Determination of Heats and Entropies of Transfer for some Univalent Ions from Water to Methanol, Acetonitrile, Dimethylsulfoxide, Pyridine and Tetrahydrothiophene

MATS JOHNSSON and INGMAR PERSSON

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

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Abstract

The heats of solution, ΔH_s°, for a large number of 1:1 salts have been determined in water, methanol, acetonitrile, dimethylsulfoxide, pyridine and tetrahydrothiophene. The heats of transfer, ΔH_{tr}°, from water to the other solvents for 21 univalent ions have been calculated from the heats of solution determined in this study and values taken from the literature. The extrathermodynamic tetraphenylarsonium tetraphenylborate assumption, stating that, $\Delta H_{tr}^\circ(AsPh_4^+) = \Delta H_{tr}^\circ(BPh_4^-)$ for all pairs of solvents, have been applied to calculate the ΔH_{tr}° values for single ions. The entropies of transfer, ΔS_{tr}°, of single ions have been calculated from Gibbs free energies and heats of transfer. The solvents used in this study represent a wide range of donor properties. Water and methanol are hard oxygen donor solvents, which solvate hard acceptors fairly well and soft acceptors poorly. Dimethylsulfoxide is, for the studied acceptors, an oxygen donor solvent. It solvates hard acceptors very well and soft acceptors fairly well. Pyridine, a nitrogen donor, and tetrahydrothiophene, a sulfur donor, are typical soft donor solvents, solvating soft acceptors very well and hard acceptors poorly. Acetonitrile shows a specific solvation of univalent d^{10} acceptors, while it solvates other acceptors fairly poorly. The halides are more weakly solvated in aprotic solvents because these are not able to form hydrogen bonds. In spite of stronger solvation of several ions in water, the heats of transfer to other solvents are generally negative. The negative ΔS_{tr}° values arise from the difference in bulk order between water which is well-ordered through hydrogen bonding, and the less ordered aprotic solvents.

Introduction

As part of transfer thermodynamic studies, the heats of transfer from water (W) to methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py) and tetrahydrothiophene (THT) for 21 univalent ions are reported in this paper, including

those taken from the literature [1]. The choice of solvents has been discussed in a previous paper, also reporting the Gibbs free energy of transfer, ΔG_{tr}°, for the same ions and solvents [2]. The tetraphenylarsonium tetraphenylborate (TATB) assumption [3, 4] has been applied as the necessary extrathermodynamic assumption in this study.

The strength of the solvation depends on the kind of interaction which is formed between the ion and the solvent molecules. Solvation through van der Waals interactions is always present in condensed phases, but it is dominating only in a very limited number of solvents, e.g. alkanes, alkenes and benzene [5]. The energy gained through van der Waals solvation of ionic compounds is never large enough on its own to exceed the lattice energies. Ionic compounds can therefore not be dissolved in this kind of solvent. Solvents with one or several donor atoms are in most cases able to form interactions with ions of varying character. The degree of electrostatic and covalent contribution varies widely between different kinds of solvents. Hard acceptors are most strongly solvated in solvents able to form strong electrostatic interactions with ions. Oxygen and nitrogen donor solvents, in general, solvate hard acceptors well, while solvents with polarizable donor atoms such as phosphorous and sulfur solvate hard acceptors poorly [1, 2, 6]. Soft acceptors form the strongest solvates with solvents able to develop strong covalent bonds, e.g. phosphorous and sulfur donor solvents [6]. Among the nitrogen donor solvents, liquid ammonia, amines and pyridine solvate soft acceptors well, while nitriles solvate these acceptors, except for the univalent d^{10} acceptors, poorly [6]. Oxygen donors, in general, solvate soft acceptors poorly [6].

Anions are solvated through the electrostatic forces formed between the ion and the solvent molecule dipoles surrounding it. The donor properties of a solvent are of no importance since anions are donors themselves. Anions prone to form hydrogen bonds are especially well solvated in protic solvents; thus the halides are more strongly solvated in protic than in aprotic solvents [2, 7].

Methanol solvates hard and soft acceptors, as well as halides more weakly than water. Methanol forms weaker electrostatic forces than water, probably because of a lower dipole moment. Methanol also forms weaker hydrogen bonds than water [6]. This causes a weaker solvation of species, such as the lighter halides, which are prone to hydrogen bonding.

Acetonitrile solvates the univalent d^{10} acceptors especially well, while the other univalent cations, as well as soft divalent d^{10} acceptors, are poorly solvated. The halides are markedly weaker solvated in acetonitrile than in water because no hydrogen bonding is possible and only weak electrostatic interactions are formed in acetonitrile.

Dimethylsulfoxide (DMSO) is an oxygen donor to all acceptors in this study. It has a high dipole moment, $\mu = 3.96$ D, and a high dielectric constant, $\epsilon = 46.7$ [8]. DMSO solvates hard acceptors such as the alkali ions, very well, while soft acceptors are fairly well solvated. DMSO, however, solvates soft acceptors more strongly than most other oxygen donor solvents [1].

Pyridine is an aprotic nitrogen donor solvent with a fairly high dipole moment, $\mu = 2.19$ D, but a relatively low dielectric constant, $\epsilon = 12.1$ [8]. It solvates soft acceptors well, while its interactions with hard acceptors are quite weak [2, 7].

