APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 499–506 (2000)

Potentiometric study of the hydrolysis of $(CH_3)Hg^+$ in $NaClO_4$: construction of a thermodynamic model†

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The hydrolysis of CH_3Hg^+ was studied potentiometrically in $NaClO_4$ media in the range 0.1–3.0 mol dm^{-3} ionic strength at 25 °C. Evaluation of data with the non-linear least-squares computer programs BSTAC and STACO led us to propose the formation of CH_3HgOH and $(CH_3Hg)_2OH^+$ species. The stoichiometric stability constants obtained for the two species at the different ionic strengths were correlated by means of Modified Bromley Methodology (MBM) to obtain the corresponding thermodynamic equilibrium constants, as well as the interaction parameters of the soluble species. This is the first of a series of potentiometric studies on the different equilibria of methylmercury with the majority of ions present in natural waters in order to simulate the behaviour of methylmercury in sea and estuary waters. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: methylmercury; hydrolysis; equilibria; potentiometry; thermodynamic model; specific interaction model

Received 30 June 1999; accepted 31 January 2000

1 INTRODUCTION

It is recognized that the toxicity of any element (e.g. mercury) is determined by the particular species occurring in the sample.[1] In general terms, organic species of metals (more hydrophobic) show a higher ability to cross through biological membranes than inorganic forms. In the case of methylmercury (CH_3Hg^+), its high affinity to sulphydryl groups and lipids of animals explains its accumulation in living organisms, particularly in the lipoid tissue of mammals. Methylmercury toxicity in mammals is primarily manifested as central nervous system damage, but it also causes blockage of binding sites of enzymes, interferes with protein synthesis and restricts thymidine incorporation into DNA.[2]

Large-scale poisonings have been reported in populations which consume fish with high methylmercury content or bread made with corn seed previously treated with methylmercury as a fungicide. During the 1971–1972 period in Iraq 6530 persons were hospitalized, of whom 459 died. Similar incidents have been occurred in Japan (Minimata, 1953–1970; Niigata, 1960s period),[3] Pakistan, Guatemala and more recently in India[1] and Brazil,[4] where a large-scale dumping of inorganic mercury from gold mining has affected the residents of the Amazon River zone. In addition, large ecological disasters due to historical use of methylmercury as a fungicide or seed dressings have also been described.[1]

Although most of the industrial uses of the organomercurials have already been banned,[1] organomercury compounds are still produced to be used in the agricultural, paper and pharmaceutical industries. But more important from the environmental point of view is the capacity for methylation of the inorganic mercury that may occur in algae[5], humic substances,[6] or via bacteria.[7] The rate and extent of methylation of mercury(II) in water and sediments depends upon factors such as the compound of mercury(II) (acetate is easier to methylate than mercuric chloride), the methylating agent, the chemical composition of the sediment, its oxygen concentration and pH.

Studies on the hydrolysis and complexation of methylmercury and the ligands commonly present

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Contract/grant sponsor: University of the Basque Country; Contract/grant number: UPV 171.310-EA 160/97.

† This paper is based on work presented at the 5th International Conference on Mercury as a Global Pollutant, Rio de Janeiro, Brazil, 23–27 May 1999.

Table 1 Chemical models proposed to explain the hydrolysis of methylmercury

Authors	Ref.	Species proposed	Experimental technique
Maynard and Howard	8	CH_3HgOH	Conductimetry
Johns *et al.*	9	CH_3HgOH	Conductimetry
Waugh *et al.*	10	CH_3HgOH	Potentiometry
Goggin and Woodward	11	CH_3HgOH and $(CH_3Hg)_2OH^+$	Raman
Schwarzenbach and Schellenberg	12	CH_3HgOH and $(CH_3Hg)_2OH^+$	Potentiometry
Zanella and Plazzogna	13	CH_3HgOH	Potentiometry
Clarke and Woodward	14	CH_3HgOH, $(CH_3Hg)_2OH^+$ and $(CH_3Hg)_3O^+$	Raman
Libich and Rabenstein	15	CH_3HgOH and $(CH_3Hg)_2OH^+$	NMR
Ingman and Liem	16	CH_3HgOH	Distribution
Anderegg	17	CH_3HgOH	Potentiometry
Rabenstein *et al.*	18	CH_3HgOH and $(CH_3Hg)_2OH^+$	NMR and Raman
Jawaid *et al.*	19	CH_3HgOH and $(CH_3Hg)_2OH^+$	Potentiometry

