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Interaction of Inorganic Mercury(II) with Polyamines, Polycarboxylates, and Amino Acids

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A study on chemical equilibria of different Hg^{2+}−organic ligand systems is reported to establish the sequestration power of N/O donor groups versus metal. Ligand classes considered are: O-donors (succinate, 1,2,3,4-butanetetracarboxylate, 1,2,3,4,5,6-benzenehexacarboxylate, polymethacrylate, and polyacrylates); N-donors (ethylenediamine, diethylenetriamine, spermidine, triethylentetramine, tetraethylenpentamine, poly(allylamine), and poly(ethylenimine)); and amino acids (glycine, histidine, and aspartic acid). Equilibria were studied potentiometrically in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C. For some systems, the dependence on ionic strength in the range $(0 \le I \le 1)$ mol·L^{-1} ($NaNO_3$) and the overall enthalpy changes, by calorimetric measurements, were also determined. The sequestering ability of ligands toward Hg^{2+} was evaluated, defining the amount of ligand necessary to sequester 50 % of the total metal cation concentration, pL_{50}. The dependence on temperature and on ionic strength of pL_{50} was determined. General trends for the formation parameters for Hg^{2+}−O-donor and −N-donor species depending on the binding sites were found. The free energy of binding for both unprotonated and monoprotonated species of carboxylates ($\Delta G_b = -21.7 \pm 3$ kJ·mol^{-1}) and for unprotonated species of amines ($\Delta G_b = -35.4 \pm 5$ kJ·mol^{-1}) was estimated.

Introduction

In the last decades, there has been an increased awareness of metal contamination in various aquatic environments, particularly concerning mercury compounds.[1−5] The effects of environmental exposure to mercury may be insidious, difficult to detect, and potentially widespread. Mercury(II) is a soft metal with a strong affinity for sulfur-donor ligands and halides, particularly chloride. The affinity of Hg(II) for sulfur donors is known to be very high in the pH range of 1 to 13, suggesting the use of sulfur-containing ligands for Hg removal from waste waters. Moreover, in biological systems, the activity of intra- and extracellular proteins and enzymes with free mercaptogroups is adversely affected by binding of the −SH groups to Hg(II).

Like other metals, mercury speciation is affected by complexation with natural organic and inorganic ligands, which influences its transport, transformation, and bioavailability in natural waters. In the literature are reported many papers on Hg^{2+}−organic matter systems.[6−11] Mercury is generally bound to the acid sites in organic matter. The most common acidic functional groups in DOM include carboxylic acids, phenols, ammonium ions, alcohols, and thiols. Among these, carboxylic acids and phenols account for 90 % of organic matter acidity.[12] Our studies on mercury(II) will concern most of these ligand classes, starting from O-, N-, and O,N-donor ligands. For the relevance of the interaction of Hg(II)−S-containing ligands, we are planning to study these systems in the future, too.

The quantitative study of the interactions between mercury(II) and different types of ligands is of utmost importance for: (1) modelling the speciation of this toxic metal ion in natural and biological systems, (2) understanding the fate of Hg^{2+}, and (3) modelling decontamination processes. The complexation process can be applied to various purposes such as the metal decontamination of waste effluents, groundwater, and seawater. Molinari and coworkers[13−15] applied polymer-assisted ultrafiltration (PAUF) to remove heavy metal ions from industrial effluent. This technique combines the binding of metal ions to a water-soluble polymer and the separation of the metal−polymer complex by means of an ultrafiltration membrane. Herrero et al.[16] report a study of the mercury adsorption by nonliving biomass of a brown marine macroalga.

In this article, we report a study on the chemical equilibria of different Hg^{2+}−organic ligand systems with a double scope: (1) to contribute to the knowledge of mercury speciation and (2) to determine the sequestering ability of organic ligands toward Hg^{2+}. Ligand classes considered were: (1) O-donor ligands, such as di- (succinate), tetra- (1,2,3,4-butanetetracarboxylate), and hexa- (1,2,3,4,5,6-benzenehexacarboxylate) carboxylates, and polyelectrolytes, such as polymethacrylate and polyacrylates, at two different molecular weights; (2) N-donor ligands, such as amines containing a different number of aminic groups (from ethylenediamine to tetraethylenepentamine), and polyelectrolytes, such as poly(allylamine) and poly(ethylenimine); and (3) amino acids such as glycine containing one carboxylic and one amino group, histidine containing an additional amino group, and aspartic acid containing an additional carboxylic group. Hg^{2+}−carboxylate, −amine, and −amino acid systems reported in the literature are collected in Table 1.[17−38] In this article, equilibria were studied potentiometrically in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C. Under the same conditions, for Hg^{2+}−1,2,3,4-butanetetracarboxylate, −1,2,3,4,5,6-benzenehexacarboxylate, −diethylenetriamine, −poly(ethylenimine), and −glycine systems, the enthalpy changes by calorimetric measurements were also determined. For some systems (1,2,3,4-butanetetracarboxylate, 1,2,3,4,5,6-benzenehexacarboxylate, polyacrylate 2 kDa and 100 kDa,

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Table 1. Literature Formation Constants of Hg^{2+}−Organic Ligands Complexes

	t	I	log β			
	°C	mol·L^{-1}	ML	ML_2	other species	ref
formic acid	25	0.1	2.85			38
	25	0.5	2.78			38
	25	1	2.88			38
	25	2 ($NaClO_4$)	3.18			38
	25	3 ($NaClO_4$)	3.66	7.10		28
	25	0	3.5			38
	25	3 ($NaClO_4$)	3.62	5.90		30
acetic acid	25	0.1	3.74			38
	25	0.5	3.59			38
	25	1	3.57			35
	25	2 ($NaClO_4$)	4.00			30
	25	3 ($NaClO_4$)	4.22	8.45		28
	25	0	4.3			38
oxalic acid	25	0.1	9.66			24
	25	0.05	9.87			25
propionic acid	25	1	3.90			35
	25	2 ($NaClO_4$)	4.00			30
	25	3 ($NaClO_4$)	4.33	8.80		28
citric acid	25	0.1	10.9			38
ethylamine	25	0.5	8.90	18.44		31
methylamine	25	0.5	8.66	17.86	ML_3 (18.2); ML_4 (18.5)	23
ethylenediamine	20	0.1	13.85	22.22		37
	25	3 ($NaClO_4$)	16.75	25.97		33
	25	0.1	14.3	23.3	MLOH (37.4); $ML_2(OH)$ (28.6); $ML_2(OH)_2$ (33.3); $ML_3(OH)_2$ (42.3)	32
putrescine	20	1	17.96		MLH (10.99);[a] MLH_2 (17.82)[b]	21
cadaverine	20	1	17.92		MLH (11.36); MLH_2 (18.41)	21
dien	20	0.5	21.8	29	MLH (25.7); MLOH (6.3)[c]	38
	25	0.1		25.0		20
	20	0.5		29		38
trien	25	0.1	24.5			27
	25	0.5	24.0			38
	25	1	24.3		MLH (26.5);	38
tetren	25	0.1	24.8			29
	25	0.1	27.7			19
ethylenedinitrilo-tetrakis (ethyleneamine)	20	0.5	29.6		MLH (38.22); MLH_2 (42.92); MLH_3 (45.52)	36
	25	1	29.3		MLH (37.76);	18
glycine	25	0.1	12.2	19.20		26
	25	0.6		18.36		22
	22	0.01		18.2		17
	25	0.1	10.5	19.10		34
aspartic acid	25	0.1	6.72			37
	25	0.1	6.10	10.18		37
	25	0.1	13.2	20.00		26

[a] Refers to reaction: M + HL. [b] Refers to reaction: M + H_2L. [c] Refers to reaction: ML + OH.

diethylenetriamine, and tetraethylenpentamine), dependence on ionic strength in the range ($0 \leq I \leq 1$) mol·L^{-1} was reported.

