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SINGLE ION THERMODYNAMICS FOR Cl^-, Br^-, I^-, Ph_4B^-, K^+, Rb^+, Cs^+ AND Ph_4As^+ IN MIXED HEXAMETHYLPHOSPHORTRIAMIDE–WATER SOLVENTS

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ABSTRACT

This paper presents a study of the Ph_4AsPh_4B assumption for the determination of thermodynamic quantities of single ions in mixed hexamethylphosphortriamide (HMPT)–water solvents. The solvation energy of Ph_4AsPh_4B is considered as a combination of electrostatic and neutral components. The neutral components are replaced by the experimental data of Ph_4Ge and Ph_4C.

Based on this study, the standard free energies of transfer for K^+, Rb^+, Cs^+, Ph_4As^+, Cl^-, Br^-, I^- and Ph_4B^- are calculated from the experimental solubilities of tetraphenyl derivatives and by the use of the asymmetric Ph_4AsPh_4B assumption.

INTRODUCTION

The determination of single ion thermodynamic quantities requires an artificial method for partitioning the values of salts for cations and anions. Among a number of extrathermodynamic methods suggested in the literature [1–4], Ph_4AsPh_4B has attained increasing acceptance [5–10]. The solvation energy of an ion is considered as a combination of neutral and electrostatic contributions. The neutral contribution predominates in the solvation energy of the reference ions [9,10]. This has been verified experimentally by Kim [10,11] using neutral molecules which are equal in size and structure to the reference cation and anion, e.g., Ph_4Ge and Ph_4C, respectively. The standard free energy of transfer for the reference electrolyte from water (w) to an organic solvent (s) can, therefore, be expressed by

$$\begin{aligned}\Delta G_t^0(Ph_4AsPh_4B) &= \Delta_w^s G^0(Ph_4AsPh_4B)\\ &= \Delta_w^s G^0(Ph_4Ge) + \Delta_w^s G^0(Ph_4C) + \Delta_w^s G^0(el) \qquad (1)\end{aligned}$$

All values in eqn. (1) are experimentally available, except the electrostatic free energy, $\Delta_w^s G^0(el)$, which will be found from this equation.

The aim of this work is to determine the standard free energies of transfer from water to mixed HMPT–H_2O for the reference electrolyte and the

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partition of their values for the cation and anion. With the help of the Ph_4AsPh_4B assumption examined in the solvent systems under discussion, the standard free energies of transfer for several cations and anions are required.

EXPERIMENTAL

HMPT was of spectroscopic purity (Uvasol, Merck) and used without further purification except the introduction of a dehydration agent for storage. The preparation of $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ was made as follows: the aqueous solutions of KCl, RbCl and CsCl were added to equivalent concentrations of $NaBPh_4$ dissolved in water, the precipitates were filtered, dissolved in acetone, crystallized by slow evaporation, repeated recrystallization in acetone two times and the final product dried in an oven at 100°C for two days. Ph_4AsBr and Ph_4AsI were prepared by a similar method using Ph_4AsCl, KBr and KI as starting materials in acetonitrile. The stoichiometric ratios of the products were analysed by gravimetric and activation analyses. The water contents in $RbBPh_4$, $CsBPh_4$, Ph_4AsBr and Ph_4AsI were determined by Karl–Fischer titration and IR spectrometry. From IR spectrometry, no peaks of OH were observed for any of the tetraphenyl derivatives, whereas the Karl–Fischer titration revealed 0.032 and 0.071 mol H_2O per mole of Ph_4AsBr and Ph_4AsI, respectively, but no detectable H_2O in the other derivatives.

The solubility data of the tetraphenyl derivatives Ph_4AsPh_4B, Ph_4C, Ph_4Ge, Ph_4AsCl, Ph_4AsBr, Ph_4AsI, $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ were analysed by neutron activation analysis (München reactor in Graching, West Germany) for the first two derivatives, UV spectrometry for the third and gravimetric analysis for the others.

The experimental values presented in this paper are the average of more than three separate determinations. The densities and dielectric constants of the mixed solvents under study were determined by a digital oscillator densimeter (Heraeous-Paar DMA-50) and a Dekameter DK 300 (WTW), respectively. The measurements were carried out at constant temperature 25 ± 1°C.

