

SOLVATION AND COMPLEX FORMATION—COMPETING AND COOPERATIVE PROCESSES IN SOLUTION

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Abstract - The interplay between solvation and complex formation in solvents of different solvating properties is discussed for a wide selection of acceptors and donors. The solvents compared are the strongly protic water, the less protic methanol and the aprotic dimethylsulfoxide, acetonitrile and pyridine. The latter ones differ considerably in their donor properties and, as a consequence, exhibit very different affinities to acceptors of different types. The relative strengths of the solvate bonds, and the bonds formed in complexes between the acceptor ion and other donors present determine to a large degree the net enthalpy change measured for complex formation reactions. Also the forces acting between the solvent molecules exert a marked influence on this term, however. The stabilities of the complexes also depend very much on entropy changes. These generally become more favourable, the stronger the solvation and the lower the internal order of the solvent. In strongly solvating, but structurally disordered solvents, the entropy terms become extremely favourable while the enthalpy terms become unfavourable, in spite of the fact that the acceptor to ligand bonds might be quite strong. In such cases, stable complexes are formed in endothermic reactions, due to an extensive entropy stabilization.

SOLVATION AND SOLUBILITY OF IONIC COMPOUNDS

Complex formation between metal ions (or other cations) and ligands in solution occurs in competition with the solvation of the species involved. The strength of the solvation depends upon the nature of the solvent, and the species concerned. In order to bring an ionic solid in solution, the solvation has to be quite strong, as the lattice forces are strong in such crystals. Such a strong solvation is possible only in strongly polar solvents, or in solvents possessing a special affinity to the ions to be solvated.

Thermodynamically, the solubility is given by the solution free energy ΔG_S^0 which is the difference between the solvation free energy ΔG_{sv}^0 and the lattice free energy ΔG_{lat}^0 . In the simple case of a fully dissociated 1:1 electrolyte ML, ΔG_{sv}^0 and ΔG_{lat}^0 refer to the reactions



respectively; ΔG_S^0 is evidently the sum of the solvation free energies of the ions present. Hence

$$\Delta G_S^0 = \Delta G_{sv}^0(M^+) + \Delta G_{sv}^0(L^-) - \Delta G_{lat}^0 \quad (3)$$

where ΔG_S^0 is directly related to the solubility product K_S :

$$\Delta G_S^0 = -RT \ln K_S \quad (4)$$

For most ionic compounds, however, the conditions are more complicated. Not only the metal ion and the anion but also complexes between these exist in solution in equilibrium with the solid phase. The function ΔG_S^0 becomes accordingly less simple.

The free energy functions are composed of enthalpy and entropy terms:

$$\Delta G_{sv}^0 = \Delta H_{sv}^0 - T\Delta S_{sv}^0 \quad (5)$$

$$\Delta G_{lat}^0 = \Delta H_{lat}^0 - T\Delta S_{lat}^0 \quad (6)$$

In these expressions, the enthalpy terms ΔH_{sv}^0 and ΔH_{lat}^0 greatly predominate over the entropy terms $T\Delta S_{sv}^0$ and $T\Delta S_{lat}^0$ (Refs. 1,2). This is due to the fact that the neutralization of electric charges is the main feature of the formation of both solvates and crystals from gaseous ions, processes which are both strongly exothermic. Moreover, if the compound is at all soluble, i.e. if the solvent is able to bring about a reasonably good neutralization of the ionic charges, $\Delta H_{sv}^0 = \Delta H_{sv}^0(M^+) + \Delta H_{sv}^0(L^-)$ has to be of the same order of magnitude as ΔH_{lat}^0 . The directly measurable solution enthalpy,

$$\Delta H_S^0 = \Delta H_{sv}^0(M^+) + \Delta H_{sv}^0(L^-) - \Delta H_{lat}^0 \quad (7)$$

is, therefore, a small difference between two large numbers. Evidently, also ΔG_{sv}^0 and ΔG_{lat}^0 must be strongly negative for ionic compounds, and of the same order of magnitude, so ΔG_S^0 is also a small difference which may be written:

$$\Delta G_S^0 = \Delta H_S^0 - T\Delta S_S^0 \quad (8)$$

where $T\Delta S_S^0 = T\Delta S_{sv}^0 - T\Delta S_{lat}^0 \quad (9)$

As a crystallization or solvation always means an increase of order relative to the gaseous state, the terms $T\Delta S_{sv}^0$ and $T\Delta S_{lat}^0$ are always negative (Ref. 2). Though they are small relative to ΔH_{sv}^0 and ΔH_{lat}^0 , the difference $T\Delta S_S^0$ is of the same order of magnitude as ΔH_S^0 , or ΔG_S^0 . For highly structured solvents, e.g. water, dissolving ionic crystals often means a sizable decrease of order, i.e. $T\Delta S_S^0$ may become strongly positive. For unstructured solvents, on the other hand, the opposite is generally true. Sometimes the value of $T\Delta S_S^0$ is so positive that a salt becomes readily soluble in spite of a quite unfavourable, i.e. strongly endothermic, value of ΔH_S^0 (e.g. NaClO_4 , KI and KNO_3 ; (Ref. 3)).

The lattice enthalpies and free energies involved in the calculation of the solvation functions ΔH_{sv}^0 and ΔG_{sv}^0 , (eqns. (3) and (7)) cannot be directly measured. For metal halides, however, they can be fairly safely calculated from a Born-Haber cycle involving i.a. the ionization potential of the metal and the electron affinity of the halogen atom, quantities which are well known (Refs. 4 and 5). For composite cations and anions, on the other hand, the ionization potentials and electron affinities leading to their formation cannot be very accurately determined. For salts containing such ions, ΔH_{lat}^0 and ΔG_{lat}^0 are therefore preferably calculated by means of some semiempirical approach. Especially for ΔH_{lat}^0 , numerous such treatments have been proposed (Refs. 4,6,7). The recent rigorous ones in all probability lead to fairly accurate results. This is also strongly indicated by the circumstance that values calculated by these methods for alkali halides agree well with those found from the Born-Haber cycle mentioned above (Ref. 5). Some disturbing discrepancies do exist between different approaches, however, which are still a matter of discussion. Values of ΔG_{lat}^0 for salts containing composite ions are generally calculated by subtracting $T\Delta S_{lat}^0$ from ΔH_{lat}^0

(eq. 6). The value of $\Delta S_{\text{lat}}^{\circ}$ is found as the difference between the entropies of the compound in the gaseous and solid state, quantities which can generally be evaluated with at least fair accuracy (Ref. 4).

SOLVATION OF SINGLE IONS

Aqueous solutions. Once the total solvation enthalpies and free energies of an ionic compound have been determined, the question arises about the contribution from the individual ions to $\Delta G_{\text{sv}}^{\circ}$ and $\Delta H_{\text{sv}}^{\circ}$. These cannot be found by purely thermodynamic methods. As the data for individual ions are of great interest, however, considerable efforts have been made to effect a reasonable partition by means of various extrathermodynamic assumptions. So far, the greatest interest has naturally been devoted to aqueous solutions. The discussion has been focussed on the best value of the real hydration enthalpy, and free energy, of the proton, $\Delta H_{\text{h}}^{\circ}(\text{H}^+)$ and $\Delta G_{\text{h}}^{\circ}(\text{H}^+)$.

For the hydration enthalpies, many different approaches have been used (Ref. 8). Several of these (including the first one, used by Fajons (9) as early as 1919) leads to values of $\Delta H_{\text{h}}^{\circ}(\text{H}^+)$ around -1100 kJ/mol at 25°C. In this treatise, the value of Morris (5), -1103 kJ/mol, has been adopted. The value has been calculated by the method of Halliwell and Nyburg (8), utilizing a new set of ionic radii derived from minima in the electron density distribution in alkali halides of rock salt structure. Later on, much the same value has been found from alkali cyanide data (Ref. 10). By the same approach, radii very close to those found by Morris have been derived by Gourary and Adrian (11). Radii calculated in this way are probably the most reliable available at present.