Experimental Section

Chemicals. Solutions of mercury(II) chloride from corresponding Riedel-de-Haen product were prepared. We prepared solutions of succinic (suc), 1,2,3,4-butanetetracarboxylic (btc), 1,2,3,4,5,6-benzenehexacarboxylic (mellitic, mlt), polymethacrylic 4 kDa (pma) and polyacrylic 2 kDa (paa2) acids, ethylenediamine (en), diethylenetriamine (dien), spermidine (spd), triethylenetetramine (trien), tetraethylenepentamine (tetren), glycine (Gly), histidine (His), aspartic acid (Asp), and poly(allylamine) 15 kDa (paam) by weighing the solid products (Fluka, Aldrich, or both) without further purification. We prepared solutions of polyacrylic 100 kDa acid (paa100) and poly(ethylenimine) 750 kDa (pei) by diluting the aqueous solution (Aldrich). The purity of ligands was checked by alkalimetric titration. We prepared standard NaOH and HCl solutions by diluting concentrated Fluka ampoules, and they were standardized against potassium hydrogenphthalate (Fluka, puriss) and sodium carbonate (Fluka, puriss), respectively. $NaNO_3$ (Fluka, puriss) was used after stove drying at 140 °C. All solutions were prepared using grade A glassware and ultrapure water (conductivity < 0.1 μS·cm^{-1}).

Apparatus. Potentiometric measurements were performed using two sets of equipment to avoid systematic errors: (1) A Metrohm model 713 potentiometer (± 0.1 mV resolution) coupled to a Metrohm 665 Dosimat burette (± 0.001 cm^3 minimum deliverable volume) and equipped with a Metrohm combined glass electrode (model 6.0222.100) was used. The potentiometer and the burette were connected to a personal computer that, using suitable software, allows automatic data acquisition. (2) A Metrohm model 809 titrando coupled to a Metrohm 800 Dosino dispenser and equipped with an Orion (Ross model 8101) glass electrode and an Ag/AgCl reference electrode was used. Data were automatically acquired by the software Metrohm TiAMO 1.0.

For all potentiometric measurements, we standardized the electrodes couple in terms of pH −log[H^+] by titrating a 10 mmol·L^{-1} HCl solution (at the same ionic strength value as that of the solution under study) with standard NaOH to determine the standard potential, $E°$, before each experiment. The potentiometric titrations were carried out in a stream of purified nitrogen gently bubbled in the titration cell to avoid O_2 and CO_2 contamination. The measurement cells were thermostatted at (25 ± 0.1) °C by means of water circulation from a thermocryostat (model D1-G Haake).

Table 2. Experimental Details of Potentiometric and Calorimetric Measurements

ligand	I^a	no. tit[b]	no. point[c]	C_H[d]	C_{Hg}[d]	C_L[d]	pH
			Potentiometric Measurements				
succ	0.1	8	50	1.5 to 5	0.5 to 1.5	1 to 2	2 to 7
btc	0.1 to 1	30	60	4 to 20	0.8 to 3	1 to 5	2 to 7
mlt	0.1 to 1	28	60	6 to 15	0.8 to 2	1 to 2.5	2 to 6.5
pma	0.1	8	60	3.5 to 7	1 to 2	1 to 3	2 to 10.5
paa2	0.1 to 1	57	60	4 to 20	0.8 to 5	2 to 10	3 to 9
paa100	0.1 to 1	42	60	4 to 20	0.8 to 5	2 to 10	3 to 9
en	0.1	8	60	6 to 8	0.8 to 2	1 to 2	2 to 10.5
dien	0.1 to 1	28	70	1 to 10	0.5 to 1.5	0.8 to 3	5.5 to 10
spd	0.1	8	50	7.5 to 12	1 to 2	1.5 to 3	2.5 to 10
trien	0.1	8	80	9 to 15	1 to 2	1.5 to 3	2 to 10
tetren	0.1 to 1	25	70	2 to 18	1 to 2	1.5 to 3	2 to 10
paam	0.1	9	50	4 to 5	0.4 to 1	0.4 to 1	3 to 10
pei	0.1	10	40	6	0.5 to 1	0.8 to 2	2 to 8
Gly	0.1	9	60	3 to 10	0.5 to 1.5	1 to 5	2 to 9.5
hys	0.1	8	60	3 to 10	0.5 to 1.5	0.8 to 1.6	2 to 10
Asp	0.1	8	80	12 to 13	0.5 to 1.5	1 to 3	2 to 10
			Calorimetric Measurements				
btc	0.1	4	30		1.5 to 3	55	4.7 to 6.5
mlt	0.1	4	30		2 to 2.5	85	4.2 to 4.6
dien	0.1	4	30		2 to 2.5	102	3.6 to 9.5
pei	0.1	4	30		1.5 to 2	79	4.6 to 5.3
Gly	0.1	4	30		1.5 to 2	213	5.0 to 9.3

[a] In $mol \cdot L^{-1}$. [b] Number of titrations. [c] Number of points for titration. [d] In $mmol \cdot L^{-1}$.

Calorimetric measurements were performed at 25.000 ± 0.001 °C by means of a Tronac 450 Isoperibol Titration calorimeter coupled to a Keithley 196 system DMM digital multimeter. The titrant was delivered by a 2.5 mL capacity Hamilton syringe (model 1002TLL). A computer program was used for the acquisition of the calorimetric data. The system accuracy was checked by the titration of TRIS (tris-(hydroxymethyl)amino-methane) buffer with HCl. The heat of dilution was measured before each experiment. The precision of calorimetric apparatus was $Q \pm 0.008$ J and $v \pm 0.001$ cm^3.

Procedure. Potentiometric experiments were carried out in $NaNO_3$ aqueous solutions at $I = 0.1$ $mol \cdot L^{-1}$ and for btc, mlt, paa2, paa100, dien, and tetren in the ionic strength range ($(0.1 \leq I \leq 1.0)$ $mol \cdot L^{-1}$) at $t = 25.0 \pm 0.1$ °C. For the investigation of ligand protonations, 25 mL of solution containing the ligand under study ($(2 \leq C_L \leq 10)$ $mmol \cdot L^{-1}$) and $NaNO_3$, to reach the prefixed ionic strength values, was titrated with standard NaOH. For the investigation of Hg^{2+}−ligand systems, 25 mL of solution containing Hg^{2+}, the ligand under study at different metal ligand ratios (from $C_{Hg}/C_L = 0.3$ to $C_{Hg}/C_L = 3$), and $NaNO_3$, to reach the prefixed ionic strength values, was titrated with standard NaOH.

We obtained the Hg^{2+} hydrolysis and Hg^{2+}−chloride species enthalpies by adding standard NaOH to its chloride salt solution ((2 to 4) $mmol \cdot L^{-1}$) in the presence of $NaNO_3$ (to reach ionic strength value of 0.1 $mol \cdot L^{-1}$). We obtained the formation enthalpies of complex species of Hg^{2+} with btc, mlt, dien, pei, and Gly by adding to 50 mL of the solution containing Hg^{2+} and $NaNO_3$ (to reach ionic strength value of 0.1 $mol \cdot L^{-1}$) the ligand under study (two carboxylates were as sodium salts, i.e., Na_4btc and Na_6mlt). The investigated metal/ligand ratios, C_{Hg}/C_L, were from 0.35 to 1.

Details of both potentiometric and calorimetric titrations are reported in Table 2.

Calculations. To determine all parameters of the acid−base titration, we performed the calculations by using the ESAB2 M nonlinear least-squares computer program.[39] This program allowed us to refine the analytical concentration of the reagents, the $E°$ electrode standard potential, the j_a coefficient relative to the acidic junction potential (according to the equation $E_j = j_a [H^+]$) and the K_w ionic product of water; it was also useful to evaluate the purity of the ligand examined. The refinement of the formation constants was performed using the BSTAC software.[40] It employed an iterative and convergent numerical method, based on the linear combination of the mass balance equations, that minimized the error square sum on electromotive force values and took into account eventual variations of ionic strength during the titrations. Calorimetric titration data were analyzed by the ES5CM computer program.[41] The ES4ECI program[40] was used to draw speciation diagrams and to calculate species formation percentages. The LIANA program[40] was used to fit linear and nonlinear equations for the dependence on ionic strength of formation constants and for the sequestration plots.