Tetrahydrothiophene (THT) is an aprotic sulfur donor solvent with a dipole moment of 1.90 D [8] and a low dielectric constant, $\epsilon \approx 8$. Sulfur donor solvents, including THT, solvate soft acceptors slightly stronger than pyridine, while they solvate acceptors such as the alkali ions extraordinarily poorly [2]. This is obviously because sulfur has limited abilities to participate in electrostatic interactions; the reason for this behaviour is however uncertain.

Transfer thermodynamics from water to liquid ammonia have been introduced in this paper for comparison. Liquid ammonia is a unique solvent in the sense that it solvates both hard and soft acceptors very well [2]. On the other hand, it solvates the halides as weakly as aprotic solvents, which indicates that the possibilities for hydrogen bonding in liquid ammonia are very limited.

Calculations

The heats of transfer, ΔH_{tr}°, for salts are calculated from the heats of solution, ΔH_s°, for the salts in water and in the solvents examined, according to

$$\Delta H_{tr}^{\circ}(w, s) = \Delta H_s^{\circ}(s) - \Delta H_s^{\circ}(w)$$

In order to determine the heats of transfer of single ions, an extrathermodynamic assumption must be applied. The tetraphenylarsonium tetraphenylborate assumption [3, 4], TATB, has been applied in this

study. The choice of extrathermodynamic assumption has been discussed in a previous paper [2]. The TATB assumption is based on the fact that the $AsPh_4^+$ and BPh_4^- ions are equally solvated in all solvent pairs, thus

$$\Delta H_{tr}^{\circ}(AsPh_4^+) = \Delta H_{tr}^{\circ}(BPh_4^-)$$

$$\Delta G_{tr}^{\circ}(AsPh_4^+) = \Delta G_{tr}^{\circ}(BPh_4^-)$$

$$\Delta S_{tr}^{\circ}(AsPh_4^+) = \Delta S_{tr}^{\circ}(BPh_4^-)$$

Tetraphenylarsonium tetraphenylborate is only slightly soluble in the solvents studied. The heat of transfer of this salt is calculated by combining the heats of transfer for some other salts. For example from water to acetonitrile it can be calculated as follows

$$\Delta H_{tr}^{\circ}(AsPh_4BPh_4) = \Delta H_{tr}^{\circ}(AsPh_4I) + \Delta H_{tr}^{\circ}(NaBPh_4)$$
$$- \Delta H_{tr}^{\circ}(NaI)$$

and from water to pyridine as follows

$$\Delta H_{tr}^{\circ}(AsPh_4BPh_4) = \Delta H_{tr}^{\circ}(AsPh_4Cl) + \Delta H_{tr}^{\circ}(NaBPh_4)$$
$$- \Delta H_{tr}^{\circ}(NaSCN) - \Delta H_{tr}^{\circ}(Et_4NCl)$$
$$+ \Delta H_{tr}^{\circ}(Et_4NSCN)$$

By definition

$$1/2\Delta H_{tr}^{\circ}(AsPh_4BPh_4) = \Delta H_{tr}^{\circ}(AsPh_4^+) = \Delta H_{tr}^{\circ}(BPh_4^-)$$

The entropies of transfer for single ions are calculated according to

$$\Delta S_{tr}^{\circ} = (\Delta H_{tr}^{\circ} - \Delta G_{tr}^{\circ})T^{-1}$$

Experimental

Solvents

The solvents were purified as described previously and stored over 3 Å molecular sieves [2, 8].

Chemicals

All commercial chemicals used in this study were of analytical grade. The elemental analysis and the melting points of prepared compounds are listed in Table I, otherwise they are given earlier [2].

Preparation of Salts

The preparation method of salts not given below is described previously [2].

Tetraphenylarsonium picrate was prepared as described by Popov and Humphrey [9].

Sodium picrate was prepared by neutralization of picric acid with sodium hydroxide. The product was recrystallized from acetone.

Sodium thiocyanate (Merck reagent) was dried at reduced pressure in 110 °C for at least 24 h.

Rubidium, cesium, thallium(I) and tetraethylammonium trifluoromethylsulfonate were prepared by

TABLE I. Melting Points (°C) of Prepared Salts used in the Measurements in This Study

	Melting point	Characteristics	Elemental analysis Found (calculated)			
			C	S	H	N
AsPh₄Pic	200–202[a]	yellow crystals				
NaPic	275–277	yellow crystals				
KPic		yellow needles				
RbCF₃SO₃	247–249	white powder	5.18–5.24 (5.2)	12.7 (13.7)		
CsCF₃SO₃	266–268	white powder	4.31–4.39 (4.3)	10.8–10.9 (11.4)		
TlCF₃SO₃	241–243	white powder	3.39–3.41 (3.4)	8.57–8.75 (9.1)		
Et₄NCF₃SO₃	141–143	white powder	38.8–38.9 (38.9)	11.3–11.5 (11.4)	7.26–7.30 (7.2)	5.02–5.04 (5.0)
Bu₄NBPh₄	231–233	white powder	85.3–85.6 (85.6)		10.1–10.2 (10.0)	2.39–2.45 (2.5)
Bu₄NPic	86–88	yellow powder	56.2 (56.2)		7.86–8.02 (8.1)	12.2 (11.9)

[a]Ref. 9 reports 203–204.

neutralization of aqueous solution of the corresponding hydroxide with trifluoromethylsulfonic acid. The obtained white salts were recrystallized from acetone and diethylether.

