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Heats of Solvation of the Mercury(II), Silver(I) and Copper(I) Ions, and of some of Their Halogeno Complexes, in Solvents of Different Coordinating Properties

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Abstract

The heats of solvation of Cu^+, Ag^+, Hg^{2+}, and of their halogeno complexes, are generally larger in pyridine than in dimethyl sulfoxide, indicating a stronger solvation of these soft acceptors by the softer solvent. However, for the complexes HgL_4^{2-}, of regular tetrahedral coordination, this does not apply; in these the mercury atom is so well shielded that it does not interact immediately with the solvent. In acetonitrile, species of copper(I) in particular are strongly solvated, in spite of the fairly weak donor properties of the nitrogen atom in this solvent. In water, the heat of solvation is not a good measure of the strength of the solvate bond. The considerable energy used for breaking the structure of the bulk solvent results in abnormally low values of the heat of solvation. Not so strongly, though still to a marked extent, the solvent structure also influences the heats of solvation in the soft solvent tetrahydrothiophene. Even though stronger solvate bonds are certainly formed by this solvent than by pyridine, the heats of solvation are generally lower in tetrahydrothiophene, though less so the softer the acceptor.

Though the electrostatic terms, depending on ionic charge and radius, are the most prominent ones in the heats of solvation of ions, the covalent terms (soft–soft interactions) contribute nevertheless quite heavily in the case of typically soft acceptors.

Introduction

Previous studies [1, 2] of the formation of halogeno and thiocyanato complexes of mercury(II), silver(I) and copper(I) indicate that these typically soft acceptors are more strongly solvated in pyridine than in dimethyl sulfoxide (DMSO), or water. The same applies [3] to copper(I) in acetonitrile (AN). This reflects the softer character of the nitrogen donors pyridine and AN relative to the oxygen donors DMSO and, especially, water. To substantiate this inference, the heats of solvation, ΔH°_{sv}, in the various solvents of the species concerned should be compared. First, this applies to the free metal ions, Hg^{2+}, Ag^+ and Cu^+, being most strongly solvated, but the heats of solvation of the complexes formed are also of immediate interest.

The heats of solvation of neutral complexes, in the present systems HgL_2, AgL and CuL ($L^- = Cl^-, Br^-, I^-$) can be determined without any extrathermodynamic assumption, by combining the heats of sublimation and the heats of solution of the complexes [4]. For the calculation of the heats of solvation of individual ions, on the other hand, extrathermodynamic assumptions have to be introduced. Previously [4, 5] the assumptions chosen have been that $\Delta H^\circ_{sv}(H^+) = -1103$ kJ/mol in aqueous solution and that, between any two solvents, the enthalpies of transfer are the same for the tetraphenylarsonium and the tetraphenylborate ions, $\Delta H^\circ_{tr}(Ph_4As^+) = \Delta H^\circ_{tr}(BPh_4^-)$ (TATB-assumption). The same assumptions have been applied here. As to the TATB-assumption, recent measurements have confirmed that it most probably represents a fairly good approximation [6].

Calculations of heats of solvation of individual ions depend moreover critically upon the possibility of calculating the lattice enthalpies ΔH°_{lat} of the salts involved [4]. These are most reliably calculated for metal halides where cycles involving well-established values of heats of formation, ionization potentials and electron affinities can be applied [7]. For other types of salts, where these quantities are not known, the calculation of ΔH°_{lat} has to be based on empirical approaches founded on the electrostatic interaction between the ions concerned. For small ions of spherical symmetry, such methods seem to work fairly well [8, 9]. For salts containing large ions of spherical symmetry, however, various approaches yield fairly different results, as has been amply demonstrated in the case of K_2PtCl_6 [10]. Even if some procedures seem to yield more trustworthy results than others, their accuracy is still somewhat in

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doubt. Salts of the large tetrahedral ions HgL_4^{2-}, formed in the mercury halide systems [1] certainly belong to this category. Though accurate values of $\Delta H^\circ_{sv}(HgL_4)$ cannot, therefore, be calculated, it is nevertheless possible to calculate reliable values of ΔH°_{tr} between the solvents concerned, as will be shown below.

