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Enthalpy Characteristics and State of *N,N*-Disubstituted Amides of Formic and Acetic Acids in Water–Formamide Mixtures

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Abstract—The enthalpies of solution of *N,N*-disubstituted amides of formic and acetic acids at 298.15 K throughout the entire range of compositions of the water–formamide mixed solvent were measured. The enthalpies of solvation and transfer of the amides from water into the mixed solvent were calculated. The effects of the structure and properties of the solutes and also of the composition of the mixed solvent on their thermochemical characteristics were considered. The monotonous weakening of solvation of the alkylamides throughout the entire range of mixture compositions results from reduced exothermicity of their nonspecific and specific solvation. Analysis of the deviations of the enthalpies of transfer from additivity in composition showed that the hydrocarbon radicals of the amides are slightly more solvated by formamide, while the polar functional groups, by water.

The characteristic thermodynamic and structural features of aqueous nonelectrolyte solutions first of all result from the presence of a three-dimensional net of hydrogen bonds in liquid water. Solvatophobic effects similar to hydrophobic effects earlier detected in aqueous solutions can be expected to appear in pure and mixed solvents strongly associated by hydrogen bonds. According to available published data, formamide [1, 2] and its mixtures with water [3] can be such solvents. The fact that water–water, formamide–formamide, and water–formamide hydrogen bonds are close in energy [4] explains the low excess volumes [5] and enthalpies of mixing [6], observed throughout the entire range of mixture compositions. It was found by computer simulation of a mixture with a low formamide content that formamide molecules form approximately four hydrogen bonds with water molecules [7]. Molecular-dynamic modeling of water–formamide solutions of various concentration showed that the local geometry of molecules linked by hydrogen bonds remains almost invariable in a wide range of compositions [3].

This work deals with the thermochemical characteristics of *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide, *N,N*-dimethylacetamide, *N,N*-diethylacetamide, hexamethylphosphoramide (HMPA), and formamide in mixed water–formamide solvents with various formamide contents at 298.15 K, and also the state of the components in the solutions under study. As far as we know, no such studies were carried out earlier.

The heat effects and standard enthalpies of solution of the amides under study, measured by calorimetry, are given in Table 1. The experimental data of this work for tertiary amides were discussed together with our previous data [6, 12] on the enthalpies of solution of formamide and HMPA (Table 2).

Let us consider the effects of the structure and properties of the solutes on the enthalpies of their solution and solvation. The enthalpies of solution (Table 1) of *N,N*-disubstituted amides with the same acid radical are close to each other within a wide range of compositions of the mixed solvent. These values become noticeably different only in solutions containing less than 0.15 mole fraction of formamide. In this case, diethylamides of formic and acetic acids are dissolved with a greater exothermic effect than the corresponding dimethylamides. As the $\Delta_{\mathrm{vap}}H$ of diethylamides is higher than the $\Delta_{\mathrm{vap}}H$ of dimethylamides, the more negative values of $\Delta_{\mathrm{s}}H^0$ for diethylamides are due to their strong interaction with water. The $\Delta_{\mathrm{s}}H^0 = f(X)$ dependence for formamide is much different. The enthalpy of solution of formamides becomes more exothermic with decreasing water contents of the mixtures, whereas the exothermic effect of solution of *N,N*-dialkylamides decreases (Table 1). The standard enthalpies of formamide solution in the water–formamide solvent are identical to the excess partial molar enthalpies of formamide, calculated with the enthalpies of mixing reported in [6].

Table 1. Heat effects ($\Delta_{s}H^{m}$, kJ/mol) and standard enthalpies ($\Delta_{s}H^{0}$, kJ/mol) of solution, van der Waals molar volumes (V_{W}, cm^{3}/mol), and enthalpies of vaporization ($\Delta_{vap}H$, kJ/mol) of DMF (**I**), *N,N*-diethylformamide (**II**), *N,N*-dimethylacetamide (**III**), and *N,N*-diethylacetamide (**IV**) in the water–formamide mixed solvent at 298.15 K[a]

