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Gibbs Free Energies, Enthalpies and Entropies of Transfer for Reference Ions Ph_4As^+ and Ph_4B^- in Mixed DMFA-H_2O Solvents at Different Temperatures

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Abstract The thermodynamic data (ΔG_t, ΔH_t and $T\Delta S_t$) of transfer for tetraphenylarsonium-tetraphenylborate (Ph_4AsBPh_4) from water to mixed dimethylformamide (DMFA)-H_2O solvents were estimated from the experimental solubility and calorimeter measurements. The experiments were done at three different temperatures 288.15, 298.15 and 308.15 K. Also the thermodynamic parameters were divided into reference anion and cation following the asymmetric deviation and their values, were discussed. Dividing all the thermodynamic functions between the cation and anion by using 1.064 factors we obtain their individual functions. The reference ion values can be easily used for evaluating the different thermodynamic parameters of any ion that contains in its counterion tetraphenyl cation or anion . By using the data given here the thermodynamic parameters for some single ion can be estimated for following their behaviour in environment. The single ion thermodynamics are helpful for predicting, explaining and mechanisms suggesting. Theoretical and engineering chemistry are in need for experimental single ion parameters for the comparison with that calculated by different solvation theories.

Keywords Gibbs Free Energies, Enthalpies, Entropies, Tetraphenylarsonium-Tetraphenyl Borate, Dimethylformamide

1. Introduction

Single ion transfer Gibbs energies, entropies and enthalpies play an important role in many areas of chemistry, such as the estimation of solubilities, electrochemical potentials, distribution ratio and complex formation constants[1].

Extra thermodynamic models must be used for the determination of single ion thermodynamic quantities[2,3].

As one of the extrathermodynamic assumptions, the refrence electrolytes such as tetrphenylphosphonium , tetraphenylarsonium and triso – amyl -n- butylammonium – tetra phenyl borate have been used for the partition of thermodynamic quantities of electrolytes into values of individual ions[4 -6] . Also thermodynamics of ion association are in need to the single ion parameters[7].

The reference electrolyte Ph_4AsBPh_4 with its caution and anion of different sizes and large tetrahedral structure in which the central ion is buried in four phenyl rings, provide the possibility of evaluating single ion thermodynamic quantities in different solvents[8].

This reference electrolyte assumption has been studied experimentally as well as theoretically in many pure solvents[9], and mixed solvents[10]. Here in this work the Gibbs energies, enthalpies and entropies of transfer for $Ph_4As BPh_4$ from water to mixed DMFA-H_2O solvents were experimentally determined at 288.15, 298.15 & 308.15 K and their values were discussed. The aim of the work is to give data about the solvation of very important reference electrolyte Ph_4AsBPh_4 in mixed DMFA-H_2O solvents and its ions, necessary for the evaluating other single ion thermodynamic parameters. These data can help the analyst for further evaluation and discussion about ion properties in solutions.

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2. Experimental

The DMFA used was of spectroscopic purity (Uvasol) from Merck and used directly without purification. Ph_4AsBPh_4 was prepared by the condensation of aqueous solutions of Ph_4AsPh_4B and $NaBPh_4$ followed by crystallization in acetonitrile as described in ref. 15. The effect of temperature was studied by shaking samples put in closed test tubes in a shaking water bath of the types "Assistant" till saturation for one week at the studied temperatures 288.15, 298.15 and 308.15 K. The solubilities were determined as explained before in ref. 12. Calorimeter like thermos shape (RMG) type 489/10 was used for measuring the enthalpies of solvation at the used temperature. The solubility were determines conductometically and gravimetrically as explained before which are ease, reproducible and cheap methods . Also it consumes little time and accurate data.

3. Results and Discussion

3.1. Gibbs Free Energies

The calculated ΔG_t and their transfer values (ΔG_t) for Ph_4AsBPh_4 at 288.15, 298.15 and 308.15 K were evaluated as explained in ref. 12 and their values are listed in Tables1-3 with standard deviation of ± 0.3 KJ/mole.