For ions of lower symmetry, such as HgL^+ and HgL_3^-, or CuL_2^- and AgL_2^-, no method for calculating ΔH°_{lat} has been devised. Moreover, many of these ions only rarely, if at all, appear in well-defined salts [11, 12]. A determination of their ΔH°_{sv} therefore seems a long way off.

As for mercury(II), all data necessary for the intended comparison already exist for water, DMSO and pyridine [1, 4, 13, 14]. In AN, only ΔH°_{sv} of $HgCl_2$ and $HgBr_2$ have been determined [14]; HgI_2 is not soluble enough for such a determination and no thermodynamic data exist that would allow the calculation of ΔH°_{sv} for Hg^{2+}, or for its ionic halogeno complexes. For silver(I), the values of $\Delta H^\circ_{sv}(Ag^+)$ are known for water and DMSO [15, 16]. On account of the low solubilities of AgL in these solvents [17], $\Delta H^\circ_{sv}(AgL)$ cannot be measured. The latter also applies to AgL in AN [17], while the solubility in pyridine is high enough to allow such a determination [2]. For copper(I), the disproportionation of Cu^+ and the low solubilities of CuL prevent the determination of heats of solvation for these species in aqueous solution. Already in DMSO, however, these obstacles have largely disappeared [18], and in acetonitrile [3] and pyridine [2] Cu^+ is perfectly stable and the halides CuL quite soluble.

The measurements were performed at 25 °C. As in previous measurements referring to pyridine and AN [1–3], a 0.1 M tetraethylammonium medium was used, with perchlorate as the non-coordinating anion. In DMSO, 1 M ammonium perchlorate was chosen as medium, also in order to conform with previous measurements [18].

Calculation and Notations

For neutral complexes

$$\Delta H^\circ_{sv} = \Delta H^\circ_{s} - \Delta H^\circ_{sub} \tag{1}$$

where ΔH°_s is the heat of solution of the solid, directly measured, and ΔH°_{sub} the heat of sublimation. Contrary to $\Delta H^\circ_{sub}(HgL_2)$, $\Delta H^\circ_{sub}(ML)$ of the neutral silver(I) and copper(I) halides cannot be very reliably determined by vapour pressure measurements [19–21]. Instead they have been calculated from the coordinate bond energies ΔH°_{CBE}, pertaining to the reaction $ML(g) \rightarrow M^+(g) + L^-(g)$, and the lattice enthalpies ΔH°_{lat}, pertaining to the reaction $M^+(g) + L^-(g) \rightarrow ML(s)$, as

$$-\Delta H^\circ_{sub} = \Delta H^\circ_{CBE} + \Delta H^\circ_{lat} \tag{2}$$

Values of ΔH°_{CBE} have been obtained by Pearson and Mawby [22], from the combination of the heats of atomization of the halides with the ionization potential of the metal, I_M, and the electron affinity of the halogen, E_L. Values of ΔH°_{lat} have been calculated according to (*cf.* ref. [4]):

$$\Delta H^\circ_{lat} = \Delta H^\circ_f(ML) - C - D - I_M - E_L \tag{3}$$

where ΔH°_f = standard heat of formation of ML(s), C = heat of sublimation of the metal, D = heat of atomization of the halogen (reaction $1/2L_2(s.s.) \rightarrow L(g)$).