Results

Thermodynamic Parameters for Ligand Protonation and Mercury(II) Hydrolysis. Calculations of Hg^{2+}−ligand complex formation constants require knowledge of the ligand protonation constants under the same ionic strength conditions. With this aim, first protonation constants of ligands in $NaNO_3$ at $I = 0.1$ $mol \cdot L^{-1}$ were determined. Results are reported in Table 3. For protonation constants of pma, paa2, paa100, and paam, two steps are reported because in our calculations, we considered two monomeric units to be the base unit of the polyelectrolytes. This model (diprotic-like model) was successfully tested for several synthetic and natural polyelectrolytes.[42,43] In this way, we are able to analyze potentiometric data for this kind of high-molecular-weight ligand by using the same computer tools as those for low-molecular-weight ligands.

Hg^{2+} hydrolyzes[44,45] to produce in dilute solutions the neutral mononuclear $Hg(OH)_2^0$ species. Other species ($Hg(OH)^+$, $Hg(OH)_3^-$, and Hg_2OH^{3+}) are formed in small amounts. Some authors also report the polynuclear $Hg_3(OH)_3^{3+}$ species, but it occurs only at high mercury(II) concentrations. Data used in our calculations for both hydrolysis and Hg^{2+}−Cl^- complex formation constants are given in Table 4. In the same Table, enthalpies of the main hydrolytic and chloride species $Hg(OH)_2^0$, $HgCl_2^0$, and $HgCl(OH)^0$, determined calorimetrically in $NaNO_3$ aqueous solution at $I = 0.1$ $mol \cdot L^{-1}$ and $t = 25$ °C, are reported. Ligand protonation enthalpies are reported in Table 5.

Table 3. Protonation Constants of Ligands in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and at $t = 25$ °C[a]

L	log β_1^H	log β_2^H	log β_3^H	log β_4^H	log β_5^H	log β_6^H
suc	5.204 ± 0.004[b]	9.17 ± 0.01[b]				
btc	6.42 ± 0.02	11.67 ± 0.03	15.84 ± 0.05[b]	19.04 ± 0.07[b]		
mlt	6.55 ± 0.01	12.11 ± 0.01	16.62 ± 0.02	19.79 ± 0.05	20.76[c]	21.5[c]
pma	6.480 ± 0.004	11.526 ± 0.008				
paa2	5.54 ± 0.02	9.62 ± 0.03				
paa100	5.78 ± 0.02	10.20 ± 0.04				
en	9.790 ± 0.005	16.818 ± 0.006				
dien	9.729 ± 0.005	18.664 ± 0.006	22.880 ± 0.006			
spd	10.24 ± 0.04	19.87 ± 0.03	28.09 ± 0.03			
trien	9.559 ± 0.007	18.588 ± 0.004	25.139 ± 0.008	28.55 ± 0.01		
tetren	9.750 ± 0.005	18.947 ± 0.003	27.120 ± 0.005	31.786 ± 0.008	34.61 ± 0.01[b]	
paam	9.56 ± 0.05	17.48 ± 0.06				
pei	8.77 ± 0.03	16.76 ± 0.03	22.76 ± 0.04	26.30 ± 0.06		
Gly	9.452 ± 0.005	11.88 ± 0.01				
His	8.98 ± 0.01	15.00 ± 0.02	16.98 ± 0.05			
Asp	9.556 ± 0.003	13.223 ± 0.004	15.281 ± 0.007			

[a] β_i refers to reaction: iH + L = H_iL (charges omitted for simplicity). [b] ± std. dev. [c] Values at $I = 0.1$ mol·L^{-1} in NaCl.[60]

Table 4. Thermodynamic Parameters for Hg^{2+} Hydrolysis and Chloride Complexes in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C

reaction	log β[a]	ΔH[b]
$Hg^{2+} + H_2O = Hg(OH)^+ + H^+$	− 3.60	
$Hg^{2+} + 2\ H_2O = Hg(OH)_2^0 + 2\ H^+$	− 6.34	43.9 ± 1.8[c]
$Hg^{2+} + 3\ H_2O = Hg(OH)_3^- + 3\ H^+$	− 21.10	
$2\ Hg^{2+} + H_2O = Hg_2(OH)^{3+} + H^+$	− 3.58	
$Hg^{2+} + Cl^- = HgCl^+$	6.82	
$Hg^{2+} + 2\ Cl^- = HgCl_2^0$	13.36	− 55 ± 2
$Hg^{2+} + 3\ Cl^- = HgCl_3^-$	14.44	
$Hg^{2+} + 4\ Cl^- = HgCl_4^{2-}$	15.06	
$Hg^{2+} + Cl^- + H_2O = HgCl(OH)^0 + H^+$	3.68	− 2.5 ± 1.5

[a] Ref 44. [b] In kJ·mol^{-1}. [c] ± std. dev.

Table 5. Ligand Protonation Enthalpies in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C[a,b]

L	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6	ref
btc	6.2	5.6	4.5	0.8			73
mlt	12.7	10.0	7.3	4.6	2.3	− 0.2	74[c]
dien	− 49.9	− 99.8	− 131.3				75
pei	− 47.2	− 92.7	− 123.0	− 133.0			76
Gly	− 44.4	− 48.7					77[c]

[a] ΔH refers to the reaction: iH + L = H_iL (charges omitted for simplicity). [b] In kJ·mol^{-1}. [c] Calculated from ref 73.

Thermodynamic Parameters for the Formation of Mercury(II)−Organic Ligand Complexes. Potentiometric measurements of Hg^{2+}−organic ligand systems, under the conditions reported in the Experimental Section, evidenced the formation of different complex species. Several models were tested, and those proposed are reported in Table 6 together with their formation constants in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C. As pointed out in the Introduction, different kinds of ligands were studied: O-donor, N-donor, and amino acids. Ligands containing O-donor groups (suc, btc, mlt, pma, paa2, and paa100) showed a similar behavior toward complexation. In all of these systems, the formation of the HgL, HgLH, and $HgLH_2$ (except for suc ligand) species was found together with the hydrolytic HgL(OH) species. As an example, in Figure 1 the distribution diagram of the Hg^{2+}−btc system is shown. As can be seen, in the acidic range, most of the Hg^{2+} is present as complex species with high formation percentages of the $Hg(btc)^{2-}$, $Hg(btc)H^-$, and $Hg(btc)H_2^0$ species. In the basic range, the most important species is the hydrolytic one, $Hg(OH)_2^0$, with a significant formation percentage (∼ 50 %) of the mixed $Hg(btc)(OH)^{3-}$ species.

Some similarities can also be evidenced for Hg^{2+}−N-donor ligand systems: the formation of the HgL, HgLH (except for en and paam), and HgL(OH) species was found, with $HgLH_2$ for tetren, the polynuclear Hg_2L for en and dien, and the $Hg_2(paam)_2$, $Hg(pei)_2$, and $Hg(pei)_2(OH)$ species. For this class of ligands, the speciation diagram of Hg^{2+}−dien is shown (Figure 2). As can be seen, under the reported experimental conditions, mercury is mostly present at pH < 5 as $Hg(dien)H^{3+}$ and at pH > 7 as $Hg(dien)^{2+}$.

The third class of ligands studied is represented by amino acids. The speciation model of these amino acids is the same and implies the formation of the HgL, HgL(OH), Hg_2L, and Hg_2L_2 species. Complex formation constants are reported in Table 6. As an example, the distribution of species versus pH for aspartic acid is shown in Figure 3. In this system, at pH < 6, ∼ 60 % of Hg^{2+} is present as $Hg_2(Asp)_2^0$ and ∼40 % is present as $Hg(Asp)^0$. At pH > 8, the most important species is $Hg(Asp)(OH)^-$, which reaches a yield of ∼ 70 %.

Temperature Dependence. The overall enthalpy changes regarding the complex formation in the Hg^{2+}−btc, −mlt, −dien, −pei and −Gly systems, together with ΔG and $T\Delta S$ values, are reported in Table 7. Partial thermodynamic parameters, according to the most probable reaction, are shown in Table 8. As can be seen, all enthalpy values are exothermic, indicating that exoergic metal−nitrogen or metal−oxygen interaction overcomes the endoergic dehydration of the cation.

