

Solvent Extraction Studies on the Complex Formation between Methylmercury(II) and Bromide, Chloride and Nitrate Ions

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Complex formation between $\text{CH}_3\text{Hg}(\text{II})$ and Cl^- , Br^- and NO_3^- ions in the two-phase system *o*-xylene/ Y M ($\text{H},\text{Na})(\text{Br},\text{Cl},\text{NO}_3)(\text{aq})$, $Y=1.0$ or 2.5 , has been studied at 25°C by radiometric measurement of the distribution of $\text{CH}_3^{203}\text{Hg}$ between the two phases as a function of the chloride, bromide and nitrate concentration. The distribution

data, which have been analyzed using the computer program LETAGROP-DISTR, may be explained by the formation of the methylmercury(II) species CH_3HgCl , CH_3HgBr in both phases and additional formation of $\text{CH}_3\text{HgBr}_2^-$ in the aqueous phase and CH_3HgNO_3 in the organic phase. The values of the equilibrium constants are:

	$Y=1.0$	$Y=2.5$
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}(\text{aq})$	$\log(K \pm 3\sigma)$ 6.37 ± 0.02	$\log(K \pm 3\sigma)$ 6.60 ± 0.25
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}(\text{org})$	8.06 ± 0.13	8.30 ± 0.20
$\text{CH}_3\text{Hg}^+ + \text{NO}_3^- \rightleftharpoons \text{CH}_3\text{HgNO}_3(\text{org})$	-0.98 ± 0.09	-1.21 ± 0.04
$\text{CH}_3\text{Hg}^+ + 2\text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}_2^-(\text{aq})$	6.09 ± 0.14	5.98 ± 0.09
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}(\text{aq})$		5.50 ± 0.01
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}(\text{org})$		6.59 ± 0.01

The coordination chemistry of organomercurial ions, e.g. CH_3Hg^+ ions, with ligands in natural waters, e.g. the halogenides, OH^- and NO_3^- ions, is of great interest for a deeper understanding of their polluting effects on the environment. Organic mercury compounds enter natural waters in different ways.^{1–3} In such forms mercury is easily absorbed by living organisms and the deleterious effects on the health of man and animals have been established.^{4,5}

In natural waters, organomercurial ions are usually found in trace concentrations complexed with ligands present in the system. Studies of the chemical state of these compounds under similar conditions are of interest for understanding their distribution in nature. In this work, we report the results of liquid-liquid extraction studies on complex formation between methylmercury(II) and Cl^- , Br^- and NO_3^- ions in the system *o*-xylene/ 1.0 M

($\text{H},\text{Na})(\text{Br},\text{Cl},\text{NO}_3)(\text{aq})$ and *o*-xylene/ 2.5 M ($\text{H},\text{Na})(\text{Br},\text{Cl},\text{NO}_3)(\text{aq})$. Studies on the complex formation of $\text{MeHg}(\text{II})$ with Cl^- in the two-phase system *o*-xylene/ 1.0 M ($\text{H},\text{Na})(\text{Cl},\text{ClO}_4)$ and its hydrolysis and complex formation with phosphate ions in *o*-xylene/ 1.0 M ($\text{H},\text{Na})(\text{Cl},\text{PO}_4,\text{NO}_3)$ have been reported previously.^{6,7} Preliminary results from this work have been reported elsewhere.⁸

Previous work

A potentiometric method of studying the complex formation between methylmercury(II) and Br^- ions has been used by Waugh *et al.*,⁹ Schwarzenbach and Schellenberg,^{10,11} and Zanella *et al.*¹² These authors reported the formation of CH_3HgBr species. Simpson¹³ assumed the formation of CH_3HgBr in the aqueous and toluene phase and calculated from a

single experimental point the distribution constant $K_D = 45$. The kinetics of the formation of the species $\text{CH}_3\text{HgX}^{1-n}$ from CH_3HgOH for $\text{X}^{n-} = \text{Cl}^-$, Br^- , I^- , SCN^- and SO_3^{2-} , have been studied by Eigen *et al.*¹⁴ The complex formation between methylmercury(II) and Br^- , Cl^- , NO_3^- and OH^- ions studied by different methods are summarized in Table 3.

