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The Solvation Thermodynamics of Methylmercury(II) Species Derived from Measurements of the Heat of Solution and the Henry's Law Constant

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Abstract

The heat of solution, ΔH_s^0, for methylmercury(II) chloride in water was determined calorimetrically. Corresponding measurements in pyridine were made for the CH_3HgX (X = Cl, Br and I) complexes, as well as for dimethylmercury(II). The ΔH_s^0 values were used in combination with ΔH_{sub}^0 or ΔH_{vap}^0 data from the literature to calculate the heats of solvation. The free energy of solvation in water, expressed as the Henry's law constant, *H*, was determined for the methylmercury(II) hydroxide complex. Mercury species of environmental importance are classified according to their ability to be transported from water to air, *i.e.* by using *H*. The ability to form hydrogen bond of the ligands is stated to be an important factor determining the magnitude of *H* in the air/water two phase system. Comparison of the solvation thermodynamics in the well-structured water with considerable weaker solvation properties than pyridine, with pyridine which has almost no solvent structure, implies the important relation between *H* and the entropy of solvation.

Introduction

Thermodynamic data for naturally-occurring mercury species are needed as basic parameters in assessing the biogeochemical cycle of mercury. The air/water exchange of uncharged mercury compounds is considered to be an important pathway in nature [1, 2]. The direction and magnitude of this transfer thus has a pronounced effect on the atmospheric residence time of mercury.

The total mercury fluxes between gas and aqueous phase are highly dependent on contributing compounds, which vary in their natural abundance and chemical properties. Several mercury species of importance have previously been given from equilibrium calculations in aqueous solution [2–6] and have been compared with analytical speciations of mercury in the environment [2]. A definite determination of existing species is, however, highly dependent on the operational procedure and therefore difficult to obtain. Furthermore, the chemical conditions in nature are usually not in equilibrium.

There is also a deficiency in basic thermodynamical knowledge regarding phase distribution equilibria and solvation strength, also for the proposed important complexes. In order to evaluate the transition tendency of the different species between air and water phase, they may be classified by the magnitude of the respective distribution constant, the Henry's law constant (*H*).

The purpose of the present study is to investigate the relationship between the Henry's law constant for mercury complexes of environmental importance and the properties of corresponding solvent–solute interactions. It may thus be possible to forecast approximate magnitudes of *H* from structural and/or heat of solvation data for other mercury species with suggested significant fluxes. The relationship is obvious since the solvation free energy, ΔG_{sv}^0, is:

$$\Delta G_{sv}^0 = \Delta H_{sv}^0 - T\Delta S_{sv}^0 = -RT\ln(1/H)$$

where ΔH_{sv}^0 and ΔS_{sv}^0 are the heat and entropy of solvation, respectively. The heat of solvation indicates the coordination strength of solvent molecules to the mercury complex.

Possible structural interactions with the solvent and a subsequent deviation from linearity in solvated uncharged mercury(II) halides [7, 8] and methylmercury(II) complexes [9, 10] in various solvents have been reported. The linear structure in the gas phase of the environmentally impor-

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tant CH_3HgX complexes, ($X = Cl, Br, I, CH_3$) [11, 12] seems to persist in aqueous solution [9, 10]. Raman spectroscopy data for the solvated inorganic mercury(II) halides indicate, however, a minor deviation from linearity due to more pronounced interactions between water and mercury [13]. It was thus of interest to study the corresponding differences in the thermodynamic data – free energy, enthalpy and entropy of solvation – to confirm the varying properties of solvation.

Heats of solvation for the methylmercury(II) species can be obtained from measurements of heats of solution, ΔH_s^0, and heats of sublimation, ΔH_{sub}^0 without any extrathermodynamic assumptions.

$$\Delta H_{sv}^0 = \Delta H_s^0 - \Delta H_{sub}^0$$

Heats of solution of methylmercury(II) chloride in water and of methylmercury(II) halides and dimethylmercury in pyridine have been determined calorimetrically in the present investigation. Heats of sublimation, ΔH_{sub}^0, were taken from the literature [14].

The heats of solvation found for the methylmercury(II) species are compared to values found for mercury(II) halides in water, dimethylsulfoxide [15] and pyridine [13]. Additional heat of solvation data for dimethylmercury and elemental mercury in water have been reported [16, 17]. The electron donor properties of two solvents, water and pyridine, and the correlated change in heat of solvation for methylmercury(II) species was subsequently resolved from the present study.

