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Thermal properties of tetraalkylammonium bromides in several solvents

V. P. Korolev · O. A. Antonova · N. L. Smirnova ·
A. V. Kustov

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Abstract Enthalpies of solution of tetra-*n*-hexylammonium bromide in anhydrous methanol (MeOH), formamide (FA), and ethylene glycol (EG) have been measured at 298.15 and 313.15 K. The integral solution enthalpies ($\Delta_{sol}H^{m}$) of Hex_4NBr and literature data for Et_4NBr and Bu_4NBr have been extrapolated to infinite dilution using the Redlich–Rosenfeld–Meyer-type equation to give the corresponding standard enthalpies of solution ($\Delta_{sol}H^{0}$). Linear correlation between $\Delta_{sol}H^{0}(Bu_4NBr)$ and $\Delta_{sol}H^{0}$ (Hex_4NBr) has been obtained in MeOH, FA, and EG. Relations allowing to predict the $\Delta_{sol}H^{0}$ value of Hex_4NBr in FA, NMF, DMF, and NMA at various temperatures have been proposed. The integral heat method has been employed to obtain partial molar heat capacities $\overline{C}^{0}_{p2}$ of the tetraalkylammonium bromides in MeOH, FA, and EG. It has been shown that the $\overline{C}^{0}_{p2}$ values of Et_4NBr and Bu_4NBr in methanol and formamide determined by this method are in good agreement with values obtained by the flow calorimetry data.

Keywords Calorimetry · Enthalpy of solution · Ethylene glycol · Formamide · Heat capacity of solution · Methanol · Partial molar heat capacity · Tetraalkylammonium bromides

Introduction

Thermal properties of organic electrolytes in aqueous and non-aqueous solvents are of great importance for investigations of various kinds of interparticle interactions, solvophobic and structural effects, and features of ions solvation in a solution [1–10]. For example, on the basis of the data of solution enthalpies of Et_4NBr and Bu_4NBr in water, formamide (FA), methanol (MeOH), and ethylene glycol (EG) solvents at 298.15 and 313.15 K, we have made the conclusion [1] that the solvophobic solvation effects weaken in the following set of solvents, namely H_2O, FA, EG, and MeOH. The study of enthalpic characteristic at different temperatures has a special significance. It allows to calculate the heat capacity data which are sufficiently sensitive to the solute—solvent interaction and the solution structure [2–5]. The sequence of solvents mentioned above has been also confirmed by the heat capacity of solution, ΔC^{0}_{p}, values of Bu_4NBr [5]. The ΔC^{0}_{p} value is necessary for determining such an important thermodynamic quantity as $\overline{C}^{0}_{p2}$—the partial molar heat capacity at infinite dilution by means of the integral solution enthalpy method. Another way of obtaining the $\overline{C}^{0}_{p2}$ values is the extrapolation of apparent molar heat capacities to an infinite dilution. These characteristics are usually calculated from flow calorimetry data.

The authors [6, 7] studied the set of tetraalkylammonium (TAA) bromides in MeOH and reported the $\overline{C}^{0}_{p2}$ values for Me_4NBr–Bu_4NBr defined by the integral solution enthalpy method. Then they reported the $\overline{C}^{0}_{p2}$ data for Pen_4NBr and Hep_4NBr determined by flow calorimetry [8]. Chen et al. [9] obtained $\overline{C}^{0}_{p2}$ values for NH_4Br, Me_4NBr–Pen_4NBr in FA by the flow calorimetry method. De Visser and Somsen [4] applied the integral heat method to the solutions of tetrabutylammonium bromide in a number of solvents including FA. It is necessary to note that the data on heat capacity properties of Hex_4NBr are not available in the studies mentioned above [1, 4–9].

V. P. Korolev (✉) · O. A. Antonova · N. L. Smirnova ·
A. V. Kustov
Institute of Solution Chemistry, Russian Academy of Sciences,
1, Academicheskaya str, 153045 Ivanovo, Russia
e-mail: korolev@isuct.ru

Marcus and Hefter [10] analysed the partial molar heat capacities of a number of R_4N^+ ions in groups of solvents. They obtained linear correlations $\overline{C}_{p2}^0 = f(n_C)$ for some solvents, where n_C—the number of carbon atoms of TAA ion.

