Determination of Gibbs Free Energy of Transfer for some Univalent Ions from Water to Methanol, Acetonitrile, Dimethylsulfoxide, Pyridine, Tetrahydrothiophene and Liquid Ammonia; Standard Electrode Potentials of some Couples in these Solvents

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Abstract

The free energy of transfer, ΔG_{tr}°, for 21 univalent ions are determined from water to methanol, acetonitrile, dimethylsulfoxide (DMSO), pyridine, tetrahydrothiophene and liquid ammonia. These solvents show a wide range of donor properties, whereby water and methanol are regarded as hard donors, dimethylsulfoxide and acetonitrile are on the borderline between hard and soft, and the remaining solvents are regarded as typical soft donors. The ΔG_{tr}° values of ionic compounds are calculated from solubility product measurements of 1:1 salts. The extrathermodynamic tetraphenylarsonium tetraphenylborate (TATB) assumption has been applied in order to calculate the contributions from the single ions. The TATB assumption implies that the two large ions Ph_4As^+ and BPh_4^- are equally solvated, thus $\Delta G_{tr}^{\circ}(AsPh_4^+) = \Delta G_{tr}^{\circ}(BPh_4^-)$, for all solvent pairs. Standard electrode potentials in non-aqueous solvents can be calculated from the standard electrode potentials in water and the ΔG_{tr}° values. The standard electrode potentials calculated from the solubility product measurements, and the potentiometrically determined ones were found to be in excellent agreement. The extrathermodynamic assumption has thereby been experimentally shown to be close to the truth.

Introduction

The determination of transfer thermodynamics of individual ions requires that an extrathermodynamic assumption is applied. The most used is that originated by Grunwald *et al.* stating that the PPh_4^+ and the BPh_4^- ions interact similarly with the solvent [1]. This assumption was later modified by Popovych and Dill [2]. They stated that the TAB^+ ion (TAB = triisoamyl-n-butylammonium) and the BPh_4^- ion interact similarly with the solvent. Alexander and Parker used the $AsPh_4^+$ and BPh_4^- ions for the determination of the medium ion activity coefficients, γ

[3]. The approaches using the PPh_4^+ and $AsPh_4^+$ cations are found to be in excellent agreement, while the assumption including the TAB^+ ion differs slightly from the other two [4].

The viscosity *B*-coefficients for the PPh_4^+, BPh_4^-, NBu_4^+ and BBu_4^- ions have been determined in dimethylsulfoxide [5], hexamethylphosphoric triamide [6] and dimethylformamide [7]. The *B*-coefficient is a function of the ion–solvent interaction. The viscosity *B*-coefficient of the PPh_4^+ and BPh_4^- ions are similar, and twice the values for NBu_4^+ and BBu_4^-. This shows that the PPh_4^+ and BPh_4^- ions interact much more strongly with the solvent than the NBu_4^+ and BBu_4^- ions. The electrostatic interactions between pi-electrons in the phenyl rings and the solvent molecules are probably stronger than the van der Waals forces [8]. One can therefore assume that the TAB^+ and BPh_4^- ions interact differently with the solvent, and that the approach including the TAB^+ and BPh_4^- ions is not preferable. The tetraphenylarsonium tetraphenylborate assumption, TATB, has been frequently used in recent years, and it has been applied in this study. The accuracy of the TATB assumption has been tested by comparing potentiometrically determined standard electrode potentials in DMSO and pyridine, with values calculated from differences in medium ion activity coefficients.

Other extrathermodynamic assumptions must be applied when Gibbs free energy of transfer is determined from electrode potentials. The bis(biphenyl)chromium assumption is based on the fact that the electrode potential of the redox couple bis(biphenyl)chromium(0)/(I) is independent from the nature of the solvent [9]. The difference in Gibbs free energy of transfer obtained from the TATB and bis(biphenyl)chromium assumptions can be up to 5 kJ mol^{-1} in some cases, corresponding to a difference in standard electrode potential of about 50 mV. A large number of other extrathermodynamic assumptions have been proposed during the years. These have been reviewed by Popovych [10].

TABLE I. Some Physical Properties of the Solvents Used in This Study

Solvent	Melting point (°C)	Boiling point (°C)	ϵ	μ (D)
Water	0.0	+100.0	78.5	1.85
Methanol	−93.9	+65.0	32.6	1.70
Acetonitrile	−45.7	+81.6	36.0	3.85
DMSO	+18.5	+189	46.4	3.96
Pyridine	−42	+115.5	12.1	2.19
THT	−96.2	+121.1	8	1.90
Liquid ammonia	−77.7	−33.4	22.4	1.47

Most transfer thermodynamic studies performed have been to hard donor solvents, while the number of studies to solvents with a soft donor atom is very limited. The soft donor solvents used are, furthermore, often not commercially available. The transfer thermodynamics from water of single ions have recently been extensively reviewed by Marcus [11, 12].