I		II		III		IV	
m	$\Delta_{s}H^{m}$	*m*	$\Delta_{s}H^{m}$	*m*	$\Delta_{s}H^{m}$	*m*	$\Delta_{s}H^{m}$
			X 0.00				
$\Delta_{s}H^{0}$ –15.22[b]		$\Delta_{s}H^{0}$ –17.97[b]		$\Delta_{s}H^{0}$ –21.42[b]		$\Delta_{s}H^{0}$ –24.08[b]	
			X 0.13				
$\Delta_{s}H^{0}$ –13.04[b]		$\Delta_{s}H^{0}$ –13.93[b]		$\Delta_{s}H^{0}$ –17.94[b]		$\Delta_{s}H^{0}$ –18.65[b]	
			X 0.25				
0.0296	–11.42	0.0202	–11.63	0.0279	–15.79	0.0212	–16.03
0.0558	–11.37	0.0413	–11.64	0.613	–15.68	0.0452	–16.19
$\Delta_{s}H^{0}$ –11.40		$\Delta_{s}H^{0}$ –11.64		$\Delta_{s}H^{0}$ –15.73		$\Delta_{s}H^{0}$ –16.11	
			X 0.50				
0.0310	–7.84	0.0150	–7.91	0.0253	–11.69	0.0305	–11.68
0.0598	–7.77	0.0381	–8.16	0.0540	–11.50	0.0590	–11.61
$\Delta_{s}H^{0}$ –7.81		$\Delta_{s}H^{0}$ –8.04		$\Delta_{s}H^{0}$ –11.60		$\Delta_{s}H^{0}$ –11.65	
			X 0.75				
0.0240	–7.42	0.0184	–7.69	0.0221	–10.05	0.0191	–10.64
0.0557	–7.19	0.0476	–7.65	0.0509	–10.20	0.0365	–10.71
$\Delta_{s}H^{0}$ –7.31		$\Delta_{s}H^{0}$ –7.67		$\Delta_{s}H^{0}$ –10.13		$\Delta_{s}H^{0}$ –10.67	
			X 0.90				
0.0299	–6.82	0.0166	–6.81	0.0197	–9.31	0.0128	–9.05
0.0551	–6.79	0.0405	–6.78	0.0375	–9.29	0.0287	–9.10
$\Delta_{s}H^{0}$ –6.81		$\Delta_{s}H^{0}$ –6.79		$\Delta_{s}H^{0}$ –9.30		$\Delta_{s}H^{0}$ –9.07	
			X 1.00				
0.0311	–6.25	0.0249	–6.45	0.0224	–8.62	0.0252	–8.83
0.625	–6.31	0.0442	–6.43	0.0408	–8.61	0.0464	–8.80
$\Delta_{s}H^{0}$ –6.28 V_{W} 46.77 $\Delta_{vap}H$ 46.89		$\Delta_{s}H^{0}$ –6.44 V_{W} 67.23 $\Delta_{vap}H$ 50.32		$\Delta_{s}H^{0}$ –8.62 V_{W} 57.04 $\Delta_{vap}H$ 50.23		$\Delta_{s}H^{0}$ –8.81 V_{W} 77.50 $\Delta_{vap}H$ 54.11	

[a] (*m*, mol/kg solvent) Molal concentration and (*X*) mole fraction of formamide. Values of V_{W} were taken from [8], and values of $\Delta_{vap}H$, from [9]. [b] Data of [10].

Table 2. Van der Waals molar volumes (V_{W}, cm^{3}/mol), enthalpies of vaporization ($\Delta_{vap}H$, kJ/mol), and standard enthalpies of solution (kJ/mol) of HMPA (**V**) and formamide (**VI**) in the water–formamide mixed solvent at 298.15 K[a]

Comp. no.	V_{W}	$\Delta_{vap}H$	*X* 0.00	*X* 0.13	*X* 0.25	*X* 0.50	*X* 0.75	*X* 0.90	*X* 1.00
V	110.65	61.1	–49.52	–42.00	–33.50	–26.00	–22.70	–20.40	–17.42
VI	26.23	60.1	1.91	1.22	0.52	0.23	0.07	0.01	0.00

[a] (*X*) Mole fraction of formamide. Values of V_{W} were taken from [8] and values of $\Delta_{vap}H$, from [9, 11].

