APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 339–346

Complexation of CH_3Hg^+ with chloride, sulfate and carbonate in $NaClO_4$: construction of thermodynamic models

J. Sanz*, J. C. Raposo, A. de Diego and J. M. Madariaga

Kimika Analitikoaren Saila, Euskal Herriko Unibertsitatea (UPV/EHU), PK 644, E-48080 Bilbao, Spain

Received 13 November 2000; Revised 26 February 2002; Accepted 3 March 2002

The complexation of CH_3Hg^+ with major ions present in sea and estuary waters (Cl^-, $SO_4{}^{2-}$ and $CO_3{}^{2-}$) was studied potentiometrically in an $NaClO_4$ medium in the ionic strength range 0.1–3.0 mol dm^{-3} at 25 °C. The potentiometric data, treated with non-linear least squares computer programs, led us to establish the formation of the species CH_3HgCl in equilibrium with chloride, $CH_3Hg(SO_4)^-$ species with sulfate and no complex with carbonate. The stoichiometric stability constants obtained at the different ionic strengths were correlated by means of the modified Bromley methodology (MBM) to determine the corresponding thermodynamic constants and interaction parameters. This study is the second of a series designed to simulate, using the MBM thermodynamic model, the behaviour of methylmercury in different conditions of sea and estuary waters. In the first study of the series, the hydrolysis equilibria of methylmercury in $NaClO_4$ ionic media were established. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: methylmercury; complexation; equilibrium; chloride; sulfate; carbonate; potentiometric study; specific ion interaction theory; thermodynamic model

INTRODUCTION

The high volatility of mercury and its compounds, and their accumulative and persistent character in the environment, have been the principal causes of the growth in social and scientific interest in mercury biogeochemistry in the last few decades. Although the use of this element and its organic compounds has decreased significantly, a recent study[1] has estimated the total anthropogenic emissions of mercury to the atmosphere as about 3600–4500 tons per year. The behaviour of mercury and its different compounds in the environment is controlled by several physicochemical mechanisms;[2,3] methylation, adsorption, deposition, complexation, evaporation, etc. are some of the processes that determine the atmospheric mercury cycle and that are necessary to study in order to gain a complete knowledge of the real distribution of mercury in the environment.

Furthermore, the toxicity of mercury compounds varies considerably, necessitating the determination of individual species to assess environmental impact accurately. Methylmercury is considered by the World Health Organization and the United Nations Chemist Security International Program as the most hazardous species of all the mercury compounds.[4]

Many studies have been made in the last 15 years on toxicity and methylmercury analytical determination, but few studies have attempted to establish the different equilibria that control the behaviour of methylmercury in natural waters. As has been previously established,[5–7] studies on the complex formation of methylmercury and the ligands that are commonly found in nature are of importance for a better understanding of their chemical behaviour in the ecological medium.

Thermodynamic models and specific interaction theories have been successfully used in many chemical systems to determine the species and concentrations present in different sets of conditions and media. For example, calculations of different nickel species concentrations, which control some processes in an automated plant for recovering metals from electroplating baths, have been performed using the modi-

---

*Correspondence to: J. Sanz, Kimika Analitikoaren Saila, Euskal Herriko Unibertsitatea (UPV/EHU), PK 644, E-48080 Bilbao, Spain.
E-mail: qabsalaj@lg.ehu.es
Contract/grant sponsor: University of the Basque Country; Contract/grant number: UPV 171.310-EA 160/97.

fied Bromley methodology (MBM)[8,9] in very variable media.[10] The MBM has also been applied to the determination of fluoride concentrations in the presence of aluminium by potentiometric measurements, a very common problem in the industrial control of fluorine production.[11] In dealing with environmental problems, MBM has been used for speciation of arsenic in natural waters,[12] and has show how the dissolved arsenic is controlled by the iron concentration in rivers and by the magnesium concentration in estuary waters, due to the formation of iron and magnesium arsenate precipitates respectively.

In order to determine the methylmercury species present in the variable conditions of different multicomponent natural waters using thermodynamic models, it is first necessary to perform systematic studies of these equilibria taking into account the ionic strength. Estimates of activity coefficients of species can be obtained empirically from experimental data by considering theories of specific ion interactions. Apart from a recent study by Sammartano and co-workers,[5] thermodynamic parameters reported on complex formation studies already carried out refer only to a single ionic medium and a single value of ionic strength.[13–17]

In this paper a potentiometric study (glass electrode–double liquid-junction reference electrode) on the complexation of the CH_3Hg^+ with Cl^-, SO_4^{2-} and CO_3^{2-} at 25 °C, in $NaClO_4$ ionic medium at different ionic strengths (0.1, 0.5, 1.0 and 3.0 mol dm^{-3}) is reported. The experimental data obtained is used to construct a thermodynamic model using the MBM. This model will help us to estimate the distribution of methylmercury in the different species that can be formed with anions present in natural environments, as a function of the composition of those chemical systems.

EXPERIMENTAL

Reagents and solutions

Methylmercury was used as hydroxide and was prepared and isolated from methylmercury iodide (Merck, p.a.) according to literature methods.[13,18] All other reagents were of analytical grade (from Merck and Fluka), with a purity always >99.5%, and were used without further purification. The concentration of the sodium perchlorate employed as ionic medium was tested gravimetrically after evaporation of different aliquots at 110 °C. The concentration of the aqueous methylmercuric hydroxide in solution was checked by photometric titration with dithizone.[19] Stock solutions of perchloric acid and sodium hydroxide were standardized against tris(hydroxymethyl)-aminomethane and potassium hydrogenphthalate respectively.[20] All the solutions were prepared using Milli Q water ($R < 18\ \Omega\,cm^{-1}$) and grade A glassware.