3.2. Enthalpies and Entropies

The enthalpies ΔH_t from water to mixed DMFA-H_2O solvents for the reference electrolyte (RE) Ph_4 As B Ph_4 were estimated calorimetrically at 288.15, 298.15 and 308.15 K and their values are given in Tables 1-3 also. The entropies T ΔS and entropies of transfer $T\Delta S_t$ for Ph_4AsBPh_4 were obtained by applying equation 1, and their values are also presented in Tables 1-3[13 - 18].

$$\Delta H_t = \Delta G_t + T\Delta S_t \quad (1)$$

For evaluating the single ion reference thermodynamic parameters for Ph_4 As^+ & Ph_4 B^- we must use the R ratio, which is the thermodynamic parameters for each reference ion, equation 2.

$$R = \frac{\Delta X_t(Ph_4As^+)}{\Delta X_t(Ph_4B^-)} \quad (2)$$

The average R value on using the Gibbs free energies for both cation and anion is 1.064 $\pm$ 0.05 as given in ref. 8. Dividing all the thermodynamic functions between the cation and anion by using 1.064 factors we obtain their individual functions which cited in Tables 1, 2 and 3. The reference ion values given in Tables 1-3 can be easily used for evaluating the different thermodynamic parameters[19 - 25] of any ion that contains in its counter ion tetra phenyl cation or anion at different temperatures.

4. Conclusions

This work is to give data about the solvation of very important reference electrolyte Ph_4AsBPh_4 in mixed DMFA-H_2O solvents and its ions, Ph_4 As^+ , Ph_4B^-

necessary for the evaluating other single ion thermodynamic parameters. These data can help the analyst for further evaluation and discussion about ion properties in solutions.

Table 1. Gibbs free energies, entropies and enthalpies for Ph_4AsBPh_4 electrolyte and Ph_4 As^+, Ph_4 B^- ions in mixed DMFA-H_2O solvents at 288.15 K (in KJ/mole)

Xs	$T\Delta S$	$T\Delta S_t$	$T\Delta S_t$ (Ph_4As^+)	$T\Delta S_t$ (Ph_4B^-)	ΔG	ΔG_t	ΔG_t (Ph_4As^+)	ΔG_t (Ph_4B^-)
0	9.2208	1.5845	0.8429	0.7415	5.9993	-6.7669	-3.5999	-3.1669
0.1744	86445	1.0085	0.5365	0.4719	6.500	-6.2599	-3.3303	-2.9296
0.3222	8.6445	1.0085	0.5365	0.4719	7.0800	-5.6799	-3.0217	-2.6582
0.449	8.6445	1.0085	0.5365	0.4719	7.6984	-5.062	-2.6929	-2.3690
0.559	8.3564	0.7204	0.3832	0.3371	8.2591	-4.5008	-2.3944	-2.1063
0.6553	8.3564	0.7204	0.3832	0.3371	8.8321	-3.9279	-2.0896	-1.8383
0.7404	8.0682	0.4332	0.2304	0.2027	9.5512	-3.2088	-1.7071	-1.5017
0.816	7.9529	0.3169	0.1686	0.1483	10.199	-2.5599	-1.3618	-1.1980
0.8838	7.7801	0.1441	7.666×10^{-2}	6.7438×10^{-2}	11.04668	-1.7133	-0.9114	-0.8018
0.9448	7.7801	0.1441	7.666×10^{-2}	6.7438×10^{-2}	11.9167	-0.8433	-0.4486	-0.3947
1.0	7.6359	0	0	0	12.7599	0	0	0

ΔH	ΔH_t	ΔH_t (Ph_4AS^+)	ΔH_t (Ph_4B^-)
-3.2215	-8.3456	-4.4398	-3.9057
-2.1445	-7.2686	-3.8668	-3.4017
-1.5645	-6.6886	-3.5583	-3.1302
-0.9461	-6.0702	-3.2293	-2.8408
-0.0972	-5.2213	-2.777	-2.4435
+0.4756	-5.6484	-2.4729	-2.1754
+1.4829	-3.6411	-1.9371	-1.7040
+2.2471	-2.8769	-1.5305	-1.3464
+3.2666	-1.8575	-0.9882	-0.8693
+4.1366	-0.9874	-0.5253	-0.4621
+5.1241	0	0	0

Table 2. Gibbs free energies, entropies and enthalpies for Ph_4AsBPh_4 electrolyte and Ph_4 As^+, Ph_4 B^- ions in mixed DMFA-H_2O solvents at 298.15 K (in KJ/mole)

