# Temperature dependence of the pair interaction between hydrophobic and hydrophilic solutes: A calorimetric study

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## Abstract

The enthalpies of tetraethyl- and tetrabutylammonium bromides solution in water and highly aqueous water–formamide (FA) mixtures were measured at 277.15, 288.15, 313.15, 319.15 and 328.15 K. The standard enthalpies of solution are obtained and compared with previously determined values at 298.15 K. Heat capacities of solution were computed. Enthalpic and heat capacity coefficients of solute–FA pair interactions were calculated. The heat capacity of methylene group interaction with FA was found to be negative, whereas the heat capacity of bromide ion–FA interaction appeared to be positive. The free energy and entropic coefficients of tetrabutylammonium bromide–FA interaction coefficients were estimated and compared with those for other non-electrolytes. It has been found that the interaction between two hydrophobic species is the entropic origin which is in agreement with classical models of hydrophobic interaction. In contrast, the interaction of tetrabutylammonium bromide with FA is the enthalpic origin, it being repulsive at all temperatures studied.
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## 1. Introduction

Recently [1], we have studied the temperature dependence of the pair-interaction energetics between tetraethyl- and tetrabutylammonium bromides and hexamethyl phosphoric triamide (HMPT) in water. The heat capacity coefficients of electrolyte–amide interaction $c_{p23}$ have been found to be negative equal to $-34$ and $-32\,\mathrm{J\,kg\,mol^{-2}\,K^{-1}}$ for $Et_4NBr$ and $Bu_4NBr$, respectively. It has appeared quite unexpected for strongly hydrophobic species, such as HMPT and tetraalkylammonium salts [2]. We have shown that such solutes behaviour resulted from the influence of bromide ion and the polar $N_3PO$ group of the amide molecule [1], i.e. the sign of the $c_{p23}$ values are defined by hydrophilic effects. Thus, it is of particular interest to study the tetraalkylammonium bromides

interaction with hydrophilic non-electrolytes and compare the interaction parameters with those for HMPT. We have chosen one of the most hydrophilic solutes, formamide (FA) which has the positive value of the hydrophobicity parameter $dB_{22}dP^{-1}$ and negative values of the entropic $s_{22}$ and enthalpic $h_{22}$ pair-interaction coefficients [2]. In contrast, the $dB_{22}dP^{-1}$ derivative is large and negative for HMPT, whereas the enthalpic and entropic parameters being the largest among other non-electrolytes are positive [2].

## 2. Experimental

Formamide ($NH_2CHO$), water and tetraalkylammonium salts were purified as in our previous studies [3–5]. The measurements were carried out using "isoperibol" ampoule calorimeters described in detail elsewhere [1,3–6]. The enthalpy of solution was determined by a comparative method. An electrical calibration was carried out before and

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after each experiment. The calorimeter was tested by measuring the enthalpies of KCl and 1-propanol solution in water at 298.15 K. The agreement between our and the best literature values was found to be excellent [5,6].

## 3. Results

The experimental enthalpies of solution were obtained in the range of the electrolyte molalities of 0.006–0.04 mol kg$^{-1}$. The enthalpies of solution at infinite dilution $\Delta_{sol}H^0$ were calculated from the following relationship: $\Delta_{sol}H^0 = \Delta_{sol}H^m + \Delta_{dil}H^{m\to 0}$. The enthalpies of dilution $\Delta_{dil}H^{m\to 0}$ were calculated in terms of Debye–Hükkel theory in the second approximation according to the method proposed elsewhere [7]. The $\Delta_{dil}H^{m\to 0}$ values are found to be from $-0.08$ to $-0.36$ kJ mol$^{-1}$. The enthalpies of solution at infinite dilution $\Delta_{sol}H^0$ in pure water reflect the results of five or more measurements, while the $\Delta_{sol}H^0$ values in the mixed solvent represent the result of one or two experiments (see Tables 1 and 2).

