Thermochemistry of Bu$_4$NBr solutions in binary solvents containing formamide

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ICTAC2008 Conference
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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 $D_{sol} H^0$ 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$_4$NBr solutions in FA–MeOH mixture at 298.15 K. Its applicaiton yields the $D_{sol} H^0$ 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$_4$NBr have been calculated in H$_2$O–FA, MeOH–FA and EG–FA mixtures using the literary and present data. The sequence of solvents H$_2$O [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$_4$NBr 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$_2$O–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
considerably more deviated from ideal behaviour on magnitude of excess volume than the water–formamide system. So, the excess volume equals $-0.55 \text{ sm}^3 \text{ mol}^{-1}$ [3, 6] for equimolar composition in the first case, in the second one $V^\infty = -0.13 \text{ sm}^3 \text{ mol}^{-1}$ (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 $\text{sm}^3 \text{ mol}^{-1}$ 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$_4$NBr in the series of amides at 278.15–328.15 K by a calorimetric method. Then they [20] have investigated the solutions of Bu$_4$NBr 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$_4$NBr and Bu$_4$NBr 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$_3$NBr in the same solvents at the same temperatures.

The solutions of Et$_4$NBr 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$_4$NBr 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$_4$NBr 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 distilled 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-$\text{sm}^3$ titanium 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 ±2 10$^{-4}$.

**Results**

The integral enthalpies of solution $\Delta_{sol}H^m$ of Bu$_4$NBr in mixed solvents in methanol–formamide and ethylene glycol–formamide mixed solvents at 313.15 K are listed in Table 1.

| Solvent System | $\Delta_{sol}H^m$ (kJ mol$^{-1}$) |
|---------------|----------------------------------|
| MeOH–FA      |                                  |
| EG–FA        |                                  |
| MeOH–EG–FA  |                                  |

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]:

$$\Delta_{sol}H^m = \Delta_{sol}H^0 + A_{Hm}^{1/2} + B m$$

(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.

$$A_H = -(\nu/2)^{1/2} \cdot [z_+z_-]^{3/2} \cdot \nu \cdot RT^2 \cdot A \cdot \left( \frac{1}{T} + \frac{\partial \ln e}{\partial T} + \frac{x}{3} \right)$$

(2)

where $\nu$ is the number of ions of charge $z_i$ per “molecule” of electrolyte.

The term $A$ can be written as follows:

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

(3)
Table 1 The integral enthalpies of solution ($\Delta_{sol}H^\alpha$)/kJ mol$^{-1}$) of Bu$_4$NBr in mixtures of formamide with methanol and ethylene glycol and the appropriate Debye–Hückel limiting law slope ($A_d$/kJ kg$^{1/2}$ mol$^{-3/2}$) at 313.15 K

| Methanol–formamide | Ethylene glycol–formamide |
|---------------------|--------------------------|
| $m$ (mol kg$^{-1}$) | $\Delta_{sol}H^\alpha$  | $m$ (mol kg$^{-1}$) | $\Delta_{sol}H^\alpha$  |
| $X_{FA}$ = 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 | 0.01419 18.94 | 0.00607 30.61 |
|  | 0.02444 18.96 | 0.01221 30.75 |
|  | 0.03441 18.98 | 0.01221 30.75 |
| $X_{FA}$ = 0.1061, $A_H$ = 11.202 | 0.00806 19.22 | 0.00756 30.21 |
|  | 0.01643 19.31 | 0.01248 30.26 |
|  | 0.02442 19.29 | 0.01248 30.26 |
| $X_{FA}$ = 0.2461, $A_H$ = 7.658 | 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 | 0.01648 29.94 |
| $X_{FA}$ = 0.4255, $A_H$ = 4.545 | 0.01098 19.30 | 0.00746 29.20 |
|  | 0.01741 19.33 | 0.01423 29.41 |
| $X_{FA}$ = 0.6042, $A_H$ = 2.584 | 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, $A_H$ = 2.432 | 0.00593 19.35 | 0.00771 27.65 |
|  | 0.01073 19.37 | 0.01540 27.71 |
| $X_{FA}$ = 0.7936, $A_H$ = 1.323 | 0.00690 19.36 | 0.00506 24.15 |
|  | 0.01923 19.27 | 0.01020 24.20 |
|  | 0.02817 19.23 | 0.01020 24.20 |
| $X_{FA}$ = 0.8933, $A_H$ = 0.887 | 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 |

