

Articles

Thermodynamic Properties of Transfer for Tetraphenylarsonium Tetraphenylborate from Water to *n*-Alkanols

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Solubilities of tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{AsB-Ph}_4$) in water, methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-octanol at $T = 293.2, 298.2, 303.2$ and 308.2 K have been determined by spectrophotometry. The standard transfer Gibbs energy ($\Delta_{\text{tr}}G_{\text{w}\rightarrow\text{s}}^0$) and entropy ($\Delta_{\text{tr}}S_{\text{w}\rightarrow\text{s}}^0$) of $\text{Ph}_4\text{AsBPh}_4$ from water to the *n*-alkanols at temperature from 293.2 K to 308.2 K have been obtained. Furthermore, the contribution of microscopic interaction to the standard Gibbs energy of transfer for $\text{Ph}_4\text{AsBPh}_4$ was calculated and discussed. The results show that the effect of hydrophobic interaction of $\text{Ph}_4\text{AsBPh}_4$ on its transfer process is the most important factor. According to the thermodynamical principle, the transfer process of $\text{Ph}_4\text{AsBPh}_4$ from water to the *n*-alkanols is the entropy dominated.

Keywords tetraphenylarsonium tetraphenylborate, *n*-alkanol, solubility, standard transfer thermodynamic property, activity coefficient, microscopic interaction

Introduction

$\text{Ph}_4\text{AsBPh}_4$ is a typical strong electrolyte which contains a large anion and cation. It plays an important role in studies and calculations of the transfer thermodynamic properties of single ions from water to another solvents owing to many thermodynamic properties of $\text{Ph}_4\text{AsBPh}_4$ distributed equally on Ph_4As^+ and BPh_4^- , such as^{1, 2}

$$\Delta_{\text{tr}}G(\text{Ph}_4\text{As}^+) = \Delta_{\text{tr}}G(\text{BPh}_4^-),$$

$$\Delta_{\text{tr}}H(\text{Ph}_4\text{As}^+) = \Delta_{\text{tr}}H(\text{BPh}_4^-)$$

$$\Delta_{\text{tr}}S(\text{Ph}_4\text{As}^+) = \Delta_{\text{tr}}S(\text{BPh}_4^-),$$

$$\Delta_{\text{s}}S(\text{Ph}_4\text{As}^+) = \Delta_{\text{s}}S(\text{BPh}_4^-)$$

and so on. So that, the thermodynamic properties of $\text{Ph}_4\text{AsBPh}_4$ in different solvents have been studied extensively by many authors.³⁻⁷ However, the systematic investigation of thermodynamic properties of $\text{Ph}_4\text{AsBPh}_4$ in a series of *n*-alkanols have not been reported. In order to study the difference of the thermodynamic properties of different uni-univalent tetraphenylborates in a series of *n*-alkanols and to get the information of microscopic interaction between the solute and solvent molecules, our previous papers,⁸⁻¹¹ reported the standard Gibbs energies of transfer for alkali metal tetraphenylborates from water to different *n*-alkanols. As part of our systematic research on the transfer thermodynamic properties for tetraphenylborates, in this paper, the standard Gibbs energy and entropy of transfer for $\text{Ph}_4\text{AsBPh}_4$ from water to different *n*-alkanols and the contribution of microscopic interaction to $\Delta_{\text{tr}}G^0$ were studied.

Experimental

Sodium tetraphenylborate (NaBPh_4), methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 1-butanol (BuOH), 1-pentanol (PeOH), 1-hexanol (HexOH) and 1-octanol (OctOH) were produced by Shanghai First Reagent Factory (A. R. grade). Tetraphenylar-

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sonium chloride (Ph_4AsCl) was purchased from Germany (A. R. grade). The solvents were purified by using the same procedure as before;⁸ their refractive indices at $T = 293.15$ K were 1.3285, 1.3614, 1.3850, 1.3996, 1.4104, 1.4155, 1.4291, respectively, in good agreement with literature.¹² $\text{Ph}_4\text{AsBPh}_4$ prepared by treating Ph_4AsCl with an excess 3% NaBPh_4 in water was recrystallized three times from acetone-water and dried *in vacuo* at $T = 323$ K. The composition of $\text{Ph}_4\text{AsBPh}_4$ is mass fraction 0.5452 Ph_4As^+ and mass fraction 0.4541 BPh_4^- , which were measured by spectrophotometry. Twice-distilled water, treated with ion exchange resin, was used and its conductivity was 1.13×10^{-4} S/m.