The enthalpies of solvation of the amides under study, calculated by Eq. (1), are given in Fig. 1a.

$$\Delta_{solv}H^{0} = \Delta_{s}H^{0} - \Delta_{vap}H. \quad (1)$$

The enthalpies of vaporization of the compounds are given in Tables 1 and 2.

It is evident from Fig. 1 that the enthalpies of hydration of the amides become more exothermic in the series formamide < DMF < *N,N*-diethylformamide < *N,N*-dimethylacetamide < *N,N*-diethylacetamide < HMPA. This series is also valid for dialkylamides throughout the entire range of mixture compositions. The possible reasons for the strengthened solvation in water and the mixed solvent can be, first, strengthening solvatophobic solvation with increasing size of the hydrocarbon radicals; second, increasing basicity of the amides (the donor numbers of formamide, DMF, *N,N*-diethylformamide, *N,N*-dimethylacetamide, *N,N*-diethylacetamide, and HMPA are 24.0, 26.6, 31.0, 27.8, 32.1, and 38 kkal/mol, respectively [13]). It is evident that the electron-donor power of the amides is more affected by increasing size of the radical at the amino nitrogen atom than by addition of CH_2 groups to acyl.

The effect of mixture composition on the enthalpies of solvation of the compounds is expedient to analyze in terms of the enthalpies of transfer from water, calculated by Eq. (2) and represented in Fig. 1b.

$$\Delta_{tr}H^0(\text{A, water} \longrightarrow \text{water–formamide})$$
$$= \Delta_{solv}H^0(\text{A, water–formamide}) - \Delta_{solv}H^0(\text{A, water})$$
$$= H^0(\text{A, water–formamide}) - \Delta_s H^0(\text{A, water}). \quad (2)$$

Here $\Delta_{solv}H^0$(A, water–formamide), $\Delta_s H^0$(A, water–formamide), and $\Delta_{solv}H^0$(A, water), ΔpH^0(A, water) are the standard enthalpies of solvation and solution of the amides (A) in the mixed solvent and water, respectively.

The ethalpies of transfer of tertiary amides are positive throughout the entire range of mixture compositions, whereas the $\Delta_{tr}H^0$ of formamide are negative. The concentration dependences of these values are controlled by the size of amide molecules. The endothermicity of the enthalpies of transfer of the amides increases with increasing van der Waals volume of their molecules (Tables 1 and 2). This fact can be explained by increasing endothermic contribution of nonspecific solvation of amides with increasing formamide content of the mixture. In this work by nonspecific solvation we mean the sum of enthalpy contributions from formation of a cavity in the solvent for accomodation of an amide molecule and also from amide–solvent van der Waals interaction. To estimate trends in the nonspecific solvation, we used the contributions of methylene radicals in the enthalpies of transfer of the amides. On the basis of the composition and structure of amide molecules, the enthalpies of transfer of a CH_2 group can formally be estimated by Eqs. (3)–(6):

$$\Delta_{tr}H^0(CH_2) = [\Delta_{tr}H^0(\mathbf{II}) - \Delta_{tr}H^0(\mathbf{I})]/2, \quad (3)$$

$$\Delta_{tr}H^0(CH_2) = [\Delta_{tr}H^0(\mathbf{IV}) - \Delta_{tr}H^0(\mathbf{III})]/2, \quad (4)$$

$$\Delta_{tr}H^0(CH_2) = [\Delta_{tr}H^0(\mathbf{III}) - \Delta_{tr}H^0(\mathbf{I})], \quad (5)$$