EXPERIMENTAL

Reagents. NaCl, *p.a.* (Merck), NaBr, AnalaR (Mallinckrodt) or Ultrapur quality were dried at 110–120 °C and used without further purification. The chloride content in the NaBr sample was determined mass spectrometrically. Typical results were 0.32 % NaCl in NaBr (*p.a.*) and 0.05 % in NaBr (Ultrapur). These values were used to correct the initial total concentration of chloride in the system. The purity of the non-radioactive methylmercuric hydroxide (Alfa Inorganics, Ventron) was checked by titration with standard acid and by an atomic absorption technique.¹⁵ It was found to be better than 97 %. The radioactive $\text{CH}_3^{203}\text{Hg}$ was purchased in the form of CH_3HgCl (Radiochemical Centre, Amersham, England) and freed from inorganic ^{203}Hg as described previously.⁶ For the distribution experiments, a stock solution of 1.6×10^{-6} M $\text{CH}_3^{203}\text{HgCl}$ in *o*-xylene was used. All the *o*-xylene (Merck *p.a.*) was purified as described previously.⁷

Distribution experiments

Manual method. Equal volumes (10–15 ml) of aqueous phase (with composition Y M (Na,H,MeHg)(Br,Cl,NO₃), $Y=1.0$ or 2.5) and organic phase (MeHgCl–*o*-xylene) were equilibrated and the distribution of $\text{CH}_3\text{Hg(II)}$ between the phases measured radiometrically as described previously.⁷

Automatic method. Some of the distribution experiments were carried out using a computer-controlled AKUFVE apparatus. The method is based on the use of PDP-11/10 computer as the controlling unit using BASIC as the program language. A detailed description of the system will be published elsewhere.¹⁶ AKUFVE is an apparatus for continuous liquid-liquid extraction experiments constructed by Rydberg *et al.*¹⁷

All experiments were carried out in thermostated rooms at 25 °C.

SYMBOLS AND EQUILIBRIUM CONSTANTS

- $[]_a, []_{org}$ = equilibrium concentration in the aqueous phase and the organic phase
- C_X = the initial total concentration of the species X referred to the aqueous phase. $X = \text{CH}_3\text{Hg(II)}$, Cl^- , Br^- or NO_3^-
- K_{pq}^{org} = formation constant of the complex $(\text{MeHg}^+)_p(\text{X}^-)_q(\text{org})$ (cf. eqn. 1)
- K_{rs}^{aq} = formation constant of the complex $(\text{MeHg}^+)_r(\text{X}^-)_s(\text{aq})$ (cf. eqn. 2)
- I_{org}, I_{aq} = radioactivity of $\text{CH}_3^{203}\text{Hg}$ in the organic and aqueous phase in counts per unit time and unit volume and corrected for background and deadtime
- D = $\Sigma[\text{MeHg}]_{org} / \Sigma[\text{MeHg}]_{aq} = I_{org} / I_{aq}$, net distribution ratio of $\text{CH}_3\text{Hg(II)}$
- D_{exp}, D_{calc} = experimental and calculated distribution ratio of $\text{CH}_3\text{Hg(II)}$
- U_{min} = the minimized error-square sum, e.g. for $val = 1$ one minimizes $U = \sum_1^{Np} (\log D_{calc} - \log D_{exp})^2$, where Np is the number of experimental points (cf. Ref. 18)

BASIC ASSUMPTIONS AND CHEMICAL MODEL

In our treatment of the data we assumed the formation of the set of species $(\text{H}^+)_p(\text{MeHg}^+)_q(\text{Cl}^-)_r(\text{Br}^-)_s(\text{NO}_3^-)_t(\text{org})$ and $(\text{H}^+)_k(\text{MeHg}^+)_l(\text{Cl}^-)_m(\text{Br}^-)_n(\text{NO}_3^-)_o(\text{aq})$ (cf. Refs. 7, 18)

However, as no evidence for any mixed complexes has been found, we will in this paper for simplicity describe these sets of species as $(\text{MeHg}^+)_p(\text{X}^-)_q(\text{org})$ and $(\text{MeHg}^+)_r(\text{X}^-)_s(\text{aq})$, where $\text{X}^- = \text{Cl}^-$, Br^- , NO_3^- or OH^- , with the formation constants

$$K_{pq}^{org} = [(\text{MeHg}^+)_p(\text{X}^-)_q]_{org} [\text{MeHg}^+]^{-p} [\text{X}^-]^{-q} \quad (1)$$

and

$$K_{rs}^{aq} = [(\text{MeHg}^+)_r(\text{X}^-)_s] [\text{MeHg}^+]^{-r} [\text{X}^-]^{-s} \quad (2)$$

It is assumed that in the organic phase, only uncharged complexes are formed and that the activity coefficient of the species is kept constant by maintaining a constant ionic strength (= 1 or 2.5 M). The distribution ratio of MeHg(II) may be expressed by

$$D_{\text{calc}} = \frac{\sum p K_{pq}^{\text{org}} [\text{MeHg}^+]^p [\text{X}^-]^q}{\sum r K_{rs}^{\text{aq}} [\text{MeHg}^+]^r [\text{X}^-]^s} \quad (3)$$

From (3) D_{calc} may be calculated for a given point, if C_{MeHg} , C_{Cl^-} , C_{Br^-} , $C_{\text{NO}_3^-}$, $\log [\text{H}^+]$ and K_{pq}^{org} and K_{rs}^{aq} for the set of species are given.

