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On the Solvation Thermodynamics of the Neutral Mercury(II) Halides in Different Solvents at 25 °C

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Abstract

Solubilities and heats of solution have been determined for the mercury(II) halides in benzene, acetone, acetonitrile, triethylamine, pyridine, di-n-butylsulfide, tetrahydrothiophene, di-n-butylamine, piperidine and hexylamine. The free energies of solution were calculated from the solubilities. The free energies of solvation were obtained by combining the free energies of solution and sublimation. The heats of solvation were obtained analogously. The entropies of solvation have then been calculated from the free energies and heats of solvation.

The heats of solvation do not follow the same sequence as the Raman active symmetric stretching frequencies, ν_1(Hg–X), which are a measure of the bond strength of the Hg–X bonds and indirectly also a measure of the strength of the Hg–solvate bonds. The heats of solvation are markedly less exothermic in solvents with a high degree of bulk order. The degree of bulk order depends on fairly strong intermolecular forces. The heat of solvation in one solvent can therefore be lower than in another one in spite of the fact that the solvate bonds are stronger. This is because energy is consumed when solvent molecules have to be taken out of the bulk structure when the solvation occurs.

Introduction

During recent years several papers have dealt with the solvation of the neutral mercury(II) halide complexes in various solvents [1–8]. In order to determine the solvation properties of the solvents, Raman spectroscopic studies on the neutral mercury(II) halide complexes have been performed [1–4]. These studies have shown that the donor properties differ greatly. Mercury(II) halides are to some extent soluble in hydrocarbons such as alkanes, alkenes and benzene [9]. The solvation properties of these solvents are very weak. Solvents donating through an oxygen atom in general solvate the soft electron acceptor mercury(II) poorly. The oxygen atom in *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) is a stronger donor than that in water, alcohols, aldehydes, organic acids and esters [1–4]. The nitrogen in nitriles is weakly coordinated to typically soft electron acceptors like mercury(II), while it solvates acceptors like gold(I), silver(I) and especially copper(I) fairly well [10]. The solvation properties of solvents donating through sulfur and nitrogen are generally very dependent on the groups bonded to the donor atom [4]. When phenyl groups are bonded to the donor atom, the donor properties decrease markedly. When protons and/or alkyl groups are bonded to the donor atom, the donor properties increase with increasing dipole moment of the solvent molecule [4]. The donor properties of the amines increase in the order: tertiary < secondary < primary. For sulfur donating solvents, sulfides have stronger solvation properties than thiols.

There is thus a wide spread in solvation properties among amines and sulfides/thiols depending on the dipole moment of the solvents. Triethylamine (TEA) and 1-buthanethiol (BuSH) have solvation properties similar to DMF and DMSO [4]. On the other hand, the primary amine hexylamine (HA) solvates mercury(II) halides very well [4]. Solvents donating through phosphorous always solvate soft electron acceptors like mercury(II) very well. Again, the donor properties decrease markedly when a phenyl group is bonded to phosphorous [4, 7].

The heats of solvation, $-\Delta H^\circ_{sv}$, of the neutral mercury(II) halides in water and DMSO have been reported previously [5]. That study showed, as the Raman spectroscopic ones did, that mercury(II) is more strongly solvated in DMSO than in water. On average, the heat of solvation of mercury(II) halides is 35 kJ mol^{-1} more exothermic in DMSO.

The structure of the solvated neutral mercury(II) halide complexes do change with increasing strength of solvation. The mercury(II) halides are linear in the gaseous phase [11]. The solvated complexes are

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four-coordinated in solvents with stronger solvating properties than water [12–15]. In solvents with weak solvation properties, the X–Hg–X angle deviates only a few degrees from linearity [12]. This angle decreases as the solvation becomes stronger; tetrahedral configuration is approached in solvents of strong solvation properties. The X–Hg–X angles in DMSO are ~160° [12, 15], ~145° in pyridine [13] and ~135° in tetrahydrothiophene (THT) [14]. $HgI_2(PPh_3)_2$ is a regular tetrahedron in the solid state [16]. The Hg–X bond distances increase and the solvate bonds become stronger and shorter with increasing solvation [4].

Graddon *et al.* have made thermodynamic studies on reactions between mercury(II) halides and organic Lewis bases in benzene solution. By using the heats of solvation of the mercury(II) halides in benzene, the heats of solvation in pure Lewis bases can be calculated. In this way, the heats of solvation for some Lewis bases which are solids at room temperature can be obtained.

The solvation themodynamics of the neutral mercury(II) halides can be determined without any extrathermodynamic assumptions. The free energy of solvation is obtained by combining the free energy of sublimation with the free energy of solution. The heat of solvation is obtained analogously. The free energies and the heats of sublimation are available from the literature [17]. The free energies are obtained from solubility measurements of the mercury(II) halides. The heats of solution have been determined calorimetrically in this study.

