

Thermal properties of n - R_4 NBr solutions in binary solvents containing formamide

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Abstract The enthalpies of solution of tetraethyl- and tetra- n -hexylammonium bromides have been measured in mixtures of formamide with ethylene glycol at 298.15 and 313.15 K in the whole mole fraction range by the calorimetric method. The standard enthalpies of solution in binary mixtures have been calculated with Redlich–Rosenfeld–Meyer type equation. The enthalpy and heat capacity parameters of pair interaction of organic electrolytes with EG in FA and with FA in EG have been computed and discussed. The enthalpy interaction parameters of single ions with EG in FA medium have been evaluated and compared with those for ion–water and ion–MeOH interaction in FA. The standard heat capacities of solution have been evaluated. The excess enthalpies of solution, $\Delta_{\text{sol}}H^E$, of Et_4NBr , Bu_4NBr , and Hex_4NBr have been determined. The $\Delta_{\text{sol}}H^E$ values are positive for Et_4NBr and negative for Bu_4NBr and Hex_4NBr and become more negative from Bu_4NBr to Hex_4NBr .

Keywords Binary solvent · Calorimetry · Enthalpy and heat capacity parameters of pair interaction · Enthalpy of solution · Ethylene glycol · Excess enthalpy of solution · Formamide · Heat capacity of solution · Tetraalkylammonium bromides

Introduction

Thermal properties of tetraalkylammonium (TAA) salt solutions in non-aqueous binary solvents containing formamide were studied in set of the works [1–4]. In the article [1], the enthalpies of solution of tetra- n -butylammonium bromides in binary mixtures of water, formamide, N -methylformamide, and N,N -dimethylformamide were obtained at 298.15 by calorimetric method.

In the studies [2–4] the enthalpies of solution of Et_4NBr in mixtures of formamide with water and methanol at 298.15 and 313.15 K [2] and Bu_4NBr in MeOH–FA and EG–FA binaries at 298.15 [3] and 313.15 K [4] were measured. Thermal properties of some TAA bromides in EG were defined for the first time. The new additive scheme of determination of the physico-chemical characteristics of binaries necessary for calculation the Debye–Hückel limiting law slope A_H required for obtaining of the standard solution enthalpies was proposed in [4]. The equations for calculation of the A_H values of any uni-univalent electrolytes in the mixtures of FA with MeOH and EG at 298.15 and 313.15 K were also cited in [4]. The data of solution enthalpies of Hex_4NBr in binary mixtures were not found by us even at one temperature.

Thermal characteristics of ion-molecular particles of different nature give an important information about energetic of intermolecular interactions in solutions. It is well known that in the formalism of McMillan–Mayer theory [5] enthalpic interaction coefficients can be considered a measure of intermolecular interactions in solution. A number of successful applications of this theory to the enthalpic properties of dilute solutions have been reported [6–8]. It was shown [8] that a functional group additivity concept developed by Savage and Wood [7] for

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non-electrolytes also applies for mixtures of electrolytes and non-electrolytes.

Since our enthalpies of solution in mixed solvent systems always covered the complete mole fraction range, it is possible to determine the enthalpic pair interaction coefficient in the initial and final region.

The present study reports the results of calorimetric measurements of solution enthalpies of tetraethyl- and tetra-*n*-hexylammonium bromides in FA–EG binaries at 298.15 and 313.15 K in the whole mole fraction range of mixture. The aim of present study is (i) to report the experimental enthalpies of solution of Et₄NBr and Hex₄NBr in FA–EG binary system at 298.15 and 313.15 K, (ii) to calculate the values of their standard enthalpies of solution, (iii) to use the enthalpies of solution data to calculate the change in molar heat capacities, ΔC_p^0 , for dissolution in mixed solvent, (iv) to compute the enthalpy and heat capacity coefficients of the solute–co-solvent pair interaction and estimate the enthalpy contributions of single ions to the parameters of pair interaction with co-solvent; (v) to compare obtained characteristics with the ones of another systems containing formamide.

Experimental

Materials

Formamide “Fluka $\geq 99\%$ (purum)” has been frozen, stored over molecular sieves 3 Å and twice distillate under reduced pressure at 348 K. The content of water in formamide has been determined by Fisher titration and never exceeded 0.04 mass%. Ethylene glycol “Sigma-Aldrich spectrophotometric grade 99+-%” with water content $< 0.01\%$ has been used without further purification. The mixtures have been prepared by weight using an electronic analytical balance (OKB Vesta) with accuracy 1 mg. The uncertainty in the mole fraction is to be lower than $\pm 2 \times 10^{-4}$. Tetraethylammonium bromide (Merck) has been used without additional purification and only dried in a vacuum at 353 K [2]. Tetra-*n*-hexylammonium bromide (Aldrich, 99%) has been used after drying in vacuum at 308 K for at least 72 h with a trap with liquid nitrogen up to a constant weight. Suitable amounts of salts have been transferred into thin glass ampoules within a glove box with dry P₂O₅.

The measurements

The enthalpies of solution have been measured with an ampoule type “isoperibol” calorimeter [9] equipped with a 60 cm³ reaction vessel. The experimental procedure and

the test of the instrument have been reported earlier [4, 10–12]. The overall uncertainty of our measurements is estimated to be within 1%.

Results

All measurements of the experimental enthalpies of solution of Et₄NBr and Hex₄NBr in formamide–ethylene glycol mixtures have been carried out at molalities 0.003–0.01 mol kg⁻¹. The experimental and standard enthalpies of solution $\Delta_{\text{sol}}H^m$ of Et₄NBr and Hex₄NBr in ethylene glycol–formamide mixture at 298.15 and 313.15 K are listed in Tables 1 and 2.

