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Enthalpy Characteristics and State of Formamides and Acetamides in Water–1,2-Ethanediol Mixtures

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Abstract—The effects exerted by the mixed solvent composition and by the structure and properties of solutes (*N,N*-disubstituted formamides and acetamides) on their thermochemical characteristics of solvation and transfer from water into water–1,2-ethanediol mixtures were considered. The composition of the solvation surrounding of the solutes was analyzed.

This work continues our studies of amide solutions in mixed solvents with hydrogen bond networks. We started these works from a water–formamide mixture [1]. The interest in amide solutions in water and mixed solvents is caused by the possibility of using them for modeling fragments of biomolecules. Fairly detailed data, including thermochemical data [2–7], are available for aqueous solutions of amides, whereas data for ternary systems water–organic solvent–amide (in infinitely dilute state) are scarce. The enthalpies of solution of some amides in mixtures of water with monohydric alcohols [8] and urea [7] were determined. At the same time, data on the effects exerted by the nature and composition of a solvent on the solvation of solutes would give insight into the state and reactivity of a substrate in solution.

The main goals of this study were, first, to find a correlation between the structures of *N,N*-dialkylamides and the thermochemical characteristics of their solvation in a mixed solvent water–1,2-ethanediol and, second, to study how the solvation and state of the amides are affected by the mixture composition. For this purpose, we measured calorimetrically the enthalpies of solution of formamide, dimethylformamide, diethylformamide, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide in water–1,2-ethanediol mixtures in the whole range of compositions at 298.15 K. The results are given in Tables 1 and 2. Earlier [12] we measured the enthalpies of solution of hexamethylphosphoramide. Its standard enthalpies of solution in the mixed solvent with compositions studied in this work are (kJ mol^{-1}) –49.52, –33.20, –23.50, –16.80, –16.70, –14.60, and –12.80.

The enthalpies of solution of *N,N*-disubstituted amides of the same acid noticeably differ from each other only in water and in mixtures with 1,2-ethanediol mole fraction less than 0.1 (Tables 1, 2). In this range of compositions, the solution of ethylamides is more exothermic as compared to methylamides.

The enthalpies of solvation of the amides under study, calculated by formula (1), are plotted in Fig. 1.

$$\Delta_{\mathrm{solv}}H^0 = \Delta_{\mathrm{soln}}H^0 - \Delta_{\mathrm{vap}}H. \tag{1}$$

Here $\Delta_{\mathrm{solv}}H^0$, $\Delta_{\mathrm{soln}}H^0$, and $\Delta_{\mathrm{vap}}H$ are the standard enthalpies of solvation, solution, and vaporization of a solute, respectively. The enthalpies of vaporization of the compounds are given in Table 2; $\Delta_{\mathrm{vap}}H$ of hexamethylphosphoramide is 61.10 kJ mol^{-1} [13], and its van der Waals molar volume is 110.65 cm^3 mol^{-1} [9].

Figure 1 shows that, in the entire range of compositions of the mixed solvent, the enthalpies of solvation of *N,N*-dialkylamides become more negative in the series dimethylformamide (DMF) < diethylformamide < *N,N*-dimethylacetamide < *N,N*-diethylacetamide < hexamethylphosphoramide. Such a trend is due, first, to strengthening solvophobic solvation of the compounds as the size of hydrocarbon radicals increases [14] and, second, to increasing basicity of the amides (donor numbers of DMF, diethylformamide, *N,N*-dimethylacetamide, *N,N*-diethylacetamide, and hexamethylphosphoramide are 26.6, 31.0, 27.8, 32.1, and 38 kcal mol^{-1}, respectively [15]).

