Complex equilibria, solvation and solubility

Sten Ahrland

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

ABSTRACT - For metal salts involved in complex formation the overall solubility is a complicated function of the solvation and stabilities of the various species present. This treatise discusses how these factors, and hence the solubilities, vary between different complex systems and different solvents. Illustrative examples are provided by the copper(I), silver(I) and mercury(II) halide systems. Their behaviour in the solvents water, dimethylsulfoxide, acetonitrile and pyridine is the main subject of the present study.

SOLVATION AND SOLUBILITY

The solubility of a compound in a given solvent depends upon the balance between the Gibbs lattice energy of the solid and the Gibbs energies of solvation of the species present in solution. The conditions in solution can differ considerably depending on the character of the solute and the solvent. The present treatise will be restricted to various types of electrolytes. These display a highly variable behaviour depending upon the interactions of the composite ions, or between the ions and neutral molecules present. Especially important among the latter are of course the solvent molecules. In every solution the solvation of the species present is a most important factor, as is indeed implied in the opening sentence above.

By definition, strong electrolytes are those where a complete dissociation into ions, generally present already in the solid, takes place in solution. This means that the solvation of the ions predominates completely over their mutual interactions. Thermodynamically this is certainly a simpler case than if interactions between the various species give rise to a number of complexes. Especially simple conditions are of course met in solutions of strong 1:1 electrolytes. It might therefore be worthwhile to state the thermodynamic solubility conditions for this case, though the present treatise will deal with solutions where complexes are formed.

In the case of the strong electrolyte ML, the Gibbs energy of solution, ΔG_s^o, is given by the difference

$$\Delta G_s^o = \Delta G_{sv}^o(M^+) + \Delta G_{sv}^o(L^-) - \Delta G_{lat}^o \qquad (1)$$

where $\Delta G_{sv}^o(M^+)$ and $\Delta G_{sv}^o(L^-)$ denote the Gibbs energies of solvation of the cation and anion, respectively, and ΔG_{lat}^o the Gibbs lattice energy. ΔG_s^o is directly related to the solubility product K_s:

$$\Delta G_s^o = -RT \ln K_s \qquad (2)$$

If the salt is just dissolved, the solubility C_s is evidently

$$C_s = \sqrt{K_s} = [M^+] = [L^-] \qquad (3)$$

If additional amounts of the anion L^- are added, the solubility of ML will decrease to:

$$C_s = [M^+] = K_s/[L^-] \qquad (4)$$

Here, as in the following, it is assumed that the activity conditions are kept constant so that concentrations ($[M^+]$, $[L^-]$, etc) could be inserted instead of activities. In the more complicated systems where complexes are formed, these simple expressions do not apply. Also in such systems, however, the solubilities evidently depend upon the strength of solvation. The solubilities of the silver halides provide informative examples. In aqueous solutions of the chloride and bromide systems, a series of mononuclear complexes up to AgL_4^{3-} are formed as the ligand concentration is increased. As the anionic complexes AgL_n^{1-n}, $n=2$ to 4, are readily soluble, the total solubility will steeply increase once the slightly soluble neutral complexes AgL are transformed into higher complexes. The solubility curves will thus pass through minima where the total solubilities are dominated by the low solubilities

of AgL (refs. 1, 2). In the iodide system, polynuclear complexes are formed besides the mononuclear ones as the total solubility increases with the ligand concentration. This implies an even steeper rise than if only nomonuclear complexes were formed (ref. 3).

In solvents where the neutral complexes AgL are more strongly solvated than in water, the minimum solubility will increase. In pyridine, the solvation has become strong enough to make the complexes AgCl and AgBr readily soluble; on dissolving the solid phases solubilities of 94 and 220 mM are reached (ref. 4). As in water, higher complexes are formed at higher concentrations of the ligands, implying even larger solubilities. In spite of the strong solvation of silver(I) species, the solids AgCl and AgBr remain unsolvated also in this solvent. The iodide, on the other hand, is transformed into a solvate of the composition AgIPy. A structure determination reveals an infinite "stairs" arrangement (ref. 5), analogous to that found for one modification of CuIPy (ref. 6) and also to the acetonitrile solvates CuClAN, CuBrAN (ref 7) and CuIAN (ref. 8). This radical phase transition means a much lower solubility of silver iodide in pyridine, 8 mM, than would be expected for a phase AgI (ref. 4).