RESULTS AND DISCUSSION

Following eqn. (1), the total standard free energies of transfer for the reference ions from water (w) to non-aqueous solvents (s) read as in eqns. (2)

TABLE 1

Standard free energies of transfer (kcal mol^{-1}) from water to mixed HMPT–H_2O solvents for Ph_4AsPh_4B, Ph_4C and Ph_4Ge at 25°C (molal scale)

X_s (HMPT)	ρ [a]	ϵ [b]	σ (10^8 cm) [c]	$\Delta^s_wG^0$ (Ph_4AsPh_4B)	$\Delta^s_wG^0$ (Ph_4C)	$\Delta^s_wG^0$ (Ph_4Ge)	$\Delta^s_wG^0$ (neut.)
0	0.99707	78.5	2.73	0	0	0	0
0.042	1.0116	70.0	3.110	−9.75	−1.323	−1.593	−2.916
0.094	1.0406	60.0	3.47	−11.55	−2.841	−3.564	−6.405
0.194	1.0453	45.4	4.08	−14.00	−4.748	−5.448	−10.196
0.292	1.0414	38.6	4.56	−15.41	−5.636	−6.172	−11.808
0.369	1.0382	35.6	4.89	−16.186	−6.075	−6.557	−12.632
0.482	1.0333	32.6	5.32	−16.809	−6.528	−6.941	−13.469
0.543	1.0326	31.7	5.52	−17.16	−6.719	−7.105	−13.824
0.618	1.0290	30.8	5.766	−17.50	−6.926	−7.312	−14.238
0.712	1.0264	30.02	6.05	−17.88	−7.091	−7.491	−14.582
0.801	1.0240	29.7	6.29	−18.19	−7.216	−7.642	−14.858
0.911	1.0220	29.3	6.57	−18.58	−7.353	−7.767	−15.12
1.0	1.0202	29	6.78	−18.82	−7.394	−7.835	−15.229

[a] Density of solvent.

[b] Dielectric constant of solvent.

[c] The average hard sphere diameter of the solvent molecule is calculated from $\sigma = 0.9275\,\sigma_0(V^0) - 0.8465 \times 10^{-8}$ [10], where $\sigma_0(V^0) = \sqrt[3]{6V^0/\pi N}$, V^0 is the partial molar volume of the mixed solvent and N Avogadro's number.

and (3).

$$\Delta^s_wG^0(Ph_4As^+) = \Delta^s_wG^0(Ph_4Ge) + \Delta^s_wG^0(el^+) \tag{2}$$

$$\Delta^s_wG^0(Ph_4B^-) = \Delta^s_wG^0(Ph_4C) + \Delta^s_wG^0(el^-) \tag{3}$$

The $\Delta^s_wG^0(Ph_4AsPh_4B)$, $\Delta^s_wG^0(Ph_4Ge)$ and $\Delta^s_wG^0(Ph_4C)$ values are available from experiment, therefore, $\Delta^s_wG^0(el^+)$ and $\Delta^s_wG^0(el^-)$ can be calculated according to eqn. (4).

$$\Delta^s_wG^0(el^+) = \Delta^s_wG^0(el^-) = 1/2\{\Delta^s_wG^0(Ph_4AsPh_4B) - [\Delta^s_wG^0(Ph_4C) + \Delta^s_wG^0(Ph_4Ge)]\} \tag{4}$$

Since for a big ion the difference between $\Delta^s_wG^0(el^+)$ and $\Delta^s_wG^0(el^-)$ will be very small due to the ion–quadrupole interactions, we took them as experimentally equal.

The standard free energies of transfer for Ph_4AsPh_4B from water to mixed HMPT–H_2O solvents are given in Table 1. The activity coefficients were determined by the Debye–Hückel equation as in ref. 12, the distance of the closest approach is estimated by assuming one solvent molecule to be placed between the ions. The distance of the closest approach is calculated by the relation: $a = r_+ + \sigma + r_-$, where r_+, r_- and σ represent the radii of

TABLE 2

Standard free energies for the reference cation and anion from water to mixed HMPT–H_2O solvents (K cal mol^{-1}) at 25°C (molal scale)

