Gibbs Free Energies, Enthalpies and Entropies of Transfer for Reference Ions Ph₄ As⁺ and Ph₄ B⁻ in Mixed DMFA-H₂O Solvents at Different Temperatures

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Abstract

The thermodynamic data (ΔG_t, ΔH_t and TΔS_t) of transfer for tetraphenylarsonium-tetraphenylborate (Ph₄AsBP₄₄) from water to mixed dimethylformamide (DMFA)-H₂O 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 reference electrolytes such as tetraphenylphosphonium, tetraphenylarsonium and triso-amyl-n-butylammonium-tetraphenyl 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 Ph₄AsBP₄ has 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 Ph₄ As BPr₄ from water to mixed DMFA-H₂O 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 Ph₄AsBP₄ in mixed DMFA-H₂O 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.

2. Experimental

The DMFA used was of spectroscopic purity (Uvasol) from Merck and used directly without purification. Ph₄AsBP₄ was prepared by the condensation of aqueous solutions of Ph₄AsPh₄B and NaBPr₄ 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 determined conductometrically 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 $\Delta G_i$ and their transfer values ( $\Delta G_i$) for Ph$_4$AsBPh$_4$ at 288.15, 298.15 and 308.15 K were evaluated as explained in ref. 12 and their values are listed in Tables 1-3 with standard deviation of ± 0.3 KJ/mole.

3.2. Enthalpies and Entropies

The enthalpies $\Delta H_i$ from water to mixed DMFA-H$_2$O 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 $\Delta S_i$ and entropies of transfer $\Delta S_{i}$, for Ph$_4$AsBPh$_4$ were obtained by applying equation 1, and their values are also presented in Tables 1-3[13 - 18].

\[
\Delta H_i = \Delta G_i + T \Delta S_i
\]  

(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.

\[
R = \frac{\Delta X_f(\text{Ph}_4 \text{As}^+)}{\Delta X_f(\text{Ph}_4 \text{B}^-)}
\]  

(2)

The average R value on using the Gibbs free energies for both cation and anion is 1.064 ± 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$_4$AsBPh$_4$ in mixed DMFA-H$_2$O solvents and its ions, Ph$_4$ As$^+$, Ph$_4$B$^-$ 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$_4$AsBPh$_4$ electrolyte and Ph$_4$ As$^+$, Ph$_4$ B$^-$ ions in mixed DMFA-H$_2$O solvents at 288.15 K (in KJ/mole)

| $\Delta H$ | $\Delta S$ | $\Delta G$ | $\Delta G_i$ | $\Delta G_{(\text{Ph}_4 \text{As}^+)}$ | $\Delta G_{(\text{Ph}_4 \text{B}^-)}$ |
|------------|------------|------------|---------------|----------------------------------|----------------------------------|
| -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$_4$AsBPh$_4$ electrolyte and Ph$_4$ As$^+$, Ph$_4$ B$^-$ ions in mixed DMFA-H$_2$O solvents at 288.15 K (in KJ/mole)

| $\Delta H$ | $\Delta S$ | $\Delta G$ | $\Delta G_i$ | $\Delta G_{(\text{Ph}_4 \text{As}^+)}$ | $\Delta G_{(\text{Ph}_4 \text{B}^-)}$ |
|------------|------------|------------|---------------|----------------------------------|----------------------------------|
| -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             |                                  |                                  |
| Xs DMFA | T ∆S | T ∆S (Ph₄As⁺) | T ∆S (Ph₄B⁻) | T ∆G | ∆G (Ph₄As⁺) | ∆G (Ph₄B⁻) | ∆G (Ph₄As⁺) | ∆G (Ph₄B⁻) |
|--------|------|----------------|----------------|------|-------------|-------------|-------------|-------------|
| 0      | 9.8608 | 1.6949        | 0.9017         | 5.36104 | -6.8789     | -6.8789     | -6.8789     | -6.8789     |
| 0.1744 | 9.2445 | 1.0786        | 0.5738         | 5.9254 | -6.3146     | -3.3593     | -2.9552     | -2.9552     |
| 0.3222 | 9.2445 | 1.0786        | 0.5738         | 6.5179 | -5.7221     | -3.0442     | -2.6779     | -2.6779     |
| 0.449  | 9.449  | 1.0786        | 0.5738         | 7.1245 | -5.1154     | -2.7214     | -2.3940     | -2.3940     |
| 0.559  | 8.9364 | 0.7705        | 0.4099         | 7.6742 | -4.5652     | -2.4286     | -2.1365     | -2.1365     |
| 0.6553 | 8.6282 | 0.4623        | 0.2459         | 8.9999 | -3.2400     | -1.72368    | -1.5163     | -1.5163     |
| 0.814  | 8.5049 | 0.3390        | 0.1803         | 9.6499 | -2.5901     | -1.3779     | -1.2121     | -1.2121     |
| 0.8838 | 8.3201 | 0.1542        | 8.203 x 10⁻² | 7.2165 x 10⁻² | 10.4904 | -1.7436  | -0.9276 | -0.8160 |
| 0.9448 | 8.3201 | 0.1542        | 8.203 x 10⁻² | 7.2165 x 10⁻² | 11.3993 | -0.8407 | -0.4472 | -0.3934 |
| 1.0    | 8.1659 | 0              | 0              | 12.2399 | 0            | 0            | 0            | 0            |

Table 3. Gibbs free energies, entropies and enthalpies for Ph₄AsBPh₄ electrolyte and Ph₄ As⁺, Ph₄ B⁻ ions in mixed DMFA-H₂O solvents at 308.15 K (in KJ/mole)

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