Calculations and Notations

The free energy and the heat of solvation, ΔG°_{sv} and ΔH°_{sv}, of the neutral mercury(II) halides, HgX_2, pertaining to the reaction

$$HgX_2(g) \longrightarrow HgX_2(solv)$$

are obtained by combining the free energy and the heat of sublimation, ΔG°_{sub} and ΔH°_{sub}, pertaining to

$$HgX_2(s) \longrightarrow HgX_2(g)$$

with the free energy and the heat of solution, ΔG°_s and ΔH°_s, pertaining to

$$HgX_2(s) \longrightarrow HgX_2(solv)$$

referring to the relations

$$\Delta G^\circ_{sv} = \Delta G^\circ_s - \Delta G^\circ_{sub}$$

and

$$\Delta H^\circ_{sv} = \Delta H^\circ_s - \Delta H^\circ_{sub}$$

The free energy of solution, ΔG°_s, is directly connected with the solubility S according to the relationship

$$\Delta G^\circ_s = RT \ln S.$$

From the free energy of solvation, $-\Delta G^\circ_{sv}$, the equilibrium constant of the distribution of HgX_2 between the gas and the solvent phase, K_{sv}, is calculated according to the relationship

$$\Delta G^\circ_{sv} = RT \ln K_{sv},$$

where

$$K_{sv} = [HgX_2(solv)]\,[HgX_2(g)]^{-1} = e^{-\Delta G^\circ_{sv}(RT)^{-1}}.$$

The Henry's law constant, H, is obtained by inversion of K_{sv},

$$H = e^{\Delta G^\circ_{sv}(RT)^{-1}} = [HgX_2(g)]\,[HgX_2(solv)]^{-1}.$$

By adding the heat of solvation in benzene, ΔH°_{sv}(benzene), the heat of reaction between a mercury(II) halide and Lewis base in benzene solution, ΔH°_R(benzene), and the heat of transfer of the complex $HgX_2(LB)_2$ from benzene to Lewis base (LB) solution, ΔH°_{sc}, the heat of solvation in the Lewis base solution, is obtained.

$$HgX_2(g) \rightleftharpoons HgX_2(benzene) \quad \Delta H^\circ_{sv}(benzene)$$

$$HgX_2(benzene) + nLB \rightleftharpoons HgX_2(LB)_n(benzene)$$
$$n = 1 \text{ or } 2 \quad \Delta H^\circ_R(benzene)$$

$$HgX_2(LB)_n(benzene) \rightleftharpoons HgX_2(LB)_n(LB) \quad \Delta H^\circ_{sc}$$

$$\Delta H^\circ_{sv}(LB) = \Delta H^\circ_{sv}(benzene) + \Delta H^\circ_R(benzene) + \Delta H^\circ_{sc}$$

The ΔH°_{sc} term is the difference in outer sphere solvation of $HgX_2(LB)_2$ between benzene and the pure Lewis base. Because of weak outer sphere solvation of complexes of this kind, this term is very small in most cases. The magnitude of this term can be measured, but that measurement has not been made in this work. The ΔH°_{sc} term has not been taken into account when the heat of solution has been calculated.

Experimental

Chemicals

The mercury(II) chloride, bromide and iodide (red) were recrystallized from hot water, alcohol and acetone, respectively, dried and stored over silica gel at reduced pressure. All solvents were freshly distilled before use according to the methods described in the literature [18]. No ionic medium was used except in the case of pyridine, where 0.1 M tetraethylammonium perchlorate was used as supporting electrolyte.

Calorimetry

The calorimeter for dissolution measurements and the procedure used have been described previously [19]. Varying amounts of salt, 0.02–0.5 g, were transferred into ampoules, which were weighed before and after the transferring, and preliminarily sealed. The glass tube on the ampoule was finally sealed by burning. The salts were dissolved in 80.0 ml solvent, which never took more than 10 min. The solvent was changed when 3 or 4 ampoules with the same salt were determined. In the systems studied, the heats of solution were not found to be dependent on the mercury(II) concentration. At least four independent experiments in agreement were performed for each salt and solvent. All measurements were carried out at 25.000 ± 0.002 °C.

Solubility Measurements

The solubilities were determined gravimetrically by weighing the amount of undissolved salt in a certain volume of the solvent. The amount of undissolved salt was kept as small as possible in order not to interfere with the volume of the solution. The measurements were performed at room temperature.

Measurements and Results

Solubilities

In solvents with strong donor properties, the mercury(II) halides react immediately with the solvent forming mercury(II) halide adduct compounds in the solid phase. It is therefore impossible to determine the solubilities of the mercury(II) halides in these solvents. In many instances, however, the solid is a mixture of the mercury(II) halide and the adduct compound. This is easily seen with mercury(II) iodide, which is red, while the adduct compounds are white or pale yellow. This shows that there are only small differences in the solubilities of the solid phases. The solubilities determined in this study are listed in Table I. The solubilities are given for the most soluble of the solid phases, the mercury(II) halide or the adduct compound. The free energies of solution, ΔG°_{sv}, calculated from the solubilities and the estimated random errors are listed in Table II. The solvents in all Tables are arranged in order of increasing solvation properties.