The distribution data were analyzed using the computer program LETAGROP-DISTR.¹⁸ In this analysis all points were given equal weights.

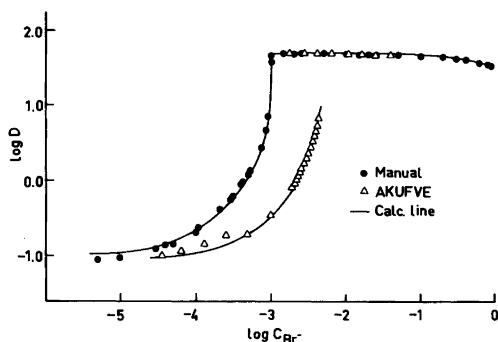


Fig. 1. The distribution of MeHg(II) between *o*-xylene and 1.0 M (Na,H)(Br,Cl,NO₃) aqueous phase as a function of initial total concentration of bromide and for two different levels of C_{MeHg} , 1.0×10^{-3} M and 4.9×10^{-4} M.

The full-drawn lines have been calculated using the equilibrium constants given in Table 2, Model No. V, for the formation of the species MeHgCl, MeHgBr and MeHgBr₂⁻ in the aqueous phase and MeHgCl, MeHgBr and MeHgNO₃ in the organic phase.

RESULTS

The primary data from the distribution experiments are available from one of the authors (D.H.L.) on request.

The system *o*-xylene/1.0 M (Na,H)(Br,Cl,NO₃). The results are illustrated in Fig. 1. $\log [\text{H}^+] = -2.00$ and $\log C_{\text{Cl}^-}$ was varied from -2.08 to -8.06 . As shown previously,^{10,6} no hydrolyzed MeHg(II) species are formed at $\log [\text{H}^+] = -2$. Fig. 1 shows that at low values of C_{Br^-} (less than 0.1 mM), $\log D$ levels off with decreasing C_{Br^-} . This indicates the extraction of MeHgCl as found previously, and other MeHg(II) species which do not contain Br⁻ ions. As will be shown, the data indicate the extraction of MeHgNO₃. The distribution curves form straight lines with increasing C_{Br^-} and level off to a horizontal line at $C_{\text{Br}^-} > 1$ mM. This may be explained by the formation of MeHgBr(org) and MeHgBr(aq). In addition, at $C_{\text{Br}^-} > 0.1$ M, $\log D$ decreases with increasing C_{Br^-} indicating the formation of MeHgBr₂⁻(aq).

The results of the computer analysis for five models are summarized in Table 1. Previous studies⁶ showed the formation of MeHgCl in the aqueous and *o*-xylene phases. The formation constants found, i.e. $K = 10^{6.39}$ M⁻¹ for MeHgCl(org), and $K = 10^{5.32}$ M⁻¹ for MeHgCl(aq), were used and not varied in the computer calculations. Minimizing the error-square sum ($Np = 72$ points) model V, in which the formation of MeHgCl(org), MeHgBr(org), MeHgNO₃(org), and MeHgCl(aq), MeHgBr(aq) and MeHgBr₂⁻(aq) species is assumed, gives the best fit. For this model the minimized error-square sum $U_{\text{min}} = 0.118$ and $\sigma(\log D) = 0.04$.

Table 1. Equilibrium constants^a $\log K$ for the formation of methylmercury(II) species in the system MeHg(II)–*o*-xylene/1.0 M (Na,H)(Br,Cl,NO₃) for various assumptions of MeHg(II) complexes that minimize the error-square sum, $U = \sum_1^{72} (\log D_{\text{calc}} - \log D_{\text{exp}})^2$.