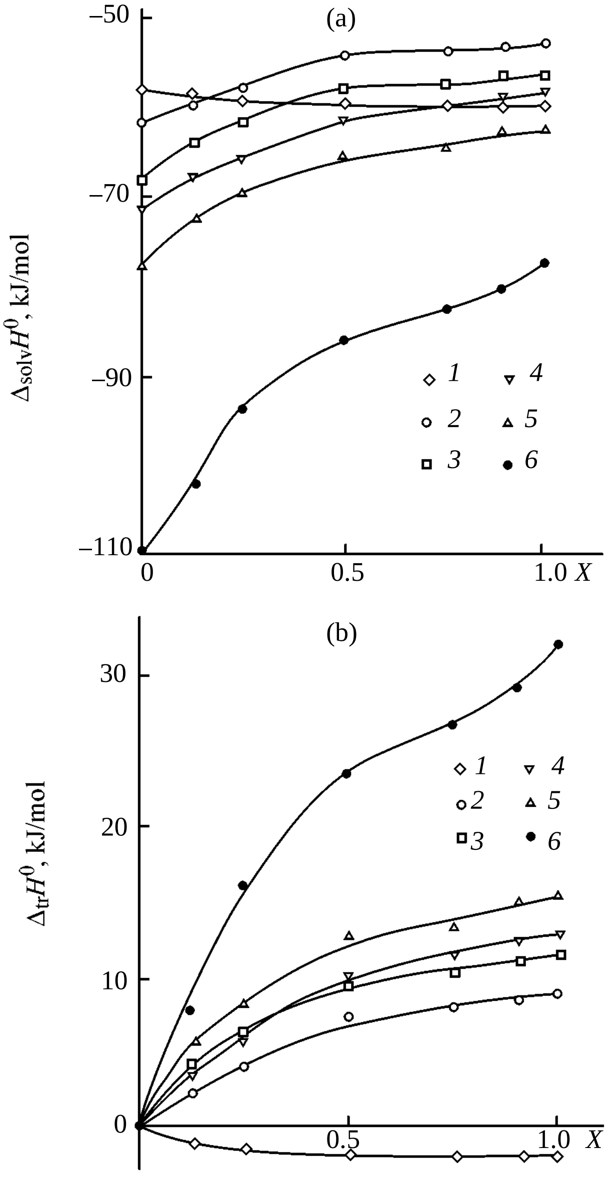

Fig. 1. Enthalpies of (a) solvation and (b) transfer of (*1*) formamide, (*2*) *N,N*-dimethylformamide, (*3*) *N,N*-diethylformamide, (*4*) *N,N*-dimethylacetamide, (*5*) *N,N*-diethylacetamide, and (*6*) hexamethylphosphoramide in the water–formamide mixed solvent at 298.15 K as functions of mixture composition.

$$\Delta_{tr}H^0(CH_2) = [\Delta_{tr}H^0(\mathbf{IV}) - \Delta_{tr}H^0(\mathbf{II})]. \quad (6)$$

Equations (3) and (4) allow calculation of the enthalpies of transfer of the CH_2 radicals of amino groups, and Eqs. (5) and (6), of the CH_2 radicals of acetyl groups. The resulting data are given in Fig. 2. As seen, compared to amino methylene radicals, acetyl CH_2 groups have more endothermic enthalpies of transfer, which vary more monotonically with increasing formamide content of the mixture. Compari-

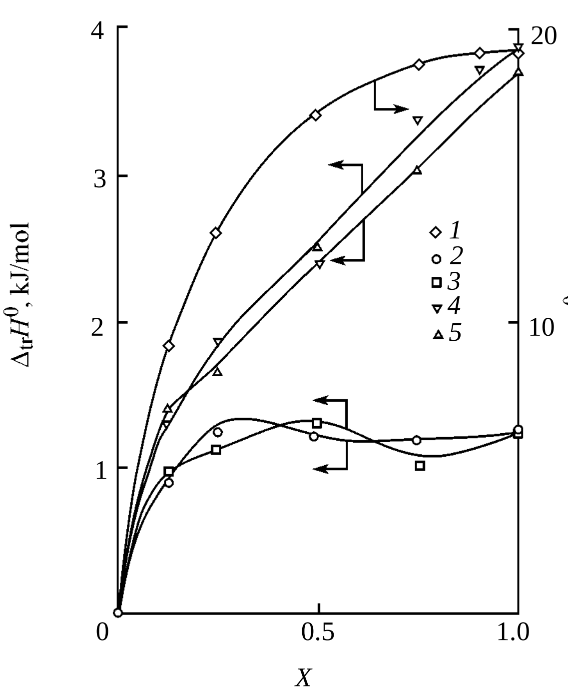

Fig. 2. Enthalpies of transfer of (*1*) argon and (*2*)–(*5*) methylene radicals of the amides from water to the water–formamide mixed solvent at 298.15 K as functions of mixture composition. The data for curves (*2*)–(*5*) are calculated by Eqs. (3)–(6), respectively.