## 4. Discussion

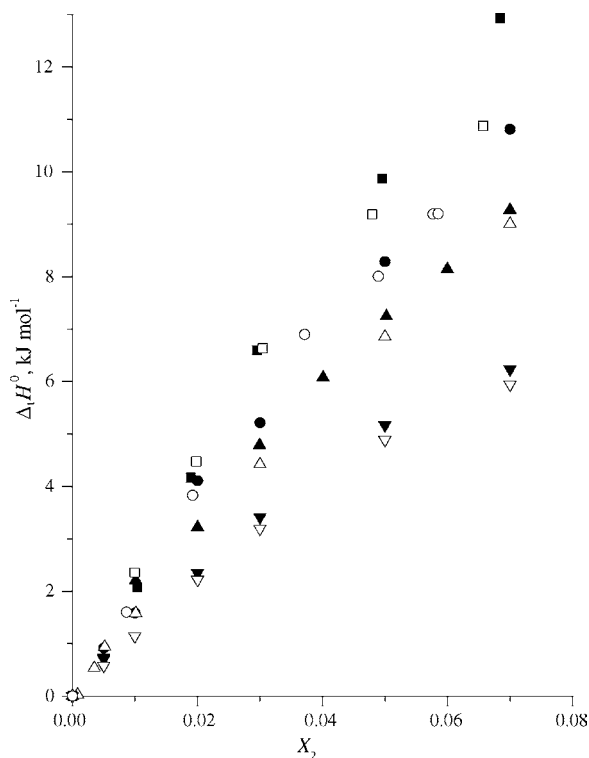The comparison of the enthalpies of a solute transfer allows to find some interesting observation. Fig. 1 shows that



Fig. 1. Enthalpies of transfer of Bu$_4$NBr (dark symbols) from water to water–FA mixtures and Et$_4$NBr (light symbols) from water to water–HMPT mixtures at 277.15 K (■, □), 288.15 K (●, ○), 298.15 K (▲, △) [3,5] and 313.15 K (▼, ▽). $X_2$, the amide mol fraction.

Table 1
Enthalpies of solution at infinite dilution ($\Delta_{sol}H^0$, kJ mol$^{-1}$) of Et$_4$NBr in water–FA mixtures at 277.15, 288.15, 313.15, 319.15 and 328.15 K

| $X_{FA}$ | $\Delta_{sol}H^{0a}$ |
|---|---|
| **277.15** | |
| 0 | $3.58 \pm 0.12$[b] |
| 0.01000 | 3.68 |
| 0.02000 | 3.86 |
| 0.03000 | 3.96 |
| 0.05000 | 4.22 |
| 0.06000 | 4.36 |
| 0.07000 | 4.66 |
| **288.15** | |
| 0 | $4.71 \pm 0.04$[b] |
| 0.00501 | 4.73 |
| 0.00884 | 4.82 |
| 0.01000 | 4.80 |
| 0.02000 | 4.95 |
| 0.02946 | 5.09 |
| 0.03000 | 5.00 |
| 0.04998 | 5.10 |
| 0.05000 | 5.12 |
| 0.0699 | 5.32 |
| 0.07000 | 5.27 |
| **313.15** | |
| 0 | $8.11 \pm 0.10$[b] |
| 0.005000 | 8.08 |
| 0.00998 | 8.07 |
| 0.02000 | 8.02 |
| 0.03000 | 8.00 |
| 0.04991 | 7.93 |
| 0.07000 | 7.85 |
| **319.15** | |
| 0 | $9.01 \pm 0.06$ |
| 0.003397 | 8.94 |
| 0.01152 | 8.90 |
| 0.03006 | 8.83 |
| 0.04777 | 8.60 |
| 0.06544 | 8.69 |
| **328.15** | |
| 0 | $10.13 \pm 0.16$ |
| 0.003130 | 10.10 |
| 0.01272 | 10.00 |
| 0.01824 | 9.95 |
| 0.02821 | 9.98 |
| 0.03282 | 9.89 |
| 0.04706 | 9.70 |
| 0.06719 | 9.84 |

[a] Uncertainties are represented as the twice standard deviation from the mean value.