in the environment are of importance for a better understanding of its ecological behaviour. Organomercury cations are considered to be acids of different hardness on the Lewis scale, depending on the groups bound to the mercury atom. Although mercury in CH_3Hg^+ has a strong tendency toward linear coordination, it retains some residual Lewis acidity. Consequently, it shows a trend to hydrolysis in aqueous solution, as shown in previous work.[8–19] However, not all authors propose the same set of hydrolytic species from methylmercury(II) (Table 1).

From those data, it is hardly possible to know the behaviour of methylmercury in a multicomponent solution sufficiently well to describe the chemical speciation of this compound in natural waters. As was pointed out previously, it is generally recognized that biological activity depends on the chemical form of the metal species (free, complexed, hydrolysed) present in the environment. Thus, studies should be conducted on the chemical speciation of methylmercury in different aqueous ionic media at a wide range of ionic strengths and containing the main constituents of natural waters.

In this first paper a potentiometric study (glass electrode–double liquid junction reference electrode) of the hydrolysis of the CH_3Hg^+ ion, at 25 °C, in sodium perchlorate ($NaClO_4$) ionic media at different ionic strengths (0.1, 0.5, 1.0 and 3.0 mol dm^{-3}) is described. With the stoichiometric formation constant for each hydrolytic species, a thermodynamic model is constructed by MBM.[20,21] This model allows us to know the different species present in the methylmercury–water system and the variation of their presence with pH and ionic strength.

2 EXPERIMENTAL

Reagents and solutions

Methylmercury hydroxide was prepared from methylmercury iodide according to the method of Sneed and Maynard[22] Methylmercury iodide (Strem Chem.; 98%+) was dissolved in methanol (Merck; p.a.) and stirred for 2 h with silver oxide obtained from a mixture of silver nitrate (Fluka; p.a.) and sodium hydroxide (Merck; p.a.). The solid was filtered off and the solution was concentrated by vacuum evaporation at 55 °C. A white solid was formed, which was redissolved in a minimum volume of warm methanol and filtered to eliminate impurities. The solution was reprecipitated by adding dry ether (Merck; p.a.). Later evaporation yielded crystals that were dried in air. The concentration of the aqueous solutions of methylmercuric hydroxide were checked by photometric titration with dithizone.[23]

All other reagents were of analytical grade (from Merck and Fluka), with a purity always greater than 99%, and were used without further purification. The concentration of the sodium perchlorate monohydrate employed as the ionic medium was tested gravimetrically after evaporation of different aliquots at 110 °C. Stock solutions of perchloric acid and sodium hydroxide were standardized against tris(hydroxymethyl)aminomethane and potasium hydrogenphthalate respectively.[24] All the solutions were prepared using Milli-Q water at the corresponding ionic strength (0.1, 0.5, 1.0 or 3.0 mol dm^{-3}).

Ag–AgCl(s) / AgCl(s)–I(mol dm^{-3}) $NaClO_4$ / I(mol dm^{-3}) $NaClO_4$ // Test solution / Glass electrode.

Scheme 1

Apparatus

For photometric titration of the methylmercury solutions, a UV/Vis diode-array Hewlett-Packard HP8452A spectrophotometer was used. The titrated solution was added to the spectrophotometric cells (Hellma 104F-QS, pathlength = 1 cm) with a Gilson Minipuls 2 peristaltic pump.

The potentiometric experiments were carried out by means of an automatic titration system developed in our laboratory,[25] which can control up to three titrations at the same time. The measurements were made with the cell given in Scheme 1, where I is the ionic strength of the solution. The glass electrode (Metrohm 6.0101.100) and the double liquid-junction Ag-AgCl(s) reference electrode (Metrohm 6-0726-100-RC) were connected to a preamplifier in order to adapt the electrical signal to a Hewlett-Packard HP 3421A voltmeter (with a resolution of 5.5 digits) connected to a computer (PC 286). The titrant additions were performed with a Metrohm Dosimat 725 automatic burette with a precision of $\pm 5\ \mu$l, connected to the computer via a RS-232C interface. An oil-bath was used to maintain the temperature of the titration vessel at 25 ± 0.1 °C while dinitrogen (N_2) presaturated in the corresponding ionic strength medium was continuously bubbled in order to avoid the presence of carbondioxide (CO_2) in the solution titrated. Magnetic stirring was employed during the titration.

