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SOLUTE–SOLVENT INTERACTIONS OF SOME UNIVALENT–UNIVALENT SALTS WITH VARIOUS ORGANIC SOLVENTS AT 25°C

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ABSTRACT

The solubilities of Ph_4AsCl, Ph_4AsBr, Ph_4AsI, $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ in about 13 organic solvents are measured gravimetrically. From their values the free energies and the free energies of transfer are estimated.

From the experimental free energy data of the tetraphenyl derivatives and using the asymmetric tetraphenylarsonium tetraphenylboride assumption, the solute–solvent free energies of transfer of the ions Cl^-, Br^-, I^-, K^+, Rb^+ and Cs^+ are evaluated and discussed.

INTRODUCTION

From the solubilities of some salts in various solvents, the Gibbs free energies of transfer [1] can be calculated by using eqn. (1) (with water as reference solvent):

$$\Delta G_t(\text{salt}) = -2.303RT \log \frac{K_{sp}(\text{organic solvent})}{K_{sp}(\text{water})} \qquad (1)$$

K_{sp} in eqn. (1) represents the thermodynamic solubility product of the salt in the desired solvent. The mean activity coefficient $\gamma_\pm$ of the salt in different solvents required for the evaluation of K_{sp} was calculated from the Debye–Hückel equation [2].

On the other hand, the standard free energy of any univalent–univalent salt can be calculated [3] by the use of eqn. (2):

$$\Delta G(\text{salt}) = -2.303RT \log K_{sp(s)} \qquad (2)$$

where $K_{sp(s)}$ is the solubility product of the salt in the solvent discussed.

The aim of this work is to estimate the thermodynamic standard free energies and free energies of transfer for some univalent–univalent salts.

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Also, using the asymmetric Ph_4AsBPh_4 assumption [4] it is possible to estimate the free energy of transfer of the individual ions used.

EXPERIMENTAL

Saturated solutions of Ph_4AsCl, Ph_4AsBr, Ph_4AsI, $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ in the organic solvents were prepared by adding excess salt to 10 ml of the solvent in a glass tube until a white precipitate persisted. The saturated solutions were shaken in a water bath (of the type Assistent) for 3 days, and allowed to stand for another day without shaking to reach the necessary equilibrium. The solubilities of these salts were determined gravimetrically by evaporating 1–2 ml of the saturated solution in a small aluminium disk (diameter, 3 cm) under an IR lamp to avoid scattering of the solution.

All the organic solvents used, i.e. acetone, dimethylformamide (DMF), acetonitrile, dimethylacetamide, *N*-methylpyrrolidone, methanol, ethanol, hexamethylphosphortriamide, formamide, dimethylsulphoxide (DMSO), propylene carbonate and *N*-methylformamide, are pure solvents from Merck and were used without purification, except that a dehydrating agent (molecular sieve) was added for storage.

RESULTS AND DISCUSSION

Solubilities, standard free energies and standard free energies of transfer of the salts Ph_4AsCl, Ph_4AsBr and Ph_4AsI, calculated using eqs. (1) and (2), are listed in Table 1, together with the mean activity coefficient values. The standard free energies of transfer presented in Table 1 are on a molal scale calculated using eqn. (3):

$$\Delta G_t(\text{molar scale}) + 2.303RT\ 2\log \rho = \Delta G_t(\text{molal scale}) \quad (3)$$

ΔG_t(molar scale) is calculated from eqn. (1) and ρ is the density of the organic solvent, which value was taken from the work of Kim [5]. The solubilities of the univalent–univalent electrolytes represented in Table 1 decrease in the series of solvents in the order: water > methanol > DMSO > DMF > acetonitrile > dimethylacetamide > propylene carbonate > *N*-methylpyrrolidone > formamide.

