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Thermochemistry of Bu_4NBr solutions in binary solvents containing formamide

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Abstract The heats of solution of tetrabutylammonium bromide have been measured in mixtures of formamide (FA) with methanol (MeOH) and ethylene glycol (EG) at 313.15 K by calorimetric method. The standard enthalpies of solution in binary mixtures have been extrapolated to infinite dilution by Redlich–Rosenfeld–Meyer type equation using the literary data at 298.15 K and the present paper data at 313.15 K. The Debye–Hückel limiting law slope A_H required for calculation of the $\Delta_{sol}H^0$ value has been obtained with application the new additive scheme of determination of the physic-chemical characteristics of binaries. The scheme is tested on the example of Bu_4NBr solutions in FA–MeOH mixture at 298.15 K. Its application yields the $\Delta_{sol}H^0$ value very closed on the ones determined with the real (non-additive) characteristics of binaries. The standard enthalpies of solution extrapolated by Redlich–Rosenfeld–Meyer type equation are in a good agreement with the ones computed in terms of the Debye–Hückel theory in the second approximation. The heat capacities characteristics of Bu_4NBr have been calculated in H_2O–FA, MeOH–FA and EG–FA mixtures using the literary and present data. The sequence of solvents $H_2O > FA > EG > MeOH$ located on their ability to solvophobic solvation found by us earlier for enthalpic characteristics is confirmed by the $\Delta C_p{}^0$ values. The comparison of thermochemical characteristics of Bu_4NBr solutions in aqueous and non-aqueous mixtures containing FA has been carried out. The own structure of water remains in the region of small additions of formamide to co-solvents. It considerably differs the H_2O–FA mixture from the investigated non-aqueous systems.

Keywords Binary solvent · Enthalpy of solution · Enthalpy of transfer · Ethylene glycol · Formamide · Heat capacity of solution · Methanol · Tetrabutylammonium bromide

Introduction

The binary solvents containing FA have been of wide interest to solution chemists during recent years. Mixtures of FA with water and alcohols including MeOH are intensively studied by various methods [1–11]. In spite of the fact that methanol and water differ strongly in the structure and properties in a liquid state their mixtures with FA have unique similar thermal features. So, the heats of mixing of components have not only the same sign for mixtures of methanol–FA and water–FA but also closed values equal for equimolar composition of given mixtures 0.28 [8] and 0.27 [11] kJ mol^{-1}, accordingly, at 298.15 K. Contrary to it the value of H^E of the ethylene glycol–formamide system is closed to zero (-0.03 kJ mol^{-1} [12]). The standard heat of solution of FA in methanol 2.22 kJ mol^{-1} (our calculation by Eq. 1 from [8]) only a little differs from the heat of solution of FA in water 2.03 [13], 1.97 [14] kJ mol^{-1} whereas the enthalpy of solution of FA in ethylene glycol is equal to -0.13 kJ mol^{-1} [15] at 298.15 K. The standard heat of solution of methanol in FA 1.02 (calculation by Eq. 1 from [8]), 0.84 [16] kJ mol^{-1} not much differs from the heat of solution of water in FA 1.18 [17], 1.17 [18] kJ mol^{-1}.

Excess volumes of mixtures of FA with methanol and water are negative, i.e. mixtures occupy smaller volume than in ideal state. But the methanol–formamide system is

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considerably more deviated from ideal behaviour on magnitude of excess volume than the water–formamide system. So, the excess volume equals -0.55 sm^3 mol^{-1} [3, 6] for equimolar composition in the first case, in the second one $V^E = -0.13$ sm^3 mol^{-1} (our calculation from the data [10]) at 298.15 K. It is interesting to note the excess volume of ethylene glycol–formamide mixture has an opposite sign and equals 0.06 sm^3 mol^{-1} for equimolar composition according to our calculation from the data [9]. Thus, within a given criteria these mixtures can be ranged by the degree of non-ideality: methanol–FA > water–FA > ethylene glycol–FA.

De Visser and Somsen in [19] have studied Bu_4NBr in the series of amides at 278.15–328.15 K by a calorimetric method. Then they [20] have investigated the solutions of Bu_4NBr in binary mixtures containing water, FA, *N*-methylformamide and DMFA at 298.15 K.

The authors of work [21] have studied the solutions of TAA salts in mixtures FA and HMPT with water at 298.15 or 328.15 K by a calorimetric method. This paper has been limited on an interval of compositions ($X \leq 0.125$ m.f. of amide).