Reliable calculation of the numerical values of $A_d$ 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 $\varepsilon$ 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:

$$V = X_{FA}V_{FA} + X_SV_S + V^E$$

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:

$$\rho = \frac{X_{FA}M_{FA} + X_SM_S}{X_{FA}V_{FA} + X_SV_S + V^E}$$

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

$$\alpha = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{X_{FA}V_{FA} + X_SV_S + \partial V^E/\partial T}{X_{FA}V_{FA} + X_SV_S + V^E}$$

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

$$\alpha = \phi_{FA}a_{FA} + \phi_Sa_S + \frac{\partial V^E/\partial T}{X_{FA}V_{FA} + X_SV_S}$$

where $\phi_{FA}$, $\phi_S$ is the volume fractions, determined by Eq. 9:

$$\phi_{FA} = \frac{X_{FA}V_{FA}}{X_{FA}V_{FA} + X_SV_S}, \phi_S = \frac{X_SV_S}{X_{FA}V_{FA} + X_SV_S}$$

For an ideal mixture it is received:

$$\alpha^{id} = \phi_{FA}a_{FA} + \phi_Sa_S$$

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

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

$$\ln\varepsilon = \phi_{FA}\ln\varepsilon_{FA} + \phi_S\ln\varepsilon_S$$

where $\rho$ is the density and the dielectric constant of pure or mixed solvent. Other symbols have their usual meanings [27].
Differentiating expression (11) is received:
\[
\frac{\partial \ln e}{\partial T} = \frac{\partial \ln e_{FA}}{\partial T} + \frac{\partial \ln e_{S}}{\partial T} + \frac{\partial \ln e_{S}(x_S - x_{FA})(\ln e_S - \ln e_{FA})}{\partial T} \tag{12}
\]

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:
\[
A_H = X_{FA} A_{H(FA)} + X_S A_{H(S)} + \Delta A_H \tag{13}
\]

The value \(\Delta A_H\) is the deviation from additivity. The values of \(\Delta A_H\) 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:
\[
\Delta A_H = X_{FA} X_S (a + b X_{FA}) \tag{14}
\]

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.

### Discussion

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

\[
\begin{align*}
\alpha &= 8.71 \times 10^{-4} \text{K}^{-1} \text{[Eq. 8], } A_H = 3.18 \text{ kJ kg}\^{1/2} \text{ mol}^{-3/2}, \Delta_{sol}H^0 = 16.87 \text{ kJ mol}^{-1}; \\
\alpha^{id} &= 9.97 \times 10^{-4} \text{K}^{-1} \text{[Eq. 10], } A_H = 3.07 \text{ kJ kg}\^{1/2} \text{ mol}^{-3/2}, \Delta_{sol}H^0 = 16.86 \text{ kJ mol}^{-1}.
\end{align*}
\]

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 \(\Delta_{sol}H^m\) vs. \(m^{1/2}\) for the investigated salts are presented in Fig. 2. The \(\Delta_{sol}H^0\) values for two

### Table 2 Properties of pure solvents [23]

| Solvent          | Methanol | Formamide | Ethylene glycol |
|------------------|----------|-----------|-----------------|
| \(T\) (K)        | 298.15   | 313.15    | 298.15          |
| \(\rho\) (kg m\(^{-3}\)) | 786.5    | 772.2     | 1129.1          |
| \(\pi\) \times 10^6 (K\(^{-1}\)) | 1203     | 1257      | 749             |
| \(\varepsilon\)  | 32.7     | 30.0      | 109.0           |
| \(-\partial ln e/\partial T\) \times 10^3 (K\(^{-1}\)) | 5.91     | 5.84      | 3.75            |
| \(A\)            | 3.870    | 4.052     | 0.762           |
| \(A_H\) (kJ kg\(^{1/2}\) mol\(^{-3/2}\)) | 12.32    | 14.69     | 0.165           |

Table 3 Coefficients \(a\) and \(b\) of Eq. 14

| \(T\) (K) | \(a\) \(\pm\) \(b\) | \(R\) | \(s_f\) |
|-----------|-----------------------|-------|--------|
| Formamide–methanol | 298.15  \(-19.14 \pm 0.12\) 10.07 ± 0.27 | 0.99998 | 0.03 |
| 313.15  \(-21.77 \pm 0.19\) 11.23 ± 0.33 | 0.99998 | 0.03 |
| Formamide–ethylene glycol | 298.15 \(-7.20 \pm 0.08\) – | 0.99996 | 0.03 |
| 313.15 \(-7.63 \pm 0.15\) – | 0.99988 | 0.06 |

\(R\) is the correlation coefficient, \(s_f\) is the standard deviation of the fit.
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 \( \Delta_{\text{sol}} H^0 \) 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 \( \Delta_{\text{sol}} H^0 \) extrapolated by various methods differ on 1.5% as much as possible.