In this study, Gibbs free energy of transfer, ΔG_{tr}°, has been determined for 21 univalent cations and anions from water (W) to methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py), tetrahydrothiophene (THT) and liquid ammonia (NH$_3$). The solvents used are all commercially available. Water has been chosen as the reference solvent, because it is by far the most used solvent in science. Two oxygen, three nitrogen and one sulfur donor solvents have been studied. The oxygen in methanol is regarded as a hard electron donor, while the oxygen in DMSO is on the borderline between hard and soft donors. This is one of the oxygen donors with the largest possibility for participating in covalent bonding [13]. Acetonitrile is regarded as a border-line nitrogen donor, which however solvates univalent d^{10} metal ions well [13]. The nitrogen in pyridine is a soft donor. Primary and secondary amines have even stronger electron donating properties than pyridine [8]. Because of low dielectric constants of these solvents, $\epsilon < 6$ [14], very few salts dissociate and consequently determinations of solubility products, and also ΔG_{tr}° values, are impossible. Most sulfur donor solvents are regarded as soft. The cyclic thioether tetrahydrothiophene, THT, has been chosen for the studies of the solvating properties of a soft sulfur donor solvent. THT has a sufficiently high dielectric constant, $\epsilon \approx 8$, for complete or at least partial dissociation of a number of salts, making determinations of solubility products possible and reliable. Some physical properties of the used solvents are given in Table I.

Standard electrode potentials in liquid ammonia for some couples have been reported [15], as well as a ΔG_{tr}° value for the proton from water to liquid ammonia [11]. These values have been used for the calculation of the ΔG_{tr}° values for the other univalent

ions. Liquid ammonia is a unique solvent in the sense that it is a very strong electron donor and at the same time it solvates hard acceptors well through electrostatic forces.

Calculations and Notations

The medium ionic activity coefficient, γ, reflects the strength of the interaction between ion and solvent. Only the difference in ionic activity coefficients between two solvents, $^{s_1}\gamma^{s_2}$, can be determined; absolute values of γ cannot be obtained. Kolthoff has described in detail the calculation of γ values from solubility products in the solvent pair s_1 and s_2 [4]. The calculations of γ values, or logarithmed, $p^{s_1}\gamma^{s_2}$, can be made from solubility products, $pK_{sp}(ML)$ as follows

$$pK_{sp}(ML)_{s_2} - pK_{sp}(ML)_{s_1} = {}^{s_1}\Delta^{s_2}pK_{sp}(ML)$$

$$= p\gamma_{M^+} + p\gamma_{L^-}$$

Water is used as the reference solvent and the TATB assumption has been applied, the calculation in all solvents therefore starts with $1/2\Delta pK_{sp}(AsPh_4BPh_4)$ = $p^w\gamma^s(AsPh_4^+) = p^w\gamma^s(BPh_4^-)$. Gibbs free energy of transfer from water to the solvent s is obtained according to the following relationship

$$\Delta G_{tr}^{\circ}(w, s) = -RT \ln \gamma_{ion} = RT \ln 10p\gamma_{ion}$$

The difference in standard electrode potential for a couple between water and another solvent is calculated from Gibbs free energy of transfer or *vice versa* according to

$$\Delta G_{tr}^{\circ} = nF(E_{solv}^{\circ} - E_{aq}^{\circ}); E_{solv}^{\circ} = \Delta G_{tr}^{\circ}n^{-1}F^{-1} + E_{aq}^{\circ}$$

where n is the number of electrons in the electrode reaction and F is Faradays constant.

Experimental

Solvents

The water used in the conductivity measurements was distilled twice in an all-glass equipment. Methanol

TABLE II. Melting Points of Synthesised Salts Used in Measurements

	Melting points (°C)		Characteristics
	This work	Literature	
AsPh₄BPh₄	298–300	293–295[a]	colorless crystals
AsPh₄Pic	200–202	203–204[a]	yellow crystals
AsPh₄Cl	258–260		white crystals
AsPh₄Br	283–285		white crystals
AsPh₄I	319–321		white crystals
AsPh₄CF₃SO₃	293–295		colorless crystals
KBPh₄	[b]		white powder
KPic	340 (dec.)[c]		yellow needles
KCF₃SO₃	145–147		white powder
RbBPh₄	[b]		white powder
CsBPh₄	[b]		white powder
TlBPh₄	310 (dec.)[c]		white powder
TlPic	320 (dec.)[c]		yellow needles

[a] Ref. 18.   [b] Denotes melting points higher than 350 °C.   [c] (dec.), decomposition.