We [22] have reported the enthalpy characteristics of Et_4NBr and Bu_4NBr in MeOH, FA and EG at 298.15 and 313.15 K. Then we [23] have added the data of the solution enthalpies of Hex_4NBr in the same solvents at the same temperatures.

The solutions of Et_4NBr in mixtures water–FA and MeOH–FA have been studied in [24] at 298.15 and 313.15 K.

The thermal characteristics of solutions Bu_4NBr in binary mixtures MeOH–FA and EG–FA in all intervals of mixed solvent have been investigated in [12]. Measurements were limited to one temperature (298.15 K).

Therefore in continuation of previous thermochemical studies it was of interest to receive new thermochemical characteristics of tetrabutylammonium bromide solutions in all intervals of compositions of methanol–formamide and ethylene glycol–formamide mixtures at several temperatures and compare the thermal properties of these mixtures with available data in the literature. Also the aim of this work was the obtaining of the standard enthalpies of solution of Bu_4NBr in binary mixtures and the comparison with the data received by the different methods of extrapolation.

Experimental

Materials

Tetrabutylammonium bromide (Merck) was dried under reduced pressure at 343.15 K for 72 h and used without further purification. Formamide «Reachem (pure)» was frozen, dried with molecular sieves 3 Å and twice distillated under reduced pressure at 348.15 K. Fisher titration indicated the presence of 0.04 mass% water in formamide. Methanol «HPLC grade Fisher Scientific 99.99%» and ethylene glycol «Sigma–Aldrich spectrophotometric grade 99+%» with water content <0.01% were used without further purification.

Solution calorimetry

The enthalpies of solution have been measured on an automated isoperibol calorimeter provided with a 60-sm^3 titanum vessel. The construction of a calorimeter and test of its work were considered in detail earlier [23, 25]. A comparative method has been used for the measurement of heat effects. The calibration of the system by an electric current was carried out before each experiment. Mixtures have been prepared by weighing the liquids in ground stoppered bottles taking due precautions to minimize the evaporation losses for slightly volatile MeOH and to penetrate the moisture for hygroscopic EG and FA. All the weighing was performed by means of an electronic analytical balance (OKB Vesta) with accuracy 1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2\ 10^{-4}$.

Results

The integral enthalpies of solution $\Delta_{sol}H^m$ of Bu_4NBr in mixed solvents in methanol–formamide and ethylene glycol–formamide mixed solvents at 313.15 K are listed in Table 1.

The dependence of the integral enthalpies of solution of electrolyte on concentration in any solvent can be represented by Redlich–Rosenfeld–Meyer type equation [26]:

$$\Delta_{sol}H^m = \Delta_{sol}H^0 + A_H m^{1/2} + B\,m \tag{1}$$

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.

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

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

The term A can be written as follows:

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

Table 1 The integral enthalpies of solution ($\Delta_{sol}H^m$/kJ mol^{-1}) of Bu_4NBr in mixtures of formamide with methanol and ethylene glycol and the appropriate Debye–Hückel limiting law slope (A_H/kJ kg$^{1/2}$ mol$^{-3/2}$) at 313.15 K