It is well known that a soft metal, such as Hg^{2+}, has higher affinity for N-donor ligands than for O-donor ligands. In the soft−soft interactions, complexation free energies are mainly of enthalpic origin.[46] O-donor ligands, such as carboxylates, are considered to be hard; instead, N-donor ligands, such as polyamines, are considered to have intermediate characteristics between hard and soft ligands. As expected, the enthalpy values of Table 7, considering the same formation reaction, referring to Hg^{2+}−dien and −pei species are considerably more exothermic than those of Hg^{2+}−btc and Hg^{2+}−mlt. Moreover, the species containing Gly show intermediate enthalpy values between carboxylates and polyamines. For example, for the ML species we obtained: ΔH = (−30.0 ± 0.4 and −40 ± 3) kJ·mol^{-1} for L = btc and mlt, respectively; ΔH = (−135.6 ± 0.9 and −143.4 ± 0.60) kJ·mol^{-1} for L = dien and pei, respectively; and ΔH = −52 ± 2 kJ·mol^{-1} for Gly. The thermodynamic data in Tables 7 and 8 show that another factor, such as charge effects, influences the metal−ligand interactions: the $-\Delta H$ value increases with increasing ligand charge. As an example, for the reaction M + LH, ΔH values are (−32 and −63) kJ·mol^{-1}, for btc ($z = -3$) and mlt ($z = -5$), respectively;

Table 6. Formation Constants for Hg^{2+} Organic Ligand Systems at $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$) and $t = 25\ °C$[a]

L	$\log \beta_{110}$	$\log \beta_{111}$	$\log \beta_{112}$	$\log \beta_{11-1}$	$\log \beta$ (other species)
suc	9.46 ± 0.04[b]	14.22 ± 0.05[b]		3.32 ± 0.02[b]	
btc	11.61 ± 0.08	17.14 ± 0.08	21.52 ± 0.07[b]	4.81 ± 0.08	
mlt	18.43 ± 0.06	22.55 ± 0.07	25.56 ± 0.05	14.30 ± 0.10	
pma	12.08 ± 0.05	18.46 ± 0.09	23.3 ± 0.13	3.6 ± 0.28	
paa2	11.06 ± 0.02	16.13 ± 0.03	20.39 ± 0.03	4.18 ± 0.01	
paa100	11.78 ± 0.02	16.57 ± 0.02	20.74 ± 0.02	4.03 ± 0.02	
en	16.47 ± 0.02			9.66 ± 0.04	22.89 ± 0.03 $Hg_2(en)$[b]
dien	19.05 ± 0.03	25.19 ± 0.03		9.37 ± 0.09	24.22 ± 0.04 $Hg_2(dien)$
spd	18.06 ± 0.01	25.40 ± 0.03		7.24 ± 0.09	
trien	24.13 ± 0.01	28.05 ± 0.03		12.1 ± 0.2	
tetren	26.87 ± 0.01	31.79 ± 0.01	36.28 ± 0.01	15.94 ± 0.07	
paam	17.76 ± 0.09			9.16 ± 0.03	39.38 ± 0.06 $Hg_2(paam)_2$
pei	22.79 ± 0.04	27.22 ± 0.06		15.87 ± 0.07	36.51 ± 0.04 $Hg(pei)_2$ 31.5 ± 0.15 $Hg(pei)_2(OH)$
Gly	13.87 ± 0.07			6.98 ± 0.03	18.82 ± 0.07 $Hg_2(Gly)$ 31.42 ± 0.07 $Hg_2(Gly)_2$
His	15.75 ± 0.03			7.37 ± 0.07	20.48 ± 0.03 $Hg_2(Asp)$ 34.44 ± 0.13 $Hg_2(Asp)_2$
Asp	14.86 ± 0.03			7.36 ± 0.01	19.15 ± 0.09 $Hg_2(His)$ 33.12 ± 0.04 $Hg_2(His)_2$

[a] β_{pqr} refers to reaction: $p\mathrm{Hg} + q\mathrm{L} + r\mathrm{H} = \mathrm{Hg}_p\mathrm{L}_q\mathrm{H}_r$ (charges omitted for simplicity). [b] ± std. dev.

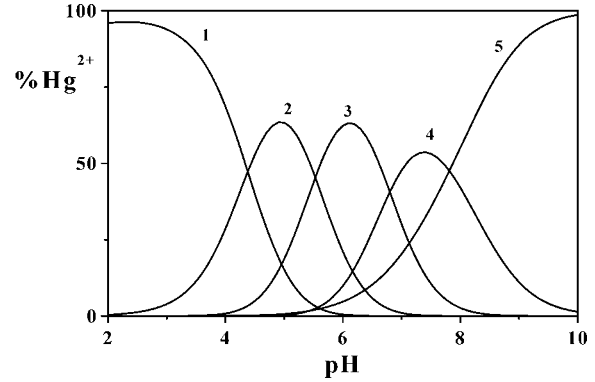

Figure 1. Speciation diagram of Hg^{2+}−btc system versus pH. Conditions: $C_{Hg} = C_{btc} = 1\ mmol\cdot L^{-1}$, $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$), $t = 25\ °C$. Species: 1, $Hg(btc)H_2^0$; 2, $Hg(btc)H^-$; 3, $Hg(btc)^{2-}$; 4, $Hg(btc)OH^{3-}$; 5, $Hg(OH)_2^0$.

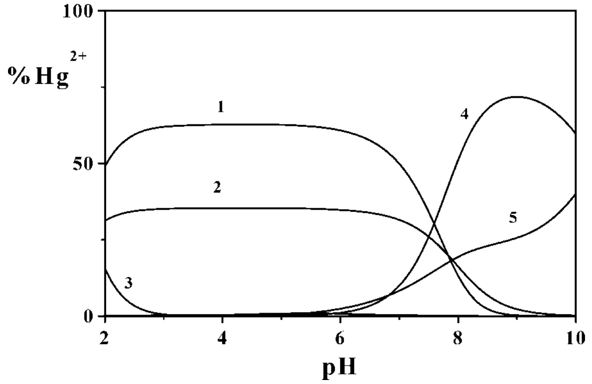

Figure 3. Speciation diagram of Hg^{2+}−Asp system versus pH. Conditions: $C_{Hg} = C_{Asp} = 1\ mmol\cdot L^{-1}$, $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$), $t = 25\ °C$. Species: 1, $Hg_2(Asp)_2^0$; 2, $Hg(Asp)^0$; 3, $Hg_2(Asp)^{2+}$; 4, $Hg(Asp)OH^-$; 5, $Hg(OH)_2^0$.

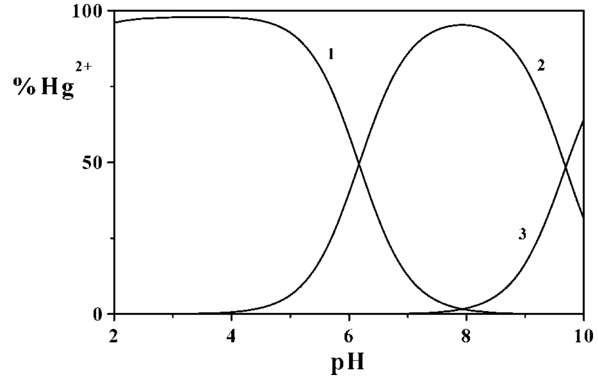

Figure 2. Speciation diagram of Hg^{2+}−dien system versus pH. Conditions: $C_{Hg} = C_{dien} = 1\ mmol\cdot L^{-1}$, $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$), $t = 25\ °C$. Species: 1, $Hg(dien)H^{3+}$; 2, $Hg(dien)^{2+}$; 3, $Hg(dien)OH^+$.

for the reaction $M + LH_2$, $\Delta H = (-69$ and $-96)\ kJ\cdot mol^{-1}$ for btc ($z = -2$) and mlt ($z = -4$), respectively.