Safety note: organomercury compounds, and especially methylmercury, are highly toxic. They can cause neurological damage and kidney malfunction. Direct contact with the skin can lead to death. Precautions and adequate clothing are necessary when manipulating the reagent. Sodium perchlorate is explosive in contact with hot surfaces. Solutions should be prepared with caution.

Apparatus

An automatic titration system developed in our laboratory,[21] which can control up to three titrations at the same time, was used in the potentiometric experiments. A glass electrode (Metrohm 6.0101.100) and a double liquid-junction Ag–AgCl(s) reference electrode (Metrohm 6-0726-100-RC) were used, as in Scheme 1, where I is the ionic strength of the solution.

$$\text{Ag–AgCl(s)}|\text{AgCl(s)}–I(\text{mol dm}^{-3}\ \text{NaClO}_4\ |\ I(\text{mol dm}^{-3})\text{NaClO}_4\ ||\ \text{Test solution}\ |\ \text{Glass electrode}$$

Scheme 1.

The electromotive force (EMF) measurements were recorded via a computer by means of a preamplifier in order to adapt the electrical signal to a Hewlett-Packard HP 3421A voltmeter. A Metrohm Dosimat 725 automatic burette with a precision of ±5 μl, was used to perform the additions. An oil bath was used to thermostat the titration vessel at 25.0 ± 0.1 °C and CO_2 was removed by bubbling nitrogen (saturated at the corresponding ionic strength to avoid evaporation of the ionic medium) through the solution. Magnetic stirring was employed during the titration. The photometric titration of the methylmercury was performed with a UV–VIS diode-array Hewlett-Packard HP8452A spectrophemeter; the titrated solution was brought into the spectrophotometric cells (Hellma 104F-QS; path length, 1 cm) using a Gilson Minipuls 2 pump.

Procedure

Higher concentrations of all the components with regard to those found in natural systems were used in order to establish more carefully all the possible equilibria of methylmercury.

Two different kinds of titration were performed. In order to calculate the chloride and sulfate complexes, a solution (70 cm^3) containing methylmercury (10^{-2}–10^{-4} mol dm^{-3}), different amounts (10^{-1}–10^{-4} mol dm^{-3}) of the corresponding sodium salt (NaCl or Na_2SO_4), a slight excess of $HClO_4$ to calculate the standard potential E_0 of the electrolytic cell, and the necessary amount of $NaClO_4$ stock solution ($0.1 \leq I \leq 3.0$ mol dm^{-3}) to keep the ionic strength constant, were titrated with $Na(OH^-,ClO_4^-)$ solution at the same ionic strength. After each addition (up to 100 additions for each titration) a waiting time of 1 min was allowed to elapse, followed by an EMF reading every 30 s up to a maximum of 20. Equilibrium was considered to have been reached when the standard deviation of the last three potential measurements was less than 0.05 mV. Each titration took between 10

Table 1. Different chemical models tested to explain the chloride and sulfate experimental data at ionic strength 1.0 mol dm^{-3} together with the sum of squared errors for each fit and the equilibrium constants obtained. In all these different models, CH_3HgOH and $(CH_3Hg)_2OH^+$ are always included; $\log \beta_{CH_3}HgOH = -4.671$[6] and $\log \beta_{(CH_3}Hg)_2OH^+ = -2.185$[6] were used as known and constants parameters for this ionic strength

Chloride				Sulfate			
Model		BSTAC		Model		BSTAC	
No.	Species	U	$\log \beta$	No.	Species	U	$\log \beta$
I	CH_3HgCl	72.9	5.17	I	$CH_3Hg(SO_4)^-$	32.9	1.41
II	$CH_3HgCl_2^-$	86.4	6.28	II	$CH_3Hg(HSO_4)$	41.2	2.63
III	$CH_3HgCl_3^{2-}$	90.7	7.01	III	$CH_3Hg(SO_4)^-$	37	2.95
					$CH_3Hg(HSO_4)$		5.72
IV	$CH_3HgClOH^-$	no fit		IV	$(CH_3Hg)_2SO_4$	no fit	
V	CH_3HgCl	no fit		V	$CH_3Hg(SO_4)^-$	no fit	
	$CH_3HgCl_2^-$				$(CH_3Hg)_2SO_4$		

and 15 h to complete. At least five titrations were performed at each ionic strength and the methylmercury concentration and the complexation agent were varied to determine if polynuclear species were present.

The titrations to calculate the carbonate complexes were carried out with the same methylmercury range of concentrations and different amounts of Na_2CO_3 but with a slight excess of NaOH to take the pH to the alkaline zone. The solutions were titrated with the $(Na^+,H^+)ClO_4$ solution until pH 8.5 in order to avoid the formation of $CO_2(aq)$. The procedure and conditions of equilibrium were exactly the same as used to carry out the calculations for the chloride and sulfate complexes.

Calculations

The free hydrogen-ion was calculated using Eqns (1) and (2)

$$E = E_0 + g \log h + E_j(h) \quad (1)$$

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

All the parameters needed (E_0, water autoprotolysis constant K_w, and the acid (j_{ac}) and base (j_{ba}) liquid junction potential coefficients) were calculated previously by means of ionic medium titrations and were refined numerically by means of the MODEL FUNCTION version[22] of the LETAGROP program.[23] All these calculations are explained in depth elsewhere.[6] Concentration and formation constants are given on a molar scale.