The enthalpies of transfer of compounds from water into a mixed solvent reflect the effect exerted by variation of the mixture composition on the enthalpies

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Table 1. Thermal effects ($\Delta_{soln}H^m$, kJ mol^{-1}) of solution of formamide (**I**), DMF (**II**), *N*,*N*-diethylformamide (**III**), *N*,*N*-dimethylacetamide (**IV**), and *N*,*N*-diethylacetamide (**V**) in water–1,2-ethanediol mixed solvent at 298.15 K[a]

I		II		III		IV		V	
$m \times 10^4$	$\Delta_{soln}H^m$	$m \times 10^4$	$\Delta_{soln}H^m$	$m \times 10^4$	$\Delta_{soln}H^m$	$m \times 10^4$	$\Delta_{soln}H^m$	$m \times 10^4$	$\Delta_{soln}H^m$
$X = 0.130$									
495	2.97	257	–9.17	219	–9.45	172	–13.98	176	–15.56
1263	2.90	490	–9.21	397	–9.47	411	–13.9	389	–15.42
$X = 0.250$									
418	2.39	227	–6.44	250	–5.63	173	–10.57	142	–9.67
1152	2.35	450	–6.47	501	–5.62	388	–10.57	324	–9.63
$X = 0.505$									
590	1.19	215	–3.73	208	–2.91	165	–7.30	229	–6.11
1115	1.15	473	–3.76	498	–2.91	349	–7.26	399	–6.08
$X = 0.750$									
396	0.50	270	–2.22	176	–1.38	175	–4.93	175	–4.48
950	0.46	496	–2.27	410	–1.36	376	–4.90	371	–4.48
$X = 0.900$									
624	0.08	187	–1.29	207	–0.71	222	–3.44	186	–2.67
1162	0.08	367	–1.30	402	–0.68	416	–3.43	368	–2.65
$X = 1.00$									
698	–0.14	327	–0.76	194	–0.21	141	–2.91	158	–2.40
1768	–0.12	629	–0.76	331	–0.22	341	–2.92	331	–2.43

[a] (X) Mole fraction of $C_2H_4(OH)_2$ (here and in Tables 2–4); (m) molal concentration of a solute (mol/kg solvent).

Table 2. Standard enthalpies of solution ($\Delta_{soln}H^0$, kJ mol^{-1}) of amides in water–1,2-ethanediol mixed solvent, their enthalpies of vaporization ($\Delta_{vap}H^0$, kJ mol^{-1}), and van der Waals molar volumes (V_W, cm^3 mol^{-1}) at 298.15 K[a]

X	I		II		III		IV		V	
	$\Delta_{soln}H^0$	δ	$\Delta_{soln}H^0$	δ	$\Delta_{soln}H^0$	δ	$\Delta_{soln}H^0$	δ	$\Delta_{soln}H^0$	δ
0.00	1.97[b]		–15.22[b]		–17.97[b]		–21.42[b]		–24.08[b]	
0.13	2.94	0.04	–9.19	0.02	–9.46	0.01	–13.94	0.04	–15.49	0.07
0.25	2.37	0.02	–6.46	0.01	–5.63	0.00	–10.57	0.00	–9.65	0.02
0.50	1.17	0.02	–3.75	0.01	–2.91	0.00	–7.28	0.02	–6.10	0.02
0.75	0.48	0.02	–2.25	2.25	–1.37	0.01	–4.92	0.01	–4.48	0.00
0.90	0.08	0.00	–1.30	0.01	–0.70	0.02	–3.44	0.00	–2.66	0.01
1.00	–0.13	0.01	–0.76	0.00	–0.22	0.01	–2.92	0.00	–2.42	0.02
$\Delta_{vap}H^0$	60.13		46.89		50.32		50.23		54.11	
V_W	26.23		46.77		67.23		57.04		77.50	

[a] The compounds are denoted as in Table 1; (δ) arithmetic mean error. The values of V_W are taken from [9], and those of $\Delta_{vap}H$, from [10]. [b] Data of [11].

of solute solvation. They are calculated by formula (2) and are given in Fig. 2.

$$\Delta_{tr}H^0 = \Delta_{solv}H^0 - \Delta_{solv}H^0_1 = \Delta_{soln}H^0 - \Delta_{soln}H^0_1. \quad (2)$$

Here $\Delta_{solv}H^0$ and $\Delta_{soln}H^0$ are the standard enthalpies of solvation and solution of amides in a mixed solvent, and $\Delta_{solv}H^0_1$ and $\Delta_{soln}H^0_1$ are the standard enthalpies of their hydration and solution in water.