(Merck p.a.) was dried over calcium oxide for at least a day. The calcium oxide was filtered off on Millipore filter (0.20 μ) immediately prior to usage. The purification of acetonitrile (Fluka p.a.) and dimethylsulfoxide (Merck) has been described elsewhere [16, 17]. Pyridine (De Haen, p.a.) was used without further purification. Tetrahydrothiophene (Fluka 97%) was distilled under nitrogen atmosphere to prevent oxidation. The fraction distilling at 119–120 °C was collected. All organic solvents except methanol were stored over 3 Å molecular sieves in dark bottles.

Preparation and Purification of Salts

The melting points of the salts used in this study are given in Table II. The elemental analyses were performed by the Department of Analytical Chemistry at the University of Lund.

Tetraphenylarsonium tetraphenylborate and picrate were prepared and purified as described elsewhere [18].

Tetraphenylarsonium bromide and iodide were prepared by mixing aqueous solutions of tetraphenylarsonium chloride and sodium halide. Tetraphenylarsonium bromide and iodide are less soluble in water than the chloride. The products were washed with several portions of water.

Tetraphenylarsonium trifluoromethylsulfonate was prepared by addition of trifluoromethylsulfonic acid to an aqueous solution of tetraphenylarsonium chloride. The hydrochloric acid formed was evaporated off. The remaining crystals were washed with water and several portions of ethanol. *Anal.* Found: S, 5.86–6.02; C, 56.4–56.5; H, 3.70–3.78. Calc.: S, 6.0; C, 56.6; H, 3.8%.

Sodium tetraphenylborate (Fluka p.a.) was recrystallized according to a previously described procedure [19].

Potassium, rubidium, cesium and thallium(I) tetraphenylborate were precipitated in aqueous solution by mixing sodium tetraphenylborate and alkali chloride or thallium(I) perchlorate. The products were washed with several portions of water. The alkali salts were recrystallized from acetone and water. Thallium(I) tetraphenylborate was only washed with water and acetone due to very low solubility.

Potassium picrate was prepared as described elsewhere [20].

Potassium trifluoromethylsulfonate was prepared and recrystallized as described by Hedwig and Parker [21].

Silver perchlorate (Fluka p.a.) was recrystallized according to Radell *et al.* [22].

Thallium(I) picrate was prepared as described previously [4].

Tetrabutylammonium picrate was prepared by neutralization of an aqueous solution of picric acid with tetrabutylammonium hydroxide (Fluka p.a. 40% in water).

Tetraethylammonium iodide and tetrabutylammonium chloride, bromide and tetrafluoroborate (all Fluka p.a.) were recrystallized from acetone.

All salts were stored in a dark desiccator over phosphorous pentoxide at reduced pressure.

Thallium amalgam containing 55% thallium was prepared by fusing metallic thallium (Alfa 99.99%) and metallic mercury (p.a.) [23] under nitrogen to prevent oxidation. Prior to use, the amalgam was washed with dilute nitric acid, water and acetone.

TABLE III. pK_{sp} of Salts at 25 °C in Water (W), Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py) and Tetrahydrothiophene (THT). Values in Parentheses are Uncertain.

Salt	W	M	AN	DMSO	Py	THT
AsPh₄BPh₄	17.3[a]	9.0[b]	5.8[b]	4.3[a]	4.0	13.7
AsPh₄Pic	8.8[b]	3.9[b]	2.6[b]			4.9
AsPh₄Cl	1.0				0.4	8.6
AsPh₄Br	2.0					4.7
AsPh₄I	5.1[b]	2.3[b]	2.7[b]		1.9	
AsPh₄CF₃SO₃	8.9	2.0				
NaBPh₄	(0.1)					4.2
NaI			(0.7)		(1.1)	
KBPh₄	7.5[b]		3.3[b]		1.9	
KPic	3.5[b]	4.4[b]	4.7[b]		3.7	
KCl	−0.9[c]		7.9[a]			
KBr	−1.1[c]		5.7[a]			
KClO₄	1.9[d]	4.7[e]	4.2[f]		5.7	
KCF₃SO₃		1.3	(0.0)		(1.0)	
RbBPh₄	8.5[c]	6.0[g]	3.9[c]		4.1	
RbPic	3.7[a]	4.8[a]	4.6[a]			
RbBr	−0.9[a]		6.1[a]			
RbClO₄	2.5[d]	5.4[e]	4.6[a]			
CsBPh₄	8.7[h]	6.2[h]	3.9[c]		8.3	
CsPic	4.2[a]	5.2[a]	4.7[a]			
CsBr	−0.8[a]		5.8[a]			
CsClO₄	2.4[d]	5.0[e]	4.0[a]			
AgBPh₄	17.2[i]	14.4[i]	7.5[b]	4.7[a]		
AgCl	9.7[a]	13.4[b]	13.2[b]	10.6[b]	6.1	
AgBr	12.2[a]	15.5[b]	13.9[k]	10.8[b]	5.8	
AgI	16.0[a]	18.6[b]	14.5[b]	11.6[b]	9.0	
AgSCN	11.9[a]	14.2[b]	10.3[b]	7.5[b]	5.4	
TlBPh₄		9.3[a]	9.5[a]	2.9[a]	6.7	
TlPic	4.1[a]	4.1[a]	5.5[a]			3.5
TlCl	3.7[l]	6.5[a]	13.2[m]	6.2[n]		
TlBr	5.4[a]	8.2[a]	13.0[m]	5.8[n]		
TlI	7.2[c]	9.3		4.7[n]	6.8	
TlClO₄	1.1[m]	2.9[a]	3.6[m]			
TlSCN	3.8[m]		8.3[m]			
NH₄ClO₄		0.7[e]	2.4			
Et₄NI	(−0.2)				4.6	

