

Solvation and complex formation in strongly solvating solvents

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Abstract - Earlier proposed concepts for estimation of donor properties of solvents are briefly discussed and a comparison between some of the concepts is made for 53 solvents. The kind of solvents which can be regarded as strongly solvating are proposed for the further discussion. A comparison is also made of the solvation of typically soft and hard acceptors for a number of solvents. The solvation of univalent and some divalent ions in methanol, acetonitrile, dimethylsulfoxide, pyridine, tetrahydrothiophene and liquid ammonia have been studied by means of transfer thermodynamics from water. Oxygen donor solvents and nitriles solvate in general hard acceptors well and soft ones poorly. Amines, sulfur and phosphorous donor solvents solvate soft acceptors strongly while on the other hand they solvate hard acceptors poorly. The stability of a complex is in general inversely proportional to the solvation of the metal ion or complex and the ligand. The complex formation will therefore be weaker in solvents where the acceptor is strongly solvated. When the dielectric constant is lower than 10 the tendency to neutralization of charge through ion pair formation becomes important and the stabilities of neutral complexes will increase dramatically.

CLASSIFICATION OF SOLVENTS

Several authors have proposed concepts for a general systematizing of the donor properties of solvents. It is, however, doubtful if such a general systematizing is possible. It is plausible that several donor scales for estimation of solvation ability of solvents are necessary because of the very different acceptor properties of metal ions and complexes.

The first concept was originated by Gutman et al. who introduced the donor numbers, D_N , for the coordinating property of a solvent (ref. 1-4). The donor number is defined as the $-\Delta H^\circ$ value, in kcal mol⁻¹, of the formation of the 1:1 adduct between the donor solvent and the chosen reference electron acceptor antimony(V) chloride in dilute 1,2-dichloroethane solution. Antimony(V) chloride is regarded as an acceptor on the border-line between hard and soft. In recent years alternative concepts to the donor numbers have been proposed (ref. 5-12) in order to simplify the measurements and to extend the number of solvents. The donor number can not be determined for all solvents by the original procedure since other chemical reactions take place beside the adduct formation (ref. 5,6,11,13). No donor numbers have been reported for sulfur and phosphorous donor solvents. These will certainly react immediately with antimony(V) chloride and direct measurements of donor numbers are therefore not possible.

Indirect measurements of donor numbers are not always reliable (ref. 11) and such will not be further discussed in this paper. It has therefore been important to find a simple approach from which it is possible to estimate the donor properties of especially soft donor solvents. Mercury in mercuric bromide is regarded as a fairly soft electron acceptor and has been chosen as probe in the concept donor strength. Donor strength, D_S , is defined as the difference between the symmetric Hg-Br stretching frequencies of the neutral mercuric bromide complex in gaseous phase and in a saturated solution of the studied solvent (ref. 6). Mercuric bromide is soluble and stable in all solvents studied except in liquid ammonia where it dissociates (ref. 14) and in isocyanates where it decomposes (ref. 6,15).

Maria and Gal have used an approach very similar to the definition of the donor numbers (ref. 5). They have used boron trifluoride as acceptor instead of antimony(V) chloride and dichloromethane as solvent instead of 1,2-dichloroethane in order to reduce the number of side reactions. The $-\Delta H_{BF_3}$ values are given in kJ mol⁻¹. There is of course a very good correlation between the D_N and $-\Delta H_{BF_3}$ scales.

Soukup and Schmid have proposed spectroscopic studies in the visible region of the copper(II) N,N,N',N'-tetramethylethylenediamine acetylacetonate complex, Cu(tmen)(acac)⁺, dissolved in the pure solvents. The donor property of the solvent is determined by the λ_{\max} of this complex, Cu- λ_{\max} (ref. 8). A very good agreement between Cu- λ_{\max} values and the donor numbers is obtained. Phosphines reduce copper(II) in the Cu(tmen)(acac)⁺ complex to copper(I), which is the reason why this approach can not be applied for these solvents (ref. 16).

The D_s , D_N , $-\Delta H_{BF_3}$ and Cu- λ_{\max} values for 53 solvents are summarized in Table 1. The D_s values are plotted against the D_N , $-\Delta H_{BF_3}$ and Cu- λ_{\max} values in Fig. 1. As can be seen in these figures a very good correlation between the D_s values and the D_N and Cu- λ_{\max} values except for sulfur donor solvents are found. The three solvents out of line in Fig. 1c are aniline and the sulfur donors tetrahydrothiophene and hexamethylthiophosphoric triamide. The sulfur donors N,N-dimethylthioformamide and N-methylthiopyrrolidone(2) could not be put within the limits of the figure.

TABLE 1. A comparison of the relative donor scales donor strength^a, D_s , donor numbers^b, D_N , Maria and Gals $-\Delta H_{BF_3}$ values^c and Soukup and Schmid's Cu- λ_{\max} values^d for Cu(tmen)(acac)(soln)[†].