Saturated solutions of $\text{Ph}_4\text{AsBPh}_4$ were prepared by adding 50 mL of MeOH, EtOH, PrOH, BuOH, PeOH, HexOH, OctOH, respectively and 100 mL of water to an excess amount of $\text{Ph}_4\text{AsBPh}_4$ in different glass bottles, which were then flushed with fresh N_2 and sealed with a tightly fitting ground stopper and parafilm, followed by equilibration in a constant-temperature shaking bath at $T = 293.2, 298.2, 303.2$ and 308.2 K in which the fluctuation of the temperature was less than ± 0.05 K. The equilibrium time were 14–20 days (depending on the temperature), which was confirmed experimentally to be sufficiently long.

The saturated solutions of $\text{Ph}_4\text{AsBPh}_4$ in different solvents at different temperatures were filtered and the absorbances were measured at 274 nm by GBC-916 spectrophotometer (Waters, Australia). In order to eliminate the influence of temperature variation, all the experimental operations were carried out in a large box in which the temperature was the same as that of the constant-tempera-

ture shaking bath. Because the solubility of $\text{Ph}_4\text{AsBPh}_4$ in water is rather low, the absorbance for its saturated solution is too low to be directly determined. In this work, the determining method of absorbance for aqueous solution of $\text{Ph}_4\text{AsBPh}_4$ was as follows: 90 mL of filtering solution was dried *in vacuo* at $T = 303$ K, then the crystal of $\text{Ph}_4\text{AsBPh}_4$ was dissolved in 3 mL of mixed solvents of acetone-water and the absorbance was determined. The absorbance is linear over a range of concentration from 1×10^{-7} mol/dm³ to 9×10^{-5} mol/dm³.

The method used to measure the densities of *n*-alkanols is the same as that of the previous paper.⁸

Results and discussion

Solubility of $\text{Ph}_4\text{AsBPh}_4$

The solubilities (C) of $\text{Ph}_4\text{AsBPh}_4$ in different *n*-alkanols and the densities (d_0) of solvents from 293.2 K to 308.2 K are presented in Table 1. It can be seen from Table 1 that the solubility of $\text{Ph}_4\text{AsBPh}_4$ decreases with increasing the number of carbon atoms (n) of the *n*-alkanols and with lowering of temperature. The experiential relation between C and n , T was obtained by using curve fitting on a microcomputer, it can be expressed as

$$\lg C = -16.049 + 0.0397T - 0.2567n \quad (1)$$

The calculated result of solubility for $\text{Ph}_4\text{AsBPh}_4$ from Eq. (1) was very approximate to the measuring value in the range of experimental temperature.

Table 1 Solubilities of $\text{Ph}_4\text{AsBPh}_4$ in different solvents and densities of the solvents

| Solvents | 293.2 K | | 298.2 K | | 303.2 K | | 308.2 K | |
|----------|-----------------------|----------|-----------------------|----------|-----------------------|----------|-----------------------|----------|
| | $10^6 C$ | ρ_1 | $10^6 C$ | ρ_1 | $10^6 C$ | ρ_1 | $10^6 C$ | ρ_1 |
| Water | 1.45×10^{-3} | 0.9983 | 2.28×10^{-3} | 0.9975 | 3.62×10^{-3} | 0.9957 | 5.63×10^{-3} | 0.9940 |
| MeOH | 21.2 | 0.7908 | 32.8 | 0.7868 | 49.9 | 0.7828 | 82.6 | 0.7788 |
| EtOH | 12.8 | 0.7895 | 20.4 | 0.7852 | 30.7 | 0.7808 | 49.6 | 0.7765 |
| PrOH | 6.40 | 0.8062 | 10.7 | 0.8021 | 16.0 | 0.7980 | 26.2 | 0.7939 |
| BtOH | 3.51 | 0.8111 | 5.86 | 0.8072 | 9.17 | 0.8032 | 14.8 | 0.7993 |
| PeOH | 2.04 | 0.8147 | 3.32 | 0.8106 | 5.08 | 0.8066 | 8.42 | 0.8025 |
| HexOH | 1.17 | 0.8206 | 1.79 | 0.8166 | 2.73 | 0.8126 | 4.52 | 0.8086 |
| OctOH | 0.341 | 0.8261 | 0.543 | 0.8224 | 0.823 | 0.8186 | 1.34 | 0.8149 |