The solvation of all the amides under study becomes less exothermic in mixtures with a low $C_2H_4(OH)_2$ content, with the slope of the curve of $\Delta_{tr}H^0$ vs. 1,2-ethanediol concentration increasing with increas-

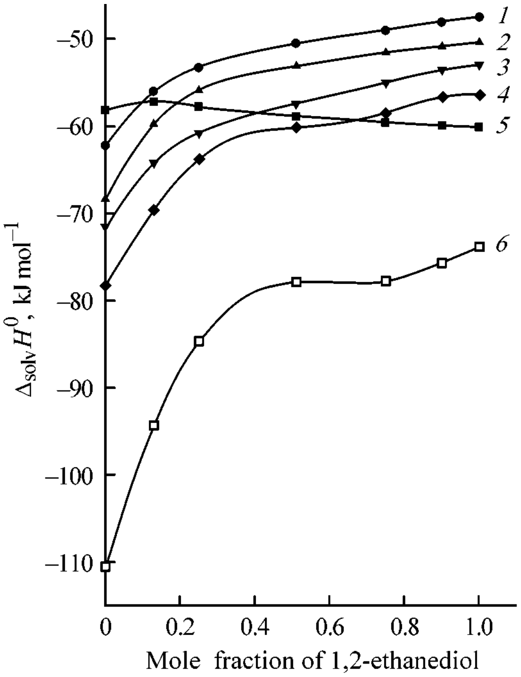

Fig. 1. Enthalpies of solvation of (*1*) dimethylformamide, (*2*) diethylformamide, (*3*) *N,N*-dimethylacetamide, (*4*) *N,N*-diethylacetamide, (*5*) formamide, and (*6*) hexamethylphosphoramide in water–1,2-ethanediol mixed solvent at 298.15 K as functions of the mixture composition.

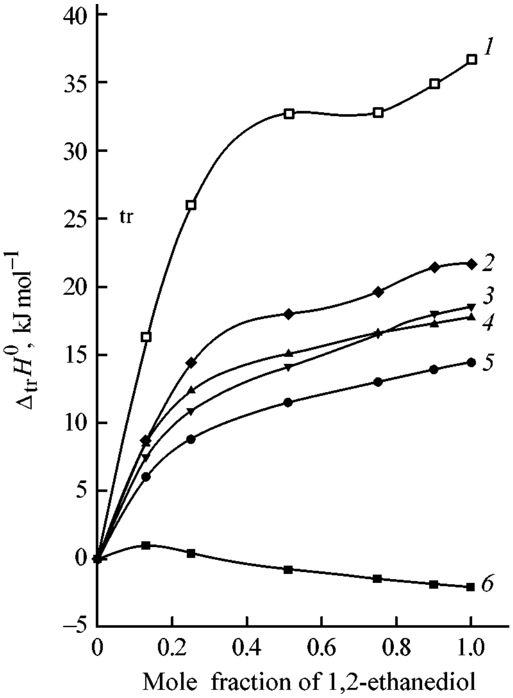

Fig. 2. Enthalpies of transfer of (*1*) hexamethylphosphoramide, (*2*) *N,N*-diethylacetamide, (*3*) *N,N*-dimethylacetamide, (*4*) diethylformamide, (*5*) dimethylformamide, and (*6*) formamide from water into $H_2O–C_2H_4(OH)_2$ mixed solvent at 298.15 K as functions of the mixture composition.

ing number of hydrocarbon (methyl and methylene) radicals in amide molecules. The weakest changes are characteristic of formamide, and the strongest, for hexamethylphosphoramide. Such a trend corresponds to a decrease in the contribution of hydrophobic hydration, which is weakened as the size of hydrocarbon radicals of solute molecules decreases [5, 6, 14] and the content of a nonaqueous component in the mixed solvent increases [16, 17].