[a]Ref. 4.   [b]Ref. 25.   [c]Ref. 26.   [d]Ref. 27.   [e]Ref. 28.   [f]Ref. 29.   [g]Ref. 30.   [h]Ref. 31.   [i]Ref. 32.   [k]Ref. 33.   [l]Ref. 34.   [m]Ref. 35.   [n]Ref. 36.

Conductivity Measurements

The conductivity measurements were performed by a Metrohm 644 Conductometer ranging from 1 μS to 100 mS. The conductance, G, was measured in several aqueous potassium chloride solutions of different concentration at 25 °C. At each concentration, the cell constant, c (cm^{-1}), was calculated according to $c = KG^{-1}$, where K is the equivalent conductances for each concentration [24]. The cell constant measured within the concentration range 0.001 to 0.1

M was consistent. The average value of the cell constant was 0.826 cm^{-1}.

The saturated solutions were not filtered prior to the conductivity measurements. A series of five consecutive solutions diluted tenfold was measured for each salt and solvent. If the logarithmed conductivities showed a linear relationship to the logarithmed concentrations and if the obtained slope was larger than 0.7, complete dissociation was assumed. The salt was not used in further calculations if the conductivi-

TABLE IV. Values of pγ_{ion} (Medium Ion Activity Coefficient) Derived from pK_{sp} Values using the Tetraphenylarsonium Tetraphenylborate Assumption at 25 °C. pγ Values Calculated from Water (W) to Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py) and Tetrahydrothiophene (THT)

Ion	W to M	W to AN	W to DMSO	W to Py	W to THT
AsPh₄⁺	−4.1	−5.8	−6.5	−6.6	−1.8
Na⁺	+1.5[a]	+2.4[a]	−2.4[a]	+2.8	+5.9
K⁺	+1.7	+1.6	−2.1[a]	+1.0	
Rb⁺	+1.6	+1.2	−1.9[a]	+2.2	
Cs⁺	+1.6	+0.9	−2.2[a]	+6.2	
Ag⁺	+1.3	−3.9	−6.0	−10.0	−9.0[b]
Au⁺ [b]		−5.4	−10.5	−17.4	
Tl⁺	+0.8	+1.8	−3.6[a]	−0.2	+1.5
H⁺	+1.9[a]	+8.1[a]	−3.3[a]	−3.8[b], −3.0[c]	
NH₄⁺	+0.9[b]	+2.8			
Et₄N⁺	+0.1[b]	−1.5[b]	−2.2[b]	+1.4	
Bu₄N⁺	−3.8[b]	−5.8[b]			
BPh₄⁺	−4.1	−5.8	−6.5	−6.6	−1.8
Pic⁻	−0.8	−0.4		−0.8	−2.1
Cl⁻	+2.4	+7.3	+6.9	+6.0	+9.4
Br⁻	+2.0	+5.5	+4.6	+3.6	+4.5
I⁻	+1.3	+3.4	+1.6	+3.4	
SCN⁻	+1.0	+2.2	+1.6	+3.5	
ClO₄⁻	+1.0	+0.7	−0.2	+2.8	
CF₃SO₃⁻	−2.8	−4.1		−2.5	

[a]Ref. 4.   [b]Calculated from ΔG_{tr}° values.   [c]Calculated from ΔG_{tr}° in ref. 11.

ty measurements indicated incomplete dissociation at saturation.

Potentiometric Measurements

In all measurements Bu₄NPic was used as the ionic medium. The potential between the half cells Ag(s)/Ag⁺ (10.0 mM) and Tl(am)/Tl⁺ (10.0 mM) was determined in DMSO, pyridine and THT. The difference in potential between thallium metal and the amalgam is corrected with 2.5 mV [24]. For the measurements in DMSO and pyridine two commercial Ingold vessels, connected through a salt bridge containing ionic medium, were used for the electrode solutions which were kept at 25.0 ± 0.1 °C. The measurements were performed with a Data Precision 3500 digital voltmeter. Because of the low dielectric constant of tetrahydrothiophene, the electrical resistance of a chemical cell containing a THT solution was of the same order of magnitude as the input resistance of the voltmeter. In order to minimize the resistance in the cell, another type of cell has been used where the salt bridge has been exchanged for a porous sintered glass filter between the half-cells. The resistance of this type of cell containing 0.1 M Bu₄NPic in THT is less than 2 MΩ. This is an acceptably low resistance when comparing it with the input resistance of the voltmeter, 1 GΩ. The difference in potential between the Ag(s)/Ag⁺ and H₂(g)/H⁺ couples was determined in DMSO and pyridine using a platinum plate with 1 atm. H₂(g) in 10.0 mM picric acid and the silver electrode described above.