The standard enthalpies of solution of electrolytes studied have been obtained by Redlich–Rosenfeld–Meyer type equation [4, 10, 13]:

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

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 a given temperature, A_H is constant for all electrolytes with the identical charge.

$$A_H = -(v/2)^{1/2} \cdot |z_+ z_-|^{3/2} \cdot v \cdot RT^2 \cdot A \cdot \left(\frac{1}{T} + \frac{\partial \ln \varepsilon}{\partial T} + \frac{\alpha}{3} \right) \quad (2)$$

where v is the number of ions of charge z_i per “molecule” of electrolyte.

The term A can be written as follows:

$$A = \sqrt{\frac{2\pi N_A \cdot e^6 \rho}{1000(\varepsilon \cdot kT)^3}} = \frac{4.201 \cdot 10^6 \rho^{1/2}}{(\varepsilon T)^{3/2}} \quad (3)$$

where ρ and ε are the density and the dielectric constant of pure or mixed solvent. Other symbols have their usual meanings [14].

Reliable calculations of the numerical A_H values requires proper physicochemical data of mixed solvent. The data of ρ and ε for investigated EG–FA mixtures necessary for determination are not found by us even at the one temperature. Parameters required for calculation of A_H for pure solvents are taken from [4]. Parameters for EG–FA mixture have been obtained with application the new additive scheme of determination of the physicochemical characteristics of binaries [4]. The A_H values of EG–FA solvent at 298.15 and 313.15 K have been calculated by the Eqs. 2 and 3 and are listed in Tables 1 and 2.

The Debye–Hückel limiting law slope for EG–FA mixtures may be written as:

Table 1 The experimental ($\Delta_{\text{sol}}H^m/\text{kJ mol}^{-1}$) and standard ($\Delta_{\text{sol}}H^0/\text{kJ mol}^{-1}$) enthalpies of solution of Et₄NBr in mixtures of ethylene glycol with formamide and the appropriate Debye–Hückel limiting law slope ($A_H/\text{kJ kg}^{1/2} \text{mol}^{-3/2}$) at 298.15 and 313.15 K

<i>m</i> /mol kg ⁻¹ 298.15 K	$\Delta_{\text{sol}}H^m$	<i>m</i> /mol kg ⁻¹ 313.15 K	$\Delta_{\text{sol}}H^m$
$X_{\text{FA}} = 0.000$ m.f., $A_H = 9.843$		$X_{\text{FA}} = 0.000$ m.f., $A_H = 11.681$	
$\Delta_{\text{sol}}H^0 = 21.02 \pm 0.08$ [10]		$\Delta_{\text{sol}}H^0 = 21.71 \pm 0.07$ [10]	
$X_{\text{FA}} = 0.027$ m.f., $A_H = 9.396$		$X_{\text{FA}} = 0.033$, $A_H = 11.079$	
0.0133	21.47	0.0065	22.10
0.0261	21.53	0.0150	22.11
$\Delta_{\text{sol}}H^0 = 20.78 \pm 0.03$		$\Delta_{\text{sol}}H^0 = 21.57 \pm 0.01$	
$X_{\text{FA}} = 0.053$ m.f., $A_H = 8.973$		$X_{\text{FA}} = 0.055$ m.f., $A_H = 10.665$	
0.0167	21.35	0.0067	21.93
0.0275	21.37	0.0137	21.95
$\Delta_{\text{sol}}H^0 = 20.67 \pm 0.01$		$\Delta_{\text{sol}}H^0 = 21.13 \pm 0.01$	
$X_{\text{FA}} = 0.099$ m.f., $A_H = 8.240$		$X_{\text{FA}} = 0.116$ m.f., $A_H = 9.606$	
0.0147	21.00	0.0134	21.43
0.0264	21.02	0.0213	21.60
$\Delta_{\text{sol}}H^0 = 20.40 \pm 0.01$		$\Delta_{\text{sol}}H^0 = 20.82 \pm 0.09$	
$X_{\text{FA}} = 0.168$ m.f., $A_H = 7.208$		$X_{\text{FA}} = 0.147$ m.f., $A_H = 9.080$	
0.0097	20.38	0.0054	20.98
0.0282	20.65	0.0111	20.99
$\Delta_{\text{sol}}H^0 = 19.81 \pm 0.08$		$\Delta_{\text{sol}}H^0 = 20.58 \pm 0.01$	
$X_{\text{FA}} = 0.246$ m.f., $A_H = 6.131$		$X_{\text{FA}} = 0.234$ m.f., $A_H = 7.708$	
0.0110	19.63	0.0088	20.47
0.0217	19.67	0.0200	20.61
0.0309	19.69	$\Delta_{\text{sol}}H^0 = 19.93 \pm 0.07$	
0.0409	19.70	$X_{\text{FA}} = 0.507$ m.f., $A_H = 4.122$	
$\Delta_{\text{sol}}H^0 = 19.17 \pm 0.03$		0.0072	17.62
$X_{\text{FA}} = 0.502$ m.f., $A_H = 3.185$		0.0151	17.65
0.0171	17.21	$\Delta_{\text{sol}}H^0 = 17.39 \pm 0.02$	
0.0281	17.26		
$\Delta_{\text{sol}}H^0 = 16.90 \pm 0.03$		$X_{\text{FA}} = 0.750$ m.f., $A_H = 1.893$	
$X_{\text{FA}} = 0.752$ m.f., $A_H = 1.220$		0.0061	15.04
0.0140	14.50	0.0141	15.11
0.0290	14.53	$\Delta_{\text{sol}}H^0 = 14.90 \pm 0.04$	
$\Delta_{\text{sol}}H^0 = 14.39 \pm 0.02$			
$X_{\text{FA}} = 1.000$ m.f., $A_H = 0.165$		$X_{\text{FA}} = 1.000$ m.f., $A_H = 0.541$	
$\Delta_{\text{sol}}H^0 = 11.55 \pm 0.02$ [10]		$\Delta_{\text{sol}}H^0 = 12.07 \pm 0.01$ [10]	

The uncertainties are the standard deviation

$$A_H = X_{\text{FA}}A_{H(\text{FA})} + X_{\text{EG}}A_{H(\text{EG})} + aX_{\text{FA}}X_{\text{EG}} \quad (4)$$

where at 298.15 K: $a = -7.20 \pm 0.08$, $R = 0.99996$, $\text{sd} = 0.03 \text{ kJ kg}^{1/2} \text{mol}^{-3/2}$, at 313.15 K: $a = -7.63 \pm 0.15$, $R = 0.99988$, $\text{sd} = 0.06 \text{ kJ kg}^{1/2} \text{mol}^{-3/2}$.