Model	MeHg(II) species in the aqueous phase ^b		MeHg(II) species in the organic phase ^c		U_{min}	$\sigma(\log D)$
	MeHgBr	MeHgBr ₂ ⁻	MeHgBr	MeHgNO ₃		
I	—	—	—	—	628	—
II	$K = 0$	—	—	—	628	2.97
III	6.43 max 6.98 ^d	—	8.11 max 8.64 ^d	—	6.63	0.31
IV	6.36(6)	—	8.03(7)	–0.99(8)	0.191	0.06
V ^e	6.37(2)	6.09(14)	8.06(13)	–0.98(9)	0.118	0.04

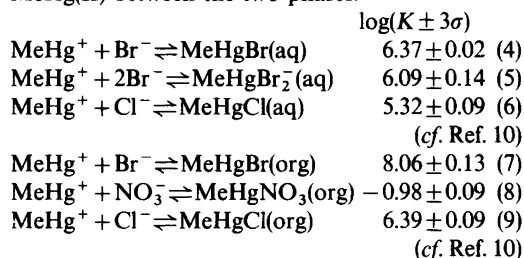
^a The limits given correspond approximately to $\log (K \pm 3\sigma)$. ^b For MeHgCl $\log K = 5.32$. The value was kept constant during the course of computer calculations. ^c For MeHgCl $\log K = 6.39$. The value was kept constant during the course of computer calculations. ^d If $\sigma(K) > 0.2K$, the maximum value = $\log [K + 3\sigma(K)]$ is given. ^e The best model assumed.

Table 2. Comparison of formation constants for the species in model V (Table 1) in the two-phase system MeHg(II)–*o*-xylene/1.0 M (Na,H)(Br,Cl,NO₃) which minimizes the three types of error-square sum $U_1 = \sum_1^{72} [\log(D_{\text{calc}} D_{\text{exp}}^{-1})]^2$, $U_2 = \sum_1^{72} (D_{\text{calc}} D_{\text{exp}}^{-1} - 1)^2$ and $U_3 = \sum_1^{72} (D_{\text{exp}} D_{\text{calc}}^{-1} - 1)^2$ respectively.

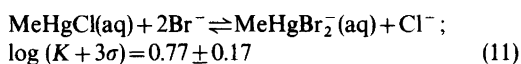
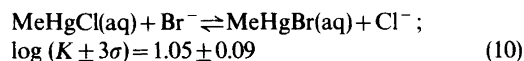
Type of error minimized	Species in the aqueous phase		Species in the organic phase		U_{\min}	$\sigma(\log D)$
		$\log(K \pm 3\sigma)$		$\log(K \pm 3\sigma)$		
U_1	MeHgBr	6.37(2)	MeHgBr	8.06(13)	0.118	0.04
	MeHgBr ₂ ⁻	6.09(14)	MeHgNO ₃	-0.98(9)		
U_2	MeHgBr	6.36(8)	MeHgBr	8.06(8)	0.626	0.09
	MeHgBr ₂ ⁻	6.13(24)	MeHgNO ₃	-0.95(4)		
U_3	MeHgBr	6.36(10)	MeHgBr	8.06(10)	0.598	0.09
	MeHgBr ₂ ⁻	6.12 max 6.32 ^a	MeHgNO ₃	-1.00(4)		

^a If $\sigma(K) > 0.2 K$, the maximum value $\log [K + 3\sigma(K)]$ is given.

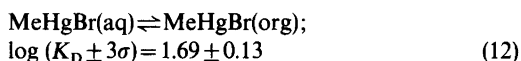
Model IV, in which the species MeHgBr₂⁻ is not considered, gives $U_{\min} = 0.191$ and $\sigma(\log D) = 0.06$, which may also be considered as an acceptable fit to the data. However, the distribution at $C_{\text{Br}} > 0.1$ M, cf. Fig. 1, indicates a systematic deviation due to the formation of MeHgBr_{*n*}^{1-*n*}, with $n > 1$. These effects indicating the formation of MeHgBr₂⁻ were found to be more pronounced in the two-phase system *o*-xylene/2.5 M (Na,H)(Br,Cl,NO₃), cf. Fig. 4. In Table 2, we compare the results obtained when other types of error-square sums are minimized. If the formation of the MeHg(II) species given in model V (Table 1) is assumed, practically the same values for the equilibrium constants are obtained for the three types of error-square sums. This supports the view that the data may be given equal weight. We conclude that the supposition of formation of the following methylmercury(II) species gives a good description of the distribution of MeHg(II) between the two phases.



Using eqns. (4), (5) and (6), we obtain the equilibrium constant for the exchange reaction:



From eqns. (4) and (7), we obtain the distribution constant for MeHgBr:



In Fig. 2, $\log D$ is plotted versus $\log [\text{Br}^-]$. All the experimental points for different C_{MeHg} are seen to fall on the same line. This strongly indicates that only mononuclear methylmercury(II) species are formed.

