

Temperature dependence of the interaction between two hydrophobic solutes: a calorimetric study

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Abstract

The enthalpies of tetraethyl- and tetrabutylammonium bromides solution in water and its mixtures with hexamethyl phosphoric triamide (HMPT) in the “water-rich” region of the mixed solvent were measured at 277.15, 288.15 and 313.15 K. The standard enthalpies of solution are computed and compared with previously determined values at 298.15 K. The enthalpic and heat capacity coefficients of solute–HMPT pair interactions in water and the temperature changes of the entropic pair interaction coefficients were computed and compared with those for other organic non-electrolytes. It was shown that bromide-ion and cosolvent nature influenced strongly both enthalpic interaction parameters and their temperature dependence, the last one in particular. The enthalpy of methylene group interaction with HMPT was found to be large, positive and independent of the temperature. It was pointed out that the energetics of non-polar solute transfer from water to various highly aqueous water-organic mixtures at room temperature is defined to a great extent by dimensions of cosolvent molecules and packing effects of solvent molecules in the solute solvation shell.

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1. Introduction

The solvent-induced forces are widely believed to drive non-polar solutes together in aqueous media, stabilize folded structures of globular proteins, define to a great extent the formation of micelles and bilayer membranes, etc., [1–5]. The so-called hydrophobic effects arising from unique properties of liquid water are the object of intensive studies during the last decades (see [1–10] and references therein).

Symmetrical tetraalkylammonium salts have broad applications [11], for instance, in biochemistry as molecular probes and blockers of ion channels in biological membranes. They are also well-known useful models for studying molecular nature of hydrophobic hydration [9,10] and interaction [12,13]. Considerable efforts are devoted to studying thermodynamic properties of their solutions in water [14,15]

and aqueous-organic mixtures [16–24]. Some of these works [17,18,20–24] have dealt with the computation of enthalpic, free energy and entropic solute–solute and solute–cosolvent pair interaction parameters in terms of McMillan–Mayer formalism [4,25]. It has been found that the enthalpic coefficients of the tetraalkylammonium salt–organic non-electrolyte pair interaction (h_{23}) are positive (enthalpically repulsive) at room temperature almost in all cases and significantly increase as the tetraalkylammonium cation dimension is increased [17,18,21,22,24]. The applicability of Savage and Wood additivity concept [26] to the enthalpic pair interaction parameters of tetraalkylammonium bromides with dimethylformamide (DMF) [21] and HMPT [22] in water has been shown. The enthalpic coefficients of non-polar $-\text{CH}_2-$ group interaction with amides are found to be large and positive, whereas the h_{23} value for bromide ion is negative [21,22]. The same conclusion appears to be valid in the case of acetonitrile and 2-methyl-2-propanol (*t*-BuOH) [18].

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Table 1
Enthalpies of solution at infinite dilution ($\Delta_{\text{sol}}H^\circ$, kJ mol⁻¹) of Et₄NBr and Bu₄NBr in water at 277.15–313.15 K

Solute	$\Delta_{\text{sol}}H^\circ$			
	277.15	288.15	298.15	313.15
Et ₄ NBr	3.58 ± 0.12 ^a	4.71 ± 0.04	6.02 ± 0.04 ^b 6.05 ± 0.02 ^c	8.11 ± 0.10
Bu ₄ NBr	-24.41 ± 0.23 -25.0 ^e	-16.01 ± 0.11 -16.40 ± 0.22 ^d	-8.59 ± 0.04 ^b -8.58 ± 0.06 ^d , -8.48 ± 0.05 ^c	2.67 ± 0.07 2.65 ^e

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

^b Values from reference [24].

^c Values from reference [23].

^d Values from reference [16].

^e The $\Delta_{\text{sol}}H^\circ$ values were interpolated from the data given in reference [15].

Our recent studies of Et₄NBr and Bu₄NBr behaviour in the highly aqueous water-organic mixtures [23,24] have indicated that the h_{23} coefficients for HMPT are the largest among other organic co-solvents. It has been found also [23] that the enthalpic coefficients of Bu₄NBr–amide pair interaction at 298.15 K increase linearly with the second virial coefficient derivative on the pressure $dB_{22} dP^{-1}$ which is the one of successful parameters of hydrophobicity [27]. Therefore, the increase of the Bu₄NBr–amide enthalpic interaction coefficients just reflects the rise of amide molecule hydrophobicity.