[b] Values in pure water at 277.15–313.15 K were taken from Ref. [1].

the enthalpies of Bu$_4$NBr transfer from water to the highly aqueous water–FA mixtures are nearly identical to those of Et$_4$NBr in the mixtures of water with HMPT. Since it is observed in a dilute aqueous solution, we should expect that the enthalpic coefficients of Et$_4$NBr–HMPT and Bu$_4$NBr–FA pair interaction in water will be very close. Additionally, since this phenomenon is observed in a wide temperature range (see Fig. 1), it is reasonable to consider that the heat capacity interaction parameters should not differ either. The

Table 2
Enthalpies of solution at infinite dilution ($\Delta_{sol}H^0$, kJ mol$^{-1}$) of Bu$_4$NBr in water–FA mixtures at 277.15, 288.15, 313.15, 319.15 and 328.15 K

| $X_{FA}$ | $\Delta_{sol}H^{0a}$ |
|---|---|
| **277.15** | |
| 0 | $-24.41 \pm 0.23$[b] |
| 0.01037 | $-20.32$ |
| 0.01892 | $-20.23$ |
| 0.02953 | $-17.81$ |
| 0.04956 | $-14.53$ |
| 0.06844 | $-11.47$ |
| **288.15** | |
| 0 | $-16.01 \pm 0.11$[b] |
| 0.005000 | $-15.10$ |
| 0.01001 | $-14.43$ |
| 0.02000 | $-11.90$ |
| 0.03000 | $-10.79$ |
| 0.05000 | $-7.23$ |
| 0.06998 | $-5.20$ |
| **313.15** | |
| 0 | $2.67 \pm 0.07$[b] |
| 0.005000 | 3.38 |
| 0.005010 | 3.41 |
| 0.01001 | 3.82 |
| 0.02002 | 5.02 |
| 0.02998 | 6.09 |
| 0.05000 | 7.84 |
| 0.07000 | 8.90 |
| **319.15** | |
| 0 | $6.46 \pm 0.11$ |
| 0.005030 | 7.33 |
| 0.01220 | 8.05 |
| 0.02358 | 9.33 |
| 0.03810 | 9.92 |
| 0.04485 | 10.60 |
| 0.06389 | 11.50 |
| **328.15** | |
| 0 | $12.62 \pm 0.07$ |
| 0.005200 | 12.84 |
| 0.01415 | 13.50 |
| 0.034500 | 15.17 |
| 0.04662 | 15.66 |
| 0.05630 | 16.12 |
| 0.07718 | 16.58 |

[a] Uncertainties are represented as the twice standard deviation from the mean value.

[b] Values in pure water at 277.15–313.15 K were taken from Ref. [1].

results obtained would seem to be explained by the simple fact that the decrease of cosolvent hydrophobicity due to the substitution of HMPT on hydrophilic FA is almost compensated by increasing a solute hydrophobicity arising from the increase of a tetraalkylammonium ion size. However, this explanation does not take into account the influence of bromide ion and a polar group in a non-electrolyte molecule which it is known to define greatly the temperature dependence of the solute–HMPT interaction parameters [1]. Thus, the real situation appears to be more complex resulting from a compensation of contributions from both hydrophobic and hydrophilic interactions.
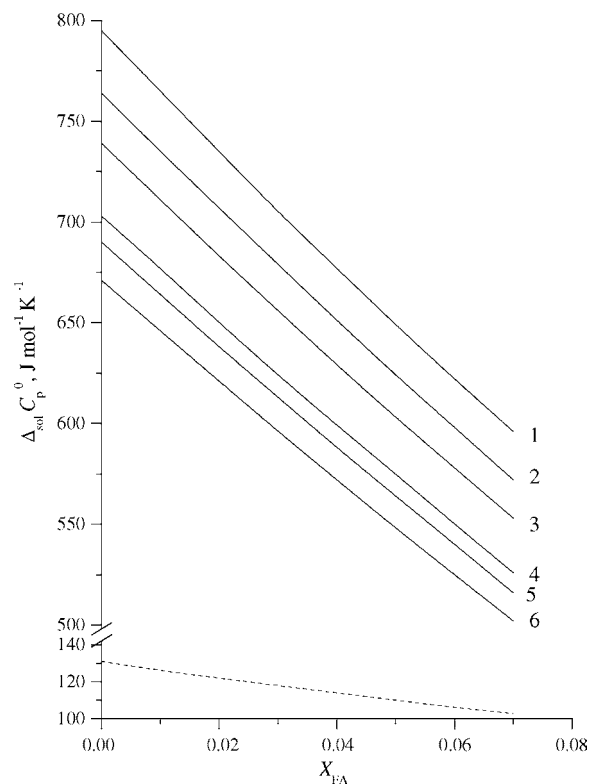


Fig. 2. Heat capacities of Et$_4$NBr (- - -) and Bu$_4$NBr (——) solutions in the water–FA mixed solvent at 277.15 (1), 288.15 (2), 298.15 (3), 313.15 (4), 319.15 (5) and 328.15 (6).