Ionic Strength Dependence. To study the dependence on ionic strength of Hg^{2+} complex formation constants, for some systems, we performed measurements in the ionic strength range of $(0.1 \le I \le 1)\ mol\cdot L^{-1}$ ($NaNO_3$). Protonation and Hg^{2+}−complex formation constants at different ionic strengths are reported in Tables 9 and 10 for btc, mlt, paa2, paa100, dien, and tetren. Dependence on ionic strength was taken into account by the SIT (specific ion interaction theory) equation.[47−56] According to the SIT model, formation constants follow the equation

$$\log \beta = \log {}^{\mathrm{T}}\beta - z^{*}\frac{0.509\mathrm{I}^{1/2}}{1 + 1.5\mathrm{I}^{1/2}} + \Delta \varepsilon I \qquad (1)$$

$$\text{with } z^{*} = \sum (\text{charge})^2_{\text{reactants}} - \sum (\text{charge})^2_{\text{products}}$$

where β is the formation constant at the ionic strength I, ${}^{\mathrm{T}}\beta$ is the formation constant at infinite dilution, and $\Delta\varepsilon = \Sigma\varepsilon_{\text{reactants}} - \Sigma\varepsilon_{\text{products}}$ (ε = specific ion interaction coefficient). In the calculations of the SIT parameters, both ionic strength and formation constants were used on the molal scale, as is required. The conversion from the molar to the molal scale was obtained using the equation (at 25 °C; d_0 is solvent density; c is molar concentration; m is molal concentration) $c/m = d_0 + a_1c + a_2c^2$, with $d_0 = 0.99987$, $a_1 = 0.02983151$, and $a_2 = -6.4516\cdot 10^{-4}$.[57] $\Delta\varepsilon$ values for each equilibrium constant, together with formation constants at infinite dilution, are reported in Table 11. Dependence of protonation and formation constants on ionic strength can also be interpreted in terms of ion pair formation.[58] The effect of ionic strength is particularly marked for O-donor ligands because of the interaction (weak complex formation) between the carboxylate anion and Na^+ present in the ionic medium.[59,60]

Table 7. Overall Thermodynamic Formation Parameters for Hg^{2+}−Ligand Systems at $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$) and $t = 25\ °C^{a,b}$

L	*pqr*	$-\Delta G$	$\Delta H \pm s$	$T\Delta S$
btc	110	66.3	−30.0 ± 0.4	36
	111	97.8	−26 ± 1	72
	112	122.8	−64 ± 2	59
	11−1	27.5	−23.0 ± 0.7	5
mlt	110	105.2	−40 ± 3	65
	111	128.7	−50 ± 3	79
	112	145.9	−91 ± 3	55
	11−1	81.6	−60.2 ± 0.6	21
dien	110	108.7	−135.6 ± 0.9	−27
	111	143.8	−197 ± 6	−53
	11−1	53.5	−88 ± 1	−35
	210	138.2	−173 ± 2	−35
pei	110	130.1	−143.4 ± 0.6	−13
	111	155.4	−235 ± 4	−80
	11−1	90.6	−96 ± 3	−5
	120	208.4	−111 ± 2	97
	12−1	179.8	−193 ± 5	−13
Gly	110	79.2	−52 ± 2	27
	11−1	39.8	−9.5 ± 0.1	30
	210	179.3	−87 ± 1	92
	220	107.4	−114 ± 1	−7

[a] Referred to the reaction: pHg + qL + rH = $Hg_pL_qH_r$ (charges omitted for simplicity). [b] In $kJ\cdot mol^{-1}$.

Table 8. Thermodynamic Formation Parameters for Hg^{2+}−Ligand Systems at $I = 0.1\ mol\cdot L^{-1}$ ($NaNO_3$) and $t = 25\ °C^{a}$

L	reaction[b]	$-\Delta G$	ΔH	$T\Delta S$
btc	M + L	66.3	−30.0	36
	M + LH	61.2	−32	29
	M + LH_2	56.2	−69	−13
	M(OH) + L	48.0	−44	4
mlt	M + L	105.2	−40	65
	M + LH	91.3	−63	29
	M + LH_2	76.8	−96	−19
	M(OH) + L	102.2	−80.9	21
dien	M + L	108.7	−135.6	−27
	M + LH	88.4	−147	−59
	M(OH) + L	74.0	−109	−35
	M + ML	29.7	−37	−8
pei	M + L	130.1	−143.4	−13
	M + LH	105.3	−188	−83
	M(OH) + L	111.1	−140	−29
	ML + L	78.3	−32	111
	ML(OH) + L	89.2	−53	36
Gly	M + L	79.2	−52	27
	M(OH) + L	60.4	−30.2	30
	ML + M	28.3	−35	−7
	M_2L + L	71.9	−79	−7

[a] Expressed in $kJ\cdot mol^{-1}$. [b] Charges omitted for simplicity.

Sequestering Ability. In previous papers,[61−66] we proposed a Boltzman-type equation to define the sequestering ability of a ligand toward a metal as a function of the sum of formation percentages of all metal−ligand complexes, $\Sigma(\%)$, versus pL, where pL $\equiv -\log\ [L]_{tot}$ ($[L]_{tot}$ is the total ligand concentration). This function is assimilable to a sigmoid curve (or a dose response curve) with asymptotes of 100 for pL → −∞ and 0 for pL → + ∞

$$\Sigma(\%) = 100\left[\frac{1}{1 + e^{(pL - pL_{50})/S}} - 1\right] \qquad (2)$$

where pL_{50} and S are empirical parameters. In particular, pL_{50} represents the ligand concentration necessary to sequester 50 % of the metal ion; therefore, this parameter can be used as a measure of the sequestering ability of different ligands. The S parameter represents the slope at the inflection of the $\Sigma(\%)$ function versus pL.

To evidence the different sequestering ability of ligands toward Hg^{2+}, we calculated the pL_{50} values for each system by means of the $\Sigma(\%)$ function versus pL in the presence of Hg^{2+} trace amounts and with pL ranging from 0 to 15. Calculations were performed at pH 5.0 and at pH 8.1, that is, the pH of seawater. Results are reported in Table 12 and are shown in Figures 4, 5, and 6 for O-donor ligands, N-donor ligands, and amino acids, respectively, at pH 8.1 as an example. As observed, at this pH value, the higher sequestering ability is that of N-donor ligands, with pL_{50} ranging from 4.23 (for spd) to > 12 (for tetren and pei).

Among O-donor ligands, mellitate shows the higher sequestering ability with $pL_{50} = 11.00$ and 9.68 at pH 5.0 and 8.1 respectively. The sequestering ability of other carboxylates is lower than that of mlt and significantly varies from pH 5.0 to pH 8.1; for example, for btc, we obtain 6.76 and 3.06, respectively. This behavior can be explained considering the speciation model of the Hg^{2+}−btc system (Figure 1) at pH 8.1; the only complex species is $Hg(btc)OH^{3-}$, whereas most of the mercury is present as the hydrolytic $Hg(OH)_2^0$ species. If we consider lower pH values, then high formation percentages of $Hg(btc)^{2-}$, $Hg(btc)H^-$, and $Hg(btc)H_2^0$ species can be found. The sequestering ability of O-donor ligands toward Hg^{2+} is comparable to that of the phytate ion.[61] If we compare the sequestering ability of btc, dien, and Asp at the two different pH values, then we obtain at pH 8.1 the trend dien > Asp > btc, whereas at pH 5.0, dien still shows the highest sequestering ability, but the differences with btc and Asp are lower than those at pH 8.1 (trend is dien > Asp ≈ btc). A comparison is shown in Figure 1S of the Supporting Information.

The influence of ionic strength on sequestering ability is significant for O-donor systems, whereas it is negligible for N-donor systems. In Figure 7, as an example, pL_{50} of Hg^{2+}−btc complexes at $I = 0.1$ and $0.5\ mol\cdot L^{-1}$ at pH 5.0 and 8.1 is reported. As can be noted, when the ionic strength is increased from (0.1 to 0.5) $mol\cdot L^{-1}$, the pL_{50} value decreases for both pH values: at pH 5.0, from 6.76 to 5.70; at pH 8.1, from 3.06 to 2.00. Therefore, it is necessary to have more ligand to sequester the mercury when the ionic strength of the medium increases.