Methanol–formamide		Ethylene glycol–formamide	
m (mol kg^{-1})	$\Delta_{sol}H^m$	m (mol kg^{-1})	$\Delta_{sol}H^m$
$X_{FA} = 0.00000$ [22]		$X_{FA} = 0.00000$ [22]	
0.01088	18.44	0.00708	30.85
0.02388	18.61	0.01302	30.88
0.03128	18.80	0.01874	30.85
0.04168	18.95	0.02440	30.84
$X_{FA} = 0.04837$, $A_H = 13.021$		$X_{FA} = 0.01708$, $A_H = 11.475$	
0.01419	18.94	0.00607	30.61
0.02444	18.96	0.01221	30.75
0.03441	18.98		
$X_{FA} = 0.1061$, $A_H = 11.202$		$X_{FA} = 0.05942$, $A_H = 10.668$	
0.00806	19.22	0.00756	30.21
0.01643	19.31	0.01248	30.26
0.02442	19.29		
$X_{FA} = 0.2461$, $A_H = 7.658$		$X_{FA} = 0.08759$, $A_H = 10.150$	
0.01099	19.29	0.00485	29.82
0.01703	19.44	0.01168	29.90
0.02289	19.51	0.01648	29.94
0.02961	19.53		
$X_{FA} = 0.4255$, $A_H = 4.545$		$X_{FA} = 0.1387$, $A_H = 9.245$	
0.01098	19.30	0.00746	29.20
0.01741	19.33	0.01423	29.41
$X_{FA} = 0.6042$, $A_H = 2.584$		$X_{FA} = 0.1738$, $A_H = 8.651$	
0.00675	19.35	0.00943	28.88
0.01084	19.33	0.01683	28.92
		0.02326	28.87
		0.03036	28.72
$X_{FA} = 0.6223$, $A_H = 2.433$		$X_{FA} = 0.2595$, $A_H = 7.292$	
0.00593	19.35	0.00771	27.65
0.01073	19.37	0.01540	27.71
$X_{FA} = 0.7936$, $A_H = 1.323$		$X_{FA} = 0.5492$, $A_H = 3.638$	
0.00690	19.36	0.00506	24.15
0.01923	19.27	0.01020	24.20
0.02817	19.23		
$X_{FA} = 0.8933$, $A_H = 0.887$		$X_{FA} = 0.7534$, $A_H = 1.880$	
0.00831	19.43	0.00617	22.30
0.01722	19.45	0.01415	22.35
$X_{FA} = 1.00000$ [22]			
0.00820	20.25	0.02442	20.20
0.01629	20.22	0.03236	20.19

where ρ and ε are the density and the dielectric constant of pure or mixed solvent. Other symbols have their usual meanings [27].

Reliable calculation of the numerical values of A_H requires proper physicochemical data. The data for investigated binary mixtures necessary for calculation are limited. There are only data of the density for the formamide–methanol system at the different temperatures [6]. The data on the electric permittivity ε of studied mixtures is not found by us even at the one temperature. In such cases it is necessary to use those or other additive schemes.

The expression for molar volume of the mixture containing formamide and component S (MeOH, EG) is written as:

$$V = X_{FA} V_{FA} + X_S V_S + V^E \tag{4}$$

where X_{FA}, X_S is the mole fractions of FA and co-solvent, respectively, V_{FA}, V_S is their molar volumes, V^E is the excess volume of mixed solvent.

Density of mixture is calculated by Eq. 5:

$$\rho = \frac{X_{FA}M_{FA} + X_S M_S}{X_{FA}V_{FA} + X_S V_S + V^E} \tag{5}$$

where M_{FA}, M_S is the molar masses.

For ideal mixture the density can be written as:

$$\rho^{id} = \frac{X_{FA}M_{FA} + X_S M_S}{X_{FA}V_{FA} + X_S V_S} \tag{6}$$

Thermal expansibility coefficient of mixed solvent is calculated by the equation:

$$\alpha = -\frac{1}{\rho}\frac{\partial \rho}{\partial T} = \frac{1}{V}\frac{\partial V}{\partial T} = \frac{\alpha_{FA}X_{FA}V_{FA} + \alpha_S X_S V_S + \partial V^E/\partial T}{X_{FA}V_{FA} + X_S V_S + V^E} \tag{7}$$

The neglecting of the term $\partial V^E/\partial T$ brings the greatest uncertainty in the α value. The ignoring of the term V^E in the denominator is received:

$$\alpha = \varphi_{FA}\alpha_{FA} + \varphi_S\alpha_S + \frac{\partial V^E/\partial T}{X_{FA}V_{FA} + X_S V_S} \tag{8}$$

where φ_{FA}, φ_S is the volume fractions, determined by Eq. 9:

$$\varphi_{FA} = \frac{X_{FA}V_{FA}}{X_{FA}V_{FA} + X_S V_S}, \quad \varphi_S = \frac{X_S V_S}{X_{FA}V_{FA} + X_S V_S} \tag{9}$$

For an ideal mixture it is received:

$$\alpha^{id} = \varphi_{FA}\alpha_{FA} + \varphi_S\alpha_S \tag{10}$$

Because of the absence of the data of V^E and $\partial V^E/\partial T$ for EG–FA the values of α are calculated by the Eq. 10.