To interpret the solubility changes between different solvents, values of the Gibbs energies of solvation for the various species present in the solutions are evidently needed, as well as the constants for the equlibria established between them. The magnitude of these quantities for some selected ions and complexes in various solvents will be discussed in the next two sections.

ENTHALPIES AND GIBBS ENERGIES OF SOLVATION IN VARIOUS SOLVENTS

For this comparison, the species selected are the metal ions Cu^+, Ag^+; Zn^{2+}, Cd^{2+}, Hg^{2+}; the halide ions, and the halido complexes of the metal ions mentioned. As to the solvents, water is an obvious choice not only because of its abundance and tremendous importance on our planet, but also as the archetype of a protic solvent, displaying the peculiarities due to the formation of strong hydrogen bonds. Dimethylsulfoxide (DMSO) has been chosen as an aprotic oxygen donor solvent. It would further be desirable to consider solvents coordinating through a softer donor atom than oxygen. As such the nitrogen donor solvents acetonitrile (AN) and pyridine (Py) have been selected which offer their nitrogen atom in very different atomic environments.

The Gibbs energies of solvation, directly connected with the solubility, are known for the metal ions quoted, and also for the heavy halide ions Cl^-, Br^-, I^- in all these solvents (with the exception for Cd^{2+} in pyridine). For the complexes, however, values of ΔG_{sv}^0 are not known. On the other hand, enthalpies of solvation are known not only for the metal and halide ions but also in several instances for the neutral complexes. In addition, the enthalpies of transfer, ΔH_{tr}^0, between different solvents are known for many ionic complexes. By comparing enthalpies and Gibbs energies in cases where both are known, it should be possible to draw conclusions also in cases where only enthalpy data are available.The values of ΔH_{sv}^0 of the metal ions, and of their neutral halido complexes determined to date are listed in Table 1. In this Table values of ΔG_{sv}^0 for the solvation of the metal ions in DMSO have also been entered, as well as the resulting entropy terms $T\Delta S_{sv}^0$. The reason for selecting DMSO as the standard for this comparison is that the data are most complete fot this solvent. The values of $-\Delta G_{sv}^0$ are throughout smaller, i.e. less favourable, than the values of $-\Delta H_{sv}^0$. This means that the entropy terms $T\Delta S_{sv}^0$ are always negative, i.e. unfavourable, as is to be expected as the solvation implies an ordering relative to the gaseous state. It should be noted, however, that the order between the ions is the same for ΔH_{sv}^0 and ΔS_{sv}^0. This certainly applies also to the complexes where the values of ΔG_{sv}^0 are so far unknown.

The same conclusion is reached from the data of Table 2, where values of ΔH_{tr}^0 and ΔG_{tr}^0, pertaining to the transfer between DMSO and the other solvents are listed. For the transfer from DMSO to water, the values of $-\Delta G_{tr}^0$ (DMSO→W) are less negative than those of $-\Delta H_{tr}^0$ (DMSO→W), implying that the favoured reversed transfers from water to DMSO become less favoured because of negative entropy terms. The same applies to the transfers from DMSO to AN, though the differences between ΔG_{tr}^0 (DMSO→AN) and ΔH_{tr}^0 (DMSO→AN) are generally small for this pair, expecially for Ag^+ and Hg^{2+}. Between ΔG_{tr}^0(DMSO→Py) and ΔH_{tr}^0 (DMSO→Py) the difference is, on the other hand, quite large; for these transfers the entropy terms are all very unfavourable. For a certain solvent pair, the entropies thus behave in much the same way for all acceptors, though they differ considerably in magnitude between different pairs. It seems safe to assume that this will apply not only to the metal ions but also to the complexes.

