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# THERMODYNAMIC STUDIES OF THE SOLVATION OF $Ph_4AsPh_4B$ IN MIXED SOLVENTS (MeOH–DMF)

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## ABSTRACT

The thermodynamic data ($\Delta G^0$, $\Delta H^0$ and $T\Delta S^0$) of the solvation of tetraphenylarsonium-tetraphenylborate ($Ph_4AsPh_4B$) and its neutral parts, tetraphenylgermanium ($Ph_4Ge$) and tetraphenylmethane ($Ph_4C$) in methanol–*N*,*N*-dimethylformamide mixed solvents are discussed.

The values of the free energy of transfer, $\Delta^s_M G^0$, are calculated from measurements of the solubilities of $Ph_4AsPh_4B$, $Ph_4Ge$ and $Ph_4C$ in the successive fractions of MeOH in DMF at three different temperatures (15, 25, 35 °C). The values of $\Delta^s_M H^0$ and $T\Delta^s_M S^0$ for the derivatives are calculated from $\Delta^s_M G^0$ values.

The values of $\Delta^s_M G^0$, $\Delta^s_M H^0$ and $T\Delta^s_M S^0$ of tetraphenylarsonium and tetraphenylborate ions have also been carefully calculated. The ratios of $\Delta^s_M G^0$ values ($\Delta^s_M G^0 = \Delta G^0(+)/\Delta G^0(-)$) were found to be greater than unity. Similarly, the ratios of $\Delta^s_M H^0$ and $T\Delta^s_M S^0$ for the positive and negative ions were found to be greater than unity.

## INTRODUCTION

The free energy of transfer from methanol (M) to dimethylformamide (DMF) and their mixtures is calculated by the following equation [1–3]

$$\Delta^s_M G^0 = {}_sG^0 - {}_MG^0 \qquad (1)$$

where ${}_sG = -RT \ln a_s$, ${}_MG^0 = -RT \ln a_M$, $G^0$ is the standard molal free energy of the solute and $a$ is the activity.

The standard enthalpy is calculated graphically by drawing the relation between $pK_{sp}$ and $1/T$ [3,7].

On applying eqn. (2), $T\Delta^s_M S^0$ of transfer could be obtained from the $\Delta^s_M G^0$ and $\Delta^s_M H^0$ values

$$\Delta^s_M H^0 = \Delta^s_M G^0 + T\Delta^s_M S^0 \qquad (2)$$

Knowing that the free energy consists of the neutral and electrostatic free energies [3]. Kim [4] proved that $Ph_4C$ and $Ph_4Ge$ are the neutral parts of the $Ph_4B^-$ and $Ph_4As^+$ ions, respectively. Also, the thermodynamic functions of $Ph_4AsPh_4B$ were separated into neutral ($Ph_4C + Ph_4Ge$) and electrostatic parts according to eqn. (3).

$$\Delta^{s}_{M}X^{0}(\mathrm{Ph_4AsPh_4B}) = \Delta^{s}_{M}X^{0}(\mathrm{Ph_4Ge}) + \Delta^{s}_{M}X^{0}(\mathrm{Ph_4C}) + \Delta^{s}_{M}X^{0}(\mathrm{el})\ldots \quad (3)$$

where $\Delta^{s}_{M}X^{0} = \Delta^{s}_{M}G^{0}$, $\Delta^{s}_{M}H^{0}$ or $T\Delta^{s}_{M}S^{0}$. The ideal condition for the reference cation and reference anion is satisfied by the relation [4,5]

$$\frac{\Delta^{s}_{M}X^{0}(+)}{\Delta^{s}_{M}X^{0}(-)} = k \quad (4)$$

where $X^{0}(+)$ and $X^{0}(-)$ are the thermodynamic functions of the reference cation and reference anion, respectively. A reference electrolyte which is applicable for the determination of the single ion thermodynamics must have a $k$ value in eqn. (4) of unity or a certain value not differing from unity.