| Solvent | D_s | D_N | $-\Delta H_{BF_3}$ | Cu- λ_{\max} |
|---|-------------------|-------------------|--------------------|----------------------|
| Dichloromethane | 7 | | | 550* |
| 1,2-Dichloroethane | 8 | 0 | 10.0 | 538* |
| Benzene | 9 | 0.1 | | NS |
| Nitromethane | 9 | 2.7 | 37.6 | 532 |
| Anisole (Methylphenylether) | 9 | 7.9 ^g | | 573* |
| Furane | 10 | 4.3 | | 578* |
| Nitrobenzene | 10 | 4.4 | 35.8 | 533 |
| Benzonitrile | 12 | 11.9 | 55.4 | 572* |
| Methyl acetate | 12 | 16.5 | 72.8 | 570* |
| Propylene carbonate | 12 | 15.1 | 64.2 | 554 |
| Diethyl ether | 12 | 19.2 | 78.8 | NS |
| Acetic acid | 14 | 10.5 ^g | | |
| Diphenyl sulfide | 14 | | | NS |
| Butyrolactone | 14 | | | 568* |
| Acetonitrile | 14 | 14.1 | 60.4 | 575* |
| Tetramethylenesulfon (TMSO ₂) | 15 | | | 562* |
| Acetone | 15 | 17.0 | 76.0 | 571 |
| Tetrahydrofurane (THF) | 15 | 20.0 | 90.4 | 579 |
| Methanol | 16 | 19 | | 589* |
| Water | 17 | 18.0 | | 591* |
| Formaldehyde | 18 | | | |
| Dioxane | 18 | 14.8 | 74.1 | 575* |
| 1-Butanol | 19 | 24.0 ^g | | 589* |
| 1,2-Ethanediol | 20 | | | 579* |
| Ethanol | 20 | 20 | | 589* |
| Formamide | 21 | | | 594* |
| Trimethylphosphate | 23 | | | 596* |
| Tri-n-butylphosphate | 23 | 23.7 | | 599 |
| N-Methylformamide | 23 | | | 604* |
| Triethylamine | 24 ^e | 31.7 ^h | | NS |
| Tetramethylurea | 24 | 31 | 108.6 | 596□ |
| N,N-Dimethylformamide | 24 | 26.6 | 110.5 | 603 |
| N,N-Dimethylacetamide | 25 | 27.8 | 112.1 | 608□ |
| Dimethyl sulfoxide (DMSO) | 27 | 29.8 | 105.3 | 613 |
| N-Methylpyrrolidone(2) | 27 | | | |
| Buthanthiol | 28 | | | NS |
| Tetramethyl sulfoxide (TMSO) | 29 | | | 613* |
| Hexamethylphosphoric triamide | 34 | 38.8 | 117.5 | 633□ |
| Aniline | 34 | 33.3 ^g | | 570* |
| Pyridine | 39 | 33.1 | 128.1 | 638 |
| Di-n-butylsulfide | 41 | | | NS |
| Tetrahydrothiophene (THT) | 43 | | | 606* |
| Cyclohexylisocyanate | 45 ^e | | | NS |
| Di-n-butylamine | 46 | | | NS |
| Piperidine | 49 | 51 ⁱ | | 692* |
| N,N-Dimethylthioformamide | 52 | | | 413□ |
| Hexamethylthiophosphoric triamide | 54 | | | 581* |
| Hexylamine | 55 | 57 ⁱ | | 673* |
| N-Methylthiopyrrolidone(2) | 56 | | | 763□ |
| Tributylphosphite | 59 | | | NS |
| Triphenylphosphine | 67 ^{e,f} | | | NS |
| Liquid ammonia | 69 ^e | 59 ⁱ | | |
| Tributylphosphine | 76 | | | RT1 |

^aRef. 6. ^bRef. 4. ^cRef. 5. ^dRef. 8. G. Gritzner, personal communication, □, and this work. * Extrapolated value. ^fValues from Raman studies on solid compounds. ^gValues calculated from p^* or B values using the following equation $D_N = -6.36 + 0.19B^*$, see ref. 7. ^hRef. 11. ⁱRef. 13. NS Cu(tmen)(acac)ClO₄ and Cu(tmen)(acac)BPh₄ are not soluble. RT1 The Cu(II) complex is reduced to Cu(I) by the solvent.

The other proposed donor concepts (refs. 9-11) show no correlations with those presented here (ref. 16).

Based on the D_s values, the solvents dichloromethane-nitrobenzene in Table 1 can be regarded as non-coordinating, solvating only through London forces. Solvents in the range benzonitrile-formamide are regarded as hard donors solvating mainly through electrostatic forces. The solvents pyridine-tributylphosphine are regarded as soft donors forming covalent bonds to soft electron acceptors. Solvents in the range trimethylphosphate-hexamethylphosphoric triamide are donors on the border-line between hard and soft.

Soft electron acceptors are most strongly solvated by solvents with strong electron donor properties, while the hard acceptors are mainly solvated through the electrostatic forces formed between the acceptor and the solvent molecules surrounding it. This means that the sequence of solvents for solvation of soft and hard acceptors will differ very much. In order to get a basis for the estimation of solvation of hard acceptors the concept hard donor strength, \underline{HD}_s , has been introduced (ref. 6). The \underline{HD}_s is defined as Gibbs free energy of transfer of the sodium ion from 1,2-dichloroethane. There is no correlation between the D_s and the \underline{HD}_s scales, as can be seen in Table 2 and Fig. 2.