The increasing hydrogen bonding properties of the ligands in the series $CH_3 < I^- < Br^- < Cl^- < OH^-$ are expected to be reflected in the heat of solvation and the Henry's law constant. The Henry's law constant for methylmercury(II) hydroxide must be considerably lower compared to other methylmercury(II) complexes, depending on the strong hydrogen bond to the bulk water (*cf.* methylmercury(II) chloride and dimethylmercury). In the present study the magnitude of H for methylmercury(II) hydroxide is determined. Other experimentally derived distribution constants for various mercury species have been given elsewhere [1, 16, 17].

Experimental

Chemicals

Commercial CH_3HgCl (Merck), CH_3HgBr (Ventron), CH_3HgI (Ventron) and CH_3HgCH_3 (Ventron) were used without any purification in the calorimetric experiments. A purified CH_3HgOH solution, used in two distribution experiments, was prepared from a 1000 ppm aqueous stock solution of methylmercury(II) chloride (Ventron) according to a method described in the literature [18]. A freshly diluted experimental solution was prepared from a commercial 1 M aqueous solution of methylmercury(II) hydroxide (Ventron). The structural determination of methylmercury(II) hydroxide in water had previously been performed on a sample from this stock solution [9]. Pyridine *p.a.* (Merck) was dried by means of 3 Å molecular sieves. Milli-Q water was used as solvent in the Henry's law constant investigation and double-distilled water in the calorimetric study. The various ionic media were prepared from carefully dried NaCl (Merck), $NaClO_4$ (Merck) and Et_4NClO_4 (Fluka). A purified NaOH solution with a known trace mercury content, 22 ng l^{-1}, was used for pH adjustment of the experimental methylmercury(II) hydroxide solution. Purification of the gas phase, oxygen (AGA), has previously been described [1]. Freshly prepared 10% $NaBH_4$ (Fluka) solutions were used for mercury analysis of the aqueous phase in the distribution experiments [1].

Calorimetric Measurements

A detailed description of the experimental set–up and techniques applied in the calorimetric measurements are reported elsewhere [19]. Weighed amounts of the methylmercury(II) species (0.005–0.4 g) were enclosed in glass ampoules within a glove-box. The volume of solvent was always 80.0 ml. The heat of solution of methylmercury(II) chloride in water was measured in three different ionic media (0.7 M NaCl, 0.7 M $NaClO_4$ and 0.1 M Et_4NClO_4). The ionic medium in pyridine was always 0.1 M Et_4NClO_4. The methylmercury(II) compounds were dissolved within 3 minutes in experiments performed at 25.000 ± 0.002 °C.

The Henry's Law Constant

The experimental technique has been previously described in detail [1]. Three vessels, connected in series, contained aqueous methylmercury(II) hydroxide. A steady flow of oxygen was purged through the system. The use of three vessels ensure a constant aqueous phase concentration in the third vessel during the experiment [1]. The Henry's law constant can thus be resolved directly from the aqueous phase concentration of methylmercury(II) hydroxide in the third vessel and the methylmercury(II) hydroxide amount distributed to a known gas phase volume. The dynamic flow system is based on the fact that an uncharged solute is distributed into the gas phase conducted through the aqueous phase. Under these circumstances a distribution equilibrium can be assumed for compounds, *e.g.* methylmercury(II) hydroxide, exhibiting low Henry's law constants [1]. The three distribution vessels used in the present

TABLE I. Heats of Solvation, ΔH_{sv}^0, Derived from Calorimetric Measurements of Heats of Solution, ΔH_s^0, for CH_3HgX (X = Cl, Br, I, and CH_3) in Water and Pyridine Media at 25 °C (kJ mol^{-1}).

Species	ΔH_{sub}^0	ΔH_s^0		ΔH_{sv}^0	
		Water[a]	Pyridine[b]	Water	Pyridine
CH_3HgCl	64.0[d]	15.9 ± 1.2[c]	−1.0 ± 1.1[c]	−48.1	−65.0
CH_3HgBr	67.4[e]		−0.2 ± 0.1[c]		−67.6[f]
CH_3HgI	64.5[d]		1.6 ± 0.6[c]		−62.9
CH_3HgCH_3	34.6[g]		−0.9 ± 0.2[c]		−35.5