The enthalpies of transfer of \( \text{Bu}_4\text{NBr} \) from formamide to its mixtures with co-solvents (S) have been calculated as:

\[
\Delta_{\text{tr}} H^0 (\text{FA} \rightarrow \text{FA} + S) = \Delta_{\text{sol}} H^0 (\text{FA} + S) - \Delta_{\text{sol}} H^0 (\text{FA})
\]

(15)

The enthalpies of transfer of \( \text{Bu}_4\text{NBr} \) 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 \( \text{Bu}_4\text{NBr} \) are observed in system FA–water.

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

\[
\Delta C_p^0 = (\Delta_{\text{sol}} H^0 (298.15 \text{ K}) - \Delta_{\text{sol}} H^0 (298.15 \text{ K}))/15
\]

(16)

The \( \Delta C_p^0 \) values of \( \text{Bu}_4\text{NBr} \) 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 \( \Delta_{\text{sol}} H^0 = f(X_{\text{FA}}) \) 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 \( \text{H}_2\text{O}–\text{FA} \) system, \( s_f \leq 0.14 \text{ kJ mol}^{-1} \) in EG–FA system and \( s_f \leq 0.05 \text{ kJ mol}^{-1} \) for \( \text{MeOH}–\text{FA} \). The

![Fig. 2: The integral enthalpies of solution of \( \text{Bu}_4\text{NBr} \) 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](Image 62x494 to 261x763)

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**Table 4** The standard enthalpies of solution (\( \Delta_{\text{sol}} H^0 / \text{kJ mol}^{-1} \)) of \( \text{Bu}_4\text{NBr} \) in methanol–formamide mixtures at 298.15 and 313.15 K

| \( X_{\text{FA}} \) | \( \Delta_{\text{sol}} H^0 \) (298.15 K) | \( X_{\text{FA}} \) | \( \Delta_{\text{sol}} H^0 \) (313.15 K) |
|---|---|---|---|
| 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 (\( \Delta_{\text{sol}} H^0 / \text{kJ mol}^{-1} \)) of \( \text{Bu}_4\text{NBr} \) in ethylene glycol–formamide mixtures at 298.15 and 313.15 K

| \( X_{\text{FA}} \) | \( \Delta_{\text{sol}} H^0 \) (298.15 K) | \( X_{\text{FA}} \) | \( \Delta_{\text{sol}} H^0 \) (313.15 K) |
|---|---|---|---|
| 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

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Fig. 2: The integral enthalpies of solution of \( \text{Bu}_4\text{NBr} \) 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

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The uncertainties are the standard deviation
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: \( \text{H}_2\text{O} > \text{FA} > \text{EG} > \text{MeOH} \) 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 \( \Delta C_p^0 \) value.

The value of \( \Delta C_p^0 \) in water is positive and large enough and the first additions of FA (\( X_{\text{FA}} \leq 0.3 \text{ m.f.} \)) result in 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 \( X_{\text{FA}} \geq 0.3 \text{ m.f.} \). The additions of amide to MeOH and EG result in inconsiderable growth of \( \Delta C_p^0 \) values on over the range of the mixed solvent. The heat capacities of \( \text{Bu}_4\text{NBr} \) solution in ethylene glycol and methanol systems in the region of \( X_{\text{FA}} \geq 0.5 \text{ m.f.} \) become practically identical. The presence of the own structure of water in the region of small additions of formamide considerably distinguishes the \( \text{H}_2\text{O}–\text{FA} \) system from the investigated non-aqueous systems.

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**Fig. 3** The enthalpies of solution of \( \text{Bu}_4\text{NBr} \) 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.

**Fig. 4** The enthalpies of transfer of \( \text{Bu}_4\text{NBr} \) 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 \( \text{Bu}_4\text{NBr} \) solution in mixtures of formamide with methanol (1), ethylene glycol (2) and water (3) in the 298.15–313.15 K temperature interval.
It is interesting to consider a deviation from additivity of the \( \Delta C_p^0 \) value for aqueous and non-aqueous systems containing formamide (Fig. 6). The \( \Delta C_p^0 \) 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 and present data at 298.15 K.