The aim of this work is to estimate the thermodynamic parameters for the $\mathrm{Ph_4As^+}$ and $\mathrm{Ph_4B^-}$ ions in the mixture of solvents under investigation and their uses for the determination of some thermodynamic data of monovalent ions.

Our results are contradictory to those reported in the literature which considered that $\mathrm{Ph_4AsPh_4B}$ is a symmetric model.

## EXPERIMENTAL

The solubilities of tetraphenylmethane, tetraphenylgermanium and $\mathrm{Ph_4AsPh_4B}$, including the analysis of equilibrium solutions, have been described elsewhere [2]. The solvents (MeOH and DMF) were spectroscopic pure (Uvasol) from Merck and used without purification, except for the addition of dehydrating agent (molecular sieve) for storage. The effect of temperature was studied in a shaking thermostat immersed in a mixture of glycol–water (40% v/v). The salts were shaken in a water bath for one week and then left for two days to reach equilibrium conditions. The solubility of $\mathrm{Ph_4C}$ was determined by UV spectrometry (model Carry 16). The solubilities of $\mathrm{Ph_4Ge}$ and $\mathrm{Ph_4AsPh_4B}$ were also estimated by the neutron activation analysis technique using the FRM (Forschungs Reaktor München, neutron flux, $2 \times 10^{13}$ n $\mathrm{s^{-1}}$ $\mathrm{cm^{-2}}$). The salt effect activity coefficients for $\mathrm{Ph_4AsPh_4B}$ in each solution were calculated by the Debye–Hückel equation [7].

The densities and dielectric constants of the mixed solvents under investigation were determined with a digital oscillator densimeter (Heraeous-Paar DMA-50) and a Dekameter DK 300 (WTW), respectively.

## RESULTS AND DISCUSSION

The values of log $S$ (solubility) and $\mathrm{p}K_{\mathrm{sp}}(-\log S)$ were calculated at three different temperatures (15, 25 and 35 °C) for the molal solubilities of $\mathrm{Ph_4C}$ and $\mathrm{Ph_4Ge}$, respectively, in a mixed solvent of methanol and DMF. In all measurements, methanol was used, due to the low solubility of these salts in water, and the similarity of the dipole moments of both water and methanol. The activity coefficients of $Ph_4C$ and $Ph_4Ge$ were taken to be unity because of the neutrality of these salts. For $Ph_4AsPh_4B$ the $pK_{sp}$ values were calculated by the following equation

$$pK_{sp} = -2 \log S + 2 \log \gamma_{\pm} \tag{5}$$

The free energy of transfer for $Ph_4AsPh_4B$ in the mixed methanol–dimethylformamide solutions were calculated from the solubility data by applying eqn. (6) in the 0–1 mole fraction range.

$$\Delta^{s}_{M}G^{0} = -RT \ln pK_{sp} \tag{6}$$

where

$$pK_{sp} = pK_{sp}(M) - pK_{sp}(s)$$

The calculated free energies for the different tetraphenyl derivatives at 25 °C are shown in Table 1. The standard enthalpies of transfer for $Ph_4C$, $Ph_4Ge$ and $Ph_4AsPh_4B$ were calculated graphically by drawing the relation between $pK_{sp}$ and $1/T$. From the slopes, the values of $\Delta H^0$ were estimated as shown in Table 1.

The standard entropy of transfer, $T\Delta^{s}_{M}S^{0}$, of the reference electrolyte ($Ph_4AsPh_4B$) and their neutral parts were calculated by using eqn. (2). The calculated values at 25 °C are listed in Table 1.

It was observed that the entropy of transfer of the neutral parts ($Ph_4C$ + $Ph_4Ge$) are approximately zero, as shown in Table 1.