Thallium(I) perchlorate was prepared by mixing barium perchlorate with thallium(I) sulfate. The solution was evaporated to leave the product which was recrystallized from acetone.

Tetrabutylammonium tetraphenylborate was precipitated when mixing aqueous solutions of tetrabutylammonium chloride and sodium tetraphenylborate.

The other tetraalkylammonium salts were recrystallized from acetone or from acetone and diethylether.

All salts were kept over phosphorous pentoxide under reduced pressure.

Calorimetric Measurements

The measurements were performed in an ampoule calorimeter described previously [10, 11]. The heats of solution were measured in a gold vessel containing 80 ml solvent. The measurements were performed in pure solvents without supporting electrolyte. The concentration of the salt during the measurements never exceeded 20 mM. The salts were dissolved within a few minutes in most cases. However, several salts with low solubility in tetrahydrothiophene took somewhat longer to dissolve. For all salts at least six experiments in close agreement were performed. Different amounts of salt were dissolved in order to check if the heats of solution varied with the con-

centration. This behaviour was, however, not seen in any of the cases. Only salts that proved to be completely dissociated, checked from conductometric studies, were examined. The salts were transferred into the ampoules in a glove box filled with dry nitrogen, to avoid contact with moisture. In water, methanol, acetonitrile and dimethylsulfoxide it is possible to use ampoules sealed with a rubber plug covered with wax. Pyridine and tetrahydrothiophene dissolve the wax and therefore another type of ampoule sealed by burning was used. The ampoules were cooled during the sealing in order to protect the salt from decomposition. All experiments were carried out at 25.000 ± 0.002 °C.

Results

The heats of solution, ΔH_s°, determined in this study and those taken from the literature are summarized in Table II. The larger errors generally found in ΔH_s° in tetrahydrothiophene are due to low solubility and slow dissolution of the salts.

The heats of transfer to tetrahydrothiophene are calculated from DMSO, since salts soluble in tetrahydrothiophene are, in general, not sufficiently soluble in water. The heats of transfer from water to tetrahydrothiophene are calculated according to

$$\Delta H_{tr}^{\circ}(W, THT) = \Delta H_{tr}^{\circ}(W, DMSO)$$

$$+ \Delta H_{tr}^{\circ}(DMSO, THT)$$

TABLE II. Heats of Solution (ΔH_s° (kJ mol^{-1})) of Salts in Water (W), Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py) and Tetrahydrothiophene (THT) at 25 °C

	H$_2$O	M	AN	DMSO	Py	THT
AsPh$_4$Pic			+26.9 ± 1.4	+26.0 ± 0.4	+15.6 ± 1.3	+24.4 ± 0.9
AsPh$_4$Cl	−10.5[a] −10.7[c]	−4.2[b]	−0.2[a]	−3.8[c] −5.9[d]	−5.4[a]	
AsPh$_4$I	+34.6[e]		+17.6[f]	+11.6[g] +14.4[e]		
NaBPh$_4$	−19.1[a] −19.9[e]	−42.1[b]	−42.5[a]	−59.7[e] −59.9[g]	−72.2[a]	−60.3 ± 3.4
NaPic	+37.0 ± 0.9	+15.6 ± 5.0		−4.2 ± 0.5 −3.7[g]		
NaCl	+3.8[f]	−7.8[b]		−7.0[h]		
NaI	−7.5[f] −7.8[e]	−29.7[b]	−27.6[f]	−48.2[e] −47.9[g]		
NaSCN	+7.0[a]	−16.7[i]	−9.0 ± 0.9	−26.8 ± 0.4	−28.2[a]	
KPic				+11.5 ± 0.8		
KI	+20.5[f] +20.3[e]	−0.5[b]	−10.2[j]	−27.0[h, d] −25.7[e]		
KCF$_3$SO$_3$	+18.4 ± 0.5 +17.2[k]	+3.7 ± 0.7 +3.2[k]	−4.7 ± 0.8 −2.9[k]	−16.3[k]	−9.5 ± 0.3	
RbCF$_3$SO$_3$	+25.5 ± 1.0				−6.2 ± 0.6	
CsCF$_3$SO$_3$	+29.0 ± 0.8				−3.0 ± 0.3	
AgClO$_4$	+9.9[m]		−47.5[m]	−60.3[m]	−115.7[m]	−90.4[m]
AgCF$_3$SO$_3$				−57.8 ± 1.0		−91.2 ± 1.5
TlClO$_4$	+38.6 ± 3.1					
TlCF$_3$SO$_3$	+19.8 ± 0.5	+3.7 ± 0.1		−22.8 ± 0.8	−41.2 ± 1.4	
NH$_4$SCN	+22.3 ± 1.5	−0.6 ± 0.4	+8.4 ± 0.5	−17.9 ± 0.3	−19.0 ± 0.7	
Et$_4$NCl	−12.1[a] −12.6[e]	+4.0[b]	+6.6[a]	+10.1[e]	+12.4[a]	
Et$_4$NBr	+6.2[a] +5.8[e]	+20.5[b]	+12.3[a]	+13.7[e]	+13.4[a]	
Et$_4$NI	+27.3[a] +28.6[e]	+34.5[b]	+18.5[a]	+18.8 ± 0.7 +20.3[e]	+15.9[a]	
Et$_4$NSCN	+19.2[a]				+11.0[a]	
Et$_4$NClO$_4$	+30.9[a]	+37.4[b]	+12.9[a]	+15.7[c]	+8.4[a]	
Et$_4$NCF$_3$SO$_3$	+4.7 ± 0.1				−2.6 ± 0.3	
Bu$_4$NBPh$_4$				+32.3 ± 0.4		+11.8 ± 1.6
Bu$_4$NPic				+38.2 ± 0.2		+25.0 ± 1.3
Bu$_4$NCl	−28.9[a] −29.8[c]			+13.5 ± 1.4 +13.5[c]	+7.2[a]	+4.8 ± 1.3
Bu$_4$NBr	−7.9[a] −8.4[c]	+17.5[b]		+20.9 ± 0.9 +20.7[c]	+10.8[a]	+13.0 ± 1.1
Bu$_4$NI	+15.0[a]	+35.8[b]	+27.2[a]	+27.7 ± 1.1 +30.4[c]	+16.1[a]	+6.0 ± 1.8
Bu$_4$NSCN				+18.3 ± 0.8		+16.1 ± 1.6
Bu$_4$NClO$_4$		+28.7[b]		+15.7 ± 0.5 +16.5[c]		+14.6 ± 0.6
Bu$_4$NBF$_4$	6.3 ± 0.6	+30.6 ± 0.9	+12.4 ± 0.5	+16.4 ± 0.4	−6.3 ± 0.1	+17.2 ± 0.7