Free Energies of Solvation

The free energies of sublimation have been reported to be 38.5, 39.3 and 41.9 kJ mol^{-1} for mercury(II) chloride, bromide and iodide, respectively [17]. The free energies of solvation have been calculated from the free energies of solution and sublimation (see 'Calculations and Notations'). The results obtained are listed in Tables II and V. The solvents can be divided into two groups based on the free energies of solvation. Solvents with hard donor atoms like acetone, acetonitrile, methanol and water show the sequence $-\Delta G^{\circ}_{sv}(HgCl)_2) > -\Delta G^{\circ}_{sv}(HgBr_2) > -\Delta G^{\circ}_{sv}(HgI_2)$. The other solvents in this study show the opposite sequence. These solvents all have a soft or fairly soft donor atom except benzene, which solvates the mercury(II) halides only through London forces, in contrast to the other solvents in this study.

TABLE I. Molar Solubilities of Mercury(II) Halides in Different Solvents at 25 °C

Solvent	$HgCl_2$	$HgBr_2$	HgI_2
Benzene	16×10^{-3}	16×10^{-3}	7.5×10^{-3}
Diethylether	0.170	67×10^{-3}	8.3×10^{-3}
Acetone	3.22	0.96	31×10^{-3}
Acetonitrile	1.83	0.26	7.6×10^{-3}
MeOH	2.0	1.5	68×10^{-3}
Water	0.254	16×10^{-3}	0.22×10^{-3}
TEA	$<0.1 \times 10^{-3}$	0.51×10^{-3}	15×10^{-3}
DMSO	2.00	3.25	4.25
Pyridine	0.90	0.80	0.70
DBS	3.67	5.02	3.22
THT	0.37	0.70	0.83
DBA	55×10^{-3}	70×10^{-3}	1.50
Piperidine	44×10^{-3}	0.97	1.20
HA	2.0×10^{-3}	0.89	2.85

Distribution Constants

The equilibrium constant for the reaction $HgX_2(solv) \rightleftharpoons HgX_2(g)$ is called the Henry's law constant, H, $H = [HgX_2(g)] [HgX_2(solv)]^{-1}$ (dimensionless). The Henry's law constant can be calculated from the free energy of solvation as described above. These equilibria are always established far to the left. The Henry's law constants for the mercury(II) halides in solvents where $HgX_2(s)$ certainly is in equilibrium with the saturated solution are listed in Table III.

Heats of Solution

The degree of dissociation or disproportionation of a salt depends on the concentration. Raman spectroscopic studies have clearly shown that the neutral mercury(II) halides neither dissociate nor disproportionate in the solvents used in this study [4]. This has been further confirmed by the fact that the same values of heats of solution have been obtained regardless of the concentration used in the experiment. The heats of solution in water and DMSO have been reported previously [5]. The heats of solution and corresponding random errors are given in Table IV.

Heats of Solvation

The heats of sublimation of the mercury(II) halides have been reported to be 82.8, 84.1 and 88.2 kJ mol^{-1} for mercury(II) chloride, bromide

TABLE II. Gibbs Free Energy of Solution, ΔG_s° (kJ mol^{-1}), and Solvation, ΔG_{sv}° (kJ mol^{-1}) of the Mercury(II) Halides in Solvents of Different Solvating Properties at 25 °C

Solvent	Constant	$HgCl_2$	$HgBr_2$	HgI_2
Benzene	ΔG_s°	10.25 ± 0.15	10.25 ± 0.15	12.1 ± 0.2
	ΔG_{sv}°	−28.3	−29.1	−29.8
AN	ΔG_s°	−1.50 ± 0.05	3.34 ± 0.05	12.1 ± 0.2
	ΔG_{sv}°	−40.0	−36.0	−29.8
Acetone	ΔG_s°	−2.90 ± 0.05	0.10 ± 0.05	8.6 ± 0.1
	ΔG_{sv}°	−41.4	−39.2	−33.3
MeOH	ΔG_s°	−1.70 ± 0.05	−1.00 ± 0.05	6.7 ± 0.1
	ΔG_{sv}°	−40.2	−40.3	−35.2
Water	ΔG_s°	3.4 ± 0.1	10.1 ± 0.1	20.9 ± 0.2
	ΔG_{sv}°	−35.1	−29.2	−21.0
TEA	ΔG_s°		18.8 ± 0.5	10.4 ± 0.2
	ΔG_{sv}°		−20.5	−31.5
DMSO	ΔG_s°	−1.7 ± 0.1	−2.9 ± 0.1	−3.6 ± 0.1
	ΔG_{sv}°	−40.2	−42.2	−45.8
Pyridine	ΔG_s°	0.26 ± 0.05	0.55 ± 0.05	0.88 ± 0.05
	ΔG_{sv}°	−38.2	−38.7	−41.0
DBS	ΔG_s°	−3.22 ± 0.05	−4.00 ± 0.05	−2.90 ± 0.05
	ΔG_{sv}°	−41.7	−43.3	−44.8
THT	ΔG_s°	2.46 ± 0.05	0.88 ± 0.05	0.45 ± 0.05
	ΔG_{sv}°	−36.0	−38.4	−41.4
DBA	ΔG_s°	7.2 ± 0.1	6.6 ± 0.1	−1.00 ± 0.05
	ΔG_{sv}°	−31.3	−32.7	−42.9
Piperidine	ΔG_s°	7.74 ± 0.05	0.08 ± 0.05	−0.45 ± 0.05
	ΔG_{sv}°	−30.8	−39.2	−42.4
HA	ΔG_s°	15.4 ± 0.2	0.29 ± 0.05	−2.60 ± 0.05
	ΔG_{sv}°	−23.1	39.0	−44.5

