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SINGLE ION FREE ENERGIES OF SOME MONOVALENT IONS IN MIXED DIMETHYLACETAMIDE-WATER SOLUTIONS USING THE ASYMMETRIC Ph_4AsBPh_4 ASSUMPTION

ESAM A. GOMAA *

Chemistry Department, Faculty of Science, Mansoura University, Mansoura (Egypt)

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ABSTRACT

The free energies of transfer ($\Delta_w^s G^\ominus$) of the ions Na^+, Rb^+, Cs^+, Ph_4As^+, Ph_4Sb^+, Cl^-, Br^-, I^- and Ph_4B^- from water to mixed dimethylacetamide (DMAC)-H_2O solvents have been estimated from solubility measurements at 25°C and by applying the modified tetraphenylarsonium-tetraphenylboride ($\Delta_w^s G^\ominus(Ph_4As^+) > \Delta_w^s G^\ominus(Ph_4B^-)$) assumption.

The evaluated single ion free energies for these ions are discussed in terms of both solute-solvent interaction and the preferential solvation of ions.

INTRODUCTION

In order to obtain the thermodynamics of single ions, it is helpful to take into account suitable extrathermodynamic assumptions based on theory [1-4]. Among all the assumptions, that as tetraphenylarsonium-tetraphenylboride (Ph_4AsBPh_4) has gained the most popularity [5-9]. Kim [10-12] proved that Ph_4AsBPh_4 is an asymmetric model and not a symmetric one as explained previously in the literature. This means that the Ph_4As^+ ion belongs more to single ion thermodynamic functions than does the Ph_4B^- ion. The ratio of single ion free energies of the reference ions $\Delta_w^s G^\ominus(Ph_4As^+)$ to $\Delta_w^s G^\ominus(Ph_4B^-)$ was found to be 1.08 ± 0.02 in some organic solvents [13]. The aim of this work is to estimate the single ion free energies of the ions under consideration in mixed dimethylacetamide (DMAC)-H_2O solvents by applying the modified asymmetric Ph_4AsBPh_4 assumption.

EXPERIMENTAL

The *N,N*-dimethylacetamide (DMAC) used was very pure (Uvasol) from Merck. All the experimental parts, including the preparation of solutes

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* All correspondence should be addressed to the author at: Teachers Training College, Salalah, P.O. Box 19905, Sultanate of Oman.

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($NaBPh_4$, $RbBPh_4$, $CsBPh_4$, Ph_4AsCl, Ph_4AsBr, Ph_4AsI, Ph_4AsBPh_4 and Ph_4SbBPh_4), the preparation of saturated solutions and the analytical determination of solubilities, are explained in previous works [14–16].

The densities and dielectric constants of the mixed DMAC–H_2O solvents were determined by using a digital oscillator, densimeter (Heraeous–Paar–DMA-50) and a dekameter DK 300 (WTW), respectively.

RESULTS AND DISCUSSION

The measured densities and dielectric constants of the mixed DMAC–H_2O solvents at 25 ° C are given in Table 1. The single ion free energies of transfer ($\Delta^s_w G^\ominus$) of Na^+, Rb^+, Cs^+, Cl^-, Br^- and I^- from water to mixed DMAC–H_2O solvents are calculated from the solubilities (C), activity coefficients ($\gamma_\pm$) of the corresponding tetraphenyl derivative salts and the single ion free energies for the reference ions, Ph_4As^+ and Ph_4B^- as follows

$$\Delta^s_w G^\ominus(\mathrm{Na}^+) = -RT\frac{\log C^2_{\mathrm{NaBPh_4(s)}} + 2\log\gamma_{\pm\,\mathrm{NaBPh_4(s)}}}{\log C^2_{\mathrm{NaBPh_4(w)}} + 2\log\gamma_{\pm\,\mathrm{NaBPh_4(w)}}} - \Delta^s_w G^\ominus(\mathrm{Ph_4B^-}) \tag{1}$$

$$\Delta^s_w G^\ominus(\mathrm{Rb}^+) = -RT\frac{\log C^2_{\mathrm{RbBPh_4(s)}} + 2\log\gamma_{\pm\,\mathrm{RbBPh_4(s)}}}{\log C^2_{\mathrm{RbBPh_4(w)}} + 2\log\gamma_{\pm\,\mathrm{RbBPh_4(w)}}} - \Delta^s_w G^\ominus(\mathrm{Ph_4B^-}) \tag{2}$$