This equation allows to define the A_H values of any univalent electrolytes in EG–FA mixture at appropriate temperatures.

Table 2 The experimental ($\Delta_{\text{sol}}H^m/\text{kJ mol}^{-1}$) and standard ($\Delta_{\text{sol}}H^0/\text{kJ mol}^{-1}$) enthalpies of solution of Hex₄NBr in mixtures of ethylene glycol with formamide and the appropriate Debye–Hückel limiting law slope ($A_H/\text{kJ kg}^{1/2} \text{mol}^{-3/2}$) at 298.15 and 313.15 K

<i>m</i> /mol kg ⁻¹ 298.15 K	$\Delta_{\text{sol}}H^m$	<i>m</i> /mol kg ⁻¹ 313.15 K	$\Delta_{\text{sol}}H^m$
$X_{\text{FA}} = 0.000$ m.f., $A_H = 9.843$		$X_{\text{FA}} = 0.000$ m.f., $A_H = 11.681$	
$\Delta_{\text{sol}}H^0 = 21.64 \pm 0.01$ [10]		$\Delta_{\text{sol}}H^0 = 23.10 \pm 0.07$ [10]	
$X_{\text{FA}} = 0.054$ m.f., $A_H = 8.954$			
0.0066	21.14	$X_{\text{FA}} = 0.114$ m.f., $A_H = 9.648$	
0.0139	21.29	0.0022	21.68
$\Delta_{\text{sol}}H^0 = 20.57 \pm 0.08$		0.0039	21.78
$X_{\text{FA}} = 0.104$ m.f., $A_H = 8.158$		$\Delta_{\text{sol}}H^0 = 21.29 \pm 0.05$	
0.0057	19.98		
0.0104	20.05	$X_{\text{FA}} = 0.252$ m.f., $A_H = 7.443$	
$\Delta_{\text{sol}}H^0 = 19.54 \pm 0.04$		0.0025	19.73
$X_{\text{FA}} = 0.139$ m.f., $A_H = 7.633$		0.0041	19.81
0.0062	19.43	$\Delta_{\text{sol}}H^0 = 19.39 \pm 0.04$	
0.0117	19.45		
$\Delta_{\text{sol}}H^0 = 19.06 \pm 0.01$		$X_{\text{FA}} = 0.404$ m.f., $A_H = 5.347$	
$X_{\text{FA}} = 0.208$ m.f., $A_H = 6.645$		0.0024	17.83
0.0059	18.21	0.0041	17.93
0.0116	18.33	$\Delta_{\text{sol}}H^0 = 17.53 \pm 0.05$	
$\Delta_{\text{sol}}H^0 = 17.79 \pm 0.06$			
$X_{\text{FA}} = 0.251$ m.f., $A_H = 6.061$		$X_{\text{FA}} = 0.508$ m.f., $A_H = 4.114$	
0.0064	17.66	0.0021	16.51
0.0118	17.78	0.0042	16.54
$\Delta_{\text{sol}}H^0 = 17.34 \pm 0.06$		$\Delta_{\text{sol}}H^0 = 16.17 \pm 0.02$	
$X_{\text{FA}} = 0.350$ m.f., $A_H = 4.814$			
0.0053	15.98	$X_{\text{FA}} = 0.664$ m.f., $A_H = 2.580$	
0.0113	16.21	0.0022	14.40
$\Delta_{\text{sol}}H^0 = 15.44 \pm 0.12$		0.0038	14.59
$X_{\text{FA}} = 0.512$ m.f., $A_H = 3.085$		$\Delta_{\text{sol}}H^0 = 14.08 \pm 0.10$	
0.0021	13.03		
0.0039	13.22	$X_{\text{FA}} = 0.742$ m.f., $A_H = 1.958$	
$\Delta_{\text{sol}}H^0 = 12.72 \pm 0.11$		0.0027	13.49
$X_{\text{FA}} = 0.643$ m.f., $A_H = 1.965$		0.0042	13.52
0.0063	11.34	$\Delta_{\text{sol}}H^0 = 13.38 \pm 0.02$	
0.0110	11.52		
$\Delta_{\text{sol}}H^0 = 11.01 \pm 0.09$		$X_{\text{FA}} = 0.901$ m.f., $A_H = 0.964$	
$X_{\text{FA}} = 0.751$ m.f., $A_H = 1.225$		0.0023	12.48
0.0021	10.36	0.0039	12.52
0.0039	10.56	$\Delta_{\text{sol}}H^0 = 12.40 \pm 0.02$	
$\Delta_{\text{sol}}H^0 = 10.11 \pm 0.10$			
$X_{\text{FA}} = 0.906$ m.f., $A_H = 0.460$		$X_{\text{FA}} = 1.000$ m.f., $A_H = 0.541$	
0.0052	9.36	$\Delta_{\text{sol}}H^0 = 8.94 \pm 0.02$ [10]	
0.0103	9.45		
$\Delta_{\text{sol}}H^0 = 9.25 \pm 0.05$			
$X_{\text{FA}} = 1.000$ m.f., $A_H = 0.165$			
$\Delta_{\text{sol}}H^0 = 8.94 \pm 0.02$ [10]			