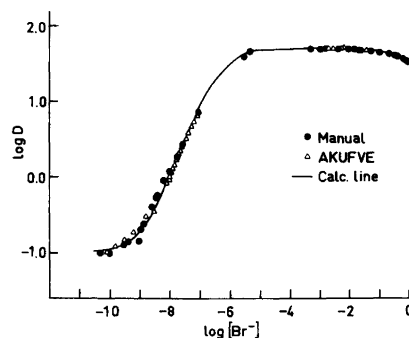


Fig. 2. The distribution of MeHg(II) between *o*-xylene and 1.0 M (Na,H)(Br,Cl,NO₃) as a function of the equilibrium concentration of bromide ions in the aqueous phase $[\text{Br}^-]$ M, and for the different initial total concentrations of methylmercury(II).

The full-drawn lines have been calculated using equilibrium constants given in Table 1, Model No. V.

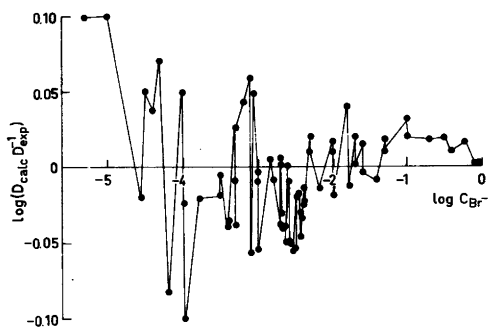


Fig. 3. The error $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ as a function of $\log C_{\text{Br}^-}$ for the two-phase system MeHg(II)–*o*-xylene/1.0 M (Na,H)(Br,Cl,NO₃) assuming the species with the equilibrium constants given in Table 1, Model No. V.

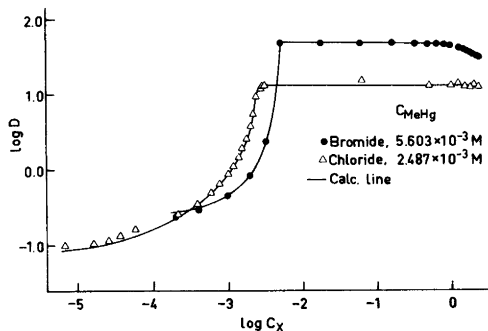


Fig. 4. The distribution of MeHg(II) in the two-phase system *o*-xylene/2.5 M (Na,H)(Br,Cl,NO₃) as a function of the total initial concentration of bromide at $C_{\text{MeHg}} = 5.603 \times 10^{-3}$ M (●) and of chloride for $C_{\text{MeHg}} = 2.487 \times 10^{-3}$ M (△). C_X represents C_{Br^-} or C_{Cl^-} .

The full-drawn lines have been calculated using the equilibrium constants given in Table 3 for the formation of the different MeHg(II) species.

In Fig. 3, the function $\log(D_{\text{calc}}D_{\text{exp}}^{-1})$ is plotted versus $\log C_{\text{Br}^-}$ assuming model V in Table 1. The distribution of the points is seen to show no systematic deviations.

In Fig. 5, the mol % distribution of the MeHg(II) species is shown as a function of $\log [\text{Br}^-]$ at constant $C_{\text{MeHg}} = 1.0 \times 10^{-3}$ M, $C_{\text{Cl}^-} = 1.0 \times 10^{-5}$ M, $C_{\text{NO}_3^-} = 1.0$ M and $\log [\text{H}^+] = -2.0$. In Fig. 6, the distribution of the dominating species is plotted as a function of $\log [\text{H}^+]$ at constant $C_{\text{MeHg}} = 1.0 \times 10^{-4}$

M, $C_{\text{Br}^-} = 1.0 \times 10^{-4}$ M, $C_{\text{Cl}^-} = 1.0 \times 10^{-3}$ M and $C_{\text{NO}_3^-} = 1.0$ M. These curves were calculated using the HALTAFALL program,²³ assuming MeHg(II) species and equilibrium constants according to model V in Table 1. For MeHgOH the equilibrium constants determined previously²² were used. The concentrations of the MeHg(II) species not repre-