For the ion solvation $M^+(g) + L^-(g) \rightarrow M^+(sv) + L^-(sv)$, the total heat of solvation is

$$\Delta H^\circ_{sv}(M^+) + \Delta H^\circ_{sv}(L^-) = \Delta H^\circ_s(M,L) + \Delta H^\circ_{lat}(ML) \tag{4}$$

where $\Delta H^\circ_s(M,L)$ refers to the reaction $ML(s) \rightarrow M^+(sv) + L^-(sv)$. This implies that

$$\Delta H^\circ_s(M,L) = \Delta H^\circ_s(ML) - \Delta H^\circ_{\beta 1} \tag{5}$$

where $\Delta H^\circ_{\beta 1}$ is the heat of the complex formation in solution $M^+(sv) + L^-(sv) \rightarrow ML(sv)$ which has already been measured [2, 3, 18]. Hence

$$\begin{aligned}\Delta H^\circ_{sv}(M,L) &= \Delta H^\circ_{sv}(M^+) + \Delta H^\circ_{sv}(L) \\ &= \Delta H^\circ_{lat} + \Delta H^\circ_s(ML) - \Delta H^\circ_{\beta 1}\end{aligned} \tag{6}$$

In the cases where ΔH°_{lat} and, consequently, ΔH°_{sv}(M,L) cannot be calculated with reasonable accuracy, the heats of transfer of pairs of ions can nevertheless be found by determining the values of $\Delta H^\circ_s(M,L)$ in the solvents concerned. As is evident from eqns. (5) and (6),

$$\begin{aligned}\Delta H^\circ_{tr}(M^+) + \Delta H^\circ_{tr}(L^-) = \Delta H^\circ_s(M,L)(II) \\ - \Delta H^\circ_s M,L)(I)\end{aligned} \tag{7}$$

for the sum of the heats of transfer from solvent I to solvent II.

A similar procedure can be applied to the anionic copper(I) complexes CuL_2^-. If the heats of reaction of $M^+(g) + 2L^-(g) \rightarrow ML_2^-(sv)$ are ΔH°_I and ΔH°_{II} in solvents I and II, respectively, then

$$\Delta H^\circ_{II} - \Delta H^\circ_I = \Delta H^\circ_{tr}(ML_2^-) \tag{8}$$

for the transfer $ML_2^-(I) \rightarrow ML_2^-(II)$. As, for solvent I,

$$\Delta H^\circ_I = \Delta H^\circ_{sv}(M^+) + 2\Delta H^\circ_{sv}(L^-) + \Delta H^\circ_{\beta 2} \tag{9}$$

and analogously for solvent II, then

$$\begin{aligned}\Delta H^\circ_{tr}(ML_2^-) = \Delta H^\circ_{tr}(M^+) + 2\Delta H^\circ_{tr}(L^-) + \Delta H^\circ_{\beta 2}(II) \\ - \Delta H^\circ_{\beta 2}(I)\end{aligned} \tag{10}$$

Analogously, for the mercury(II) complexes ML_j^{j-2}:

$$\begin{aligned}\Delta H^\circ_{tr}(ML_j^{j-2}) = \Delta H^\circ_{tr}(M^{2+}) + j\Delta H^\circ_{tr}(L^-) \\ + \Delta H^\circ_{\beta j}(II) - \Delta H^\circ_{\beta j}(I)\end{aligned} \tag{11}$$

where j = 1, 3 and 4 mean ionic complexes.

Experimental

Chemicals

The copper(I) halides were prepared as described in ref. 23. The silver perchlorate p.a. was dried at 100 °C and used without further purification. The silver halides were prepared by precipitation from aqueous silver perchlorate solution with sodium halides. The crystals were washed with ethanol and acetone and dried at 100 °C. DMSO and AN were distilled over calcium hydride (DMSO *in vacuo*). Pyridine p.a. was used without further purification. All solvents were kept over molecular sieves of pore size 3 Å to avoid contamination with moisture.

Calorimetric Measurements

The apparatus and procedure have been described previously [24]. In a dry-box, varying amounts of copper(I) or silver halide, or silver perchlorate (5–100 mg) were transferred to a weighed ampoule which was then sealed in the box, and weighed again. The substance was dissolved in $V = 80$ ml of solution.