As to the hydration free energies, two quite different approaches lead to almost the same values of $\Delta G_{\text{h}}^{\circ}(\text{H}^+)$, viz. 1090 and 1086 kJ/mol, at 25°C. Of these, the method applied by Randles (12), based on measurements of the Volta potential, makes no assumption about the dimensions of the ions involved. The value of Blandamer and Symons (13), on the other hand, is obtained on the assumptions that the radii of Rb^+ and Cl^- are the same, as found by Gourary and Adrian, and that the values of $\Delta G_{\text{h}}^{\circ}$ is therefore the same for these ions. Also calculations based on semiempirical extensions of the Born equation yield values of much the same magnitude (Ref. 4). It seems reasonable to adopt $\Delta G_{\text{h}}^{\circ}(\text{H}^+) = -1088$ kJ/mol as a fairly accurate value.

With these values of $\Delta H_{\text{h}}^{\circ}(\text{H}^+)$ and $\Delta G_{\text{h}}^{\circ}(\text{H}^+)$, a value of the hydration entropy $\Delta S_{\text{h}}^{\circ}(\text{H}^+) = -50$ J/Kmol at 25°C is calculated. This quantity can, however, also be found in a more direct way, as the difference between the absolute entropies of H^+ in the gaseous and aqueous phases. By the Sackur-Tetrode equation, the former is found to be $S_{\text{g}}^{\circ}(\text{H}^+) = 109$ J/K mol (Ref. 14). Several approaches have been used to calculate the entropy in the aqueous phase. The results are in satisfactory agreement, so a value of $S_{\text{aq}}^{\circ}(\text{H}^+) = -21$ J/Kmol can be confidently adopted (Ref. 4). Consequently, $\Delta S_{\text{h}}^{\circ}(\text{H}^+) = -130$ J/K mol, i.e. a considerably more negative value than found from the difference $\Delta H_{\text{h}}^{\circ}(\text{H}^+) - \Delta G_{\text{h}}^{\circ}(\text{H}^+)$. This discrepancy is certainly larger than would be expected from the errors ascribed to the various quantities used in the calculations. It remains so far unresolved but as both $\Delta H_{\text{h}}^{\circ}(\text{H}^+)$ and $S_{\text{aq}}^{\circ}(\text{H}^+)$ seem quite well established, it might be reasonable to assume that either $-\Delta G_{\text{h}}^{\circ}(\text{H}^+)$, or $S_{\text{g}}^{\circ}(\text{H}^+)$, or both, have been accorded to large values.

Once values of $\Delta H_{\text{h}}^{\circ}(\text{H}^+)$ and $\Delta G_{\text{h}}^{\circ}(\text{H}^+)$ have been settled, values for other single ions can be

calculated from a suitable combination of the values of ΔH_h^0 and ΔG_h^0 determined for various electrolytes.

Non-aqueous solutions. Once the hydration enthalpies and free energies have been established for single ions, their solvation enthalpies and free energies in other solvents are generally found by the addition of the enthalpies and free energies of transfer, $\Delta H_{tr}^0(W \rightarrow S)$ and $\Delta G_{tr}^0(W \rightarrow S)$, between water and the solvent concerned. Again, only quantities referring to salts can be determined by purely thermodynamic methods. To effect the separation of these into the contributions from the single ions takes an extrathermodynamic assumption. Several such procedures have been proposed, yielding more or, sometimes, less concordant results (Refs. 15,16). In later years, however, a rather general consensus has been reached that a modification of the assumption originally suggested by Grunwald et al (17) is presumably closest to the truth. Its basic idea is that two large monovalent ions of much the same size and outer appearance must interact with any given solvent in much the same manner. This should especially apply if the interactions are weak and non-specific. The original pair suggested was Ph_4P^+ and BPh_4^- , later on Arnett and McKelvey (18) introduced the pair Ph_4As^+ and BPh_4^- which has now been taken as a standard (Refs. 16,19). The assumption implies that $\Delta H_{tr}^0(\text{Ph}_4\text{As}^+) = \Delta H_{tr}^0(\text{BPh}_4^-)$, $\Delta G_{tr}^0(\text{Ph}_4\text{As}^+) = \Delta G_{tr}^0(\text{BPh}_4^-)$ and, consequently, $\Delta S_{tr}^0(\text{Ph}_4\text{As}^+) = \Delta S_{tr}^0(\text{BPh}_4^-)$ for all pairs of solvents.

Solvation of various classes of ions, as a function of the solvent. Thermodynamic quantities found in the manner described are presented in Tables 1 and 2 for different classes of cations and anions. The solvents have been chosen in order to represent a wide spectrum of properties. Those range from the strongly protic water via the more weakly protic methanol to the aprotic DMSO, AN and pyridin. Among the latter, DMSO, like water and methanol, coordinates all the cations discussed here via oxygen. Pyridine and AN coordinate cations via nitrogen. Generally, however, the donor properties of the nitrogen atom are much stronger in pyridine than in AN.

For most ions, the heats of solvation are more exothermic in a strongly solvating aprotic solvent, such as DMSO, than they are in a strongly solvating protic solvent such as water, Table 1. This is to be expected, as more energy is presumably needed to break the strong hydrogen bonds of the water structure than to disrupt the structure of liquid DMSO. Also as expected, methanol generally takes an intermediate position. The solvents coordinating via nitrogen exhibit more special preferences. The fairly soft donor pyridine has, as expected, a very high affinity for the markedly soft acceptors Ag^+ and Hg^{2+} . As to AN, the most striking feature is the very low affinity to certain hard acceptors such as Zn^{2+} and, especially, H^+ . Also in this solvent, soft acceptors are preferred. The pattern is more subtle than in pyridine, however. While the very soft Ag^+ slightly prefers DMSO to AN, Cu^+ markedly prefers AN to DMSO (Table 5). Remarkably enough, ΔH_{tr}^0 between DMSO and AN is almost as unfavourable for the border-line ion Cd^{2+} as for the typically hard Zn^{2+} , and for both ions more unfavourable than for Ba^{2+} .

Ligands able to form hydrogen bonds in protic solvents are striking exceptions from the trends described. Thus for Cl^- , and to some extent also for Br^- , the transfer from water to an aprotic solvent is endothermic in all cases listed, Table 1. These ligands favour solvents where their hydrogen bonding capacity can be utilized. For I^- , on the other hand, the trend is similar to that found for other ions, as might be expected for a species of little, if any, capacity to form hydrogen bonds. Contrary to this, the strongly hydrogen

TABLE 1. Hydration enthalpies, ΔH_h^0 , and enthalpies of transfer, $\Delta H_{tr}^0(W \rightarrow S)$, between water and solvents of different solvating and dielectric properties, for a representative selection of cations and anions (kJ mol^{-1}), at 25°C . Internally consistent crystallographic radii of these ions are also given (r_c/A).