In this article, we report the integral enthalpies of solution of tetra-*n*-hexylammonium bromide in anhydrous MeOH, FA, and EG at 298.15 and 313.15 K. The experimental $\Delta_{sol}H^m$ values have been extrapolated to an infinite dilution for calculating the standard $\Delta_{sol}H^0$ values by Redlich–Rosenfeld–Meyer-type equation [9]. By the same method, we have determined the standard solution enthalpies of Et_4NBr and Bu_4NBr in these solvents using the data obtained earlier by us [1].

We have used the $\Delta_{sol}H^0$ values for computing the molar heat capacity of solution ΔC_p^0 data in the investigated solvents. The corresponding $\overline{C}_{p2}^0$ values have been calculated from ΔC_p^0 data and the molar heat capacity of crystalline salt $\overline{C}_{pcryst}^0$

The aims of this article are (i) to analyse the solution enthalpies data of Et_4NBr, Bu_4NBr, and Hex_4NBr in several solvents (ii) to compare the data on the partial molar heat capacity obtained by the integral heat method for salts being investigated in non-aqueous H-bonded solvents MeOH, FA, and EG with the literature data, and (iii) to check up the existence of the linear dependence of $\overline{C}_{p2}^0$ values of the solutes being studied on the size of cation. Similar study on the thermochemical properties of TAA salts solutions in binary mixtures on the basis of MeOH, FA, and EG will be reported in further publication in this Journal.

Experimental

Materials

MeOH «HPLC grade Fisher Scientific 99.99%» and EG «Sigma–Aldrich spectrophotometric grade 99+%» have been used without further purification, FA (Reachem) has been purified as in our previous study [1]. Hex_4NBr (Aldrich, 99%) has been dried in vacuum at 308 K for 72 h with a trap with liquid nitrogen up to a constant mass [11]. Suitable amounts of salt have been transferred into thin glass ampoules in a glove box filled with P_2O_5.

Apparatus and methods

The calorimetric measurements have been carried out with an ampoule "isoperibol" calorimeter [12] fitted with a 60-cm^3 vessel. Thermistor resistance of calorimeter has been measured by the Standard Temperature Measuring Instrument [13]. The signal of the instrument has been converted to the degrees of the International Temperature Scale of 1990. The detection limit of the apparatus is 10 μK. The temperature instability in the bath is 1 mK in the temperature range of 278–333 K. The calorimeter has been tested by measuring the enthalpies of solution of potassium chloride (KCl) and 1-propanol (1-PrOH) in water at 298.15 K [13] according to the recommendations given elsewhere [14]. Our results $\Delta_{sol}H^m$ $(m = 0.111 \text{ mol kg}^{-1}) = 17.61 \pm 0.02 \text{ kJ mol}^{-1}$ for KCl and $\Delta_{sol}H^0 = -10.18 \pm 0.03 \text{ kJ mol}^{-1}$ for 1-PrOH [13] are in good agreement with the recommended values 17.58 ± 0.02 and $-10.16 \pm 0.02 \text{ kJ mol}^{-1}$ for KCl and 1-PrOH, respectively [14]. The probes of salts have been weighed on analytical balances (Ohaus Analytical plus) with 0.1 mg accuracy.

Results and discussion

The integral enthalpies of solution $\Delta_{sol}H^m$ of Hex_4NBr in MeOH, FA, and EG at 298.15 and 313.15 K are given in Table 1. We have found the only measurement of the solution enthalpy of Hex_4NBr in MeOH. Krishnan and Friedman [15] reported the value 6.82 kJ mol^{-1} obtained at molality $m < 5\ 10^{-4}$ mol kg^{-1} at 298.15 K. This value is in satisfactory agreement with the $\Delta_{sol}H^m$ data given in Table 1.