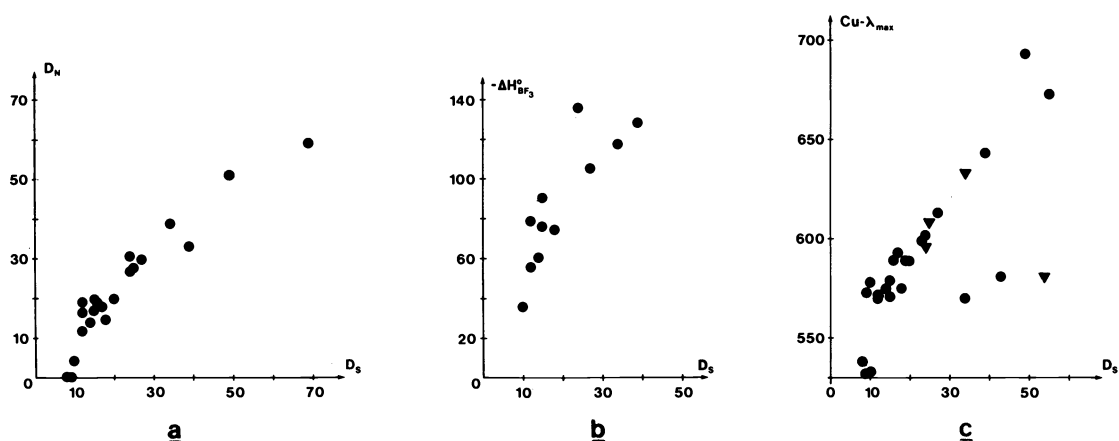


Fig. 1. The donor numbers, Maria and Gals $-\Delta H_{BF_3}$ values and Soukup and Schmid's $Cu-\lambda_{max}$ values are plotted against the donor strength in a, b and c, respectively. ∇ in lc denotes data from Gritzner, see references to Table 1.

TABLE 2. The hard donor strength, \underline{HD}_s , the donor strength, D_s , values for some solvents at 25°C.

| Solvent | \underline{HD}_s | D_s |
|--------------------------------|--------------------|-------|
| N,N-Dimethylthioformamide | -14 | 52 |
| Nitrobenzene | -9 | 10 |
| Tetrahydrothiophene | -4.4 | 43 |
| Nitromethane | -1 | 9 |
| Benzonitrile ^b | -0.1 | 12 |
| 1,2-Dichloroethane | 0.0 ^a | 8 |
| Propanol | 7.9 | 19 |
| Pyridine ^b | 8.7 | 39 |
| Acetonitrile ^b | 9.9 | 14 |
| Propylene carbonate | 10.1 | 12 |
| 1-Butanol ^b | 11.0 | 19 |
| Methylacetate ^b | 13.3 | 12 |
| Ethanol | 14 | 20 |
| Metanol ^b | 16.7 | 16 |
| Acetone | 20.7 | 15 |
| Water | 24.7 | 17 |
| Tetrahydrofuran | 34 | 15 |
| N,N-Dimethylformamide | 34.3 | 24 |
| N,N-Dimethylacetamide | 36.8 | 25 |
| Dimethylsulfoxide ^b | 37.8 | 27 |
| Liquid ammonia | 38 | 69 |
| N-Methylpyrrolidone | 40 | 56 |

^a By definition

^b Ref. 17, remaining data from ref. 18.

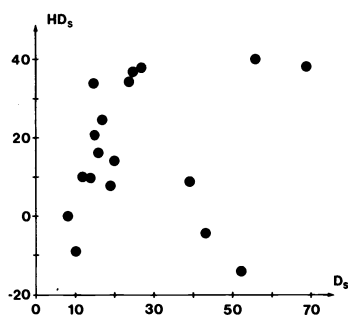


Fig. 2. The hard donor strength \underline{HD}_s is plotted against the donor strength D_s of some solvents. The correlation is 0.23; thus there is no correlation between the \underline{HD}_s and D_s scales.

SOLVATION OF SINGLE IONS

The Gibbs free energies and heats of solvation of ionic compounds can easily be determined by means of solubility product (ref. 19) and potentiometric, and calorimetric measurements, respectively. An extrathermodynamic assumption must be applied in order to calculate the contributions from the single ions. A large number of such assumptions have been proposed during the years (ref. 20). The assumption originated by Grunwald (ref. 21) and later adjusted by Arnett and McKelvey (ref. 22) seems to be very close to the truth (ref. 23). This assumption implies that the two large univalent ions Ph_4As^+ and BPh_4^- are equally solvated, thus $\Delta G_{\text{tr}}^{\circ}(\text{Ph}_4\text{As}^+) = \Delta G_{\text{tr}}^{\circ}(\text{BPh}_4^-)$, $\Delta H_{\text{tr}}^{\circ}(\text{Ph}_4\text{As}^+) = \Delta H_{\text{tr}}^{\circ}(\text{BPh}_4^-)$, $\Delta S_{\text{tr}}^{\circ}(\text{Ph}_4\text{As}^+) = \Delta S_{\text{tr}}^{\circ}(\text{BPh}_4^-)$, for all pair of solvents.

The standard electrode potentials in non-aqueous solvents can be calculated from the standard electrode potentials in water and Gibbs free energies of transfer according to the relationship $\Delta G_{\text{tr}}^{\circ} = nF(E_{\text{sol}}^{\circ} - E_{\text{aq}}^{\circ})$; $E_{\text{sol}}^{\circ} = \frac{\Delta G_{\text{tr}}^{\circ}}{nF} + E_{\text{aq}}^{\circ}$.