[a] Determined in a 0.7 M NaCl medium. ΔH_s^0 in 0.7 M $NaClO_4$ was found to be 13.5 ± 1.3 kJ mol^{-1} and ΔH_s^0 in 0.1 M Et_4NClO_4 resulted in 15.6 ± 0.7 kJ mol^{-1}. [b] Determined in 0.1 M Et_4NClO_4 medium. [c] Present work. [d] Ref. 14. [e] Ref. 14. Present value is probably somewhat too large. [f] Expected to be less negative if ΔH_{sub}^0 is too high. [g] Ref. 27.

study were made of welded polyvinylidenfluoride. The vessels were cleaned with *aqua regia,* extensively soaked with Milli-Q, water and finally rinsed with the experimental solution. The total mercury amount distributed to the gas phase was collected on gold traps [1]. Contribution from reduction or disproportionation reactions resulting in the volatile elemental mercury or eventually dimethylmercury species were checked, by inserting a fourth vessel containing 10 ml Milli-Q water after the third distribution vessel but before the gold traps. In one experiment, Milli-Q water acidified with HNO_3 suprapur (Merck) to pH 1 was used. The methylmercury(II) hydroxide content in the gas phase may be considered as being completely trapped in the Milli-Q water while the volatile compounds are passing through the vessel, due to the much larger tendency to distribute to the gas phase (*cf.* the *H* in Table III). The methylmercury(II) ion formed in the acidified water completely lacks the ability to distribute to the gas phase.

The concentration of methylmercury(II) hydroxide was between 3.3 and 63.7 μM and a volume of 5 to 8 ml was added to each of the three vessels. The aqueous phase concentration in the third vessel was found from subsamples which were added to a quartz reduction/volatilization vessel described elsewhere [20]. The quartz vessel was purged with mercury free helium gas (AGA) in connection with sodium borohydride treatment, and the volatilized mercury was collected on a gold trap. The gold traps containing mercury were analysed by use of a helium dc plasma emission spectrometer [1]. Calibration and precision of the analytical procedure can be found elsewhere [20]. The oxygen gas flow was always around 0.050 l min^{-1}. A temperature range of 11.5 to 25 °C was covered. Three different ionic media were used, 0.7 M sodium perchlorate, 0.2 × 10^{-3} M sodium chloride, with the pH adjusted to 11.2–11.5 and 0.1 × 10^{-3} M NaOH (pH adjusted Milli-Q water). The duration of the distribution experiments was always less than 24 h.

Results

The heats of solution for methylmercury(II) chloride in water and CH_3HgX (X = Cl, Br, I and CH_3) in pyridine, derived from the present calorimetric measurements, are listed in Table I. Variation in the dissolved amount of the various species had no effect on the ΔH_s^0 value, indicating that no other complexes are formed and that no dissociation occurs in the concentration range studied. The dissolution of methylmercury(II) chloride in water was also used to study the media dependence of the heat of solution. The three various ionic media gave no significant differences, see Table I.

The low solubilities of methylmercury(II) bromide and iodide in water make it difficult to perform precise calorimetric investigations [21]. The heats of solvation of these complexes in water was not studied in the present work. The solubility of dimethylmercury in water seems feasible for a calorimetric study [22], even though some contradicting solubility data have been reported [23]. Calorimetric measurements on $(CH_3)_2Hg$ in aqueous solution have, however, not been performed. The present investigation was undertaken in order to obtain the heat of solvation. A ΔH_{sv}^0 value for $(CH_3)_2Hg$ in water has previously been reported [16]. The heat of solvation for dimethylmercury was in this study derived from the temperature dependence of the Henry's law constant and may thus exhibit a lower accuracy compared to a value achieved by a calorimetric technique.

The heats of solution of the four various methylmercury(II) compounds in pyridine were determined without difficulty. The solubilities of the species in pyridine are much larger than are those in water,

TABLE II. Experimentally Determined Henry's Law Constant H for CH_3HgOH in Various Media and at some Different Temperatures.