Procedure

In order to calculate the protonation equilibrium constants, aliquots (70 cm^3) of a solution containing methylmercury (10^{-2}–10^{-4} mol dm^{-3}) a small excess of $HClO_4$ in order to calculate the standard potential (E_0) of the electrolytic cell, and the necessary amount of $NaClO_4$ stock solution to keep the ionic strength constant, were titrated with a $Na(OH^-, ClO_4^-)$ solution at the same ionic strength. After each addition (total = 200), 1 min was allowed to elapse, then a reading was performed every 30 s to a maximum of 20 readings. It was considered that the equilibrium was reached when the standard deviation of the last three measurements was less than 0.05 mV. Each titration took between 10 and 15 hour to complete. At least five titrations were performed at each ionic strength and the methylmercury concentration was varied in order to determine whether polynuclear species were present.

Determination of *h*

Making use of the Nernst equation,[26] the free hydrogen-ion concentration (h) can be calculated from Eqns [1] and [2].

$$E = E_0 + g \cdot \log h + E_i(h) \qquad [1]$$

$$E_j(h) = j_{ac}h + j_{ba}K_w h^{-1} \qquad [2]$$

Therefore, in order to be able to determine h, it is necessary to know the values of K_w (water autoprotolysis constant) and the acid (j_{ac}) and basic (j_{ba}) liquid junction potential coefficients. E_0 is determined for each titration since it may vary from day to day. As the j_{ac}, j_{ba} and K_w values can be considered constant, since the ionic strength was kept constant throughout the titrations,[26] we have used the values for 0.5, 1.0 and 3.0 mol dm^{-3} determined previously.[27] The values for the 0.1 mol dm^{-3} ionic strength were determined by means of ionic medium titrations. First Gran's method[28] was

Table 2 log K_w and the liquid-junction coefficients at different ionic strengths in $NaClO_4$ medium

I (mol dm^{-3})	log K_w	j_{ac} (mV dm^3 mol^{-1})	j_{ba} (mV dm^3 mol^{-1})
0.1	-13.71 ± 0.01	-449 ± 3	681 ± 3
0.5[a]	-13.69 ± 0.01	-103 ± 2	140 ± 1
1.0[a]	-13.75 ± 0.01	-71 ± 2	92 ± 2
3.0[a]	-14.12 ± 0.01	-17 ± 2	69 ± 1

[a] Values taken from Ref 27.

used and later the values were refined numerically by means of the MODEL FUNCTION version[29] of the LETAGROP program.[30] The values used are shown in Table 2.

Once the values of these constants are known and E_0 is calculated for each titration by Gran's method,[28] h can be calculated for each experimental point. Since the equation to calculate the value of h cannot be solved analytically, an iterative (Excel) procedure (the Newton–Raphson method[26]) was used.

3 CALCULATIONS AND RESULTS

The chemical system studied can be described by the following general reaction (Eqn [3]):

$$p\mathrm{CH_3Hg^+} + q\mathrm{OH^-} \leftrightarrow \mathrm{(CH_3Hg)}_p\mathrm{OH}_q{}^{p-q} \qquad [3]$$

The corresponding formation equilibrium constant can be expressed as Eqn [4]

$$^{I}\beta_{pq} = \frac{\left[\mathrm{(CH_3Hg)}_p\mathrm{OH}_q{}^{p-q}\right]}{[\mathrm{CH_3Hg^+}]^p[\mathrm{OH^-}]^q} \qquad [4]$$

where $^{I}\beta_{pq}$ is the stoichiometric equilibrium constant at the corresponding I (ionic strength) and [ ] represents the molar concentration. In a first approximation the composition and the formation constant values were intended to be evaluated graphically by means of the Z function,[26] which is defined as the average number of ligands bound to a central ion (Eqn [5]):

$$Z = \frac{\sum[\mathrm{(CH_3Hg)}_p\mathrm{OH}_q{}^{p-q}]}{C_\mathrm{M}} \qquad [5]$$