Figure 8 shows the influence of temperature on sequestering ability. $\Sigma(\%)$ versus pL, for Hg^{2+}−btc as an example, at three different temperatures ((15, 25, and 37) °C) is reported. For this system, pL_{50} decreases from (15 to 37) °C: at pH 5.0, pL_{50} = 7.10, 6.76, and 6.30 at t = (15, 25, and 37) °C, respectively; at pH 8.1, pL_{50} = 3.42, 3.06, and 2.71 at t = (15, 25, and 37) °C, respectively. The same trend is observed for the Hg^{2+}−dien system (Figure 2S in the Supporting Information): at pH 8.1, pL_{50} = 7.12, 6.68, and 5.32 at t = (15, 25 and 37) °C, respectively. The decreasing effect of temperature on pL_{50} is higher for N-donor systems than for O-donor ligand−Hg^{2+} systems.

General Trend for the Stability of Hg^{2+}−O-Donor and −N-Donor Ligand Complexes. The stability of complex species between metal ion and different classes of ligands depends on several factors, such as the number and the type of binding sites, the charges in the ligand, the formation of chelate rings, and other structural effects (e.g., distance between coordinating groups, steric hindrance, etc.). By examining the formation parameters reported here, we can observe some regularities that allowed us to estimate some general parameters for each ligand class.

Sixteen formation constants for Hg^{2+}−carboxylate complexes (suc, btc, mlt, pma, paa2, and paa100, both unprotonated and monoprotonated; formate, acetate, oxalate, and citrate (literature data, Table 1)) at $I = 0.1\ mol\cdot L^{-1}$ were considered. Each

Table 9. Ligand Protonation Constants in $NaNO_3$ at Different Ionic Strengths (in mol·L^{-1}) and at t = 25 °C[a]

L	I	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6
btc	0.25	6.15 ± 0.01[b]	11.20 ± 0.02[b]	15.24 ± 0.02[b]	18.36 ± 0.04[b]		
	0.50	6.01 ± 0.01	10.93 ± 0.03	14.92 ± 0.03	17.98 ± 0.04		
	1.00	5.87 ± 0.01	10.71 ± 0.01	14.66 ± 0.01	17.68 ± 0.02		
mlt	0.25	6.01 ± 0.03	11.16 ± 0.03	15.34 ± 0.04	18.32 ± 0.01	19.41[c]	20.1[c]
	0.50	5.60 ± 0.06	10.41 ± 0.07	14.31 ± 0.08	17.16 ± 0.01	18.36	19.1
	1.00	5.12 ± 0.03	9.55 ± 0.05	13.15 ± 0.06	15.94 ± 0.02	17.49	18.2
paa2	0.25	5.360 ± 0.008	9.34 ± 0.09				
	0.50	5.23 ± 0.02	9.122 ± 0.009				
	1.00	5.173 ± 0.005	9.08 ± 0.06				
paa100	0.25	5.61 ± 0.02	9.85 ± 0.02				
	0.50	5.429 ± 0.007	9.55 ± 0.01				
	0.75	5.383 ± 0.004	9.458 ± 0.006				
	1.00	5.329 ± 0.003	9.372 ± 0.004				
dien	0.25	9.818 ± 0.001	18.882 ± 0.002	23.379 ± 0.004			
	0.50	9.872 ± 0.003	18.990 ± 0.002	23.592 ± 0.005			
	1.00	9.98 ± 0.02	19.19 ± 0.01	24.01 ± 0.02			
tetren	0.25	9.69 ± 0.03	18.99 ± 0.02	27.26 ± 0.03	32.19 ± 0.04	35.40 ± 0.05[b]	
	0.50	9.87 ± 0.02	19.36 ± 0.01	27.87 ± 0.01	33.04 ± 0.02	36.34 ± 0.02	
	1.00	9.97 ± 0.01	19.571 ± 0.005	28.240 ± 0.008	33.577 ± 0.009	37.12 ± 0.01	

[a] β_i refers to reaction: iH + L = H_iL (charges omitted for simplicity). [b] ± std. dev. [c] Values in NaCl.[60]

Table 10. Formation Constants of Hg^{2+}−Ligand Systems in $NaNO_3$ at Different Ionic Strengths and at t = 25 °C[a]

L	I/mol·L^{-1}	log β_{110}	log β_{111}	log β_{112}	log β_{11-1}	log β_{210}
btc	0.25	10.78 ± 0.01[b]	16.11 ± 0.02[b]	20.43 ± 0.03[b]	4.10 ± 0.01[b]	
	0.50	10.33 ± 0.02	15.47 ± 0.04	19.67 ± 0.09	3.79 ± 0.03	
	1.00	9.67 ± 0.01	14.48 ± 0.02	18.63 ± 0.04	3.08 ± 0.02	
mlt	0.25	18.02 ± 0.01	21.96 ± 0.09	24.83 ± 0.08	13.92 ± 0.09	
	0.50	17.43 ± 0.09	21.25 ± 0.06	24.10 ± 0.08	13.10 ± 0.10	
	1.00	17.27 ± 0.01	21.07 ± 0.04	23.98 ± 0.04	12.10 ± 0.08	
paa2	0.25	10.80 ± 0.02	15.93 ± 0.03	20.15 ± 0.06	3.78 ± 0.02	
	0.50	10.70 ± 0.02	15.73 ± 0.04	19.86 ± 0.06	3.68 ± 0.03	
	1.00	10.64 ± 0.03	15.52 ± 0.06	19.97 ± 0.09	3.47 ± 0.05	
paa100	0.25	11.54 ± 0.009	16.28 ± 0.02	20.04 ± 0.04	3.96 ± 0.01	
	0.50	11.38 ± 0.006	16.16 ± 0.01	20.28 ± 0.01	3.90 ± 0.01	
	1.00	11.29 ± 0.006	16.06 ± 0.01	20.20 ± 0.01	3.90 ± 0.01	
dien	0.25	19.15 ± 0.05	25.35 ± 0.04		9.45 ± 0.14	24.49 ± 0.09[b]
	0.50	19.53 ± 0.01	25.55 ± 0.01		9.95 ± 0.02	25.15 ± 0.02
	1.00	19.85 ± 0.01	25.91 ± 0.01		10.21 ± 0.03	25.82 ± 0.03
tetren	0.25	26.94 ± 0.03	32.06 ± 0.02	36.40 ± 0.06	15.77 ± 0.06	
	0.50	27.30 ± 0.01	32.50 ± 0.01	36.90 ± 0.01	15.54 ± 0.06	
	1.00	27.55 ± 0.01	32.92 ± 0.01	37.24 ± 0.01	13.75 ± 0.05	

[a] β_{pqr} refers to reaction: pHg + qL + rH = $Hg_pL_qH_r$ (charges omitted for simplicity). [b] ± std. dev.

formation constant was divided by the number of binding groups (i.e., the number of carboxylic groups, except for btc (3), mlt (5), and all high-molecular-weight carboxylates (3); in parentheses is the reported number of considered groups). The mean value of log K/n is 3.8 ± 0.5, which corresponds to the free energy per bond $\Delta G_b = -21.7 \pm 3$ kJ·mol^{-1}. The relatively low confidence interval indicates that other factors play a less relevant role.

Analogous treatment of amine complexes formation data gives (en (2), dien (3), spd (3), trien (4), tetren (5), paam (3), and pei (4); in parentheses is reported the number of binding groups) log $K/n = 6.2 \pm 0.8$ or $\Delta G_b = -35.4 \pm 5$ kJ·mol^{-1}. In this case, we considered only unprotonated complexes because for monoprotonated complexes, significantly different values are obtained: log $K/n = 4.8 \pm 0.3$ or $\Delta G_b = -27.4 \pm 2$ kJ·mol^{-1}. This decrease in the stability is likely due to the presence of a positive charge on the ligand, which makes the complex species less stable. Amino acids show the additivity of $-COO^-$ and $-NH_2$ contributions, in particular, for histidine and aspartate.