Standard electrode potentials for some couples containing univalent or divalent ions in water, methanol, acetonitrile, DMSO, pyridine, tetrahydrothiophene and liquid ammonia are shown in Table 3 and Fig. 3. With increasing solvation of the oxidized species in a couple the standard electrode potential will decrease and consequently with increasing solvation of the

TABLE 3. Standard electrode potentials in Volts vs. $E^{\circ}(\text{H}_2(\text{g})/\text{H}^+(\text{aq}))$ in water (W), methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py), tetrahydrothiophene (THT) and liquid ammonia (NH_3) at 25°C, ref. 17.

| | W | M | AN | DMSO | Py | THT | NH_3 |
|--|-------|-------|-------|-------|-------|-------|---------------|
| $\text{H}_2(\text{g})/\text{H}^+$ | 0.00 | +0.12 | +0.48 | -0.20 | -0.18 | | -1.00 |
| $\text{Na}(\text{s})/\text{Na}^+$ | -2.71 | -2.61 | -2.56 | -2.85 | -2.54 | -2.41 | -2.89 |
| $\text{K}(\text{s})/\text{K}^+$ | -2.92 | -2.82 | -2.83 | -3.06 | -2.86 | | -3.04 |
| $\text{Rb}(\text{s})/\text{Rb}^+$ | -2.93 | -2.83 | -2.86 | -3.04 | -2.69 | | -3.06 |
| $\text{Cs}(\text{s})/\text{Cs}^+$ | -2.92 | -2.83 | -2.87 | -3.01 | -2.61 | | -3.08 |
| $\text{Cu}(\text{s})/\text{Cu}^+$ | +0.52 | | -0.02 | +0.09 | -0.33 | +0.21 | -0.64 |
| $\text{Cu}(\text{s})/\text{Cu}^{2+}$ | +0.34 | | +0.60 | +0.08 | +0.08 | | -0.60 |
| $\text{Cu}^+/\text{Cu}^{2+}$ | +0.16 | | +1.21 | +0.07 | +0.49 | | -0.56 |
| $\text{Ag}(\text{s})/\text{Ag}^+$ | +0.80 | +0.87 | +0.58 | +0.45 | +0.25 | +0.27 | -0.24 |
| $\text{Au}(\text{s})/\text{Au}^+$ | +1.83 | | +1.51 | +1.21 | +0.80 | | |
| $\text{Zn}(\text{s})/\text{Zn}^{2+}$ | -0.77 | -0.62 | -0.41 | -1.01 | | | -1.54 |
| $\text{Cd}(\text{s})/\text{Cd}^{2+}$ | -0.41 | -0.24 | -0.19 | -0.69 | | | -1.20 |
| $\text{Hg}(\text{s})/\text{Hg}_2^{2+}$ | +0.80 | | | +0.46 | +0.46 | | |
| $\text{Hg}(\text{s})/\text{Hg}^{2+}$ | +0.85 | | | +0.50 | +0.44 | | -0.33 |
| $\text{Hg}^{2+}/\text{Hg}^{2+}$ | +0.91 | | | +0.54 | +0.41 | | |
| $\text{Tl}(\text{s})/\text{Tl}^+$ | -0.34 | -0.29 | -0.23 | -0.56 | -0.35 | -0.25 | |
| $\text{Cl}^-/\text{Cl}_2(\text{g})$ | +1.36 | +1.22 | +0.93 | +0.95 | +1.02 | +0.84 | +0.91 |
| $\text{Br}^-/\text{Br}_2(\text{l})$ | +1.07 | +0.95 | +0.74 | +0.80 | +0.86 | +0.80 | +0.73 |
| $\text{I}^-/\text{I}_2(\text{s})$ | +0.54 | +0.46 | +0.34 | +0.45 | +0.34 | | +0.28 |

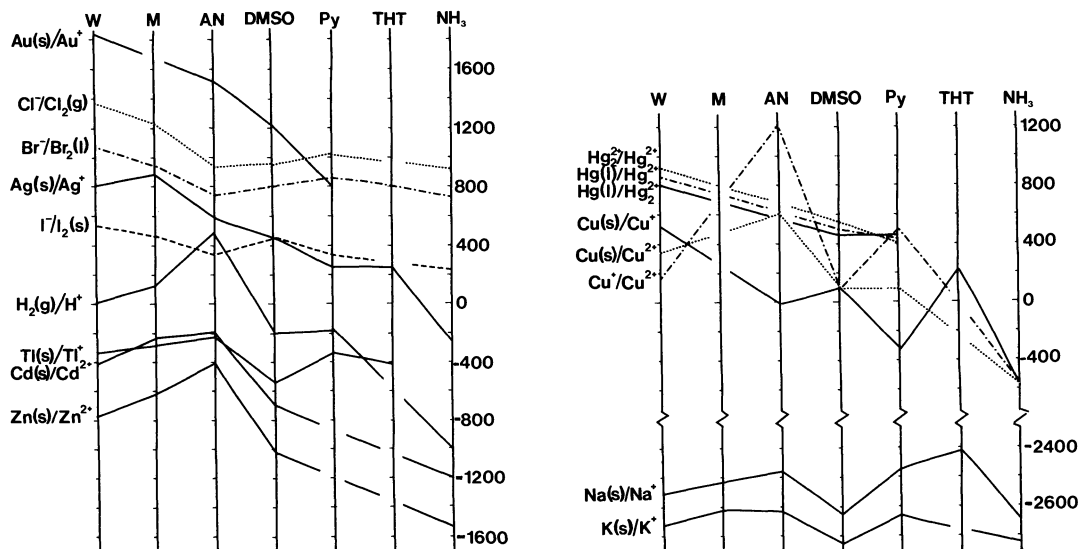


Fig. 3. Changes in standard electrode potentials between water (W), methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py), tetrahydrothiophene (THT) and liquid ammonia (NH_3).

reduced species in a couple the standard electrode potential will increase. The transfer thermodynamics of some univalent ions from water to methanol, acetonitrile, dimethylsulfoxide, pyridine and tetrahydrothiophene are shown in Fig. 4.