It might thus be concluded, that the values of ΔG_{sv}^0 are generally more favourable in DMSO than in water. Consequently, all systems considered here tend to be more soluble in DMSO than in water. For the soft copper(I), silver(I) and mercury(II), however, pyridine is an even better solvent than DMSO. For copper(I), this is

TABLE 1. Enthalpies of solvation[a], $\Delta H_{sv}°$/kJ mol^{-1}, of the cations Cu^+, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, and of their neutral halido complexes, in solvents of various donor properties; Gibbs energies, and entropies of solvation for the cations in DMSO[b]; at 25 °C. Ionic radii, r_{ion}/Å[c].

| | r_{ion} | Water | DMSO | AN | Py | DMSO | |
			$-\Delta H_{sv}°$			$-\Delta G_{sv}°$	$T\Delta S_{sv}°$
Cu^+	0.86		649	679	734	609	-40
Ag^+	1.12	488	539	529	595	511	-28
CuCl			247.5	250.6	303.8		
CuBr			237.6	242.2	292.9		
CuI			231	235	291		
AgCl					235.2		
AgBr					224.6		
AgI					219.3		
Zn^{2+}	0.75	2063	2123	2043	2149	2071	-52
Cd^{2+}	0.95	1831	1898	1819	1955	1853	-45
Hg^{2+}	1.02	1845	1921	1851	2006	1890	-31
$ZnCl_2$			219				
$ZnBr_2$			221				
ZnI_2			224.5				
$CdCl_2$		194	221				
$CdBr_2$		170	209				
CdI_2		141	191				
$HgCl_2$		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] For copper(I), silver(I) and mercury(II) (except for Hg^{2+} in AN) ref. 9; for zinc(II) and cadmium(II) in water and DMSO ref 10; for Zn^{2+} in AN and Py, and Hg^{2+} in AN, ref. 11; for Cd^{2+} in AN and Py, ref. 12.
[b] Ref. 13; values slightly modified as described in Ref. 14; values of Cu^+ and Hg^{2+} less reliable.
[c] For Zn^{2+}, Cd^{2+} and Hg^{2+} ref. 15; for Ag^+ ref. 16; the radius of Cu^+ is 0.26 A smaller than that of Ag^+, see Table 5 of ref. 17.

also the case for AN. The latter is, on the other hand, not at all a good solvent for divalent states, being increasingly worse as their softness decreases from mercury(II) to zinc(II).

The preference of the aprotic solvents for soft acceptors also brings about a large stabilization of the softer copper(I) relative to the harder copper(II). This means that the extensive disproportionation of copper(I) which is such a characteristic feature of its chemistry in aqueous solution is much less extensive in DMSO and practically suppressed in the two solvents coordinating via nitrogen (refs. 14, 24, 25). As to the halide ions, values of both $\Delta H_{sv}°$ and $\Delta G_{sv}°$ are known for many solvents. In Table 3, data are listed not only for the solvents so far discussed but also for methanol, which is protic, though less so than water, and for tetrahydrothiophene, THT, which is aprotic and coordinating via sulfur. In all instances, $-\Delta G_{sv}° < -\Delta H_{sv}°$, on account of the unfavourable entropy change accompanying the solvation. Due to hydrogen bonding, the values of $\Delta G_{sv}°$ are more favourable in protic than in aprotic solvents for Cl^-, and slightly also for Br^-; for I^- the difference is insignificant. For F^-, values are available only for the protic solvents; in aprotic ones fluorides tend to be slightly soluble on account of their high lattice energies, not compensated in these solvents by high solvation energies due to hydrogen bonding.

TABLE 2. Enthalpies[a] and Gibbs energies of transfer[b] (kJ mol^{-1}) between dimethylsulfoxide and water, acetonitrile, pyridine, for Cu^+, Ag^+, Hg^{2+} and for halido complexes of these acceptors, at 25 °C.