Discussion

This article is a part of a general work that we are performing to develop a Hg^{2+} speciation model in natural waters. With this aim, here we took into account three different ligand classes (O-donors, N-donors, and amino acids). As expected, for a soft cation, Hg^{2+} shows higher affinity for N-donor than for O-donor ligands and an intermediate behavior for amino acids. Model speciation for different systems has been widely described in previous paragraphs, but to evidence the soft nature of Hg^{2+}, it is necessary to pay attention to the strength of the interactions. As can be seen in Table 6, when we compared, for example, the stability constant of HgL species, we found for O-donor ligands log β values that vary from 9.46 (for suc) to 12.08 (for pma), except for Hg(mlt) species (log β = 18.43). The stability of HgL species for amines is higher and varies from 16.47 (for en) to 26.87 (for tetren). Intermediate values are observed for amino acids (containing both O-donor and N-donor groups) with log β values, referring to HgL species, of 13.87, 14.86, and 15.75 for Gly, Asp, and His, respectively. The highest value obtained refers to His species and can be attributed to the presence in the molecule of two amino groups and further confirms the soft nature of the metal. If we also compare enthalpy values of Table 7, then those of Hg^{2+}−dien and −pei are considerably more exothermic than those of Hg^{2+}−btc and −mlt, whereas Hg^{2+}−Gly species present intermediate enthalpy values. The strong affinity for amino groups is reflected on the sequestering ability that is higher for all N-donor ligands,

Table 11. Empirical Parameters of Equation *1* for the Dependence on Ionic Strength (in $\mathrm{mol \cdot kg^{-1}}$) of Protonation and Hg^{2+} Complex Formation Constants at t = 25 °C

L	*pqr*	$\log {}^{T}\beta_{pqr}$[a]	$\Delta\varepsilon$	σ[b]	L	$\log {}^{T}\beta_{pqr}$[a]	*pqr*	$\Delta\varepsilon$	σ[b]
btc	011	7.18	0.35	0.06	paa100	6.55 ± 0.02[c]	011	0.21	0.02
	012	13.01	0.58	0.09		11.49 ± 0.02	012	0.31	0.02
	013	17.36	0.83	0.10		13.33 ± 0.09	110	0.81	0.07
	014	20.92	0.87	0.11		18.45 ± 0.09	111	1.07	0.09
	110	13.32 ± 0.06[c]	−0.38	0.07		22.56 ± 0.09	112	1.26	0.10
	111	19.34 ± 0.06	−0.76	0.07		5.06 ± 0.09	11−1	0.69	0.07
	112	23.92 ± 0.04	−0.79	0.07					
	11−1	5.91 ± 0.07	−0.75	0.08	dien	9.79	011	0.16	0.04
						18.54	012	0.19	0.06
mlt	011	7.90	−0.34	0.03		22.20	013	0.55	0.08
	012	14.60	−0.57	0.05		18.96 ± 0.04	110	0.86	0.06
	013	20.01	−0.76	0.07		24.68 ± 0.04	111	0.36	0.02
	014	23.88	−0.60	0.10		9.49 ± 0.07	112	1.12	0.11
	110	21.10 ± 0.07	1.06	0.10		23.22 ± 0.07	11−1	0.90	0.07
	111	26.09 ± 0.10	1.49	0.12					
	112	29.72 ± 0.11	1.98	0.13	tetren	9.78	011	0.16	0.07
	11−1	16.09 ± 0.09	−1.07	0.10		18.79	012	0.33	0.10
						26.53	013	0.42	0.14
paa2	011	6.17 ± 0.01	0.21	0.003		30.39	014	0.66	0.11
	012	10.67 ± 0.01	0.42	0.01		32.39	015	0.54	0.07
	110	12.36 ± 0.04	0.72	0.05		26.79 ± 0.05	110	0.73	0.06
	111	17.75 ± 0.08	0.63	0.09		31.28 ± 0.06	111	0.78	0.05
	112	21.85 ± 0.06	0.91	0.05		35.08 ± 0.09	112	0.06	0.09
	11−1	5.02 ± 0.06	0.09	0.05		16.63 ± 0.07	11−1	−2.30	0.2

[a] β_{pqr} refers to reaction: $p\mathrm{Hg} + q\mathrm{L} + rH = \mathrm{Hg}_p\mathrm{L}_q\mathrm{H}_r$ (charges omitted for simplicity). [b] Std. dev. in the fit of eq 1. [c] ± std. dev.

Table 12. $\mathrm{pL_{50}}$ Values of Equation *2* for Different Ligands at pH 5.0 and 8.1 and t = 25 °C[a]

	$\mathrm{pL_{50}}$	
L	pH 5.0	pH 8.1
suc	5.58	1.56
btc	6.76	3.06
mlt	11.00	9.68
pma	8.22	2.37
paa2	7.00	2.47
paa100	7.42	2.38
en	5.94	6.16
dien	7.78	6.68
spd	3.60	4.23
trien	10.33	11.69
tetren	11.20	> 12
paam	6.62	6.33
pei	11.38	> 12
Gly	5.76	3.88
His	7.00	4.23
Asp	6.58	5.14

[a] $S = 1.00 \pm 0.05$.

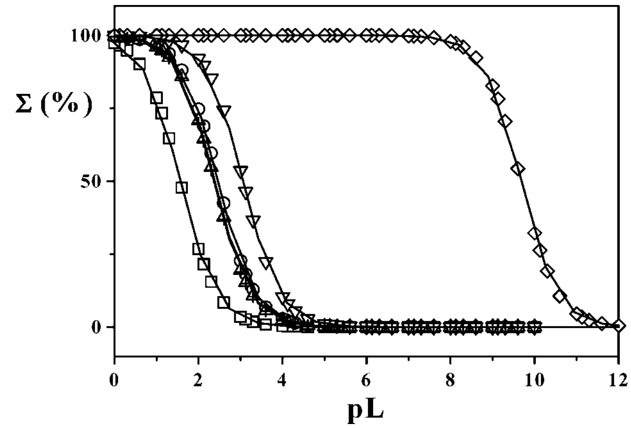

Figure 4. Sum of percentages of Hg^{2+}−O-donor ligand species versus pL in $NaNO_3$ at I = 0.1 $\mathrm{mol \cdot L^{-1}}$ and t = 25 °C. Concentration: $C_{Hg^{2+}}$ = trace, pH 8.1. Symbols: □, suc; +, pma; ○, paa2; △, paa10; ▽, btc; ◇, mlt.

particularly for trien, tetren, and pei, as can be seen from $\mathrm{pL_{50}}$ values reported in Table 12. Among carboxylates, only the mlt sequestering ability ($\mathrm{pL_{50}}$ = 11.00, at pH 5.0) is comparable to that of these amines. In general, both temperature and ionic strength must be suitably taken into account because they have a strong effect on the sequestering ability of all ligand classes studied here.

Literature Comparisons

Speciation studies of natural waters need the knowledge of interaction between Hg^{2+} and high- and low-molecular-weight ligands. Whereas many papers can be found in the literature on high-molecular-weight ligands,[6−11] very few data on low-molecular-weight ligands are reported. In Table 1, formation constants of complexes between Hg^{2+} and ligand classes studied in this article (carboxylates, amines, and amino acids) are collected. As can be seen, these data are few and are often fragmentary. In some cases, the data refer to only one ionic strength value, and whereas there are data at different ionic strengths, they refer to different ionic media or to different speciation models. Authors have mainly taken into account the formation of deprotonated species only and two systems (en and dien) of protonated or hydrolytic ones. In the present article, the formation of mixed hydrolytic HgL(OH) species assumes remarkable importance with significant formation percentages, particularly in the alkaline pH range (see Figures 1, 2, and 3).

