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Determination of Heats of Solvation of Copper(I) and Silver(I) Ions and Halide Complexes in Tetrahydrothiophene

MATS JOHNSSON and INGMAR PERSSON

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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Abstract

The heats of solution of the copper(I) and silver(I) halides have been determined in tetrahydrothiophene (THT). THT is a sulfur donor solvent, which coordinates soft metal ions and complexes such as copper(I) and silver(I) strongly. THT has a low dielectric constant, which means that salts rarely dissociate in this solvent. The heats of solvation of the neutral copper(I) and silver(I) halides are obtained by combining the heats of solution and heats of sublimation from the literature. The heats of solvation of the copper(I) and silver(I) ions have been calculated by combining the heats of solution of the neutral metal halides, the heats of complex formation of these complexes, and the heats of solvation of the halide ions in THT. The heats of solvation of the copper(I) and silver(I) ions in THT are –698 and –583 kJ mol^{-1}, respectively. The obtained heats of solvation show that copper(I) and silver(I) ions and neutral halide complexes are strongly solvated in THT.

Introduction

In order to determine the heats of solvation of individual ions an extrathermodynamic assumption must be applied. The TATB assumption stating that $\Delta H^\circ_{tr}(\text{AsPh}_4^+) = \Delta H^\circ_{tr}(\text{BPh}_4^-)$ is the most generally accepted [1, 2] and it has been applied in this study. The heats of solvation of metal ions can be determined from the thermodynamics of formation of the first halide complexes, the heats of solvation of the halide ions, together with the heats of solution of the metal halides. The thermodynamics of complex formation of the copper(I) and silver(I) halides in THT have been studied earlier [3]. Soft metal ions such as silver(I) and copper(I) coordinate the soft sulfur donor solvent THT strongly. In diluted THT solution, two mononuclear complexes are formed, the first one being the strongest. A major desolvation of the metal ion occurs most probably when the second complex is formed [3]. The heats of solvation of the halide ions are determined from the heats of hydration and the heats of transfer [4, 5]. The heats of solution of the copper(I) and silver(I) halides are measured in this study. These are determined without any extrathermodynamic assumptions, by combining the heat of sublimation and solution both which can be experimentally determined. Heats of solvation of the copper(I) and silver(I) ions, and the copper(I) halides have already been determined in acetonitrile, dimethylsulfoxide and pyridine, and of the silver(I) halides in pyridine [6–9].

Experimental

Chemicals

Tetrahydrothiophene (THT) (Fluka 97%) was purified as described elsewhere [10]. The copper(I) halides (Merck p.a.) were recrystallized from acetone and diethylether, kept over phosphorpentoxide at reduced pressure and handled under dry nitrogen. The silver(I) nitrate and sodium halides, used for preparation of the silver(I) halides, were of analytical grade. The silver(I) halides were precipitated from water, carefully washed, dried over phosphorous pentoxide under reduced pressure and kept in dark vessels.

Calorimetry

The ampoule calorimeter and procedure used are described elsewhere [11, 12]. Glass ampoules with varying amounts of salt were used in order to check if the heats of solution were dependent on concentration. The ampoules were sealed by melting, and cooled during the sealing. The salts were dissolved within a few minutes in 80 ml of solvent. At least six experiments were performed for each salt. All measurements were performed at 25.000 ± 0.002 °C.

Calculations

For the reaction

$$\text{M}^+(\text{g}) + \text{L}^-(\text{g}) \longrightarrow \text{M}^+(\text{solv}) + \text{L}^-(\text{solv})$$

the overall enthalpy change of the two ions M, L is determined by

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$$\Delta H^\circ_{\mathrm{sv}}(\mathrm{M,L}) = \Delta H^\circ_{\mathrm{sv}}(\mathrm{M}) + \Delta H^\circ_{\mathrm{sv}}(\mathrm{L}) \tag{1}$$

The quantity $\Delta H^\circ_{\mathrm{sv}}(\mathrm{M,L})$ is calculated from the heat of solution of the two ions according to

$$\Delta H^\circ_{\mathrm{sv}}(\mathrm{M,L}) = \Delta H^\circ_{\mathrm{lat}}(\mathrm{ML}) + \Delta H^\circ_{\mathrm{s}}(\mathrm{ML}) - \Delta H^\circ_{\beta 1}(\mathrm{ML}) \tag{2}$$

where $\Delta H^\circ_{\mathrm{lat}}$ is the lattice enthalpy of ML(s) in the reaction

$$\mathrm{M^+(g) + L^-(g) \longrightarrow ML(s)}$$

$\Delta H_{\mathrm{s}}^\circ(\mathrm{ML})$ is the heat of solution of the salt ML

$$\mathrm{ML(s) \longrightarrow M^+(solv) + L^-(solv)}$$

$\Delta H^\circ_{\beta 1}(\mathrm{ML})$ is the enthalpy change of the reaction

$$\mathrm{M^+(solv) + L^-(solv) \longrightarrow ML(solv)}$$

determined from a calorimetric titration of a metal solution with a solution of the ligand.