[a]Ref. 7.   [b]Ref. 12.   [c]Ref. 13.   [d]Ref. 14.   [e]Ref. 1.   [f]Ref. 15.   [g]Ref. 16.   [h]Ref. 17.   [i]Calc. from ref. 12.
[j]Ref. 18.   [k]Ref. 19.   [m]Ref. 20.

The heats of transfer for the salt AsPh$_4$BPh$_4$ from water to methanol, acetonitrile, dimethylsulfoxide and pyridine have been calculated previously [4, 7].

No values of heats of solution in tetrahydrothiophene seem to have been reported earlier. The heat of transfer for the salt AsPh$_4$BPh$_4$ to tetrahydrothio-

TABLE III. Heats of Transfer (ΔH_{tr}° (kJ mol^{-1})) of ions from Water (W) to Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py), Tetrahydrothiophene (THT) and Liquid Ammonia (NH₃) at 25 °C, Calculated from Heats of Solution in Table I. Values in Parentheses are Uncertain

	W to M	W to AN	W to DMSO	W to Py	W to THT	W to NH₃ [a]
AsPh₄⁺	−2.6	−10.2	−11.2	−22.8	−15.6	
Na⁺	−20.5	−13.1	−28.9	−30.3	−25.0	−36
K⁺	−19.3	−23.9	−35.7	−24.1		−26
Rb⁺	−16.5[a]	−24.6[a]	(−35[a])	−27.8		−25
Cs⁺	−14.1[a]		−33.0[a]	−28.1		−33
Cu⁺		−72[b]	−42[b]	−127[b]	−91[c]	
Ag⁺	−20.9[a]	−41.4	−51.3	−106.5	−96.3	−106
Tl⁺	−20.7		−44.7	−57.1		
NH₄⁺	−19.7	−11.2	−35.3	−36.4		
Et₄N⁺	+7.8	−1.9	+3.7	−3.4		
Bu₄N⁺	+20.7	+19.0	+24.6	+8.2	+8.6	
H⁺		+56.0[d]	−11.5[d]	−43.6[d]		
BPh₄⁻	−2.6	−10.2	−11.2	−22.8	−15.6	
Pic⁻	−0.9	−12.4	−12.3	−12.0	−9.5	
Cl⁻	+8.9	+20.5	+18.1	+27.9	+25.4	+6
Br⁻	+6.5	+8.0	+3.8	+10.6	+11.9	−16
I⁻	−1.7	−6.8	−11.8	−8.0	(−17.5)	−29
SCN⁻	−3.2	−2.7	−4.9	−4.9	+8.9	
ClO₄⁻	−1.3	−16.1	−18.9	−19.1	−4.0	
CF₃SO₃⁻	+4.6	+0.8	+2.1	−3.9	+13.7	
BF₄⁻	+3.6	−12.9	−14.5	−20.8	+2.3	

[a]Ref. 1.   [b,c]The heats of transfer for Cu⁺ are calculated from the heats of solvation of Cu⁺ ([b]ref. 20 and [c]ref. 21) and ΔH_{hydr}(Cu⁺) = −607 kJ mol^{-1}, a value given by D. R. Rosseinsky, *Chem. Rev.*, 65, 467 (1967).   [d]Ref. 22.