The analysis of the temperature dependence of the $\Delta_{sol}H^0$ values in the water–FA system was performed as in our previous studies [1,8]. The curves $\Delta_{sol}H^0$ versus $X_{FA}$ were described by polynomial expressions, the results of calculation at a fixed FA mol fraction being treated by the following equations:

$$\Delta_{sol}H^0(T) = \Delta_{sol}H^0(\Theta) + \Delta_{sol}C_p^0\Theta\left(\frac{T}{\Theta} - 1\right) \tag{1}$$

$$\Delta_{sol}H^0(T) = \Delta_{sol}H^0(\Theta) + \Delta_{sol}C_p^0\Theta\left(1 - \frac{\Theta}{T}\right) \tag{2}$$

$$\Delta_{sol}H^0(T) = \Delta_{sol}H^0(\Theta) + \Delta_{sol}C_p^0\Theta\ln\left(\frac{T}{\Theta}\right) \tag{3}$$

where $\Delta_{sol}H^0(T)$ and $T$ (current temperature, K) are variables, $\Delta_{sol}H^0(\Theta)$ and $\Delta_{sol}C_p^0$ are the enthalpy and heat capacity parameters desired at a reference temperature $\Theta$ (K), respectively. Eq. (1) assumes that the heat capacity of solution $\Delta_{sol}C_p^0$ (the change of the heat capacity in the salt transfer process from a solid state into water) does not depend on temperature $T$, while Eqs. (2) and (3) require that the heat capacity should be proportional to $T^{-2}$ and $T^{-1}$, respectively. It has been found that Eq. (1) gives a better description of the Et$_4$NBr data while the $\Delta_{sol}H^0$ values for Bu$_4$NBr are described better by Eq. (3). The heat capacities of solution $\Delta_{sol}C_p^0$ given in Fig. 2 are positive for both solutes. Never-

Table 3
Enthalpic coefficients of Et$_4$NBr and Bu$_4$NBr pair interaction ($h_{23}$, J kg mol$^{-2}$) with HMPT and FA in water

| $T$ | Et$_4$NBr | | Bu$_4$NBr | |
|---|---|---|---|---|
| | HMPT[a] | FA | HMPT[a] | FA |
| 277.15 | 2350 (42)[b] | 130 (9) | 7925 (501) | 2167 (126) |
| 288.15 | 2023 (116) | 73 (6) | 7681 (378) | 1810 (144) |
| 298.15 | 1635 (90) | 54 (1)[c] | 7215 (200) | 1545 (100)[c] |
| 313.15 | 1130 (56) | −32 (4) | 6808 (270) | 1190 (44) |
| 319.15 | 928 (30) | −51 (12) | 6602 (81) | 1091 (126) |
| 328.15 | 620 (38) | −96 (35) | 6313 (105) | 835 (63) |

[a] Values from Ref. [1]; the data at 319.15 and 328.15 K are the extrapolated values according to Eqs. (3) and (4) given in Ref. [1].
[b] Uncertainties represent the standard deviation of the coefficients obtained.
[c] Values from Ref. [3].

theless, it is obvious that both the heat capacity values and the initial slope of the curve $\Delta_{sol}C_p^0$ versus $X_{FA}$ for Bu$_4$NBr are significantly larger than those for Et$_4$NBr (see Fig. 2).