The values of electrical permittivity ε of mixtures are defined using the equation offered in the present work:

$$\ln\varepsilon = \varphi_{FA}\ln\varepsilon_{FA} + \varphi_S\ln\varepsilon_S \tag{11}$$

Differentiating expression (11) is received:

$$\frac{\partial \ln\varepsilon}{\partial T} = \varphi_{\mathrm{FA}}\frac{\partial \ln\varepsilon_{\mathrm{FA}}}{\partial T} + \varphi_S\frac{\partial \ln\varepsilon_S}{\partial T} + \varphi_{\mathrm{FA}}\varphi_S(\alpha_S - \alpha_{\mathrm{FA}})(\ln\varepsilon_S - \ln\varepsilon_{\mathrm{FA}}) \qquad (12)$$

The values A, A_{H} and also parameters required for their calculation for pure solvents at 298.15 and 313.15 K are listed in Table 2, taken from [23]. The values A_{H} for mixed solvents are listed in Table 1. The values A_{H} for the studied mixtures in all intervals of compositions of mixed solvent at 298.15 K are presented in Fig. 1.

The appropriate Debye–Hückel limiting law slope for mixture may be written as:

$$A_{\mathrm{H}} = X_{\mathrm{FA}}\,A_{\mathrm{H(FA)}} + X_S A_{\mathrm{H(S)}} + \Delta A_{\mathrm{H}} \qquad (13)$$

The value ΔA_{H} is the deviation from additivity. The values of ΔA_{H} for binary mixtures of FA with MeOH and EG were approximated by Redlich–Kister type equation, usually applicable for describing excess functions of binary mixtures:

$$\Delta A_{\mathrm{H}} = X_{\mathrm{FA}}\,X_S(a + b\,X_{FA}) \qquad (14)$$

where a and b are coefficients presented in Table 3.

The Eq. 13 can be used for calculation of the values of A_{H} of any uni-univalent electrolytes in the mixtures of FA with MeOH and EG at appropriate temperatures.

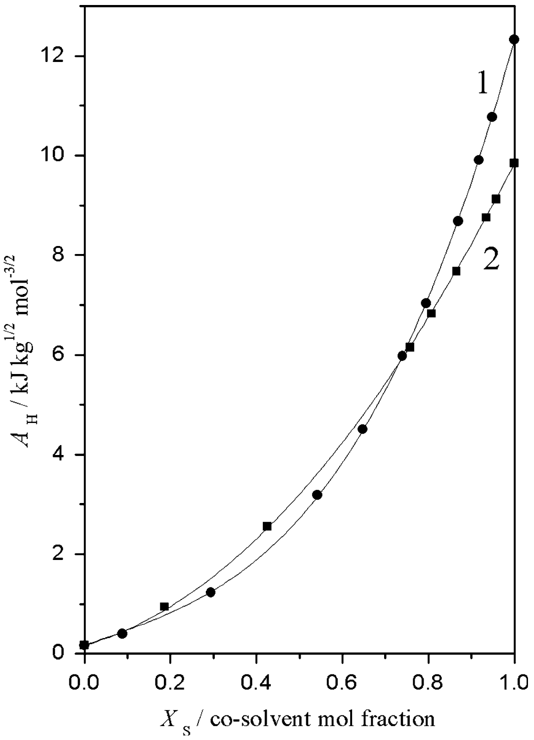

Fig. 1 The appropriate Debye–Hückel limiting law slope A_{H} of formamide–methanol (1) and formamide–ethylene glycol (2) mixed solvents at 298.15 K. Lines—Eq. 13

Table 3 Coefficients a and b of Eq. 14

T (K)	a	b	R	s_{f}
Formamide–methanol				
298.15	−19.14 ± 0.12	10.07 ± 0.27	0.99998	0.03
313.15	−21.77 ± 0.19	11.23 ± 0.33	0.99998	0.03
Formamide–ethylene glycol				
298.15	−7.20 ± 0.08	–	0.99996	0.03
313.15	−7.63 ± 0.15	–	0.99988	0.06

R is the correlation coefficient, s_{f} is the standard deviation of the fit

Discussion

There is a possibility to compare the two variants of the calculation A_{H} for FA–MeOH system. For example, for $X_{\mathrm{FA}} = 0.4582$ m.f. at 298.15 K $\Delta_{\mathrm{sol}}H^m = 17.05$ kJ mol^{-1} at $m = 0.00488$ mol kg^{-1}, $\Delta_{\mathrm{sol}}H^m = 17.13$ kJ mol^{-1} at $m = 0.0140$ mol kg^{-1} [12]:

$$\alpha = 8.71\ 10^{-4}\mathrm{K}^{-1}(\mathrm{Eq.\ 8}),\ A_{\mathrm{H}} = 3.18\ \mathrm{kJ\ kg}^{1/2}\ \mathrm{mol}^{-3/2},\ \Delta_{\mathrm{sol}}H^0 = 16.87\ \mathrm{kJ\ mol}^{-1};$$

$$\alpha^{\mathrm{id}} = 9.97\ 10^{-4}\mathrm{K}^{-1}(\mathrm{Eq.\ 10}),\ A_{\mathrm{H}} = 3.07\ \mathrm{kJ\ kg}^{1/2}\ \mathrm{mol}^{-3/2},\ \Delta_{\mathrm{sol}}H^0 = 16.86\ \mathrm{kJ\ mol}^{-1}.$$

It is obviously that the using of coefficient of the thermal expansion calculated by the additive scheme is quite admissible for calculation A_{H} in non-aqueous mixtures (Eq. 10). The curves $\Delta_{\mathrm{sol}}H^m$ vs. $m^{1/2}$ for the investigated salts are presented in Fig. 2. The $\Delta_{\mathrm{sol}}H^0$ values for two

Table 2 Properties of pure solvents [23]

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
$\alpha \cdot 10^6$ (K^{-1})	1203	1257	749	762	662	686
ε	32.7	30.0	109.0	102.9	37.9	34.9
$-\partial\ln\varepsilon/\partial T \cdot 10^3$ (K^{-1})	5.91	5.84	3.75	3.88	5.38	5.30
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

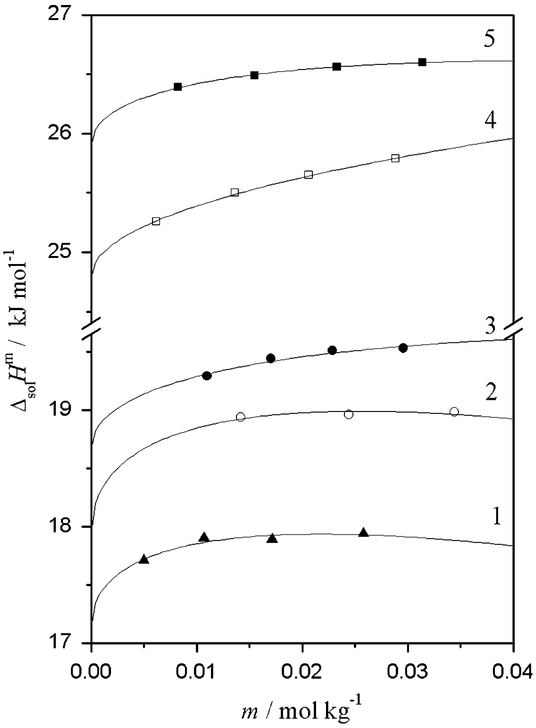

Fig. 2 The integral enthalpies of solution of Bu_4NBr vs. molality of salt. Mixed solvent formamide–methanol: 1—0.0514, 2—0.0484, 3—0.2461 m.f. of FA. Mixed solvent formamide–ethylene glycol: 4—0.2420, 5—0.1926 m.f. of FA. Temperatures: 1, 4, 5—298.15; 2, 3—313.15 K. *Lines*—Eq. 1

different temperatures calculated by Eq. 1 are given in Tables 4 and 5. The comparison of the previously received values with the data [12] where the values $\Delta_{sol}H^0$ were calculated in terms of Debye–Hückel theory in the second approximation [28] is presented at 298.15 K in Fig. 3. The values of $\Delta_{sol}H^0$ extrapolated by various methods differ on 1.5% as much as possible.

The enthalpies of transfer of Bu_4NBr from formamide to its mixtures with co-solvents (S) have been calculated as follow:

$$\Delta_{tr}H^0(\mathrm{FA} \rightarrow \mathrm{FA} + S) = \Delta_{sol}H^0(\mathrm{FA} + S) - \Delta_{sol}H^0(\mathrm{FA}) \quad (15)$$

The enthalpies of transfer of Bu_4NBr from formamide to its mixtures with the studied solvents at 298.15 K are given in Fig. 4. Also, the data from [20] for mixtures of FA–water, FA–*N*-MFA and FA–DMFA are presented here for comparison. As is seen from Fig. 4 additions of co-solvents to formamide influence the enthalpic component of Gibbs energy of the mixed solvent differently. So, addition of ethylene glycol and *N*-MFA weakens, of methanol practically does not change, and of water and DMFA strengthen solvation of the salt in mixture in comparison with pure formamide. The greatest changes of the transfer enthalpy characteristics of model solvophobic substance Bu_4NBr are observed in system FA–water.