Solubility Measurements

The solubilities of alkali and tetraalkylammonium halides in methanol, acetonitrile and tetrahydrothiophene were determined by potentiometric titrations with silver(I) nitrate in aqueous solution. The tetrahydrothiophene was oxidized by concentrated nitric acid prior to the analysis. The other solubilities were determined by adding a known amount of salt to a certain volume of solvent followed by several days of stirring. The saturated solutions were filtered, undissolved salt was dried and weighed. The remaining solution was evaporated to dryness and the salt was weighted. If this amount of salt was larger than the added one, the salt was assumed to form crystalline solvates and was not used in further calculations.

Results

The solubility products determined in this study and those taken from the literature are summarized in Table III. The solubility products are only given for salts assumed to be completely dissociated at saturation and for the silver(I) halides in pyridine, where the complex formation thermodynamics have been determined previously [37].

The medium ionic activity coefficients, pγ, calculated from the solubility products in Table III are given in Table IV. Salts containing a tetraphenyl-

TABLE V. ΔG_{tr}° Values Calculated from $p\gamma_{ion}$, Transfer from Water (W) to Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py), Tetrahydrothiophene (THT) and Ammonia (NH$_3$). Values in Parentheses are Uncertain

Ion	W to M	W to AN	W to DMSO	W to Py	W to THT	W to NH$_3$ [a]
AsPh$_4^+$	−23.4	−33.1	−37.1	−37.7	−10.3	
Na$^+$	+8.0	+14.8	−13.1	+16.0	+33.7	−17.4
K$^+$	+9.7	+9.1	−13.1	+5.7		−11.6
Rb$^+$	+9.7	+6.8	10.8	+12.6		−12.5
Cs$^+$	+9.1	+5.1	−12.6	+35.4		−15.4
Cu^{+} [a]		−52.1	−41.5	−82.0	−29.9	−109.0
Ag$^+$	+7.4	−22.3	−34.2	−57.1	−51.1 [a]	−100.3
Au^{+} [a]		−30.9	−59.8	−99.4		
Tl$^+$	+4.6	+10.3	−20.5	−1.1	+8.6	
H$^+$	+10.8	+46.2	−18.8	−28 [a], −24 [b]		−96.5
NH$_4^+$	+4.9 [c]	+16.0				
Et$_4$N$^+$	+0.6 [d]	−8.8 [d]	−12.5 [d]	+8.0		
Bu$_4$N$^+$	−21.7 [d]	−33.1 [d]				
BPh$_4^-$	−23.4	−33.1	−37.1	−37.7	−10.3	
Pic$^-$	−4.6	−2.3		−4.6	−12.0	
Cl$^-$	+13.7	+41.7	+39.4	+34.2	+53.7	+43.4
Br$^-$	+11.4	+31.4	+26.3	+20.5	+25.7	+32.8
I$^-$	+7.4	+19.4	+9.1	+19.4		(+25.1)
SCN$^-$	+5.7	+12.6	+9.1	+20.0		
ClO$_4$	+5.7	+4.0	−1.1	+16.0		
CF$_3$SO$_3^-$	−16.0	−23.4		−14.3		

[a] Calculated from E° values.   [b] Ref. 47.   [c] Ref. 48.   [d] Ref. 19.

borate ion were, if possible, used for determination of pγ values. If the pγ values could be calculated in several ways, the average value has been selected if the obtained values are in agreement. If they were not in agreement, the most reliable way has been selected.

The Gibbs free energy of transfer for the univalent cations and anions in Table V are in most cases obtained from the pγ values in Table IV. The values of copper(I) and gold(I) in all solvents [17, 38–44], silver(I) in tetrahydrothiophene and all ions in liquid ammonia except the proton [15], are calculated from the standard electrode potentials.

The standard electrode potential in a non-aqueous solvent for a couple has been calculated from Gibbs free energy of transfer and the standard electrode potential in water, see 'Calculations and Notations'. The standard electrode potentials for some couples have been determined potentiometrically as noted above. The standard electrode potentials in liquid ammonia are taken from the literature [15] and adjusted to the NHE in water via Gibbs free energy of transfer for the proton from water to liquid ammonia [11]. The standard electrode potentials vs. NHE in water for some couples in water, methanol, aceto-nitrile, DMSO, pyridine, tetrahydrothiophene and liquid ammonia are given in Table VI and Figs. 1 and 2.