X_s (HMPT)	$\Delta^s_w G^0(Ph_4As^+)$	$\Delta^s_w G^0(Ph_4B^-)$
0	0	0
0.042	−2.693	−2.423
0.094	−5.185	−4.462
0.194	−7.13	−6.43
0.292	−7.929	−7.394
0.369	−8.334	−7.852
0.482	−8.611	−8.198
0.543	−8.773	−8.387
0.618	−8.943	−8.557
0.712	−9.14	−8.74
0.801	−9.308	−8.882
0.911	−9.487	−9.083
1.0	−9.631	−9.189

the reference cation and anion [10], and the hard sphere diameter (Table 1), respectively. The solubility products are determined with a precision of ±1.8% or better. The total free energy of transfer of the neutral parts Ph_4Ge and Ph_4C are also determined from the solubility measurements and their values are given in Table 1.

From the free energies of transfer of Ph_4C, Ph_4Ge and Ph_4AsPh_4B, therefore, the partition of $\Delta^s_w G^0(Ph_4AsPh_4B)$ into the values of the individual ions (eqns. 2–4) are calculated and given in Table 2. The mean value of the ratio of $\Delta^s_w G^0(Ph_4As^+)$ to $\Delta^s_w G^0(Ph_4B^-)$ is found to be 1.0708 ± 0.04, indicating that Ph_4AsPh_4B is an asymmetric model. Once the standard free energies of transfer for the reference ions are known, the values of the ions Cl^-, Br^-, I^-, K^+, Rb^+ and Cs^+ can be determined by using the following equations.

$$\Delta^s_w G^0(Cl^-) = RT \ln\left(\frac{[Ph_4AsCl]_s^2 \cdot {}_s\gamma_\pm^2 Ph_4AsCl}{[Ph_4AsCl]_w^2 \cdot {}_w\gamma_\pm Ph_4AsCl}\right) - \Delta^s_w G^0(Ph_4As^+) \tag{5}$$

$$\Delta^s_w G^0(Br^-) = RT \ln\left(\frac{[Ph_4AsBr]_s^2 \cdot {}_s\gamma_\pm^2 Ph_4AsBr}{[Ph_4AsBr]_w^2 \cdot {}_w\gamma_\pm Ph_4AsBr}\right) - \Delta^s_w G^0(Ph_4As^+) \tag{6}$$

$$\Delta^s_w G^0(I^-) = RT \ln\left(\frac{[Ph_4AsI]_s^2 \cdot {}_s\gamma_\pm^2 Ph_4AsI}{[Ph_4AsI]_w^2 \cdot {}_w\gamma_\pm Ph_4AsI}\right) - \Delta^s_w G^0(Ph_4As^+) \tag{7}$$

$$\Delta^s_w G^0(K^+) = RT \ln\left(\frac{[KBPh_4]_s^2 \cdot {}_s\gamma_\pm^2 KBPh_4}{[KBPh_4]_w^2 \cdot {}_w\gamma_\pm^2 KBPh_4}\right) - \Delta^s_w G^0(Ph_4B^-) \tag{8}$$

TABLE 3

Solubility products and standard free energies of transfer (kcal mol^{-1}) from water to mixed HMPT–H_2O solvents of some tetraphenyl derivatives (at 25°C, molal scale)

X_s (HMPT)	Ph_4AsCl		Ph_4AsBr		Ph_4AsI		$KBPh_4$		$PbBPh_4$		$CsBPh_4$	
	pK_{sp}	$\Delta^s_wG^0$	pK_{sp}	$\Delta^s_wG^0$	pK_{sp}	$\Delta^s_wG^0$	pK_{sp}	$\Delta^s_wG^0$	pK_{sp}	$\Delta^s_wG^0$	pK_{sp}	$\Delta^s_wG^0$
0	0.455	0	2.943	0	5.189	0	7.673	0	8.447	0	9.402	0
0.042	0.72	0.362	2.461	−0.657	–	–	4.25	−4.669	5.75	−3.678	–	–
0.194	–	–	–	–	–	–	0.106	−8.957	1.595	−9.346	1.646	−10.58
0.292	2.269	2.474	2.627	−0.431	3.62	−2.14	0.849	−9.311	1.311	−9.734	1.341	−10.99
0.369	2.649	2.993	2.691	−0.344	3.63	−2.126	0.935	−10.466	1.179	−9.914	1.344	−10.99
0.482	3.381	3.991	2.98	0.05	3.615	−2.147	0.913	−9.22	1.089	−10.04	1.139	−11.271
0.662	3.692	4.415	2.951	0.011	3.6	−2.167	0.873	−9.275	0.994	−10.23	1.225	−11.53
0.84	3.715	4.447	3.118	0.239	3.59	−2.18	0.709	−9.498	1.0403	−10.103	1.267	−11.096
1.0	3.482	4.129	3.214	0.369	3.55	−2.24	0.9135	−9.219	0.93	−11.52	1.022	−11.430