The exothermicity or endothermicity of the free energy of transfer values shown in Table 1 depends on the nature of the anion. The endothermic transfers from water occur with those anions which are strong hydrogen-bond acceptors (e.g. Cl^-) and thus interact strongly with water, which is a strong hydrogen-bond donor [6,7]. The endothermicity is greatest for transfer from water to dipolar aprotic solvents, which are not hydrogen-bond donors as in

TABLE 1

Solubilities and standard free energies of transfer from water to organic solvents for Ph_4AsCl, Ph_4AsBr and Ph_4AsI (kcal mol^{-1} on a molal scale at 25 °C)

Organic solvents	Molal solubility	log γ_+	ΔG	ΔG_t
Ph_4AsCl				
Methanol	1.406	−0.480	0.906	0.186
DMF	0.526	−0.370	1.771	1.051
Acetonitrile	0.459	−0.371	1.934	1.214
Dimethylacetamide	0.224	−0.305	2.605	1.886
DMSO	1.076	−0.312	0.764	0.044
N-Methylpyrrolidone	0.229	−0.375	2.769	2.0496
ΔG (in H_2O) = 0.7197				
Ph_4AsBr				
Methanol	1.447	−0.473	0.853	−3.171
DMF	0.665	−0.377	1.513	−2.511
Acetonitrile	0.666	−0.391	1.548	−2.476
DMSO	0.797	−0.294	1.071	−2.953
N-Methylpyrrolidone	0.389	−0.406	2.226	−1.798
ΔG (in H_2O) = 4.024				
Ph_4AsI				
Acetone	5.159×10^{-2}	−0.440	4.711	−2.207
DMF	0.257	−0.313	2.463	−4.455
Acetonitrile	0.104	−0.263	3.396	−3.522
Dimethylacetamide	0.108	−0.249	3.313	−3.605
DMSO	0.251	−0.234	2.276	−4.64
N-Methylpyrrolidone	0.184	−0.345	2.946	−3.972
Formamide	0.171	−0.304	1.876	−5.042
Propylene carbonate	0.218	−0.153	2.222	−4.696
ΔG (in H_2O) = 6.918				

the case of $\Delta G_t(Ph_4AsCl)$ in *N*-methylpyrrolidone, dimethylacetamide and DMF (see Table 1). The free energies of transfer of Ph_4AsBr and Ph_4AsI are exothermic because Br^- and I^- are weak hydrogen-bond acceptors and also highly polarizable [8].

Standard free energies of solution ΔG of $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ in water and standard free energies of transfer ΔG_t of the electrolytes from water to acetone, DMF, acetonitrile, dimethylacetamide, DMSO, *N*-methylpyrrolidone, methanol, ethanol, hexamethylphosphortriamide, formamide, glycol, *N*-methylformamide and propylene carbonate, all at 25 °C, are shown in Table 2. The free energy data on the molal scale, obtained from the solubility products, have been adjusted to allow for ion association and Debye–Hückel salt effects ($\gamma_\pm$) as described previously. All electrolytes in Table 2 are more soluble in water than in non-aqueous solvents at 25 °C. The free energies of transfer of $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ are exothermic. The increase in the exothermicity of these salts on transfer from

TABLE 2

Solubilities and standard free energies of transfer from water to organic solvents for $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ (kcal mol^{-1} on a molal scale at 25 °C)

