ for selected data with $C_{MeHg(II)} = 4.15 \times 10^{-5}$ M, $C_{Cl} = 1.27 \times 10^{-3}$ M and approximately constant values of $[H_2PO_4^-] = 0$ (O); $10^{-3.01}$ M (●); $10^{-2.12}$ M (◓); $10^{-1.74}$ M (□); $10^{-1.54}$ M (▽) and $10^{-1.34}$ M (△). The lines drawn have been calculated assuming the formation of MeHgCl(org), MeHgCl(aq), MeHgOH(aq), and MeHgHPO$_4^-$(aq) with the formation constants given in Table 2, model 14. The distribution data is given in Table 1.

Table 2. Equilibrium constants [a] log β_{pqrs} for the formation of $(H^+)_p(CH_3Hg^+)_q(Cl^-)_r(H_2PO_4^-)_s$ species in the system $CH_3Hg(II) - 1.0$ M $(Na,H)(NO_3,Cl,PO_4)$/o-xylene for various assumptions of $CH_3Hg(II)$ species which minimize the error-square sum $U = \sum_1^{98} (\log D_{calc} - \log D_{exp})^2$.

Model No.	(p,q,r,s) log β_{pqrs}(org)	(p,q,r,s) log β_{pqrs}(aq)	U_{min}	$\sigma(\log D)$
1	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32$	43.864	
2	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (0,1,0,1)\ 4.54$ (max. 4.77)	27.311	0.531
3	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-2,1,0,0) -11.06$ (max. -10.73)	25.158	0.509
4	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-2,1,0,0) -13.27$ (max. -12.83); $(0,1,0,1)\ 4.52 \pm 0.23$	14.481	0.388
5	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-2,1,0,0)\ \beta = 0; (-2,1,0,1) -8.45 \pm 0.21$	10.306	0.328
6	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-2,1,0,1) -8.45 \pm 0.21$	10.306	0.326
7	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (0,1,0,1)\ 3.93$ (max. 4.23); $(-2,1,0,1) -8.45 \pm 0.25$	8.627	0.300
8	$(0,1,1,0)^{nv}6.39$	$(-1,1,0,0) -3.79 \pm 0.11; (0,1,1,0)^{nv}5.32$	3.555	0.191
9	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-1,1,0,0) -3.86 \pm 0.11; (0,1,0,1)3.76$ (max. 4.00)	2.714	0.168
10	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-1,1,0,1) -1.58 \pm 0.07; (0,1,0,1)\ \beta = 0$ (max. 3.47)	1.761	0.135
11	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-1,1,0,1) -1.58 \pm 0.07$	1.761	0.135
12	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-1,1,0,1) -1.61 \pm 0.06; (-2,1,0,1) -10.42$ (max. -10.18)	1.163	0.110
13	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-2,1,0,0) -13.65$ (max. -13.41); $(-1,1,0,1) -1.61 \pm 0.06$	1.132	0.109
14[b]	$(0,1,1,0)^{nv}6.39$	$(0,1,1,0)^{nv}5.32; (-1,1,0,0) -4.40 \pm 0.07; (-1,1,0,1) -1.74 \pm 0.03$	0.150	0.040

[a] $\beta_{pqrs} = [(H^+)_p(CH_3Hg^+)_q(Cl^-)_r(H_2PO_4^-)_s]_t[H^+]^{-p}[CH_3Hg^+]^{-q}[Cl^-]^{-r}[H_2PO_4^-]^{-s}$, where the subindex t indicates the phase referred to in the reaction. The limits given correspond approximately to log $[\beta \pm 3\sigma(\beta)]$ and if $\sigma(\beta) < 0.2\beta$, the value max. $= \log[\beta + 3\sigma(\beta)]$ is given. [nv] The given value of β for the species was not varied during the course of computer calculation. [b] The "best" model assumed.