However, most part of these studies was performed at room temperature and, therefore, the temperature dependence of interaction parameters remained unknown. The thermochemical data are available only for Bu₄NBr in the mixtures of water with acetone (Me₂CO), *t*-BuOH and 1,4-dioxane (DO) at 288.15, 298.15 and 308.15 K [16]. Thus, the principal objective of the present study is to obtain and compare experimental information on the energetics of Et₄NBr and Bu₄NBr interaction with hydrophobic cosolvent–HMPT in water at different temperatures. Since both HMPT and *t*-BuOH are strongly hydrophobic cosolvents, i.e. for their dilute aqueous solutions $dB_{22} dP^{-1} < 0$, $g_{22} < 0$, $h_{22} \gg 0$ and $v_{22} < 0$ [27], we would expect a similar behaviour of tetraalkylammonium salts in the highly aqueous water–HMPT and water–*t*-BuOH mixtures. At the same time, polar groups of the HMPT and *t*-BuOH molecules interact in a different way with surrounding water molecules, which may cause the difference of the hydrophobic electrolytes behaviour in the systems above.

2. Experimental

Hexamethyl phosphoric triamide ((CH₃)₆N₃PO), water and tetraalkylammonium salts were purified as in our previous study [23]. The measurements were carried out using a precise “isoperibol” ampoule calorimeter fitted with 75 cm³ vessel [23,28]. A calorimetric vessel was equipped with a calibrated heater, a titanium stirrer and a thermistor. A glass ampoule containing a solute was attached to a stirrer. An ampoule crushing against a vessel bottom initiated a dissolution process. A thermistor was connected with a precise resistance bridge and a recorder potentiometer. The enthalpy of solution

was determined by a comparative method. An electrical calibration was carried out before and after each experiment. The calorimeter was tested by measuring the enthalpies of potassium chloride (KCl) and 1-propanol solution in water at 298.15 K. The agreement between our and best literature values was found to be excellent [23,28].

3. Results

The experimental enthalpies of solution were obtained in the range of the solute molalities of 0.002–0.038 mol kg⁻¹. The enthalpies of solution at infinite dilution $\Delta_{\text{sol}}H^\circ$ values were calculated from the following relationship: $\Delta_{\text{sol}}H^\circ = \Delta_{\text{sol}}H^{\text{m}} + \Delta_{\text{dil}}H^{\text{m} \rightarrow 0}$. The enthalpies of dilution $\Delta_{\text{dil}}H^{\text{m} \rightarrow 0}$ were calculated in terms of Debye–Hückel theory in the second approximation according to the method proposed elsewhere [29]. The $\Delta_{\text{dil}}H^{\text{m} \rightarrow 0}$ values are found to be from -0.05 to -0.2 kJ mol⁻¹. The enthalpies of solution at infinite dilu-

Table 2
Enthalpies of solution at infinite dilution ($\Delta_{\text{sol}}H^\circ$, kJ mol⁻¹) of Et₄NBr in the water–HMPT mixtures at 277.15, 288.15 and 313.15 K

X_{HMPT}	$\Delta_{\text{sol}}H^\circ$
277.15	
0.00993	5.95
0.01977	8.07
0.03045	10.22
0.04795	12.78
0.06568	14.46
288.15	
0.00864	6.31
0.01923	8.54
0.03719	11.61
0.04893	12.71
0.05769	13.90
0.05852	13.92
313.15	
0.00500	8.69
0.01001	9.26
0.01999	10.33
0.03002	11.31
0.05000	13.00
0.06998	14.05

Table 3
Enthalpies of solution at infinite dilution ($\Delta_{\text{sol}}H^\circ$, kJ mol^{-1}) of Bu_4NBr in the water–HMPT mixtures at 277.15, 288.15 and 313.15 K

X_{HMPT}	$\Delta_{\text{sol}}H^\circ$
277.15	
0.00927	−17.33
0.02005	−8.54
0.03053	0.12
0.04853	15.37
0.06477	24.83
288.15	
0.00679	−11.27
0.01130	−8.21
0.02032	−0.84
0.03018	6.73
0.05343	21.66
0.07067	29.45
313.15	
0.00500	6.35
0.00934	10.30
0.02001	16.15
0.02999	21.92
0.04714	30.67
0.05203	31.37
0.06855	36.81

tion $\Delta_{\text{sol}}H^\circ$ in pure water given in Table 1 reflect the results of five or more measurements, while the $\Delta_{\text{sol}}H^\circ$ values in the mixed solvent represent the result of two or usually a single experiment (see Tables 2 and 3). Table 1 shows a good agreement between our enthalpies of solution and those available in literature [15,16].