To calculate the complex formation constants, numerical treatment was carried out using the BSTAC[24] and STACO[25] programs. These programs minimize for all the N_p experimental points the sum of square errors U defined by Eqn. (3), where X is the EMF potential in BSTAC or the volume of titrant added in STACO.

$$U = \sum_{N_p} (X_{calc} - X_{exp})^2 \quad (3)$$

RESULTS AND DISCUSSION

Chloride and sulfate species

For each experimental data set, several chemical models were tested with both BSTAC and STACO programs. In all these different models, the CH_3HgOH and $(CH_3Hg)_2OH^+$ species that were stated as the products of methylmercury hydrolysis in previous work[6] are always included. As an example, results for the data at 1.0 mol dm^{-3} ionic strength are summarized in Table 1. As can be seen, the best fit is obtained by considering only the formation of 1:1 complexes

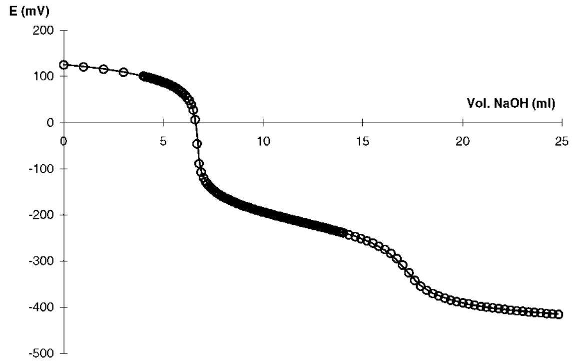


Figure 1. Titration of 8.7 × 10^{-3} mol dm^{-3} CH_3HgOH and 2.42 × 10^{-2} mol dm^{-3} NaCl with NaOH in 1.0 mol dm^{-3} $NaClO_4$ (○, experimental values; —, values calculated by BSTAC with the formation of the single species CH_3HgCl).

Table 2. Calculated stoichiometric stability constants (molar scale) for the methylmercury–chloride and methylmercury–sulfate systems at different ionic strengths in $NaClO_4$ medium at 25 °C. For both systems the corresponding formation constant values of CH_3HgOH and $(CH_3Hg)_2OH^+$, at the given ionic strength value, are considered[6]

	$\log {}^{I}\beta_{11}$ (CH_3HgCl)		$\log {}^{I}\beta_{11}$ ($CH_3Hg(SO_4)^-$)	
I (mol dm^{-3})	BSTAC	STACO	BSTAC	STACO
0.1	5.28 ± 0.01	5.28 ± 0.01	1.59 ± 0.02	1.61 ± 0.02
0.5	5.18 ± 0.01	5.20 ± 0.01	1.40 ± 0.02	1.37 ± 0.04
1.0	5.17 ± 0.01	5.17 ± 0.01	1.41 ± 0.03	1.45 ± 0.04
3.0	5.31 ± 0.01	5.29 ± 0.01	1.74 ± 0.04	1.80 ± 0.07

[Eqn. (4)] for both the chloride and sulfate.

$$CH_3Hg^+ + X^- \rightleftharpoons CH_3HgX \quad (\text{where } X = Cl^- \text{ and } SO_4{}^{2-}) \tag{4}$$

As an example, Figure 1 shows the agreement between experimental and calculated data for the titration of CH_3HgOH and NaCl with NaOH in 1.0 mol dm^{-3} $NaClO_4$. The same results were obtained for the other ionic strengths and other methylmercury concentrations investigated in this work. The formation of the HSO_4^- complex in the sulfate system was also considered, using the stability constant values reported in the literature.[26,27] The results obtained at each ionic strength using both programs are shown in Table 2.

Tables 3 and 4 summarize the proposed species and formation constant values reported by other authors. As can be seen, the stoichiometry of the complex species of methylmercury agrees with that suggested previously,[5,13–17] but the formation constant values depend not only on the ionic strength but also on the composition of the ionic medium.

Table 3. Stoichiometric stability constants found in the literature for the methylmercury–chloride equilibrium

I (mol dm^{-3})	T (°C)	$\log {}^{I}\beta_{11}$	Ref.
0	25	5.45	13
0.1 $NaNO_3$	20	5.25	14
0.1 KNO_3	25	4.90 ± 0.03	15
1.0 $NaClO_4$	25	5.32 ± 0.09	16
0.1 NaCl	25	5.25 ± 0.03	5
0.25 NaCl	25	5.19 ± 0.02	5
0.5 NaCl	25	5.16 ± 0.02	5
1.0 NaCl	25	5.13 ± 0.03	5
2.0 NaCl	25	5.14 ± 0.03	5
3.0 NaCl	25	5.22 ± 0.04	5

Table 4. Stoichiometric stability constants found in the literature for the methylmercury–sulfate equilibrium

I (mol dm^{-3})	T (°C)	$\log {}^{I}\beta_{11}$	Ref.
0.7 Na_2SO_4	25	0.94	17
0.09 Na_2SO_4	25	2.54 ± 0.04	5
0.16 Na_2SO_4	25	2.51 ± 0.04	5
0.25 Na_2SO_4	25	2.51 ± 0.05	5
0.36 Na_2SO_4	25	2.52 ± 0.05	5
0.49 Na_2SO_4	25	2.55 ± 0.05	5
0.64 Na_2SO_4	25	2.59 ± 0.05	5
0.81 Na_2SO_4	25	2.63 ± 0.07	5
1.00 Na_2SO_4	25	2.68 ± 0.07	5