The concentration dependence of $\Delta\ _{sol}H^m$ of electrolyte in various solvents is frequently described by means of Redlich–Rosenfeld–Meyer-type equation [9]:

$$\Delta_{sol}H^m = \Delta_{sol}H^0 + A_H m^{1/2} + Bm, \qquad (1)$$

where A_H is the appropriate Debye-Hückel limiting law slope and B is the empirical constant varying with electrolyte, solvent, and temperature. For a given solvent at constant temperature, A_H is constant for all electrolytes with the identical charge.

$$A_H = -(v/2)^{0.5}|z_+z_-|^{1.5} vRT^2 A\left(\frac{1}{T} + \frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial T} - \frac{1}{3\rho}\frac{\partial\rho}{\partial T}\right) \qquad (2)$$

where v—the number of ions of charge z_i per "molecule" of electrolyte. The term A can be written as follows:

$$A = \sqrt{\frac{2\pi N_A e^6 \rho}{1000\,(\varepsilon kT)^3}}, \qquad (3)$$

where ρ and ε are the density and the dielectric constant of solvent, respectively. Other symbols have their usual meanings [16].

Reliable calculation of the numerical values of A_H requires proper physicochemical data for the pure solvents: such as ρ and ε and their first temperature derivatives. For pure methanol, the third order polynomial of $\rho = f(T)$ cited by Sun et al. [17] has been taken. We have also collected

Table 1 The integral enthalpies of solution ($\Delta_{\mathrm{sol}}H^{\mathrm{m}}$/kJ mol^{-1}) of Hex_4NBr in non-aqueous solvents

m/mol kg^{-1} 298.15 K	$\Delta_{\mathrm{sol}}H^{\mathrm{m}}$	m/mol kg^{-1} 313.15 K	$\Delta_{\mathrm{sol}}H^{\mathrm{m}}$
Methanol			
0.0032	6.32	0.0030	7.56
0.0045	6.13	0.0031	7.80
0.0057	6.52	0.0067	7.83
0.0078	6.16	0.0069	8.05
0.0080	6.69	0.0117	7.87
		0.0118	7.87
		0.0157	7.94
		0.0193	7.97
Formamide			
0.0050	9.11	0.0026	12.28
0.0080	9.17	0.0050	12.29
0.0111	9.27	0.0074	12.32
01390	9.37	0.0100	12.35
Ethylene glycol			
0.0021	21.97	0.0033	23.62
0.0030	22.00	0.0061	23.62
0.0039	22.02	0.0088	23.66
0.0089	22.03	0.0114	23.73

the ε values for methanol given elsewhere [18–20] as shown in Table 2 and have fitted these data to the equation:

$$\varepsilon = 32.68 \pm 0.02 + (17174 \pm 91)(1/T - 1/298.15),$$
$$R = 0.9998, \mathrm{sd} = 0.09 \qquad (4)$$

The temperature derivative of the dielectric constant of methanol, $\partial\varepsilon/\partial T$, calculated by Eq. 4, and represented in Table 3, equals -0.193 K^{-1} at 298.15 K. This value is in good agreement with that -0.197 K^{-1} given by Abraham et al. [21].

Table 2 Dielectric constants of methanol at different temperatures [18–20]

T/K	ε	T/K	ε
250.7	43.53	298.15	32.70
273.2	37.92	303.15	31.76
278.15	36.88	308.15	30.74
283.15	35.76	313.15	30.01
288.15	34.70	318.15	28.92
288.15	34.74	323.15	28.34
293.15	33.68	328.15	27.21
298.15	32.66	333.15	26.75

Table 3 Physic-chemical characteristics of non-aqueous solvents calculated by Eqs. 4–6 and equations given in [17, 24]