This function can be directly calculated by Eqn [6], where H_T and C_M are the total concentrations of protons and methylmercury respectively and h is the free concentration of protons. As it can be seen in Fig. 1, the Z function is dependent on the total concentration of methylmercury, which suggests the formation of polynuclear species involving methylmercury. As polynuclear complexes are formed, numerical treatments were carried out using the BSTAC[31] and STACO[32] programs. These programs minimize for all the N_p experimental points the sum of squared errors U defined in Eqn [7], where X = emf potential in BSTAC and X = volume of titrant added in STACO. These programs allow the detection and correction of any possible systematic errors, e.g. in total concentration of methylmercury or H_T. It is also possible to treat simultaneously all the titrations corresponding to the same ionic strength.

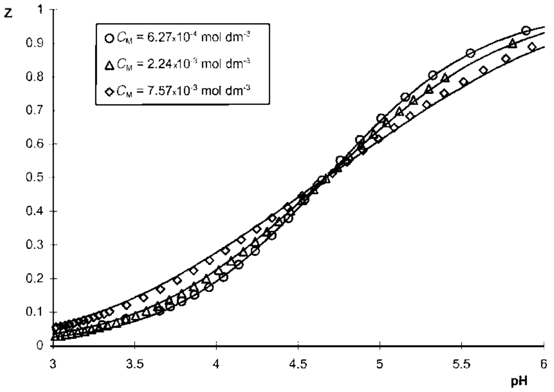

Figure 1 Representation of Z vs. $-\log h$, for $I = 1.0\ \mathrm{mol\ dm^{-3}}$ in $\mathrm{NaClO_4}$ at different methylmercury total concentrations (C_M).

$$Z = -\left[\frac{H_\mathrm{T} - h + K_\mathrm{w}h^{-1}}{C_\mathrm{M}}\right] \qquad [6]$$

$$U = \sum_{N_\mathrm{p}}(X_\mathrm{calc} - X_\mathrm{exp})^2 \qquad [7]$$

Several models were tested with both programs. First, the model with the $\mathrm{CH_3HgOH}$ and $\mathrm{(CH_3Hg)_2OH^+}$ species was processed as it is the one proposed in most of the studies.[11,12,15,18,19] The model with a single complex species $\mathrm{CH_3HgOH}$ was also tried as it has been proposed by numerous authors. Other models including $\mathrm{(CH_3Hg)_3O^+}$ or $\mathrm{CH_3Hg(OH)_2{}^-}$ species were also tested. The results of the sum of squared errors (Eqn [7]) for these models with both programs are summarized in Table 3 for ionic strength $1.0\ \mathrm{mol\ dm^{-3}}$. As can be observed, the simplest model that satisfactorily explains the experimental data is that formed by the neutral $\mathrm{CH_3HgOH}$ and cationic $\mathrm{(CH_3Hg)_2OH^+}$ species, in agreement with some of the previous studies.[11,12,15,18,19] The same set of species explains better the experimental data for the other ionic strengths used in this work.

The proposed values of the stoichiometric formation constants for the two species at the four levels of ionic strengths (Table 4) were set as a compromise between the mean and uncertainty values given by the two numerical programs.

In order to construct a suitable thermodynamic model it is an advantage to have as many

Table 3 Different chemical models tested to explain the experimental data at 1.0 mol dm^{-3} ionic strength together with the equilibrium constants obtained and the sum-of-squares errors for each fit

Model		BSTAC		STACO	
No.	Species	U	log β	U	log β
I	CH_3HgOH	91.3	9.191 ± 0.008	6.7	9.292 ± 0.011
II	$(CH_3Hg)_2OH^+$	75.8	11.003 ± 0.011	12.7	10.994 ± 0.038
III	CH_3HgOH	7.5	9.079 ± 0.001	1.2	9.081 ± 0.006
	$(CH_3Hg)_2OH^+$		11.565 ± 0.002		11.569 ± 0.005
IV	CH_3HgOH	82.5	9.113 ± 0.020	Not adjusted	
	$(CH_3Hg)_3O^+$		22.906 ± 0.057		
V	CH_3HgOH	Not adjusted		Not adjusted	
	$CH_3Hg(OH)_2{}^-$				
VI	CH_3HgOH	383.5	9.15 ± 0.16	Not adjusted	
	$(CH_3Hg)_2OH^+$		10.75 ± 0.18		
	$(CH_3Hg)_3O^+$		14 ± 94.2		

stoichiometric stability constant values at different ionic strengths and in different ionic media as possible. As stated above, the studies on the hydrolysis of methylmercury found in the literature[8–19] have been performed in different ionic media and at unique ionic strengths, so that bibliographic information is not enough to correlate and construct the thermodynamic model. The construction of the thermodynamic model proposed in this work has consequently been performed using only the set of stoichiometric formation constants collected in Table 4.