Contrary to what is found for the mercury(II) halides [1], the neutral halide complexes of copper(I) and silver(I) have no extended range of existence in the solvents used [2]. This means that the reactions $2\ \mathrm{ML} \rightleftharpoons \mathrm{M}^+ + \mathrm{ML}_2^-$ occur rather extensively and must be corrected for when the values of $\Delta H_s(\mathrm{ML})$ are to be calculated. In the case of the silver halides, the formation of the dimers $\mathrm{Ag_2L^+}$ has also to be taken into account. The distribution between the different species can be computed, however, from the overall concentrations C_M and C_L of metal and ligand, respectively, and the known stability constants [2, 3, 18]. From the heats Q actually measured $\Delta H_s^\circ(\mathrm{ML})$ can then be found from

$$Q = -V(C_\mathrm{M}\Delta H_s^\circ(\mathrm{ML}) - [\mathrm{M^+}]\Delta H_1^\circ + [\mathrm{ML_2}]\Delta H_2^\circ) \quad (12)$$

for the copper(I) systems and from

$$Q = -V(C_\mathrm{M}\Delta H_s^\circ - [\mathrm{M^+}]\Delta H_1^\circ + [\mathrm{ML_2}]\Delta H_2^\circ + [\mathrm{M_2L^+}]\Delta H_{-2}^\circ) \quad (13)$$

for the silver(I) systems.

Generally, the substance was dissolved in the pure ionic medium (0.1 M $\mathrm{Et_4NClO_4}$), but in some cases a solution of the ligand had to be used. This applies to the copper(I) halides in DMSO where a disturbing disproportionation would otherwise take place [18]. By dissolving the respective halides in solutions containing 5.7 mM chloride, 10.0 mM bromide or 20 mM iodide, where copper(I) exists mainly as $\mathrm{CuL_2^-}$, the disproportionation was almost completely suppressed. Another example is the dissolving of silver iodide in pyridine. In the pure medium this reaction is too slow for precise measurements of Q. In 13 mM iodide solution, however, where mainly $\mathrm{AgL_2^-}$ is formed, the reaction proceeds smoothly enough. Also in such cases, eqns. (12) and (13) are of course valid for the calculation of $\Delta H_s^\circ(\mathrm{ML})$.

Results

The heats of solution for the neutral complexes CuL and AgL, calculated from eqns. (12) and (13), are listed in Table I. The values of $\Delta H_\mathrm{lat}^\circ$ and $\Delta H_\mathrm{sub}^\circ$ involved in the following calculations of solvation enthalpies are given in Table II. As already mentioned, values of $\Delta H_\mathrm{sub}^\circ$ for CuL and AgL have to be obtained indirectly; vapour pressure measurements yield at the most very approximate values, Table II. For $\mathrm{HgL_2}$, on the other hand, such measurements give the most reliable results. From the data collected, the solvation enthalpies of the metal ions $\mathrm{Cu^+}$, $\mathrm{Ag^+}$ and $\mathrm{Hg^{2+}}$ have been calculated for the solvents used, Table III. The values found for the three halide systems measured in each case agree satisfactorily.

Though values of $\Delta H_s^\circ(\mathrm{ML})$ cannot be measured for the silver halides in water, DMSO, or AN, values of $\Delta H_s^\circ(\mathrm{M,L})$ can nevertheless be determined from the heats of precipitation. In pyridine where these halides are soluble, values of $\Delta H_s^\circ(\mathrm{M,L})$ have been calculated from eqn. (5). For the non-complex perchlorate, $\Delta H_s^\circ(\mathrm{M,L})$ is obtained as the heat of solution. The values of $\Delta H_s^\circ(\mathrm{Ag,L})$ thus obtained, and of the transfer enthalpies $\Delta H_\mathrm{tr}^\circ(\mathrm{W} \rightarrow \mathrm{S})$ hence calculated, are in Table IV. The latter agree only approximately when calculated from different silver salts. The discrepancies are presumably due to difficulties in determining the heats of precipitation of the silver halides in water, DMSO and AN. Consequently, the values derived from the perchlorate measurements are considered as the most accurate ones. From these, and the value of $\Delta H_\mathrm{sv}^\circ(\mathrm{Ag^+})$ in pyridine presently determined (Table III), values of $\Delta H_\mathrm{sv}^\circ(\mathrm{Ag})$ have