The enthalpic coefficients of the electrolyte (3)–FA (2) pair interaction $h_{23}$ were computed as in our previous studies [1,3–5] according to the equation proposed by Heuvelsland et al. [9]:

$$\Delta_{sol}H^0 = A_0 + A_1 X_{FA} + A_2 X_{FA}^2 \tag{4}$$

The $A_1$ coefficient is connected with the enthalpic coefficient of the solute–cosolvent pair interaction $h_{23}$ by a simple relationship:

$$A_1 = \frac{2h_{23}}{M_w} \tag{5}$$

where $M_w$ is molar mass of water. The $h_{23}$ coefficients given in Table 3 are positive at lower temperatures indicating that the solute–cosolvent interaction is repulsive in a thermochemical sense [10]. However, as temperature is increased, the Et$_4$NBr–FA interaction becomes gradually attractive. The analysis of the temperature dependence of the $h_{23}$ coefficients shows that it can be represented by the following equations:

$$h_{23}(\text{Et}_4\text{NBr}, T) = 40(5) - 4.4(0.3)298.15\left(\frac{T}{298.15 - 1}\right)$$
$$s_f = 10 \text{ J kg mol}^{-2} \tag{6}$$

$$h_{23}(\text{Bu}_4\text{NBr}, T) = 1575(14) - 26(1)298.15\ln\left(\frac{T}{298.15}\right)$$
$$s_f = 32 \text{ J kg mol}^{-2} \tag{7}$$

where values in brackets represent the standard deviation of the coefficients obtained and $s_f$ is the standard deviation of the fit. Eqs. (6) and (7) indicate that the heat capacity coefficients of the solute–amide pair interaction $c_{p23}$ are negative, as it has been observed in the case of hydrophobic HMPT [1]. It is interesting to compare the parameters of Et$_4$NBr–HMPT and Bu$_4$NBr–FA pair interactions. Table 3 shows that the
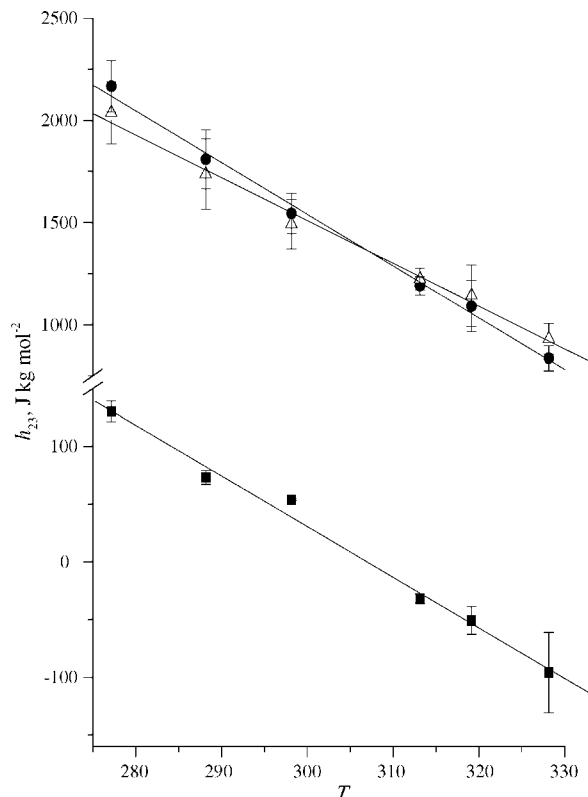


Fig. 3. Temperature dependence of the enthalpic pair-interaction coefficients of Et$_4$NBr (■), Bu$_4$NBr (●) and Bu$_4$N$^+$–Et$_4$N$^+$ (△) with FA in water. Error bars represent the standard deviation of the coefficient obtained. Lines are the linear description.

$h_{23}$ are nearly identical, which is in agreement with the prediction made above from the data given in Fig. 1. The $c_{p23}$ interaction parameters equal to −34 (1) [1] and −26 (1) J kg mol$^{-2}$ K$^{-1}$ are also close to each other.