Organic solvent	Molal solubility	Log $\gamma_{\pm}$	ΔG	ΔG_t
$KBPh_4$				
Acetone	1.659×10^{-1}	-0.627	3.839	-6.63
DMF	1.1187	-0.455	1.108	-9.361
Acetonitrile	6.912×10^{-2}	-0.2527	3.855	-6.614
Dimethylacetamide	1.107	-0.427	1.087	-9.382
DMSO	1.2111	-0.3396	0.699	-9.770
N-Methylpyrrolidone	1.0516	-0.5584	1.464	-9.005
Methanol	4.879×10^{-3}	-0.1284	6.657	-3.812
Ethanol	6.251×10^{-4}	-0.0684	8.927	-1.541
Hexamethylphosphortriamide	0.8255	-0.579	1.807	-8.662
Formamide	0.0319	-0.0157	4.124	-6.076
Glycol	1.0012	-0.381	1.038	-9.431
N-Methylformamide	0.4579	-0.0538	1.072	-9.397
ΔG (in H_2O) = 10.469				
$RbBPh_4$				
Acetonitrile	0.0192	-0.105	5.133	-6.466
Dimethylacetamide	0.714	-0.395	1.471	-10.128
Formamide	0.68×10^{-2}	-0.0226	5.975	-5.625
Propylene carbonate	0.0618	-0.1126	7.902	-3.698
ΔG (in H_2O) = 11.6				
$CsBPh_4$				
Acetone	3.37×10^{-2}	-0.408	5.129	-7.501
DMF	0.4784	-0.372	1.888	-1.074
Acetonitrile	2.136×10^{-2}	-0.169	5.018	-7.613
Dimethylacetamide	0.686	-0.381	1.486	-11.145
DMSO	0.7211	-0.3008	1.208	-11.423
N-Methylpyrrolidone	0.785	-0.4699	1.569	-11.062
Methanol	8.077×10^{-4}	-0.0498	8.573	-4.058
Ethanol	1.114×10^{-4}	-0.0301	10.866	-1.765
Hexamethylphosphortriamide	0.5996	-0.495	1.956	-10.675
Formamide	2.11×10^{-3}	-0.0132	7.335	-4.665
Glycol	1.589×10^{-3}	-0.0483	17.712	+5.082
N-Methylformamide	0.105	-0.033	2.760	-9.871
Propylene carbonate	2.58×10^{-2}	-0.0819	4.557	-7.4434
ΔG (in H_2O) = 12.63				

water to dipolar aprotic solvents is the result of a substantial loss of entropy. The free energies of transfer of the Cs^+ salt are more exothermic than those of both Rb^+ and K^+ salts as a result of the combined effects of dispersion and cavity-forming interactions [9].

The standard free energies of transfer of KCl, KBr, KI, RbCl, RbBr, RbI, CsCl, CsBr and CsI are evaluated indirectly from the experimental data for

TABLE 3

Standard free energies of transfer from water to organic solvents for KCl, KBr and KI calculated by eqns. (4)–(6) (kcal mol^{-1} on a molal scale at 25 °C)

Organic solvent	KCl	KBr	KI
Methanol	8.284	4.927	–
DMF	10.150	6.588	4.644
Acetonitrile	10.880	7.190	6.144
Dimethylacetamide	11.284	–	5.793
DMSO	7.804	4.807	3.12
N-Methylpyrrolidone	12.185	8.337	6.163
Formamide	–	–	0.072

the tetraphenyl derivatives tabulated in Tables 1 and 2 and from the ΔG_t values for Ph_4AsBPh_4 reported by Kim [5] by using the following equations:

$$\Delta G_t(KCl) = \Delta G_t(Ph_4AsCl) + \Delta G_t(KBPh_4) - \Delta G_t(Ph_4AsBPh_4) \quad (4)$$

$$\Delta G_t(KBr) = \Delta G_t(Ph_4AsBr) + \Delta G_t(KBPh_4) - \Delta G_t(Ph_4AsBPh_4) \quad (5)$$

$$\Delta G_t(KI) = \Delta G_t(Ph_4AsI) + \Delta G_t(KBPh_4) - \Delta G_t(Ph_4AsBPh_4) \quad (6)$$

On applying eqns. (4)–(6) to Rb^+ and Cs^+, the salts $RbBPh_4$ and $CsBPh_4$ instead of $KBPh_4$ are substituted into the previous equations. The calculated values are recorded in Tables 3–5. The orders of ΔG_t for MX salts are

$KCl > KBr > KI$ $\quad$ $RbCl > RbBr > RbI$ $\quad$ $CsCl > CsBr > CsI$

being the result of competitive effects [10]. The relative order, $\Delta G_t(KCl) > \Delta G_t(KBr) > \Delta G_t(KI)$, is probably due to increased destabilization of the simple anions.