TABLE I. Heats of Solution, ΔH_s° (kJ/mol), for the Neutral Copper(I) and Silver(I) Halogeno Complexes, at 25 °C[a]

	DMSO	AN	Pyridine		Pyridine
CuCl	−10.2 ± 0.7	−13.3 ± 0.6	−66.5 ± 1.3	AgCl	−13.2 ± 0.5
CuBr	−11.3 ± 0.3	−15.9 ± 0.3	−66.6 ± 1.7	AgBr	−14.7 ± 0.2
CuI	−1.8 ± 0.2	−6.1 ± 0.1	−61.7 ± 1.2	AgI	−22.0 ± 0.8

[a] The random errors indicated refer to three standard deviations.

TABLE II. Calculation of Lattice and Sublimation Enthalpies for the Copper(I), Silver(I) and Mercury(II) Halides

	$-\Delta H^\circ_f$ [a]	$-\Delta H^\circ_{lat}$ [b]	ΔH°_{CBE} [c]	ΔH°_{sub} [d]	ΔH°_{sub} [e] (vap)
CuCl	136.8	994.6	757.3	237.3	
CuBr	105.4	976.9	750.6	226.3	
CuI	71	967	738.1	229	
AgCl	127.1	917.4	695.4	222.0	204
AgBr	100.4	904.4	694.5	209.9	197
AgI	61.9	890.2	692.9	197.3	202
$HgCl_2$	224.3	2647	2566	81	82.8
$HgBr_2$	170.7	2621	2537	84	84.1
HgI_2	105.4	2604	2518	86	88.2

[a] Refs. 25–27. [b] Eqn. (3), with values of C from ref. 28, D from ref. 29, I_M from ref. 30 and E_L from ref. 31. [c] Ref. 22. [d] Eqn. (2). [e] From vapour pressure measurements; refs. 19 (AgCl, AgBr), 20 (AgI) and 27 ($HgCl_2$, $HgBr_2$, HgI_2I).

TABLE III. Solvation Enthalpies (kJ/mol) of Pairs of Ions, and of the Single Ions Cu^+, Ag^+ and Hg^{2+}, Calculated from Measurements on Their Halogeno Complexes, at 25 °C

		$-\Delta H^\circ_{\beta j}$ [a]	$-\Delta H^\circ_{sv}(\mathrm{M}, j\ \mathrm{L})$ [b]	$-\Delta H^\circ_{sv}(\mathrm{M}^{n+})$ [c]
DMSO	$Cu^+ + Cl^-$	6.4	998.4	651
	$Cu^+ + Br^-$	9.3	978.9	648
	$Cu^+ + I^-$	13.6	955.1	648
AN	$Cu^+ + Cl^-$	−16.8	1024.7	680
	$Cu^+ + Br^-$	−10.5	1003.3	676
	$Cu^+ + I^-$	−8.5	981.5	681
Pyridine	$Cu^+ + Cl^-$	−13.0	1074.1	736
	$Cu^+ + Br^-$	−10.2	1053.7	730
	$Cu^+ + I^-$	−8.5	1037.1	736
Pyridine	$Ag^+ + Cl^-$	−1.0	931.6	594
	$Ag^+ + Br^-$	3.3	915.8	592
	$Ag^+ + I^-$	12.3	899.9	599
Pyridine	$Hg^{2+} + 2Cl^-$	20.9	2681.5	2006
	$Hg^{2+} + 2Br^-$	22.3	2650.4	2002
	$Hg^{2+} + 2I^-$	35.1	2611.0	2009

[a] Heat of complex formation for the neutral complex; $j = 1$ for CuL and AgL, $j = 2$ for HgL_2 [1, 2]. [b] Eqn. (6); for mercury(II) systems values of $\Delta H^\circ_s(\mathrm{ML_2})$ from ref. 14. [c] Values of $\Delta H^\circ_{sv}[\mathrm{L}]$ from ref. 5.