The lattice enthalpies $\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML})$ at 25 ℃ for the copper(I) and silver(I) halides are calculated from the standard heats of formation $\Delta H^\circ_{\mathrm{f}}(\mathrm{ML})$, the heats of sublimation of the metal, L_{M}, the heats of atomisation of the halogens, D_{L}, the ionisation potentials of the metal ions, I_{M} and the electron affinities of the halogen atoms, E_{L} according to

$$\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML}) = \Delta H^\circ_{\mathrm{f}}(\mathrm{ML}) - L_{\mathrm{M}} - D_{\mathrm{L}} - I_{\mathrm{M}} - E_{\mathrm{L}} \tag{3}$$

The heat of solution $\Delta H_{\mathrm{s}}^\circ(\mathrm{M,L})$ is related to the heat of solution of the salt ML, $\Delta H^\circ_{\mathrm{s}}(\mathrm{ML})$ by

$$\Delta H_{\mathrm{s}}^\circ(\mathrm{M,L}) = \Delta H_{\mathrm{s}}^\circ(\mathrm{ML}) - \Delta H^\circ_{\beta 1}(\mathrm{ML}) \tag{4}$$

The heat of solvation of the ligand, $\Delta H^\circ_{\mathrm{sv}}(\mathrm{L})$ is determined from the heat of hydration and the heat of transfer from water to the solvent according to

$$\Delta H^\circ_{\mathrm{sv}}(\mathrm{L}) = \Delta H^\circ_{\mathrm{hydr}}(\mathrm{L}) + \Delta H^\circ_{\mathrm{tr}}(\mathrm{L}) \tag{5}$$

The heat of solvation of the metal ion can be determined in two ways. According to eqn. (1)

$$\Delta H^\circ_{\mathrm{sv}}(\mathrm{M}) = \Delta H^\circ_{\mathrm{sv}}(\mathrm{M,L}) - \Delta H^\circ_{\mathrm{sv}}(\mathrm{L}) \tag{6}$$

or as for the ligand by

$$\Delta H^\circ_{\mathrm{sv}}(\mathrm{M}) = \Delta H^\circ_{\mathrm{hydr}}(\mathrm{M}) + \Delta H^\circ_{\mathrm{tr}}(\mathrm{M}) \tag{7}$$

The heat of sublimation $\Delta H^\circ_{\mathrm{sub}}(\mathrm{ML})$ from the relation

$$\mathrm{ML(s) \longrightarrow ML(g)}$$

is determined from the coordinate bond energy, $\Delta H^\circ_{\mathrm{CBE}}(\mathrm{ML})$ and the lattice enthalpies $\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML})$.

$$\Delta H^\circ_{\mathrm{sub}}(\mathrm{ML}) = \Delta H^\circ_{\mathrm{CBE}}(\mathrm{ML}) - \Delta H^\circ_{\mathrm{lat}}(\mathrm{ML}) \tag{8}$$

The heat of sublimation together with the heat of solution $\Delta H^\circ_{\mathrm{s}}(\mathrm{ML})$ from

$$\mathrm{ML(s) \longrightarrow ML(solv)}$$

gives the heat of solvation of the neutral complex $\Delta H^\circ_{\mathrm{sv}}(\mathrm{ML})$ in the reaction

$$\mathrm{ML(g) \longrightarrow ML(solv)}$$

according to

$$\Delta H^\circ_{\mathrm{sv}}(\mathrm{ML}) = \Delta H_{\mathrm{s}}^\circ(\mathrm{ML}) - \Delta H^\circ_{\mathrm{sub}}(\mathrm{ML}) \tag{9}$$