The values calculated for the methylmercury–chloride complex are in agreement with the values reported in the literature, mainly with the recent Sammartano and co-workers study,[5] which is the only systematic study of the influence of ionic strength on the value of the stoichiometric constants. As can be seen, the values in chloride media are slightly lower than in perchlorate, as can be expected from the behaviour of other metal–ligand equilibria.[28–32]

In other ways, the complexation data proposed for the sulfate complex are significantly divergent with the data found by Sammartano and co-workers[5] (Table 4). This divergence can be easily explained by the use in the Sammartano model of an additional complex, the formation of the ionic species $NaSO_4^-$. In the present work this labile complex is not considered as a species, but only as an ionic interaction between Na^+ and $SO_4{}^{2-}$. The other stoichiometric constant value taken from the literature ($\log {}^{1}\beta_{11} = 0.94$ in 0.7 mol dm^{-3} Na_2SO_4),[17] taking into account that the ionic medium is different, is in agreement with the value proposed in the present work.

Dependence on ionic strength was taken into account by using a Debye–Hückel-type equation, which has been successfully employed to construct thermodynamic models of various hydrolysis and complexation equilibria,[28–32] and to explain thermodynamic data of mixtures of electrolytes.[33] In the MBM the individual activity coefficient of a charged species is expressed by Eqn. (5) where $A = 0.511$ dm$^{3/2}$ mol$^{-1/2}$, I is the ionic strength on the molar scale, Z_M the charge of the M ion, Z_X that of the ionic species with opposite sign to M and c_X its molarity.

$$\log \gamma_M = -\frac{AZ_M^2 I^{1/2}}{1 + I^{1/2}} + \sum_X \dot{B}_{MX}(|Z_M| + |Z_X|)^2 \cdot \frac{c_X}{4} \tag{5}$$

$\dot{B}_{MX}$ is expressed by Eqn. (6), where B_{MX} is the interaction parameter proposed by Bromley for each ion pair MX on the molar scale (mol dm^{-3}).

$$\dot{B}_{MX} = \frac{(0.06 + 0.6B_{MX})|Z_M Z_X|}{\left[1 + \left(\frac{1.5}{|Z_M Z_X|}\right)I\right]^2} + B_{MX} \qquad (6)$$

To calculate the activity coefficients in the case of uncharged species, as the methylmercuric chloride, the MBM uses the expression in Eqn. (7), where $S_{MX,\text{ionic medium}}$ is the salt coefficient on the molar scale (dm^3 mol^{-1}) of the neutral species MX. Equation (7) is similar to that of Long and McDevit.[34]

$$\log \gamma_{MX} = S_{MX,\text{ ionic medium}} c_{\text{ionic medium}} \qquad (7)$$

In general, the different equilibria taking place between methylmercury and chloride or sulfate can be described by Eqn. (4) and their thermodynamic stability constants can be written as in Eqn. (8), where $^\circ\beta_{pq}$ is the thermodynamic stability constant, { } indicates activity, [ ] molar concentration and γ denotes the molar activity coefficient.

$$^\circ\beta_{pq} = \frac{\{(CH_3Hg)X\}}{\{CH_3Hg^+\}\{X\}} = \frac{[(CH_3Hg)X]\gamma_{CH_3HgX}}{[CH_3Hg^+]\gamma_{CH_3Hg^+}[X]\gamma_X} \qquad (8)$$

Combination of Eqns (5–8) gives the expression in Eqn. (9) for the chloride equilibrium and in Eqn. (10) for the sulfate equilibrium, in which $\dot{B}_{MX}$ are the functions of the corresponding Bromley terms described in Eqn. (6).

$$\begin{aligned}\log^I \beta_{11} = {} & \log^\circ \beta_{11} - 2\frac{-AZI^{1/2}}{1+I^{1/2}} \\ & + \left[\dot{B}_{CH_3Hg^+,ClO_4^-} + \dot{B}_{Cl^-,Na^+} - S_{CH_3HgCl,NaClO_4}\right]I \qquad (9)\end{aligned}$$

$$\begin{aligned}\log^I \beta_{11} = {} & \log^\circ \beta_{11} - 4\frac{-AZI^{1/2}}{1+I^{1/2}} \\ & + \left[\dot{B}_{CH_3Hg^+,ClO_4^-} - \dot{B}_{CH_3HgSO_4^-,Na^+}\right]I + \left[\dot{B}_{SO_4^{2-},Na^+}\right]\frac{9}{4}I \qquad (10)\end{aligned}$$

By using the experimentally determined formation constants (Table 2) and making use of the nonlinear regression analysis program NLREG[35] (with the B_{Na^+,Cl^-}, $B_{Na^+,SO_4^{2-}}$ and $B_{CH_3Hg^+,ClO_4^-}$ interaction parameters necessary for this fit having already been determined previously[6,7]) the values of the thermodynamic constants, two Bromley interaction parameters and the salts' coefficients necessary to construct the corresponding thermodynamic models were thus determined. Those values are as follows:

$$\log^\circ \beta_{11} = 5.50 \pm 0.02 \quad \text{for} \quad CH_3Hg^+ + Cl^- \rightleftharpoons CH_3HgCl$$

$$\log^\circ \beta_{11} = 2.00 \pm 0.02 \quad \text{for} \quad CH_3Hg^+ + SO_4{}^{2-} \rightleftharpoons CH_3HgSO_4{}^-$$

$$S_{CH_3HgCl,NaClO_4} = -0.067 \pm 0.004$$

$$B_{CH_3HgSO_4^-,Na^+} = -0.330 \pm 0.004$$

Figures 2 and 3 show the fit between the proposed stoichiometric formation constant values and the theoretical functions. As can be seen, the thermodynamic models explain satisfactorily all the formation constant values.