TABLE III. The Henry's Law Constants, H (dimensionless), Expressed as $-\log H$, for the Mercury(II) Halides Between Air and some Solvents of Different Solvation Properties at 25 °C

Solvent	$HgCl_2$	$HgBr_2$	HgI_2
n-Hexane	2.8	3.2	3.8
Benzene	5.0	5.1	5.2
Acetone	7.3	6.9	5.8
AN	7.0	6.3	5.2
MeOH	7.0	7.1	6.2
Water	6.2	5.1	3.7
TEA		3.6	5.5
DMSO	7.0	7.4	8.0

and iodide, respectively [17]. In all solvents except the sulfides tetrahydrothiophene (THT) and di-n-butylsulfide (DBS), the sequence $-\Delta H_{sv}^\circ(HgCl_2) > -\Delta H_{sv}^\circ(HgBr_2) > -\Delta H_s^\circ(HgI_2)$ is obtained. In the sulfides the ΔH_{sv}° values are similar for all mercury(II) halides, with the $\Delta H_{sv}^\circ HgBr_2)$ value as the most exothermic one. The heats of solvation determined in this study are summarized in Tables IV and V.

Graddon *et al.* have made a large number of calorimetric studies on reactions between mercury(II) halides and Lewis bases, including many common solvents, in benzene solution. They have proposed that only one solvent molecule is added to HgX_2 in benzene solution, with the exception of phosphines. A recalculation of Graddon's data shows that two solvent molecules are added to HgX_2 in some cases where fairly high free ligand concentrations have been obtained, e.g., in the $HgCl_2$–pyridine and –tri-n-butyl amine systems. In the base concentrations Graddon *et al.* studied, the $HgX_2(LB)$ complex was strongly dominating and only small amounts of the complex $HgX_2(LB)_2$ were formed in some cases. Larger portions of $HgX_2(LB)_2$ occur only in concentrated or pure base solutions. For some other Lewis bases, e.g., THF and triphenylarsine, only one complex is formed. THF forms one weak complex, and further complex formation is not to be expected at the free THF concentrations reached. Triphenylarsine forms two complexes with

TABLE IV. Heats of Solution, ΔH°_s (kJ mol^{-1}), and Solvation, ΔH°_{sv} (kJ mol^{-1}), of the Mercury(II) Halides in Solvents of different Solvating Properties in kJ mol^{-1} at 25 °C

Solvent	Constants	$HgCl_2$	$HgBr_2$	HgI_2
Benzene	ΔH°_s	11.3 ± 0.7	15.7 ± 0.3	
	ΔH°_{sv}	−71.5	−68.4	
Acetone	ΔH°_s	13.0 ± 3.8	18.9 ± 0.6	
	ΔH°_{sv}	−69.8	−65.2	
AN	ΔH°_s	9.9 ± 0.5	13.3 ± 0.3	
	ΔH°_{sv}	−72.9	−70.8	
Methanol	ΔH°_s	−0.9 ± 0.2	+3.1 ± 1.1	+12.4 ± 1.0
	ΔH°_{sv}	−83.7	−81.0	−75.8
TEA	ΔH°_s			−23.2 ± 1.8
	ΔH°_{sv}			−111.4
Pyridine	ΔH°_s	−55.2 ± 2.0	−51.7 ± 0.7	−41.8 ± 1.4
	ΔH°_{ev}	−138.0	−135.8	−130.0
DBS	ΔH°_s	−31.1 ± 0.6	−35.1 ± 0.7	−29.4 ± 0.9
	ΔH°_{sv}	−113.9	−119.2	−117.6
THT	ΔH°_s	−36.1 ± 1.1	−40.0 ± 0.9	−31.8 ± 0.9
	ΔH°_{sv}	−118.9	−124.1	−120.0
DBA	ΔH°_s		−75.9 ± 2.0	−63.0 ± 1.6
	ΔH°_{sv}		−160.0	−151.2
Piperidine	ΔH°_s	−84.4 ± 2.9	−82.8 ± 1.2	−71.6 ± 2.2
	ΔH°_{sv}	−167.2	−166.8	−159.8
HA	ΔH°_s	−146.1 ± 3.2	−116.8 ± 1.4	−99.4 ± 1.7
	ΔH°_{sv}	−228.9	−200.9	−187.6
Tri-n-butylphosphine	ΔH°_s			−149.5 ± 2.0
	ΔH°_{sv}			−237.7

mercury(II) in DMSO solution, where the first complex is much stronger than the second one [20]. It is therefore likely that only one arsine is added to HgX_2 in solutions with a high arsine activity.