Cations

The standard electrode potentials of metal/metal ion couples are more positive in methanol than in water. This shows that the solvation of cations is in general weaker in methanol than in water. The donor properties of methanol are of the same order of magnitude as water, but water develops stronger electrostatic interactions, see Table 2. In spite of positive free energies of transfer to methanol the heats of transfer are negative and consequently the entropies of transfer are negative. The negative entropies of transfer indicate that the overall order in the solutions increases on the transfer of a metal ion from an aqueous to a methanol solution. When an ion is hydrated in an aqueous solution, the order of the water molecules coordinating to the ion increases slightly, but at the same time the very well-ordered aqueous bulk structure is partly disrupted since water molecules have left for the hydration and the hydrated ions do not fit into it. In methanol, a larger increase in order around the ions is obtained, because the methanol bulk structure is not at all as well-ordered as the aqueous one. At the same time the loss in order because of disruption of the bulk structure is thus much less. The negative heats of transfer are mainly due to more

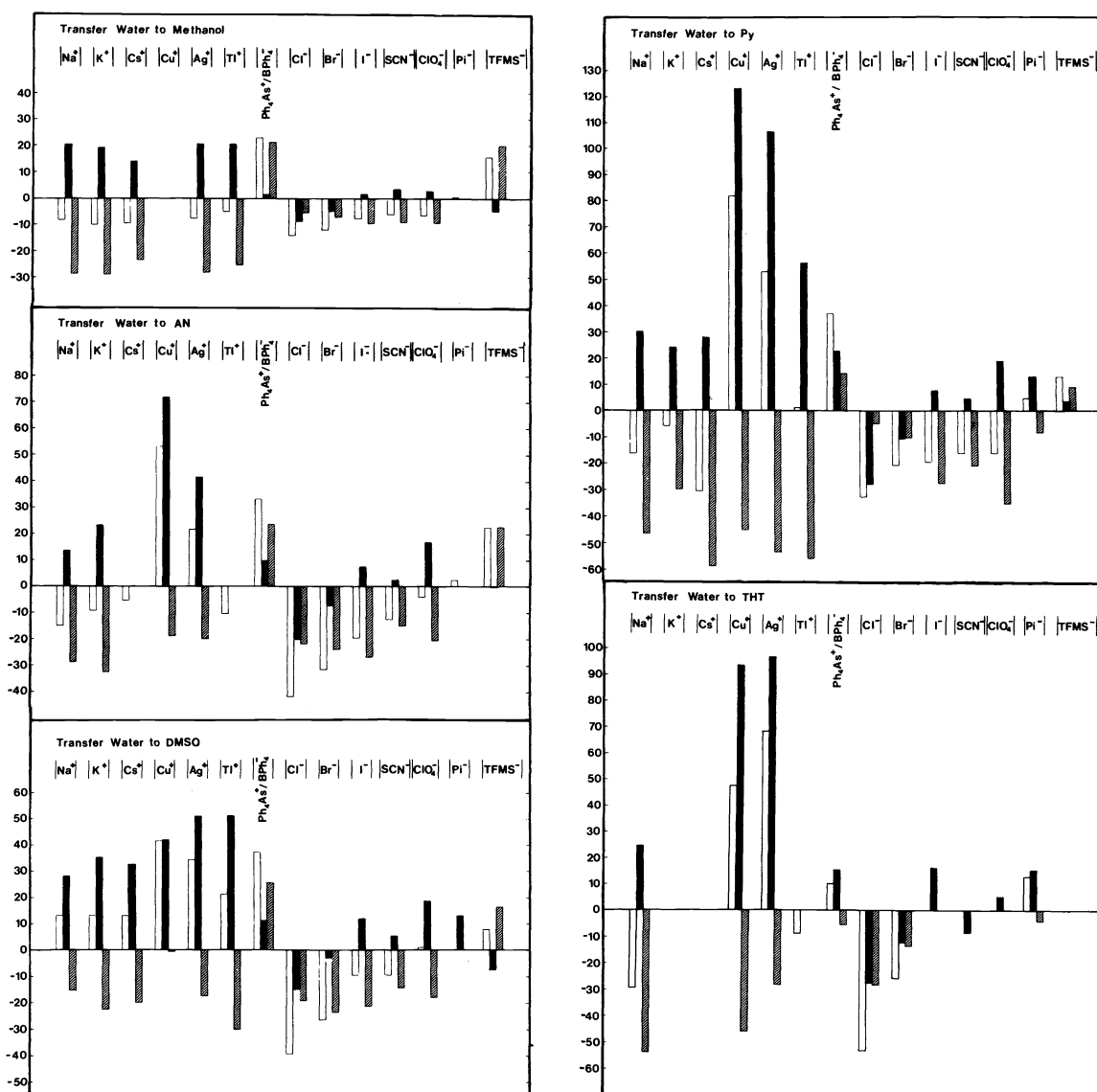


Fig. 4. The changes of free energy, $-\Delta G_{\text{tr}}^{\circ}$, (white), enthalpy, $-\Delta H_{\text{tr}}^{\circ}$, (black) and entropy, $T\Delta S_{\text{tr}}^{\circ}$, (hatched) in kJ mol^{-1} for the transfer of univalent single ions from water to methanol, acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py) and tetrahydrothiophene (THT) at 25°C .

energy being consumed in water than in methanol when solvent molecules are forced out of the bulk structure for the solvation.