Results

The lattice enthalpies, $\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML})$ at 25 ℃ were calculated from the Born–Haber cycle according to eqn. (3). Data used in these calculations are given in Table I. The heats of solution, $\Delta H_{\mathrm{s}}^\circ(\mathrm{ML})$ of the copper(I) and silver(I) halides are negative, Table II. The random errors in $\Delta H^\circ_{\mathrm{s}}(\mathrm{ML})$ were estimated to be less than 2 kJ mol^{-1}. The heats of solution were independent of the amounts of salt dissolved for all systems. The heats of solvation of the neutral copper(I) and silver(I) halides, calculated from heats of solution and sublimation, are given in Table III. The

TABLE I. Lattice Enthalpies, $\Delta H^\circ_{\mathrm{lat}}$, for the Reaction, $\mathrm{M^+(g) + L^-(g) \rightarrow ML(s)}$, Calculated from the Born–Haber Cycle, $\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML}) = \Delta H^\circ_{\mathrm{f}}(\mathrm{ML}) - L_{\mathrm{M}} - D_{\mathrm{L}} - I_{\mathrm{L}} - E_{\mathrm{L}}$. Heat of Sublimation, $\Delta H^\circ_{\mathrm{sub}}(\mathrm{ML})$ Calculated from Lattice Enthalpies, $\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML})$ and the Coordinate Bond Energy, $\Delta H^\circ_{\mathrm{CBE}}$, According to $\Delta H^\circ_{\mathrm{sub}}(\mathrm{ML}) = \Delta H^\circ_{\mathrm{CBE}}(\mathrm{ML}) - \Delta H^\circ_{\mathrm{lat}}(\mathrm{ML})$. All Values in kJ mol^{-1}

ML	$\Delta H^\circ_{\mathrm{f}}(\mathrm{ML})^{\mathrm{a}}$	$L_{\mathrm{M}}{}^{\mathrm{b}}$	$D_{\mathrm{L}}{}^{\mathrm{c}}$	$I_{\mathrm{M}}{}^{\mathrm{d}}$	$E_{\mathrm{L}}{}^{\mathrm{e}}$	$\Delta H^\circ_{\mathrm{lat}}(\mathrm{ML})$	$\Delta H^\circ_{\mathrm{CBE}}(\mathrm{ML})^{\mathrm{f}}$	$\Delta H^\circ_{\mathrm{sub}}(\mathrm{ML})$
CuCl	−136.4	+339.3	+121.8	+745.3	−348.6	−994.2	−756.9	+237.3
CuBr	−105.9	+339.3	+111.7	+745.3	−324.5	−977.7	−750.3	+227.4
CuI	−68.5	+339.3	+106.7	+745.3	−295.3	−964.3	−737.7	+226.6
AgCl	−127.0	+286.2	+121.8	+730.8	−348.6	−917.2	−695.0	+222.2
AgBr	−99.6	+286.2	+111.7	+730.8	−324.5	−903.8	−694.2	+209.6
AgI	−62.3	+286.2	+106.7	+730.8	−295.5	−890.5	−692.5	+198.0

[a] Standard heats of formation of the crystalline halides, $\Delta H^\circ_{\mathrm{f}}(\mathrm{ML})$ for the reaction $\mathrm{M(s) + 1/2L_2(s,s) \rightarrow ML(s)}$, at 298 K from ref. 15, (s, s) denotes standard state. [b] Heats of sublimation of the metals, L_{M}, for the reaction $\mathrm{M(s) \rightarrow M(g)}$, at 298 K from ref. 15. [c] Heats of atomization of the halogenes, D_{L}, for the reaction $\mathrm{1/2L_2(s,s) \rightarrow L(g)}$, at 298 K from ref. 16. [d] The ionization potentials of the metal atoms, I_{M}, for the reaction $\mathrm{M(g) \rightarrow M^+(g) + e^-}$, at 0 K from ref. 17. [e] Electron affinities of the halogen atoms, E_{L}, for the reaction $\mathrm{L(g) + e^- \rightarrow L^-(g)}$, at 0 K from ref. 18. [f] Coordinate bond energies, $\Delta H^\circ_{\mathrm{CBE}}$, at 298 K from ref. 19.

TABLE II. Heats of Solvation of the Neutral Halide Complexes of Copper(I) and Silver(I) in THT Determined from ΔH_s°(ML) and ΔH_{sub}°(ML) According to $\Delta H_{sv}^\circ(ML) = \Delta H_s^\circ(ML) - \Delta H_{sub}^\circ(ML)$. All Values in kJ mol^{-1}

ML	ΔH_s°(ML)	ΔH_{sub}°(ML)[a]	ΔH_{sv}°(ML)
CuCl	−41.8 ± 1.4	+237.3	−279.1
CuBr	−48.3 ± 0.5	+227.4	−275.7
CuI	−39.6 ± 1.5	+226.6	−266.2
AgCl	−11.5 ± 2.0	+222.2	−233.7
AgBr	−17.0 ± 0.9	+209.6	−226.6
AgI	−19.4 ± 0.9	+198.0	−217.4

[a] The heats of sublimation from Table I.