TABLE IV. Heats of Solution (kJ/mol) of Pairs of Ions $Ag^+ + L^-$, $\Delta H^\circ_s(\mathrm{Ag, L})$, and Heats of Transfer (kJ/mol) from Water to DMSO, AN and Pyridine for the Silver Ion, $\Delta H^\circ_{tr}(Ag^+)$, at 25 °C

	$-\Delta H^\circ_s(\mathrm{Ag,L})$ [a]				$-\Delta H^\circ_{tr}(Ag^+)$ [b]		
	Water	DMSO	AN	Pyridine	W → DMSO	W → AN	W → Py
$Ag^+ + ClO_4^-$	−9.9 ± 0.3	60.3 ± 0.6	47.5 ± 0.5	115.7 ± 1.8	51.0	41.2	106.8
$Ag^+ + Cl^-$	−65.7	−28.9		14.2	55.6		108.1
$Ag^+ + Br^-$	−84.8	−38.1	−38.9	11.4	43.2	53.8	107.1
$Ag^+ + I^-$	−111.1	−52.3	−52.7	9.7	46.0	51.8	113.5

[a] Data referring to the perchlorate in all solvents, and to the halides in pyridine, from the present investigation. Data for the halides in the other solvents are from refs. 32 (water) and 33 (DMSO, AN), and refer to solutions of an ionic strength zero, or close to zero. [b] Eqn. (10), with values of $\Delta H^\circ_{tr}(L^-)$ from ref. 5.

TABLE V. Heats of Solvation ($-\Delta H^\circ_{sv}$; kJ/mol) of the Copper(I), Silver(I) and Mercury(II) Ions[a], and of their Neutral Complexes[b], in Solvents of Different Solvating Properties, at 25 °C

	Water	DMSO	AN	Pyridine	THT
Cu^+		649	679	734	698
CuCl		247.5	250.6	303.8	279.1
CuBr		237.6	242.2	292.9	274.6
CuI		231	235	291	269
Ag^+	488	539	529	595	585
AgCl				235.2	233.5
AgBr				224.6	226.9
AgI				219.3	216.7
Hg^{2+}	1845	1921		2006	
$HgCl_2$	68.8	104.0	72.9	138.0	
$HgBr_2$	64.1	101.1	70.8	135.8	
HgI_2	59.3	92.5		130.0	

[a] Tables III and IV; for Hg^{2+} in water and DMSO from ref. 4; for Cu^+ and Ag^+ in THT from ΔH°_{sv} in pyridine, with values of ΔH°_{tr}(Py → THT) from ref. 34. [b] Eqn. (1), data for mercury(II) from ref. 14, for copper(I) and silver(I) halides in THT from values of ΔH°_s in ref. 35 and the present values of ΔH°_{sub}, Table II.

TABLE VI. Heats of Transfer (kJ/mol) of Cu^+ and Ag^+, and of their Halogeno Complexes ML and ML_2^- between Solvents of Different Solvation Properties, at 25 °C[a]

	ΔH°_{tr}(DMSO → AN)			ΔH°_{tr}(AN → Py)			ΔH°_{tr}(Py → THT)		
Cu^+		−30			−55			34	
Ag^+		10			−66			10	
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
CuL	−3.1	−4.6	−4.3	−53.8	−50.7	−55.6	24.7	18.3	22.1
CuL_2^-	9	13	13	−30	−46		50	25	
AgL							1.7	−2.3	2.6
AgL_2^-							19	18	

[a] Values for Cu^+ and Ag^+ from data in Tables III and IV, respectively; for CuL and AgL from Table I. Values for CuL_2^- and AgL_2^- calculated from eqn. (10), with values of $\Delta H^\circ_{tr}(L^-)$ and $\Delta H^\circ_{\beta 2}$ pertaining to DMSO, AN and Py from refs. 2, 3, 5, to THT from refs. 34 and 36.