Media	pH[a]	Temperature (°C)	Concentration of Hg (M)	Volatile Hg contribution[b] (%)	H[c] (dimensionless)	ΔG^0_{sv} (kJ mol^{-1})
Milli-Q water	10.1	15.0	6.4×10^{-5} [d]	30.5[e]	1.73×10^{-7}	−37.3
Milli-Q water	10.1	20.0	6.4×10^{-5} [d]	17.9	2.69×10^{-7}	−36.9
2×10^{-4} M NaCl	11.5	11.5	5.9×10^{-6} [f]	38.9	5.27×10^{-8}	−39.7
2×10^{-4} M NaCl	11.5	25.0	5.9×10^{-6} [f]	3.7	2.48×10^{-7}	−37.7
0.7 M $NaClO_4$	11.2	20.0	3.3×10^{-6} [f]	38.6	3.19×10^{-7}	−36.5
0.7 M $NaClO_4$	11.2	25.0	3.3×10^{-6} [f]	54.7	3.83×10^{-7}	−36.6

[a] The pH adjustment was performed with NaOH, which will contribute to the total ionic strength. [b] Determined by passage of Milli-Q water. [c] The Henry's law constant was defined as $[CH_3HgOH_{(g)}]\,[CH_3HgOH_{(aq)}]^{-1}$. [d] A dilution from the purified methylmercury(II) hydroxide solution. [e] The polymer Porapack was used as an alternative way to separate Hg^0 from CH_3HgOH. A good agreement was found considering that the effectiveness of this trap is defined by the operational conditions (C. Brosset, personal communication). [f] Diluted from the 1 M stock solution of CH_3HgOH.

due to the stronger solvation and a markedly lower degree of solvent structure.

The heats of sublimation were taken from the literature and are listed in Table I. It should be noted that the ΔH^0_{sub} value for methylmercury(II) bromide is probably too high. A re-determination of this value would be reassuring. The trend in the calculated heats of solvation for methylmercury(II) species are thus influenced by the enlarged ΔH^0_{sub} for methylmercury(II) bromide (see Table I).

A direct indication of the strength of solvent–solute interaction, beside the heat of solvation, can be resolved from the Henry's law constant. The Henry's law constant for methylmercury(II) hydroxide was determined in the present study. Representative primary data are shown in Figs. 1 and 2. The correction for a more volatile mercury species, Hg^0, derived by inserting water between the third distribution vessel and the gold trap, is displayed in Fig. 1 and Table II. Three various ionic media were used in order to study the 'salting-out' tendency [24, 25]. The values found reveal an increase in magnitude of H in the 0.7 M sodium perchlorate medium compared to the other two media, see Table II.

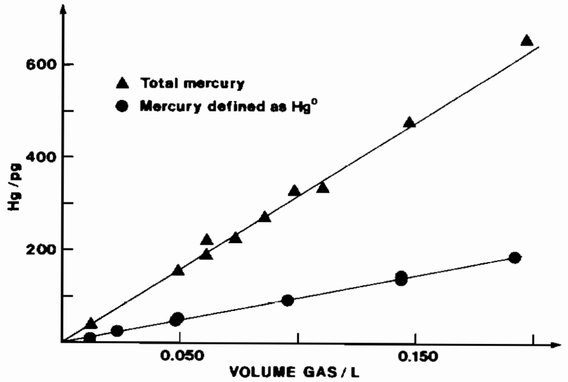

Fig. 1. Primary data for the gaseous phase in a representative determination of the Henry's law constant for methylmercury(II) hydroxide. Milli-Q water, pH adjusted to 10.1, was used as aqueous phase at the temperature 15.0 ± 0.5 °C.

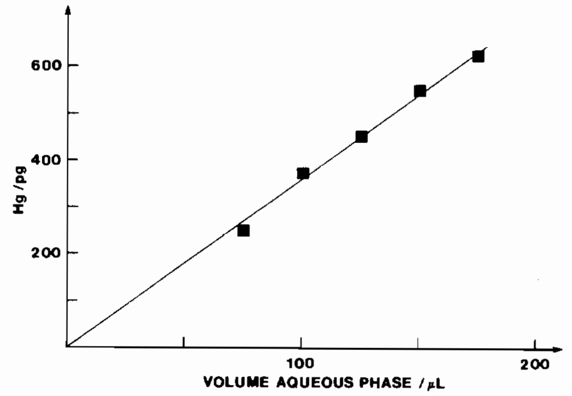

Fig. 2. Primary data for the aqueous phase mercury concentration in the same experiment (see Fig. 1). The water phase was diluted by a factor of 3.58×10^3 before the analyses.

Discussion

Heat of Solvation

The heats of solvation in pyridine and water show a marked difference in solvation between mercury(II), methylmercury(II) halides and dimethylmercury, see Table III. The heat of solvation value of dimethylmercury is only a half and a quarter of those values found for methylmercury(II) and mercury(II) halides, respectively. The ability to form solvate bonds to the mercury decreases when the softness of the ligands coordinated to mercury(II) is increased [9]. Pyridine forms solvate bonds to mercury in mercury(II) and methylmercury(II) halides [8, 10], while such bonds are probably not formed to dimethylmercury. Water forms hydrate bonds to mercury only in the mercury(II) halides. The halide groups in the complexes are solvated, and this is especially pronounced in water when hydrogen bonds are formed.