In the case of *N,N*-dialkylamides, the enthalpies of transfer increase within the whole range of compositions of the $H_2O–C_2H_4(OH)_2$ mixtures. Along with the above-mentioned decrease in the effect of hydrophobic hydration, there are two more factors acting in the same direction and determining a decrease in solvation of the amides. First, positive $\Delta_{tr}H^0$ values may be due to the fact that an increase in the diol content in a mixture leads to a greater endothermic contribution of nonspecific solvation of amides. Here, by this value is meant the sum of enthalpy contributions from the formation of a cavity in a solvent to accommodate an amide molecule and also from van der Waals interaction of an amide with a solvent. The increase in the endothermicity of xenon transfer with increasing content of 1,2-ethanediol in a mixture [18] (Fig. 3) and also the positive enthalpy of hexane transfer from H_2O to $C_2H_4(OH)_2$ (4.3 kJ mol^{-1}), as calculated from the data of [19, 20], indicate that the nonspecific solvation of amides is weakened. The change in the nonspecific solvation of amides can also be estimated using the contributions of methylene radicals to the enthalpies of transfer of amides. The enthalpies of transfer of a CH_2 group can be formally calculated by relationships (3)–(7) based on the compositions and structures of amide molecules.

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

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

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

$$\Delta_{tr}H^0(CH_2) = [\Delta_{tr}H^0(\mathbf{V}) - \Delta_{tr}H^0(\mathbf{III})], \quad (6)$$

$$\Delta_{tr}H^0(CH_2) = [\Delta_{tr}H^0(\mathbf{V}) - \Delta_{tr}H^0(\mathbf{IV})]/2. \quad (7)$$

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

Formulas (3), (4), and (7) allow us to calculate the enthalpies of transfer of methylene radicals bound to

Table 3. Some properties of the $H_2O–C_2H_4(OH)_2$ mixture at 298.15 K[a]

Parameter	X						
	0	0.13	0.25	0.51	0.75	0.9	1
E_T^N	1.00	0.94	0.89	0.84	0.81	0.80	0.79
H^E	0	–536	–713	–607	–343	–144	0
V	18.07	22.61	27.23	36.85	46.26	52.05	55.92
p	2.297	1.991	1.769	1.468	1.290	1.211	1.167

[a] Values of E_T^N are taken from [22]; H^E (J mol^{-1}), from [23]; and V (cm^3 mol^{-1}), from [24]. p (kJ cm^{-3}) is the cohesion energy density of the solvent. The enthalpies of vaporization of water and 1,2-ethanediol are 43.99 [25] and 61.1 kJ mol^{-1} [25], respectively.

the nitrogen atom, and formulas (5) and (6), the enthalpies of transfer of acetyl CH_2 groups. The values thus calculated are plotted in Fig. 3, showing that the enthalpies of transfer of methylene groups are positive and increase as the content of 1,2-ethanediol in a mixture grows. However, variation of the mixture composition affects the solvation of methylene groups differently, which is not unexpected. The structure of amide molecules is such that the N-bonded and acetyl CH_2 groups have different closest surroundings. Therefore, they are not energetically equivalent and have different equilibrium geometries [21]. The solvation of N-bonded [formula (3)] and acetyl [formulas (5) and (6)] methylene groups is weakened to a greater extent as compared to CH_2 fragments remote from the polar group in a chain [formulas (4) and (7)]. Functional groups are known to affect solvation of nonpolar radicals in compounds of other homologous series also. For example, in alcohols the contribution of the methylene group to the enthalpy of hydration varies from 7.6 kJ mol^{-1} for $C_1–C_2$ to 3.9 kJ mol^{-1} for $C_5–C_6$ [17].

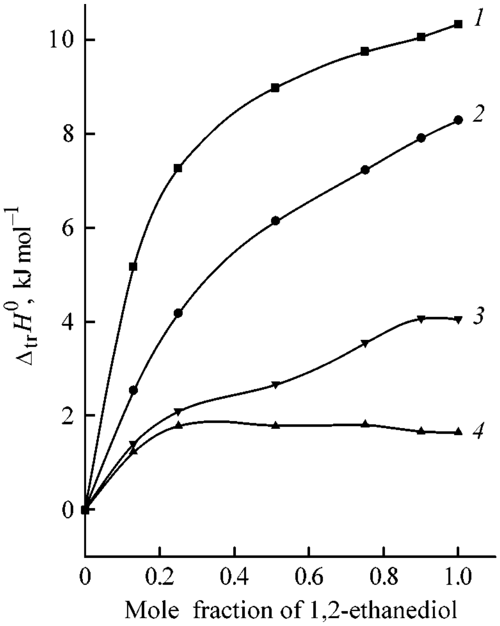

Fig. 3. Enthalpies of transfer of (*1*) xenon and (*2–4*) methylene radicals of amides from water into a mixed solvent $H_2O–C_2H_4(OH)_2$ as functions of the mixture composition at 298.15 K. Curves *2–4* were calculated by formulas (3), (5), and (4), respectively.