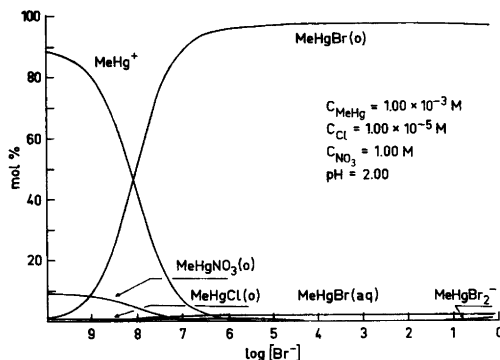


Fig. 5. The mol % distribution of different MeHg(II) species in the two-phase system *o*-xylene/1 M (Na,H)(Br,Cl,NO₃) as a function of $\log [\text{Br}^-]$ for constant values of $C_{\text{MeHg}} = 1.00 \times 10^{-3}$ M, $C_{\text{Cl}^-} = 1.00 \times 10^{-5}$ M, $C_{\text{NO}_3^-} = 1.00$ M and $[\text{H}^+] = 1.00 \times 10^{-2}$ M.

The curves have been calculated assuming the species and equilibrium constants according to Model No. V in Table 1.

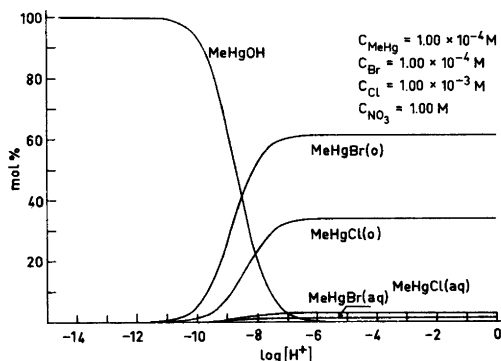
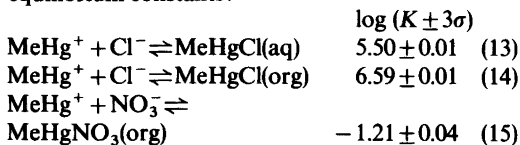


Fig. 6. The mol % distribution of the predominant MeHg(II) species in the two-phase system *o*-xylene/1 M (Na,H)(Br,Cl,NO₃) as a function of $\log [\text{H}^+]$ at constant $C_{\text{MeHg}} = 1.0 \times 10^{-4}$ M, $C_{\text{Br}^-} = 1.00 \times 10^{-4}$ M, $C_{\text{Cl}^-} = 1.00 \times 10^{-3}$ M and $C_{\text{NO}_3^-} = 1.0$ M. The MeHg(II) species not represented in the figure were found to be negligible under the extraction conditions studied.

sented in these figures were found to be negligible under the extraction conditions studied.

The system *o*-xylene/2.5 M (Na,H)(Br,Cl,NO₃). In Fig. 4, the distribution of MeHg(II) in the two-phase system *o*-xylene/2.5 M (Na,H)(Cl,NO₃) is illustrated for $C_{\text{MeHg}} = 2.487 \times 10^{-3}$ M, $\log [H^+] = -2.0$ and varying chloride concentration. In agreement with the previous conclusions,⁶ the distribution curve indicates the formation of the species MeHgCl(aq) and MeHgCl(org). LETAGROP analysis of the data ($N_p = 23$ points) shows that these can be explained ($U_{\text{min}} = 0.462$, $\sigma(\log D) = 0.0145$) by assuming the following set of MeHg(II) species and equilibrium constants:



The distribution constant of MeHgCl may thus be calculated from (13) and (14):

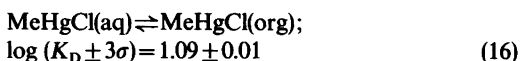
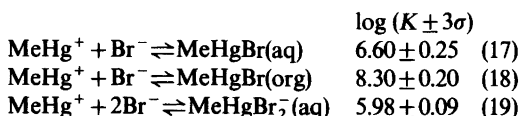


Fig. 4 also illustrates $\log D$ versus $\log C_{\text{Br}^-}$ for the system *o*-xylene/2.5 M (Na,H)(Br,Cl,NO₃). Comparing Fig. 4 and Fig. 1, we see not only the similarity of the curves but also the more pronounced effects on D , due to the formation of MeHgBr_{*n*}^{1-*n*} species with $n > 1$ at $C_{\text{Br}^-} > 0.1$ M. Computer analyses of the data assuming the set of methylmercury(II) species found previously (Model V, Table 1), gives $U_{\text{min}} = 0.018$ and $\sigma(\log D) = 0.032$ for $N_p = 20$ points and the following values of the equilibrium constants:



The values of K for the formation of MeHgCl(aq), MeHgCl(org) and MeHgNO₃(org) given in (13), (14) and (15) were not varied during the computer calculations. From (17) and (18) we obtain the distribution constant of MeHgBr:

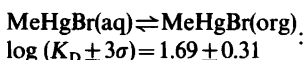


Table 3. Equilibrium constant for formation of methylmercury(II) species in various systems. The temperature is 25 °C, if not otherwise stated.