The heats of solvation in the pure Lewis bases have been calculated from the heats of complex formation in benzene according to the description above. In these calculations the heats of transfer from benzene to the pure Lewis bases have been neglected. A comparison between the heats of solvation obtained from direct measurements in the solvent and from reactions in benzene shows no differences for pyridine, tertiary amines and tri-n-butylphosphine. The assumption $\Delta H^\circ_{sc} = 0$ is valid for these solvents with low bulk order. For THT, which has a significant bulk structure [4, 14], this assumption can not be used. THT is the only solvent with a pronounced bulk order among those that Graddon and coworkers have studied. The heats of solvation calculated from reactions between mercury(II) halides and Lewis bases in benzene solution are summarized in Table VI. The heats of solvation determined both in the pure solvent and in benzene solution are compared in Table VII. The heats of solvation determined in these two ways agree very well.

Solvation Entropies

The solvation entropies have been calculated from the determined values of free energies and of heats of solvation. The solvation entropies together with the free energies and the heats of solvation are summarized in Table V.

Discussion

The solvents in this study can be divided into three groups depending on the way they solvate the neutral mercury(II) halides. These groups are: (1) solvents without donor atoms, (2) solvents with hard donor atoms, which form mainly electrostatic solvate bonds, and (3) solvents with soft donor atoms, which form mainly covalent solvate bonds.

The solvents with no or weak donor properties solvate the neutral mercury(II) halides only through

TABLE V. Gibbs Free Energy of Solvation, ΔG°_{sv}, the Heat of Solvation, ΔH°_{sv}, in kJ mol^{-1}, and the Entropy of Solvation, $T\Delta S^\circ_{sv}$, in kJ mol^{-1}, and ΔS°_{sv}, in J mol^{-1} K^{-1}, of Mercury(II) Halides in Solvents of Different Solvating Properties at 25 °C

Solvent	Compound	ΔG°_{sv}	ΔH°_{sv}	$T\Delta S^\circ_{sv}$	ΔS°_{sv}
Benzene	$HgCl_2$	−28.3	−71.5	−43.2	−145
	$HgBr_2$	−29.1	−68.4	−39.3	−131
	HgI_2	−29.8	∼−70	−41	−138
Acetone	$HgCl_2$	−41.4	−69.8	−28.4	−95
	$HgBr_2$	−39.2	−65.2	−26.0	−87
	HgI_2	−33.3	–	–	–
AN	$HgCl_2$	−40.0	−72.9	−32.9	−110
	$HgBr_2$	−36.0	−70.8	−34.8	−117
	HgI_2	−29.8	–	–	–
MeOH	$HgCl_2$	−40.2	−83.7	−43.5	−146
	$HgBr_2$	−40.3	−81.0	−40.7	−137
	HgI_2	−35.2	−75.8	−40.6	−136
Water	$HgCl_2$	−35.1	−68.8	−33.7	−113
	$HgBr_2$	−29.2	−64.1	−34.9	−117
	HgI_2	−21.0	−59.3	−38.3	−128
TEA	$HgCl_2$	–	–	–	–
	$HgBr_2$	−20.5	–	–	–
	HgI_2	−31.5	−111.4	−79.9	−268
DMSO	$HgCl_2$	−40.2	−104.0	−63.8	−214
	$HgBr_2$	−42.2	−101.1	−58.9	−198
	HgI_2	−45.8	−92.5	−46.7	−157
Pyridine	$HgCl_2$	−38.2	−138.0	−99.8	−335
	$HgBr_2$	−38.7	−135.8	−97.1	−326
	HgI_2	−41.0	−130.0	−89.0	−298
DBS	$HgCl_2$	−41.7	−113.9	−72.2	−242
	$HgBr_2$	−43.3	−119.2	−75.9	−255
	HgI_2	−44.8	−117.6	−72.8	−244
THT	$HgCl_2$	−36.0	−118.9	−82.9	−278
	$HgBr_2$	−38.4	−124.1	−85.7	−287
	HgI_2	−41.4	−120.0	−78.6	−264
DBA	$HgCl_2$	−31.3	–	–	–
	$HgBr_2$	−32.7	−160.0	−127.3	−427
	HgI_2	−42.9	−151.2	−108.3	−363
Piperidine	$HgCl_2$	−30.8	−167.2	−136.4	−457
	$HgBr_2$	−39.2	−166.8	−127.6	−428
	HgI_2	−42.4	−159.8	−117.4	−394
HA	$HgCl_2$	−23.1	−228.9	−205.8	−690
	$HgBr_2$	−39.0	−200.9	−161.9	−543
	HgI_2	−44.5	−187.6	−143.1	−480
Tri-n-butylphosphine	HgI_2		−237.7		