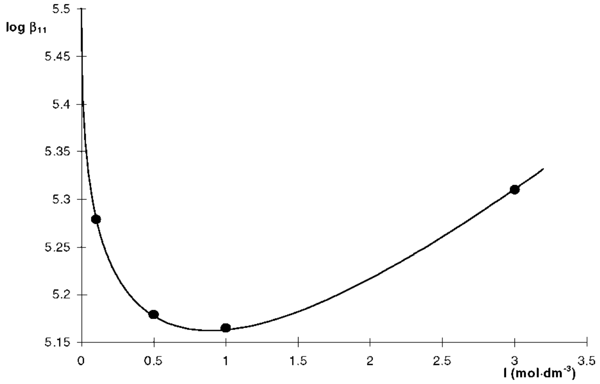


Figure 2. Variation of log β_{11} for the CH_3HgCl species with the ionic strength in $NaClO_4$ media: (—) theoretical function (MBM); (●) experimental values.

Carbonate species

An appropriate treatment of the experimental data requires the use of the carbonate acid–base stoichiometric constants at the ionic strengths of the work for use in the calculations of the methylmercury–carbonate complexes. As has been described in the Experimental section, the study has been performed in the alkaline zone in order to eliminate errors in the total concentration of carbonate which occur at pH values below 8.5 due to the equilibria described in Eqns (11) and (12).

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad (11)$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \qquad (12)$$

In the pH working range, the chemical model for carbonate only requires the use of the equilibrium described in Eqn. (13).

$$HCO_3{}^- \rightleftharpoons CO_3{}^{2-} + H^+ \qquad (13)$$

The thermodynamic model of this equilibrium in $NaClO_4$

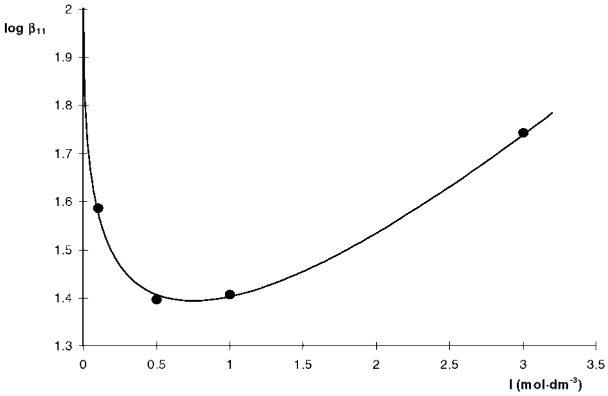


Figure 3. Variation of log β_{11} for the $CH_3HgSO_4^-$ species with the ionic strength in $NaClO_4$ media: (—) theoretical function (MBM); (●) experimental values.

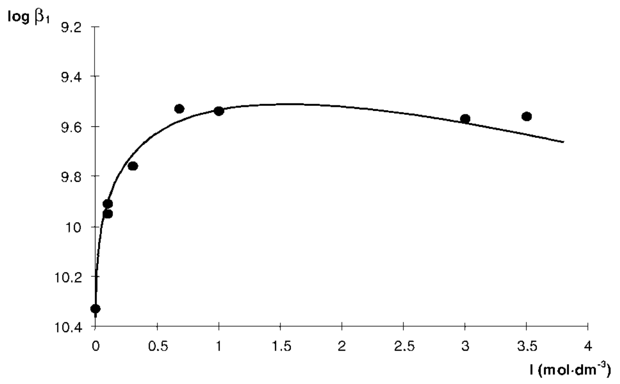


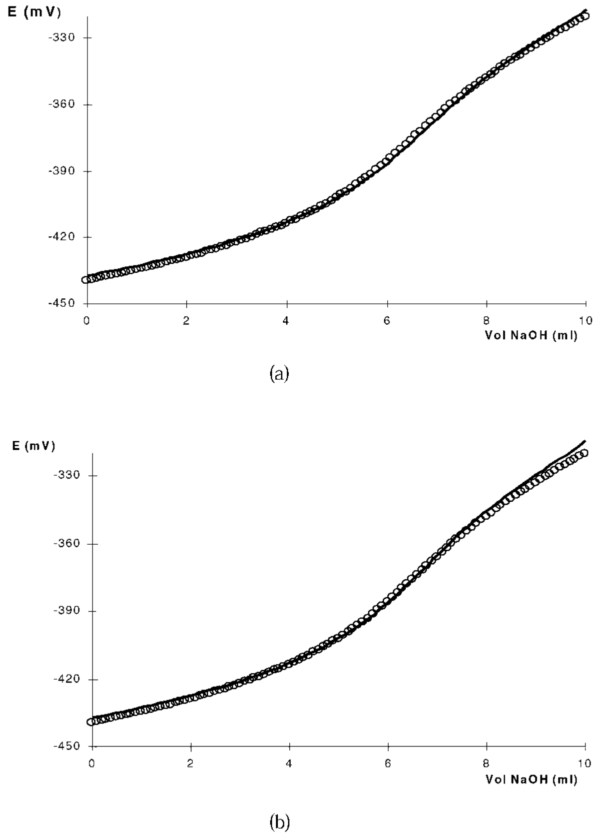
Figure 4. Values of the experimental (●) log β_1 obtained from literature together with the theoretical function (—) predicted by the MBM thermodynamic model for the $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ equilibrium.