Discussion

The standard enthalpies have been used to obtain the enthalpic pair interaction coefficients h_{xy} for interaction between TAA salt and co-solvent of EG–FA mixture in dilute solutions of mixed solvent according to the modified McMillan–Mayer model [5]. The calculation of the enthalpy parameters of pair interaction has been carried out as well as in our studies [11, 15]. All enthalpies have proved to be smooth functions of the mole fraction of one of the solvent components. For a certain combination of solute x and co-solvent y , we subjected the enthalpies of solution at low of X_y to a least-squares analysis with regard to the equation:

$$\Delta_{\text{sol}}H^0(x \text{ in } S + y) = \Delta_{\text{sol}}H^0(x \text{ in } S) + bX_y + cX_y^2 \quad (5)$$

where X_y is a co-solvent mole fraction.

The adjustable parameter b in this equation is related to the limiting slope. The enthalpic pair interaction coefficient may be written as [8]:

$$h_{xy} = \frac{1}{2}M_S b \quad (6)$$

where M_S is the molar mass of the solvent.

The calculated (Eqs. 5 and 6) enthalpy parameters of pair interactions of TAA salts with FA in EG (h_{13}) and with EG in FA (h_{23}) listed in Table 3. The h_{13} and h_{23} values for Bu_4NBr at 298.15 K have been taken from [3] and calculated using the solution enthalpies data from [4] at 313.15 K. As seen from the Table 3 the h_{13} values are negative. It indicates that the pairwise interaction of TAA salts with FA in EG is enthalpically attractive in a thermochemical sense [16]. The increasing of the cation size induces the decrease of the h_{13} parameters which become more negative. The parameters become less negative with enhancing temperature, excluding Et_4NBr . The values of h_{23} parameters are positive and decrease with the rise of cation size and show the linear dependences on n_C :

$$298.15 \text{ K} : h_{23} = (356 \pm 21) - (11.2 \pm 1.2)n_C, \quad (7)$$

$$R = 0.994, \quad \text{sd} = 14 \text{ J kg mol}^{-2}$$

$$313.15 \text{ K} : h_{23} = (341 \pm 16) - (9.4 \pm 0.9)n_C, \quad (8)$$

$$R = 0.996, \quad \text{sd} = 10 \text{ J kg mol}^{-2}.$$

The h_{23} values increase weakly (see Table 3) with growth of the temperature excluding Et_4NBr .

The heat capacity parameters of pair interactions of TAA salts with FA in EG (c_{p13}) and with EG in FA (c_{p23}) have been computed as in [2] by Eq. 9 and also presented in Table 3.

$$c_{pi3} = (h_{i3}(313.15 \text{ K}) - h_{i3}(298.15 \text{ K}))/15 \quad (9)$$

where $i = 1$ or 2 .

The values of c_{p13} parameter of TAA salts–FA interaction in EG are positive. They increase approximately linearly with the increasing n_C :

$$c_{p13} = (-6.0 \pm 1.9) + (0.69 \pm 0.11)n_C, \quad (10)$$

$$R = 0.991, \quad \text{sd} = 1.2 \text{ J kg K}^{-1} \text{ mol}^{-2}.$$

The heat capacity parameters, c_{p23} , are closed to zero in the limit of uncertainty (Table 3). The TAA bromides–EG interaction is enthalpically repulsive.

The values of parameters discussed relate to electrolyte as a sum of contributions of cation and anion interactions in infinite dilute solution. For enthalpy coefficients it can be written as:

$$h_{23}(\text{EG} - \text{R}_4\text{NBr}) = h_{23}(\text{EG} - \text{R}_4\text{N}^+) + h_{23}(\text{EG} - \text{Br}^-). \quad (11)$$

It is obviously important to estimate the contributions of single ions to the parameters of pair interaction. According to the articles [7, 17, 18], we assume that the contribution of each methyl group is equivalent to one and a half contributions of the methylene group. The contributions of ($>\text{CH}_2$) group to the h_{23} value of TAA salts interaction with EG in FA medium equal $-11.2 \text{ J kg mol}^{-2}$ (Eq. 7) and $-9.4 \text{ J kg mol}^{-2}$ (Eq. 8) at 298.15 and 313.15 K, respectively. We can admit that the nitrogen atom in R_4N^+ cation does not yield the contribution to interaction of the large organic cation with solvent. A charge of nitrogen atom in cation R_4N^+ is screened by alkyl groups [19, 20].

Table 3 Enthalpy (h_{13} and $h_{23}/\text{J kg mol}^{-2}$) and heat capacity (c_{p13} and $c_{p23}/\text{J kg K}^{-1} \text{ mol}^{-2}$) parameters of pair interactions in FA (1)–EG (2)–TAA bromide (3) systems

Salt	h_{13}		h_{23}		c_{p13}	c_{p23}
	298.15 K	313.15 K	298.15 K	313.15 K		
Et_4NBr	-213 ± 5	-225 ± 10	272 ± 4	270 ± 8	-1 ± 1	0 ± 1
Bu_4NBr	-481 ± 12 [3]	-387 ± 16^a	166 ± 13 [3]	182 ± 13^a	6 ± 2	1 ± 2
Hex_4NBr	-542 ± 9	-398 ± 46	93 ± 29	119 ± 32	10 ± 4	2 ± 4

^a Calculated from the $\Delta_{\text{sol}}H^0$ values given elsewhere [4]

$$h_{23}(\text{EG} - (\text{C}_n\text{H}_{2n+1})_4\text{N}^+) = h_{23}(\text{EG} - (4n + 2)(\text{CH}_2)). \quad (12)$$