Solvent \rightarrow		Water ^a	Meth ^b	DMSO ^c	AN ^d	Py ^e
$\epsilon \rightarrow$		78.5	32.6	46.4	36.0	12.3
$\mu/D \rightarrow$		1.85	1.70	3.96	3.92	2.23
	r_c^f	$-\Delta H_h^0$		$\Delta H_{tr}^0(W \rightarrow S)$		
H^+		1103		-25.5	56.1	
Na^+	1.17	417	-20.5	-27.7	-13.0	-30.3
Cs^+	1.83	289	-13.8	-30.0		
Et_4N^+	2.7	127	9.2	-2.8	-1.8	-3.4
Ph_4As^+	4.3	42	<u>-1.7</u>	<u>-11.9</u>	<u>-10.2</u>	<u>-22.8</u>
Ag^+	1.12	483	-20.9	-54.0	-41.2	-106
Ba^{2+}	1.50	1330	-59.2	-78.5	-8.5	
Zn^{2+}	0.75	2063	-45.6	-60	20.1	
Cd^{2+}	0.95	1830	-40.4	-67	8.2	
Hg^{2+}	1.02	1940		-76		-160
F^-	1.16	502	13.8			
Cl^-	1.64	366	8.4	18.8	20.5	27.9
Br^-	1.80	335	4.6	3.5	7.9	10.6
I^-	2.04	294	-2.1	-12.8	-7.0	-7.9
SCN^-			-3.4			-4.9
ClO_4^-	1.86	219	-2.5	-19.2	-16.2	
BPh_4^-	4.05	47	<u>-1.7</u>	<u>-11.9</u>	<u>-10.2</u>	<u>-22.8</u>

^aAs in Refs 2, 19, with values for Ba^{2+} (Ref. 20) corrected to the present value of $\Delta H_h^0(\text{H}^+)$ and ClO_4^- (Ref. 6) added.

^bRef 21.

^cAs in Ref 19, with the value for Ba^{2+} added (Ref. 22).

^dRef 23, except for H^+ (Ref. 24) and Na^+ , Ph_4As^+ , Ba^{2+} , Zn^{2+} , Cd^{2+} , BPh_4^- (Ref. 22).

^eRef 23.

^fAs in Ref 19, except that the value for Ba^{2+} has been added (Ref. 25) and the value of ClO_4^- revised (Ref. 6).

bonding F^- shows a fairly endothermic ΔH_{tr}^0 already between water and methanol. For this ion, hydrogen bonding is indeed essential if the solvate bonds should be strong enough to compete with the high lattice energies. Consequently, fluorides are generally slightly soluble in aprotic solvents. The conditions discussed are further illustrated by Fig. 1. The line referring to water is much steeper than the approximately parallel lines referring to aprotic solvents. Also here, methanol exhibits an intermediate behaviour.

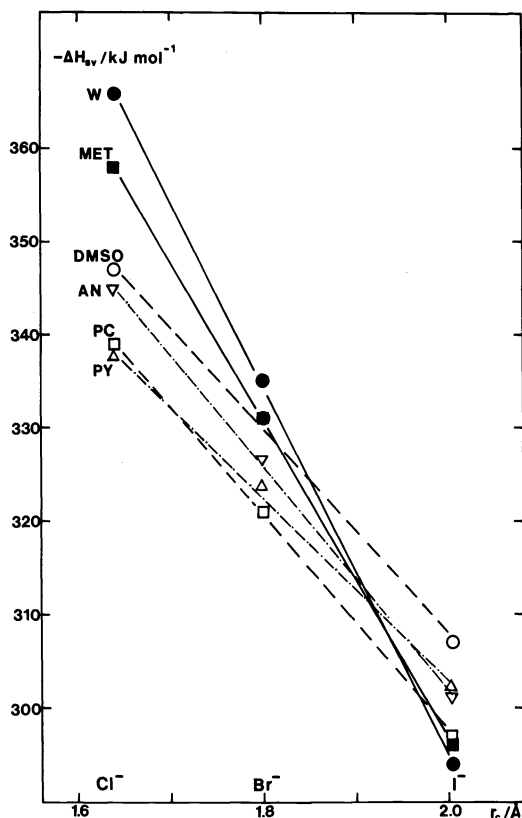


Fig. 1. Solvation enthalpies of the halide ions as a function of their ionic radii, in water (W), methanol (MET), dimethylsulfoxide (DMSO), propylene carbonate (PC), acetonitrile (AN) and pyridine (PY).

It is striking that the large differences in the macroscopic dielectric constant ϵ between the solvents seem to be of no decisive importance, even for ions where the interactions are mainly electrostatic, Table 1. This applies both to the halides and to cations such as Na^+ , Et_4N^+ and Ba^{2+} . Nor is the relation between ΔH_{SV}^0 and the dipole moment μ of the solvent molecule a simple one.

As pointed out above, compatible sets of ΔH_{h}^0 , ΔG_{h}^0 and ΔS_{h}^0 are seemingly not yet possible to calculate. In Table 2, only values of ΔG_{h}^0 are therefore listed. As stated above, they are not very different from ΔH_{h}^0 ; $T\Delta S_{\text{h}}^0$ is generally a small difference. Values of ΔG_{tr}^0 are known for methanol, DMSO and AN, but so far not for pyridine.

For the transfer reactions, the entropy terms are generally very important. In most cases they are negative, counteracting the reaction. The effect is often quite strong, especially for the divalent cations. Positive values are found for ions which are large and certainly weakly solvated, such as Et_4N^+ , Ph_4As^+ and BPh_4^- . Very significantly, a positive value is also found for the transfer of H^+ to AN, i.e. to a solvent where H^+ is very weakly solvated, as indicated by the very positive value of ΔH_{tr}^0 , Table 1. The transfer from water thus implies a net increase of order except for ions which are very disfavoured by the solvent they are entering. This is to be expected as water is certainly the most structured of the solvents, due to the strong intermolecular hydrogen bonds. Moving an ion out of a hydrate shell into a solvate shell in another solvent therefore means a relatively small decrease

TABLE 2. Hydration free energies, ΔG_h^0 , and free energies of transfer, ΔG_{tr}^0 , between water and various solvents for the ions listed in Table 1 (and also for Cu^+ and Cu^{2+}). The entropy contributions $T\Delta S_{tr}^0$ to the transfer are also given. Energies in kJ mol^{-1} ; temperature 25°C .

Solvent \rightarrow	Water ^a		Meth ^b		DMSO ^c		AN ^d	
	$-\Delta G_h^0$	ΔG_{tr}^0	$T\Delta S_{tr}^0$	ΔG_{tr}^0	$T\Delta S_{tr}^0$	ΔG_{tr}^0	$T\Delta S_{tr}^0$	
H^+	1088	10.8		-18.8	-6.7	46.2	9.9	
Na^+	409	8.6	-29.1	-13.7	-14.0	13.7	-26.7	
Cs^+	282	9.7	-23.5	-12.6	-17.4	5.1		
Et_4N^+		0.8	8.4	-12.6	9.8	-8.8	7.0	
Ph_4As^+		<u>-23.4</u>	<u>21.7</u>	<u>-37.1</u>	<u>25.2</u>	<u>-32.5</u>	<u>22.3</u>	
Cu^+	(568)			-40.9		-52.6		
Ag^+	477	7.4	-28.3	-33.7		-21.7	-19.5	
Ba^{2+}	1314	18.4	-77.6	-25.1	-53.4	57.3	-65.8	
Cu^{+2}	2083			-50.1		48.2		
Zn^{2+}	2024	27.6	-73.2	-46.9	-13	68.6	-47.5	
Cd^{2+}	1797	32.6	-73.0	-55.9	-11	42.3	-34.1	
Hg^{2+}				-67.9	-8			
F^-	436	16.3	-2.5					
Cl^-	319	12.6	-4.2	38.8	-20.0	42.2	-21.7	
Br^-	305	11.4	-6.8	25.7	-22.2	32.0	-24.1	
I^-	259	6.8	-8.9	9.1	-22.9	18.8	-25.8	
SCN^-		5.7	-9.1	8.6		12.6		
ClO_4^-		5.7	-8.2	-1.3	-17.9	4.6	-20.8	
BP_4^-		<u>-23.4</u>	<u>21.7</u>	<u>-37.1</u>	<u>25.2</u>	<u>-32.5</u>	<u>22.3</u>	

^a $\Delta G_h^0(\text{H}^+)$ chosen as described in text; other values from Ref 26, slightly revised so as to refer to the present value of $\Delta G_h^0(\text{H}^+)$.