Solvent	Methanol		Formamide		Ethylene glycol	
T/K	298.15	313.15	298.15	313.15	298.15	313.15
ρ/kg m^{-3}	786.5	772.2	1129.1	1116.4	1109.1	1098.1
$-\partial\rho/\partial T$/ kg m^{-3} K^{-1}	0.946	0.971	0.846	0.851	0.734	0.753
ε	32.7	30.0	109.0	102.9	37.9	34.9
$-\partial\varepsilon/\partial T$/K^{-1}	0.193	0.175	0.409	0.399	0.204	0.185
A	3.870	4.052	0.762	0.767	3.689	3.847
A_{H}/kJ kg$^{1/2}$ mol$^{-3/2}$	12.32	14.69	0.165	0.541	9.84	11.68

The data of ρ from [22] at 264–422 K and the data of ε from [23] at 293–373 K for ethylene glycol have been fitted as functions of temperature:

$$\rho = 1109.10 \pm 0.11 - (733.7 \pm 4.3)10^{-3}(T - 298.15)$$
$$- (640 \pm 45)10^{-6}(T - 298.15)^2,$$
$$R = 0.99997, \mathrm{sd} = 0.3\mathrm{kg\ m}^{-3} \qquad (5)$$

$$\varepsilon = 37.88 \pm 0.05 + (18105 \pm 113)(1/T - 1/298.15),$$
$$R = 0.99994, \mathrm{sd} = 0.07 \qquad (6)$$

Dunn and Stokes [24] cited the equation of $\rho(T)$ for liquid formamide based on their own data. Later, Chen et al. [9] obtained the dependence of molar volume of formamide versus temperature using the values calculated from data [24]. Our analysis has shown that the equation offered by Chen et al. [9] is incorrect. Therefore, we have used the equation of $\rho(T)$ from [24] and the equation of $\varepsilon(T)$ from the same work for calculations. The values A, A_{H} as well as parameters required for their calculation at 298.15 and 313.15 K are listed in Table 3.

The curves $\Delta_{\mathrm{sol}}H^{\mathrm{m}}$ versus $m^{1/2}$ for Hex_4NBr are presented in Fig. 1. The $\Delta_{\mathrm{sol}}H^0$ values for Hex_4NBr calculated by Eq. 1 are listed in Table 4. The $\Delta_{\mathrm{sol}}H^0$ data of Et_4NBr and Bu_4NBr in MeOH, FA and EG determined by Eq. 1 are also presented in Table 4. The integral solution enthalpies of Et_4NBr and Bu_4NBr in these solvents from [1] and A_{H} values from Table 3 have been used for calculating their standard enthalpies of solution. The solution enthalpy of Bu_4NBr in FA measured by us $\Delta_{\mathrm{sol}}H^0 = 17.71 \pm 0.02$ kJ mol^{-1} at 298.15 K is in good agreement with the value 17.65 ± 0.05 [4].

It should be noted that the properties of individual solvents are necessary for solving a problem of determination of the mixed solvent properties using various additive schemes. In paper [5], we have realized this approach for FA–MeOH and FA–EG mixtures.

According to the work [1] where we considered the connection between $\Delta_{\mathrm{sol}}H^0(Et_4NBr)$ and $\Delta_{\mathrm{sol}}H^0(Bu_4NBr)$ in this article we have decided to make the same analysis