Accounting the Eq. 12 the dependence of the enthalpic and heat capacity of pair interactions on the number of CH₂ groups has been described by the Eqs. 13–15:

$$298.15 \text{ K} : h_{23} = (378 \pm 21) - (11.2 \pm 1.2)n_{\text{CH}_2}, \quad (13)$$

$$R = 0.994, \quad \text{sd} = 14 \text{ J kg mol}^{-2}$$

$$313.15 \text{ K} : h_{23} = (360 \pm 16) - (9.4 \pm 0.9)n_{\text{CH}_2}, \quad (14)$$

$$R = 0.996, \quad \text{sd} = 10 \text{ J kg mol}^{-2}$$

$$c_{p13} = (-7.4 \pm 1.9) + (0.69 \pm 0.11)n_{\text{CH}_2}, \quad (15)$$

$$R = 0.991, \quad \text{sd} = 1.2 \text{ J kg K}^{-1} \text{ mol}^{-2}.$$

On the base of the assumptions formulated above and Eqs. 11 and 12, we have obtained the parameters of pair interactions of single ions with EG in FA medium which are presented in Table 4.

We have added to the data for FA-EG-R₄NBr systems the values for the other systems containing formamide. In the article [21] at 298.15 K the enthalpic coefficients of pair interactions of Et₄NBr and Bu₄NBr in FA-H₂O-R₄NBr were obtained and equal -134 ± 3 and $-135 \text{ J kg mol}^{-2}$, accordingly. We have taken the data for Et₄NBr [2] at 298.15 and 313.15 K and Bu₄NBr [3] at 298.15 K in FA-H₂O and FA-MeOH mixtures and unpublished results for Bu₄NBr in FA-H₂O at 313.15 K for determination of the h_{23} values of R₄N⁺ and Br⁻, which for these systems are also listed in Table 4. Procedure of calculation of h_{23} for FA-H₂O-R₄NBr and FA-MeOH-R₄NBr systems is similar to the one for FA-EG-R₄NBr systems. The h_{23} parameters of interaction of Hex₄N⁺ with H₂O and MeOH in FA medium has been obtained by extrapolation assuming that the dependences $h_{23} = f(n_C)$ are linear for these systems.

Table 4 The enthalpy ($h_{23}/\text{J kg mol}^{-2}$) parameters of pair interactions of single ions (3) with co-solvents (2) in formamide

T (K)	Et ₄ N ⁺	Bu ₄ N ⁺	Hex ₄ N ⁺	Br ⁻
Water				
298.15	18	32	46 ^a	-147
313.15	86	155	224 ^a	-155
Ethylene glycol				
298.15	-112	-202	-291	378
313.15	-94	-169	-244	360
Methanol				
298.15	-263	-473	-683 ^a	385
313.15	-385	-693	-1001 ^a	536

^a Obtained by extrapolation

It is seen from the Table 4 that the interaction of organic cations with EG and MeOH in FA medium is enthalpically favorable ($h_{23} < 0$) whereas in water the h_{23} values are positive. The attraction strengthens with growth of the organic cation size. In the formamide medium the organic cation interacts more strongly with methanol than with ethylene glycol.

Let's discuss the feature of interaction of bromide-ion with co-solvents in FA (Table 4). It is repulsive with MeOH and EG. The h_{23} parameters slightly differ by the value in these cases. Bromide-ion is more strongly solvated by formamide than MeOH or EG. On the contrary, the interaction of anion with water is attractive in the formamide medium. Anion is more strongly solvated by co-solvent–water than the basic solvent–formamide.

Summarizing the data from Table 4 for cation and anion we have obtained the parameters of pair interaction, h_{23} , of Bu₄NBr with MeOH and EG in formamide system which are equal 83 and 176 J kg mol⁻², respectively. Using the data [22] we have also calculated the interaction parameters of Bu₄NBr with MeOH and EG in an aqueous solution which are equal $3,721 \pm 279$ and $3,865 \pm 627 \text{ J kg mol}^{-2}$, respectively. These values coincide in the limit of uncertainties. It is interesting to note that in aqueous medium $h_{23}(\text{MeOH–BuOH}) = 586 \text{ J kg mol}^{-2}$ and $h_{23}(\text{EG–BuOH}) = 643 \pm 27 \text{ J kg mol}^{-2}$ [23] are also closed.

The mean heat capacities of solution, ΔC_p^0 , at 298–313 K temperature interval have been obtained from the enthalpies of solution by the Eq. 16:

$$\Delta C_p^0 = (\Delta_{\text{sol}}H^0(313.15 \text{ K}) - \Delta_{\text{sol}}H^0(298.15 \text{ K}))/15. \quad (16)$$

The ΔC_p^0 values of Bu₄NBr in formamide–ethylene glycol mixture in the investigated temperature interval have been calculated using the data of solution enthalpies [4]. The $\Delta_{\text{sol}}H^0 = f(X_{\text{FA}})$ dependences have been approximated by polynomials of the conforming power. The obtained values of ΔC_p^0 have been used for determination the heat capacities of transfer from ethylene glycol to ethylene glycol–formamide mixtures by:

$$\Delta_{\text{tr}}C_p^0 = \Delta C_p^0(\text{EG} + \text{FA}) - \Delta C_p^0(\text{EG}). \quad (17)$$

The $\Delta_{\text{tr}}C_p^0$ values for salts investigated are presented in Fig. 1. The heat capacities of transfer are negative for Et₄NBr and positive for Bu₄NBr and Hex₄NBr. The $\Delta_{\text{tr}}C_p^0$ values become more positive from Bu₄NBr to Hex₄NBr and have endothermic maxima at $X_{\text{FA}} \approx 0.7$ – 0.75 m.f.