The contribution of the specific interaction amide (electron donor)–solvent (electron acceptor) should also become more endothermic as the content of 1,2-ethanediol in a mixture increases. A change in the solvatochromic parameter E_T^N suggests a decrease in the acidity of a solvent [22] (Table 3). As expected, an increase in the enhalpy of transfer due to weakening specific interaction is more pronounced for hexamethylphosphoramide (Fig. 2) having the highest electron-donor power among the compounds under study [14].

Figure 2 shows that the dependence of the enthalpy of transfer of formamide on the mixed solvent composition differs from those obtained for tertiary amides in that it passes through a maximum at the 1,2-ethanediol mole fraction of 0.1. The weakening of the formamide solvation at mole fractions of $C_2H_4(OH)_2$ of 0 – 0.1 is due to the same reasons as for *N,N*-dialkylamides. At the same time, it is difficult to explain an increase in the formamide solvation with further increase in the 1,2-ethanediol content (Table 3) in terms of variation of the mixture properties responsible for the energy of nonspecific solvation and specific interaction. It should be noted that not only electron-acceptor power of a mixed solvent (Table 3), but also its electron-donor power decrease with increasing concentration of 1,2-ethanediol. The donor number (*DN*) of associated liquid water (33 kcal mol^{-1} [25]) is much greater than that of 1,2-ethanediol (20 kcal mol^{-1} [25]).

The molecular-statistical approach [26] shows that, when considering the enthalpy of solvation, three contributions should be taken into account: the enthalpy of formation of a cavity in a solvent, the enthalpy of the intermolecular interaction solute–solvent, and the enthalpy of the solvent structural reorganization caused by introduction of a solute. The estimation of the structural contribution to thermodynamic characteristics is still the matter of discussions. Traditionally, the difference between an experimental thermodynamic characteristic and its value calculated in the framework of a certain model approximation is considered as the structural contribution. In [27], we showed that the ratio of the difference between the experimental enthalpy of solvation and that calculated within the framework of the scale-particle theory (SPT) to the van der Waals molar volume of a solute is proportional to the cohesion energy density of the solvent [Eq. (8)].

$$[\Delta_{\mathrm{solv}}H^0 - \Delta_{\mathrm{solv}}H^{\mathrm{SPT}}]/V_{\mathrm{W}} = \Delta_{\mathrm{str}}H^0/V_{\mathrm{W}} = a + b\,(p - p_{\mathrm{A}}). \qquad (8)$$

Here $\Delta_{\mathrm{solv}}H^{\mathrm{SPT}}$ is the enthalpy of solvation of a solute calculated within the framework of the scale-particle theory; $\Delta_{\mathrm{str}}H^0$ is the enthalpy of structural reorganization of the solvent; p and p_{A} are the cohesion energy densities of the solvent and solute, respectively; V_{W} is the van der Waals molar volume of a solute calculated from group contributions [9]; a and b are the fitting factors calculated by regression analysis.

Using expression (8), we can calculate $\Delta_{\mathrm{str}}H^0$ by formula (9) and its change upon transfer of a solute from a reference solvent into a solvent under study, by expression (10).

$$\Delta_{\mathrm{str}}H^0 = aV_{\mathrm{W}} + b(p - p_{\mathrm{A}})V_{\mathrm{W}}, \qquad (9)$$

$$\Delta_{\mathrm{tr,\,str}}H^0 = b(p - p_1)V_{\mathrm{W}}. \qquad (10)$$

Here p_1 is the cohesion energy density of a reference solvent.