The difference in standard electrode potential between the couples Ag(s)/Ag$^+$ and Tl(s)/Tl$^+$ have been determined potentiometrically and calculated from
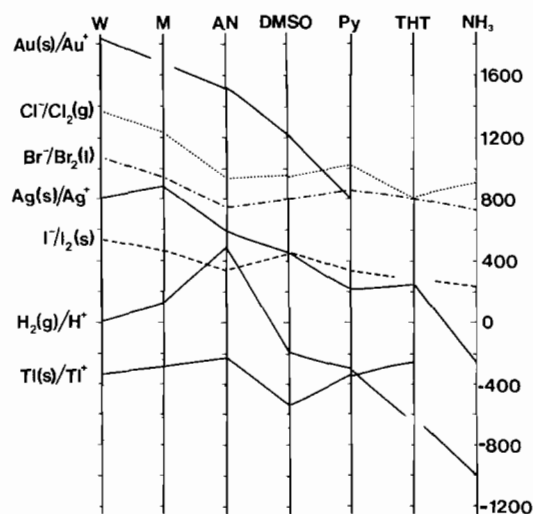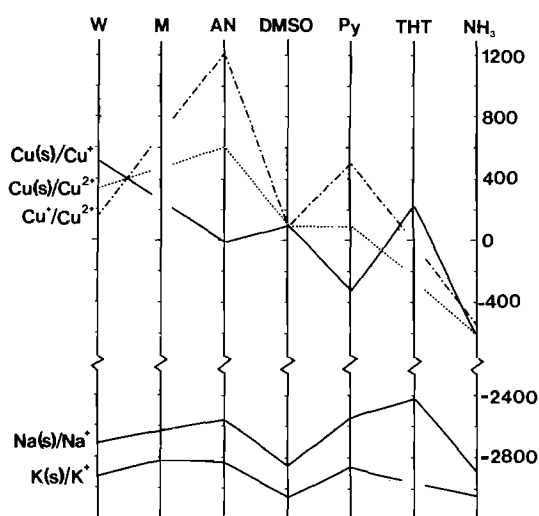

Fig. 1. Standard electrode potentials of some metal couples and the halogen couples X$^-$/X$_2$, X = Cl, Br, I, in water (W), methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py), tetrahydrothiophene (THT) and liquid ammonia (NH$_3$) at 25 °C. All values are referred to the NHE in water.

solubility measurements in DMSO and pyridine. The obtained results are given in Table VII. The results obtained from the two procedures are in close agreement. The observed differences, less than 30 mV, corresponds to errors of about 3.0 kJ mol^{-1} or less in

TABLE VI. Standard Potentials in Volts vs. $E°(H_2(g)/H^+(aq))$ in Water (W), Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py), Tetrahydrothiophene (THT) and Ammonia (NH_3) at 25 °C. Values in Parentheses are Uncertain

Couple	W	M	AN	DMSO	Py	THT	NH_3[a]
$H_2(g)/H^+$	0	+0.11	+0.48	−0.20	−0.28		−1.00
Na/Na^+	−2.71	−2.63	−2.56	−2.85	−2.54	−2.36	−2.89
K/K^+	−2.92	−2.82	−2.83	−3.06	−2.86		−3.04
Rb/Rb^+	−2.93	−2.83	−2.86	−3.04	−2.80		−3.06
Cs/Cs^+	−2.92	−2.83	−2.87	−3.06	−2.55		−3.08
Cu/Cu^+	+0.52		−0.02	+0.09	−0.33	+0.21	−0.61
Cu/Cu^{2+}	+0.34		+0.60	+0.08	+0.08		−0.60
Cu^+/Cu^{2+}	+0.16		+1.21	+0.07	+0.49		−0.56
Ag/Ag^+	+0.80	+0.87	+0.57	+0.45	+0.21	+0.27	−0.24
Au/Au^+	+1.83[b]		+1.51	+1.21[c]	+0.80		
Tl/Tl^+	−0.34	−0.29	−0.23	−0.56	−0.35	−0.25	
Cl^-/Cl_2	+1.36	+1.22	+0.93	+0.95	+1.01	+0.80	+0.91
Br^-/Br_2	+1.07	+0.95	+0.74	+0.80	+0.86	+0.80	+0.73
I^-/I_2	+0.54	+0.46	+0.34	+0.45	+0.34		(+0.28)

[a] Ref. 15. [b] Ref. 39. [c] Ref. 40, recalculated to reference NHE in water.

Fig. 2. Standard electrode potentials of some metal and metal ion couples, in water (W), methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py), tetrahydrothiophene (THT) and liquid ammonia (NH_3) at 25 °C. All values are referred to the NHE in water.