S→	W	AN	Py		W	AN	Py
				$-\Delta H_{tr}{}^o$(DMSO→S)			
Cu^+		30	85	Hg^{2+}	-76	-70	85
CuCl		3	57	$HgCl^+$	-52		71
CuBr		5	55	$HgBr^+$	-54		67
CuI		4	60	HgI^+	-46		66
$CuCl_2{}^-$		-9	21	$HgCl_2$	-35	-31	34
$CuBr_2{}^-$		-13	33	$HgBr_2$	-37	-30	35
$CuI_2{}^-$		-13		HgI_2	-33		38
				$HgCl_3{}^-$	-26		19
Ag^+	-51	-10	56	$HgBr_3{}^-$	-51		15
				$HgI_3{}^-$			20
Zn^{2+}	-60	-80	26	$HgCl_4{}^{2-}$	-24		0
				$HgBr_4{}^{2-}$	-52		6
Cd^{2+}	-67	-79	57	$HgI_4{}^{2-}$	-66		5
				$-\Delta G_{tr}{}^o$(DMSO→S)			
Cu^+	-41	12	41	Zn^{2+}	-47	-116	-57
Ag^+	-34	-12	23	Cd^{2+}	-56	-98	
				Hg^{2+}	-68	-71	11

[a] For metal ions and neutral complexes, from values of Table 1; for ionic complexes from ref. 9.

[b] Values pertaining to water and AN, from ref. 14, except the transfer of Hg^{2+} to AN, taken from ref. 11. Values pertaining to pyridine from ref. 18 (Cu^+, Ag^+) and from ref. 11 (Zn^{2+}, Hg^{2+})

TABLE 3. Enthalpies[a] and Gibbs energies[b] of solvation, (kJ mol^{-1}) of the halide ions in solvents of different characteristics, at 25 °C. Ionic radii[c], r_{ion}/Å, of the halide ions.

		Water	Methanol	DMSO	AN	Py	THT
	r_{ion}			$-\Delta H_{sv}{}^o$			
F^-	1.16	502	488				
Cl^-	1.64	366	358	347	345	338	341
Br^-	1.80	335	330	331	327	324	323
I^-	2.04	294	296	307	301	301	311
				$-\Delta G_{sv}{}^o$			
F^-		436	420				
Cl^-		319	303	280	277	285	265
Br^-		305	294	279	273	284	279
I^-		259	252	250	240	240	

[a] Water, ref. 19; methanol, ref. 20, for F^- cf. also ref. 21; DMSO, AN, Py, ref. 22; THT, ref. 23.

[b] Water, Methanol, DMSO, AN, ref. 14; Py, THT, ref. 18 [c] Ref. 19.

HALIDO COMPLEX FORMATION OF COPPER(I), SILVER(I) AND MERCURY(II)

As pointed out above, formation of anionic complexes might strongly contribute to an increase of the overall solubility in systems where the neutral complexes tend to be slightly soluble. In cases where only one anionic complex is formed the conditions are particularly simple. In practice, this applies to the copper(I) halide systems in the aprotic solvents considered here, up to fairly high ligand concentrations, and also to the chloride system in aqueous solution. The total solubility of copper(I) is then given by

$$C_S=[Cu^+]+[CuL]+[CuL_2^-] \text{ i.e. } C_S=K_S(1/[L]+K_1+K_1K_2[L]) \qquad (5)$$

where K_S is the solubility product of CuL and K_1 and K_2 the stepwise stability constants. Once the term $1/[L]$ referring to $[Cu^+]$ is negligible, the solubility will increase linearly with [L], and more steeply the larger the value of K_2. The constant contribution from the neutral complex equals K_SK_1. In systems where higher complexes are formed, additional terms containing higher powers of [L] will appear.

In aqueous solutions, the conditions are complicated by the disproportionation of Cu^+. Here addition of halide acts in two ways. The unstable species Cu^+ is suppressed, and the slightly soluble neutral complexes CuL are transformed into anionic complexes CuL_2^-.