The analysis of the temperature dependence of the $\Delta_{\text{sol}}H^\circ$ values in water and the mixed solvent were performed using two equations obtained from the relationships given in the comprehensive work of Benson and Krause [30]:

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

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

where $\Delta_{\text{sol}}H^\circ(T)$ and T (current temperature, K) are variables, $\Delta_{\text{sol}}H^\circ(\Theta)$ and $\Delta_{\text{sol}}C_p^0$ are the enthalpy and heat capacity parameters desired at a reference temperature Θ (K), respectively. Eq. (1) assumes that the heat capacity of solution $\Delta_{\text{sol}}C_p^0$ (the change of the heat capacity in the solute transfer process from a solid state into water) does not depend

Table 4
Parameters of Eqs. (1) and (2) for Et_4NBr and Bu_4NBr aqueous solutions at 298.15 K

Solute	Eq. (1)			Eq. (2)		
	$\Delta_{\text{sol}}H^\circ(\Theta)$ (kJ mol^{-1})	$\Delta_{\text{sol}}C_p^0$ ($\text{J mol}^{-1} \text{K}^{-1}$)	S (kJ mol^{-1}) ^a	$\Delta_{\text{sol}}H^\circ(\Theta)$ (kJ mol^{-1})	$\Delta_{\text{sol}}C_p^0$ ($\text{J mol}^{-1} \text{K}^{-1}$)	S (kJ mol^{-1})
Et_4NBr	6.12 (0.08) ^b	127 (6)	0.16	6.19 (0.13)	124 (9)	0.25
Bu_4NBr	−8.58 (0.04)	751 (3) ^c	0.07	−8.16 (0.26)	733 (18)	0.49

^a S is a standard deviation of the fit.

^b Values in brackets represent the standard deviation of the coefficients of Eqs. (1) and (2).

^c The $\Delta_{\text{sol}}C_p^0$ value interpolated from the data given in reference [15] is $765 \text{ J mol}^{-1} \text{K}^{-1}$.

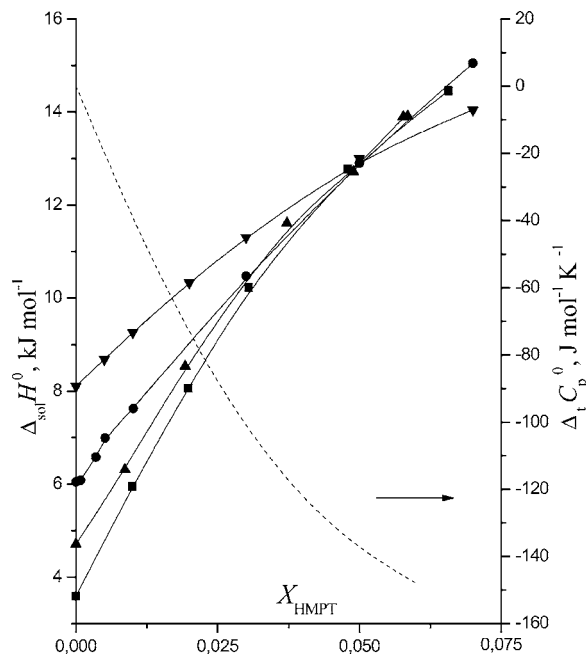


Fig. 1. Enthalpies of solution of Et_4NBr in the water–HMPT mixed solvent (left-hand scale) at 277.15 (■), 288.15 (▲), 298.15 (●) [23] and 313.15 (▼). Lines are spline functions; the dashed line is the heat capacity of Et_4NBr transfer from water to the mixed solvent (right-hand scale).

on temperature T , while Eq. (2) requires that the heat capacity should be proportional to T^{-2} . One important advantage of Eqs. (1) and (2) in comparison with usual polynomials is that the equation parameters have clear physical meaning, these equations allowing to estimate easily the $\Delta_{\text{sol}}H^\circ$ value at a reference temperature Θ . It can be seen from Table 4 that both equations describe the data given in Table 1 well. However, it is obvious that Eq. (1) gives a better description of the $\Delta_{\text{sol}}H^\circ$ values and a smaller standard deviation of the heat capacity of solution. Table 4 shows that, the $\Delta_{\text{sol}}C_p^0$ values are large and positive for both electrolytes as observed usually for hydrophobic solutes [1,3,27], the heat capacity of Bu_4NBr solution at 298.15 K being in a good agreement with the value reported by Ahluwalia and Sarma [15].