In acetonitrile, the picture is more complicated. The sodium and thallium(I) ions are even weaker solvated than in methanol. The other alkali ions are equally solvated in the two solvents. The univalent d^{10} ions copper(I), silver(I) and gold(I) are on the other hand stronger solvated in acetonitrile than in both water and methanol. The specific solvation of univalent d^{10} acceptors is especially pronounced for copper(I). The heats and entropies of transfer to acetonitrile of metal ions are negative for the same reason as with methanol. The especially strong solvation of the copper(I) and silver(I) ions are accompanied by substantially more negative heats of transfer than for the other metal ions, giving entropies of transfer similar to the other cations.

The standard electrode potentials of all couples are lower, and the metal ions are more strongly solvated in DMSO than in water. DMSO forms stronger interactions to both hard and soft acceptors than water, see Tables 1 and 2. The heats and entropies of transfer are negative for most cations. DMSO is an oxygen donor to most cations including all cations in Fig. 4. DMSO act, however, as a sulfur donor to especially soft acceptors as palladium(II) and platinum(II) (refs. 24-26).

The transfer thermodynamics of single ions to pyridine have many similarities with those to acetonitrile. The alkali ions are more weakly solvated, the thallium(I) ion is equally solvated and the copper(I), silver(I) and gold(I) ions are more strongly solvated in pyridine than in water. The heats and entropies of transfer in pyridine show the same trends as in acetonitrile, but the absolute values are much larger in pyridine. Pyridine is a markedly stronger donor solvent than acetonitrile and pyridine has an even lower degree of bulk order than acetonitrile.

It has only been possible to determine the complete transfer thermodynamics for a limited number of ions to tetrahydrothiophene because of low solubilities and incomplete dissociation. In spite of a very positive ΔG_{tr}° value for the sodium ion, marked negative heat and entropy of transfer are observed. The soft acceptors copper(I) and silver(I) ions are as expected strongly solvated in tetrahydrothiophene. It is of interest to notice that silver(I) is more strongly solvated in tetrahydrothiophene than in pyridine, while the opposite is found for copper(I). Of these ions and solvents silver(I) and tetrahydrothiophene are regarded as the most soft ones, respectively. It has also been found that sulfur donor solvents only solvate typically soft acceptors well, because these solvents form strong covalent interactions but only very weak electrostatic ones, see Table 2.

All cations are solvated markedly stronger in liquid ammonia than in any other solvent studied as can be seen from the very low standard electrode potentials of all metal/metal ion couples, see Table 3 and Fig. 3.

Anions

The solvation of anions follows a quite different pattern than the cations. The differences in solvation between the solvents examined are furthermore fairly small. This is because only electrostatic forces are formed between the anion and the dipoles of the solvent molecules surrounding it, apart from the substantially weaker London forces, are due to the solvation. The donor properties of the solvents are of no importance for the solvation of anions, which are donors themselves. The halides are especially strongly solvated in solvents prone to form hydrogen bonds. The strength of the hydrogen bonds of the halides decreases in the order $Cl^{-} > Br^{-} > I^{-}$.

COMPLEX FORMATION IN STRONG DONOR SOLVENTS

A fundamental difference between complex formation reactions with charged ligands in protic and aprotic solvents is that the entropy terms are generally much more favourable in the aprotic solvents. This is because of the lower degree of bulk order often found in these solvents. The overall decrease in order is a result of desolvation processes where strongly coordinated solvent molecules leave the metal ion upon complex formation for the solvent bulk. This is especially pronounced in strongly donating solvents with low bulk order; protic solvents are always well-ordered because of the hydrogen bonding. Another difference between the two categories of solvents is that ligands forming hydrogen bonds are especially well solvated by protic solvents. The complex formation with such ligands in protic solvents will therefore be weaker than in aprotic solvents.

The dielectric constant of the solvent must be considered when stabilities of complexes are accounted. Salts very rarely dissociate in solvents with dielectric constants lower than 6-7. It has not been possible to determine any transfer thermodynamic parameters for the Ph_4As^{+} and BPh_4^{-} ions in such solvents and consequently not for other ions either because of the

applied TATB assumption. Solvents belonging to this category are alkanes, alkenes, many ethers, amines, several sulfides and thiols, thiophenes, phosphines and organic phosphites. Many salts can be dissolved in these solvents, but because of the low dielectric constants they do not dissociate. In solvents with low dielectric constant, the charge on ions can not be neutralized through solvation and instead the charge is neutralized by formation of neutral ion pairs. The electrostatic forces between ions become therefore more predominant in such solvents. The stability constants of neutral complexes will thus be very high in such solvents. The effect on the complex formation in a solvent with a low dielectric constant is shown by thermodynamic studies on the complex formation in tetrahydrothiophene. The estimated constant of tetrahydrothiophene is about 8, a value just above where the ion pair formation predominates.

The formation of copper(I) and silver(I) halide and thiocyanate complexes have been studied in water (ref. 27), acetonitrile (ref. 28), DMSO (ref. 29), pyridine (ref. 30) and tetrahydrothiophene (ref. 31). The results of the investigations in the non-aqueous solvents are summarized in Figs. 5 and 6.