It is interesting to consider a deviation from additivity of the values $\Delta_{\text{sol}}H^0$ of TAA salts in mixture formamide with ethylene glycol at two temperatures with the increasing of cation size. The $\Delta_{\text{sol}}H^E$ values are computed by Redlich–Kister type Eq. 18 and shown graphically in Fig. 2:

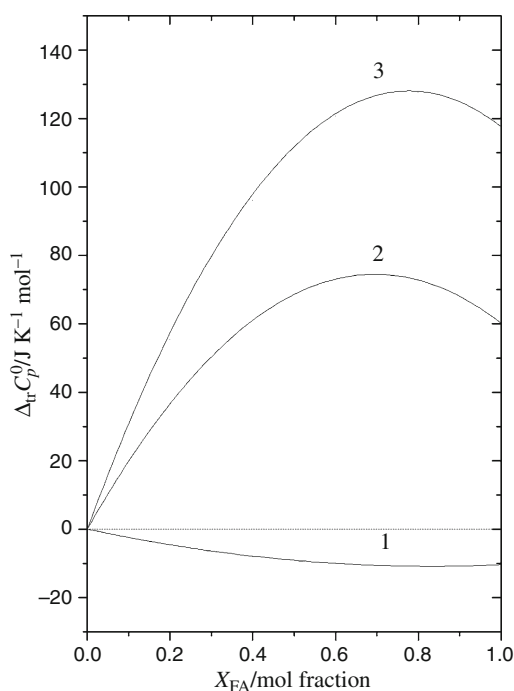


Fig. 1 The heat capacities of transfer of Et₄NBr (1), Bu₄NBr (2) and Hex₄NBr (3) from ethylene glycol to its mixtures with formamide. X_{FA} is the mole fraction of formamide. Lines are the description by the Redlich–Kister type equation

$$\Delta_{\text{sol}}H^E = X_{\text{EG}}X_{\text{FA}}(a + b \cdot X_{\text{FA}}) \quad (18)$$

where X_{EG} and X_{FA} are the mole fraction of ethylene glycol and formamide, respectively, a and b are the empirical coefficients. The excess enthalpies of solution are positive (endothermic) for Et₄NBr and negative (exothermic) for Bu₄NBr [4] and Hex₄NBr over the entire range of formamide composition at both temperatures. The temperature increase induces the decrease of the $\Delta_{\text{sol}}H^E$ values from Et₄NBr to Hex₄NBr (Fig. 2).

In order to gain information on ion–solvent interactions in binary mixtures and to examine the effect of the presence of a co-solvent it was interesting to collect the experimental data of the solution enthalpies of one of the TAA salt in both aqueous and non-aqueous binaries. Tetra-*n*-butylammonium bromide is the most investigated solute in this sense. De Visser and Somsen [1] in the article reported the enthalpies of solution of Bu₄NBr in some amide–water and amide–amide mixtures. We have added to this data the own ones [3] and early obtained in our laboratory [22]. For the sake of convenience of comparing we consider the excess enthalpy of solution. This characteristic has been defined by:

$$\Delta_{\text{sol}}H^E = \Delta_{\text{sol}}H^0 - X_1 \Delta_{\text{sol}}H_1^0 - X_2 \Delta_{\text{sol}}H_2^0. \quad (19)$$

The dependences of $\Delta_{\text{sol}}H^E(X)$ of Bu₄NBr in the different mixtures are shown in the Fig. 3. In the aqueous systems,

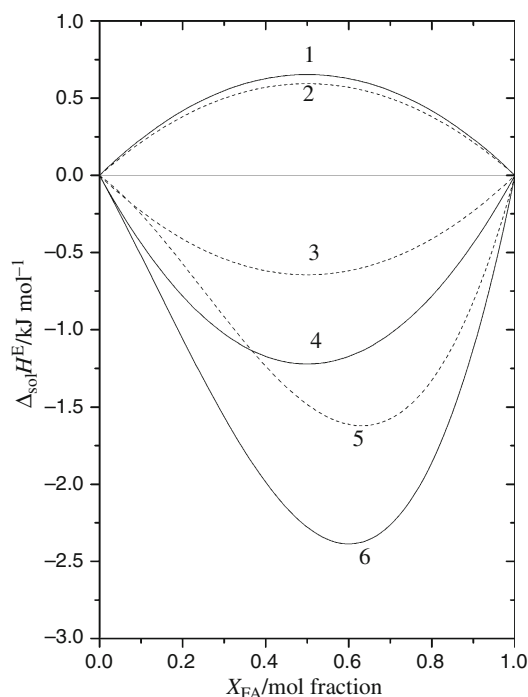


Fig. 2 The excess enthalpies of solution of Et₄NBr (1, 2), Bu₄NBr (3, 4) and Hex₄NBr (5, 6) in mixture of formamide with ethylene glycol. (1, 4, 6)—298.15 K, (2, 3, 5)—313.15 K. X_{FA} is the mole fraction of formamide. Lines are the description by the Redlich–Kister type equation

the curves of $\Delta_{\text{sol}}H^E(X)$ do display the endothermic maxima in the aqueous region of mixtures at $X_{\text{H}_2\text{O}} \approx 0.7$ – 0.75 m.f. The maximum height in a given binaries strongly depends primarily on the nature of non-aqueous co-solvent. The similar $\Delta_{\text{sol}}H^E$ composition profiles rather suggest that they are determined by one and the same effect. According the approach proposed in the articles of Somsen and co-authors [1, 24–26] the $\Delta_{\text{sol}}H^E$ value is connected with the enthalpic effect of hydrophobic hydration of solutes containing non-polar groups. For aqueous DMF the maxima of the values of number properties [27–30] has been found at $X_{\text{DMF}} \approx 0.25$ – 0.33 m.f. and interpreted by the existence of molecular complexes DMF·2H₂O and DMF·3H₂O. The authors [1] do also not exclude the possibility of formation of the DMF·3H₂O molecular complex.