weak electrostatic forces. This group includes such solvents as benzene, 1,2-dichloroethane, furane, nitromethane, carbon tetrachloride and hydrocarbons. The symmetric stretching frequencies ν_1(Hg–X) of the mercury(II) halides in this group of solvents are almost the same and only a few wavenumbers below those found in gas phase [4]. This indicates that the mercury(II) halides have only very weak interactions with these solvents. The solubilities of the mercury(II) halides in these solvents are in general low. For each solvent there are only small differences in solubility between the halides. The free energies of solvation of the mercury(II) halides are thus of the same order of magnitude, with a slight increase in the order $-\Delta G^\circ_{sv}(HgCl_2) < -\Delta G^\circ_{sv}(HgBr_2) < -\Delta G^\circ_{sv}(HgI_2)$.

TABLE VI. The Heats of Solvation of the Mercury(II) Halides, ΔH°_{sv}, kJ mol^{-1}, Calculated from Reactions between Mercury(II) Halides and Lewis Bases in Benzene Solution [6–8]

Solvent	$HgCl_2$	$HgBr_2$	HgI_2
THF	86.6	80.9	
NBu_3 (TBA)	114.8	112.2	115.7
Pyridine	135.1	136.4	135.1
THT	138.2	136.8	129.2
$P\phi_3$	180	187	177
$P\phi_2Bu$	198	203	201
$P\phi Bu_2$	229	220	204
PBu_3	249	248	239
$P(C_6H_{11})_3$	250	239	232
$P\phi_2Me$	201	203	192
$P\phi Me_2$	215	220	199
$As\phi_3$	126	135	
$As\phi_2Me$	144	145	144
$As\phi Me_2$	147	135	127
$AsMe_3$	147	140	142

TABLE VII. The Heats of Solvation of the Mercury(II) Halides, $-\Delta H^\circ_{sv}$, kJ mol^{-1}, Calculated from Reactions between Mercury(II) Halides and Lewis Bases in Benzene Solution and from Determined Values of Heat of Solution and Sublimation

Solvent	$HgCl_2$	$HgBr_2$	HgI_2
Pyridine[a]	135.1	136.4	135.1
Pyridine[b]	138.0	135.8	130.0
Tri-n-butyl amine[a]	114.8	112.2	115.7
Triethyl amine[b]			111.4
Tri-n-butylphosphine[a]	249	248	239
Tri-n-butylphosphine[b]			237.7
Tetrahydrothiophene[a,c]	138.2	136.8	129.2
Tetrahydrothiophene[b,c]	118.9	124.1	120.0

[a] From reactions in benzene solution, ref. 6. [b] From heats of solution and sublimation, this work. [c] Tetrahydrothiophene has a bulk structure, with possible S–S distances which have been determined in the liquid THT.

TABLE VIII. The Free Energies of Solvation, $-\Delta G^\circ_{sv}$, kJ mol^{-1}, in Some Hydrocarbons Calculated from Solubility Measurements[a]

Solvent	$HgCl_2$	$HgBr_2$	HgI_2
n-Hexane[b]	15.8	18.2	21.6
Cyclohexane[b]	16.6	19.6	22.8
Cyclohexene[b]	27.7	28.5	28.4
Benzene[c]	28.3	29.1	29.8
Toluene[b]	29.1	29.6	29.5

[a] The solubilities of the mercury(II) halides in carbontetrachloride are lower than in n-hexane and we have not been able to determine them accurately. [b] Ref. 10. [c] This work.

The free energies of solvation of the mercury(II) halides in some hydrocarbons are listed in Table VIII. The free energies of solvation are considerably smaller in the alkanes than in the hydrocarbons with double bonds or conjugated systems. The alkanes are solvating only through London forces, while alkenes and benzene derivatives also develop electrostatic interactions through their pi orbitals. The pattern of the alkanes is expected from the nature of the London forces. The molecular surface area of the mercury(II) halides increases slightly when the atom number of the halide increases. The strength of the London forces on the mercury(II) halides is thus increasing in the same order. The strength of the electrostatic pi bond interactions increases with increasing charge density of the solute, and should therefore be the strongest for mercury(II) chloride. This is confirmed by the results in Table VIII. The free energies of solvation are about 10 kJ mol^{-1} larger for the alkenes and benzene than for the alkanes. The expected increase of the $-\Delta G^\circ_{sv}$ values with increasing atom number of the halide has been counter-balanced by the differences in the electrostatic interaction.

Among the solvents in this group, the heats of solvation, ΔH°_{sv}, have been determined only in benzene. The ΔH°_{sv} values in benzene are of the same order of magnitude as in acetone, acetonitrile and water, in spite of the fact that the latter solvents solvate the mercury(II) halides better than benzene (Table II). This behaviour, as well as the entropy terms, will be discussed below.