indicate the formation of hydrolyzed $CH_3Hg(II)$ species in the aqueous phase as seen from the decrease of log D with increasing pH for constant values of $[H_2PO_4^-]$. This conclusion is further supported by the plot shown in Fig. 2 which illustrates the distribution of $CH_3Hg(II)$ as a function of $-\log[H^+]$ for sets of experimental points which have approximately constant values of $[H_2PO_4^-] = 0$, $10^{-3.01}$, $10^{-2.12}$, $10^{-1.74}$, $10^{-1.54}$, and $10^{-1.34}$ M. The limiting horizontal line which may be drawn through the experimental points with value of $-\log[H^+]$ less than 5 indicates that in this concentration range only CH_3HgCl is extracted into the organic phase and that in the aqueous phase phosphate or hydrolyzed complexes of $CH_3Hg(II)$ are negligible compared with $CH_3HgCl(aq)$ (cf. Ref. 13). For the range of $-\log[H^+]$ greater than 5 the data show decreasing values of D with increasing pH for all sets of experimental points, with the limiting

slope $\dfrac{\mathrm{d}\log D}{\mathrm{d}\,pH} \approx -1$. This strongly indicates the formation of hydrolyzed $CH_3Hg(II)$ species in the aqueous phase with CH_3HgOH as a predominant complex. Graphical analysis of the data in Figs. 1 and 2 thus strongly indicates the formation of 1:1 complex between $CH_3Hg(II)$ and $H_2PO_4^-$ or OH^- ions. Furthermore Figs. 1 and 2 seem to indicate that the distribution curves are not affected by the variation of C_{MeHg} from 4.15×10^{-5} to 5.35×10^{-4} M. This indicates the predominant formation of only mononuclear methylmercury species in the system, which is not unexpected considering the

low concentration range of metal ions studied. As will be seen in a later part of this paper this view is also supported by the results obtained by the Letagrop analysis.

Letagrop analysis of the data. The results of the graphical analysis give us a good starting point in the analysis of the data with the Letagrop-Distr computer program. Part of the results of the computer analysis of the distribution data are given in Table 2. In this analysis we assumed the formation of MeHgCl(aq) and MeHgCl(org) with the equilibrium constants

$K_{0110}{}^{org} = [MeHgCl]_{org}[MeHg^+]^{-1}[Cl^-]^{-1} = 10^{6.39}$ M^{-1} and

$K_{0110}{}^{aq} = [MeHgCl][MeHg^+]^{-1}[Cl^-]^{-1} = 10^{6.32}$ M^{-1}

as was found in our previous work,[13] and during the computer calculations the given value of the formation constant for each of these two species was kept constant.

In Table 2 the different chemical models which have been assumed for the description of the experimental data are summarized. Table 3 summarizes the different types of methylmercury(II) species which have been included in the Letagrop analysis of the data. The results of the analysis given in Table 2 indicate that of all the different models tried, the "best" model, which describes the distribution data satisfactorily within the experimental error, is model No. 14 with $U_{min} = 0.150$ for $Np = 98$ points, and $\sigma(\log D) = 0.040$. In this model the formation of MeHgOH(aq) and MeHgHPO$_4^-$-(aq) species is assumed. No significant improvement of the U value or $\sigma(\log D)$ value was found

Table 3. Summary of the different $(H^+)_p(MeHg^+)_q(Cl^-)_r(H_2PO_4^-)_s$ species included in the Letagrop analysis of the distribution data of MeHg(II) in the two-phase system 1.0 M (Na,H)(NO$_3$,Cl,PO$_4$)/ o-xylene. $C_{Cl} = 1.27 \times 10^{-3}$ M.

Aqueous phase	Organic phase
MeHgCl[a]; MeHgOH[b]; MeHg(OH)$_2^-$; (MeHg)$_2$(OH)$_2$; (MeHg)$_2$OH$^+$; (MeHg)$_2$(OH)$_3^-$ MeHgHPO$_4^-$ [b]; MeHgH$_2$PO$_4$; MeHgPO$_4^{2-}$; (MeHg)$_2$PO$_4^-$; (MeHg)$_3$HPO$_4$; (MeHg)$_2$H$_2$PO$_4^+$; (MeHg)$_2$OHPO$_4^{2-}$.	MeHgCl[a]; MeHgOH; MeHgH$_2$PO$_4$; NaMeHgHPO$_4$; NaMeHg(OH)$_2$.

[a] The value of the equilibrium constant (cf. Ref. 13) is not varied during the computer calculations.
[b] Methylmercury(II) species assumed to be formed which may account for the available distribution data (cf. Table 2, model 14).