System	Equilibrium reaction	$\log K^a$	Method	Ref.
Water/toluene 0–7 mM Cl ⁻	MeHgCl(aq) \rightleftharpoons MeHgCl(org)	1.0 ^b	DISTR	13
	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(aq)	5.45	EMF	9
Water 0.1 M KCl	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(s)	7.16	SOL	9
	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(aq)	5.25	EMF	10, 11
0.1 M KNO ₃ <i>o</i> -Xylene/1.0 M (Na,H)ClO ₄	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(aq)	4.90 ^c	EMF	12
	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(aq)	5.32(9)	DISTR	6
<i>o</i> -Xylene/2.5 M (Na,H)NO ₃	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(org)	6.39(9)		
	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(aq)	5.64(1)	DISTR	This work
	MeHg ⁺ + Cl ⁻ \rightleftharpoons MeHgCl(org)	6.73(1)		
	MeHg ⁺ + NO ₃ ⁻ \rightleftharpoons MeHgNO ₃ (org)	-1.21(4)		
Water/toluene 0–7 mM	MeHgBr(aq) \rightleftharpoons MeHgBr(org)	1.7 ^b	DISTR	13
	MeHg ⁺ + Br ⁻ \rightleftharpoons MeHgBr(aq)	6.70	EMF	9
	MeHg ⁺ + Br ⁻ \rightleftharpoons MeHgBr(s)	8.92	SOL	9
0.1 M (K,H)NO ₃ 0.1 M KNO ₃	MeHg ⁺ + Br ⁻ \rightleftharpoons MeHgBr(aq)	6.62	EMF	10, 11
	MeHg ⁺ + Br ⁻ \rightleftharpoons MeHgBr(aq)	5.98 ^c	EMF	12
<i>o</i> -Xylene/1.0 M (Na,H)NO ₃	MeHg ⁺ + Br ⁻ \rightleftharpoons MeHgBr(org)	8.06(13)	DISTR	This work
	MeHg ⁺ + Br ⁻ \rightleftharpoons MeHgBr(aq)	6.37(2)	DISTR	This work
<i>o</i> -Xylene/1.0 M (Na,H)NO ₃	MeHg ⁺ + 2Br ⁻ \rightleftharpoons MeHgBr ₂ (aq)	6.09(14)		
	MeHg ⁺ + NO ₃ ⁻ \rightleftharpoons MeHgNO ₃ (org)	-0.98(9)		
	MeHg ⁺ + OH ⁻ \rightleftharpoons MeHgOH(s)	13.66	SOL	22

^a The limits given correspond approximately to $\log [K \pm 3\sigma(K)]$. ^b Calculated from one single experimental point available. ^c At 20 °C.

DISCUSSION

Equilibrium constants for the formation of the species between methylmercury(II) and Cl^- , Br^- and NO_3^- ions in different systems are summarized in Table 3. The present work shows that in the aqueous as well as in the organic phase, MeHg(II) and Cl^- ions form only the 1:1 complex, MeHgCl , up to C_{Cl^-} around 2.5 M. However, with Br^- ions and $C_{\text{Br}^-} > 0.1$ M, the formation of 1:2 species, MeHgBr_2^- is also indicated.

Barbieri and Bjerrum¹⁹ reported solubility measurements in 1 M $\text{Na(X,ClO}_4)$ indicating the formation of negatively charged complexes RHgX_n^{1-n} (R = ethyl and 2-butyl, $n = 1, 2, 3$) for $\text{X} = \text{SCN}$ and I. Rizzardi *et al.*²⁰ explained their ion exchange data by assuming the formation of $\text{C}_2\text{H}_5\text{HgCl}$ at $C_{\text{Cl}^-} \leq 1$ M and the formation of $\text{C}_2\text{H}_5\text{HgCl}_2^-$ species at high chloride concentrations ($C_{\text{Cl}^-} = 1-10$ M). In the present work, however, no negatively charged methylmercury(II) chloride complexes have been found for $C_{\text{Cl}^-} \leq 2.5$ M.