Units: C , mol/dm³; ρ_1 , g/cm³.

Standard Gibbs energy of transfer for Ph₄AsBPh₄

Since Ph₄AsBPh₄ is sparingly in the solvents as mentioned above, its standard transfer Gibbs energy ($\Delta_{tr}G^0$) could be determined accurately by the solubility method. For a sparingly soluble 1-1 electrolyte MX undergoing complete ionization to M⁺ and X⁻ ions in the saturated solution, $\Delta_{tr}G^0$ of MX for transfer from the reference solvent to another solvent is given by¹³

$$\Delta_{tr}G^0(M^+ + X^-)_{w \rightarrow s} = (\ln 10) RT[(pK_{sp})_s - (pK_{sp})_w] \quad (2)$$

where the subscripts w and s refer to water and organic solvent, respectively; K_{sp} is the thermodynamic solubility (ion-activity) product constant of the electrolyte in the particular solvent. If the associated phenomenon of Ph₄AsBPh₄ in solution is considered, pK_{sp} can be calculated by¹⁴

$$pK_{sp} = [C(1 - \alpha)\gamma_{\pm}]^2 \quad (3)$$

where α is the degree of association of the electrolyte into ion pairs, and γ_{\pm} is the mean activity coefficient of the electrolyte in the saturated solution on the molar scale, and its value can be calculated by the extended form of the Debye-Hückel formula¹⁵

$$\lg \gamma_{\pm} = A(C_1)^{1/2} \{ [1 + a_+^0 B(C_1)^{1/2}]^{-1} + [1 + a_-^0 B(C_1)^{1/2}]^{-1} \} / 2 + \lg [(d - 0.001 C_1 M + 0.002 C_1 M_0) / d_0] \quad (4)$$

Here, $C_1 = C(1 - \alpha)$, A and B are Debye-Hückel constants given by $1.8246 \times 10^6 (DT)^{-3/2} (\text{mol}^{-1} \cdot \text{dm}^3)^{1/2}$ and $50.29 \times 10^8 (DT)^{-1/2} (\text{mol}^{-1} \cdot \text{dm}^3)^{-1/2} \cdot \text{cm}^{-1}$, respectively, D is the dielectric constant of the solvents, d the density of the solution (assumed to be approximately equal to that of the pure solvent d_0), M and M_0 are molecular weight of the electrolyte and solvent, respectively, a_+^0 and a_-^0 the ion-size parameters for the cation and anion of the electrolyte, assumed to have the following constant value, $a^0(\text{Ph}_4\text{As}^+) = a^0(\text{BPh}_4^-) = 5 \times 10^{-8} \text{ cm}$,¹³ in different solvents. The α may be calculated by¹⁴

$$\alpha = [2CK_A\gamma_{\pm}^2 + 1] - (4CK_A\gamma_{\pm}^2 + 1)^{1/2} / 2CK_A\gamma_{\pm}^2 \quad (5)$$