Table 4. Comparison of equilibrium constants [a] log β_{pqrs} for the formation of $(H^+)_p(CH_3Hg^+)_q$-$(Cl^-)_r(H_2PO_4^-)_s$ species in the system $CH_3Hg(II) - 1.0$ M $(Na,H)(NO_3,Cl,PO_4)/o$-xylene which minimize different error-square sums $U = \sum_{1}^{98} fel[i]^2$. The computer calculations are based on the assumption of the formation of the species $CH_3HgCl(org)$, $CH_3HgCl(aq)$, $CH_3HgOH(aq)$ and $CH_3HgHPO_4^-$ (aq) (*cf.* Table 2, model No. 14).

Mimimized error $fel[i]$	(p,q,r,s)log β_{pqrs}(org)	(p,q,r,s)log β_{pqrs}(aq)	U_{min}	$\sigma(y)$
$Fel[1] = \log~(D_{calc}D_{exp}^{-1})$	$(0,1,1,0)6.39^{nv}$	$(0,1,1,0)5.32^{nv};~(-1,1,0,0)$ $-4.40 \pm 0.07;~(-1,1,0,1)$ -1.74 ± 0.03	0.150	0.040
$Fel[2] = D_{exp}D_{calc}^{-1} - 1$	$(0,1,1,0)6.39^{nv}$	$(0,1,1,0)5.32^{nv};~(-1,1,0,0)$ $-4.40 \pm 0.07;~(-1,1,0,1)$ -1.74 ± 0.03	0.844	0.094
$Fel[3] = D_{calc}D_{exp}^{-1} - 1$	$(0,1,1,0)6.39^{nv}$	$(0,1,1,0)5.32^{nv};~(-1,1,0,0)$ $-4.39 \pm 0.06;~(-1,1,0,1)$ -1.73 ± 0.03	0.756	0.089

[a] $\beta_{pqrs} = [(H^+)_p(CH_3Hg^+)_q(Cl^-)_r(H_2PO_4^-)_s]_t[H^+]^{-p}[CH_3Hg^+]^{-q}[Cl^-]^{-r}[H_2PO_4^-]^{-s}$, where the subindex t indicates the phase referred to in the reaction. The limits given correspond approximately to log $[\beta \pm 3\sigma(\beta)]$.
[nv] The given value of β for the species was not varied during the course of the computer calculation.

when, in an extension of model No. 14, the following additional species were assumed to be formed in the aqueous phase: $(0,1,0,1)$ $(= MeHgH_2PO_4), (-2,1,0,1)(= MeHgPO_4^{2-})$, and $(-2,1,0,0)[= MeHg(OH)_2]$. In the computer calculations it was found that the value of the constant β_{pqrs} for the formation of these additional species was either reduced to zero or their standard deviation $\sigma(\beta)$ found to be bigger than the value of the constant β itself, which we may take as indication that the formation of those species is negligible for the extraction conditions studied. No improvements of U_{min} were found by assuming the additional formation of dimeric methylmercury(II) species in the aqueous phase, such as $(-2,2,0,0)[= (MeHg)_2-(OH)_2], (-1,2,0,0)[= (MeHg)_2OH^+]$ $(-3,2,0,0)$ $[= (MeHg)_2(OH)_3^-], \quad (-1,2,0,1)[= (MeHg)_2-HPO_4], (-2,2,0,1)[= (MeHg)_2PO_4^-], (-3,2,0,1)-[= (MeHg)_2OHPO_4^{2-}]$ and $(0,2,0,1)[= (MeHg)_2-H_2PO_4^+]$. Some improvement of the value of the minimized error-square sum was found when to model No. 14 the additional formation of the species $(-1,1,0,1)$ $(= Na^+MeHgHPO_4^-)$ in the organic phase and $(-2,1,0,0)$ $[= MeHg-(OH)_2]$ in the aqueous phase was assumed $[U_{min} = 0.129, \sigma(\log D) = 0.037]$. However, the $\sigma(\log D)(= 0.037)$ then found was not significantly lower than that found in model No. 14 $[\sigma(\log D) = 0.040]$. It may be noted also that

for all the models tried practically the same value for β was found for the formation of the species $(-1,1,0,0)(= MeHgOH)$ and $(-1,1,0,1)$ $(= MeHgHPO_4^-)$ in the aqueous phase, which thus supports our previous conclusion that these are the predominant species in the system studied.