4. Discussion

The curves $\Delta_{\text{sol}}H^\circ$ versus HMPT mol fraction X_{HMPT} are shown in Figs. 1 and 2. It can be seen that the dissolution

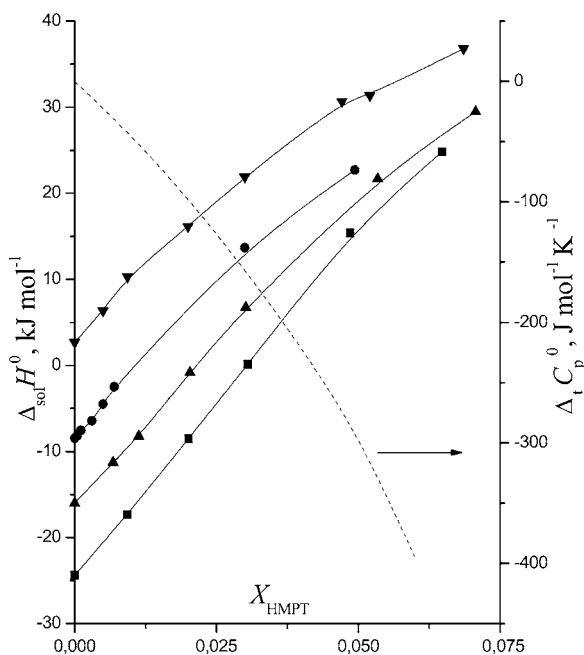


Fig. 2. Enthalpies of solution of Bu_4NBr in the water–HMPT mixed solvent (left-hand scale) at 277.15 (■), 288.15 (▲), 298.15 (●) [23] and 313.15 (▼). Lines are spline functions; the dashed line is the heat capacity of Bu_4NBr transfer from water to the mixed solvent (right-hand scale).

of both solutes becomes more endothermic as temperature is increased, the experimental curves for Et_4NBr crossing each other at $X_{\text{HMPT}} \approx 0.05$ mol fractions. It indicates that the change of the heat capacity in the Et_4NBr transfer from a solid state into the mixed solvent at this fixed composition equals zero. The dependences $\Delta_{\text{sol}}H^\circ$ versus HMPT mol fraction were described by the second-order polynomial equations for both electrolytes in the temperature range studied. The heat capacities of solute transfer from water to the mixed solvent were computed using the coefficients of the polynomials above. The $\Delta_t C_p^0$ values are seen from Figs. 1 and 2 to be negative and strongly dependent of the HMPT content. It should be noted that the Bu_4NBr behaviour differs sharply from that in the water–*t*-BuOH mixed solvent, where the $\Delta_t C_p^0$ curve versus X passes through a slight maximum at $X \approx 0.04$ alcohol mol fraction after which a sharp decrease of the $\Delta_t C_p^0$ values is observed [16]. This difference apparently should be attributed to the formation of alcohol microaggregates in the water–*t*-BuOH mixture [17,31], since the sharp decrease of the $\Delta_t C_p^0$ values corresponds to the alcohol microphase transition region ($X \approx 0.04$ – 0.08 alcohol mol fraction) [31].