The solvents with hard donor atoms, in this study acetone, acetonitrile, methanol and water, solvate mercury(II) halides fairly poorly. Still, the solvation is considerably stronger than in solvents without donor atoms, as indicated by the ν_1(Hg–X) frequencies. In these solvents the solubilities of the mercury(II) halides decrease markedly in the order $HgCl_2 > HgBr_2 > HgI_2$ (Table I). The free energies of solvation, $-\Delta G^\circ_{sv}$, decrease in the same way except in methanol where the $-\Delta G^\circ_{sv}$ values of the chloride and the bromide are similar. The solvation occurs beside the London forces mainly through electrostatic interactions with both the mercury and the halide groups. The strength of the solvent interactions with the mercury atom depends on the degree of covalency in the solvate bond. This can be estimated from the dipole moment of the solvent, which has been described previously [4]. The halide groups are especially well solvated in water and alcohols because of hydrogen bond formation in these solvents. The ability to form hydrogen bonds decreases markedly in the order $Cl^- > Br^- > I^-$ [21]. The halides are especially well solvated in aqueous solution. With increasing strength of solvation one expects increasing heats of solvation. In spite of the considerably stronger solvation in this group of solvents, the heats of solvation are of the same order of magnitude as in benzene. The $-\Delta H^\circ_{sv}$ values are lower than expected in all solvents, and especially in water. The reason is that the solvents, and especially water, have a pronounced bulk structure because of hydrogen bonding between solvent molecules and/or high dielectric constants of the solvent. High dielectric constants show that the solvent molecules are permanent dipoles, which are arranged in a fairly strict pattern. Before solvation can occur, the solvent molecules must be taken out of the bulk structure. This process, where several bonds have to be broken, is certainly endothermic with some 10 kJ mol^{-1}. The bulk structure is certainly further affected because the solvated mercury(II) halide complexes do not fit into it. This can raise the endothermic term some kJ mol^{-1} more. The heat gained from the London force solvation is about the same in all solvents. It is impossible to determine the heat of London force solvation separately from the present measurements. The solubilities of the mercury(II) halides in alkanes are too low to allow calorimetric measurements. The heat gained from the formation of weak electrostatic interactions, such as London forces and pi bond interactions, is assumed to be similar and independent of its specific nature. The $-\Delta G^\circ_{sv}$ values of the hydrocarbons show that the solvation by benzene consists of about 2/3 of London force solvation and about 1/3 of pi bond interactions. The heat gained from London force solvation of mercury(II) halides can therefore assume to be in the range 40–60 kJ mol^{-1}. The $-\Delta H^\circ_{sv}$ value found in benzene, 70 kJ mol^{-1}, includes heat from both the London force solvation and the pi bond interactions. Acetone and acetonitrile solvate mercury(II) halides considerably more weakly than water does, but the heats of solvation in these three solvents are almost the same. The heat from forming solvate bonds will increase with increasing solvation. Acetone and acetonitrile are expected to have a markedly lower bulk order than water in order to compensate for the smaller heat from the solvate bond formation. Methanol has a bulk order comparable to acetone and acetonitrile, but its solvation properties are similar to water. The heats of solvation in methanol are indeed larger, around 10 kJ mol^{-1}, than in the other solvents in this group.

The free energies of solvation of the mercury(II) halides increase in the order $-\Delta G^\circ_{sv}(HgCl_2) < -\Delta G^\circ_{sv}(HgBr_2) < -\Delta G^\circ_{sv}(HgI_2)$ in the remaining solvents in this study. From Raman spectroscopic studies these solvents can be divided into two groups depending on their solvation properties [4]. Triethylamine (TEA) and dimethylsulfoxide (DMSO) are on the borderline between hard and soft donors, while the other solvents are typical soft donors. Besides the London forces, the solvation occurs through two solvate bonds to mercury [12–15] and through electrostatic interactions with the halide groups [21]. These solvents are all aprotic and have no ability to form hydrogen bonds. The halides are solvated in the order $Cl^- > Br^- > I^-$ independent of solvent. The difference between chloride and iodide is, however, smaller in aprotic than in protic solvents [10]. This is why the order $-\Delta H^\circ_{sv}(HgCl_2) > -\Delta H^\circ_{sv}(HgBr_2) > -\Delta H^\circ_{sv}(HgI_2)$ is obtained in all solvents, except in the sulfides di-n-butylsulfide (DBS) and tetrahydrothiophene (THT). There are three solvents in this group, DMSO, DBS and THT, in which lower heats of solvation than expected have been found (see Table V). This indicates that these solvents have a bulk structure. X-ray scattering studies on DMSO [12, 15] and THT [14] solutions have shown large peaks at 5.5 and 10 Å in the radial distribution functions. These peaks are certainly due to intermolecular solvent distances, probably S–S ones. X-ray scattering studies of pyridine solutions show no such peaks. What kind of intermolecular interactions, considerably stronger than London forces, there are in these solvents is uncertain. These interactions are weaker than hydrogen bonds. They are ~20 kJ mol^{-1} compared to ~35 kJ mol^{-1} for hydrogen bonds expressed in $-\Delta H^\circ_{sv}$ values of the mercury(II) halides. The other solvents in this study lack bulk structure, and the heats of solvation increase as expected with increasing donor properties of the solvent.