An interaction between mercury in the methylmercury(II) and mercury(II) halides and two pyridine molecules in the inner coordination sphere have been reported [8, 10]. The structural determination of these mercury(II) complexes can also be correlated with changes in reported ν(Hg–X) stretching frequencies determined by Raman spectroscopy [10, 13]. The difference in heat of solvation for methylmercury(II) chloride in water and pyridine reflects the various degrees of solvation strength. Linear structures of the methylmercury(II) halides in water were inferred from a direct structural investigation of methylmercury(II) hydroxide in water [9]. The solvated methylmercury(II) hydroxide has no other types of interaction with the surrounding bulk water, apart from van der Waals forces and hydrogen bonding to the hydroxide group. Water is in fact found at the approximate sum of van der Waals radii for Hg and O. The methylmercury(II) halides solvated in water are thus expected to behave in a similar manner. This statement is further evidenced by the comparison between reported ν(Hg–X) stretching frequencies for methylmercury(II) halides in various solvents and the solvated structures in water and pyridine ([9, 10]. The larger heat of solvation found for methylmercury(II) chloride in pyridine compared to water depends on a mercury-solvent interaction in addition to the van der Waals forces found in pyridine. The mercury is thus solvated in the inner coordination sphere, by pyridine, while in aqueous solution this kind of solvation is absent.

The Henry's law Constant

The determination of a very low Henry's law constant, as for CH_3HgOH in aqueous solution, has to be performed with extreme care. Contributions from a more volatile compound, believed to be elemental mercury, are found in all experiments (see Table II). This additional amount found in the gas phase was always, however, a minor fraction compared to methylmercury(II) hydroxide and was also very constant with time (see Fig. 1). An accurate correction of the gas phase data is thus possible. Trace amounts of inorganic mercury(II) and a reduction to elemental mercury enhanced by the high pH is considered to be the source of the evolution of volatile mercury. It has previously been observed that a high pH has considerable influence on the reduction rate of inorganic mercury(II) even in oxygen saturated aqueous solutions [20].

The relative occurrence of inorganic mercury(II) in the 1 M methylmercury(II) hydroxide solution, with a pH of 9.45, can be disregarded because of the low solubility of HgO(s) [26]. A fresh dilution of this stock solution or the purified 1000 ppm stock solution, together with a short experimental time, minimized the inorganic mercury(II) content to trace amounts compared with the methylmercury(II) hydroxide species. Methylmercury(II) compounds are regarded as thermodynamically metastable [6] and transformation into inorganic mercury(II) under the present experimental conditions is considered to be slow. Inorganic mercury(II) is thus of no importance in the relative speciation of the water phase. A reduction of these trace amounts, however, contributes significantly to the gas phase.

The magnitude of the Henry's law constant seems quite reasonable in comparison with the H derived for other methylmercury(II) species, *e.g.* methylmercury(II) chloride [1]. A change in degree of solvent–ligand interaction is expected to be the only difference between the solvation of these two species. The presence of stronger hydrogen bonds to the hydroxide ligand compared to the chloride is thus directly reflected in a lower H. The difference displayed in Table II between the various ionic media is considered to be partly a 'salting out' effect. The salting out of elemental mercury has previously been determined in various aqueous media [25].

Implications from Thermodynamic Data

The solvation of the methylmercury(II) halides in water occurs through the ever present (and in this case probably important) van der Waals forces and through hydrogen bonds to the halide ligand. Solvation of dimethylmercury and elemental mercury in water occur only through van der Waals forces.

The relative ability of the various species to form hydrogen bonds and interact through van der Waals forces with water can be related to the magnitude of the Henry's law constant, partly also shown by the heat of solvation, see Table III. The coordination of solvent molecules will, in addition, result in a change of the entropy of solvation, where more negative values are obtained.

The entropy of solvation consists of mainly two terms. One term is negative and is derived from the increased degree of order obtained when solvent molecules are solvating the mercury and the halide groups. This term becomes more negative with increasing solvation. The second term is positive and arises when solvent molecules have to be broken out of the bulk structure and the degree of order of the bulk is decreased. This term is especially large in solvents such as water with a pronounced bulk structure. The first entropy term is always larger than the second one, giving a totally negative

TABLE III. Summary of Known Thermodynamic Data Concerning the Relative Ability of Various Mercury Species to be Distributed Between a Gaseous and a Solvent Phase at 25 °C.