The enthalpic coefficients of the electrolyte (3)–HMPT (2) pair interaction h_{23} were computed as in our previous studies [22,23,28] using the equation proposed by Heuvelsland et al. [21]. The coefficients given in Table 5 are large and positive indicating that the interaction between hydrophobic solutes is repulsive in a thermochemical sense [32]. The analysis of the temperature dependence of the h_{23} coefficients (see Fig. 3) was carried out using the above type of the equation as for

the $\Delta_{\text{sol}}H^\circ$ values:

$$h_{23}(\text{Et}_4\text{NBr}, T) = 1647(15) - 34(1)298.15 \left(\frac{T}{298.15} - 1 \right),$$

$$R = 0.9991, \quad S = 28 \text{ J kg mol}^{-2} \quad (3)$$

$$h_{23}(\text{Bu}_4\text{NBr}, T) = 7279(40) - 32(3)298.15 \left(\frac{T}{298.15} - 1 \right),$$

$$R = 0.9922, \quad S = 75 \text{ J kg mol}^{-2} \quad (4)$$

where values in brackets from here on represent the standard deviation of the coefficients obtained. Eqs. (3) and (4) show that the c_{p23} coefficients are negative for both solutes and equal each other.

Fig. 4 compares the enthalpic pair interaction coefficients of Bu_4NBr with various organic cosolvents at different temperatures. The h_{23} coefficients were computed in the present study using the $\Delta_{\text{sol}}H^\circ$ values given elsewhere [16]. It was found that the temperature dependence of the h_{23} coefficients obtained could be expressed by the following equations:

$$h_{23}(\text{DO}) = 3563(1) - 15(0.1)298.15 \left(\frac{T}{298.15} - 1 \right),$$

$$R = 0.9999, \quad S = 1 \text{ J kg mol}^{-2} \quad (5)$$

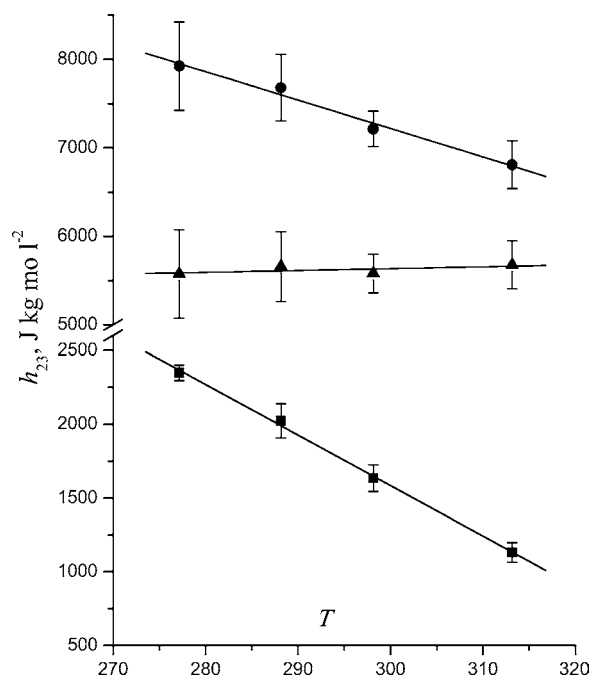


Fig. 3. Temperature dependence of the enthalpic pair interaction coefficients of Et_4NBr (■), Bu_4NBr (●) and $\text{Bu}_4\text{N}^+ - \text{Et}_4\text{N}^+$ (▲) with HMPT in water. Error bars represent the standard deviation of the coefficient obtained; lines are the description according to Eqs. (3) and (4).

Table 5
Enthalpic (h_{23} , J kg mol⁻²) and temperature changes of entropic (s_{23} , J kg mol⁻² K⁻¹) pair interaction coefficients of Et₄NBr and Bu₄NBr with HMPT in water

Solute	T (K)			
	277.15	288.15	298.15	313.15
Et ₄ NBr	h_{23}			
	2350 (42) ^a	2023 (116)	1635 (90) ^b	1130 (56)
	$s_{23}(T) - s_{23}(277.15)$			
	0	-1.32 (0.04)	-2.48 (0.07)	-4.15 (0.12)
Bu ₄ NBr	h_{23}			
	7925 (501)	7681 (378)	7215 (200) ^b	6808 (270)
	$s_{23}(T) - s_{23}(277.15)$			
	0	-1.25 (0.12)	-2.34 (0.22)	-3.91 (0.37)

^a Values in the brackets represent the standard deviation of the coefficients obtained.