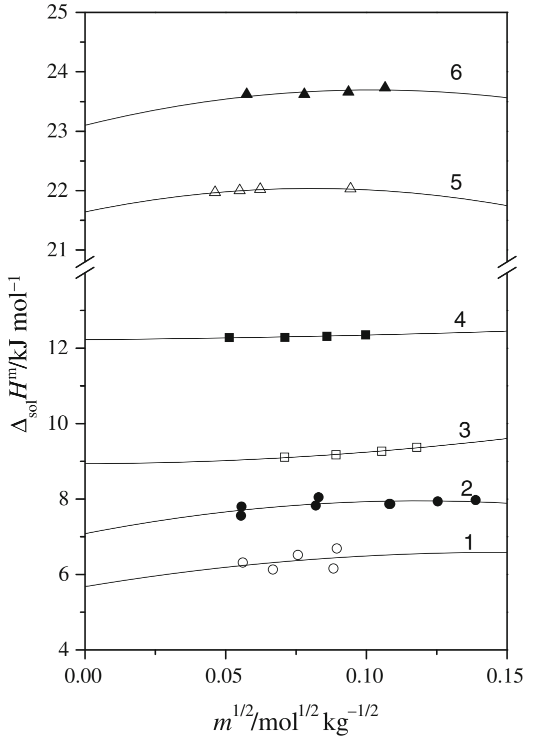

Fig. 1 The enthalpies of solution of tetra-*n*-hexylammonium bromide versus $m^{1/2}$ of salt in methanol (1, 2), formamide (3, 4) and ethylene glycol (5, 6). *Light symbols* 298.15 K, *dark symbols* 313.15 K. *Lines* Eq. 1

Table 4 The standard enthalpies of solution ($\Delta_{sol}H^0$/kJ mol^{-1}) of Et_4NBr, Bu_4NBr and Hex_4NBr in non-aqueous solvents at 298.15 and 313.15 K and the change of molar heat capacity of solution ΔC_p^0/J K^{-1} mol^{-1}) in the 298.15–313.15 K temperature range

	T/K	Methanol	Formamide	Ethylene glycol
Et₄NBr				
$\Delta_{sol}H^0$	298.15	18.27 ± 0.13	11.55 ± 0.02	21.02 ± 0.08
	313.15	18.10 ± 0.04	12.07 ± 0.01	21.71 ± 0.07
ΔC_p^0		−11 ± 9	35 ± 2	46 ± 7
Bu₄NBr				
$\Delta_{sol}H^0$	298.15	16.72 ± 0.08	17.71 ± 0.02	28.66 ± 0.03
	313.15	17.18 ± 0.12	20.23 ± 0.01	30.20 ± 0.03
ΔC_p^0		31 ± 10	168 ± 2	103 ± 3
Hex₄NBr				
$\Delta_{sol}H^0$	298.15	5.44 ± 0.11	8.94 ± 0.02	21.64 ± 0.01
	313.15	7.08 ± 0.08	12.23 ± 0.01	23.10 ± 0.07
ΔC_p^0		109 ± 13	219 ± 2	97 ± 5

The uncertainties are the standard deviations

for Bu_4NBr and Hex_4NBr. It has appeared that the solution enthalpies of Bu_4NBr and Hex_4NBr in solvents investigated are connected by a linear relation:

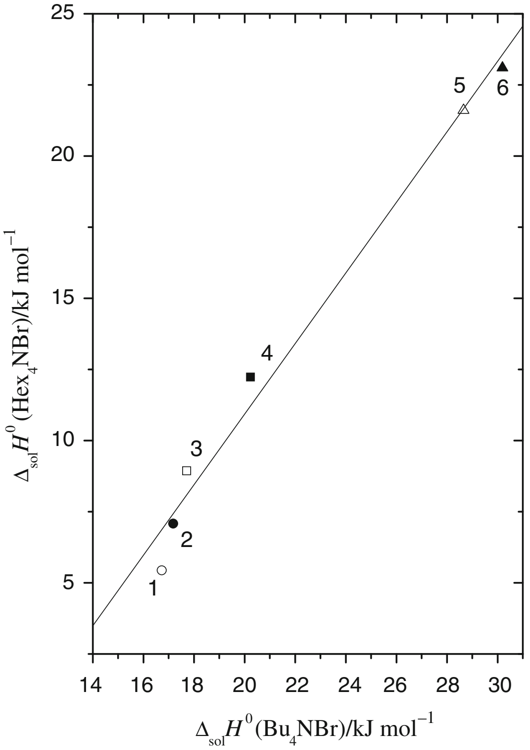

Fig. 2 The enthalpies of solution of tetra-*n*-hexylammonium bromide versus the enthalpies of solution of tetra-*n*-butylammonium bromide in methanol (1, 2), formamide (3, 4) and ethylene glycol (5, 6). *Light symbols* 298.15 K, *dark symbols* 313.15 K. *Line* Eq. 7

$$\begin{aligned}\Delta_{sol}H^0(\mathrm{Hex_4NBr}) &= (-13.9 \pm 1.7)\\ &\quad + (1.237 \pm 0.075)(\Delta_{sol}H^0(\mathrm{Bu_4NBr})),\\ R &= 0.993,\ \mathrm{sd} = 1.0\,\mathrm{kJ\ mol^{-1}}\end{aligned} \tag{7}$$

This dependence is presented in Fig. 2.