Species		H [a]			ΔG^0_{sv} [a]		ΔH^0_{sv} [b]		ΔS^0_{sv} [c]	
		Benzene	Water	Pyridine	Water	Pyridine	Water	Pyridine	Water	Pyridine
$HgCl_2$	expr						-68.8 [d]	-138 [e]		
	calc	1.1×10^{-5} [f]	6.4×10^{-7} [g]	2.0×10^{-7} [h]	-35.4 [g]	-38.2 [h]			-112	-335
$HgBr_2$	expr						-64.1 [d]	-136 [e]		
	calc	8.3×10^{-6} [i]	7.7×10^{-6} [j]	1.7×10^{-7} [k]	-29.2 [j]	-38.6 [k]			-117	-327
HgI_2	expr						-59.3 [d]	-130 [e]		
	calc	5.9×10^{-6} [i]	2.1×10^{-4} [j]	6.7×10^{-8} [k]	-21.0 [j]	-40.6 [k]			-128	-299
CH_3HgOH	expr		2.5×10^{-7} [l]		-37.7 [l]					
CH_3HgCl	expr		1.9×10^{-5} [m]		-26.9 [m]		-48.1 [l]	-65.0 [l]	-70.4	
	calc		2.7×10^{-5} [n]		-26.1 [n]					
CH_3HgBr	expr							-67.6 [l]		
	calc		1.1×10^{-4} [o]		-22.5 [o]					
CH_3HgI	expr							-62.9 [l]		
	calc		7.0×10^{-4} [o]		-18.0 [o]					
CH_3HgCH_3	expr		0.31 [p]		-2.9 [p]		-18.8 [p]	-35.5 [l]	-53.4	
	calc		0.13 [q]		-5.1 [q]					
Hg^0	expr		0.29 [r]		-3.1 [r]		-22.2 [r]		-64	
	calc		0.35 [s]		-2.6 [s]					

[a] Dimensionless Henry's law constant expressed as $[XHgX'_{(g)}][XHgX'_{(aq)}]^{-1}$ or free energy of solvation in kJ mol^{-1}. It should be noted that the experimental H have been determined in varying ionic strengths of the media, from pure water up to 0.1 M Cl^-. No correction for 'salting-out' has been applied in the Table. [b] Heat of solvation in kJ mol^{-1}. [c] Entropy of solvation in J K^{-1} mol^{-1}. Calculated from ΔG^0_{sv} and ΔH^0_{sv} values given in Table. The entropy value denoted experimental was calculated by use of experimentally determined values only. [d] Data from ref. 15 and refs. therein. [e] Data from ref. 13. [f] Data from refs. 28, 29, 31. [g] Data from refs. 29, 30. [h] Data from refs. 29, 31. [i] Data from refs. 27, 28, 31. [j] Data from refs. 27, 32. [k] Data from refs. 21, 31. [l] Present study. [m] Data from ref. 1. [n] Data from refs. 14, 16, 21. [o] Data from refs. 14, 21. [p] Data from ref. 16. [q] Data from refs. 14, 22. [r] Data from ref. 17. Defined as experimental. [s] Data from ref. 33. Defined as calculated.

entropy of solvation. The mercury(II) halides are expected to have the most negative entropies of solvation, depending on the fact that two solvent molecules are interacting with mercury and at least two with the halides. The entropies will be considerable more negative in pyridine than in water, depending on the stronger solvation and the marked lower bulk order. This pattern is indeed found, see Table III.

The ΔS^0_{sv} values for elemental mercury and dimethylmercury is as high as 50% of those found for the mercury(II) halides, in spite of the fact that the former species are solvated only through van der Waals forces. This is interpreted as that elemental mercury, dimethylmercury and to some extent methylmercury(II) halides fit very well in the water bulk structure, depending on their size and weak solvation. On the other hand, the mercury(II) halides, hydrated through both mercury and halide groups, are certainly bulky and fit poorly into the bulk structure. The bulk structure will be strongly affected and the degree of bulk order decrease markedly.

In conclusion, the hydrogen bonding properties of the ligands are responsible for a significant part of the variation in the Henry's law constant for mercury species in aqueous solution.

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