Table 4 The standard enthalpies of solution ($\Delta_{sol}H^0$/kJ mol^{-1}) of Bu_4NBr in methanol–formamide mixtures at 298.15 and 313.15 K

298.15 K		313.15 K	
X_{FA}	$\Delta_{sol}H^0$	X_{FA}	$\Delta_{sol}H^0$
0.0	16.72 ± 0.08 [23]	0.0	17.18 ± 0.12 [23]
0.0514	17.14 ± 0.04	0.0484	17.95 ± 0.07
0.0825	17.21 ± 0.05	0.1061	18.54 ± 0.01
0.1304	17.33 ± 0.01	0.2461	18.77 ± 0.04
0.2049	17.28 ± 0.12	0.4255	18.98 ± 0.01
0.2602	17.41 ± 0.01	0.6042	19.26 ± 0.01
0.3521	17.19 ± 0.01	0.6223	19.22 ± 0.01
0.4582	16.87 ± 0.01	0.7936	19.32 ± 0.03
0.7061	16.98 ± 0.03	0.8933	19.36 ± 0.01
0.9116	17.32 ± 0.01	1.0	20.23 ± 0.01 [23]
1.0	17.71 ± 0.02 [23]		

The uncertainties are the standard deviation

Table 5 The standard enthalpies of solution ($\Delta_{sol}H^0$, kJ mol^{-1}) of Bu_4NBr in ethylene glycol–formamide mixtures at 298.15 and 313.15 K

298.15 K		313.15 K	
X_{FA}	$\Delta_{sol}H^0$	X_{FA}	$\Delta_{sol}H^0$
0.0	28.66 ± 0.03 [23]	0.0	30.20 ± 0.03 [23]
0.0419	28.13 ± 0.01	0.0171	29.95 ± 0.01
0.0648	27.79 ± 0.07	0.0594	29.61 ± 0.01
0.1343	26.69 ± 0.01	0.0876	29.30 ± 0.04
0.1926	25.90 ± 0.01	0.1387	28.51 ± 0.01
0.2420	24.79 ± 0.01	0.1738	28.44 ± 0.05
0.5742	21.45 ± 0.01	0.2595	27.21 ± 0.01
0.8134	18.86 ± 0.01	0.5492	23.95 ± 0.01
		0.7534	22.17 ± 0.01

The uncertainties are the standard deviation

The heat capacities of solution, $\Delta C_p{}^0$, have been determined from the enthalpies of solution by the equation:

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

The $\Delta C_p{}^0$ values of Bu_4NBr in formamide–water mixture in investigated temperature interval have been calculated using the data of enthalpies of solution from [20] at 298.15 K and our data at 313.15 K (unpublished results). For this purpose dependences $\Delta_{sol}H^0 = f(X_{FA})$ have been approximated by polynomials of the conforming power so that the standard deviation s_f did not exceed 0.18 kJ mol^{-1} in case of H_2O–FA system, $s_f \leq 0.14$ kJ mol^{-1} in EG–FA system and $s_f \leq 0.05$ kJ mol^{-1} for MeOH–FA. The

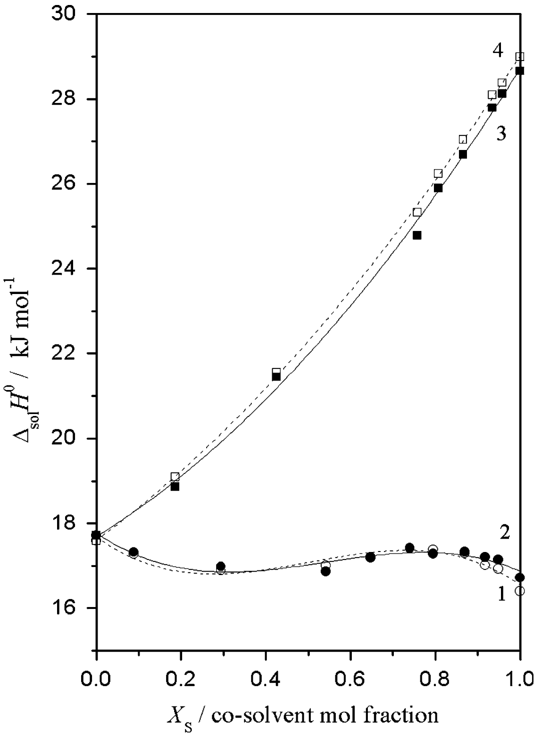

Fig. 3 The enthalpies of solution of Bu_4NBr vs. composition of mixed solvents formamide–methanol (1, 2) and formamide–ethylene glycol (3, 4) at 298.15 K. 1, 4—[12]; 2, 3—the present work

calculated values of the heat capacities of solution are presented in Fig. 5.