where K_A is the association constant and can be calculated by¹⁶

$$\ln K_A = \ln \frac{4\pi N b^3}{3000} + \frac{|Z_+ Z_-| e^2}{bkTD} \quad (6)$$

where N is the Avogadro constant, k the Boltzmann constant ($1.38 \times 10^{-16} \text{ erg/K}$), Z_+ and Z_- are the charge numbers of the cation and anion, e the electronic charge ($4.802 \times 10^{-10} \text{ CGSE}$), T the Kelvin temperature, B the distance of shortest approach between cation and anion when the electrolyte forms ion pairs in solution. Here, $b(\text{Ph}_4\text{AsBPh}_4) = 10 \times 10^{-8} \text{ cm}$. The activity coefficients and the degree of association of ions were calculated by using the iterative method on a microcomputer. The condition of convergence is that the difference in values of mean activity coefficients for the last two iterations must be less than 10^{-10} . The calculated results of γ_{\pm} , α , $\Delta_{tr}G^0$ and $\Delta_{tr}S^0$ are given in Tables 2 and 3.

Table 2 Degree of association and mean activity coefficient for Ph₄AsBPh₄ in different solvents

| Solvents | 293.2 K | | 298.2 K | | 303.2 K | | 308.2 K | |
|----------|----------------|---------------|----------------|---------------|----------------|---------------|----------------|---------------|
| | γ_{\pm} | $10^4 \alpha$ | γ_{\pm} | $10^4 \alpha$ | γ_{\pm} | $10^4 \alpha$ | γ_{\pm} | $10^4 \alpha$ |
| Water | 0.9999 | 0 | 0.9999 | 0 | 0.9999 | 0 | 0.9999 | 0 |
| MeOH | 0.9816 | 1.84 | 0.9756 | 4.39 | 0.9707 | 6.22 | 0.9641 | 9.13 |
| EtOH | 0.9763 | 2.24 | 0.9701 | 4.86 | 0.9625 | 6.90 | 0.9569 | 9.81 |
| PrOH | 0.9782 | 1.75 | 0.9711 | 4.03 | 0.9636 | 5.89 | 0.9586 | 8.38 |
| BtOH | 0.9792 | 1.50 | 0.9729 | 3.64 | 0.9667 | 5.49 | 0.9604 | 7.77 |
| PeOH | 0.9802 | 1.67 | 0.9733 | 3.89 | 0.9674 | 5.87 | 0.9600 | 8.75 |
| HexOH | 0.9817 | 1.66 | 0.9757 | 3.80 | 0.9703 | 5.86 | 0.9640 | 8.93 |
| OctOH | 0.9860 | 1.68 | 0.9810 | 3.86 | 0.9765 | 6.37 | 0.9712 | 10.51 |

Table 3 Standard Gibbs energies and entropies of transfer for $\text{Ph}_4\text{AsBPh}_4$ from water to the different n -alkanols

| Solvents | 293.2 K | | 298.2 K | | 303.2 K | | 308.2 K | |
|----------|--------------------------|-------------------------|--------------------------|-------------------------|--------------------------|-------------------------|--------------------------|-------------------------|
| | $-\Delta_{\text{tr}}G^0$ | $\Delta_{\text{tr}}S^0$ | $-\Delta_{\text{tr}}G^0$ | $\Delta_{\text{tr}}S^0$ | $-\Delta_{\text{tr}}G^0$ | $\Delta_{\text{tr}}S^0$ | $-\Delta_{\text{tr}}G^0$ | $\Delta_{\text{tr}}S^0$ |
| MeOH | 46.73 | 142 | 47.35 | 146 | 48.05 | 150 | 48.88 | 155 |
| EtOH | 44.27 | 128 | 44.96 | 136 | 45.61 | 145 | 46.54 | 153 |
| PrOH | 40.89 | 114 | 41.77 | 127 | 42.31 | 139 | 43.28 | 152 |
| BtOH | 37.95 | 100 | 38.79 | 117 | 39.51 | 134 | 40.36 | 150 |
| PeOH | 35.33 | 86.5 | 35.98 | 108 | 36.53 | 128 | 37.45 | 149 |
| HexOH | 32.60 | 75.6 | 32.93 | 97.5 | 33.40 | 123 | 34.27 | 148 |
| OctOH | 26.61 | 44.8 | 26.91 | 78.0 | 27.36 | 112 | 28.05 | 145 |

Unit: $\Delta_{\text{tr}}G^0$, $\text{kJ}\cdot\text{mol}^{-1}$; $\Delta_{\text{tr}}S^0$, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