^b Treating the experimental data upto 0.05 HMPT mol fraction gives the h_{23} values of 1489 (66) and 8151(207) J kg mol⁻² for Et₄NBr and Bu₄NBr, respectively [23].

$$h_{23}(t\text{-BuOH}) = 6191(30) + 134(4)298.15 \left(\frac{T}{298.15} - 1 \right),$$

$$R = 0.9996, \quad S = 51 \text{ J kg mol}^{-2} \quad (6)$$

$$h_{23}(\text{Me}_2\text{CO}) = 4031(31) + 9(4)298.15 \left(\frac{T}{298.15} - 1 \right),$$

$$R = 0.9140, \quad S = 54 \text{ J kg mol}^{-2} \quad (7)$$

Fig. 4 shows that non-electrolyte nature greatly influences both the enthalpic electrolyte–organic cosolvent pair interaction coefficients and their temperature dependence, the last

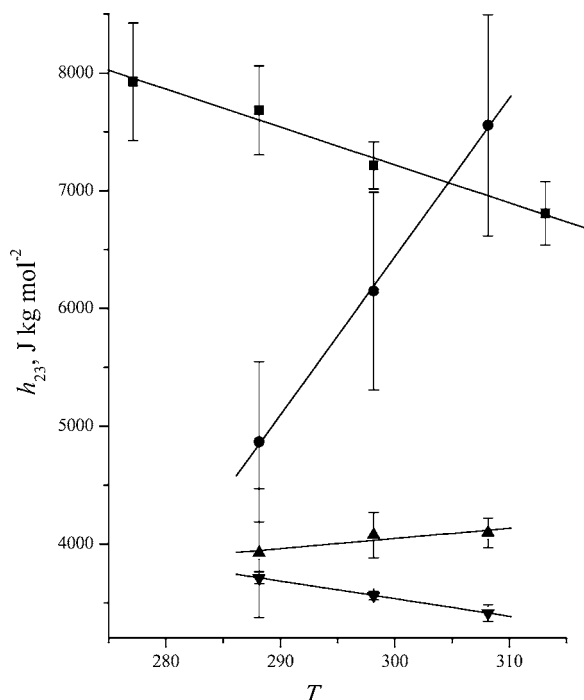


Fig. 4. Temperature dependence of the enthalpic pair interaction coefficients of Bu₄NBr with HMPT (■), DO (▼), Me₂CO (▲) and *t*-BuOH (●) in water. Error bars represent the standard deviation of the coefficient obtained; lines are the description according to Eqs. (4) and (5)–(7).

one in particular. In fact, the heat capacity coefficient of Bu₄NBr–*t*-BuOH pair interaction is large and positive, as one should expect for hydrophobic solutes [27]. At the same time, the c_{p23} values are negative for strongly hydrophobic HMPT and slightly hydrophobic DO. Since the coefficients obtained reflect the sum of cation and anion contributions [21], it would be useful to eliminate the influence of bromide ion. Fig. 3 shows that the difference of the h_{23} coefficients for Bu₄NBr and Et₄NBr is large and positive, it being independent of the temperature. It is obvious that the h_{23} (Bu₄N⁺–Et₄N⁺) value can be considered as the interaction effect of eight –CH₂– groups with HMPT molecule. Therefore, the enthalpy of the –CH₂– group interaction with HMPT is large, positive and independent of the temperature, i.e. the heat capacity value equals zero. It is possible to show that such –CH₂– group behaviour results from the compensation of the increments of polar and non-polar groups in the HMPT molecule. It is known [27] that the heat capacity pair interaction coefficient between –CH₂– groups in water at 298.15 K equals to 1.12 J kg mol⁻² K⁻¹, but the c_{p22} value for HMPT equal to –50 J kg mol⁻² K⁻¹ is negative. These interaction parameters are related to the second temperature derivative of the osmotic second virial coefficients via the integral of $[\exp(-W(r, \Omega)/kT) - 1]$ [4,27], where $W(r, \Omega)$ is the mean force potential for pairs of particles, this orientally averaged potential reflecting the contribution from all groups in interacting solute molecules [26,27]. Thus, comparing the heat capacity coefficients above and taking into account that the CH₃– group equals to the 1.5 –CH₂– one [26], we can roughly estimate the CH₃–N₃PO, CH₂–N₃PO and N₃PO–N₃PO group increments to the c_{p22} and c_{p23} values using Savage and Wood additivity principle [26]. The results can be summarized as follows. The CH₂–N₃PO and N₃PO–N₃PO heat capacity interaction parameters are found to be –8.4 and –34.9 J kg mol⁻² K⁻¹, respectively. It indicates that the negative c_{p22} value for HMPT results from the CH₃–N₃PO and N₃PO–N₃PO interactions. Similar situation is observed for the tetraalkylammonium ion interaction with HMPT, i.e. the solute interaction with CH₃– groups of HMPT molecule gives the positive contribution to the c_{p23} coefficient.

cient, but the interaction with the polar N_3PO group gives a negative one, these contributions cancel each other (see the h_{23} ($Bu_4N^+-Et_4N^+$) value given in Fig. 3). Thus, we can draw the important conclusion that negative signs of the heat capacity coefficients of the hydrophobic electrolyte–HMPT pair interaction (see Eqs. (3) and (4)) result from the influence of bromide-ion.