TABLE VII. Difference in standard electrode potential between $Ag(s)/Ag^+$ and $Tl(s)/Tl^+$ in dimethylsulfoxide (DMSO) and pyridine (Py) at 25 °C

	$E°$ (mV)	
	Solubility measurements	Potentiometric determination
DMSO	1000	1010
Pyridine	530	560
	480[a]	

[a] Ref. 45.

Gibbs free energy of transfer for single ions using the TATB assumption and solubility products determined from solubility measurements. A somewhat different potential difference between $Ag(s)/Ag^+$ and $Tl(s)/Tl^+$ in pyridine is reported by Cisak and Elving [45].

The difference in standard electrode potential between $Ag(s)/Ag$ and $H_2(g)/H^+$ has been determined in DMSO and pyridine. The difference was 630 mV in DMSO and 480 mV in pyridine. In pyridine, a difference in standard electrode potential of 500 mV is reported in perchlorate media [43]. The standard electrode potentials of NHE in DMSO and pyridine are earlier determined against NHE in water [4, 46]. The standard electrode potential of $Ag(s)/Ag^+$ in DMSO and pyridine determined from solubility products with the TATB assumption agree well with the potential difference from NHE in these solvents. Mukherjee *et al.* have determined the difference between $Ag(s)/Ag^+$ and NHE in pyridine to 551 mV [47]. The standard electrode potential of $Ag(s)/Ag^+$ in pyridine in reference to NHE in water determined from this value is +320 mV. This value deviates more than 100 mV from our value of +210 mV.

Discussion

The close agreement between standard electrode potentials determined potentiometrically and those calculated from medium ionic activity coefficients through solubility products, Table VII, implies that the TATB assumption is valid in the studied solvents. This proves that solubility product measurements can be as reliable a method as emf measurements for determination of ΔG_{tr}° values of univalent single ions. The determination of the medium ionic activity coefficients from solubility products of 1:1 salts can

be erroneous if the salt is incompletely dissociated or if the solubility product is determined for a solid solvate of the salt [10]. The selection of salts is therefore crucial. Pyridine and THT both have low dielectric constants. The salts used in the calculations in this work have been proved to be completely dissociated. The amines triethylamine, piperidine and hexylamine have dielectric constants lower than THT and pyridine and very few salts are found to dissociate in these solvents.

The original assumption by Grunwald *et al.*, where the PPh_4^+ ion is used instead of the $AsPh_4^+$ ion, is certainly as good as the TATB assumption. It is to be assumed that the PPh_4^+ ion has an ionic volume closer to the BPh_4^- ion, than to the $AsPh_4^+$ ion [5]. Thus it is possible that the original assumption is even better than the TATB. However, the difference in physical properties between the PPh_4^+ and $AsPh_4^+$ ions is very small and the choice of cation will probably not affect the results [26].

Methanol is a protic solvent with many physical properties similar to water, and therefore the difference in solvating properties between water and methanol should be fairly small. Previous studies have shown that methanol solvates hard acceptors significantly weaker than water, while the difference in solvation of soft acceptors is fairly small [48, 49]. Methanol is therefore expected to solvate metal ions slightly weaker than water, and this is indeed found for the univalent metal cations studied, Table V. This means also that the standard electrode potentials of the $M(s)/M^+$ couples are more positive, and the metals are more noble, in methanol than in water, Table VI and Figs. 1 and 2. The halides are slightly weaker solvated in methanol than in water because methanol forms weaker hydrogen bonds than water. Ions like tetraphenylarsonium, tetraphenylborate, tetraalkylammonium, picrate and trifluoromethylsulfonate with organic groups facing the solvent are on the other hand more strongly solvated in methanol since methanol interacts more strongly through van der Waals forces with organic groups than water.

Acetonitrile is an aprotic solvent which solvates metal ions in a unique and irregular pattern. The alkali ions are poorly solvated by acetonitrile, Table V. This shows that acetonitrile solvates typically hard acceptors poorly in spite of a high dipole moment and dielectric constant. The univalent d^{10} acceptors silver(I) and gold(I), and especially copper(I), are strongly solvated by acetonitrile, Table V. The difference in standard electrode potential between $Ag(s)/Ag^+$ and $Cu(s)/Cu^+$ is larger in acetonitrile, 590 mV, than in water, 280 mV. The reason for this specific solvation of copper(I) is not fully understood. The soft divalent d^{10} acceptor mercury(II) as well as the borderline d^{10} acceptors zinc(II) and cadmium(II) are, on the other hand, poorly solvated in acetonitrile [49, 50]. Acetonitrile is furthermore a

poor solvent for the proton [4], Table V. It should be regarded as a weak donor in general, but with especially strong solvation properties towards univalent d^{10} acceptors.