As has been discussed in a previous paper, the donor properties of an atom depend on the groups bonded to the donor atom and on the dipole moment of the solvent [4]. The donor properties decrease when phenyl groups are bonded to the donor atom. This is clearly demonstrated by the heats of solvation in phosphines, Table VI. The same pattern is shown for oxygen-, nitrogen- and sulfur-donating solvents. Triphenylarsine has weaker solvation properties than the other arsines, which on the other hand have similar properties in spite of varying number of phenyl groups bonded to the arsenic.

The increase in the solvation properties, determined from the symmetric stretching frequencies, ν_1(Hg–X), is directly correlated with an increased Hg–X bond distance in the solvated mercury(II) halide complex, Table IX. The X–Hg–X angle is found to decrease with increasing solvation [12–14]. This angle is 180° in the gas phase and probably also in solvents solvating through London forces and/or electrostatic pi bonding interactions [22]. The Hg–X bond distances in these solvents are probably also close to those obtained in the gas phase. The increase in bond distances and the decrease in X–Hg–X angles in solvents with hard donor atoms are certainly very small relative to the gas

TABLE IX. The Symmetric Stretching Frequencies, ν_1(Hg–X) [4], the Heats of Solvation $-\Delta H^\circ_{sv}$, and the Hg–X Bond Distances, d(Hg–X) [12–15], for the Solvated Neutral Mercury(II) Halides in Solution

	Gas	Benzene	Acetone	AN	MeOH	Water	TEA	DMSO	Py	DBS	THT	DBA	Pip	HA	Bu_3P
ν_1 (cm^{-1})															
$HgCl_2$	360	339	328	325	324	320	a	305	283	279	278	a	a	a	210^b
$HgBr_2$	225	213	207	208	208	205	a	195	183	181	179	176	173	167	146
HgI_2	156	a	151	148	151	a	148	145	142	140	140	137	135	132	113
$-\Delta H^\circ_{sv}$ (kJ mol^{-1})															
$HgCl_2$		72	70	73	84	69	a	104	138	114	119	a	167	229	249
$HgBr_2$		68	65	71	81	64	a	101	136	119	124	160	167	201	248
HgI_2		a	a	a	76	59	111	93	130	118	120	151	160	188	238
d(Hg–X) (Å)															
$HgCl_2$	2.27^c	a			2.308		a	2.320	2.38		a	a	a	a	2.60^b
$HgBr_2$	2.41^d	a				a	a	2.455	2.50		2.51	a			–
HgI_2	2.59^d	a	a	a	a	a	a	2.62	2.67		2.68				–

^{a}Too low solubility for accurate determination. ^{b}Average bond distance in the solid $HgCl_2(PBu_3)_2$, ref. 23. ^{c}Ref. 24. ^{d}Ref. 11.

phase. In DMSO, a solvent on the borderline between hard and soft donating ones, the X–Hg–X angles have decreased to 160° and the bond distances have increased around 0.04 Å [12, 15], Table IX. In soft donating solvents, the increase in bond distances and the deviation from linearity are substantial [13–14], Table IX. With increasing solvation, the solvated mercury(II) halide complexes approach tetrahedral configuration.

The heats of solvation do not follow the same solvent sequence as the solvation strength. As discussed above, this deviation depends on different bulk orders in the solvents. Solvents with hydrogen bonds and/or high dielectric constants have a high bulk order. The heats of solvation are considerably smaller in these solvents because solvent molecules must be broken out of the bulk structure upon solvation, Table IX. There are sulfur-containing solvents with a pronounced bulk order. The forces building this bulk structure are unknown. The degree of bulk order is also displayed in the solvation entropies, Table V. The more negative the solvation entropy obtained compared with the solvation properties, the lower the degree of bulk order is assumed. The solvation entropies are negative in all solvents studied, Table V. This shows that the total degree of order in the solutions increases upon solvation of the mercury(II) halides. The solution order is increasing especially in solvents with strong solvation properties and with low bulk order. In general, the solvation entropies and the heats of solvation in a solvent increase in the order $HgI_2 < HgBr_2 < HgCl_2$. This is because the solvation of the halide groups in the mercury(II) halide complexes increases in the same order. The reversed sequence is found in aqueous solution because water forms hydrogen bonds to the halide groups. This affects the water bulk structure because these hydrogen bonds do not fit into the ordinary bulk structure. Therefore, the water bulk will be more affected with increasing hydrogen bonding strength.

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