The $\Delta_{\text{sol}}H^E(X)$ in non-aqueous DMF–FA binary has a maximum also as in DMF–H₂O ones. Since this result can hardly be interpreted as due to structural effects it may be the result of a complex formation between formamide and *N,N*-dimethylformamide [1].

In the non-aqueous systems MeOH–FA, NMF–FA, and EG–FA the excess enthalpies of solution of Bu₄NBr are closed to zero for the whole composition range. It is possible to assume that the structure of the solvent mixtures

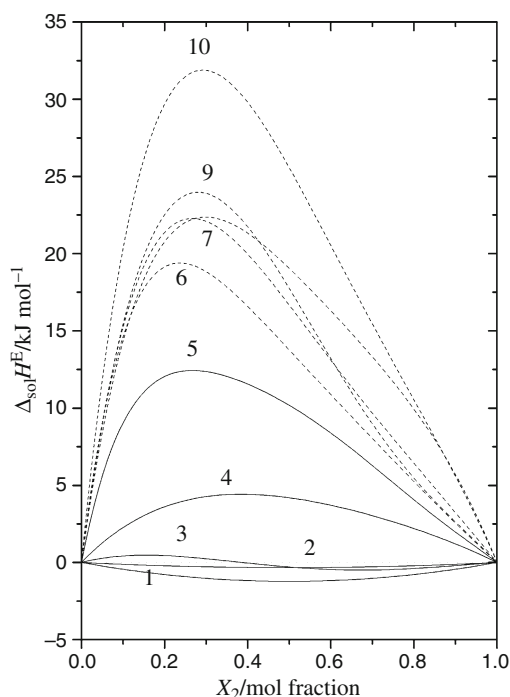


Fig. 3 The excess enthalpies of solution of Bu₄NBr in mixtures of formamide (first component) with ethylene glycol (1), *N*-methylformamide (2), methanol (3), *N,N*-dimethylformamide (4), water (5) or in mixtures of water (first component) with *N*-methylformamide (6), glycerol (7), ethylene glycol (8), methanol (9) and *N,N*-dimethylformamide (10) at 298.15 K. X_2 is the mole fraction of the second component

changes gradually and excludes the formation of complexes or associates. In addition it suggests that preferential solvation of Bu₄NBr in these mixtures is absent [1, 31].

Conclusions

The results obtained show that the pair interaction of TAA bromides with FA in EG is enthalpically attractive. The increase of the cation size induces decreasing the h_{13} values which become more negative. The parameters become less negative with increasing the temperature, i.e., the c_{p13} values of the heat capacity parameter of R₄NBr–FA interaction in EG are positive. The values of h_{23} parameters of interaction with EG in FA are positive, decrease with the rise of cation size and depend linearly on the carbon atoms number. The h_{23} values increase weakly with growth of the temperature, indicating that the c_{p23} values are closed to zero.

The enthalpy contributions of single ions R₄N⁺ and Br[−] to the parameters of pair interaction indicates that the interaction of organic cations with EG and MeOH in FA medium is enthalpically favorable ($h_{23} < 0$) whereas in water the h_{23} values are positive. The attraction strengthens

with growth of the R₄N⁺ size. In the formamide medium the organic cation interacts more strongly with methanol than with ethylene glycol. The interaction of Br[−] with MeOH and EG in FA is energetically unfavorable.

The mean heat capacities of solution, ΔC_p^0 , of TAA salts in EG–FA mixture at 298–313 K temperature interval have been obtained from the enthalpies of solution. The heat capacities of transfer for R₄NBr investigated have been calculated. It has been shown that the $\Delta_{tr}C_p^0$ values are negative for Et₄NBr and positive for Bu₄NBr and Hex₄NBr and have endothermic maxima at $X_{FA} \approx 0.7$ – 0.75 m.f.

The excess enthalpies of solution, $\Delta_{sol}H^E$, are positive (endothermic) for Et₄NBr and negative (exothermic) for Bu₄NBr and Hex₄NBr. The $\Delta_{sol}H^E$ values become more negative from Bu₄NBr to Hex₄NBr. The temperature increase induces the decrease of the $\Delta_{sol}H^E$ values from Et₄NBr to Hex₄NBr.

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References

- De Visser C, Somsen G. Enthalpies of solution of tetra-*n*-butylammonium bromide in binary mixtures of water, formamide, *N*-methylformamide, and *N,N*-dimethylformamide. *J Solut Chem.* 1974;3:847–55.
- Kustov AV, Smirnova NL, Antonova OA, Korolev VP. Thermodynamic characteristics of solution and interparticle interactions in water–formamide–Et₄NBr and methanol–formamide–Et₄NBr systems. *Russ J Phys Chem.* 2008;82:1549–54.
- Korolev VP, Smirnova NL, Antonova OA, Kustov AV. Heat properties of Bu₄NBr solutions in binary mixtures based on formamide. *Russ J Gen Chem.* 2008;78:2013–8.
- Korolev VP, Antonova OA, Smirnova NL, Kustov AV. Thermochemistry of Bu₄NBr solutions in binary solvents containing formamide. *J Therm Anal Calorim.* 2009;96:903–10. doi:10.1007/s10973-009-0047-y.
- McMillan WG, Mayer JE. The statistical thermodynamics of multicomponent systems. *J Chem Phys.* 1945;13:276–305.
- Desnoyers JE, Perron G, Avédikian L, Morel JP. Enthalpies of the urea-*tert*-butanol-water system at 25 °C. *J Solut Chem.* 1976;5:631–44.
- Savage JJ, Wood RH. Enthalpy of dilution of aqueous mixtures of amides, sugars, urea, ethylene glycol, and pentaerythritol at 25 °C: enthalpy of interaction of the hydrocarbon, amide, and hydroxyl functional groups in dilute aqueous solutions. *J Solut Chem.* 1976;5:733–50.
- Heuvelsland WJM, de Visser C, Somsen G. Enthalpic pair-interaction coefficients between electrolytes and non-electrolytes in water and *N,N*-dimethylformamide. *J Chem Soc Faraday Trans 1.* 1981;77:1191–9.
- Belousov VP, Shutin SG. Kalorimetriya smesheniya (calorimetry of mixing). In: Krestov GA, editor. *Eksperimental'nye metody khimii rastvorov (experimental methods of solution chemistry): spektroskopiya i kalorimetriya (spectroscopy and calorimetry)*. Moscow Nauka;1995. pp. 287–339.
- Korolev VP, Antonova OA, Smirnova NL, Kustov AV. Thermal properties of tetraalkylammonium bromides in several solvents. *J Therm Anal Calorim.* 2010. doi:10.1007/s10973-009-0639-6.