phene has been calculated from the values in Table II as follows

$$\Delta H_{tr}^{\circ}(W, THT)(AsPh_4BPh_4) = \Delta H_{tr}^{\circ}(DMSO, THT) \cdot$$

$$(AsPh_4Pic) + \Delta H_{tr}^{\circ}(DMSO, THT)(Bu_4NBPh_4)$$

$$- \Delta H_{tr}^{\circ}(DMSO, THT)(Bu_4NPic)$$

$$+ \Delta H_{tr}^{\circ}(W, DMSO)(AsPh_4BPh_4) = -32.9 \text{ kJ mol}^{-1}$$

By introduction of the TATB assumption we obtain

$$1/2\Delta H_{tr}^{\circ}(AsPh_4BPh_4) = \Delta H_{tr}^{\circ}(AsPh_4^+) = \Delta H_{tr}^{\circ}(BPh_4^-)$$

$$= -16.5 \text{ kJ mol}^{-1}$$

Once the heats of transfer of the AsPh₄⁺ and BPh₄⁻ ions from water to the various solvents have been determined, the other ΔH_{tr}° values for single ions are obtained from suitable combinations of the values in Table II. Because the number of salts and solvents, where heats of solution have been determined, both in this work and in the literature, exceeds the number of ΔH_{tr}° of single ions to be calculated, it has been possible to do some cross-checks. The difference in values calculated by different routes is in most cases very small. The heats of transfer for single ions determined in this study and those taken from the literature are given in Table III. The complete transfer thermodynamics for these single ions

are summarized in Table IV, and in Fig. 1. Due to low solubility of many cesium and thallium(I) salts in acetonitrile it has been impossible to determine ΔH_{tr}° values for the cesium(I) and thallium(I) ions from water to acetonitrile.

Discussion

The heats of transfer from water to methanol and the aprotic solvents examined, are negative for the univalent ions studied, except for the chloride, bromide, trifluoromethylsulfonate and the tetrabutylammonium ions. The heat of solvation can be divided into two main terms; the energy gained at the coordination of solvent molecules to the ion, and the energy consumed when solvent molecules are forced out of the bulk structure and made available for coordination. The first term increases with increasing strength and covalency of the formed solvate bonds. The second term becomes positive, unfavourable, for solvents with a high degree of bulk order, because of fairly strong intermolecular forces. Water, methanol and other protic solvents are well-ordered due to hydrogen bonding between the solvent molecules. Liquid ammonia is in this sense

TABLE IV. Free Energy of Transfer (ΔG_{tr}° (kJ mol^{-1}))[a], Heat of Transfer (ΔH_{tr}° (kJ mol^{-1}))[b] and Entropy of Transfer (given as $T\Delta S_{tr}^{\circ}$ (kJ mol^{-1})) of Ions from Water (W) to Methanol (M), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py), Tetrahydrothiophene (THT) and Liquid Ammonia (NH$_3$) at 25 °C

		W to M	W to AN	W to DMSO	W to Py	W to THT	W to NH$_3$
AsPh$_4^+$	ΔG_{tr}°	−23.4	−33.1	−37.1	−37.7	−10.3	
	ΔH_{tr}°	−2.6	−10.2	−11.2	−22.8	−15.6	
	$T\Delta S_{tr}^{\circ}$	+20.8	+22.9	+25.9	+14.9	−5.3	
Na$^+$	ΔG_{tr}°	+8.0	+14.8	−13.1	+16.0	+33.7	−17.4
	ΔH_{tr}°	−20.5	−13.1	−28.9	−30.3	−25.0	−36
	$T\Delta S_{tr}^{\circ}$	−28.5	−27.9	−15.8	−46.3	−58.7	−19
K$^+$	ΔG_{tr}°	+9.7	+9.1	−13.1	+5.7		−11.6
	ΔH_{tr}°	−19.3	−23.9	−35.7	−24.1		−26
	$T\Delta S_{tr}^{\circ}$	−29.0	−33.0	−22.6	−29.8		−14
Rb$^+$	ΔG_{tr}°	+9.7	+6.8	−10.8	+12.6		−12.5
	ΔH_{tr}°	−16.5	−24.6	−35	−27.8		−25
	$T\Delta S_{tr}^{\circ}$	−26.2	−31.4	−24.2	−40.4		−13
Cs$^+$	ΔG_{tr}°	+9.1	+5.1	−12.6	+30.3		−15.4
	ΔH_{tr}°	−14.1		−33.0	−28.1		−33
	$T\Delta S_{tr}^{\circ}$	−23.2		−20.4	−58.4		−18
Cu$^+$	ΔG_{tr}°		−52.1	−41.5	−82.0	−29.9	−109
	ΔH_{tr}°		−72	−42	−127	−91	
	$T\Delta S_{tr}^{\circ}$		−20	−1	−45	−61	
Ag$^+$	ΔG_{tr}°	+7.4	−22.3	−34.2	−57.1	−51.1	−100.3
	ΔH_{tr}°	−20.9	−41.4	−51.3	−106.4	−96.3	−106
	$T\Delta S_{tr}^{\circ}$	−28.3	−19.1	−17.1	−49.3	−45.2	−6
Tl$^+$	ΔG_{tr}°	+4.6	+10.3	−20.5	−1.1	+8.6	
	ΔH_{tr}°	−20.7		−44.7	−57.1		
	$T\Delta S_{tr}^{\circ}$	−25.3		−24.2	−56.0		
NH$_4^+$	ΔG_{tr}°	+4.9	+16.0				
	ΔH_{tr}°	−19.7	−11.2	−35.3	−36.4		
	$T\Delta S_{tr}^{\circ}$	−24.6	−27.2				
Et$_4$N$^+$	ΔG_{tr}°	+0.6	−8.8	−12.5	+8.0		
	ΔH_{tr}°	+7.8	−1.9	+3.7	−3.4		
	$T\Delta S_{tr}^{\circ}$	+7.2	+6.9	+16.2	−11.4		
Bu$_4$N$^+$	ΔG_{tr}°	−21.7	−33.1				
	ΔH_{tr}°	+20.7	+19.0	+24.6	+8.2	+8.6	
	$T\Delta S_{tr}^{\circ}$	+42.4	+52.1				
H$^+$	ΔG_{tr}°	+10.8	+46.2	−18.8	−28		−96.5
	ΔH_{tr}°		+56.0	−11.5	−43.6		
	$T\Delta S_{tr}^{\circ}$		+9.8	+7.3	−16		
BPh$_4^-$	ΔG_{tr}°	−23.4	−33.1	−37.1	−37.7	−10.3	
	ΔH_{tr}°	−2.6	−10.2	−11.2	−22.8	−15.6	
	$T\Delta S_{tr}^{\circ}$	+20.8	+22.9	+25.9	+14.9	−5.3	
Pic$^-$	ΔG_{tr}°	−4.6	−2.3		−4.6	−12.0	
	ΔH_{tr}°	−0.9	−12.4	−12.3	−12.0	−9.5	
	$T\Delta S_{tr}^{\circ}$	+3.7	−10.1		−7.4	+2.5	