In work [22] it is shown that the solutions of tetraalkylammonium salts in FA have properties similar to those of aqueous rather than methanol solutions. Although solvophobic solvation effects are weaker than those in water they are possible in FA. The results obtained allow the solvent studied to be arranged as: $H_2O > FA > EG > MeOH$ in order of weakening of solvophobic solvation effects [22]. The same sequence of individual solvents studied is shown in Fig. 5 in order of decreasing of the ΔC_p^0 value.

The value of ΔC_p^0 in water is positive and large enough and the first additions of FA (X_{FA} <0.3 m.f.) result in to its sharp decrease (Fig. 5). It is possible to assume the fragments of the own structure of water are conserved in this area. And the own structure of formamide is formed in the field of a mixed solvent $X_{FA} \geq 0.3$ m.f. The additions of amide to MeOH and EG result in inconsiderable growth of ΔC_p^0 values on over the range of the mixed solvent. The heat capacities of Bu_4NBr solution in ethylene glycol and methanol systems in the region of $X_{FA} \geq 0.5$ m.f. become practically identical. The presence of the own structure of water in the region of small additions of formamide considerably distinguishes the H_2O–FA system from the investigated non-aqueous systems.

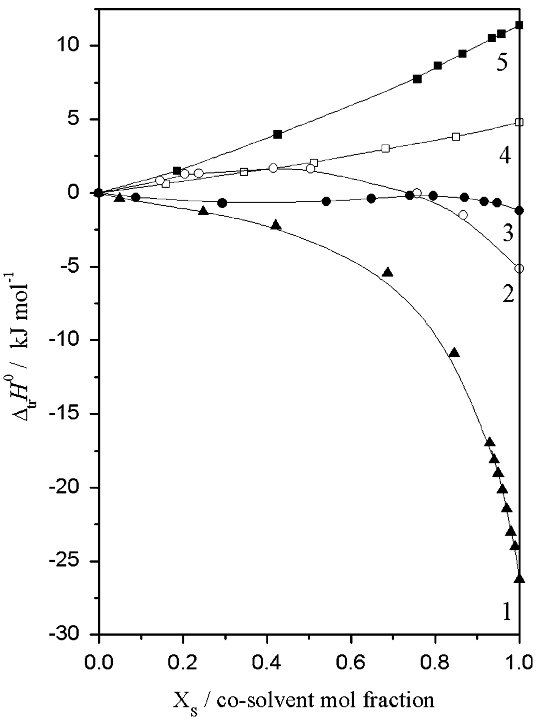

Fig. 4 The enthalpies of transfer of Bu_4NBr from formamide to mixtures of formamide with water (1), dimethylformamide (2), methanol (3), N-methylformamide (4) and ethylene glycol (5) at 298.15 K (see text). *Lines* are the polynomial description

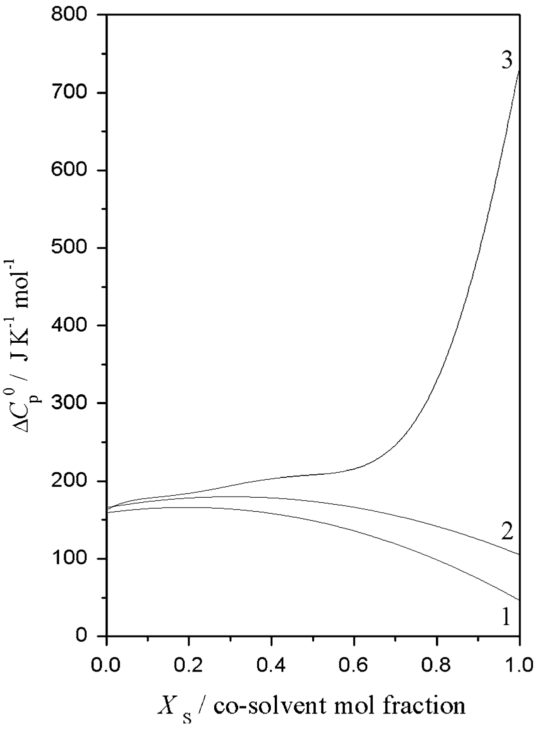

Fig. 5 The heat capacities of Bu_4NBr solution in mixtures of formamide with methanol (1), ethylene glycol (2) and water (3) in the 298.15–313.15 K temperature interval