^bRef 27, except for Et_4N^+ , F^- (Ref. 21), Ba^{2+} , Zn^{2+} , Cu^{2+} (Ref. 28).

^cRef 27, except for Et_4N^+ , ClO_4^- (Ref. 21), Ba^{2+} (Ref. 28) and Cu^+ , Cu^{2+} , Cd^{2+} , Hg^{2+} (Ref. 29).

^dRef 27, except for Et_4N^+ (Ref. 21), Cu^+ , Cu^{2+} (Ref. 30) and Ba^{2+} , Zn^{2+} , Cd^{2+} (Ref. 28). - For Ag^+ , Cl^- , Br^- , I^- , cf. also Ref 31.

of order in the aqueous solution but a large increase of order in the other solvent.

In methanol, the unfavourable entropy terms make almost all values of ΔG_{tr}^0 positive for cations, in spite of the often strongly negative values of ΔH_{tr}^0 . In DMSO, ΔG_{tr}^0 stays negative. For all the halides, and also for SCN^- , $\Delta G_{tr}^0 > 0$ in all the solvents discussed.

STANDARD POTENTIALS AND DISPROPORTIONATION CONSTANTS

Once the value of ΔG_{tr}^0 has been established for an ion M^{n+} , the difference ΔE^0 between the

standard potential $E^0(W)$ in water and $E^0(S)$ in the solvent S of the couple $M(s)/M^{n+}$ can be calculated according to

$$\Delta E^0 = E^0(W) - E^0(S) = -\Delta G_{tr}^0/nF \quad (10)$$

Hence $E^0(S)$ can immediately be found from the well-established values of $E^0(W)$.

In so far as they are known, all values of $E^0(S)$ are higher in methanol than in water. In DMSO, on the other hand, the values of $E^0(S)$ are throughout lower than in water. This means that all metals so far investigated are less noble in DMSO than in aqueous solution. In AN, the conditions are more complicated. While for most couples $E^0(S)$ is considerably higher than $E^0(W)$, striking exceptions occur for those involving M^+ ions of configuration d^{10} . Thus the value for $Cu(s)/Cu^+$ is lower than for any of the other solvents, being in fact < 0 . As $Cu(s)/Cu^{2+}$ follows the ordinary trend, this means that the couple Cu^+/Cu^{2+} becomes strongly oxidizing. The couple $Ag(s)/Ag^+$ shows an intermediate behaviour. The value of E^0 in AN is much lower than in water, but slightly higher than in DMSO. The trends described are very clearly illustrated in Fig. 2.

The changes of E^0 for the copper couples bring about drastic changes in the relative stabilities of the oxidation states involved. Thus the constant $K_D(Cu)$ of the disproportionation reaction $2Cu^+ \rightleftharpoons Cu^{2+} + Cu(s)$ which has a very high value in water is about unity in DMSO and becomes extremely small in AN, Table 4. At equilibrium, the ion Cu^+ , completely suppressed in water, becomes important in DMSO and is completely predominating in AN. The value of $K_D(Cu)$ has been determined also in pyridine, Table 4. The value is very low, though considerably higher than in AN. From the strongly exothermic value of ΔH_{tr}^0 between AN and pyridine, Table 5, one may conclude that this increase is certainly not due to a weaker solvation of Cu^+ in pyridine. The reason must rather be that Cu^{2+} is even more favoured by pyridine. Also in this solvent, however, Cu^+ predominates completely at equilibrium.

For mercury, the data so far available indicate that Hg^{2+} is stabilized in the same solvent order as Cu^+ , implying that the constant $K_D(Hg)$ of the disproportionation reaction $Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(l)$ increases in that order, Table 4. For both metals, therefore, the d^{10} configuration is stabilized. Compared to the changes in the copper system, those in the mercury system are quite small, however.

SOLVATION OF UNCHARGED SPECIES

For molecular compounds, solvation, or crystallization, does not at all imply as extensive a neutralization of charges as for ionic ones. Consequently, the heats involved are much smaller. Moreover, they may be determined by purely thermodynamic methods, without any resort to extrathermodynamic assumptions.

For the present discussion, comparisons between the solvation of neutral and charged complexes should be of immediate interest. This applies especially to series of complexes $ML_j(jq-n)^-$, formed consecutively between a metal ion M^{n+} and a ligand L^q- . Unfortunately, such data have so far hardly existed. Recently, however, they have been determined for a few systems as will be discussed below, Table 7.

Also comparisons between neutral complexes and the free metal ions and ligands involved in their formation are of great interest. For such purposes, a fairly extensive material is

TABLE 3. Standard potentials, mV, referred to the usual convention $E^0 = 0$ for the normal hydrogen electrode in aqueous solution. Temperature 25°C.

Electrode	Water ^a	Meth	DMSO	AN
H ₂ (g)/H ⁺	0	112	-195	479
Na/Na ⁺	-2710.9	-2622	-2853	-2569
Ag(s)/Ag ⁺	799.6	877	451	574
Cu(s)/Cu ⁺	518.2		94	-27
Cu(s)/Cu ²⁺	338.4		79	587
Cu ⁺ /Cu ²⁺	158.6		66	1201
Cu(Hg)/Cu ⁺	528.4		104	-17
Cu(Hg)/Cu ²⁺	343.5		84	592
Zn(s)/Zn ²⁺	-762.8	-620	-1006	-408
Cd(s)/Cd ²⁺	-402.6	-234	-692	-184
Cd(Hg)/Cd ²⁺	-352.1	-183	-641	-133
Hg(l)/Hg ²⁺	796.1		458 ^b	
Hg(l)/Hg ²⁺	851		499	
Hg ₂ ²⁺ /Hg ²⁺	905		539	

^aRef 3, except for the copper couples where the values of Ref 32 have been adopted.

^bFrom $\Delta G_{tr}^0 = -65$ kJ/mol, Ref 29.

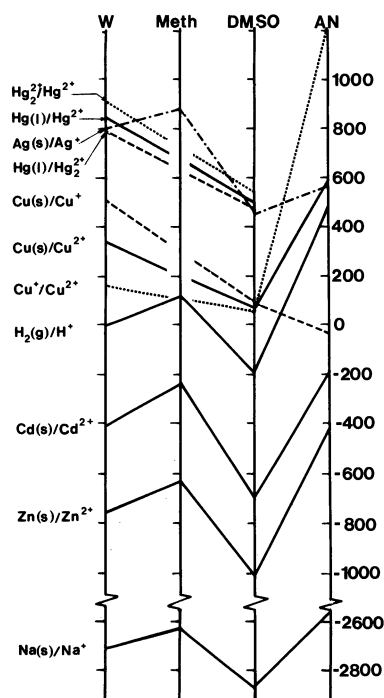


Fig. 2. Changes in standard potentials between different solvents.

TABLE 4. Disproportionation constants $K_D(\text{Cu})/M^{-1}$ and $K_D(\text{Hg})$ for the reactions $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu}(s)$ and $\text{Hg}_2^{2+} \rightleftharpoons \text{Hg}^{2+} + \text{Hg}(l)$ in various media, at 25°C.

	$\log K_D(\text{Cu})^a$	$\log K_D(\text{Hg})^b$	
Water	6.26	-1.94	I → 0
		-2.00	0.15 M NaClO ₄
		-2.24	1 M NaClO ₄
	5.95		5 M NaClO ₄
DMSO	0.18	-1.54	0.1 M NH ₄ ClO ₄ ^c
	0.64	-1.39	1 M NH ₄ ClO ₄
Py	-14	0.77	0.1 M Et ₄ NClO ₄
AN	-20.8		0.1 M Et ₄ NBF ₄

^aRefs 32, 34 (W, DMSO), 33 (Py), 30 (AN).