Xs DMFA	$T\Delta s$	$T\Delta S_t$	$T\Delta s_t$ (Ph_4As^+)	$T\Delta s_t$ (Ph_4B^-)	ΔG	ΔG_t	ΔG_t (Ph_4As^+)	ΔG_t (Ph_4B^-)
0	9.5408	1.6398	0.8723	0.7674	5.6742	-6.8064	-3.6210	-3.1854
0.1744	8.9445	1.0435	0.5551	0.4883	6.2199	-6.2607	-3.3306	-2.9300
0.3222	8.9445	1.0435	0.5551	0.4883	6.7899	-5.6907	-3.0274	-2.6632
0.449	8.9445	1.0435	0.5551	0.4883	7.3999	-5.0807	-2.7029	-2.3777
0.559	8.6464	0.7454	0.3965	0.3488	7.94994	-4.5307	-2.4103	-2.1203
0.6553	8.6464	0.7454	0.3965	0.3488	8.5659	-3.9147	-2.0826	-1.8320
0.7404	8.3482	0.4472	0.2379	0.2093	9.2799	-3.2007	-1.7027	-1.4979

0.814	8.2289	0.3279	0.1744	0.1534	9.9199	-2.5607	-1.3623	-1.1985
0.8838	8.0501	0.1491	7.932×10^{-2}	6.9778×10^{-2}	10.7698	-1.7108	-0.9101	-0.8006
0.9448	8.0501	0.1491	7.932×10^{-2}	6.9778×10^{-2}	11.669	-0.8107	-0.4312	-0.3794
1.0	7.9009	0	0	0	12.4866	0	0	0

ΔH	ΔH_t	$\Delta H_t (Ph_4AS^+)$	$\Delta H_t (Ph_4B^-)$
-3.8666	-8.4462	-4.4933	-3.9528
-2.7246	-7.3043	-3.8858	-3.4184
-2.1546	-6.7343	-3.5826	-3.1516
-1.5446	-6.1243	-3.2581	-2.8662
-0.6964	-5.2762	-2.8069	-2.4692
-0.0805	-5.6602	-2.4792	-2.1809
+0.9317	-3.6480	-1.9407	-1.7073
+1.6910	-2.8887	-1.5368	-1.3519
+2.7197	-1.86	-0.9895	-0.8705
+3.6198	-0.9599	-0.5107	-0.4492
+4.5797	0	0	0

Table 3. Gibbs free energies, entropies and enthalpies for Ph_4AsBPh_4 electrolyte and Ph_4As^+, Ph_4B^- ions in mixed DMFA-H_2O solvents at 308.15 K (in KJ/mole)

Xs DMFA	$T\Delta S$	$T\Delta S_t$	$T\Delta S_t (Ph_4As^+)$	$T\Delta S_t (Ph_4B^-)$	ΔG	ΔG_t	$\Delta G_t (Ph_4As^+)$	$\Delta G_t (Ph_4B^-)$
0	9.8608	1.6949	+0.9017	0.7932	5.36104	-6.8789	-3.6595	-3.2193
0.1744	9.2445	1.0786	0.5738	0.5047	5.9254	-6.3146	-3.3593	-2.9552
0.3222	9.2445	1.0786	0.5738	0.5047	6.5179	-5.7221	-3.0442	-2.6779
0.449	9.2445	1.0786	0.5738	0.5047	7.1245	-5.1154	-2.7214	-2.3940
0.559	8.9364	0.7705	0.4099	0.3606	7.6742	-4.5652	-2.4286	-2.1365
0.6553	8.9364	0.7705	0.4099	0.3606	8.2955	-3.9444	-2.0984	-1.8459
0.7404	8.6282	0.4623	0.2459	0.2163	8.9999	-3.2400	-1.72368	-1.5163
0.814	8.5049	0.339	0.1803	0.1586	9.6499	-2.5901	-1.3779	-1.2121
0.8838	8.3201	0.1542	8.203×10^{-2}	7.2165×10^{-2}	10.4904	-1.7436	-0.9276	-0.8160
0.9448	8.3201	0.1542	8.203×10^{-2}	7.2165×10^{-2}	11.3993	-0.8407	-0.4472	-0.3934
1.0	8.1659	0	0	0	12.2399	0	0	0

ΔH	ΔH_t	$\Delta H_t (Ph_4AS^+)$	$\Delta H_t (Ph_4B^-)$
-4.4997	-8.5738	-4.5612	-4.0125
-3.3191	-7.33932	-3. 9332	-3.4600
-2.7266	-6.8007	-3.6179	-3.1827
-2.1199	-6.194	-3.2952	-2.8987
-1.2616	-5.3357	-3.8385	-2.4971
-0.6409	-4.7149	-2.5083	-2.2065
+0.3717	-3.7024	-1.9696	-1.7327
+1.145	-2.9291	-1.5582	-1.3709
+2.1763	-1.8978	-1.0096	-0.8882
+3.0792	-0.9049	-0.5293	-0.4656
+4.0741	0	0	0

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