TABLE VII. Heats of Transfer (kJ/mol) of Hg^{2+} and Halogeno Complexes HgL_j^{j-2} between Water, DMSO and Pyridine, at 25 °C[a]

	ΔH°_{tr}(W → DMSO)			ΔH°_{tr}(DMSO → Py)		
Hg^{2+}		−76			−85	
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
HgL^+	−52	−54	−46	−71	−67	−66
HgL_2	−35.2	−37.0	−33.2	−34.0	−34.7	−37.5
HgL_3^-	−26	−51		−19	−15	−20
HgL_4^{2-}	−24	−52	−66	0	6	5

[a] Values for Hg^{2+} and HgL_2 from data in Table V, for the ionic complexes calculated from eqn. (11), with values of $\Delta H^\circ_{tr}(L^-)$ and $\Delta H^\circ_{\beta j}$ from refs. 1, 5 and 13.

been obtained. These have been entered in Table V. For water and DMSO they agree well with values found previously (*cf.* ref. 15).

The solvation enthalpies presently determined have all been listed in Table V, together with data on mercury(II) in the solvents concerned. For copper(I) and silver(I), values of ΔH°_{sv} of the species discussed here have also recently been determined in the solvent tetrahydrothiophene, THT, coordinating via sulfur. These have also been entered in Table V, for comparison.

The heats of transfer calculated for the ionic complexes CuL_2^- and AgL_2^- are given in Table VI. These also include transfers pyridine → THT where the data wanted for THT have been taken from refs. 34 and 36. For comparison, the values of $\Delta H^\circ_{sv}(M^+)$ and $\Delta H^\circ_{sv}(ML)$ in the solvents concerned have also been listed. Finally, the heats of transfer of the ionic mercury(II) complexes have been listed in Table VII, together with $\Delta H^\circ_{sv}(Hg^{2+})$ and $\Delta H^\circ_{sv}(HgL_2)$.

Discussion

The present results fully confirm the conclusions drawn from the complex formation thermodynamics that copper(I), silver(I), and mercury(II) are more strongly solvated in the soft solvent pyridine than in DMSO and water. Both for the metal ions Cu^+, Ag^+ and Hg^{2+}, and for their neutral halogeno complexes CuL, AgL and HgL_2, the solvation enthalpies are much larger in pyridine, Table V. The same applies very much to the complexes HgL^+ which are known [37] to have solvent molecules left in the inner coordination sphere, Table VII.

As has often been stated, the magnitude of $\Delta H^\circ_{sv}(M^{n+})$ of metal ion acceptors depends primarily upon their charge density. This is also borne out by the results presented in Table V. The values of ΔH°_{sv} are much higher for the divalent Hg^{2+} than for the monovalent Cu^+ and Ag^+. While the solvates of Hg^{2+} are octahedral [37, 38], those of Cu^+ and Ag^+ are tetrahedral in all the solvents discussed [37, 39–43]. In the two cases (AN, pyridine) where the distances metal to solvating atom can be compared so far, the copper distances are about 0.26 Å shorter than the silver ones [37, 41, 42]. The resulting higher charge density of Cu^+ is very clearly reflected in the values of $-\Delta H_{sv}(M^+)$ which are throughout considerably higher for Cu^+ than for Ag^+, Table V. A special trait is moreover that the solvents coordinating via nitrogen especially favour Cu^+. The largest difference $-(\Delta H^\circ_{sv}(Cu^+) - \Delta H^\circ_{sv}(Ag^+))$ is found for AN, *viz.* 150 kJ/mol, while for DMSO or THT it is only around 110 kJ/mol.

The solvation enthalpies of Cu^+ and Ag^+ are much higher than for hard ions of the same size, and more so the softer the solvent. As might be expected, the ability of these soft acceptors to form bonds of a partly covalent character strongly enhances the strength of the solvate bond, and more so the stronger the donor properties of the coordinating atom of the solvent. This is well illustrated by a comparison between Ag^+ and the hard Na^+, of about the same size [15]. The values of $-\Delta H^\circ_{sv}(M^+)$ are much higher for Ag^+ than for Na^+, and the difference increases from 71 kJ/mol for water to 148 kJ/mol for pyridine and 143 kJ/mol for THT, Table V and ref. 34.