From the values of $\Delta G_t(Ph_4As^+)$ and $\Delta G_t(Ph_4B^-)$ measured by the asymmetric Ph_4AsBPh_4 model [5] and by using eqns. (7) and (8) the single-ion free energies of transfer for Cl^-, Br^-, I^-, K^+, Rb^+ and Cs^+ are calculated and displayed in Tables 6 and 7:

$$\Delta G_t(X^-) = \Delta G_t(Ph_4AsX) - \Delta G_t(Ph_4As^+) \quad (7)$$

TABLE 4

Standard free energies of transfer from water to organic solvents for RbCl, RbBr and RbI calculated by eqns. (4)–(6) (kcal mol^{-1} on a molal scale at 25 °C)

Organic solvent	RbCl	RbBr	RbI
Acetonitrile	11.028	7.338	6.292
Dimethylacetamide	6.766	–	4.727
Formamide	–	–	0.523
Propylene carbonate	–	–	8.646

TABLE 5

Standard free energies of transfer from water to organic solvents for CsCl, CsBr and CsI calculated by eqns. (4)–(6) (kcal mol^{-1} on a molal scale at 25 °C)

Organic solvent	CsCl	CsBr	CsI
Methanol	15.268	11.91	–
Acetone	–	–	6.232
DMF	18.437	14.875	12.931
Acetonitrile	9.881	6.191	5.145
Dimethylacetamide	9.521	–	4.030
DMSO	6.151	3.154	1.467
N-Methylpyrrolidone	10.127	6.28	4.106
Formamide	–	–	1.483
Propylene carbonate	–	–	4.9006

where $X^- \equiv Cl^-, Br^-, I^-$.

$$\Delta G_t(M^+) = \Delta G_t(MBPh_4) - \Delta G_t(Ph_4B^-) \qquad (8)$$

where $M^+ \equiv K^+, Rb^+, Cs^+$.

The exothermicity or endothermicity of the free energies of transfer of single ions depends on the nature of the cation, anion and solvent.

Several factors influence ΔG_t for single ions and it is difficult to isolate one interaction mechanism as being responsible for a particular value. These factors are the following [11,12]:

(i) Coulombic-type ion–dipole electrostatic interactions.

(ii) Special interactions between ion and solvent, such as hydrogen bonding, π-complexing and Lewis acid–base interactions.

(iii) The breaking of solvent–solvent intermolecular hydrogen bonds especially in highly structured solvents such as water or formamide.

(iv) Dispersion forces or mutual polarizability between solute and solvent.

(i) Coulombic ion–dipole interactions

$\Delta G_t(Cs^+)$ is exothermic by 6.98 kcal mol^{-1} for transfer from propylene carbonate to dimethylformamide. Structural polarizability or hydrogen-bonding differences between the solvents are not great. The exothermicity is due to the presence of a highly polar, much less crowded single oxygen, carrying a much greater negative charge density in the dimethylformamide.

(ii) Special interactions

$\Delta G_t(Cl^-)$ is exothermic by 2.43 kcal mol^{-1} for transfer from dimethylformamide to methanol, whereas $\Delta G_t(I^-)$ for transfer between these solvents is endothermic by 6.10 kcal mol^{-1}. This exothermic value of $\Delta G_t(Cl^-)$ is largely a function of hydrogen-bond donation from methanol to Cl^-, an

TABLE 6

Single-ion free energies of transfer from water to non-aqueous solvents at 25 °C for Ph_4B^-, Cl^-, Br^- and I^-