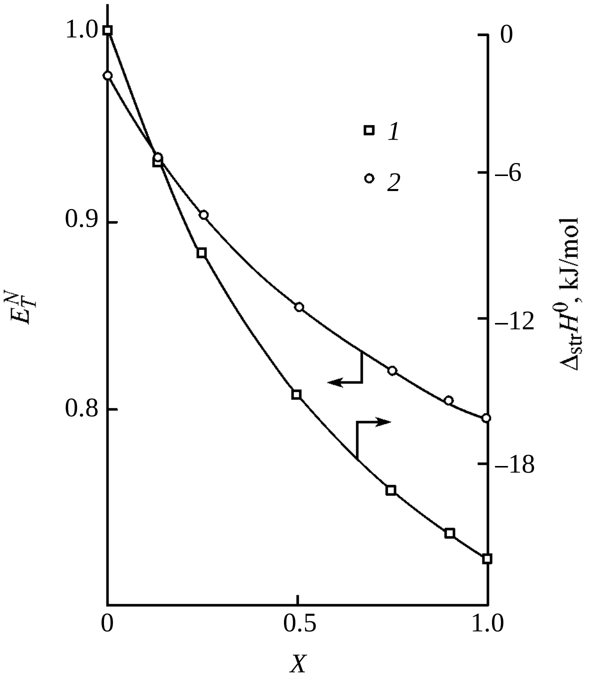

Fig. 3. Changes in the enthalpy of the structural contribution $\Delta\Delta_{str}H = [\Delta_{str}H(\text{water–formamide}) - \Delta_{str}H(\text{water})]$ of (*1*) formamide and (*2*) the parameter E_T^N [16] as functions of the composition of the water–formamide mixed solvent at 298.15 K.

son of the enthalpies of transfer from water into formamide of CH_2 groups of the amides with the corresponding values for argon [14] and ethane (10 kJ/mol, as calculated with data of [15]) shows that the enthalpies of transfer of CH_2 groups qualitatively correctly reflect the trends in variation of nonspecific solvation of the amides. It is also evident that the concentration dependence of the enthalpy of transfer for argon is similar to that for amino methylene radicals in that the enthalpy of transfer most strongly varies in the range 0–0.4 mole fraction formamide. As the content of formamide in the mixture increases, the contribution of amide (electron donor)–solvent (electron acceptor) specific interaction should become more endothermic owing to the decreasing acidity of the solvent. The change in the parameter E_T^N [16] is shown in Fig. 3. The increase in the endothermic effect of transfer owing to weakening specific interaction should affect to a greater extent the enthalpy of transfer of HMPT, which is the strongest electron donor among the compounds under study [13].

As already noted, the enthalpies of transfer of formamide from water into the mixed solvent have opposite signs in relation to the $\Delta_{tr}H^0$ values of *N,N*-disubstituted amides. There are several possible reasons for this situation. The structure of formamide suggests no or slight contribution of hydrophobic hydration [17]. The energy of the formamide (electron acceptor)–solvent (electron donor) specific interaction increases with increasing basicity of the mixture [18]. At last, the increase in the exothermic effect of transfer of formamide can be associated with decreased contribution of structural reorganization of the solvent. It is supposed [19, 20] that the structural contribution arises from differences in the intensity of intermolecular interactions in solvent and in solute and in the size of their molecules. The value of the structural contribution depends on the degree of structurization of the solvent and on its fraction available for reorganization. The degree of structurization can be measured by the cohesion energy density of the solvent. In [19, 20], one of the authors of the present work proposed Eq. (7) for the structural contribution in the enthalpy of solvation.

$$\Delta_{str}H^0 = pV_W. \qquad (7)$$

Here *p* is the cohesion energy density of the mixed solvent, calculated by Eq. (8) [21, 22] with data of [5, 6, 9].