^bRefs 29 (W, DMSO), 33 (Py).

^cFor $K_D(\text{Hg})$ 0.15 M NH₄ClO₄.

available, especially pertaining to the halides of mercury(II), silver(I), and copper(I).

The mercury(II) halides exist as discrete neutral molecules HgX₂ not only in the solid and gaseous phases (Ref. 35) but also in many solvents, of widely differing properties (Refs. 36-39). For these halides, the functions ΔH_{sv}^0 and ΔG_{sv}^0 are especially easy to determine, by combining the quantities ΔH_{sub}^0 and ΔG_{sub}^0 , referring to the sublimation $\text{HgX}_2(s) \rightarrow \text{HgX}_2(g)$, with ΔH_s^0 and ΔG_s^0 , referring to the solution $\text{HgX}_2(s) \rightarrow \text{HgX}_2(sv)$:

$$\Delta G_{sv}^0 = \Delta G_s^0 - \Delta G_{sub}^0; \quad \Delta H_{sv}^0 = \Delta H_s^0 - \Delta H_{sub}^0 \quad (11,12)$$

Here ΔG_s^0 is directly connected with the solubility S according to

$$\Delta G_s^0 = -RT \ln S \quad (13)$$

For HgX₂, the solvation functions ΔH_{sv}^0 and ΔG_{sv}^0 can thus be obtained in a rather direct manner.

For the copper(I) and silver(I) halides, where precise experimental determinations of the sublimation functions are not possible, more complicated, but still purely thermodynamic calculations are necessary in order to find ΔH_{sv}^0 and ΔG_{sv}^0 .

So far, most determinations concern ΔH_{sv}^0 . The results so far found for the various halides are listed in Table 5. The technique used does not allow the determination of ΔH_{sv}^0 for AgX in benzene, water, DMSO or AN, and for CuX in benzene or water, on account of the low solubilities of these complexes in these solvents. In so far as they have been determined, the values for the free ions have also been entered for comparison. As to Cu⁺, a determination

TABLE 5. Heats of solvation of the mercury(II), silver(I) and copper(I) ions, and of their neutral halide complexes, in solvents of different solvating properties, in kJ mol^{-1} , 25°C .

	$-\Delta H_{\text{SV}}^{\circ}$						
	Benz ^a	W ^b	DMSO ^b	AN ^c	Py ^c	THT ^a	Bu ₃ P ^d
Hg ²⁺		1845	1921		2005		
HgCl ₂	72	69	104		138	119	249
HgBr ₂	68	64	101		135	124	248
HgI ₂	74	62	96		133	123	241
Ag ⁺		488	539	529	594		
AgCl					235		
AgBr					225		
AgI					219		
Cu ⁺			649	679	734		
CuCl			247	250	303		
CuBr			238	243	293		
CuI			228	232	288		

^aRef 41 ^bRefs 40 (Hg), 33 (Ag, Cu) ^cRef 33

^dDetermined by combination of $\Delta H_{\text{SV}}^{\circ}$ in benzene with ΔH° for the reaction $\text{HgX}_2 + 2\text{Bu}_3\text{P} \rightarrow \text{HgX}_2(\text{Bu}_3\text{P})_2$ in benzene (Ref. 42). Solution in liquid Bu₃P causes displacement of X, except for HgI₂.

of its $\Delta H_{\text{SV}}^{\circ}$ in water will hardly ever be possible, on account of the extensive disproportionation.

As expected, the values of $-\Delta H_{\text{SV}}^{\circ}$ are very much smaller for the neutral complexes than for the free ions. In a given solvent, they are moreover much smaller for HgX₂, where a stable linear coordination exists in the gaseous phase, than for AgX or CuX where the unsolvated complexes are coordinatively unsaturated.

For HgX₂, the values of $\Delta H_{\text{SV}}^{\circ}$ are about the same in benzene and water. As will be discussed below, the solvate bonds are much weaker in benzene, but this is fully compensated by the stronger interaction between the water molecules. In DMSO, the values are considerably higher, just as has been found for the free ion Hg²⁺ (Table 1), and evidently much for the same reason, viz. the stronger interaction between the solvent molecules in water. The present neutral complexes should act as soft acceptors, like their central ions. The further increase of $-\Delta H_{\text{SV}}^{\circ}$ between the oxygen donor DMSO and the softer nitrogen donor pyridine is therefore expected. The nitrogen of AN is a poorer donor so the values of $-\Delta H_{\text{SV}}^{\circ}$ are lower than for pyridine, for CuX only slightly higher than in DMSO. For HgX₂, the measurements have been extended to tetrahydrothiophene, THT, coordinating via sulfur, and to tributylphosphine, Bu₃P, coordinating via phosphorus. As sulfur generally behaves as a softer donor

atom than nitrogen, one would expect a further increase of $-\Delta H_{SV}^0$ between pyridine and THT. This is not so, however, even if the solvate bond is in fact stronger for THT, as will be shown below. For the very soft phosphorus donor, on the other hand, values of $-\Delta H_{SV}^0$ are measured which are by far the largest found so far.

As already pointed out, the value of ΔH_{SV}^0 depends not only on the strength of the solvate bond but also upon the strength of the forces acting between the solvent molecules. To discern between these factors, quantities measuring the solvate bond strength should be considered. Among these, the Raman stretching frequency of the M-X bond and the bond distance M-X have been determined for the mercury(II) halides in various solvents, and also compared with the values found in the gaseous phase.

When solvent molecules are coordinated to the central atom of the complex HgX_2 , the strength of the bond Hg-X decreases. Consequently, its stretching frequency decreases, and more so, the stronger the solvation. With modern technique, well resolved Raman spectra can be obtained even for fairly dilute solutions. Under favourable conditions, the concentrations may be as low as ≈ 0.05 M.

The weakening of the Hg-X bond further means that it becomes longer. The elongation relative to the gaseous phase can be found with fair precision by X-ray diffraction, provided that sufficiently concentrated solutions can be prepared (not much lower than 0.5 M). This restriction excludes the aqueous solutions, however.

The stretching frequencies decrease considerably between the gaseous phase and the solvents, Table 6. Among these, ν_1 decreases in the order benzene > AN > water > DMSO > pyridine > THT > Bu_3P which would thus be the order of increasing strength of the solvate bond. The result is completely confirmed by the bond distances. As far as these can, and have, been measured, they increase in exactly the same order as the stretching frequencies decrease. The solvation also means a bending of the HgX_2 molecules which are linear in the gaseous phase. As might be expected, the bending generally increases with the strength of the solvate bond. When the solvent is as good a donor as the ligand X, a tetrahedral configuration is reached, as in the solid $HgI_2(PPh_3)_2$. Finally, by very strong donors such as Bu_3P , the ligand X may even be displaced.

As already pointed out, the weak intermolecular forces in benzene completely compensate the stronger solvate bond in water, resulting in about the same values of ΔH_{SV}^0 for both solvents. Also in AN the solvate bonds are in fact weaker than in water. In pyridine they are, on the other hand, much stronger which is reflected in the large solvation enthalpies found in this solvent. In DMSO, the solvate bonds are, as might be expected, weaker than in pyridine. They are considerably stronger than in water, however. The strong increase of $-\Delta H_{SV}^0$ found between water and DMSO is therefore due not only to the stronger interactions between the solvent molecules in water but also to the stronger solvate bonds in DMSO.

In THT, the solvate bonds are, as expected, very strong. As the values of $-\Delta H_{SV}^0$ are not particularly high, the conclusion would be that the intermolecular forces are quite strong in this solvent. In Bu_3P , the strong solvate bonds indicated are compatible with the exceptionally high values of $-\Delta H_{SV}^0$.