In general, the different equilibria taking place in the methylmercury(II)–water system can be expressed by Eqn [3] and their thermodynamic stability constants can be written as in Eqn [8], where { } indicates activity and [ ] molar concentration, and γ denotes the molar activity coefficient. Combining Eqns [4] and [8] gives Eqn [9].

$$ {}^0\beta_{pq} = \frac{\{(CH_3Hg)_pOH_q{}^{p-q}\}}{\{CH_3Hg^+\}^p\{OH^-\}^q} = \frac{[(CH_3Hg)_pOH_q{}^{p-q}]\gamma_{(CH_3Hg)_pOH_q{}^{p-q}}}{[CH_3Hg^+]^p\gamma^p_{CH_3Hg^+}[OH^-]^q\gamma^q_{OH^-}} \qquad [8] $$

$$ \log{}^1\beta_{pq} = \log{}^0\beta_{pq} + p\log\gamma_{CH_3Hg^+} - \log\gamma_{(CH_3Hg)_pOH_q{}^{p-q}} + q\log\gamma_{OH^-} \qquad [9] $$

MBM has been successfully employed elsewhere to construct the thermodynamic models of several hydrolysis and complexation equilibria,[33–36] so it has been applied to explain thermodynamic data of mixture of electrolytes.[37] It has been used in this work to evaluate the activity coefficient. According to MBM, the individual activity coefficient of a charged species can be expressed as Eqn [10], where $A = 0.511\ dm^{3/2}\ mol^{-1/2}$, I is the ionic strength on the molar scale, Z_M the charge on the M ion, Z_X that of the ionic species with opposite sign to M and c_X its molarity. The $\dot{B}_{MX}$ term is expressed as Eqn [11], where B_{MX} is the interaction parameter for each ion-pair MX on the molar scale ($dm^3\ mol^{-1}$).

$$ \log\gamma_M = -\frac{AZ_M^2I^{1/2}}{1+I^{1/2}} + \sum_N \dot{B}_{MX}(|Z_M|+|Z_X|)^2\frac{c_X}{4} \qquad [10] $$

$$ \dot{B}_{MX} = \frac{(0.06+0.6B_{MX})|Z_MZ_X|}{\left[1+\left(\frac{1.5}{|Z_MZ_X|}\right)I\right]^2} + B_{MX} \qquad [11] $$

Equation [12] was used to calculate the activity

Table 4 Proposed stoichiometric stability constants for the methylmercury(II)–water system at different ionic strengths in $NaClO_4$ medium at 25 °C

I (mol dm^{-3})	log ${}^1\beta_{11}$	log ${}^1\beta_{21}$
0.1	9.22 ± 0.01	11.63 ± 0.01
0.5	9.10 ± 0.01	11.55 ± 0.01
1.0	9.08 ± 0.01	11.56 ± 0.01
3.0	9.18 ± 0.01	11.80 ± 0.01

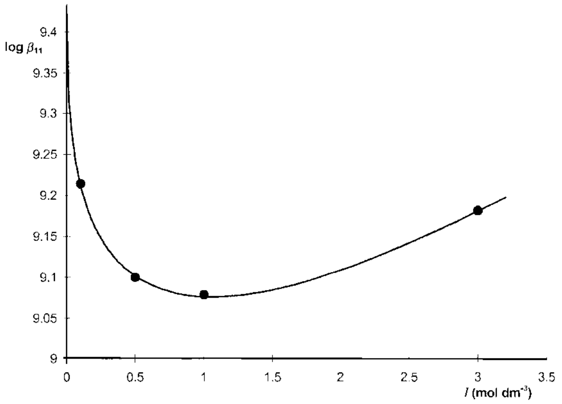

Figure 2 Variation of log β_{11} with the ionic strength in $NaClO_4$ media: —, theoretical function; ●, experimental values.