It is necessary to note that Bu_4NBr is the most experimentally investigated salt in non-aqueous solvents. Therefore, De Visser and Somsen [4] obtained the solution enthalpies of Bu_4NBr in formamide, *N*-methylformamide (NMF), and *N*,*N*-dimethylformamide (DMF) from 278 to328 K and in *N*-methylacetamide (NMA) from 308 to328 K at 10 K intervals. They fitted the $\Delta_{sol}H^0 = \mathrm{f}\ (T)$ dependence by the second-order polynomial. This polynomial contains three adjustable parameters and provides the precision of fitting about 0.1 kJ mol^{-1}. We have found, however, that similar result can be obtained using linear dependence $\Delta_{sol}H^0$ versus $1/T$ [25]. This equation contains only two adjustable parameters and is more reliable for extrapolation [25]. Taking it into account, we have fitted the $\Delta_{sol}H^0$ data of Bu_4NBr in amides [4] by the next equations:

$$\begin{aligned}\Delta_{sol}H^0(\mathrm{FA}) &= 17.67 \pm 0.06\\ &\quad - (14809 \pm 299)(1/T - 1/298.15), R\\ &= 0.9992,\ \mathrm{sd} = 0.14\,\mathrm{kJmol^{-1}}\end{aligned} \tag{8}$$

$$\begin{aligned}\Delta_{\mathrm{sol}}H^0(\mathrm{NMF}) = {} & 22.48 \pm 0.05 \\ & - (6402 \pm 253)(1/T - 1/298.15), \\ R = {} & 0.9969, \mathrm{sd} = 0.12\,\mathrm{kJmol}^{-1}\end{aligned} \tag{9}$$

$$\begin{aligned}\Delta_{\mathrm{sol}}H^0(\mathrm{DMF}) = {} & 12.29 \pm 0.06 \\ & - (12087 \pm 301)(1/T - 1/298.15), \\ R = {} & 0.9988, \mathrm{sd} = 0.14\,\mathrm{kJmol}^{-1}\end{aligned} \tag{10}$$

$$\begin{aligned}\Delta_{\mathrm{sol}}H^0(\mathrm{NMA}) = {} & 23.89 \pm 0.09 \\ & - (4695 \pm 406)(1/T - 1/298.15), \\ R = {} & 0.9963, \mathrm{sd} = 0.06\,\mathrm{kJmol}^{-1}\end{aligned} \tag{11}$$

Equations 8–11 combined with Eq. 7 allow to predict the $\Delta_{\mathrm{sol}}H^0$ values of $\mathrm{Hex_4NBr}$ in amides at various temperatures knowing the $\Delta_{\mathrm{sol}}H^0$ values of $\mathrm{Bu_4NBr}$ in the same solvents at the appropriate temperatures. For example, determined by us calorimetrically at 298.15 K, the $\Delta_{\mathrm{sol}}H^0$ value of $\mathrm{Hex_4NBr}$ in FA 8.9 kJ mol^{-1} is close to that of 8.0 kJ mol^{-1} calculated by Eqs. 8 and 7.

The standard solution enthalpies have been treated by the integral heat method to obtain heat capacities of solution, ΔC^0_p,, and partial molar heat capacities of the solutes, $\overline{C^0_{p2}}$, have been evaluated as follows:

$$\Delta C^0_p = \Delta\Delta_{\mathrm{sol}}H^0/\Delta T = \overline{C^0_{p2}} - C^0_{p\mathrm{cryst}} \tag{12}$$

where $C^0_{p\mathrm{cryst}}$ is the heat capacity of the crystalline salt.