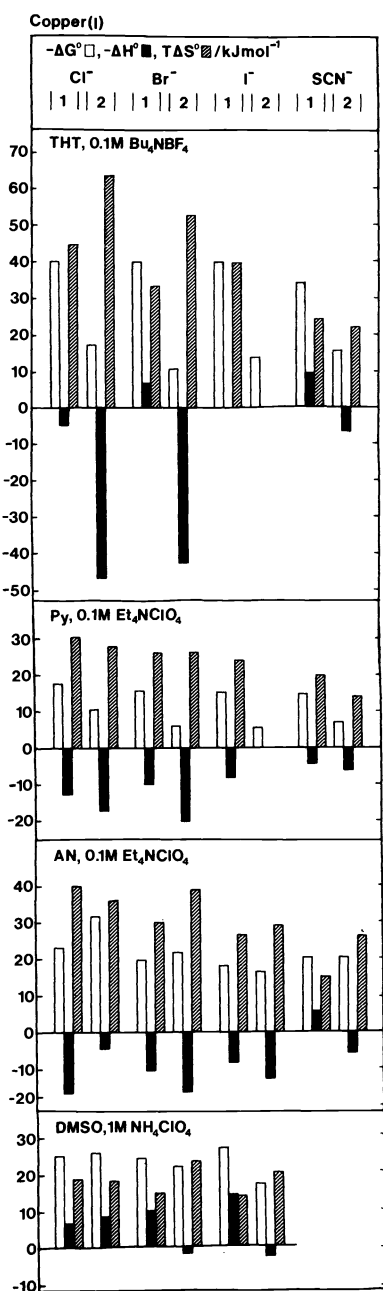


Fig. 5

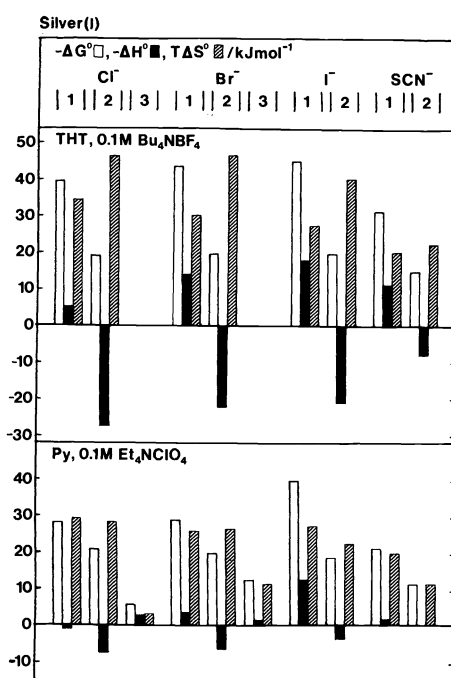


Fig. 6

Fig. 5. Stepwise changes of free energy, enthalpy and entropy for the copper(I) halide and thiocyanate systems in tetrahydrothiophene (THT) (ref. 31), pyridine (Py) (ref. 30), acetonitrile (AN) (ref. 29) and dimethylsulfoxide (DMSO) (ref. 28) at 25°C.

Fig. 6. Stepwise changes of free energy, enthalpy and entropy for the silver(I) halide and thiocyanate systems in tetrahydrothiophene (THT) (ref. 31) and pyridine (Py) (ref. 30) at 25°C.

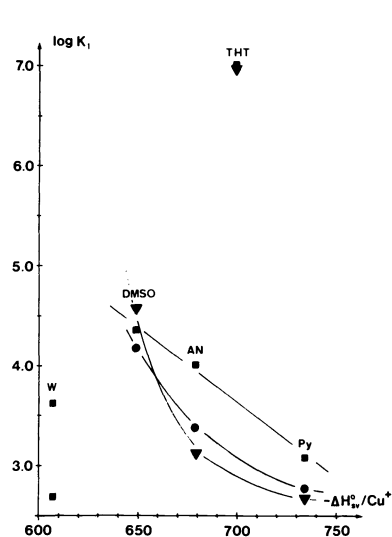


Fig. 7. The stability constants of the formation of the first copper(I) halide complexes are plotted against the heat of solvation of the copper(I) ion. ■, ● and ▼ denote chloride, bromide and iodide complexes, respectively.

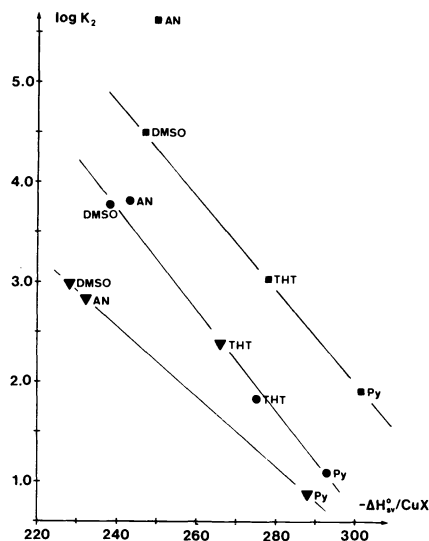


Fig. 8. The stability constants of the formation of the second copper(I) halide complexes are plotted against the heat of solvation of the copper(I) halides. ■, ● and ▼ represents the same ions as in Fig. 7

The stability constants of the first neutral copper(I) complexes are proportional to the solvation of the copper(I) ion in each solvent respectively, except in water and tetrahydrothiophene, see Fig. 7. The CuCl complex is weaker than expected in aqueous solution because of strong hydrogen bonding between water and chloride ions, free as well as coordinated. The neutral copper(I) halide complexes are about ten to the power of three stronger than expected from the solvation of the copper(I) ion in tetrahydrothiophene. This increase in stability is certainly due to increased tendency to ion pair formation in solvents with low dielectric constants. On the other hand, the stabilities of the second copper(I) complexes are proportional to the solvation of the first complex in all solvents, see Fig. 8. This is to be expected when a charged complex is formed and no charges are neutralized as when the first complex is formed.