It is obvious that the interaction parameters obtained reflect the sum of cation and anion contributions, therefore, it would be useful to eliminate the influence of bromide ion. Fig. 3 shows that the $h_{23}$ (Bu$_4$N$^+$–Et$_4$N$^+$) value is positive and strongly dependent of the temperature. It is reasonable to consider that the (Bu$_4$N$^+$–Et$_4$N$^+$) difference represents the interaction effect of eight −CH$_2$− groups with FA molecule [9,11]. This assumption allows to estimate the enthalpy and heat capacity of interaction of a single −CH$_2$− group with FA. It can be seen from Fig. 3 that the enthalpy of the −CH$_2$− group interaction with FA is large and positive. The heat capacity coefficient can be estimated as follows: $c_{p23}$ (CH$_2$–FA) = (−26 + 4.4)/8 = −2.7 J kg mol$^{-2}$ K$^{-1}$. This value differs strongly from that obtained in the previous study [1], where the $c_{p23}$ (CH$_2$–HMPT) parameter is found to equal to zero. It is known that the interaction heat capacity between two −CH$_2$− groups in water is positive [2]. It indicates that the negative $c_{p23}$ (CH$_2$–FA) value results from the methylene group interaction with a polar part of the amide molecule, but not with a >CH− group. A similar situation is observed in the case of HMPT where the $c_{p23}$ (CH$_2$–N$_3$PO) interaction is found to be equal to −8.4 J kg mol$^{-2}$ K$^{-1}$. The
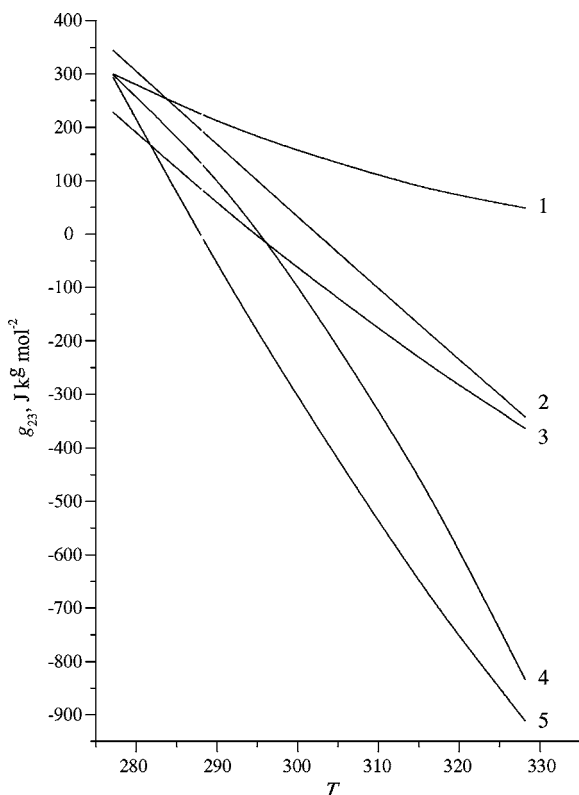
Fig. 4. Temperature dependence of the free energy pair-interaction coefficients of $Bu_4NBr$ with FA (1), $Me_2CO$ (2), DO (3), $t$-BuOH (4) and HMPT (5) in water.



Fig. 5. Temperature dependence of the entropic pair-interaction coefficients of $Bu_4NBr$ with FA (1), $Me_2CO$ (2), DO (3), $t$-BuOH (4) and HMPT (5).

principle difference between FA and HMPT is the behaviour of bromide ion. In fact, the $c_{p23}$ ($Br^-$–HMPT) coefficient is found to be large and negative [1], defining the sign of the electrolyte–HMPT pair coefficients. On the contrary, the results obtained clearly indicate that the $Br^-$–FA value is rather positive. Thus, since bromide ion shows different behaviour in the water–HMPT and water–FA systems, we can conclude that the identical $Et_4NBr$ and $Bu_4NBr$ behaviour in these mixtures (see Fig. 1) arises from the compensation of both hydrophobic and hydrophilic interactions.

To calculate the temperature changes of the free energy and entropic pair-interaction parameters, we use the Gibbs–Helmholtz equation:

$$\frac{\partial (g_{23}/T)}{\partial T} = -\frac{h_{23}}{T^2} \tag{8}$$

This method appears to give some smaller uncertainty of the $s_{23}$ and especially the $g_{23}$ parameters in comparison with the results of the previous study [1], where the calculation has been performed from heat capacity coefficients and, therefore, free energy parameters have been defined as the difference between two large values, i.e. the $h_{23}$ and $Ts_{23}$ parameters. To compute free energy pair-interaction coefficients for $Bu_4NBr$, we use the same way as in our previous study [1]. Treiner and co-workers have shown that the $Bu_4NBr$–organic non-electrolyte free energy coefficients at 298.15 K are a lin-