TABLE 4
Standard free energies of transfer (kcal mol^{-1}) for single ions from water to mixed HMPT–H_2O solvents at 25°C (molal scale)

X_s (HMPT)	Cl^-	Br^-	I^-	K^+	Rb^+	Cs^+
0	0	0	0	0	0	0
0.042	3.2	2.6	1.8	−0.26	−0.36	−0.53
0.094	5.9	4.6	3.55	−0.52	−0.74	−1.04
0.194	8.65	6.45	5.05	−1.0	−1.53	−2.36
0.292	10.4	7.45	5.80	−2.07	−2.86	−3.95
0.369	11.45	8.0	6.20	−1.58	−2.40	−3.56
0.482	12.45	8.57	6.50	−1.26	−2.08	−3.96
0.543	12.85	8.80	6.670	−0.92	−1.78	−2.96
0.618	13.3	9.07	6.85	−0.84	−1.65	−2.79
0.712	13.60	9.37	7.0	−0.72	−1.50	−2.62
0.801	13.80	9.60	7.12	−0.60	−1.35	−2.42
0.911	13.87	9.77	7.25	−0.55	−1.25	−2.26
1.0	13.85	9.9	7.35	−0.50	−1.15	−2.10

$$\Delta^{s}_{w}G^{0}(Rb^{+}) = RT\ \ln\left(\frac{[RbBPh_4]_s^2 \cdot {}_s\gamma_\pm^2 RbBPh_4}{[RbBPh_4]_w^2 \cdot {}_w\gamma_\pm^2 RbBPh_4}\right) - \Delta^{s}_{w}G^{0}(Ph_4B^{-}) \tag{9}$$

$$\Delta^{s}_{w}G^{0}(Cs^{+}) = RT\ \ln\left(\frac{[CsBPh_4]_s^2 \cdot {}_s\gamma_\pm^2 CsBPh_4}{[CsBPh_4]_w^2 \cdot {}_w\gamma_\pm^2 CsBPh_4}\right) - \Delta^{s}_{w}G^{0}(Ph_4B^{-}) \tag{10}$$

where the brackets indicate concentration in the molal scale, and $\gamma_\pm$ is the activity coefficient. Multiplication of the square of the molal concentration with the square of the activity coefficient gives the pK_{sp} values after taking the logarithm. The pK_{sp} values of Ph_4AsCl, Ph_4AsBr, Ph_4AsI, $KBPh_4$, $RbBPh_4$, $CsBPh_4$ and their $\Delta^s_wG^0$ values are listed in Table 3. The data for $\Delta^s_wG^0$ shown in Table 3 are plotted against X_s values (mole fraction of HMPT). From the curves obtained, $\Delta^s_wG^0$ values for the ions Cl^-, Br^-, I^-, K^+, Rb^+ and Cs^+ at other X_s values, not recorded experimentally, can be read and are tabulated in Table 4.

It can be seen from Table 4 that the $\Delta^s_wG^0$ values for the anions are of opposite sign to those of the cations. Thus, it is indicated that the cations K^+, Rb^+ and Cs^+ are more solvated by HMPT, whereas the anions Cl^-, Br^- and I^- are more solvated by water. The free energy of interaction of the ions with the mixed solvent decrease as the radius increases due to the decrease in the electrostatic interaction on increasing the distance between the reacted ions.

Based on this system and from the literature values [13–16], it was possible to estimate the free energies of transfer of some cations and anions. Their values are: 9.459, −10.845, −1.368, 5.004 and 11.204 K cal mol^{-1} for the ions H^+, Ag^+, ClO_4^-, SCN^- and N_3^-, respectively.

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