The results of the computer analysis show that the constants for the formation of the species MeHgBr(aq) and MeHgBr(org) have smaller standard deviations from data of 1.0 M compared with those of 2.5 M ionic medium. This may be explained statistically by the greater number of data available for the case of 1.0 M ionic medium ($Np = 72$ points) compared with that of 2.5 M medium ($Np = 23$ points). For the formation of MeHgBr_2^- (aq) species, however, a smaller value of $\sigma(K)$ was found in the case of 2.5 M ionic medium compared with that of 1.0 M, which is understandable since according to the mass-action law the formation of MeHgBr_2^- is expected to be more predominant at higher bromide concentrations.

The decrease of the constant for the formation of $\text{MeHgNO}_3(\text{org})$ found for 1.0 M ionic medium compared with that of 2.5 M medium may, in part, be due to the formation of $\text{MeHgNO}_3(\text{aq})$ which is expected to increase at higher nitrate concentrations in the aqueous medium. However, from the available data no definite conclusions on this matter can be made.

Mercury(II) is a typically soft acceptor. Since the methyl group must be regarded as an extremely soft donor, it is to be expected that the character of the methylmercury(II) ion will be pronouncedly harder than that of Hg(II) . Comparison of the stabilities of the halide complexes of Hg(II) and MeHg(II) seems to support this hypothesis. The

Table 4. Stability constants for the halides MeHgX and HgX^+ (cf. Refs. 11, 24).

X	$\log K_{\text{MeHgX}}$	$\log K_{\text{HgX}^+}$
F^-	1.5	1.0
Cl^-	5.2	6.7
Br^-	6.6	9.0
I^-	8.6	12.9

methylmercury ion is still soft, as indicated by the fact that the bromide complex of MeHg(II) is more stable than the chloride complex, but the difference is much less pronounced than for the corresponding first Hg(II) complexes.

Comparison of the other halide complexes also supports the hypothesis. This can be seen from Table 4, which illustrates for similar media, obtained by Schellenberg (MeHg^+)¹¹ and Paul (Hg^{2+}).²⁴

The difference in charge between Hg^{2+} and CH_3Hg^+ is expected to affect the stability of a given methyl halide complex, which thus makes a direct comparison between the two types of metal complexes rather difficult. However, the effect of the metal group in $\text{CH}_3\text{Hg(II)}$ on the stability of a halide complex may in part be seen by comparing the stability constants of MeHgX for different X, with that found in the case for the formation of HgX^+ (Table 4).

The distribution constants, K_D , for MeHgCl and MeHgBr , respectively, prove to be practically independent of the ionic strength. Thus, we find for $\text{MeHgCl(aq)} \rightleftharpoons \text{MeHgCl(org)}$, $K_D = 10^{1.07}$ at ionic strength 1.0 M (cf. Ref. 6) and $K_D = 10^{1.09}$ at 2.5 M. For MeHgBr , K_D is found to be $10^{1.69}$ at both these

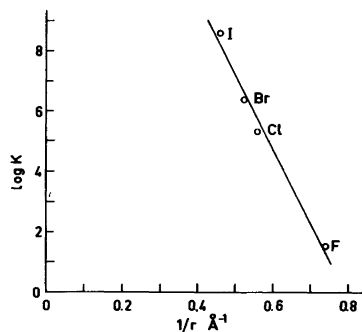


Fig. 7. The equilibrium constant for the formation of MeHgX , ($\text{X} = \text{F}^-$, Cl^- , Br^- , I^-) as a function of $1/r$, where r is the ionic radius of X taken from Ref. 27.

levels of ionic strength. This result is in agreement with the assumption that only uncharged species are involved in the relevant distribution equilibrium.

In Fig. 7 the value of $\log K$ for the formation of MeHgX is plotted as a function of the inverted value of the ionic radius. The points fall practically on a straight line indicating the formation of predominantly ionic bonds. A theoretical explanation for this has been given previously by Dyrssen.²⁵ A similar relation was shown by Dyrssen and Liem²⁶ to exist for complex formation between lanthanides, actinides and dialkylphosphoric acid.

Table 2 illustrates the results of minimizing different types of error-square sums. Practically the same values were found for the equilibrium constants for the formation of the methylmercury(II) species. This means that giving the same weight to the points, as was done during the computer analysis, is justified.

The extraction of methylmercury as methylmercury chloride in an organic phase has found application in analytical separation and assay of methylmercury.²¹ The higher distribution constant of MeHgBr compared with MeHgCl ($\Delta \log K_D = 0.62$) indicates that the extraction efficiency will be increased considerably if bromide is substituted for chloride.

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