In Table 4 we compare the equilibrium constants found for the formation of methylmercury(II) species by assuming model No. 14 (Table 2), and minimizing the following three different types of error-square sum:

$$U = \sum[\log~(D_{calc}D_{exp}^{-1})]^2;~~U = \sum(D_{exp}D_{calc}^{-1} - 1)^2$$

and

$$U = \sum(D_{calc}D_{exp}^{-1} - 1)^2.$$

The results of the calculations indicate practically the same values for the equilibrium constants for the formation of the species assumed, $MeHgOH(aq)$ and $MeHgHPO_4^-(aq)$, which indicates that the assignment of the same weight factor to the experimental points is not unjustified. In this work the weight factor is given the value $w = 1$.

CONCLUSION

We may thus conclude that for the extraction conditions studied the distribution data, within the experimental errors, can be described satis-
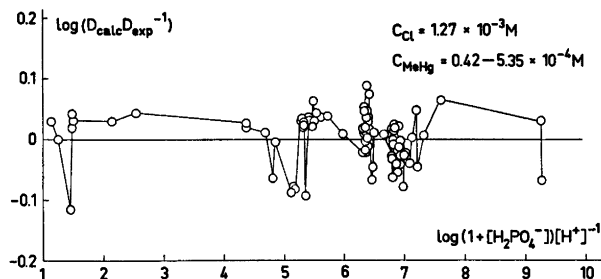
Fig. 3. The minimized error $Fel(1) = \log\ (D_{calc}D_{exp}^{-1})$ as a function of $\log\ (1+[H_2PO_4^-])[H^+]^{-1}$ for the two-phase system 1.0 M (Na,H)(NO$_3$,Cl,PO$_4$)/o-xylene, assuming the formation of MeHg-Cl(aq), MeHgCl(org), MeHgOH(aq) and MeHgHPO$_4^-$(aq) species with the equilibrium constants given in Table 2, model 14. The data are given in Table 1.

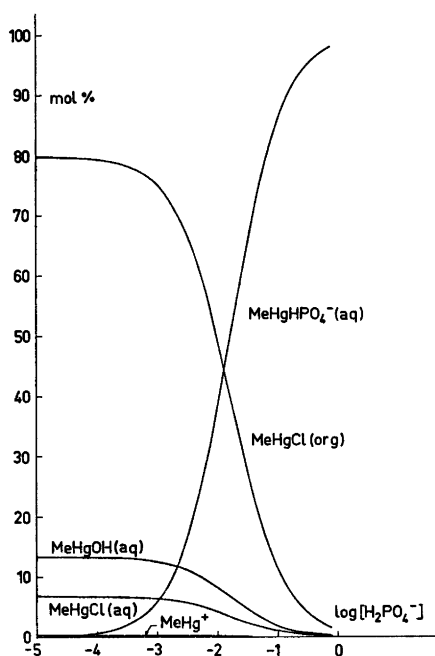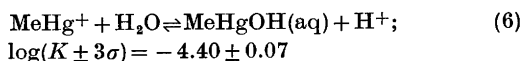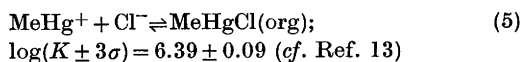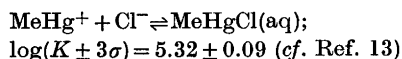factorily by assuming the following methylmercury(II) species:

$$MeHg^+ + Cl^- \rightleftharpoons MeHgCl(aq);$$

$$\log(K \pm 3\sigma) = 5.32 \pm 0.09\ (cf.\ Ref.\ 13) \qquad (4)$$

$$MeHg^+ + Cl^- \rightleftharpoons MeHgCl(org); \qquad (5)$$

$$\log(K \pm 3\sigma) = 6.39 \pm 0.09\ (cf.\ Ref.\ 13)$$

$$MeHg^+ + H_2O \rightleftharpoons MeHgOH(aq) + H^+; \qquad (6)$$

$$\log(K \pm 3\sigma) = -4.40 \pm 0.07$$

Fig. 4. The distribution of the different methylmercury(II) species as mol % *versus* [H$_2$PO$_4^-$] in the two-phase system 1.0 M (Na,H)(NO$_3$,Cl, PO$_4$)/o-xylene for a given value $-\log[H^+]=$ 7.10, $C_{Cl}=1.2\times10^{-3}$ M and $C_{MeHg}=4.15\times10^{-5}$ M. The lines have been calculated using the Haltafall program [29] assuming the formation of the set of (H$^+$)$_p$(MeHg$^+$)$_q$(Cl$^-$)$_r$(H$_2$PO$_4^-$)$_s$ species with the equilibrium constants given by model No. 14 in Table 2.
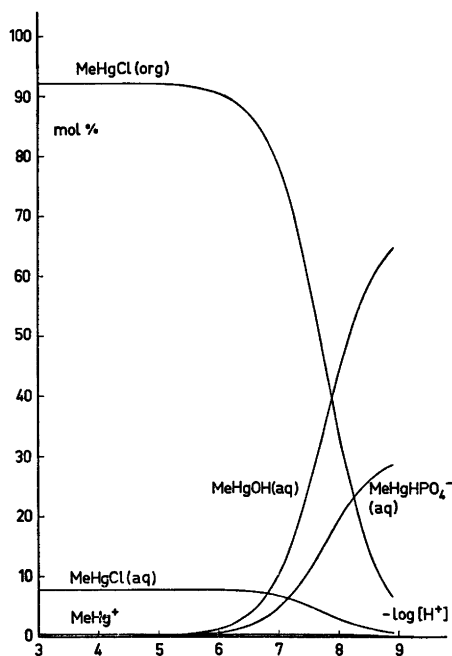

Fig. 5. The mol percentage of the different MeHg(II) species as a function of $-\log[H^+]$ in the two-phase system 1.0 M (Na,H)(NO$_3$,Cl,PO$_4$)/o-xylene for a given value of [H$_2$PO$_4^-$] = 10$^{-3.010}$ M, $C_{MeHg}=4.15\times10^{-4}$ M and $C_{Cl}=$ 1.27 × 10^{-3} M. The lines have been calculated using the Haltafall program [29] assuming the formation of the set of MeHg(II) species with the equilibrium constants given by model No. 14 in Table 2.

$MeHg^+ + H_2PO_4^- \rightleftharpoons MeHgHPO_4^-(aq) + H^+;$ (7)
$\log(K \pm 3\sigma) = -1.74 \pm 0.03$
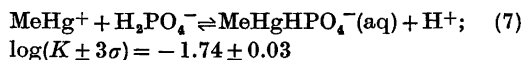
Using the value $K_w = [H^+][OH^-] = 10^{-13.95} M^2$ for the ionization of water at $I = 1.0$ M (*cf.* Refs. 22 and 28) the formation of the MeHgOH species may be described by the equilibrium:

$MeHg^+ + OH^- \rightleftharpoons MeHgOH(aq);$ (8)
$\log(K \pm 3\sigma) = 9.55 \pm 0.07$
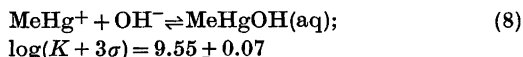
Furthermore we may calculate the constant for the hydrolysis of MeHgCl(aq) from (8) and (4) and that of MeHgHPO$_4^-$ from (7), (8) and the acid constant $K_{a2} = [HPO_4^{2-}][H^+][H_2PO_4^-]^{-1} = 10^{-6.48}$ M:

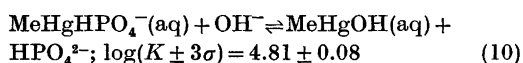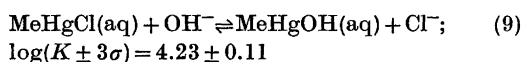$MeHgCl(aq) + OH^- \rightleftharpoons MeHgOH(aq) + Cl^-;$ (9)
$\log(K \pm 3\sigma) = 4.23 \pm 0.11$

$MeHgHPO_4^-(aq) + OH^- \rightleftharpoons MeHgOH(aq) + $
$HPO_4^{2-}; \log(K \pm 3\sigma) = 4.81 \pm 0.08$ (10)