It is assumed that solvent structurization (hardness) is responsible for its structural reorganization upon introducing a solute [28]. All solvents have certain hardness. The cohesion energy density of a solvent can serve as its measure. The $\Delta_{\mathrm{str}}H^0$ values calculated by formula (9) seem to be relative and different from the real values. However, such an approach to the determination of the enthalpy of structural reorganization allows us to make consistent the experimental and calculated enthalpies of transfer of a solute and the corresponding conclusions on the effect of solvent properties on the solvation. The data of [27] show that the difference ($\Delta_{\mathrm{solv}}H^0 - \Delta_{\mathrm{solv}}H^{\mathrm{SPT}}$) increases with increasing cohesion energy density of the solvent. Therefore, the coefficient b is positive. Its value calculated from the data in [27] is 0.5. It was found in [29] that the calculated values of $\Delta_{\mathrm{tr,\,str}}H^0$ differ from each other insignificantly in the range $1 > b > 0.5$. Therefore, in this study, as in the previous papers [27, 29, 30], we used the value of b equal to unity. The cohesion energy density of a mixed solvent was calculated by formula (11) [30, 31].

$$p = [(1 - X)\Delta_{\mathrm{vap}}H_1 + X\Delta_{\mathrm{vap}}H_2 - H^E - RT]/V. \qquad (11)$$

Here X is the mole fraction of a nonaqueous component in a mixture, $\Delta_{\mathrm{vap}}H_1$ and $\Delta_{\mathrm{vap}}H_2$ are the enthalpies of vaporization of water and cosolvent, H^E is the enthalpy of mixing of the components, and V is the molar volume of the mixture.

The contribution of $\Delta_{\mathrm{tr,\,str}}H^0$ to the enthalpy of solute transfer will decrease with increasing content of the nonaqueous component in the mixture because of decreasing cohesion energy density of the mixed solvent (Table 3). Just this factor is responsible for the shape of the composition dependences of the enthalpy of formamide transfer in a water–1,2-ethanediol mixture, namely, strengthening of its solvation in the range of 1,2-ethanediol mole fractions 0.1–1.0. A different trend could be expected from the above conclusions that the nonspecific solvation of the compounds weakens in the mixed solvent under study and from the tendency toward a decrease in the amide–solvent specific interaction due to weakening of the electron-acceptor and electron-donor power with increasing 1,2-ethanediol content. For *N,N*-dialkylamides, the changes in the enthalpies of nonspecific solvation and specific interaction dominate over the change in the contribution of the solvent structural reorganization.

In [30], we proposed a technique for estimating the composition of solvation shells of solute molecules in a binary mixture from thermochemical data. For this purpose, we used the enthalpy of solvent transfer minus the enthalpy of solvent structural reorganization ($\Delta_{\mathrm{tr}}H^*$) calculated by formula (12).

$$\Delta_{\mathrm{tr}}H^* = \Delta_{\mathrm{tr}}H^0 - \Delta_{\mathrm{tr,\,str}}H^0. \qquad (12)$$

The calculation of the composition of the solute solvation shell is based on the assumption that the deviation of $\Delta_{\mathrm{tr}}H^*$ from an additive value with respect to the composition is associated with the difference between the composition of the solvate shell and the bulk composition of the mixed solvent expressed in volume fractions. It should be noted that the use of $\Delta_{\mathrm{tr}}H^*$

Table 4. Composition (mol % of 1,2-ethanediol) of the solvation shell of amide molecules, their hydrocarbon radicals, and xenon (Xe) in a water–1,2-ethanediol mixture at 298.15 K[a]

X	**I**	**II**	**III**	**IV**	**V**	**VI**	(3)	(4)	(5)	(6)	(7)	Xe
13	14	12	13	12	12	13	11	14	12	8	11	14
25	26	24	25	24	25	26	23	28	23	23	28	27
51	51	49	50	48	50	52	47	53	45	48	55	52
75	76	73	74	73	73	73	71	78	72	67	75	76
90	90	89	89	90	90	88	88	91	92	96	93	90

[a] For notation of the compounds (Roman numerals), see Table 1; (3)–(7) are the numbers of the equations by which the enthalpies of transfer of the methylene radicals were calculated.

has two important advantages in the determination of the solvation shell composition: it characterizes not the total enthalpy of transfer, but its components, except for the structural contribution; for all the compounds studied, the dependences of $\Delta_{tr}H^*$ on the mixture composition have no extrema.