The solvation of halide ions is substantially weaker in acetonitrile than in water. Acetonitrile is an aprotic solvent and it is not able to form hydrogen bonds. The ΔG_{tr}^o values from water to acetonitrile decrease in the order $Cl^- > Br^- > I^-$, because the strength of the hydrogen bonds decreases in the same order. Ions with a hydrocarbon surface are much more strongly solvated in acetonitrile than in water for the same reason as in methanol, discussed above.

DMSO is an aprotic solvent with a high dipole moment, 3.96 D, and a dielectric constant of 46.7. It can coordinate via its oxygen or sulfur atom. Coordination via the sulfur atom is only found for the very soft acceptors palladium(II), platinum(II), ruthenium(II, III), iridium(III) and rhodium(III) [51–53]. The cations in this study are all coordinating DMSO through its oxygen atom. There is however an uncertainty about the coordination to the soft acceptor gold(I). Previous studies have shown that DMSO forms stronger electrostatic and covalent bonds than water [46]. All ions except the halide and thiocyanate ions are indeed more strongly solvated in DMSO than in water, Table V.

Pyridine is regarded as a strong donor solvent. It is a fairly strong base in aqueous solution. The dipole moment of pyridine is 2.24 D. The dielectric constant, $\epsilon = 12.1$, is low. Pyridine is a typical soft donor solvent, which solvates soft acceptors well and hard ones poorly [49]. This is shown nicely by the very negative ΔG_{tr}^o values for the soft d^{10} acceptors and by positive ΔG_{tr}^o values for the alkali ions. This indicates that pyridine participates preferably in covalent bonds, while the electrostatic interactions to pyridine are fairly weak because of the low dipole moment.

Tetrahydrothiophene, THT, is a sulfur donor solvent with a low dielectric constant, $\epsilon \simeq 8$. This strongly affects the solution chemistry for this solvent. Ion pairs are easily formed in solvents with low dielectric constants. A very limited number of salts are completely dissociated in THT. Therefore only a few ΔG_{tr}^o values have been possible to determine. THT is a very typical soft donor solvent, solvating soft acceptors very well; e.g. the soft acceptor mercury(II) in $HgBr_2$ complexes is slightly stronger solvated by THT than by pyridine [49]. On the other hand, sulfur donor solvents, including THT, form extraordinarily weak electrostatic interactions to hard and borderline acceptors [49, 50]. Among the alkali ions, only the ΔG_{tr}^o value for the sodium ion has been determined. The transfer of the sodium ion from water to THT is, as expected, very unfavorable; the standard electrode potential of the $Na(s)/Na^+$ couple is 350 mV more positive in THT

than in water. The softer the acceptor is, the more strongly it is solvated by THT. This is shown by the ΔG_{tr}° values to THT, where ΔG_{tr}° is considerably larger for Ag^+ than for Cu^+, while the opposite is found for the other aprotic solvents.

Liquid ammonia is a unique solvent in the sense that it solvates both hard and soft acceptors very well, Table V. It has a fairly high dielectric constant compared to pyridine, and the highest dipole moment of the NR_3 compounds ($R = H$ or alkyl), $\mu = 1.47$ D. This is partly the reason for its physical and solvating properties. Liquid ammonia is an even stronger electron donor than THT and pyridine [49]. This is also shown by the very low standard electrode potentials of the $Cu(s)/Cu^+$ and $Ag(s)/Ag^+$ couples, Table VI and Figs. 1 and 2. The alkali ions are solvated to the same extent in liquid ammonia and DMSO. This shows that liquid ammonia is able to form fairly strong electrostatic interactions to hard metal ions [15, 50]. The halide ions are poorly solvated in liquid ammonia, Table V. This indicates that the possible hydrogen bonding between ammonia and the halides is very weak or does not exist at all. The standard electrode potential reflects the solvation of the ion in the $M(s)/M^+$ couple, see 'Calculations and Notations'. The variation in standard electrode potential of the alkali ions is small, e.g. the difference in standard electrode potential, ΔE°, between THT and liquid ammonia for the sodium ion is 630 mV. The solvation of the proton differs very much between the solvents studied, Table VI. ΔE° for the proton between the extremes acetonitrile and liquid ammonia is as large as 1480 mV. For the soft d^{10} acceptors, ΔE° exceeds 1000 mV between water and the soft donor solvents. This shows that it is easier to vary the standard electrode potentials of soft acceptors, through increasing solvation of the cation, than it is for the hard acceptors. Thallium(I), an acceptor on the borderline between hard and soft is less sensitive to solvent transfer than acceptor extremes discussed above, e.g. ΔE° is only 330 mV for thallium(I) in the solvents studied, Table VI.

The solvation of anions follows a quite different pattern than that of the cations. The differences in solvation between the solvents examined are furthermore fairly small, Fig. 1. 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. The donor properties of the solvents are of no importance for the solvation of anions, which are donors themselves. The halides are especially well solvated in solvents prone to hydrogen bonds.

Acknowledgement

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