Standard thermodynamic relationships allow to link the heat capacity pair interaction coefficient and temperature changes of the entropic ones. Since the c_{p23} coefficients are found to be constants in the temperature range studied, we can write:

$$s_{23}(T_2) - s_{23}(T_1) = \int_{T_1}^{T_2} \frac{c_{p23}}{T} dT = c_{p23} \ln \frac{T_2}{T_1} \quad (8)$$

The $s_{23}(T) - s_{23}(277.15)$ parameters obtained according to Eq. (8) are given in Table 5. It is widely known that pair hydrophobic interaction is characterized by the following values of the interaction parameters: $Ts_{23} > h_{23} \gg 0$, $g_{23} < 0$ [27,33]. As it was mentioned above, the h_{23} coefficients are large and positive. The experimental data for calculating the g_{23} and s_{23} parameters are unavailable. Nevertheless, there is an empirical way to estimate these values. The free energy pair interaction coefficient g_{23} of various non-electrolytes with Bu_4NBr at 298.15 K was found to be a linear function of the non-electrolyte hard-sphere diameter [18]:

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

Using the $\sigma = 6.98 \text{\AA}$ value for HMPT [34] and the h_{23} and $s_{23}(T) - s_{23}(277.15)$ coefficients given in Table 5 we are able to estimate the corresponding free energy and entropic parameters according to Eq. (10):

$$g_{23} = h_{23} - Ts_{23} \quad (10)$$

Table 6 compares the g_{23} and Ts_{23} values for Bu_4NBr with various organic non-electrolytes at different temperatures. The electrolyte–cosolvent interaction is seen to be repulsive at low temperatures due to $h_{23} > Ts_{23}$. However, the temperature rise results in the opposite situation, i.e. $h_{23} < Ts_{23}$, the interaction becoming increasingly attractive. Table 6 shows that the solute–cosolvent pair interaction is entropy favourable in the temperature range studied, the g_{23} being sufficiently small due to the enthalpy/entropy compensation phenomenon [27].

It seems important to turn to Fig. 4. The enthalpic pair interaction coefficients of Bu_4NBr with HMPT and DO differ in about two times in the temperature range studied. It indicates that the enthalpies of Bu_4NBr transfer from water to the highly aqueous water–HMPT mixture are about twice as much as those in the water–DO mixed solvent. The similar situation is observed for formamide (FA) at 298.15 K, the enthalpic coefficient of Bu_4NBr –FA pair interaction being almost five times less than that for HMPT [24]. It would be reasonable to compare the $Bu_4N^+-Et_4N^+$ difference in various aqueous organic mixtures, since this value does not

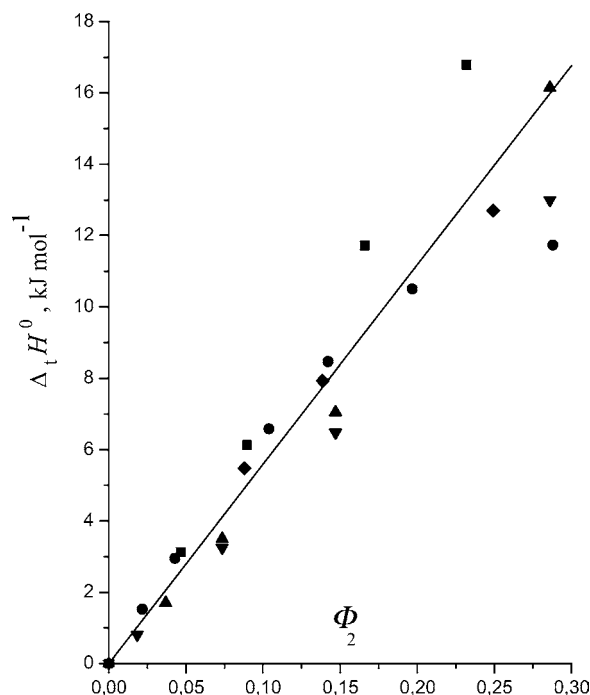


Fig. 5. Enthalpies of $Bu_4N^+-Et_4N^+$ transfer from water to its mixtures with HMPT (■) [23], Me_2CO (▲) [23], FA (●) [24], DMF (▼) [35] and DO (◆) [35] at 298.15 K. Line is the description according to Eq. (12).