$$\Delta^s_w G^\ominus(\mathrm{Cs}^+) = -RT\frac{\log C^2_{\mathrm{CsBPh_4(s)}} + 2\log\gamma_{\pm\,\mathrm{CsBPh_4(s)}}}{\log C^2_{\mathrm{CsBPh_4(w)}} + 2\log\gamma_{\pm\,\mathrm{CsBPh_4(w)}}} - \Delta^s_w G^\ominus(\mathrm{Ph_4B^-}) \tag{3}$$

$$\Delta^s_w G^\ominus(\mathrm{Cl}^-) = -RT\frac{\log C^2_{\mathrm{Ph_4AsCl(s)}} + 2\log\gamma_{\pm\,\mathrm{Ph_4AsCl(s)}}}{\log C^2_{\mathrm{Ph_4AsCl(w)}} + 2\log\gamma_{\pm\,\mathrm{Ph_4AsCl(w)}}} - \Delta^s_w G^\ominus(\mathrm{Ph_4As^+}) \tag{4}$$

$$\Delta^s_w G^\ominus(\mathrm{Br}^-) = -RT\frac{\log C^2_{\mathrm{Ph_4AsBr(s)}} + 2\log\gamma_{\pm\,\mathrm{Ph_4AsBr(s)}}}{\log C^2_{\mathrm{Ph_4AsBr(w)}} + 2\log\gamma_{\pm\,\mathrm{Ph_4AsBr(w)}}} - \Delta^s_w G^\ominus(\mathrm{Ph_4As^+}) \tag{5}$$

$$\Delta^s_w G^\ominus(\mathrm{I}^-) = -RT\frac{\log C^2_{\mathrm{Ph_4AsI(s)}} + 2\log\gamma_{\pm\,\mathrm{Ph_4AsI(s)}}}{\log C^2_{\mathrm{Ph_4AsI(w)}} + 2\log\gamma_{\pm\,\mathrm{Ph_4AsI(w)}}} - \Delta^s_w G^\ominus(\mathrm{Ph_4As^+}) \tag{6}$$

where C is the molal solubility. The subscripts s and w denote mixed solvent and water, respectively. The activity coefficient ($\gamma_\pm$) for the salts $NaBPh_4$, $RbBPh_4$, $CsBPh_4$, Ph_4SbBPh_4, Ph_4AsCl, Ph_4AsBr and Ph_4AsI in each

TABLE 1

Physical parameters for mixed DMAC–H_2O solvents, solubilities and free energies of transfer of $NaBPh_4$, $RbBPh_4$ and $CsBPh_4$ from water to mixed DMAC–H_2O solutions at 25 °C (kJ mol^{-1})

X_s (DMAC)	ρ ($g\ cm^{-3}$)	ϵ	σ_{SPT} (Å)	$NaBPh_4$			
				C (molal)	$\log \gamma_{\pm}$	ΔG	$\Delta^s_w G^{\ominus}$
0	0.99707	78.5	2.730	2.118	−0.389	−1.501	0
0.129	0.9985	67.2	3.270	2.248	−0.427	−1.582	−0.081
0.163	0.9990	65.0	3.350	2.275	−0.437	−1.581	−0.080
0.226	0.9975	61.0	3.550	2.326	−0.455	−1.586	−0.088
0.312	0.9910	56.8	3.801	2.392	−0.475	−1.611	−0.113
0.341	0.9880	55.9	3.905	2.414	−0.477	−1.649	−0.146
0.636	0.9640	45.0	4.616	2.531	−0.550	−1.879	−0.381
1.0	0.9370	37.8	5.327	2.489	−0.600	−1.038	−0.460

$RbBPh_4$				$CsBPh_4$			
C	$\log \gamma_{\pm}$	ΔG	$\Delta^s_w G^{\ominus}$	C	$\log \gamma_{\pm}$	ΔG	$\Delta^s_w G^{\ominus}$
–	–	48.55 [a]	0	–	–	52.86 [a]	0
1.584×10^{-3}	−0.023	32.229	−16.317	2.326×10^{-3}	-3.996×10^{-3}	30.111	−22.745
3.414×10^{-3}	−0.0322	28.540	−20.004	3.166×10^{-3}	−0.032	28.901	−23.955
0.012	−0.059	22.648	−25.898	0.012	−0.059	22.553	−30.304
0.044	−0.098	16.610	−31.936	0.041	−0.095	16.956	−35.899
0.157	−0.135	10.729	−37.510	0.153	−0.144	10.959	−41.897
0.683	−0.207	4.249	−44.298	0.263	−0.180	8.678	−44.178
0.754	−0.251	4.273	−44.273	0.686	−0.234	4.536	−48.320