coefficients of uncharged species, such as methylmercuric hydroxide, where $S_{MX.ionic\ medium}$ is the salt coefficient on the molar scale (dm^{3}mol^{-1}) of the neutral species MX.

$$\log \gamma_{MX} = S_{MX.ionic\ medium} \cdot C_{ionic\ medium} \qquad [12]$$

Combining Eqns [9]–[12], Eqn [13] can then be written for the equilibrium of formation of CH_3HgOH, and Eqn [14] for the equilibrium of formation of $(CH_3Hg)_2OH^+$.

$$\log^1 \beta_{11} = \log^0 \beta_{11} - 2\frac{-AZI^{1/2}}{1+I^{1/2}} + [\dot{B}_{CH_3Hg^+,ClO_4^-} + \dot{B}_{OH^-,Na^+} - S_{CH_3HgOH,NaClO_4}]I \qquad [13]$$

$$\log^1 \beta_{21} = \log^0 \beta_{21} - 2\frac{-AZI^{1/2}}{1+I^{1/2}} + [2\dot{B}_{CH_3Hg^+,ClO_4^-} + \dot{B}_{OH^-,Na^+} - \dot{B}_{(CH_3Hg)_2OH^+,ClO_4^-}]I \qquad [14]$$

From these last two equations, and using all the experimentally determined formation constants, the values of the thermodynamic constants, Bromley's interaction parameters and salt coefficients necessary to construct the corresponding thermodynamic models were determined. The B_{OH^-,Na^+} interaction parameter, necessary for this fit, had been determined previously.[21] This calculation was carried out making use of an Excel spreadsheet (Microsoft Corp., Redmond WA, USA, 1992) and the NLREG program.[38] The following values of thermodynamic constants and interaction parameters were obtained:

$$\log^0 \beta_{11} = 9.433 \pm 0.006$$

$$\log^0 \beta_{21} = 11.841 \pm 0.006$$

$$B_{CH_3Hg^+,ClO_4^-} = -0.0593 \pm 0.0009$$

$$B_{(CH_3Hg)_2OH^+,ClO_4^-} = -0.2382 \pm 0.0009$$

$$S_{CH_3HgOH,NaClO_4} = -0.1075 \pm 0.0010$$

Figures 2 and 3 show the fit between the experimental stoichiometric formation constant values and the theoretical functions proposed by the thermodynamic model.

4 DISCUSSION

This work is the first part of an attempt to construct a thermodynamic model that informs us of the chemical behaviour of methylmercury in the different conditions of pH and ion composition that can be found in natural waters: rivers, lakes, estuaries, and coastal and marine waters.

According to the proposed model the hydrolysis of methylmercury can be explained with the simultaneous presence of three species, two cationic (CH_3Hg^+ and $(CH_3Hg)_2OH^+$) and one neutral (CH_3HgOH), in the range $2 < pH < 8$. The variation of the molar fractions of these species

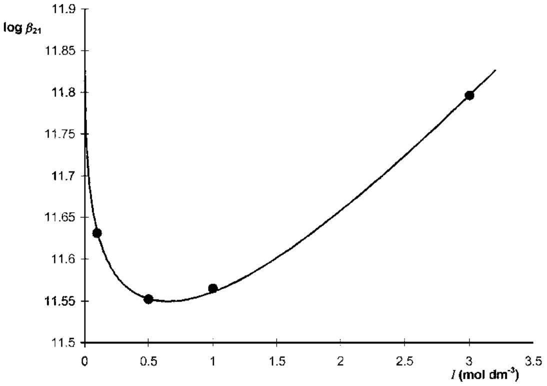

Figure 3 Variation of log β_{21} with the ionic strength in $NaClO_4$ media: —, theoretical function; ●, experimental values.