Table 5. Proposed stoichiometric stability constants for $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ equilibrium obtained using the MBM model at different ionic strengths in $NaClO_4$

I (mol dm^{-3})	log $^I\beta_1$ ($CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$)
0.1	9.901
0.5	9.626
1.0	9.535
3.0	9.587

Table 6. Different chemical models tested to explain the carbonate experimental data at ionic strength 1.0 mol dm^{-3} together with the sum of square errors for each fit and the equilibrium constants obtained (log $\beta_{HCO_3^-}$ = 9.535 (present work), log β_{CH_3HgOH} = −4.671,[6] log $\beta_{(CH_3Hg)_2OH^+}$ = −2.185[6] as known and constant parameters)

Model		BSTAC	
No.	Species	U	logβ
I	HCO_3^- CH_3HgOH $(CH_3Hg)_2OH^+$	67.3	
II	HCO_3^- CH_3HgOH $(CH_3Hg)_2OH^+$ $(CH_3HgCO_3)^-$	294	 −2.70 ± 0.05
III	HCO_3^- CH_3HgOH $(CH_3Hg)_2OH^+$ $(CH_3HgCO_3)^-$ $(CH_3HgOHCO_3)^{2-}$	272	 −1.89 ± 0.09 14.37 ± 0.16



(a)

(b)

Figure 5. Titration of methylmercury (8 × 10^{-3} mol dm^{-3}) and carbonate (2.4 × 10^{-2} mol dm^{-3}) with $HClO_4$ in 1.0 mol dm^{-3} $NaClO_4$: (a) experimental data, — data predicted by SOLGASWATER using only the hydroxide species; (b) experimental data, — data predicted by SOLGASWATER also using in the model the carbonate species $(CH_3HgCO_3)^-$ as proposed by Rabenstein *et al.*[12] (log $^I\beta_{11}$ = 6.10 in Na_2SO_4, ionic strength <1.0 mol dm^{-3}).

ionic medium was constructed by means of the MBM,[8,9] using the literature data[36–43] and some interaction parameters obtained previously.[16] The correlation between the stoichometric constants and ionic strength is shown in Figure 4. The corresponding calculated stoichiometric constant values in $NaClO_4$ are summarized in Table 5.

With the calculated stoichiometric formation constants of the carbonate protonation as known parameters, together with the hydrolytic equilibria of methylmercury, several chemical models of carbonate complexes were tested in an attempt to explain the experimental data. As shown in Table 6 (data for the 1.0 mol dm^{-3} ionic strength), no improvements are detected in the fit by introducing different methylmercury–carbonate complexes. Other chemical models have been tested, but the results obtained were always worse that those already mentioned. This is not in agreement with the only study found in literature that reports on carbonate complex studies.[17] The proton mag-

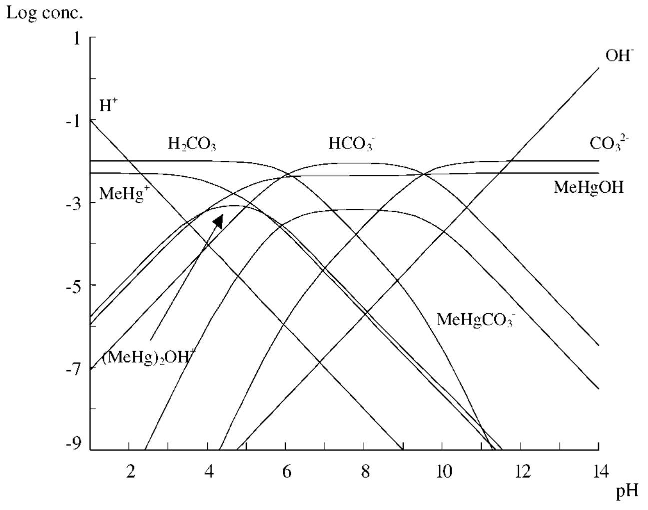


Figure 6. Theoretical logarithmic diagram of methylmercury species as a function of the pH at 25 °C and constant ionic strength ($NaClO_4$, 0.1 mol dm^{-3}) also using in the model the carbonate species $(CH_3HgCO_3)^-$ proposed by Rabenstein *et al.*[17] (log $^1\beta_{11} = 6.10$ in Na_2SO_4, ionic strength <1.0 mol dm^{-3}; $c_{CH_3Hg} = 5 \times 10^{-3}$ mol dm^{-3}, $c_{CO_3} = 10^{-2}$ mol dm^{-3}).

netic resonance and Raman spectroscopic studies of methylmercury complexes of inorganic anions carried out by Rabenstein *et al.*[17] led to a stoichiometric constant value for a 1:1 complex of log $^1\beta_{11} = 6.10$ in Na_2SO_4 of ionic strength <1.0 mol dm^{-3}.

A comparison between the experimental data and two simulations of the potentiometric titration, achieved using the computer program SOLGASWATER,[44] one without a methylmercury–carbonate complex (Figure 5a) and the other with the complex reported by Rabenstein *et al.*[17] (Figure 5b), shows a better fit for the simulation without the carbonate complex, mainly in the last part of the titration curve–where it is supposed to exist as the complex according to Rabenstein *et al.*[17] (Figure 6). So, in the conditions of this study, no carbonate complexes are necessary to explain the experimental data better. This result is in agreement with the conclusions of Sammartano and co-workers,[5] who established that no carbonate complex is formed in natural waters.