[a] From ref. 16.

solution was evaluated by applying the Debye–Hückel equation [16]

$$\log \gamma_{\pm} = -\frac{A z_1 z_2 \sqrt{C}}{1 + Ba\sqrt{C}} \tag{7}$$

where z_1 and z_2 are the charges of the ions, $A = 1.8246 \times 10^6/(T\epsilon)^{3/2}$, $B = 50.29 \times 10^8/(T\epsilon)^{1/2}$; ϵ is the dielectric constant of the solvent, T is the absolute temperature, and a is the solvated radius. The solvated radii for tetraphenyl derivative salts were estimated by adding the crystal radii to the hard sphere diameters (σ_{SPT}) of the solvents. This last was evaluated by the use of the following relation [17]

$$\sigma_{SPT} = -0.8465 + 0.9275\sigma_0 \tag{8}$$

where $\sigma_0 = \sqrt[3]{(6V_0/N\pi)}$ and V_0 = molecular weight (MW)/density (ρ), and N is Avogadro's number.

The free energies of transfer of the reference cation (Ph_4As^+) and the reference anion (Ph_4B^-) were estimated experimentally as described in previous work from the solubilities of Ph_4C, Ph_4Ge and Ph_4AsBPh_4, and their free energies of transfer from water to mixed DMAC–H_2O solvents (see Fig. 1). $\Delta^s_w G^\ominus$ values for Ph_4As^+ and Ph_4B^- ions are calculated by applying eqns. (9) and (10) as explained in previous work [13,14]

$$\Delta^s_w G^\ominus(Ph_4As^+) = 1/2\Delta^s_w G^\ominus(el) + \Delta^s_w G^\ominus(Ph_4Ge) \qquad (9)$$

$$\Delta^s_w G^\ominus(Ph_4B^-) = 1/2\Delta^s_w G^\ominus(el) + \Delta^s_w G^\ominus(Ph_4C) \qquad (10)$$

where $\Delta^s_w G^\ominus(el)$ is the electrostatic free energy for Ph_4AsBPh_4, calculated from the difference between $\Delta^s_w G^\ominus(Ph_4AsBPh_4)$ and the sum of the corresponding values for Ph_4C and Ph_4Ge. The individual experimental data for each solute in the mixed DMAC–H_2O solvents are given in Tables 1 and 2, and the values of their single ion free energies of transfer from water to mixed DMAC–H_2O solvents are shown in Table 3 and Fig. 2.

The free energies of transfer of the electrolytes, $NaBPh_4$, $RbBPh_4$ and $CsBPh_4$, increased in negativity with an increase in the solvated radii (a), mainly as a result of the increase in both electrostatic and cavity energy of interaction for the electrolytes in mixed DMAC–H_2O solvents.

Recently [13], Ph_4AsBPh_4 was strongly supported for the estimation of single ion thermodynamics in pure organic solvents. It was also noted that Ph_4SbBPh_4 is plausible as a reference electrolyte. In the present work the reference electrolyte Ph_4SbBPh_4 was studied in mixed DMAC–H_2O solvents and its reference cation free energies estimated; these are cited in Table 3.

By adding Δ values from ref. 13 (the difference between $\Delta^s_w G^\ominus(Ph_4Sb^+)$ and $\Delta^s_w G^\ominus(Ph_4As^+)$) to the single free energy values for halogen ions, the upper limit for their values was obtained. This indicated that the halogen ions have a range of $\Delta^s_w G^\ominus$ values using both the Ph_4AsBPh_4 and Ph_4SbBPh_4 assumptions, as shown in Fig. 2.

It was observed from the final results of single ion free energies that Ph_4Sb^+, Ph_4As^+, Ph_4B^-, Rb^+ and Cs^+ have negative $\Delta^s_w G^\ominus$ values in all

TABLE 2

Solubilities and free energies of transfer of Ph_4AsCl, Ph_4AsBr, Ph_4AsI and Ph_4SbBPh_4 from water to mixed DMAC–H_2O solutions at 25°C (kJ mol^{-1})

X_s (DMAC)	Ph_4AsCl				Ph_4AsBr			
	C	$\log \gamma_\pm$	ΔG	$\Delta^s_w G^\ominus$	C	$\log \gamma_\pm$	ΔG	$\Delta^s_w G^\ominus$
0	–	–	3.012 [a]	0	–	–	16.840 [a]	0
0.129	0.845	−0.146	2.499	−0.513	0.173	−0.111	9.961	−6.880
0.163	0.762	−0.148	3.043	0.031	0.203	−0.118	9.264	−7.575
0.226	0.664	−0.153	3.776	0.764	0.233	−0.129	8.709	−8.131
0.312	0.565	−0.161	4.665	1.653	0.225	−0.138	8.974	−7.868
0.341	0.483	−0.159	5.428	2.417	0.227	−0.140	8.948	−7.893
0.636	0.402	−0.189	6.673	3.661	0.240	0.174	9.056	−7.784
1.0	0.224 [a]	−0.203	9.733	6.721	0.202	−0.198	10.197	−6.642

[a] From ref. 16.