TABLE IV. Heat of Solvation of the Metal Ion, ΔH_{sv}°(M), in kJ mol^{-1} Calculated According to eqn. (6), from ΔH_{sv}°(M, L) in Table III and ΔH_{sv}°(L), in Table IV

	ΔH_{sv}°(M, L)	ΔH_{sv}°(L)	ΔH_{sv}°(M)	Average
CuCl	−1040.6	−341	−700	
CuBr	−1019.7	−323	−697	
CuI	−1008	−311	−697	−698
AgCl	−923.9	−341	−583	
AgBr	−907.1	−323	−584	
AgI	−892.2	−311	−581	−583

heats of solution of the two ions, ΔH_s°(M, L) are calculated from ΔH_s°(ML) and $\Delta H_{\beta 1}^\circ$(ML) according to eqn. (4), Table III. The heats of solvation of the two ions ΔH_{sv}(M, L) were determined from ΔH_s°(M, L) and ΔH_{lat}°(ML) according to eqn. (2), Table III. Heats of solvation of the halide ions, ΔH_{sv}°(L), were calculated according to eqn. (5) from ΔH_{hydr}°(L) and ΔH_{tr}°(L) [5]. The ΔH_{sv}°(L) values are −341, −323 and −311 kJ mol^{-1} for chloride, bromide and iodide in THT.

Heats of transfer of the halide ions, ΔH_{tr}°(L) have been determined earlier using the TATB assumption, stating that $\Delta H_{tr}^\circ(AsPh_4^+) = \Delta H_{tr}^\circ(BPh_4^-)$ [1, 5]. The heats of hydration of the ligands, ΔH_{hydr}°(L) have been determined by Morris [4] employing a calculated heat of solvation of the hydrogen ion, $\Delta H_{sv}^\circ(H^+) = -1103 \pm 13$ kJ mol^{-1}. The errors in ΔH_{sv}°(L) and ultimately in ΔH_{sv}°(M) depend mainly on the errors in ΔH_{hydr}°(L) and $\Delta H_{sv}^\circ(H^+)$.

Heats of solvation of the copper(I) and silver(I) ions were determined according to eqn. (6) from the heat of solvation of the ligand, ΔH_{sv}°(L), and the heat of solvation of the two ions, ΔH_{sv}°(M, L). The values of, ΔH_{sv}°(M) in Table IV determined from the chloride, bromide and iodide salts agree well. The heat of solvation of the copper(I) is −698 kJ mol^{-1} and −583 kJ mol^{-1} for silver(I). The heat of solvation of the metal ion, ΔH_{sv}°(M), was determined, according to eqn. (7), from the heat of hydration, ΔH_{hydr}°(M), and the heat of transfer, ΔH_{tr}°(M). The heat of hydration of the silver(I) ion was determined to be −488 kJ mol^{-1} [13]. The heat of transfer of the silver(I) ion to THT is −96.3 kJ mol^{-1} [5]. The $\Delta H_{sv}^\circ(Ag^+)$ determined from eqn. (7) to be −584 kJ mol^{-1}, agrees very well with $\Delta H_{sv}^\circ(Ag^+)$ of −583 kJ mol^{-1} calculated from ΔH_{sv}°(M, L) and ΔH_{sv}°(L).

The heat of hydration of the copper(I) has been reported to be −607 kJ mol^{-1} [14]. The heat of transfer from water, $\Delta H_{tr}^\circ(Cu^+)$, to other solvents has been calculated using this value and the $\Delta H_{sv}^\circ(Cu^+)$ values. The heat of solvation of copper(I) in THT, −698 kJ mol^{-1} gives $\Delta H_{tr}^\circ(Cu^+) = -91$ kJ mol^{-1}, according to eqn. (5).