As is certainly expected, the solvation enthalpies are much smaller for the neutral complexes than for the free metal ions, Table V. They are moreover much smaller for HgL_2 where a fairly stable linear coordination exists than for CuL and AgL where the inner coordination shell is incomplete. For these species, the solvation means a much more intimate metal–solvent interaction than in the case of HgL_2.

The difference $-(\Delta H^\circ_{sv}(CuL) - \Delta H^\circ_{sv}(HgL_2))$ is especially large for AN, a solvent which, as already stated, seems to have a special preference for copper(I) species, Table V. Not only for HgL_2 but also for Cd^{2+}, Zn^{2+} and H^+ this solvent is, on the other hand, particularly unattractive [44, 45].

For the mercury(II) species, the values of $-\Delta H^\circ_{tr}$ of the transfers DMSO → pyridine show a rather smooth decrease as the number of coordinated ligands increases until, for HgL_4^{2-}, the transfers are no longer exothermic, Table VII. In these tetrahedral complexes [46] the mercury ion is, as might be expected, so well shielded that the transfers are not much influenced by the donor properties of the solvent.

The transfers water → DMSO present a more complicated picture. For Hg^{2+} and HgL^+, $\Delta H^\circ_{tr}(W \rightarrow DMSO)$ is less exothermic than $\Delta H^\circ_{tr}(DMSO \rightarrow Py)$ while for HgL_2 the values are much the same. For HgL_3^- and HgL_4^{2-}, the values of $\Delta H^\circ_{tr}(W \rightarrow DMSO)$ are still markedly exothermic, and increasingly so in the order $Cl^- < Br^- < I^-$; for HgI_4^{2-} the large negative value of −66 kJ/mol is reached, Table VII. This pattern is no doubt mainly due to the large energy gains accompanying the reformation of the water structure which takes place on the departure of these large complexes. Such species certainly disrupt the water structure quite extensively and the disruption should become more severe the larger the complex and the less electronegative the ligand L. The trends of $\Delta H^\circ_{tr}(W \rightarrow DMSO)$ actually found are evidently consistent with this interpretation.

For the copper(I) species, the transfers DMSO → pyridine show much the same picture as for mercury(II), *i.e.* a smooth decrease of $-\Delta H^\circ_{tr}$ from Cu^+ via CuL to CuL_2^-, Table VI. It is also obvious that the strong preference of AN for Cu^+ is less marked for the complexes CuL and CuL_2^-. Evidently, a really strong solvation by AN demands a tetrahedral coordination.

The circumstance that the enthalpies of solvation, and hence the enthalpies of transfer, also involve terms due to the structure of the bulk solvent means of course that they are no unequivocal measures of the strength of the solvate bonds. Especially the structures due to hydrogen bonding in protic solvents cause marked discrepancies. Persson *et al.* [14] have studied the solvation of HgL_2 in a variety of solvents by measuring the wave number ν_1(Hg–L) of the Hg–L stretching. As the strength of the solvate bond increases, that of the bond Hg–L decreases, and consequently also ν_1(Hg–L). Generally, the values of $-\Delta H^\circ_{sv}(HgL_2)$ increase as those of ν_1(Hg–L) decrease. In water, however, the values of $-\Delta H^\circ_{sv}$-(HgL_2) are abnormally low, as much energy has to be spent to break the water structure. More surprising is that THT, and the closely related dibutyl sulfide, also show abnormally low values, indicating strong interactions between the solvent molecules. That liquid THT in fact possesses a fairly well-developed structure has also recently been indicated by X-ray diffraction studies [43].

It might be postulated that not only the values of $-\Delta H^\circ_{sv}(HgL_2)$ are abnormally low in THT, but also those of the copper(I) and silver(I) species listed in Tables V and VI. Most probably all these species are indeed more strongly solvated in THT than in pyridine. Especially the silver(I) species, with solvation enthalpies which are not very different in the two solvents, must in fact be much more strongly solvated in THT. This is also to be expected as sulfur generally behaves as a considerably softer coordinating atom than nitrogen.

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