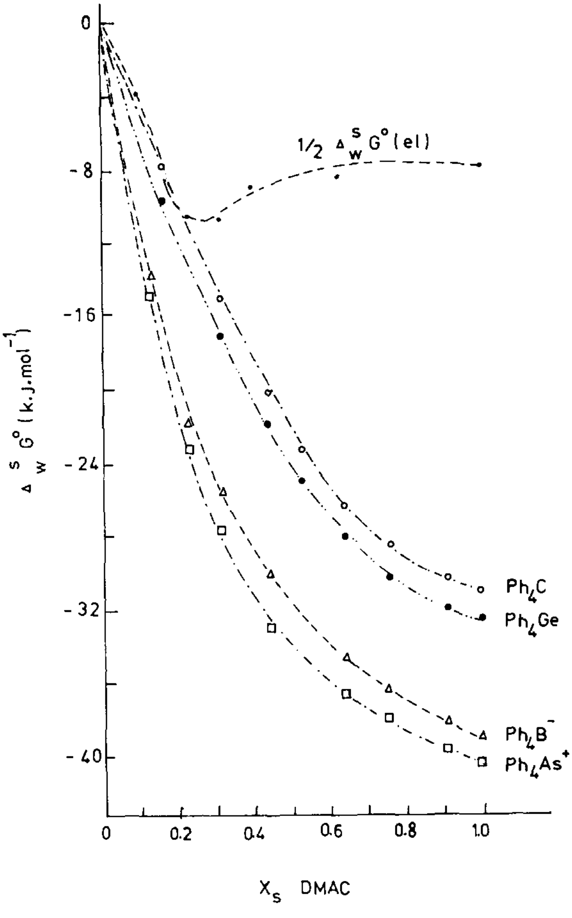


Fig. 1. Transfer free energies for Ph_4C, Ph_4Ge, Ph_4B^- and Ph_4As^+ from water to mixed DMAC–H_2O solvents.

Ph_4AsI				Ph_4SbBPh_4			
C	log $\gamma_\pm$	ΔG	$\Delta^s_w G^\ominus$	C	log $\gamma_\pm$	ΔG	$\Delta^s_w G^\ominus$
–	–	28.952 [a]	0	2.826×10^{-9}	-2.707×10^{-5}	97.594	0
0.021	−0.009	19.213	−9.738	3.167×10^{-6}	-1.295×10^{-3}	62.792	−34.802
0.029	−0.072	18.389	−10.563	9.450×10^{-6}	-2.331×10^{-3}	57.393	−40.201
0.045	−0.088	16.401	−12.551	5.972×10^{-5}	-5.554×10^{-3}	48.286	−49.308
0.063	−0.104	14.919	−14.032	3.191×10^{-4}	−0.014	40.067	−57.527
0.075	−0.110	14.099	−14.853	5.373×10^{-4}	−0.018	37.531	−60.063
0.127	−0.154	16.175	−12.777	0.0146	−0.083	21.904	−75.689
0.108 [a]	−0.177	13.051	−15.900	0.0534	−0.139	16.116	−81.478

TABLE 3

Single ion free energies for transfer of Ph_4As^+, Ph_4B^-, Ph_4Sb^+, Na^+, Rb^+, Cs^+, Cl^-, Br^- and I^- from water to mixed DMAC–H_2O solvents at 25 °C (kJ mol^{-1}) based on the asymmetric Ph_4AsBPh_4 assumption