Table 6. Mercury(II) halides in gaseous phase, and in solvents of increasing solvating strength. Symmetric stretching frequencies,^a ν_1/cm^{-1} , bond distances,^b $d(\text{Hg-X})/\text{\AA}$, and bond angles $\angle \text{X-Hg-X}$.

	Gas	Benz	W	DMSO	AN	Py	THT	Bu ₃ P
	ν_1/cm^{-1}							
HgCl ₂	360	339	320	303	325	283	d	
HgBr ₂	225	213	205	195	208	186		177
HgI ₂	156	c		145	c		137	133
	$d(\text{Hg-X})/\text{\AA}$							
HgCl ₂	2.29	c		2.35		2.38	d	
HgBr ₂	2.41			2.45		2.50		
HgI ₂	2.59			2.62		2.66	2.68	(2.73) ^e
	$\angle \text{X-Hg-X}$							
HgCl ₂	180	c				146	d	
HgBr ₂	180			165		145		
HgI ₂	180			159		145		(110.4) ^e

^aRefs 37 (Gas), 36 (Benz, W, AN), 38 (DMSO), 41.

^bRefs 43 (Gas), 38 (DMSO), 39 (Py), 44 (THT).

^cSolubility too low.

^dDisplacement of X by solvent.

^eIn the solid HgI₂(Ph₃P)₂, with a P atom of lower donor strength than in Bu₃P, Ref 45.

THE MERCURY(II) AND COPPER(I) HALIDE AND THIOCYANATE SYSTEMS IN VARIOUS SOLVENTS

Mercury(II). A fundamental difference between complex formation reactions in protic and aprotic solvents is, as has been stressed before (Refs. 2,19) that the entropy terms are generally much more favourable in the aprotic solvents. This is a consequence of the lower structural order typical for these solvents. The overall decrease of order resulting from the desolvation processes accompanying the complex formation will be much larger than in protic solvents of more well-ordered structures. All complexes whose formation involves extensive desolvation of species involved are therefore heavily entropy stabilized in aprotic solvents.

Another most characteristic difference between the two categories of solvents is that ligands apt to form hydrogen bonds are especially strongly solvated by protic solvents and consequently less available for complex formation. In aprotic solvents, therefore, complexes of such ligands become more stable relative to complexes of ligands forming no hydrogen bonds than they are in protic solvents.

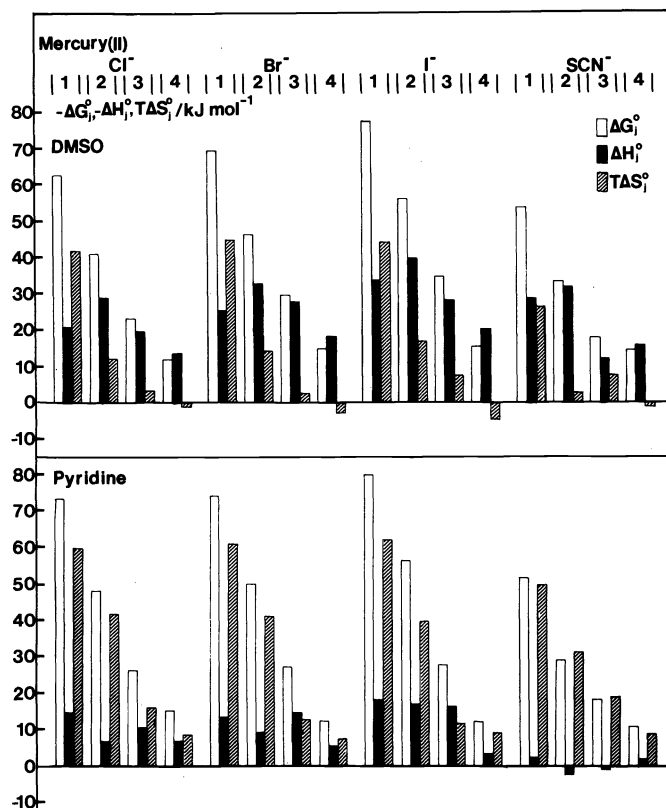


Fig. 3. Changes of free energy, enthalpy and entropy for the mercury(II) halide and thiocyanate systems in DMSO (Ref. 46) and pyridine (Ref. 33). Media: DMSO, 1 M NH_4ClO_4 ; pyridine, 0.1 Et_4NClO_4 ; 25°C.

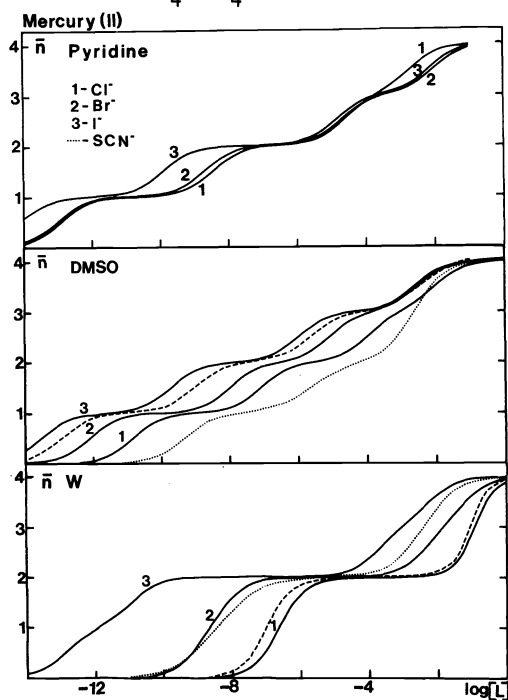


Fig. 4. Complex formation curves of the mercury(II) halide and thiocyanate systems in pyridine (Ref. 33), DMSO and water (Ref. 46). Media: pyridine, 0.1 M Et_4NClO_4 ; DMSO, 1 M NH_4ClO_4 (dashed curve bromide in 0.1 M NH_4ClO_4); water, 0.5 M (SCN^- 1 M) NaClO_4 (dashed curve chloride in 3 M NaClO_4); 25°C.

These points are both very clearly borne out by the formation of mercury(II) halide and thiocyanate complexes in various solvents. In water, the enthalpy terms predominate over the entropy terms even in the earlier steps of the complex formation, Refs. 19,46. For the softest ligands, I^- and SCN^- , the entropy terms are very small, or even negative. In aprotic solvents, the conditions are completely changed, Fig. 3. Already in DMSO, the values of $T\Delta S_1^0$ are not only positive but also quite large in all the systems. The strong desolvation that brings about this large entropy gain takes much energy, however, so ΔH_1^0 is fairly low, for all the halides $< T\Delta S_1^0$. In the next step, the desolvation is still fairly extensive but takes nevertheless much less energy. The enthalpy terms therefore becomes more favourable, $-\Delta H_2^0 > -\Delta H_1^0$. In the following steps, the desolvation is less important. The net entropy changes are ≈ 0 , and the reactions become enthalpy controlled. As the strength of the Hg-X bonds decreases as more ligands are coordinated, (Refs. 19,38), the value of ΔH_j^0 now decreases for each consecutive step, however. In pyridine, more strongly solvating than DMSO, the trends described become more strongly marked, Fig. 3. The entropy gains due to desolvation become very large while the net enthalpy changes all become small. The changes of ΔS_j^0 and ΔH_j^0 compensate each other extensively, so the resulting stabilities, represented by ΔG_j^0 , do not differ widely between the two solvents.