As shown in Table 3, negative values of the standard Gibbs energy of transfer of $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols decrease either with the increase in the number of carbon atoms of the n -alkanols or with lowering of temperature. This shows that spontaneous transfer of $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols is easier with the increase of temperature and with the decrease of number of carbon atoms of the n -alkanols, and the following information can be given: first, the interaction between $\text{Ph}_4\text{AsBPh}_4$ and water is weaker than that between $\text{Ph}_4\text{AsBPh}_4$ and the n -alkanols owing to the $\Delta_{\text{tr}}G^0$ is negative, and the larger the value of $-\Delta_{\text{tr}}G^0$, the stronger the interaction between $\text{Ph}_4\text{AsBPh}_4$ and the n -alkanol; second, the difference of interaction between ($\text{Ph}_4\text{AsBPh}_4$ -water) and ($\text{Ph}_4\text{AsBPh}_4$ - n -alkanol) increases with increasing temperature. However, the interaction between $\text{Ph}_4\text{AsBPh}_4$ and water do not weaken with increasing temperature, this show that the interaction between $\text{Ph}_4\text{AsBPh}_4$ and the n -alkanol enhances with increase in the temperature.

By using the curve fitting on a microcomputer, the relation between $\Delta_{\text{tr}}G^0$ and n , T was obtained, as following

$$\Delta_{\text{tr}}G^0 = -3.965 - 0.156T - (37.176 - 0.259T + 4.18 \times 10^{-4}T^2)n \quad (7)$$

The calculated values of $\Delta_{\text{tr}}G^0$ from Eq. (7) were very approximate to experimental results.

Contribution of microscopic interaction to Gibbs energy of transfer for $\text{Ph}_4\text{AsBPh}_4$

The standard Gibbs energy of transfer for electrolyte

from water to nonaqueous solvent can be expressed by

$$\Delta_{\text{tr}}G_{\text{w}\rightarrow\text{s}}^0 = (\Delta G_{+}^0 + \Delta G_{-}^0)_{\text{s}} - (\Delta G_{+}^0 + \Delta G_{-}^0)_{\text{w}} \quad (8)$$

where ΔG_{+}^0 and G_{-}^0 are the solvation Gibbs energies of cation and anion, respectively. The ΔG^0 of an ion is expressed in a simplified form by^{2,4,17,18}

$$\Delta G^0 = G_{\text{c}} + G_{\text{i}} + G_{\text{r}} + G_{\text{e}} + \Delta G' \quad (9)$$

The Gibbs energy terms in Eq. (9) can be calculated and explained as follows: G_{c} is the partial molar Gibbs energy of cavity formation for an ion in the solvent, which can be calculated by Pierotti's formula¹⁹ based on the scaled particle theory (SPT)²⁰ and knowledge of the hard sphere diameters of the solute and solvent molecules, that is

$$G_{\text{c}} = RT\{-\ln(1-\gamma) + [3\gamma/(1-\gamma)]R' + [3\gamma/(1-\gamma) + (9/2)(\gamma^2/(1-\gamma)^2)(R')^2]\} + \gamma p n \rho / (R')^3 \quad (10)$$

where $\gamma = (\pi\rho_0\sigma_0)/6$ which implies the packing density of the solvent, σ_0 and ρ_0 are the hard sphere diameter and number density of the solvent molecules, P the pressure of the system, N Avogadro constant, $R' = \sigma/\sigma_0$ where σ is the hard sphere diameter of the ion. In this paper $\sigma(\text{Ph}_4\text{As}^+) = 8.56 \times 10^{-8}$ cm, $\sigma(\text{BPh}_4^-) = 8.42 \times 10^{-8}$ cm,⁴ σ_0 can be calculated from⁵

$$\sigma_0(\text{SPT}) = (0.9275 \pm 0.0126)(6V_0/N\pi)^{1/3} - (0.8465 \pm 0.0084) \times 10^{-8} \quad (11)$$

where V_0 is molar volume of the solvent.