X_s (DMAC)	Ph_4As^+	Ph_4B^-	Ph_4Sb^+	Na^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
0	0	0	0	0	0	0	0	0	0
0.129	−15.149	−13.266	−21.619	15.070	−1.168	−2.180	12.750	8.504	−5.658
0.163	−19.284	−17.840	−22.360	19.205	−0.719	−4.670	17.874	10.266	7.278
0.226	−23.687	−22.013	−27.295	23.599	−2.209	−6.616	22.779	13.882	9.462
0.312	−27.968	−25.725	−31.802	27.822	−3.967	−7.931	27.378	17.857	11.693
0.341	−29.843	−29.383	−33.279	29.697	−7.667	−12.053	29.341	19.377	14.530
0.636	−36.836	−34.953	−38.908	36.456	−12.178	−7.340	38.615	27.169	22.176
1.0	−40.858	−39.603	−41.875	41.319	−3.415	−7.462	46.323	32.961	23.704

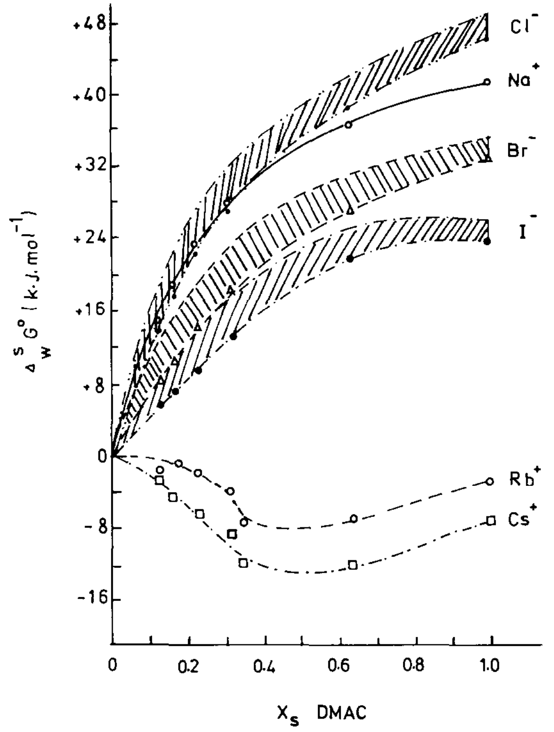


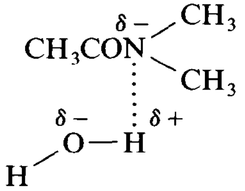
Fig. 2. Single ion free energies of transfer for Na^+, Rb^+, Cs^+, Cl^-, Br^- and I^- from water to mixed DMAC–H_2O solvents at 25 °C.

mixed DMAC–H_2O solvents. Their negative values increase in DMAC-rich solvents in the following order: $Ph_4Sb^+ > Ph_4As^+ > Ph_4B^- > Cs^+ > Rb^+$. The other ions, Cl^-, Br^-, I^- and Na^+, have positive free energies in the mixed DMAC–H_2O solvents, increasing in the following order: $Cl^- > Na^+ > Br^- > I^-$. Among the cations shown in Fig. 2, only the curve for Na^+ is shown over the whole composition range as nearly coinciding with Cl^- up to an X_s (DMAC) of 0.4. The large positive value for Na^+ and anions indicates that DMAC is not at all a good solvator for these ions. The observed increasing destabilization of halide ions as evidenced from the order $\Delta^{s}_{w}G^{\ominus}(Cl^-) > \Delta^{s}_{w}G^{\ominus}(Br^-) > \Delta^{s}_{w}G^{\ominus}(I^-)$ in mixed DMAC–H_2O solvents is due to the combined effects of destabilizing Born-type electrostatic interactions, decreasing acidity, i.e. "anion–H–centre type" interactions of the mixed solvents, and increasing strength of the "soft–soft" interactions down the group [18].

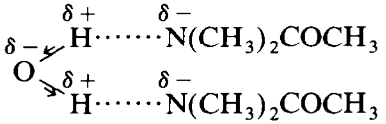
Alkali cations other than Na^+ are increasingly stabilized by the organic solvent due chiefly to the observed "basicity" or "cation–O–centre type" of interaction [18].

The observed minima in $\Delta^{s}_{w}G^{\ominus}$ for Rb^+, Cs^+ and $\Delta^{s}_{w}G^{\ominus}(el)$ can be attributed to the water structure breaking of the organic solvent [19–21].

Also, water and DMAC molecules together may lead to the formation in situ of intercomponent hydrogen-bonded complexes (A) and (B) resulting in an increased basicity of the hydroxyl oxygen itself due to the presence of the N lone pair [22].



(A)



(B)

The increasing stabilization of Ph_4B^-, Ph_4As^+ and Ph_4Sb^+ ions in mixed DMAC–H_2O solvents was due partly to dispersion interactions between the four phenyl groups and organic cosolvent and partly to the cavity-forming interaction [23].

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