The ΔC^0_p data determined from the enthalpies of solution by Eq. 12 are given in Table 4. The ΔC^0_p value equals 165 ± 6 J mol^{-1} K^{-1} at 298.15 K [4] and is in an excellent agreement with our 168 ± 2 J mol^{-1} K^{-1}.

The $\overline{C^0_{p2}}$ values for $\mathrm{Et_4NBr}$ and $\mathrm{Bu_4NBr}$ in MeOH, FA and EG at 298.15 K have been calculated using the $\Delta_{\mathrm{sol}}H^0$ data and $C^0_{p\mathrm{cryst}}$ values from [26] given in Table 5. Because of the lack of heat capacity data for the crystalline $\mathrm{Hex_4NBr}$ the available $C^0_{p\mathrm{cryst}}$ data for $\mathrm{Me_4NBr}$–$\mathrm{Pen_4NBr}$ from [7, 26–28] at 298.15 K have been described as a function of carbon atoms number in cation:

$$\begin{aligned}C^0_{p\mathrm{cryst}} = {} & 53 \pm 14 + (25.5 \pm 1.1)\,n_{\mathrm{c}}, R = 0.995, \mathrm{sd} \\ = {} & 15\ \mathrm{J\ mol^{-1}K^{-1}}\end{aligned} \tag{13}$$

The $C^0_{p\mathrm{cryst}}$ values for $\mathrm{Hex_4NBr}$ determined by Eq. 13 and $\overline{C^0_{p2}}$ values of $\mathrm{Et_4NBr}$, $\mathrm{Bu_4NBr}$, and $\mathrm{Hex_4NBr}$ in ethylene glycol, formamide and methanol calculated by Eq. 12 are also listed in Table 5.

Marcus and Hefter [10] found that for cations of $(\mathrm{C}_n\mathrm{H}_{2n+1})_4\mathrm{N}^+$ type the dependences of $\overline{C^0_{p2}}$ against n_{C} are linear in some groups of solvents. Figure 3 presents the $\overline{C^0_{p2}}$ values of $\mathrm{R_4NBr}$ salts versus n_{C} for water [8], MeOH [8], and FA [9] solvents. We have analysed these data in more details.

We have described the $\overline{C^0_{p2}}$ data for $\mathrm{Et_4NBr}$, $\mathrm{Pr_4NBr}$, and $\mathrm{Bu_4NBr}$ in aqueous solution [8] by the equation:

Table 5 Heat capacities (J K^{-1} mol^{-1}) of organic salts in ethylene glycol at 298.15 K

Solute	$C^0_{p\mathrm{cryst}}$	$\overline{C^0_{p2}}$		
		MeOH	FA	EG
$\mathrm{Et_4NBr}$	247 [26]	236	282	293
$\mathrm{Bu_4NBr}$	477 [26]	508	645	580
$\mathrm{Hex_4NBr}$	665	774	884	762