Speciation of methylmercury in natural waters

The thermodynamic models proposed here to explain the complexation of methylmercury with chloride, sulfate and carbonate, and that were proposed previously for the hydrolysis of methylmercury,[6] constitute excellent tools to simulate the chemical behaviour of methylmercury in aquatic natural systems.

For example, some of the results presented in the present work, together with other studies on mercury complexation,[45,46] can be used to explain mercury methylation dependence on pH and salinity.[7,47] The study of Compeau and Bartha[7] established a negative relationship between methylation of mercury in sediments with an increase in salinity. A decrease in methylation in carbonate medium in comparison with chloride media is also reported. Those authors explain this decrease by the formation of an $HgCO_3$ complex that inhibits methylation. This is not fully true, because it is well established that in natural waters, and especially in estuarine or sea waters, chloride complexes of mercury(II) are more stable than carbonate complexes.[45,46] The increase in methylation in chloride media compared with carbonate media can be explained by taking into account the formation of a methylmercury–chloride complex that displaces the reaction towards methylation. In carbonate media there is no complex to displace the reaction.

In a general sense, we can conclude that the aqueous species and solid forms of chemical elements in natural

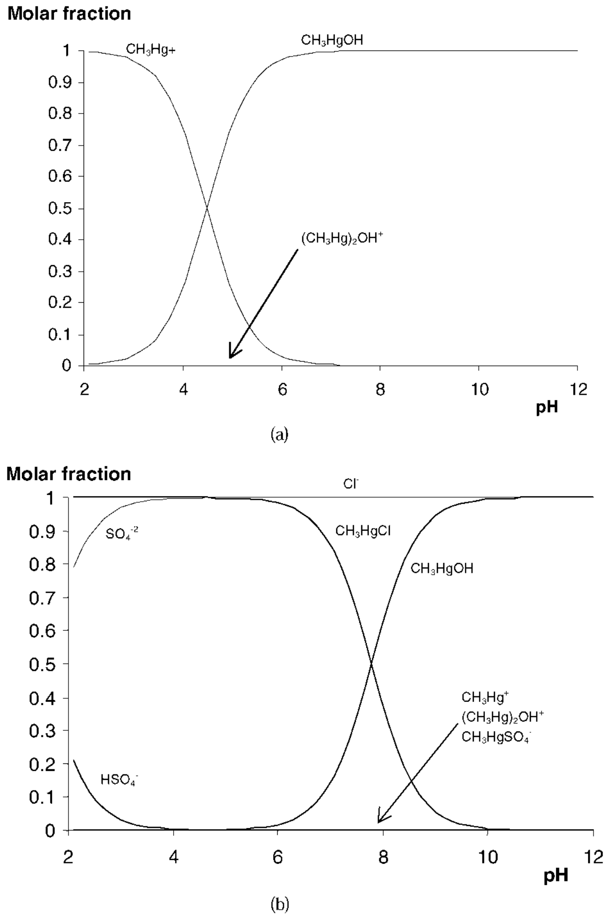


Figure 7. Distribution diagram of methylmercury species as a function of the pH at 25 °C and constant ionic strength ($NaClO_4$, 0.125 mol dm^{-3}): (a) in a water sample without any other salt ($c_{CH_3Hg} = 10^{-8}$ mol dm^{-3}, ~2 μg l^{-1}); (b) in a water sample with Cl^- and SO_4^{2-} ($c_{CH_3Hg} = 10^{-8}$ mol dm^{-3}, ~2 μg l^{-1}, $c_{Cl} = 10^{-2}$ mol dm^{-3}, $c_{SO_4} = 5 \times 10^{-3}$ mol dm^{-3}).

aqueous systems are typically established by the specific local and chemical environment of the system. The chemical context that determines the specific distribution of species of an element is system dependent. In addition, the biological, chemical, and physical characteristics of such natural systems vary in time and space. To appreciate the importance of the species formed with the main salts present in natural waters, two molar fraction diagrams have been constructed using the MEDUSA program,[48] and employing the stability constants proposed in this and previous studies[6] (Figure 7). As can be observed in this figure, in the pH range of most important natural waters (freshwater pH 7.5, seawater pH 8.2) methylmercury is hydrolysed, but in the presence of Cl^- and SO_4^{2-} anions, high percentages of the complexes are formed. Therefore, it is necessary to know the real conditions of the natural water (pH, salinity, chloride and sulfate content, etc.) in order to predict exactly the distribution of methylmercury species.