In regard to enthalpy values, we obtained ΔH = 43.9 $\mathrm{kJ \cdot mol^{-1}}$ (refers to the reaction: $Hg^{2+} + 2H_2O = Hg(OH)_2^0 + 2H^+$), which is very close to ΔH = 45.2 $\mathrm{kJ \cdot mol^{-1}}$ reported by Anderegg et al.[67] under the same conditions of ionic medium, ionic strength, and temperature. Moreover, in the literature are also reported ΔH = (41.2 and 41.1) $\mathrm{kJ \cdot mol^{-1}}$ at I = (1 and 3) $\mathrm{mol \cdot L^{-1}}$, respectively, in $NaClO_4$.[68,69] For the reaction $Hg^{2+} + 2Cl^- = HgCl_2^0$, we obtained $\Delta H = -55$ $\mathrm{kJ \cdot mol^{-1}}$, which is close to ΔH = (− 53.6, − 50.9, and − 51.4) $\mathrm{kJ \cdot mol^{-1}}$ in $NaClO_4$ at I = (0.5, 1, and 3) $\mathrm{mol \cdot L^{-1}}$, respectively.[68−70] For the ternary species $HgCl(OH)^0$, referred to the reaction $Hg^{2+} + Cl^- + H_2O = HgCl(OH)^0 + H^+$, we obtained $\Delta H = -2.5$ $\mathrm{kJ \cdot mol^{-1}}$, which is in absolute agreement with $\Delta H = -3.2$ $\mathrm{kJ \cdot mol^{-1}}$ at I = 1 $\mathrm{mol \cdot L^{-1}}$ in $NaClO_4$.[71] In the literature, there

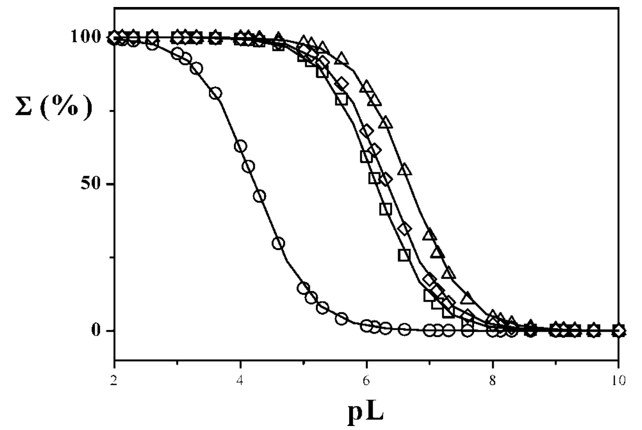

Figure 5. Sum of percentages of Hg^{2+}−N-donor ligand species versus pL in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C. Concentration: $C_{Hg^{2+}}$ = trace, pH 8.1. Symbols: ○, spd; □, en; ◇, paam; △, dien.

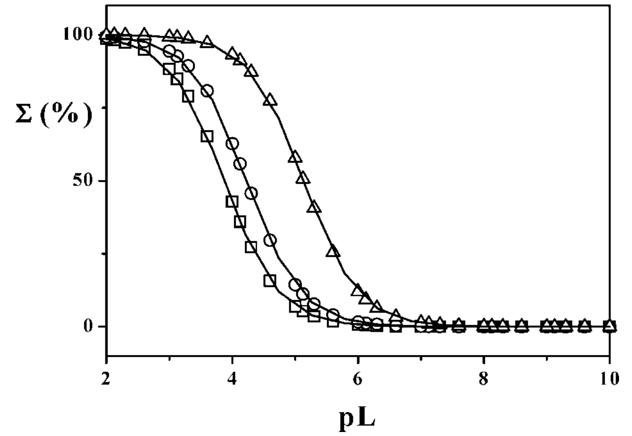

Figure 6. Sum of percentages of Hg^{2+}−amino acid species versus pL in $NaNO_3$ at $I = 0.1$ mol·L^{-1} and $t = 25$ °C. Concentration: $C_{Hg^{2+}}$ = trace, pH 8.1. Symbols: □, Gly; ○, Asp; △, His.

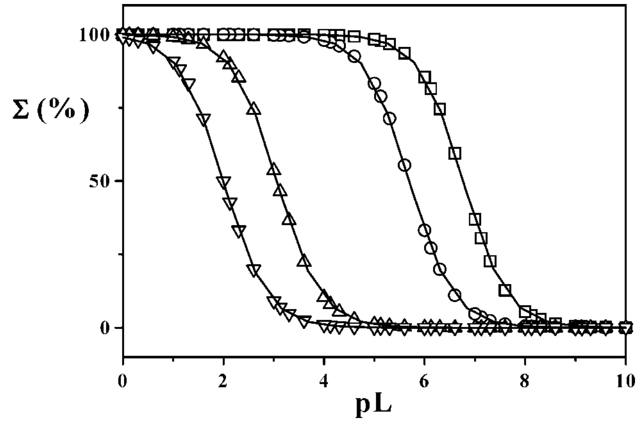

Figure 7. Sum of percentages of Hg^{2+}−btc species versus pL in $NaNO_3$ at $I = 0.1$ and 0.5 mol·L^{-1} and at two different pH values (pH 5.0 and 8.1). Concentration: $C_{Hg^{2+}}$ = trace. Symbols: □, pH 5.0, $I = 0.1$ mol·L^{-1}; ○, pH 5.0, $I = 0.5$ mol·L^{-1}; △, pH 8.1, $I = 0.1$ mol·L^{-1}; ▽, pH 8.1, $I = 0.5$ mol·L^{-1}.

are only a few works regarding enthalpy values of species containing Hg^{2+} and amines.[20,29,72] No ΔH or $T\Delta S$ values have been reported for the Hg^{2+}−btc, −mlt, and −pei systems. In the papers of Roe et al.[20] and Partridge et al.,[72] for the systems containing en, dien, and Gly, the formation of M_2L species is proposed. Our speciation models for the same systems are more complicated because they present the formation of four species for each system. By way of comparison, in ref 72, $\Delta H = -92.8$ kJ·mol^{-1} is reported for $Hg_2(Gly)$ species, which is close to our result of $\Delta H = -87$ kJ·mol^{-1}. (See Table 7.) Moreover, some species with different stoichiometries show comparable formation enthalpy values: in ref 20, $\Delta H = -151$ kJ·mol^{-1} was attributed to the $Hg(dien)_2$ species, which is fairly close to our result of $\Delta H = -173$ kJ·mol^{-1} regarding the $Hg_2(dien)$ species. The comparison of formation enthalpy values of the HgL species for dien ($\Delta H = -135.6$ kJ·mol^{-1}, this work), trien ($\Delta H = -126.3$ kJ·mol^{-1}),[29] and tetren ($\Delta H = -139.7$ kJ·mol^{-1})[29] shows that the increase in the number of $-NH_2$ groups from three to five induces little enthalpy difference.

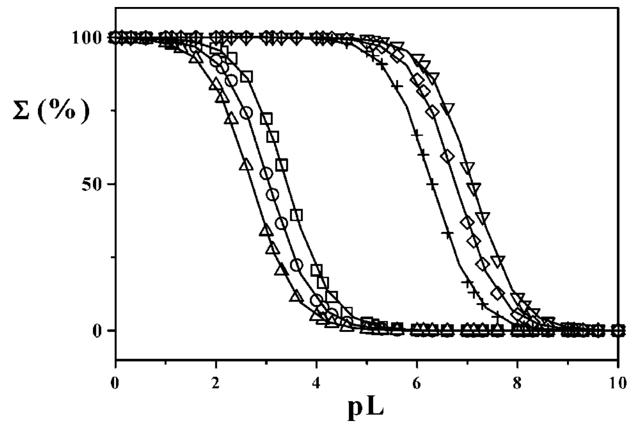

Figure 8. Sum of percentages of Hg^{2+}−btc species versus pL in $NaNO_3$ at $I = 0.1$ mol·L^{-1}, at two different pH values (pH 5.0 and 8.1), and at t = 15, 25, and 37 °C. Concentration: $C_{Hg^{2+}}$ = trace. Symbols at pH 8.1: □, 15 °C; ○, 25 °C; △, 37 °C. At pH 5.0: ▽, 15 °C; ◇, 25 °C; +, 37 °C.

Supporting Information Available:

Sum of percentages of Hg^{2+}−dien, −Asp, and −btc species versus pL in $NaNO_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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