Discussion

Tetrahydrothiophene is regarded as a soft donor solvent and it coordinates strongly to soft metal ions such as copper(I) and silver(I). Electrostatic as well as covalent bonding forces between metal ion and solvent molecules contribute to the solvation. The

TABLE III. Heat of Complex Formation, $\Delta H_{\beta 1}^\circ$(ML), Heat of Solution ΔH_s°(ML) from Table II, Heat of Solution of the Two Ions, ΔH_s°(M, L), Lattice Enthalpies, ΔH_{lat}°(ML) from Table I and the Heat of Solvation of the Two Ions, ΔH_{sv}°(M, L). All values in kJ mol^{-1}

ML	$\Delta H_{\beta 1}^\circ$(ML)[a]	ΔH_s°(ML)	ΔH_s°(M, L)[b]	ΔH_{lat}°(ML)	ΔH_{sv}°(M, L)
CuCl	+4.6	−41.8	−46.4	−994.2	−1040.6
CuBr	−6.3	−48.3	−42.0	−977.7	−1019.7
CuI	+4	−39.6	−44	−964.3	−1008
AgCl	−4.8	−11.5	−6.7	−917.2	−923.9
AgBr	−13.7	−17.0	−3.3	−903.8	−907.1
AgI	−17.7	−19.4	−1.7	−890.5	−892.2

[a] Ref. 3. [b] Calculated according to eqn. (4).

TABLE V. The Heats of Solvation, $-\Delta H^{\circ}_{sv}$, in kJ mol^{-1}, of Copper(I) and Silver(I) Ions and Halide Complexes in Water (W), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py) and Tetrahydrothiophene (THT)

	W	AN^c	DMSO^c	Py^c	THT
Cu^+	607^a	679	649	734	698
Ag^+	488^b	529	539	594	583
CuCl		250.2	247.1	303.4	279.1
CuBr		242.7	238.1	293.4	275.7
CuI		232.4	228.1	288.0	265.2
AgCl				235.1	233.7
AgBr				223.8	226.6
AgI				219.7	217.4

^{a}Ref. 14. ^{b}Ref. 13. ^{c}Ref. 9.

degree of covalency in the solvate bond depends on the softness of both the metal ion and the solvent. Silver(I) is somewhat more polarizable than copper(I), and due to the soft character of silver(I) and THT the covalent contribution is expected to predominate. The stronger electrostatic forces of copper(I) make the solvation, in general, stronger than for silver(I), Table V.

The heats of solvation of the neutral copper(I) and silver(I) halide complexes are markedly lower than the heats of solvation of the metal ions, since no charge is neutralized on the neutral complexes. Furthermore, a desolvation takes place when the neutral copper(I) and silver(I) halide complexes are formed [31]. The heat of solvation is strongly dependent on the effective charge on the metal. The effective charge on the metal becomes smaller the more covalent the bonds are within the complex. The iodide complexes have lower values of heat of solvation than the bromide and chloride complexes. The softness of the ligand and the covalency in the metal halide bond increase in the order $Cl^- < Br^- < I^-$. The effective charge on the metal thus decreases in the opposite order.

The heats of solvation of the copper(I) and silver(I) ions and halides are larger in pyridine than in THT, Tables IV and V. This is somewhat surprising since the soft acceptor mercury(II) forms markedly stronger bonds to THT than to pyridine [20] and as silver(I) forms complexes with THT in pyridine solution [21]. For sulfur donor solvents, lower heats of solvation than expected from the solvate bond strength have been reported for neutral mercury(II) halide complexes [23]. This is explained by THT and other sulfur donor solvents having a pronounced bulk structure built up by S–S intermolecular interactions. Such S–S interactions have indeed been observed in large angle X-ray scattering studies on THT solutions [23]. This means that much more energy is required to make THT molecules available for solvation, *i.e.* they are taken out of the bulk structure, than pyridine molecules, due to much stronger intermolecular forces. Pyridine has no pronounced bulk structure since it is built up mainly by van der Waals forces.

The heats of solvation of neutral mercury(II) halides also showed that the bromide complex is more strongly solvated than the other halide complexes in THT, contrary to the other solvents where the heat of solvation increases in the order $HgI_2 < HgBr_2 < HgCl_2$ [22]. The tendency for an especially strong solvation of bromide complex in THT is also seen for the silver(I) and copper(I) bromide complexes, Table V. It is less striking for the AgBr and CuBr complexes because these contain only one bromide atom. One reason for this behaviour can be that the bromide ion, free or in complexes, fits better into the THT bulk structure and less energy is required for restructuring the bulk than for the smaller chloride ion and the larger iodide ion. This is supported by the stability of the dibromocuprate(I) complex in THT being weaker than the corresponding chloride and iodide complexes [3].

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