Table 3. Composition of the solvation shells (mol % formamide) of amide molecules and their hydrocarbon radicals in the water–formamide mixed solvent at 298.15 K[a]

X	**I**	**II**	**III**	**IV**	**V**	**VI**	CH_2[b]			
							(3)	(4)	(5)	(6)
13	13	14	13	14	13	12	16	16	14	15
25	25	27	25	26	26	23	31	30	26	25
50	53	54	52	53	52	48	55	56	48	50
75	76	76	76	76	74	74	77	74	76	72
90	90	91	90	92	88	90	93	96	91	95

[a] (*X*) is the formamide content, mol %. [b] The enthalpies of solvation of methylene radical calculated by formulas (3)–(6) were used in calculations by Eq. (10).

$$p = [(1 - X)\Delta_{vap}H_1 + X\Delta_{vap}H_2 - \Delta_{mix}H - RT]/V. \qquad (8)$$

Here *X* is the mole fraction of formamide in the mixture, $\Delta_{vap}H_1$ and $\Delta_{vap}H_2$ are the enthalpies of vaporization of water and formamide, $\Delta_{mix}H$ is the enthalpy of mixing of the components, *V* is the molar volume of the mixture, and V_W is the van der Waals molar volume of a solute, calculated from group contributions [8].

The dependence of changes in the enthalpy of the structural contribution of formamide on mixture composition $\Delta\Delta_{str}H = [\Delta_{str}H^0(\text{water–formamide}) - \Delta_{str}H^0(\text{water})]$ is given in Fig. 3.

The enthalpies of solution and solvation in mixed solvents are frequently interpreted in terms of resolvation and selective solvation of solute by examining deviations of its thermodynamic or spectral properties in the mixture from additive values. A number of approaches to employing thermochemical data in studying the solvation shells of solutes in mixed solvents are known, but here we will not dwell on them. We earlier considered this problem in detail in [20], where also proposed a new procedure for calculating the composition of the solvation shell of a solute in a binary mixture. The composition of the solvation shell is usually calculated via the enthalpy of solvation of the substance minus the enthalpy of structural reorganization [Eq. (9)].

$$\Delta_{solv}H^* = \Delta_{solv}H^0 - \Delta_{str}H^0. \qquad (9)$$

$\Delta_{str}H$ is calculated by Eq. (7), and the volume fraction of formamide in the solvation shell, by Eq. (10):

$$\varphi^* = \varphi + [\Delta_{solv}H^*_{exp}(\text{water–formamide}) - \Delta_{solv}H^*_{ad}(\text{water–formamide})]/[\Delta_{solv}H^*(\text{formamide}) - \Delta_{solv}H^*(\text{water})] = \varphi + [\Delta_{tr}H^*_{exp}(\text{water}\rightarrow\text{water–formamide}) - \Delta_{tr}H^*_{ad}(\text{water-}\rightarrow\text{water–formamide})]/\Delta_{tr}H^*(\text{water–formamide}). \qquad (10)$$

Here φ is the volume fraction of formamide in the mixture. The $\Delta_{tr}H^*$ values are calculated from $\Delta_{solv}H^*$ by an equation similar to (2); $\Delta_{solv}H^*_{ad}$ and $\Delta_{tr}H^*_{ad}$ are the enthalpies of solvation and transfer, additive with respect to φ. The mole fraction of formamide in the solvation shell can be calculated by Eq. (11):

$$X^* = \varphi^*V_1/[\varphi^*V_1 + (1 - \varphi^*)V_2]. \qquad (11)$$

Here V_1 and V_2 are the molar volumes of water and formamide, respectively.

The resulting data (Table 3) show that the hydrocarbon radicals bound to nitrogen in the amide molecules under study are slightly more solvated by formamide in the mixed solvent. Therefore, amide groups should be selectively solvated by water, as no selective solvation of amide molecules as a whole is observed throughout the entire range of compositions, except for the region of equimolar contents of the components, where *N*,*N*-alkylamide molecules tend to be preferentially solvated by formamide. Considering the parameter E_T^N, Bosch and Roses [16] concluded that the solvatochromic indicator (Dimroth betaine) is preferentially solvated by formamide, but our data suggest that the selective solvation of the indicator involves preferentially its hydrocarbon radical.