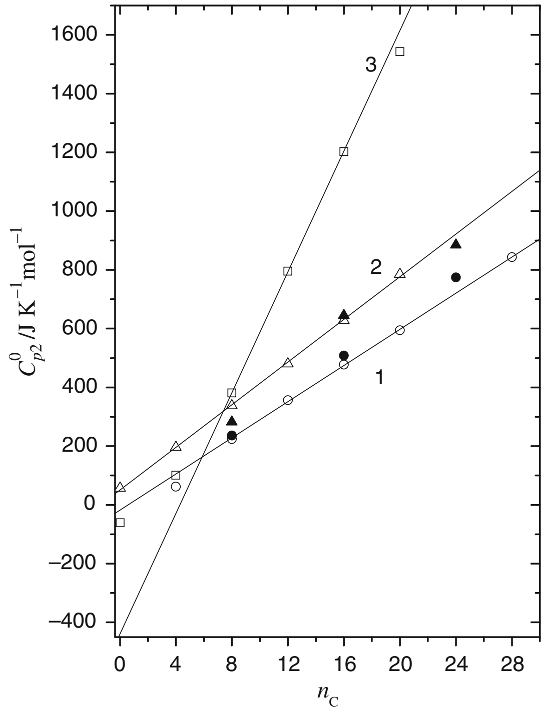

Fig. 3 Partial molar heat capacities of tetraalkylammonium bromides in methanol (1), formamide (2) and water (3) versus n_{C} (for $\mathrm{NH_4Br}$ $n_{\mathrm{C}} = 0$). *Light symbols* the literature values [8, 9], *dark symbols* the data of the present work. *Lines* Eqs. 14–16

$$\begin{aligned}\overline{C^0_{p2}} = {} & -439.7 \pm 7.2 + (102.75 \pm 0.58)\,n_{\mathrm{C}}, R = 0.9998, \mathrm{sd} \\ = {} & 3\ \mathrm{J\ mol^{-1}K^{-1}}\end{aligned} \tag{14}$$

As it is seen from Fig. 3, the points for $\mathrm{NH_4Br}$ and $\mathrm{Me_4NBr}$ have a positive deviation from linearity but the value for $\mathrm{Pen_4NBr}$ has an insignificant negative one.

In formamide, the $\overline{C^0_{p2}}$ data from [9] have been described by the equation:

$$\begin{aligned}\overline{C^0_{p2}} = {} & 50.9 \pm 4.7 + (36.28 \pm 0.39)\,n_{\mathrm{C}}, R = 0.9998, \\ & \mathrm{sd} = 6\ \mathrm{J\ mol^{-1}\ K^{-1}}\end{aligned} \tag{15}$$

Apparently from Fig. 3, the points for all the investigated salts $\mathrm{NH_4Br}$, $\mathrm{Me_4NBr}$–$\mathrm{Pen_4NBr}$ belong to line (15).

In methanol, the $\overline{C}_{p2}^{0}$ values for Et_4NBr–Pen_4NBr and Hep_4NBr have been taken from [8] and described by Eq. 16. The point for Me_4NBr has a negative deviation from linearity.

$$\overline{C}_{p2}^{0} = -17.7 \pm 5.2 + (30.75 \pm 0.29)\, n_{C}, R = 0.9999, \text{sd} = 4\ \text{J mol}^{-1}\ \text{K}^{-1} \qquad (16)$$

The slope in Eqs. 14–16 is the increment of the methylene group to the $\overline{C}_{p2}^{0}$ value. It is possible to note that this value decreases in sequence of solvents water, FA and MeOH. This sequence coincides with the one indicated in Introduction.

In Fig. 3, our $\overline{C}_{p2}^{0}$ values for the studied TAA bromides (dark symbols) are also given for comparing. Figure 3 reflects a good agreement of ours and literature data obtained by different methods.

Conclusions

The enthalpies of solution of tetra-*n*-hexylammonium bromide in anhydrous MeOH, FA, and EG have been measured at 298.15 and 313.15 K by calorimetric method for the first time. The integral solution enthalpies of Hex_4NBr and literature data for Et_4NBr and Bu_4NBr have been extrapolated to infinite dilution using the Redlich–Rosenfeld–Meyer-type equation to give the corresponding standard enthalpies of solution $\Delta_{sol}H^0$. Linear correlation between $\Delta_{sol}H^0(Bu_4NBr)$ and $\Delta_{sol}H^0$ (Hex_4NBr) has been obtained in MeOH, FA and EG at 298.15 and 313.15 K. Relations allowing to predict the $\Delta_{sol}H^0$ value of Hex_4NBr in FA, NMF, DMF, and NMA at different temperatures have been proposed. The integral heat method has been employed to determine the $\overline{C}_{p2}^{0}$ values of the Et_4NBr, Bu_4NBr, and Hex_4NBr in MeOH, FA, and EG. It has been shown that our partial molar heat capacity values of TAA bromides in MeOH and FA are in good agreement with the literature ones obtained by the flow calorimetry data.

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