All copper(I) halide and thiocyanate complexes are strongly entropy stabilized in all non-aqueous solvents studied. The most favourable enthalpy terms are found in DMSO, thus the solvent solvating copper(I) most poorly of those used. Copper(I) is strongly solvated in the nitrogen donor solvents acetonitrile and pyridine. All complex formation reactions with halides and thiocyanate are endothermic in these solvents. This means that more energy is consumed for the desolvation compared to what is gained through the formation of a copper(I)-halide/thiocyanate bond; this is valid for both steps. In tetrahydrothiophene the enthalpy change at the formation of the first step is around zero, while the formation of the second complex is very strongly endothermic. It can be assumed that a substantial desolvation takes place when the second complex is formed. The CuX_2 complexes are more weakly solvated in tetrahydrothiophene than in the other solvents. It is plausible that no solvent molecules are coordinated in the inner coordination sphere and the solvation is therefore proportional to the strength of the electrostatic forces the solvent can exert. As shown above, tetrahydrothiophene forms considerably weaker electrostatic forces than the other solvents studied, see Table 2.

The formation of silver(I) halide and thiocyanate complexes have only been studied in pyridine and tetrahydrothiophene because of very low solubilities of the neutral complexes in the other solvents. As found for copper(I) complexes, the silver(I) halide and thiocyanate complexes are considerably more stable in tetrahydrothiophene than in pyridine for the same reason as discussed above. The enthalpy changes become more negative in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$, since also the covalency of the formed bond also increases. This is to be expected for a typical soft acceptor as silver(I), where the degree of covalency in a bond depends on the nature of the donor. As for the copper(I) halide systems, a very extensive desolvation takes place for the silver(I) systems when the second complex is formed.

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REFERENCES

1. V. Gutman and E. Wychera, *Inorg. Nucl. Chem. Letters*, **2**, 257-260 (1966).
2. V. Gutman, A. Steininger and E. Wychera, *Monatsh. Chem.*, **97**, 460-467 (1966).
3. U. Meyer and V. Gutmann, *Struct. Bond.*, **12**, 113-140 (1972).
4. V. Gutman, *The Donor-Acceptor Approach to Molecular Interactions*, Ch. 2, Plenum Press, New York and London 1978.
5. P.-C. Maria and J.-F. Gal, *J. Phys. Chem.*, **89**, 1296-1304 (1985).
6. I. Persson, M. Sandström and P.L. Goggin, *Inorg. Chim. Acta*, submitted for publication.
7. R. Schmid, *J. Solution Chem.*, **12**, 135-152 (1983).
8. R.W. Soukup and R. Schmid, *J. Chem. Edc.*, **62**, 459-462 (1985).
9. R.W. Soukup and K. Sone, *Bull. Chem. Soc. Japan*, in press.
10. S. Hahn, W.M. Miller, R.N. Lichtenthaler and J.M. Prautsnitz, *J. Solution Chem.*, **14**, 129-137 (1985).
11. R.W. Taft, N.J. Pienta, M.J. Kamlet and E.M. Arnett, *J. Org. Chem.*, **46**, 661-667 (1981).
12. M. Munakata, S. Kitagawa and M. Miyazima, *Inorg. Chem.*, **24**, 1638-1643 (1985).
13. M. Harlem and A.I. Popov, *J. Am. Chem. Soc.*, **94**, 1431-1434 (1972).
14. D.J. Gardiner, A.H. Haji and B. Straughan, *J. Chem. Soc., Dalton Trans.*, 705-710 (1978).
15. H. Sawai and T. Takizawa, *Bull. Chem. Soc. Japan*, **49**, 1906-1908 (1976).
16. I. Persson and P. Persson, to be published.
17. M. Johnsson and I. Persson, to be published.
18. Y. Marcus, *Pure Appl. Chem.*, **55**, 977-1021 (1983).
19. I.M. Kolthoff and M.K. Chantooni, Jr., *J. Phys. Chem.*, **76**, 2024-2034 (1972).
20. O. Popovych, *Crit. Rev. Anal. Chem.*, **1**, 73-117 (1970).
21. E. Grundwald, C. Baughman and C. Kohnstan, *J. Am. Chem. Soc.*, **82**, 5801-5811 (1960).
22. E.M. Arnett and D.R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598-2599 (1966).
23. M. Johnsson and I. Persson, to be published.
24. F.A. Cotton, R. Francis and W.D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534-1536 (1960).
25. J. Selbin, W.E. Bull and L.H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **16**, 219-224 (1961).
26. I. Persson, *Thesis*, University of Lund, Lund 1980.
27. S. Ahrland and J. Rawsthorne, *Acta Chem. Scand.*, **24**, 157-172 (1970).
28. S. Ahrland, K. Nilsson and B. Tagesson, *Acta Chem. Scand.*, **A37**, 193-201 (1983).
29. S. Ahrland, P. Bläuenstain, B. Tagesson and D. Tuhtar, *Acta Chem. Scand.*, **A34**, 265-272 (1980).
30. S. Ahrland, S.-I. Ishiguro and I. Persson, *Acta Chem. Scand.*, **A40**, in press.
31. M. Johnsson, I. Persson and R. Portanova, to be published.