Organic solvent	$\Delta G_t(Ph_4B^-)$ [a]	$\Delta G_t(Cl^-)$	$\Delta G_t(Br^-)$	$\Delta G_t(I^-)$
Methanol	−5.86	6.246	2.889	–
Acetone	−7.73	–	–	6.013
DMF	−8.98	10.531	6.969	5.025
Acetonitrile	−7.96	9.544	5.854	4.808
Dimethylacetamide	−9.14	11.536	–	6.045
DMSO	−8.44	9.134	6.137	4.450
N-Methylpyrrolidone	−9.35	11.849	8.002	5.828
Formamide	−5.48	–	–	0.668
Propylene carbonate	−8.37	–	–	3.984

[a] See ref. 5.

interaction which is absent between dimethylformamide and the Cl^- ion. The endothermic transfer of $\Delta G_t(I^-)$ from dimethylformamide to methanol occurs because I^- is a much weaker hydrogen acceptor than Cl^-.

(iii) Solvent–solvent hydrogen bonds

The free energy of transfer of K^+ is + 0.215 kcal mol^{-1} from dimethylformamide to formamide. The endothermicity of this transfer is due to the breaking of the hydrogen bonds of the formamide structure when K^+ is introduced into formamide.

TABLE 7

Single-ion free energies of transfer from water to non-aqueous solvents at 25 °C for Ph_4As^+, K^+, Rb^+ and Cs^+

Solvents	$\Delta G(Ph_4As^+)$ [a]	$\Delta G_t(K^+)$	$\Delta G_t(Rb^+)$	$\Delta G_t(Cs^+)$
Acetone	−8.22	1.100	–	0.229
DMF	−9.48	−0.381	–	7.906
Acetonitrile	−8.33	1.346	1.494	0.347
Dimethylacetamide	−9.65	−0.221	−0.988	−2.005
DMSO	−9.09	−1.33	–	−2.983
N-Methylpyrrolidone	−9.80	0.345	–	−1.712
Methanol	−6.06	2.048	–	1.802
Ethanol	−5.36	3.478	–	3.255
Hexamethylphosphortriamide	−9.56	0.508	–	−1.505
Formamide	−5.71	−0.596	−0.145	0.815
Glycol	−5.06	−4.691	–	9.822
N-Methylformamide	−7.93	–	–	−2.251
Propylene carbonate	−8.68	–	4.672	0.9266

[a] See ref. 5.

(iv) Dispersion forces

$\Delta G_t(Ph_4As^+)$ and $\Delta G_t(Ph_4B^-)$ as shown in Tables 6 and 7 are exothermic by up to 5 kcal mol^{-1}. The greater polarizability of the organic solvents used relative to water leads to a strong dispersion force interaction between them and the phenyl groups of these ions, and thus to an exothermic transfer of these ions from water to organic solvents.

REFERENCES

1 C. Kalidas and H. Schneider, Z. Phys. Chem., N.F., 120 (1980) 145.
2 O. Popovych, Crit. Rev. Anal. Chem., 1 (1970) 73.
3 J.I. Kim and E.A. Gomaa, Bull. Soc. Chim. Belg., 90 (1981) 391.
4 J.I. Kim, J. Phys. Chem., 82 (1978) 191.
5 J.I. Kim, Z. Phys. Chem., N.F., 113 (1978) 129.
6 B.G. Cox and A.J. Parker, J. Am. Chem. Soc., 95 (1973) 6879.
7 A.J. Parker, Chem. Rev., 1 (1969) 69.
8 B.G. Cox, G.R. Hedwig, A.J. Parker and D.W. Wattes, Aust. J. Chem., 27 (1974) 477.
9 R.G. Bates, in A.K. Covington and P. Jones (Eds.), Hydrogen-bonded Solvent Systems, Taylor and Francis, London, 1968.
10 I.M. Kolthoff and M.K. Chantooni, J. Phys. Chem., 76 (1972) 2024.
11 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry 2nd edn., Interscience, New York, 1966.
12 A.J. Parker, Search, 4 (1973) 426.