include the bromide ion contribution. However, the experimental data for Et_4NBr are available at 298.15 K only and we are unable to compare the $\Delta_t C_p^0$ values. Fig. 5 compares the enthalpies of $Bu_4N^+-Et_4N^+$ transfer from water to its mixtures with five organic cosolvents. Since cosolvent dimensions differ strongly (the molar volumes vary from 39.9 upto $175.7 \text{ cm}^3 \text{ mol}^{-1}$ for FA and HMPT, respectively [34]), we express the mixed solvent composition in the volume fraction scale Φ_2 , which allows to take into account the packing effects and the difference in the non-electrolyte molecule dimension:

$$\Phi_2 = X_2 \left(\frac{V_{M,2}}{X_2 V_{M,2} + X_1 V_{M,1}} \right) \quad (11)$$

where $V_{M,1}$ and $V_{M,2}$ are the molar volumes of water and organic cosolvent, respectively. As can be seen from Fig. 5, the solute behaviour is nearly identical, the enthalpies of $Bu_4N^+-Et_4N^+$ transfer for all systems being described successfully up to the $\Phi_2 = 0.2$ organic cosolvent volume fraction by the following linear dependence:

$$\Delta_t H^\circ = 55.9(4.3)\Phi_2, \quad R = 0.9590, \quad S = 1 \text{ kJ mol}^{-1} \quad (12)$$

As a cosolvent concentration is increased, the triplet and high-order solute–cosolvent interactions give increasing contributions to the $\Delta_t H^\circ$ values causing the deviation of the experimental points from the linear dependence observed (see Fig. 5). Thus, the considerable difference

Table 6
Free energy (g_{23} , J kg mol⁻²) and entropic (Ts_{23} , J kg mol⁻²) coefficients of Bu₄NBr pair interaction with HMPT, *t*-BuOH, Me₂CO and DO in water

Cosolvent	γ_{23}	T (K)				
		277.15	288.15	298.15	308.15	313.15
HMPT	g_{23}	323	137	-264	-391	-557
	Ts_{23}	7602	7544	7479	7407	7365
<i>t</i> -BuOH	g_{23}	–	193	-50 ^a	-215	–
	Ts_{23}	–	4675	6200	7771	–
Me ₂ CO	g_{23}	–	128	57 ^a	-150	–
	Ts_{23}	–	3795	4018	4245	–
DO	g_{23}	–	81	-43 ^a	-159	–
	Ts_{23}	–	3632	3605	3573	–

^a The g_{23} coefficients were taken from reference [18].

in the energetics of the tetraalkylammonium salt–organic cosolvent pair interaction (see Fig. 4) results from the difference of the cosolvent molecule dimension and the influence of bromide ion. It is of particular importance that nature of a polar group in the cosolvent molecule does not influence the solute behaviour at low Φ_2 values. We believe that Eq. (12) has a predictive value at least for the enthalpies of non-polar solute transfer from water to its mixtures with aprotic solvents being oxygen electron pair donors such as dimethylsulfoxide, dimethylacetamide, etc.

5. Conclusions

We have studied the temperature dependence of the interaction parameters between hydrophobic solutes—tetraethyl- and tetrabutylammonium bromides and hexamethyl phosphoric triamide in water. The solute interaction with various cosolvents in water was found to be enthalpically repulsive, but entropically favourable in the temperature range studied. The results do indicate that bromide ion and cosolvent nature define to a great extent the enthalpic and heat capacity interaction parameters, the last one in particular. It was also shown that the difference in the enthalpies of the solute transfer from water to its highly aqueous mixtures with various organic cosolvents results from the influence of bromide ion as well as the difference in dimensions of the cosolvent molecules.

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