In water, the strong solvation of Cl^- relative to Br^- and, especially, I^- results in a marked increase of the complex stabilities in the order $Cl^- < Br^- < I^-$, Fig. 4. The changes in ΔH_{SV}^0 of the halide ions between water and aprotic solvents (Table 1 and Fig. 1) result in stability changes that makes this difference very much smaller. The values of ΔG_j^0 for a certain step do not differ very much between the various halides, especially not in pyridine, Fig. 3. This is even more strikingly demonstrated by the complex formation curves of Fig. 4. These also show that the consecutive steps are much better separated in the aprotic solvents.

Copper(I). While the complex formation of Cu^+ in water is much hampered by the extensive disproportionation, complete investigations of e.g. the halide and thiocyanate systems are feasible in aprotic solvents where Cu^+ is much more stable (Table 4). Results of such investigations in DMSO, AN and pyridine are reported in Figs. 5 and 6. The entropy terms are obviously even more preponderant than in the case of Hg^{2+} , and their relative importance increases from DMSO to the two solvents coordinating via nitrogen. The enthalpy terms are of subordinate importance in DMSO while in both AN and pyridine they are generally counteracting the complex formation, for many steps quite strongly. The b-sequence $Cl^- < Br^- < I^-$ found in water (Ref. 47) has been turned into a mixed sequence in DMSO, into a mild a-sequence $Cl^- > Br^- > I^-$ in pyridine, and into a quite marked a-sequence in AN, Fig. 6.

Transfer enthalpies of mercury(II) and copper(I) complexes. By combining the complex formation enthalpies reported (Figs. 3 and 5) with the solvation enthalpies of Tables 1 and 5, the enthalpies of transfer can be calculated for the complexes consecutively formed in the mercury(II) and the copper(I) halide systems. For both metals, values pertaining to the transfer DMSO \rightarrow pyridine can be found, for mercury(II) also values pertaining to water \rightarrow DMSO. For copper(I) the latter transfer is not accessible, on the other hand DMSO \rightarrow AN is, Table 7.

The transfers DMSO \rightarrow Py for $HgX_j^{(j-2)-}$ follow a simple energetic pattern. For each X^- entering, the values of ΔH_{tr}^0 decrease by ≈ 20 , or, by addition of the second X^- , by $\approx 30 \text{ kJ mol}^{-1}$. For the complexes HgX_4^{2-} , $\Delta H_{tr}^0 \approx 0$, indicating that these coordinatively saturated complexes have no stronger affinity to the softer pyridine than to the harder DMSO. Obviously, the complexes

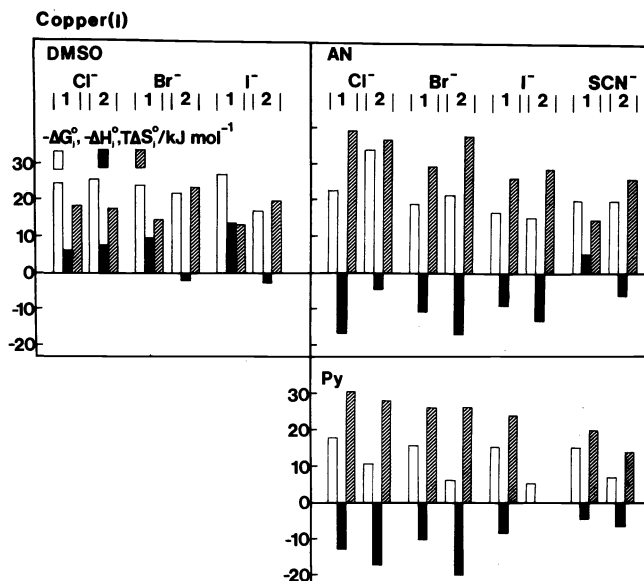


Fig. 5. Changes of free energy, enthalpy and entropy for the copper(I) halide and thiocyanate systems in DMSO (Ref. 32), AN (Ref. 30) and pyridine (Ref. 33).

Media: DMSO, 1 M NH_4ClO_4 ; AN, Py: 0.1 M Et_4NCIO_4 ; 25°C.

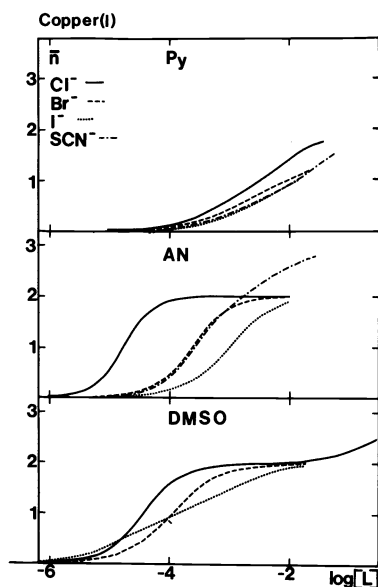


Fig. 6. Complex formation curves of the systems reported in Fig. 5.

CuX_2^- are not coordinatively saturated in this sense, in spite of the fact that a third halide ligand is only very reluctantly coordinated, if at all, Fig. 6.

The transfers of $\text{HgX}_j^{(j-2)-}$ between water and DMSO have a character very different from that found for the transfers DMSO \rightarrow Py. The values of ΔH_{tr}^0 do not decrease to ≈ 0 as HgX_4^{2-} is formed. Even in the chloride system where a monotonous decrease occurs, HgCl_4^{2-} has still $\Delta H_{\text{tr}}^0 = -20 \text{ kJ mol}^{-1}$. For bromide and iodide, a minimum is observed for ΔH_{tr}^0 at HgX_2 . The coordinatively saturated iodide complex HgI_4^{2-} has a very exothermic value of $\Delta H_{\text{tr}}^0 = -63 \text{ kJ mol}^{-1}$. Obviously, the complexes HgX_4^{2-} (and especially HgI_4^{2-}) fit badly into the

Table 7. Enthalpies of transfer between solvents stated, kJ mol^{-1} , for mercury(II) and copper(I) halide complexes, at 25°C .

X \rightarrow	W \rightarrow DMSO ^a			DMSO \rightarrow Py ^c		
	Cl	Br	I	Cl	Br	I
HgX ⁺	-52	-55	-47	-69	-65	-64
HgX ₂	-33	-38	-32	-38	-35	-37
HgX ₃ ⁻	-25	-49		-19	-15	-21
HgX ₄ ²⁻	-20	-48	-63	-4	5	1
X ⁻	18.8	3.5	-12.8			
	DMSO \rightarrow AN ^b					
CuX	-3.1	-4.6	-4.3	-56.3	-55.3	-59.9
CuX ₂ ⁻	9	14	16	-22		
X ⁻	1.7	4.4	5.8	9.1	7.0	4.7

$${}^a\Delta H_{\text{tr}}^{\text{O}}(\text{Hg}^{2+}) = -76 \text{ kJ mol}^{-1} \quad {}^b\Delta H_{\text{tr}}^{\text{O}}(\text{Cu}^{+}) = -30 \text{ kJ mol}^{-1}$$

$${}^c\Delta H_{\text{tr}}^{\text{O}}(\text{Hg}^{2+}) = -84 \text{ kJ mol}^{-1}; \Delta H_{\text{tr}}^{\text{O}}(\text{Cu}^{+}) = -85 \text{ kJ mol}^{-1}$$

water structure while they are more acceptable in DMSO. To a lesser extent, this applies also to the complexes HgX_3^- . The transfers of such complexes involves a restoration of the water structure which is reflected in values of $\Delta H_{\text{tr}}^{\text{O}}$ which are much more exothermic than would otherwise be the case.