G_i and G_r are the partial molar energies of nonelectrostatic attractive and repulsive interaction between the ion and surrounding solvent molecule, respectively. G_i can be calculated from^{19,21}

$$\begin{aligned} G_i &= G(\text{dispersion}) + G(\text{inductive}) \\ &= (-32/9)R\pi\rho_0\sigma_1^3(\epsilon_0\epsilon/k^2)^{1/2} - \\ &\quad (12/9)N\pi\rho_0\mu_0^2\theta/\sigma_1^3 \end{aligned} \quad (12)$$

where $\sigma_1 = (\sigma_0 + \sigma)/2$ and μ_0 is dipole moment of a solvent molecule.¹² Dipole moments of PeOH and OctOH molecules under investigation are unknown, so the calculation for $G(\text{inductive})$ can not be made for those solvents. θ is the ionic polarizability, and $\theta(\text{Ph}_4\text{As}^+) \approx \theta(\text{BPh}_4^-) = 40.91 \times 10^{-24} \text{ cm}^3$, ϵ_0/k and ϵ/k are the energy parameters of solvent and ion, respectively. In this paper, the energy parameter of the ion was calculated from²²

$$\epsilon/k = 2.28 \times 10^{-8} [(Z_{\pm})^{1/2}\theta^{3/2}/\sigma^6] \quad (13)$$

where Z_{\pm} is charge number of cation and anion. The energy parameter of the n -alkanol ϵ_0/k can be estimated from¹⁰

$$\lg(\epsilon_0/k) = 2.366 + 0.5027 \lg n \quad (14)$$

where n is the number of carbon atoms of the n -alkanols. G_r can be calculated using¹⁸

$$\begin{aligned} G_r &= (Ne^2r/8D_0n_0)(1/D - 1) \{ [(r + \sigma_0)^2 - \\ &\quad r^2]/(r + r_e)^4 - 1/(r + \sigma_0)^2 - 4/3[(r + \\ &\quad \sigma_0)^3 - r^3]/(r + r_e)^5 \} \end{aligned} \quad (15)$$

In Eq. (15), D_0 is vacuum dielectric constant, n_0 Born's index, e electronic charge, $r = \sigma/2$ and $r_e \approx \sigma_0/2$.

G_e is the partial molar Gibbs energy of electrostatic between ion and solvent molecules, and it can be calculated from²³

$$\begin{aligned} G_e &= Ne^2 \{ -[(r + r_0) + r]/4r(r + r_0) + \\ &\quad 1/2(r + r_0)D \} \end{aligned} \quad (16)$$

where $r_0 = \sigma_0/2$. In Eq. (9), $\Delta G' = RT \ln(RT/V_{0,m})$, $V_{0,m}$ is the partial molar volume of solvent (in this paper $V_{0,m} \approx V_0$).

The contribution of microscopic interaction to the solvation Gibbs energy and standard Gibbs energy of transfer for $\text{Ph}_4\text{AsBPh}_4$ are presented in Table 4.

From Table 4 the following information can be drawn:

(1) The positive values of Gibbs energies of cavity formation for $\text{Ph}_4\text{AsBPh}_4$ in the solvents and the repulsive interaction between $\text{Ph}_4\text{AsBPh}_4$ and the solvents decrease with increasing hard sphere diameters of the solvent molecules. This result leads to a more and more easy transfer of $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols with increasing the number of carbon atoms of the n -alkanols. As the difference between $G_c(\text{in water})$ and $G_c(\text{in } n\text{-alkanol})$ is most distinct in all of Gibbs energies of microscopic interaction between $\text{Ph}_4\text{AsBPh}_4$ and the solvents, the contribution of $\Delta_{tr}G_c$ to $\Delta_{tr}G^0$ of $\text{Ph}_4\text{AsBPh}_4$ is largest. In other words, the effect of cavity formation on the transferring process of $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols is most important.