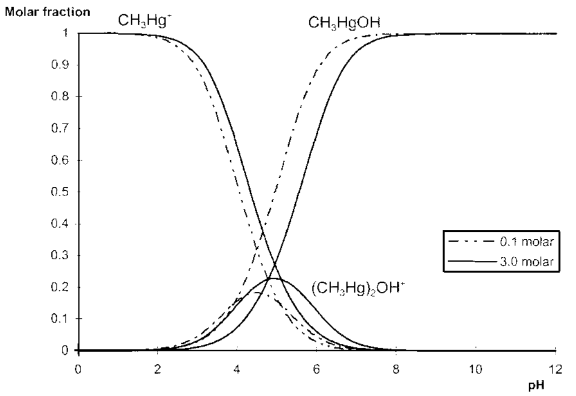

Figure 4 Distribution diagram of methylmercury(II) species as a function of the pH at different ionic strengths and constant methylmercury total concentration ($C_M = 7.5 \times 10^{-3}$ mol dm^{-3}).

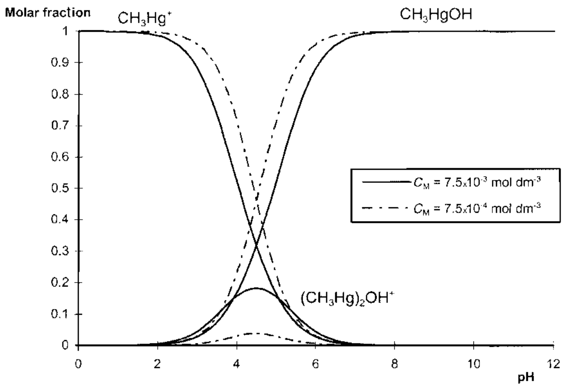

Figure 5 Distribution diagram of methylmercury(II) species as a function of the pH at constant ionic strength (0.1 mol dm^{-3}) and different methylmercury total concentrations.

with the ionic strength and methylmercury total concentration is shown in Figs 4 and 5 respectively for synthetic water samples.

As can be seen, the distribution of the hydrolytic species of methylmercury depends on the pH, the ionic strength and the total concentration. Below 5 ppm total methylmercury, the dimeric species is negligible; that is, in natural water systems only the cationic CH_3Hg^+ and the neutral CH_3HgOH species should be considered. In highly contaminated waters or in soil remediation processes this dimeric species must be important due to its cationic nature.

The ionic strength of the water system under study is another very important variable. Thus, for the same pH, the distribution of the hydrolytic species of methylmercury is expected to be different in river, estuary and coastal waters.

The most important variable is the pH of the waters. In standard continental and marine waters ($pH > 6.5$) the neutral species is more important than the others. But in acidic waters (rivers, lakes, industrial waste waters) the cationic species becomes predominant.

The different behaviour of the hydrolytic species of methylmercury as a function of these three variables can be used to explain adsorption processes in particulate suspended matter or mobility of methylmercury in soils, as well as to design new remediation processes for soil or sediments that contain undesirable amounts of this pollutant. The use of suitable computer programs, such as MINIQL, with an appropriate chemical model will help us to perform these new designs by simulating the effects of the addition of several chemicals to soils or sediments.

In natural waters, anions such as Cl^-, SO_4^{2-} or CO_3^{2-} are present and all of them are complexing agents of methylmercury[39]—thus the distribution map shown in Fig. 5 is expected to shift to the basic region of pH. According to MBM, the activity coefficients of the hydrolytic species of methylmercury depend on the concentration of both the anions in the natural waters (for the cationic species, CH_3Hg^+ and $(CH_3Hg)_2OH^+$) and the cations (for possible anionic species such as complexes CH_3HgL^- with L^{2-} ligands as suggested by Rabenstein).[39] The quantitative effects of these interactions are computed by the B_{MX} parameters. The problem arises when both interaction and complex formation are present at the same time. For example, the interaction between CH_3Hg^+ and Cl^- is calculated by the parameter but there is a complexation reaction between the two ions.[39] Thus, $B_{CH_3Hg^+}$ cannot be evaluated from experimental data like those shown in this work albeit using chloride media, because the complexation effect of Cl^- will be greater than the specific interaction on the cationic CH_3Hg^+ species.

Work is now in progress to define the complexation of CH_3Hg^+ with the major anions present in natural waters in $NaClO_4$ media with variable ligand concentration. Once the formation constants of the complexes involved are calculated, the interaction parameters $B_{CH_3Hg^+,L^{n-}}$ will be determined experimentally from experiments in Na_nL medium.

Acknowledgements We thank the University of the Basque Country for financial support (UPV 171.310-EA 160/97). J. Sanz is grateful to the MEC for his pre-doctoral fellowship.

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