The Debye–Hückel limiting law slope \( A_H \) required for calculation of the \( \Delta_{ad} H^0 \) 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 \( \Delta_{ad} H^0 \) 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 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.).

**Acknowledgements**

The financial support of this work by the Russian Foundation of Basic Researches (Grant No. 06-03-32169) is gratefully acknowledged.

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**References**

1. Pikkarainen L. Excess enthalpies of binary solvent mixtures of methanol, ethanol and 1-propanol with formamide, \( N \)-methylformamide and \( N,N \)-dimethylformamide. Thermochim Acta. 1991; 178:311–9.
2. Puhovski YuP, Rode BM. Molecular dynamics simulations of aqueous formamide solution. 1. Structure of binary mixtures. J Phys Chem. 1995;99:1566–76.
3. Garcia B, Alcalde R, Leal JM, Matos JS. Formamide—(C \(_1\)–C\(_5\)) alkan-1-ols solvent systems. J Chem Soc Faraday Trans. 1996;92: 3347–52.
4. Hersodes K, Leito I, Koppel I, Rosés M. Solute-solvent and solvent-solvent interactions in binary solvent mixtures. Part 8. The ET(30) polarity of binary mixtures of formamides with hydroxilic solvents. J Phys Org Chem. 1999;12:109–15.
5. Marcus Y. Preferential solvation in mixed solvents. X. Completely miscible aqueous co-solvent binary mixtures at 298.15 K. Monatsh Chem. 2001;132:1387–411.
6. Gómez Marigliano AC, Sólamo HN. Density, viscosity, excess molar volume, viscosity deviation, and their correlations for formamide + three alkan-1-ols binary systems. J Chem Eng Data. 2002;47:796–800.
7. Sukhno IV, Panyushkin VT, Buz’ko VYu, Joioev TE, Kovaleva IA. Solvates in formamide–water system according to a proton magnetic relaxation. Zh Fiz Khim. 2003;77:1599–604.
8. Zarei HA, Iloukhani H. Excess molar enthalpies of formamide + some alkan-1-ols (C5–C10) and their correlations at 298.15 K. Thermochim Acta. 2003;405:123–8.
9. Ali A, Nayn AK, Kumar N, Ibrahim M. Density and viscosity of magnesium sulphate in formamide + ethylene glycol mixed solvents. Proc Indian Acad Sci (Chem Sci). 2002;114(5):495–500.
10. Subbarangaiah K, Manohara Murthy N, Subrahmanyam SV. Excess thermodynamic functions of the system: water–formamide. Acustica. 1985;58(2):105–8.
11. Egan EP, Luff BB. Heat of solution, heat capacity, and density of aqueous formamide solutions at 25°C. J Chem Eng Data. 1966;11:194–6.
12. Korolev VP, Smirnova NL, Antonova OA, Kustov AV. The thermal properties of Bu4NBr solutions in binary mixtures on the base of formamide. Russ J Gen Chem. 2008;78(11):2013–8.
13. Sco¨ ld R, Suurkuusk J, Wadso¨ I. Thermochemistry of solutions of biochemical model compounds. 7. Aqueous solutions of some amides, t-butanol and pentanol. J Chem Thermodyn. 1976;8:1075–80.
14. Rouw A, Somsen G. Solvation and hydrophobic hydration of alkyl-substituted ureas and amides in N,N-dimethylformamide + water mixtures. J Chem Soc Faraday Trans II. 1982;78:3397–408.
15. Batov DV, Manin NG, Zaichikov AM. Enthalpic characteristics and state of amides of formic and acetic acids in water + 1,2-ethanediol mixtures. Russ J Gen Chem. 2002;72(7):1041–8.
16. Krishnan CV, Friedman HL. Solvation enthalpies of hydrocarbons and normal alcohols in highly polar solvents. J Phys Chem. 1971;75:3598–606.
17. Berling D, Olofsson G. Solvation of small hydrophobic molecules in formamide: a calorimetric study. J Solut Chem. 1994;23:911–23.
18. Rocha F, Bastos M. Enthalpies of solution of n-alcohols in formamide and ethylene glycol. J Solut Chem. 1997;26:989–96.