Table 4 Contribution to the transfer Gibbs energy from the terms in Eq. (9) at 298.2 K

| Solvents | G_c | $-\Delta_{tr}G_c$ | G_r | $-\Delta_{tr}G_r$ | $-G_e$ | $\Delta_{tr}G_e$ | $-G_i$ | $\Delta_{tr}G_i$ | $\Delta G'$ | $-\Delta_{tr}G'$ | $\Delta G^0(\text{solv.})$ | $\Delta_{tr}G^0$ |
|----------|--------|-------------------|-------|-------------------|--------|------------------|--------|------------------|-------------|------------------|----------------------------|------------------|
| water | 186.00 | 0 | 56.64 | 0 | 285.78 | 0 | 155.46 | 0 | 35.75 | 0 | 162.85 | 0 |
| MeOH | 133.84 | 52.16 | 39.44 | 17.20 | 271.98 | 13.80 | 144.24 | 11.22 | 31.73 | 4.02 | 211.21 | 48.36 |
| EtOH | 124.20 | 61.80 | 37.90 | 18.74 | 264.68 | 21.10 | 134.66 | 20.8 | 29.88 | 5.87 | 207.36 | 44.51 |
| PrOH | 120.56 | 65.44 | 36.62 | 20.02 | 259.74 | 26.04 | 131.20 | 24.26 | 28.67 | 7.08 | 205.09 | 42.24 |
| BuOH | 118.02 | 67.98 | 35.44 | 21.2 | 255.98 | 29.80 | 127.14 | 28.32 | 27.74 | 8.01 | 201.92 | 39.07 |
| PeOH | 114.98 | 71.02 | 34.26 | 21.98 | 251.34 | 34.44 | 122.84 | 32.62 | 26.89 | 8.86 | 198.05 | 35.20 |
| HexOH | 112.10 | 73.90 | 33.26 | 23.38 | 247.28 | 38.50 | 119.38 | 36.08 | 26.17 | 9.58 | 195.13 | 32.28 |
| OctOH | 109.16 | 76.84 | 31.42 | 25.22 | 239.38 | 46.40 | 114.48 | 40.98 | 25.00 | 10.75 | 188.28 | 25.43 |

Units: G and $\Delta_{tr}G^0$, kJ/mol, $\Delta_{tr}G = \Delta_{tr}G_c + \Delta_{tr}G_r + \Delta_{tr}G_e + \Delta_{tr}G_i + \Delta_{tr}G'$.

(2) The negative values of Gibbs energies of non-electrostatic and electrostatic attractive interaction between $\text{Ph}_4\text{AsBPh}_4$ and the solvents gradually decrease with increasing hard sphere diameters of the solvent molecules. This result leads to a more and more difficult transfer of $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols with increasing number of carbon atoms in the n -alkanols. On the other hand, although there is an evident difference of contribution between nonelectrostatic and electrostatic interaction to the Gibbs energy of solvation of $\text{Ph}_4\text{AsBPh}_4$, the contribution to the Gibbs energy of transfer of $\text{Ph}_4\text{AsBPh}_4$ is approximative, which is different from the character of interaction between alkali metal tetraphenylborate (MBPh_4) and the solvents.^{10,11} Virtually, electrostatic interaction constitutes the main contribution to the Gibbs energy of solvation for MBPh_4 , and the contribution of electrostatic interaction to $\Delta_{\text{tr}}G^0$ is apparent larger than that of non-electrostatic interaction to $\Delta_{\text{tr}}G^0$ of MBPh_4 . While the nonelectrostatic interaction between $\text{Ph}_4\text{AsBPh}_4$ and these solvents is more strong obviously than that between MBPh_4 and the solvents.

(3) The ability of spontaneous transfer for $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols is mainly due to the total result of contribution (1) and (2) as mentioned above. The various microscopic interactions between $\text{Ph}_4\text{AsBPh}_4$ and the solvents lead to the stronger solvation of $\text{Ph}_4\text{AsBPh}_4$ in the n -alkanols is stronger than that $\text{Ph}_4\text{AsBPh}_4$ in water, and the smaller the hard sphere diameter of the n -alkanol is, the stronger the solvation of $\text{Ph}_4\text{AsBPh}_4$ is.