TABLE IV. *(continued)*

		W to M	W to AN	W to DMSO	W to Py	W to THT	W to NH₃
Cl⁻	ΔG_{tr}°	+13.7	+41.7	+39.4	+34.2	+53.7	+43.4
	ΔH_{tr}°	+8.9	+20.5	+18.1	+27.9	+25.4	+6
	$T\Delta S_{tr}^{\circ}$	−4.8	−21.2	−21.3	−6.3	−28.3	−37
Br⁻	ΔG_{tr}°	+11.4	+31.4	+26.3	+20.5	+25.7	+32.8
	ΔH_{tr}°	+6.5	+8.0	+3.8	+10.6	+11.9	−16
	$T\Delta S_{tr}^{\circ}$	−4.9	−23.4	−22.5	−9.9	−13.8	−49
I⁻	ΔG_{tr}°	+7.4	+19.4	+9.1	+19.4		+25.1
	ΔH_{tr}°	−1.7	−6.8	−11.8	−8.0	−17.5	−29
	$T\Delta S_{tr}^{\circ}$	−9.1	−26.2	−20.9	−27.4		−54
SCN⁻	ΔG_{tr}°	+5.7	+12.6	+9.1	+20.0		
	ΔH_{tr}°	−3.2	−2.7	−5.3	−4.9	+8.9	
	$T\Delta S_{tr}^{\circ}$	−8.9	−15.3	−14.0	−24.9		
ClO₄⁻	ΔG_{tr}°	+5.7	+4.0	−1.1	+16.0		
	ΔH_{tr}°	−1.3	−16.1	−18.9	−19.1	−4.0	
	$T\Delta S_{tr}^{\circ}$	−7.0	−20.1	−17.8	−35.1		
CF₃SO₃⁻	ΔG_{tr}°	−16.0	−23.4		−14.3		
	ΔH_{tr}°	+4.6	+0.8	+2.1	−3.9	+13.7	
	$T\Delta S_{tr}^{\circ}$	+20.6	+24.2		+10.4		

[a]Ref. 2.　[b]Values from Table III.

more like the aprotic solvents because of very weak hydrogen bonding. The hydrogen bonding is strong in aqueous solution and of medium strength in alcohols. Tetrahydrothiophene and DMSO also have bulk structure [23], but the intermolecular forces are markedly weaker than the hydrogen bonds [5]. The bulk orders in acetonitrile and pyridine are only due to weak intermolecular electrostatic forces. The energy consumed when solvent molecules are forced out of the bulk structure is, for aprotic solvents, almost negligible compared to the heat of solvation. The negative heats of transfer from water to a solvent with less bulk structure, as seen with ions more strongly solvated in water, strongly indicates that more energy is consumed when water is forced out of the bulk structure upon solvation compared with less structured solvents.

The entropies of transfer are negative for the univalent ions studied except for the tetraphenyl-arsonium, tetraphenylborate, tetraalkylammonium and trifluoromethylsulfonate ions. The entropy of solvation can be divided into two main terms. It is affected firstly by the change in order of the solvent bulk solvating the solute. In most cases, the bulk order decreases with the introduction of a solute because it does not fit into the bulk structure. A well structured solvent will be more affected than a more or less unstructured one, when salts are dissolved. Water is the most well structured of the solvents in

this study and therefore the first entropy of transfer term will be negative on the transfer reaction from aqueous solution. The order of a solvent molecule increases when it is coordinated to an ion. The order of coordinated solvent molecules increases proportionally to the increasing solvate bond strength. The second ΔS_{tr}° term will therefore be more negative with increasing solvation. The second entropy of transfer term will be negative on transfer to a solvent where the ion is more strongly solvated than in water.