For $Ph_4AsPh_4B$, the increase in mole fraction of DMF (decrease of MeOH mole fraction) is accompanied by an increase in the entropy of transfer. This observation indicates that the entropy of transfer is mainly dependent on the electrostatic ions and/or the electrostatic part and not on the neutral one.

The thermodynamic parameters for the ions $Ph_4As^+$ and $Ph_4B^-$ are given below [2,4]

$$\Delta^{s}_{M}X^{0}(Ph_4As^{+}) = \Delta^{s}_{M}X^{0}(Ph_4Ge) + \tfrac{1}{2}\Delta^{s}_{M}X^{0}(el) \tag{7}$$

$$\Delta^{s}_{M}X^{0}(Ph_4B^{-}) = \Delta^{s}_{M}X^{0}(Ph_4C) + \tfrac{1}{2}\Delta^{s}_{M}X^{0}(el) \tag{8}$$

$X^0$(el) values are calculated from eqn. (3).

The free energy, entropy and enthalpy of transfer of the two reference ions are calculated from eqns. (7) and (8), are presented in Table 2.

The mean value of $k$, given by eqn. (4), for the thermodynamic parameters ($\Delta^{s}_{M}G^{0}$ and $\Delta^{s}_{M}H^{0}$) is found to be 1.027 indicating the plausability of $Ph_4AsPh_4B$ as reference electrolyte in the mixed solvents under discussion.From a knowledge of the values of enthalpy of transfer for $Ph_4As^+$ (−4.45 kcal) and $Ph_4B^-$ (−3.99 kcal), the enthalpy of transfer of some monovalent ions is calculated from the enthalpy values of the corresponding salts, by subtracting the values of the reference ions from those given in the literature [8,9] as shown in Table 3.

TABLE 1

Free energies, enthalpies and entropies of transfer of $Ph_4C$, $Ph_4Ge$ and $Ph_4AsPh_4B$ in MeOH–DMF solutions at 25 °C (kcal $mol^{-1}$) in the molal scale

| Mole fraction of methanol, $X_s$ | Density, $\rho$ | Dielectric constant, $\epsilon$ | $\Delta^s_M G^0$ | | | $\Delta^s_M H^0$ | | | $T\Delta^s_M S^0$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $Ph_4C$ | $Ph_4Ge$ | $Ph_4AsPh_4B$ | $Ph_4C$ | $Ph_4Ge$ | $Ph_4AsPh_4B$ | $Ph_4C$ | $Ph_4Ge$ | $Ph_4AsPh_4B$ |
| 0 | 0.9440 | 36.6 | 1.60 | 1.82 | 6.81 | 1.98 | 1.52 | 8.45 | −0.37 | 0.31 | 1.64 |
| 0.174 | 0.9313 | 36.6 | 1.53 | 1.68 | 6.26 | 1.83 | 0.79 | 7.30 | −0.29 | 0.46 | 1.04 |
| 0.322 | 0.9240 | 36.7 | 1.41 | 1.54 | 5.69 | 1.71 | 1.39 | 6.73 | −0.29 | 0.15 | 1.04 |
| 0.449 | 0.9170 | 36.7 | 1.27 | 1.34 | 5.08 | 1.72 | 1.34 | 6.12 | −0.45 | 0 | 1.04 |
| 0.559 | 0.9028 | 36.5 | 1.14 | 1.15 | 4.53 | 1.59 | 1.15 | 5.28 | −0.29 | 0 | 0.75 |
| 0.655 | 0.8880 | 36.3 | 0.99 | 0.95 | 3.91 | 1.29 | 1.72 | 4.66 | −0.45 | 0.24 | 0.75 |
| 0.740 | 0.8775 | 35.9 | 0.79 | 0.76 | 3.20 | 1.24 | 0.76 | 3.65 | 0 | 0 | 0.45 |
| 0.816 | 0.8565 | 35.4 | 0.57 | 0.59 | 2.56 | 0.61 | 1.03 | 2.89 | 0 | 0 | 0.33 |
| 0.884 | 0.8405 | 34.8 | 0.43 | 0.38 | 1.71 | 0.61 | 0.83 | 1.86 | 0 | −0.15 | 0.15 |
| 0.945 | 0.8055 | 34.1 | 0.25 | 0.18 | 0.81 | 0.61 | 1.52 | 0.96 | 0 | −0.31 | 0.15 |
| 1.000 | 0.7868 | 32.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE 2