Table 4 lists the coefficients and regression parameters of Eqs. (12) that describe the enthalpies of transfer of the amides.

$$\Delta_{tr}H^0 = a_1\varphi + a_2\varphi^2. \qquad (12)$$

Table 4. Coefficients and regression parameters of Eq. (12)[a]

Amide	a_1	a_2	s	R^2
I	10.92	–1.96	0.45	0.9865
II	18.79	–7.40	0.34	0.9950
III	15.45	–2.70	0.28	0.9973
IV	23.09	–8.00	0.48	0.9941
V	38.90	–7.90	1.01	0.9941
VI	–].83	1.94	0.07	0.9925

[a] Notation of the compounds is the same as in Tables 1 and 2; (s) standard deviation, and (R^2) correlation coefficient.

As seen from Table 4, the enthalpies of transfer of the amides are fairly fit by a polynomial of the second degree in volume fraction. The approximation error is no higher than 0.5 kJ/mol. Correlation of the resulting coefficients with the composition and structure of amide molecules shows that the coefficients a_1 and b_2 regularly change as the numbers of carbon atoms in the acid residue and in the substituents in the amino groups increase. The coefficients for tertiary formamides and acetamides have Eqs. (13) and (14):

$$a_1 = -1.21 + 4.42N_C(C) + 3.88N_C(N);$$

$$n\ 4\ (\text{compounds } \mathbf{I}\text{–}\mathbf{IV}),\ s\ 0.06, \qquad (13)$$

$$a_2 = 4.06 - 0.67N_C(C) - 2.69N_C(N);$$

$$n\ 4\ (\text{compounds } \mathbf{I}\text{–}\mathbf{IV}),\ s\ 0.04. \qquad (14)$$

In Eqs. (14) and (15), $N_C(C)$ is the number of carbon atoms in acid residue [for formyl, $N_C(C) = 1$, *etc.*] and $N_C(N)$ is the number of carbon atoms in radicals bound to nitrogen [for *N,N*-dimethyl derivatives, $N_C(N) = 2$, etc.]. The average deviation of the enthalpies of transfer of DMF, *N,N*-diethylformamide, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide, calculated by Eqs. (12)–(14), from the corresponding experimental values was 0.26 kJ/mol.

Thus, the obtained relationships can be used both for calculation of the enthalpies of transfer of the amides under study in the water–formamide mixed solvent throughout the entire range of compositions and for prediction of $\Delta_{tr}H^0$ for others alkylamides of carboxylic acids.

To conclude, the following results of the research can be noted. Solvation of tertiary amides of carboxylic acids and of HMPA throughout the entire range of compositions of the mixed solvent enhances in the order DMF < *N,N*-diethylformamide < *N,N*-dimethylacetamide < *N,N*-diethylacetamide < HMPA. Solvation of tertiary alkylamides weakens, as the formamide content of the mixture increases. The main increase in the enthalpies of transfer from water into the mixed solvent, that occurs in the range 0–0.45 mole fraction, results from weakening of both nonspecific and specific solvation. The compositions of the solvation shells suggest no selective solvation of amide molecules throughout the entire range of compositions, except for the region of equimolar contents of the components. Correlation equations for description and prediction of the enthalpies of transfer of tertiary amides of carboxylic acids in the water–formamide mixed solvent are deduced.

EXPERIMENTAL

Formamide, *N,N*-dimethylformamide, *N,N*-diethylformamide, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide were purified as described in [10]. The water contents of the organic solvents did not exceed 0.03 wt% (by Fisher titration [23].

Mixed solvents were prepared by the gravimetric method with an accuracy of 0.001 mole fraction, using freshly twice distilled water (specific electrical conductivity 10^{-5} S/cm).

The enthalpies of solution were measured on a variable-temperature isothermic-shell calorimeter. For the standard enthalpies of solution we took the mean heat effects of solution ($\Delta_s H^m$), since no dependence of $\Delta_s H^m$ on amide concentration was observed (Table 1). As shown in [10], our standard enthalpies of solution of the compounds in water are in a good agreement with published data.

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