Tetraphenylarsonium and Tetraphenylborate Ions

By the definition of the TATB assumption the solvation of these ions is identical in all solvents. These ions are more strongly solvated in non-aqueous solvents than in water, which is shown by negative ΔG_{tr}° values. The positive entropies of transfer indicate a decrease in the overall order. When these ions are 'hydrated', the aqueous bulk structure is supposed to be partly reorganized in such a way that small holes are formed around the AsPh₄⁺ and BPh₄⁻ ions [15]. This means that no water molecules are forced out of the aqueous bulk structure for hydration. The aqueous bulk structure remains almost unaffected at dissolution of these ions. The energy consumed for this reorganization is certainly very small, likewise the change in bulk order and the entropy change. Inter-
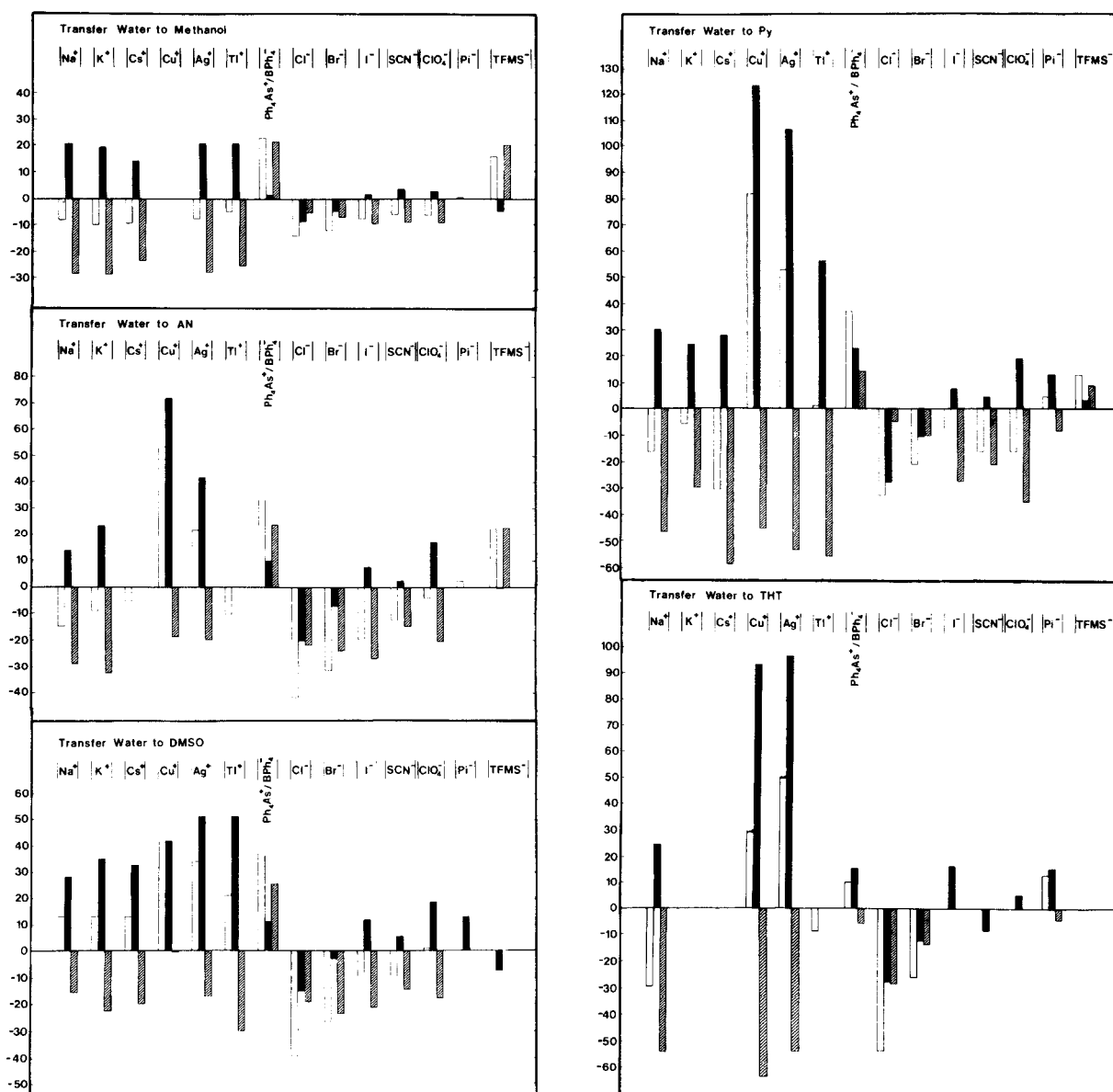
Fig. 1. The changes of free energy, $-\Delta G_{tr}^{\circ}$, (white), enthalpy, $-\Delta H_{tr}^{\circ}$, (black) and entropy, $T\Delta S_{tr}^{\circ}$, (hatched) in kJ mol^{-1} for the transfer of univalent single ions from water to methanol (M), acetonitrile (AN), dimethylsulfoxide (DMSO), pyridine (Py) and tetrahydrothiophene (THT) at 25 °C.

actions are formed between conjugated electron systems as phenyl rings and permanent or induced dipoles of the solvent molecules [2]. In non-aqueous media these interactions are stronger than van der Waals forces [5], and thus stronger than inter-molecular forces in non-structured solvents. The solvent molecules will therefore be forced out of their bulk structure upon solvation and a reorganization of the solvent structure is necessary due to the large size of the ions. All this means that the bulk order decreases and that an overall decrease in order is expected at the transfer of AsPh$_4^+$ and BPh$_4^-$ ions

from water to non-aqueous solvents. These solvation models in aqueous and non-aqueous solution of AsPh$_4^+$ and BPh$_4^-$ ions agree with the transfer thermodynamics, Table IV.