As mentioned, the disproportionation of Cu^+ is much less extensive in DMSO than in water, and practically suppressed in acetonitrile and pyridine. Simultaneously, the complexes CuL become readily soluble. This must mean that their Gibbs energies of solvation are more favourable than in water, though the difference cannot be measured, or estimated, just on account of the low solubility of CuL in aqueous solution, and of the disproportionation of Cu^+ taking place there.

No disproportionation takes place in the case of silver(I). On the other hand, it takes a solvent with very high affinity for soft acceptors to overcome the Gibbs lattice energies of the silver halides. Among the present ones, only pyridine can achieve this, though, as mentioned above, only for AgCl and AgBr, while a phase change complicates matters for AgI. Once anionic complexes are formed the solubility increases rapidly, however. This occurs not only in water but also in an array of other solvents, protic as well as aprotic, including DMSO and acetonitrile (ref. 26). Values of $\beta_2=K_1K_2$ can therefore be readily determined, while separate values of K_1 and K_2 are difficult to measure.

The pertinent values of K_s, K_1, K_2 and β_2 so far determined for the halido copper(I) and silver(I) complexes are listed in Table 4. In aqueous solutions the solubility products decrease while the complex stabilities increase from Cl$^-$ to I$^-$. The first trend decreases, the second increases the solubilities in the order mentioned, as is

TABLE 4. Solubility products [a] and stability constants [b] for copper(I) and silver(I) halido complexes in solvents of various donor properties, at 25 °C.

	Water			DMSO			AN			Py		
	Cl$^-$	Br$^-$	I$^-$	Cl$^-$	Br$^-$	I$^-$	Cl$^-$	Br$^-$	I$^-$	Cl$^-$	Br$^-$	Cl$^-$
						Copper(I)						
pK_{sp}	7.38	8.89	12.72									
log K_1				4.37	4.19	4.59	4.02	3.39	3.13	3.09	2.78	2.69
log K_2				4.50	3.75	2.99	5.53	3.82	2.84	1.91	1.10	0.9
log β_2	6.06	6.28	8.7	8.87	7.94	7.58	9.55	7.21	5.97	5.00	3.88	3.6
						Silver(I)						
pK_{sp}	9.7	12.2	16.0	10.6	10.8	11.6	13.2	13.9	14.5	6.1	5.8	
log K_1	2.85	4.15	6.58							4.95	5.03	6.87
log K_2	1.87	2.96	5.16							3.61	3.41	3.20
log β_2	4.72	7.11	11.74	11.9	11.7	13.1	12.6	13.4	14.6	8.56	8.44	10.7

[a] Copper(I), ref. 27; silver(I), ref. 18; [b] Copper(I), water, ref. 27; DMSO, refs. 28, 29; AN, ref. 24; Py ref. 25, silver(I), water, refs. 1,2,30; DMSO and AN, ref. 26; Py, ref. 25.

evident from eq. (5). In the aprotic solvents, the same trends are found for silver(I) though much less marked. For copper(I), however, the stability trends are reversed; no values of K_s are known for these systems. The characteristic differences between protic and aprotic solvents are mainly due to the hydrogen bonding of Cl^-, and to some extent Br^-, in the former. The special affinity of these ions for protic solvents is reflected in especially high values of the solvation enthalpies, Table 3; under these conditions the ions will evidently be less prone to form complexes. In pyridine, the strong solvation brings about high solubilities (cf. the high values of K_s) though the complex formation is fairly weak, for the same reason.

The second complex in all the mercury(II) halido systems is very stable in all the solvents (refs. 11, 31). Dissolving HgL_2(s) yields practically only HgL_2(sv). In water, the solubility of HgI_2 is low, $\sim$ 0.1 mM, and that of $HgBr_2$ modest, $\sim$ 15 mM, at 25 $^{\circ}$C (refs. 32, 33). In the aprotic solvents they are readily soluble, evidently because of the stronger solvation of the neutral complexes (cf. Table 1). Addition of extra halide will further increase the solubilities, however, by formation of complexes HgL_3^- and HgL_4^{2-}, the latter ones being the final complexes formed in these systems.

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