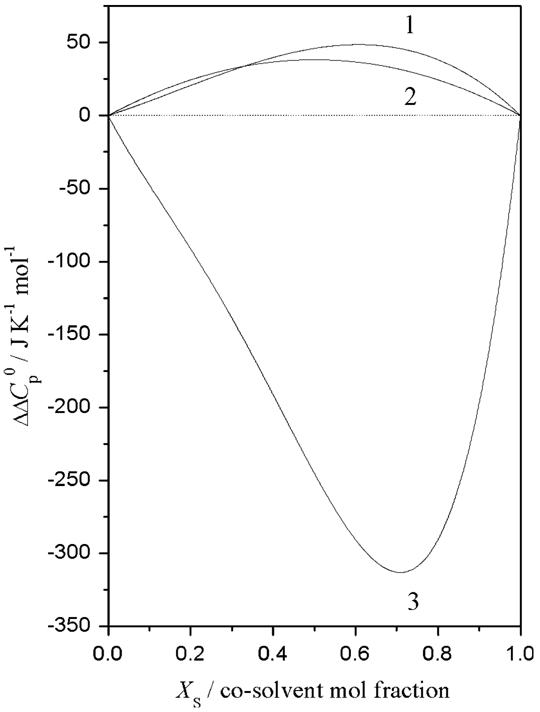

Fig. 6 The values of $\Delta\Delta C_p^0$ of Bu_4NBr vs. composition of mixtures of formamide with methanol (1), ethylene glycol (2) and water (3). *Lines* are the description by the Redlich–Kister type equations

It is interesting to consider a deviation from additivity of the ΔC_p^0 value for aqueous and non-aqueous systems containing formamide (Fig. 6). The ΔC_p^0 values were computed by Redlich–Kister type equations of the conforming powers. In aqueous system of formamide the deviation values are negative and very great. And for non-aqueous systems of formamide the values of deviation are practically equal and positive.

Thus it is reasonable to guess that the appearance of the own structure of water in $X_{FA} < 0.3$ m.f. is responsible for essential different behaviour of electrolyte in the region of small additions of FA to water and non-aqueous solvents.

Conclusions

The heats of solution of Bu_4NBr have been measured in mixtures of formamide with methanol and ethylene glycol at 313.15 K by calorimetric method for the first time.

The standard enthalpies of solution in binary mixtures have been extrapolated to infinite dilution by Redlich–Rosenfeld–Meyer type equation using the literary data at 298.15 K and the present paper data at 313.15 K.

The Debye–Hückel limiting law slope A_H required for calculation of the $\Delta_{sol}H^0$ value has been obtained with application the new additive scheme of determination of the physico-chemical characteristics of binaries. The scheme is tested on the example of Bu_4NBr solutions in FA–MeOH mixture at 298.15 K. Its application yields the $\Delta_{sol}H^0$ value very closed on the ones determined with the real (non-additive) characteristics of binaries.

The standard enthalpies of solution extrapolated by Redlich–Rosenfeld–Meyer type equation are in a good agreement with the ones computed in terms of the Debye–Hückel theory in the second approximation.

The heat capacities characteristics of Bu_4NBr have been calculated in H_2O–FA, MeOH–FA and EG–FA mixtures using the literary and present data. The sequence of solvents H_2O > FA > EG > MeOH located on their ability to solvophobic solvation found by us earlier for enthalpic characteristics is confirmed by the ΔC_p^0 values.

The investigations carried out allow revealing the important differences in behaviour of hydrophobic electrolyte Bu_4NBr in mixtures of formamide with water, methanol and ethylene glycol. It is found that the presence of the own structure of water in the region of small additions of formamide to co-solvents considerably differs the H_2O–FA system from investigated non-aqueous systems. Some common features of behaviour of Bu_4NBr in formamide mixtures with water, methanol and ethylene glycol occur only in the region rich enough in formamide content ($X_{FA} > 0.7$ m.f.).

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