Thermodynamic parameters of transfer of $Ph_4As^+$ and $Ph_4B^-$ ions in mixed MeOH–DMF solutions at 25 °C (kcal $mol^{-1}$)

| $X_s$ MeOH | $\Delta^s_M G^0$ | | | $T\Delta^s_M S^0$ | | | $\Delta^s_M H^0$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | el | $Ph_4As^+$ | $Ph_4B^-$ | el | $Ph_4As^+$ | $Ph_4B^-$ | el | $Ph_4As^+$ | $Ph_4B^-$ |
| 0 | 3.39 | 3.51 | 3.29 | 1.69 | 1.16 | 0.48 | 4.95 | 4.45 | 3.99 |
| 0.174 | 3.05 | 3.21 | 3.06 | 0.87 | 0.59 | 0.15 | 4.68 | 4.17 | 3.13 |
| 0.322 | 2.74 | 2.91 | 2.78 | 1.18 | 0.74 | 0.30 | 3.63 | 3.53 | 3.21 |
| 0.449 | 2.47 | 2.57 | 2.51 | 1.49 | 0.75 | 0.29 | 3.06 | 3.25 | 2.87 |
| 0.559 | 2.24 | 2.27 | 2.27 | 1.19 | 0.59 | 0.15 | 2.54 | 2.86 | 2.42 |
| 0.655 | 1.95 | 1.95 | 1.97 | 0.79 | 0.64 | 0.11 | 1.65 | 2.94 | 3.37 |
| 0.740 | 1.65 | 1.59 | 1.61 | 0.89 | 0.45 | 0.00 | 1.65 | 2.06 | 1.58 |
| 0.816 | 1.40 | 1.29 | 1.27 | 0.33 | 0.16 | 0.16 | 1.25 | 1.23 | 1.65 |
| 0.884 | 0.90 | 0.83 | 0.88 | 0.29 | 0.00 | 0.15 | 0.44 | 0.82 | 1.04 |
| 0.945 | 0.38 | 0.37 | 0.44 | 0.46 | −0.08 | 0.23 | 1.17 | 0.02 | 0.93 |
| 1.000 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE 3

Standard enthalpies of transfer of some single ions from MeOH to DMF at 25 °C (kcal $mol^{-1}$)

| No. | Ion | $\Delta^s_M H^0$ |
|---|---|---|
| 1 | $Li^+$ | −2.56 |
| 2 | $Na^+$ | −2.59 |
| 3 | $Ag^+$ | −4.82 |
| 4 | $K^+$ | −4.17 |
| 5 | $Rb^+$ | −4.88 |
| 6 | $Cs^+$ | −5.51 |
| 7 | $Me_4N^+$ | −3.29 |
| 8 | $Et_4N^+$ | −2.26 |
| 9 | $Pr_4N^+$ | −1.53 |
| 10 | $Bu_4N^+$ | −4.41 |
| 11 | $Ph_4As^+$ | −4.45 |
| 12 | $Am_4N^+$ | −0.31 |
| 13 | $HeX_4N^+$ | −0.58 |
| 14 | $CH_3CO_2^-$ | 3.63 |
| 15 | $Cl^-$ | 3.00 |
| 16 | $Br^-$ | −0.59 |
| 17 | $I^-$ | −2.99 |
| 18 | $ClO_4^-$ | −5.06 |
| 19 | $N_3^-$ | 0.99 |
| 20 | $Ph_4B^-$ | −3.99 |

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