Fig. 3 shows the observed error function $= \log (D_{calc} D_{exp}^{-1})$ as a function of $\log (1 + [H_2PO_4^-])[H^+]^{-1}$ for the different experimental points, assuming the formation of the set of $(H^+)_p (MeHg^+)_q (Cl^-)_r (H_2PO_4^-)_s$ species and formation constants in the "best" model found previously (*cf.* Table 2, model No. 14). From the

distribution of the error in Fig. 3 no systematic deviation seems to be indicated. Fig. 4 shows the distribution of the different methylmercury species under given extraction conditions $(C_{MeHg} = 4.15 \times 10^{-4}$ M; $C_{Cl} = 1.27 \times 10^{-3}$ M and $[H^+] = 10^{-7.10}$ M) as a function of $[H_2PO_4^-]$ and Fig. 5 gives the distribution of the different methylmercury species with varying $[H^+]$. The lines in Figs. 4 and 5 have been calculated using the Haltafall program [29] assuming the formation of the complexes MeHgCl(aq), MgHgCl(org), MeHgOH(aq), and MeHgHPO$_4^-$(aq) with the equilibrium constants given in (4), (5), (6) and (7).

DISCUSSION

In Table 5 we summarise the results found in the present work together with those reported earlier by other authors for similar studies. As can be seen there is rather fair agreement between the values for the formation constant of MeHgOH(aq) and MeHgHPO$_4^-$(aq) found in this work and those reported by, *e.g.*, Schwarzenbach and Schellenberg [4-6] from their potentiometric studies. The formation of (CH$_3$Hg)$_2$-OH$^+$ species found by these authors, however, is not indicated by the data of the present work.

Table 5. Equilibrium constant ^{a} log K_{pqr} for formation of $(H^+)_p (RHg^+)_q (H_2PO_4^-)_r$ complexes in various systems.

R	System	Temp °C	$\log K_{-110}$ RHgOH	$\log K_{-120}$ (RHg)$_2$OH$^+$	$\log K_{-111}$ RHgHPO$_4^-$	Exp. method	Ref.
CH$_3$	aqueous	25	-3.59^b			Cond.	9
CH$_3$	0.1 M(H,K)NO$_3$	20	-4.59	-2.53		EMF	4 – 6
CH$_3$	0.1 M(H,K)(NO$_3$,PO$_4$)	20			-1.60	EMF	4 – 6
CH$_3$	0 – 5 mM NO$_3^-$	24 – 25	-4.50^b			EMF	7
CH$_3$	0.1 M(H,K)NO$_3$	25	-4.78^c			EMF	8
		20	-4.64^d				8
CH$_3$	aqueous	25	-4.70^b	-2.33^b		NMR	14
CH$_3$	1 M(Na,H)(NO$_3$, Cl,PO$_4$)	25	-4.40 ± 0.07		-1.74 ± 0.03	Distr.	this work
C$_2$H$_5$	0 – 5 mM ClO$_4^-$	24 – 25	-4.9^b			EMF	7
C$_3$H$_7$	0.1 M(H,K)NO$_3$	25	-5.12^c			EMF	7
C$_4$H$_9$	0.1 M(H,K)NO$_3$	25	-5.17^c			EMF	8
C$_6$H$_5$	0 – 5 mM NO$_3^-$	24 – 25	-4.9^b			EMF	7
C$_6$H$_5$	0 – 4.3 mM ClO$_4^-$	25	-4.11^b			EMF	11
CF$_3$	dilution ClO$_4^-$	25	-3.24^b			EMF	12
C$_2$H$_5$	dilution ClO$_4^-$	25	-3.42^b			EMF	12
C$_3$F$_7$	dilution ClO$_4^-$	25	-3.50^b			EMF	12

$^a K_{pqr} = [(H^+)_p (RHg^+)_q (H_2PO_4^-)_r][H^+]^{-p}[RHg^+]^{-q}[H_2PO_4^-]^{-r}$. The limits given correspond approximately to log $[K \pm 3\sigma(K)]$. ^{b} Assuming the ionization constant of water $K_w = (H^+)(OH^-) = 10^{-14.00} M^2$.[22] ^{c} Assuming $K_w = 10^{-13.78} M^2$.[30] ^{d} Assuming $K_w = 10^{-13.96} M^2$.[4]

This may be explained as due to the very low value found for the methylmercury(II) concentrations under the present extraction conditions ($[MeHg^+] < 10^{-6.5}$ M). Using the calculated value found for $[MeHg^+] < 10^{-6.5}$ M and $K = [(MeHg)_2OH^+][MeHgOH]^{-1}[MeHg^+]^{-1} = 10^{2.37}$ M^{-1} given by Schwarzenbach and Schellenberg,[4-6] we may calculate the ratio $[(MeHg)_2OH^+][MeHgOH]^{-1} < 10^{-4.13}$. In natural waters with low concentration of $MeHg^+$, due to the presence of chloride and phosphate ions among others, and $pH = 6 - 7$ we may expect MeHgOH to predominate over $(MeHg)_2OH^+$ species.