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REFERENCES

1. M. Salomon, *J. Phys. Chem.* **74**, 2519-2524 (1970).
2. S. Ahrland, *The Chemistry of Nonaqueous Solvents* (J.J. Lagowski, ed.) Vol V A p. 1, Academic Press, New York, 1978.
3. *Handbook of Chemistry and Physics* 61 ed., CRC Press, 1980.
4. C.M. Criss and M. Salomon, *Physical Chemistry of Organic Solvent Systems* (A.K. Covington and T. Dickinson, eds.) p. 253, Plenum Press, London, 1973.
5. D.F.C. Morris, *Structure and Bonding* **4**, 63-82 (1968), **6**, 157-159 (1969).
6. H.D.B. Jenkins and K.F. Pratt, *J. Chem. Soc. Faraday* **74**, 968-981 (1978).
7. H.D.B. Jenkins, K.F. Pratt and T.C. Waddington, *J. Inorg. Nucl. Chem.* **39**, 213-220 (1977).
8. H.F. Halliwell and S.C. Nyburg, *Trans. Faraday Soc.* **59**, 1126-1140 (1963).
9. K. Fajans, *Verh. deutsche physik. Ges.* **21**, 709 (1919) (as quoted in Refs. 5 and 8).
10. H.D.B. Jenkins and D.F.C. Morris *Mol. Phys.* **33**, 663-669 (1977).
11. B.S. Gourary and F.J. Adrian, *Solid State Physics* **10**, 127-247 (1960).
12. J.E.B. Randles, *Trans. Faraday Soc.* **52**, 1573-1581 (1956).
13. M.J. Blandamer and M.C.R. Symons, *J. Phys. Chem.* **67**, 1304-1306 (1963).

14. G. Kortüm, Treatise on Electrochemistry, 2. ed., p. 123, Elsevier, Amsterdam, 1965.
15. R. Alexander, A.J. Parker, J.H. Sharp and W.E. Waghorne, J. Am. Chem. Soc. **94**, 1148-1158 (1972).
16. B.G. Cox and A.J. Parker, J. Am. Chem. Soc. **95**, 402-407 (1973).
17. E. Grunwald, G. Baughman and G. Kohnstam, J. Am. Chem. Soc. **82**, 5801-5811 (1960).
18. E.M. Arnett and D.R. McKelvey, J. Am. Chem. Soc. **88**, 2598-2599 (1966).
19. S. Ahrland, Pure Appl. Chem. **51**, 2019-2039 (1979).
20. R.M. Noyes, J. Am. Chem. Soc. **84**, 513-522 (1962).
21. B.G. Cox, G.R. Hedwig, A.J. Parker and D.W. Watts, Austr. J. Chem. **27**, 477-501 (1974).
22. G.R. Hedwig and A.J. Parker, J. Am. Chem. Soc. **96**, 6589-6593 (1974).
23. S. Ahrland, S. Ishiguro and R. Portanova, to be published.
24. R. Domain, M. Rinfret and R.L. Benoit, Can. J. Chem. **54**, 2101-2109 (1976).
25. R.D. Shannon and C.T. Prewitt, Acta Cryst. B **25**, 925-946 (1969).
26. D.R. Rosseinsky, Chem. Rev. **65**, 467-490 (1965).
27. I.M. Kolthoff and M.K. Chantooni, Jr., J. Phys. Chem. **76**, 2024-2034 (1972).
28. G.R. Hedwig, D.A. Owensby and A.J. Parker, J. Am. Chem. Soc. **97**, 3888-3894 (1975).
29. S. Ahrland and I. Persson, Acta Chem. Scand. A **34**, 645-650 (1980).
30. S. Ahrland, K. Nilsson and B. Tagesson, to be published.
31. M.K. Chantooni and I.M. Kolthoff, J. Phys. Chem. **77**, 1-7 (1973).
32. S. Ahrland, P. Bläuenstein, B. Tagesson and D. Tuhtar, Acta Chem. Scand. A **34**, 265-272 (1980).
33. S. Ahrland, S. Ishiguro, A. Marton and I. Persson, to be published.
34. S. Ahrland and J. Rawsthorne, Acta Chem. Scand. **24**, 157-172 (1970).
35. A.F. Wells, Structural Inorganic Chemistry, 4th ed., Clarendon Press, Oxford, 1975.
36. J.H. Smith and T.B. Brill, Inorg. Chem. Acta **18**, 225-229 (1976).
37. K. Sone, M. Aritaki, K. Hiraoka and Y. Fukuda, Bull. Chem. Soc. Japan **49**, 2015-2016 (1976).
38. M. Sandström, Acta Chem. Scand. A **32**, 627-641 (1978).
39. M. Sandström, I. Persson and A. Mosset, to be published.
40. S. Ahrland, L. Kullberg and R. Portanova, Acta Chem. Scand. A **32**, 251-258 (1978).
41. S. Ahrland and I. Persson, to be published.
42. Y. Farhangi and D.P. Graddon, Austr. J. Chem. **26**, 983-989 (1973).
43. P.A. Akishin, V.P. Spiridonov and A.N. Khodchenkov, Zhur. fiz. Khim. **33**, 20 (1959) (as quoted in Tables of Interatomic Distances and Configurations in Molecules and Ions, Suppl. 1956-1959, Special Publication No 18, Chemical Society, London, 1965).
44. I. Persson and M. Sandström, to be published.
45. L. Fälth, Chem. Scripta **9**, 71-73 (1976).
46. S. Ahrland and I. Persson, Acta Chem. Scand. A **35**, 49-60 (1981).
47. S. Ahrland and B. Tagesson, Acta Chem. Scand. A **31**, 615-624 (1977).

ERRATA

Volume, Issue and Year	Page no. and location	Correction				
49, 5 (1977)	671-673	In the "Recommended Reference Materials for the Realization of Physicochemical Properties - Section: Absorbance and Wavelength" infrared absorption bands were suggested as reference for wavenumber calibration. More recent revised data have been published by IUPAC in a book entitled <u>Tables of Wavenumbers for the Calibration of Infrared Spectrometers</u> compiled by A.R.H. COLE (Pergamon Press, Oxford, 1977). Wavenumbers appearing in sections II/8, II/9, II/10 and II/11 of Recommendations on Reference Materials should be replaced by the values published by COLE.				
54, 1 (1982)	208, Abstract, line 2	<u>for</u> 'dexcy' <u>read</u> 'deoxy'				
	209, column 2, 3rd name	<u>for</u> 1,1,2,2-Tetrahydro <u>read</u> 1,1,2,2-Tetradehydro				
	210, column 1, 4th name	<u>for</u> 6,7,7,8-Tetrahydro <u>read</u> 6,7,7,8-Tetradehydro				
	214, column 2, structure for Cladinose	<table style="width: 100%; border: none;"> <tr> <td style="text-align: center; vertical-align: middle;"><u>for</u></td> <td style="text-align: center; vertical-align: middle;"> $\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$ </td> <td style="text-align: center; vertical-align: middle;"><u>read</u></td> <td style="text-align: center; vertical-align: middle;"> $\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$ </td> </tr> </table>	<u>for</u>	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$	<u>read</u>	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$
<u>for</u>	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$	<u>read</u>	$\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$			
54, 3 (1982)	681, Abstract, line 3	<u>for</u> TiO ₂ 1892±30 <u>read</u> TiO ₂ 1843±15 (in air) <u>for</u> ZnO ₂ 2710±25 <u>read</u> ZnO ₂ 2710±35				
54, 8 (1982)	1455, Table 1 (i) column -ΔH _h ^o for Hg ²⁺	<u>for</u> 1940 <u>read</u> 1845				
	(ii) footnote a to Table 1	<u>add</u> ΔH _h ^o of Hg ²⁺ has been misprinted in Ref. 19				
	1457, Table 2 column 1, last item	<u>for</u> BP ₄ ⁻ <u>read</u> BPh ₄ ⁻				
	1459, Table 3 column 1, 12th item	<u>for</u> Hg(l)/Hg ²⁺ <u>read</u> Hg(l)/Hg ₂ ²⁺				
54, 10 (1982)	1859, Eq.(14)	correct version is as follows:				