As mentioned above, the effect of cavity formation of $\text{Ph}_4\text{AsBPh}_4$ in water and the n -alkanol on its transferring process from water to the n -alkanols is very important. Kronberg *et al.*²⁴ thought that the cause of hydrophobic interaction for a apolar molecule is the large energy required to form a cavity in the water in order to accommodate it. Thus the driving force of hydrophobic interaction is attributed mainly to the extricating energy of the cavity breakdown. Evidently, the more the required energy of cavity formation for a apolar molecule in water (or other solvent), the stronger the hydrophobic (or solvophobic) interaction is. We know that many special properties of water are due to the strong cohesive forces which is found in the hydrogen bonding connectivity in liquid water. Generally, water molecules are much smaller than ordinary organic hydrocarbons, resulting in a large number of

hydrogen bonds to be broken to accommodate a hydrocarbon molecule. In comparison with water, the cohesive forces in the n -alkanols are weakened obviously. As containing a large hydrophobic anion (BPh_4^-) and cation (Ph_4As^+), $\text{Ph}_4\text{AsBPh}_4$ require more energies for the cavity formation in water than in the n -alkanol. Therefore, it can be concluded that the effect of hydrophobic interaction of $\text{Ph}_4\text{AsBPh}_4$ on its transferring process from water to the n -alkanol is the most important factor.

Standard entropy of transfer of $\text{Ph}_4\text{AsBPh}_4$

From Eq. (7), the standard entropy of transfer for $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols can be given by

$$\Delta_{\text{tr}}S_{\text{w} \rightarrow \text{s}}^0 = - \left(\frac{\partial \Delta_{\text{tr}}G_{\text{w} \rightarrow \text{s}}^0}{\partial T} \right)_{\text{P}} = 0.156 - (0.259 - 8.36 \times 10^{-4} T) n \quad (17)$$

the calculated result of $\Delta_{\text{tr}}S^0$ is presented in Table 3. It can be seen from Table 3 that all of $\Delta_{\text{tr}}S^0$ are positive under the experimental conditions, which is different from the $\Delta_{\text{tr}}S^0$ of alkali metal tetraphenylborate from water to the same solvent,²⁵ and the values of $\Delta_{\text{tr}}S^0$ ($\text{Ph}_4\text{AsBPh}_4$) decrease with increasing the number of carbon atoms of the n -alkanols and lowering of temperature. As the difference between $\Delta_{\text{tr}}G^0$ and $T\Delta_{\text{tr}}S^0$ is comparatively small, according to the thermodynamical principle, the transfer process of $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols should be entropy dominated.

Generally, there are two opposite contributions to the entropy of solvation when an ion is introduced into a solvent, *i. e.* the loss of entropy results from increasing the solvent structure and decreasing the solvent structure leads to the increase of entropy. When an inorganic ion is introduced into a solvent, the stronger the solvent structure is, the larger the entropy of solvation. It is obviously from the breaking for the solvent structure. In comparison with ordinary organic solvent, the structure of water is formed highly by the intermolecular hydrogen bonding, so that, the entropy of transfer for an inorganic ion from water to the organic solvent is negative. However, when Ph_4As^+ and BPh_4^- ions are introduced into water, the forming structure of water molecules around these strong hydrophobic ions leads to the strengthening of hydrogen bonds in a surface about these ions²⁶ (*i. e.* increasing

the water structure) and the large loss of entropy. While when introducing Ph_4As^+ and BPh_4^- ions into the n -alkanols are to produce only a slight order, *i. e.* small loss of entropy. Therefore, the entropies of transfer for $\text{Ph}_4\text{AsBPh}_4$ from water to the n -alkanols are positive. The reasons for the $\Delta_{\text{tr}}S^0$ of $\text{Ph}_4\text{AsBPh}_4$, which decreases with the increase of the number of carbon atoms of the n -alkanols, may be mainly the dispersion force interaction between Ph_4As^+ , BPh_4^- ions and the n -alkanol. This interaction increases with increasing the number of carbon atoms of the n -alkanol, which leads to increase the ordering of the solvent molecules and the loss of entropy of solvation of these ions.

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