11. Kustov AV, Korolev VP. Temperature and length scale dependence of tetraalkylammonium ion–amide interaction. *J Phys Chem B*. 2008;112:2040–4.
12. Kustov AV, Emel'yanov AA, Syschenko AF, Krest'yaninov MA, Zheleznyak NI, Korolev VP. Calorimetric apparatus for measurement of thermal effects of processes in solutions. *Russ J Phys Chem*. 2006;80:1532–6.
13. Chen T, Hefter G, Buchner R, Senanayake G. Molar volumes and heat capacities of electrolytes and ions in nonaqueous solvents: 1. Formamide. *J Solut Chem*. 1998;27:1067–95.
14. Pitzer KS. Activity coefficient in electrolyte solutions. 2nd ed. Boca Raton, FL: CRC Press; 1991.
15. Kustov AV, Bekeneva AV, Antonova OA, Korolev VP. Enthalpic pair–interaction coefficients of benzene, aniline and nitrobenzene with N,N-dimethylformamide and acetonitrile in water at 298.15 K. *Thermochim Acta*. 2003;398:9–14.
16. Fernández J, García-Lisbona MN, Lilley TH, Linsdell H. Enthalpy of interaction of some amides with ammonium methanoate in water at 25 °C. Interactions between ionic group and peptide and hydrophobic groups. *J Chem Soc Faraday Trans*. 1997;93:407–11.
17. Palecz B. The enthalpies of interaction of glycine with some alkan-1-ols in aqueous solutions at 298.15 K. *Fluid Phase Equilib*. 1996;126:299–303.
18. Korolev VP, Kustov AV. Temperature dependence of the pair interaction between hydrophobic and hydrophilic solutes: a calorimetric study. *Thermochim Acta*. 2005;437:190–5.
19. Krestov GA, Korolev VP, Vandyshev VN. Enthalpies of solvation of ions and donor–acceptor ability of atom-molecular particles in solution. *Dokl AN SSSR*. 1988;302:132–4.
20. Korolev VP, Serebryakova AL, Krestov GA. Enthalpic characteristics of individual ions in mixed solvent acetonitrile–methanol at 298.15 K. *Zh Obsch Khim*. 1991;61:2129–35.
21. Kustov AV, Manin NG, Korolev VP. Enthalpies of solution of tetraethyl- and tetrabutylammonium bromides in water–formamide system. *Zh Fiz Khim*. 2003;77:2170–4.
22. Manin NG, Korolev VP, Krestov GA. Termokhimiya solvatatsii ionov v vodno-spirovnykh rastvoritelyakh pri 298.15 K (thermochemistry of solvation of ions in water–alcohol solvents at 298.15 K). *Zh Khim Termodin Termokhim (J Chem Thermodyn Thermochem) RAS. Inst Non-aqueous Solut Chem*. 1992;1:27–54.
23. Korolev VP. Parameters of the interaction between components; structural and hydrophobic effects in systems water–ethylene glycol–n-butyl alcohol and water–ethanol–xenon at 248–348 K. *J Struct Chem*. 2006;47:699–710.
24. De Visser C, Somsen G. Hydrophobic interactions in mixtures of N,N-dimethylformamide and water. Model calculations and enthalpies of solution. *J Phys Chem*. 1974;78:1719–22.
25. Heuvelsland WJM, de Visser C, Somsen G, LoSurdo A, Wen W-Y. Hydrophobic hydration of some different types of quaternary ammonium bromides in mixtures of water and N,N-dimethylformamide. *J Solut Chem*. 1979;8:25–34.
26. Rouw AC, Somsen G. The solvation of some alcohols in binary solvents: enthalpies of solution and enthalpies of transfer. *J Chem Thermodyn*. 1981;13:67–76.
27. Della Volpe C, Guarino G, Sarlorio K, Vitagliano V. Diffusion, viscosity, and refractivity data on the system dimethylformamide–water at 20 and 40 degree C. *J Chem Eng Data*. 1986;31:37–40.
28. Kawaizimi F, Ohno M, Miyahara Y. Ultrasonic and volumetric investigation of aqueous solutions of amides. *Bull Chem Soc Jpn*. 1977;50:2229–33.
29. Manohara MN, Sivakumar KV, Rajagopal E, Subrahmanyam SV. Excess thermodynamic functions of the systems water + N-methyl formamide and water + N,N-dimethyl formamide. *Acustica*. 1981;48:341–5.
30. Singh D, Bahadur L, Ramanamurthi MV. Conductance studies in amide–water mixtures. II. Sodium salts in N,N-dimethylformamide–water mixtures at 35 °C. *J Solut Chem*. 1977;6:703–15.
31. Korolev VP. Preferential solvation of non-electrolytes in mixed solvents. *Zh Obsch Khim*. 2000;70:1976–84.