The results of this work may be of interest not only from the ecological point of view, but also for further studies of the complex chemistry of methylmercury, e.g. by solvent extraction technique. In these studies the use of a buffer substance to control the pH of the aqueous solution is frequently required. However, acids and bases which are suitable for use as buffer substances may form complexes with $MeHg^+$ under the experimental conditions used. The effect of this complex formation can be corrected for if the stability constants for the reactions between $MeHg^+$ and the buffer substances are known. Phosphates being effective buffers over a wide pH range are thus particularly suitable for this purpose.

REFERENCES

1. Borg, K., Wanntorp, H., Erne, K. and Hanko, E. *Viltrevy (Swedish Wildlife) 6* (1969) 301; *J. Appl. Ecol. 3* (1966) 171.
2. Westöö, G. and Rydälv, M. *Vår Föda 7 – 8* (1971) 1; Report on Mercury in Foods, by the Joint FAO/WHO Expert Committee on Food Additives, 1970.
3. FAO Fisheries Reports, No. 99, Rome 1971.
4. Schellenberg, M., *Diss.*, ETH, Zürich 1963.
5. Schellenberg, M. and Schwarzenbach, G. *Proc. 7th Int. Conf. Coord. Chem.*, Stockholm 1962, p. 157.
6. Schwarzenbach, G. and Schellenberg, M. *Helv. Chim. Acta 48* (1965) 28.
7. Waugh, T. D., Harold, F. W. and Laswick, J. A. *J. Phys. Chem. 59* (1955) 395.
8. Zanella, P., Plazzogna, G. and Tagliavini, G. *Inorg. Chim. Acta 2* (3) (1968) 340.
9. Maynard, J. L. and Howard, H. C. *J. Chem. Soc. 123* (1923) 960.
10. Johns, I. B., Peterson, W. D. and Hixon, R. M. *J. Phys. Chem. 34* (1930) 2218.
11. Parikh, S. S. and Sweet, T. R. *J. Phys. Chem. 65* (1961) 1909.
12. Powell, H. B. and Lagowski, J. J. *J. Chem. Soc.* (1962) 2047.
13. Budevsky, O., Ingman, F. and Liem, D. H. *Acta Chem. Scand. 27* (1973) 1277.
14. Libich, S. and Rabenstein, D. L. *Anal. Chem. 45* (1973) 118.
15. Liem, D. H. and Ingman, F. *Proc. XVth Int. Conf. Coord. Chem.*, Moscow 1973, p. 648.
16. Some laboratory methods in current use at the Department of Inorganic Chemistry, the Royal Institute of Technology, Stockholm, Mimeograph 1959 (available on request).
17. Biedermann, G. and Douhéret, G. *Personal communications.*
18. Irani, R. R. and Callis, C. F. *J. Phys. Chem. 65* (1961) 934.
19. Drozdov, N. S. and Krylov, V. P. *Zh. Fiz. Khim. 35* (1961) 2557.
20. Cher, M. and Davidson, N. *J. Amer. Chem. Soc. 77* (1955) 793.
21. Thamer, J. *J. Amer. Chem. Soc. 79* (1957) 4298.
22. Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-ion Complexes*, Spec. Publ. No. 17, The Chemical Society, London 1964.
23. Ingri, N. and Sillén, L. G. *Ark. Kemi 23* (1964) 97.
24. Sillén, L. G. and Warnqvist, B. *Ark. Kemi 31* (1969) 315.
25. Sillén, L. G. and Warnqvist, B. *Ark. Kemi 31* (1969) 341.
26. Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi. 31* (1969) 353.
27. Liem, D. H. *Acta Chem. Scand. 25* (1971) 1521.
28. Anderegg, G. *Helv. Chim. Acta 50* (1967) 2333.
29. Ingri, N., Kakolowicz, W., Sillén, L. G. and Warnqvist, B. *Talanta 14* (1967) 1261.
30. Fischer, R. and Byé, J. *Bull. Soc. Chim. Fr.* (1964) 2920.
31. Ingman, F. *Talanta 18* (1971) 744.