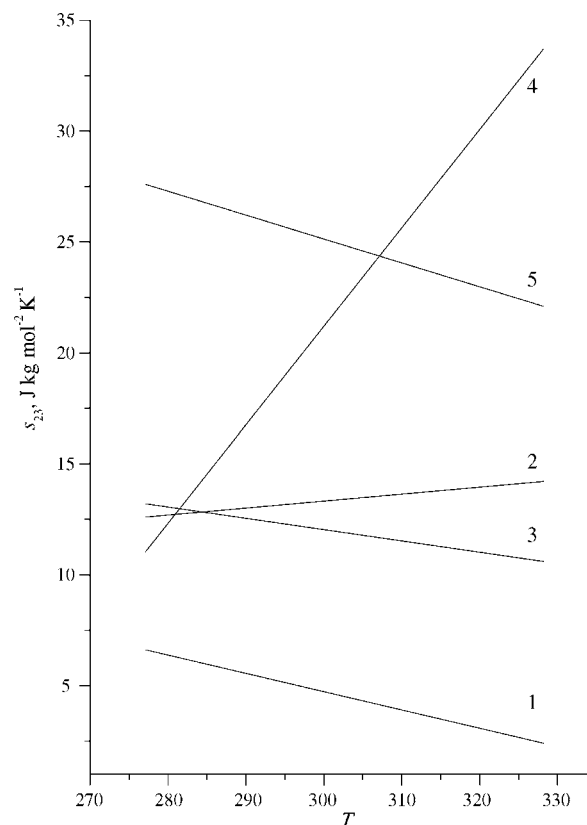ear function of the non-electrolyte hard-sphere diameter [12]:

$$g_{23} = 0.678 - 0.135\,\sigma(\text{Å}), \quad R = 0.990 \tag{9}$$

Using the $\sigma = 3.81$ Å value for FA [13] and the $g_{23}$ ($T_2$)–$g_{23}$ ($T_1$) difference computed according to Eq. (8), we are able to estimate the $g_{23}$ and then the $s_{23}$ parameters:

$$s_{23} = \frac{(h_{23} - g_{23})}{T} \tag{10}$$

Figs. 4 and 5 compare the free energy and entropic pair-interaction coefficients of tetrabutylammonium bromide with some non-electrolytes at different temperatures. The values for HMPT, acetone ($Me_2CO$), 1,4-dioxane (DO) and 2-methyl-2-propanol ($t$-BuOH) were computed using previously determined $h_{23}$ parameters [1]. The uncertainty of the $g_{23}$ coefficients appears to be large, however, our current interest is to observe and compare their temperature dependence. The $Bu_4NBr$–organic non-electrolyte interaction is seen to be repulsive at low temperatures due to $h_{23} > Ts_{23}$. As the temperature is increased, the free energy pair interaction becomes increasingly attractive especially for strongly hydrophobic HMPT and $t$-BuOH, while the interaction is always repulsive for hydrophilic FA (see Fig. 4).

The $s_{23}$ parameters are given in Fig. 5. Although they are positive in all cases, it is obvious that the $s_{23}$ coefficients are significantly larger for strongly hydrophobic species such as HMPT and $t$-BuOH. Thus, we are able to conclude

that the $g_{23}$ and $s_{23}$ parameters show typical hydrophobic behaviour, which are in an agreement with classical models of hydrophobic interaction [2,14]. In fact, the interaction between hydrated hydrophobic particles invoking the overlapping of their hydration shells results in the displacement of some amount of water to a bulk solvent. This process is accompanied by large positive values of entropic interaction parameters and negative values of free energy ones [2,14], increasing with the temperature rise until a maximum is reached, after which there should be a reversal of the trend [2,15]. It is obvious that almost a similar situation is observed in our study (see Figs. 4 and 5). The results obtained emphasise the entropic origin of the Bu$_4$NBr interaction with HMPT and $t$-BuOH, especially at higher temperatures. We could not find any reversal trends in the free energy pair-interaction parameters apparently due to a limited temperature range studied. Moreover, bromide ion and polar groups in the non-electrolyte molecules giving some contributions to interaction parameters may shift or almost eliminate the extremum on the curve $g_{23}$ versus $T$. Thus, to draw more detailed conclusions, the $g_{23}$ interaction parameters of Et$_4$NBr with hydrophobic HMPT and hydrophilic FA should be obtained.

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