Alkali Ions

The alkali ions are more strongly solvated in DMSO and liquid ammonia than in water, while they are more weakly solvated in the other solvents. The heats and entropies of transfer are negative for these ions to all solvents studied. The alkali ions follow the general solvation pattern discussed above.

The alkali ions are regarded as typical hard electron acceptors, but the charge density is fairly low. The electrostatic forces between the alkali ions and the solvent molecules are therefore fairly weak. The ability of the alkali ions to accept electrons from soft donor solvents is poor. The solvation of the alkali ions is therefore proportional to the ability of a solvent to form electrostatic interactions. Among the solvents in this study, liquid ammonia, DMSO and water form the strongest electrostatic interactions [6].

Thallium(I)

Thallium(I) is a large ion, which is regarded to have acceptor properties on the borderline between hard and soft. In comparison with the alkali ions, the solvation of thallium(I) becomes stronger the softer the solvent becomes. This is nicely illustrated by the differences in ΔG_{tr}° between thallium(I) and sodium; methanol:+6.6, acetonitrile:−4.5, DMSO:−8.0, pyridine:−17.1 and tetrahydrothiophene:−20.4 kJ mol⁻¹. The heats and entropies of transfer for thallium(I) are negative and thus follow the pattern described above.

Copper(I) and Silver(I) Ions

The univalent d¹⁰ ions are regarded as soft acceptors. Silver(I) is somewhat softer than copper(I). Copper(I) is especially strongly solvated by the nitrogen donor solvents acetonitrile, pyridine and liquid ammonia. This can be seen in the very negative ΔG_{tr}° values to these solvents, Table IV. The solvation of silver(I) increases the softer the solvent becomes and special affinity for nitrogen donor solvents is not observed, Table IV. The large negative ΔG_{tr}° values for copper(I) to the nitrogen donor solvents are accompanied by larger negative ΔH_{tr}° values, giving negative ΔS_{tr}° values, comparable to other univalent cations in this study, Table IV.

Tetraalkylammonium Ions

The tetraethylammonium ion is equally solvated in water and methanol, while it is more strongly solvated in acetonitrile and pyridine. The heats and entropies of transfer are positive to methanol and negative to acetonitrile and pyridine. The tetrabutylammonium ion shows a markedly weaker solvation in water than in methanol. In spite of this the heats of transfer are positive to all solvents studied. The tetrabutylammonium ion is thus weakly solvated in water. It seems that the butyl groups of the tetrabutylammonium ion can be orientated in such a way that a water surface is formed around the ion [15], as discussed above; in this only weak van der Waals forces, which are not strong enough to break the hydrogen bonds between the water molecules, develop between the Bu_4N^+ ion and water. In the other solvents, which consist of larger molecules, van der Waals forces stronger than the intermolecular interactions, are formed between the Bu_4N^+ ions and the solvents. When the Bu_4N^+ ions are solvated in non-aqueous solvents, the bulk structure is affected, as discussed for the $AsPh_4^+$ and BPh_4^- ions, and a decrease in the order is obtained.

Halide and Thiocyanate Ions

The halide and thiocyanate ions are more strongly solvated in water than in any of the studied solvents. This is due to the hydrogen bonds formed between water and the anions. The strength of the hydrogen bonds decrease in the order $Cl^- > Br^- > I^- > SCN^-$. The Gibbs free energies of transfer to methanol are positive but not as large as to the aprotic solvents. This shows that methanol is a protic solvent but that it forms weaker hydrogen bonds than water. The heats of transfer for chloride and bromide are positive, while they are negative for iodide and thiocyanate, except for SCN^- to tetrahydrothiophene. The positive ΔH_{tr}° values show that the hydrogen bonds between chloride or bromide and water are stronger than the intermolecular hydrogen bonds in water. In the aprotic solvents there are no specific interactions between molecules and these ions. This agrees with our knowledge that the hydrogen bonds to iodide and thiocyanate are quite weak and that the interactions between water molecules in aqueous solution are at least as strong as the interaction between water and the iodide or thiocyanate ions. The entropies of transfer are, as expected, negative for all systems.

Picrate and Perchlorate Ions

Picrate and perchlorate ions are almost equally solvated in the solvents studied, with picrate slightly stronger solvated and perchlorate slightly weaker solvated than in water. The heats and entropies of transfer are negative, except for a very small positive ΔS_{tr}° value for picrate in tetrahydrothiophene. These ions are only solvated through weak electrostatic forces and any large differences in the solvation of these ions are not expected.

Trifluoromethylsulfonate

The trifluoromethylsulfonate ion is markedly weaker solvated in water than in the other solvents. In spite of this, the heats of transfer are slightly positive, except to pyridine where a small negative value is obtained. This gives large positive entropies of transfer, indicating an overall decrease in order at transfer of the $CF_3SO_3^-$ ion from water to the solvents examined. The solvation of the trifluoromethylsulfonate ion follows the same pattern as the tetrabutylammonium ion discussed above.

Acknowledgement

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