Acknowledgements

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

REFERENCES

1. Fitzgerald WF and Mason RP. The global mercury cycle: oceanic and anthropogenic aspects. In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*, Baeyens W, Ebinghans R, Vasiliev O (eds). NATO-ASI Series 2, Environment, vol. 21. Kluwer: Dordrecht, The Netherlands, 1996.
2. Kester DR. Chemical species in marine and estuarine systems. In *The Importance of Chemical "Speciation" in Environmental Processes*, Bernhard E, Brinckman FE, Sadler PJ (eds). Springer-Verlag: Berlin, 1986; 275–300.
3. Craig PJ. Organomercury compounds in the environment. In *Organometallic Compounds in the Environment*, Craig P (ed.). Longman Group: Harlow. London, UK, 1986; 65–110.
4. *Environmental Health Criteria 101: Methylmercury*. World Health Organization: Geneva, 1990.
5. De Robertis A, Foti C, Patanè G and Sammartano S. *J. Chem. Eng. Data* 1998; **43**: 957.
6. Sanz J, Raposo JC and Madariaga JM. *Appl. Organomet. Chem.* 2000; **14**: 499.
7. Compeau G and Bartha R. *Bull. Environ. Contam. Toxicol.* 1983; **31**: 486.
8. Bromley LA. *Am. Inst. Chem. Eng. J.* 1973; **13**: 313.
9. Borge G, Castaño R, Carril MP, Corbillón MS and Madariaga JM. *Fluid Phase Equilibria* 1996; **121**: 85.
10. Henstock ME and Skov HR. *Advances in Recovery and Recycling*. Hexagon Ltd: Copenhagen, 1993.
11. Corbillón M. *Determination of total fluoride in high aluminium samples with ion selective electrodes*. Ph.D. Thesis, University of the Basque Country, Bilbao, 1997.
12. Raposo JC. *Contribution to the study of interactions of inorganic arsenic species with natural medium*. Ph.D. Thesis, University of the Basque Country, Bilbao, 2001.
13. Waugh TD, Walton HF and Laswick JA. *J. Phys. Chem.* 1955; **59**: 395.
14. Schwarzenbach G and Schellenberg M. *Helv. Chim. Acta* 1965; **48**: 28.
15. Zanella P, Plazzogna G and Tagliavini G. *Inorg. Chim. Acta* 1968; **2**: 340.
16. Budevsky O, Ingman F and Liem DH. *Acta Chem. Scand.* 1973; **27**: 1277.
17. Rabenstein DL, Tourangeau MC and Evans CA. *Can. J. Chem.* 1976; **54**(16): 2517.
18. Sneed MC and Maynard JL. *J. Amr. Chem. Soc.* 1922; **44**: 2943.
19. Ingman F. *Talanta* 1971; **18**: 744.
20. Jeffery GH, Basset J, Mendham J and Denney RC. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th edn. Longman: London, 1989.
21. Cazallas R, Fernandez LA, Etxebarria N and Madariaga JM. *Lab. Robot. Automat.* 1993; **5**: 161.
22. Fonseca JL. *The MOD/89 program for the calculation of stability constants: an extended version of LETAGROP*. BSc Thesis, University of the Basque Country, Bilbao, 1989.
23. Ingri N and Sillén LG. *Acta Chem. Scand.* 1962; **16**: 173.
24. De Stefano C, Mineo P, Rigano C and Sammartano S. *Ann. Chim.* 1993; **83**: 243.
25. De Stefano C, Foti C, Giuffré O, Mineo P, Rigano C and Sammartano S. *Ann. Chim.* 1996; **86**: 257.
26. Zvyagintsev O and Lyakhmanov S. *Zhr. Neorg. Khim.* 1969; **14**: 1822.
27. De Robertis A, De Stefano C, Gianguzza A and Sammartano S. *Chem. Spec. Bioavailab.* 1994; **6**: 65.
28. Lopategi A, Castaño R, Etxebarria N and Madariaga JM. *J. Chem. Soc. Dalton Trans.* 1995; 3843.
29. Etxebarria N, Fernandez LA and Madariaga JM. *J. Chem. Soc. Dalton Trans.* 1994; 3055.
30. Arana G, Etxebarria N, Fernandez LA and Madariaga JM. *J. Solution Chem.* 1995; **24**: 661.
31. Castaño R, Etxebarria N and Madariaga JM. *J. Chem. Soc. Dalton Trans.* 1994; 2729.
32. Zubiaur J, Castaño R, Etxebarria N, Fernadez LA and Madariaga JM. *Talanta* 1998; **45**: 1007.
33. Raposo JC, Sanz J, Borge G, Olazabal MA and Madariaga JM. *Fluid Phase Equilibria* 1999; **155**: 1.
34. Long FA and McDevit WF. *Chem. Rev.* 1952; **51**: 119.
35. Sherrod PH. *NLREG – Nonlinear Regression Analysis Program*, Nashville, TN, 1995.
36. Frydman M, Nilsson G, Rengemo T and Sillen LG. *Acta Chem. Scand.* 1958; **12**: 878.
37. Riese W, Gamsjäger H and Schindler PW. *Geochim. Cosmochim. Acta* 1977; **4**: 1193.
38. Maya L. *Inorg. Chem.* 1982; **21**: 2895.
39. Wagman DP, Evans WH, Parker VB. *J. Phys. Ref. Data* 1982; **11**(Suppl. 2).
40. Bilinski H and Schindler P. *Geochim. Cosmochim. Acta* 1982; **46**: 921.
41. Maya L. *Inorg. Chem.* 1983; **22**: 2093.
42. Cantrell KJ and Byrne RH. *J. Solution Chem.* 1987; **16**: 555.
43. Fanghägel Th, Neck V and Lim JI. *J. Solution Chem.* 1996; **25**(4): 327.
44. Eriksson G. *Anal. Chim. Acta* 1979; **112**: 375.
45. Nagypal I and Beck M. *Talanta* 1982; **29**: 473.
46. Bilinski H, Markovic M and Gessner M. *Inorg. Chem.* 1980; **19**: 3440.
47. Blum J and Bartha R. *Bull. Environ. Contam. Toxicol.* 1980; **25**: 404.
48. Puigdomenech I. *Technical report TRITA-OOK-3010 (ISSN 0348-825X)*, September 1983, Royal Institute of Technology, Stockholm.