To calculate the volume fraction of 1,2-ethanediol in the solvation shell of amide molecules, we used expression (13).

$$\phi^* = \phi + \frac{\Delta_{tr}H^*(\text{water} \to \text{water–1,2-ethanediol})}{\Delta_{tr}H^*(\text{water} \to \text{1,2-ethanediol})} - \frac{\Delta_{tr}H^*_{ad}(\text{water} \to \text{water–1,2-ethanediol})]}{\Delta_{tr}H^*(\text{water} \to \text{1,2-ethanediol})}. \qquad (13)$$

Here ϕ^* and ϕ are the volume fractions of 1,2-ethanediol in the solvation shell and in the solvent bulk, respectively; $\Delta_{tr}H^*_{ad}$ is the enthalpy of transfer additive with respect to ϕ.

The mole fraction of 1,2-ethanediol in the solvation shell can be calculated by formula (14).

$$X^* = \phi^* V_1/[\phi^* V_1 + (1 - \phi^*)V_2]. \qquad (14)$$

Here X^* is the mole fraction of 1,2-ethanediol in the solvation shell of an amide molecule, and V_1 and V_2 are the molar volumes of water and 1,2-ethanediol, respectively. The calculated data are given in Table 4.

Table 5. Coefficients and regression parameters of Eq. (13)[a]

Compound no.	a_1	a_2	s	R^2
I	4.12	–6.34	0.19	0.9782
II	20.32	–6.20	0.32	0.9968
III	30.69	–13.32	0.37	0.9972
IV	24.19	–6.06	0.51	0.9952
V	32.66	–11.25	0.55	0.9960
VI	64.19	–28.71	1.10	0.9943

[a] For the notation of compounds, see Table 1. (s) Standard deviation and (R) correlation coefficient.

The data obtained using this model show that, in the water–1,2-ethanediol mixture, the amide molecules under consideration are not solvated selectively. It can be noted that hydrocarbon radicals bound to the nitrogen atom are somewhat preferentially solvated with 1,2-ethanediol, and the amide group, with water. The preferential coordination of water molecules at the amide group seems to affect the solvation of the acetyl methylene group. These phenomena may be due to both energy and steric factors. The energy of the specific interaction amide–water is higher, compared to amide–1,2-ethanediol, owing to the higher electron-acceptor power of water. At the same time, $C_2H_4(OH)_2$ molecules are larger than H_2O molecules; therefore, the arrangement of large molecules near polar groups can be hindered sterically.

The enthalpies of transfer of amides from water into a mixed solvent H_2O–$C_2H_4(OH)_2$ are satisfactorily described by second-order polynomials with respect to the solvent composition expressed in $C_2H_4(OH)_2$ volume fractions [Eq. (15)].

$$\Delta_{tr}H^0 = a_1\phi + a_2\phi^2. \qquad (15)$$

Here a_1 and a_2 are the coefficients to be determined by regression analysis.

The coefficients and regression parameters of Eq. (15) are given in Table 5. It is seen that the coefficients a_1 and a_2 regularly change with increasing, on the one hand, number of carbon atoms in the acid residue and, on the other hand, number of carbon atoms in substituents at the amino groups. For *N,N*-dialkylformamides and -acetamides (compounds **II**–**V**, Tables 1 and 2), these coefficients are described by Eqs. (16) and (17).

$$a_1 = 8.46 + 2.927N_C(C) + 4.717N_C(N);\ n\ 4,\ s\ 0.47, \qquad (16)$$

$$a_2 = -1.62 + 1.1N_C(C) - 3.08N_C(N);\ n\ 4,\ s\ 0.48. \qquad (17)$$

Here $N_C(C)$ is the number of carbon atoms in the acid residue [for formyl, $N_C(C) = 1$ etc.], and $N_C(N)$ is the number of carbon atoms in radicals bound to the nitrogen atom [for *N,N*-dimethyl derivatives, $N_C(N) = 2$ etc.]. The average error of approximating the enthalpies of transfer of DMF, diethylformamide, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide was $0.43\ \mathrm{kJ\ mol^{-1}}$.

The coefficients of Eqs. (15) for formamide and hexamethylphosphoramide (Table 5) also fit the above-mentioned tendency. As expected, among the compounds studied, formamide has the largest coefficient a_1, and hexamethylphosphoramide, the smallest. On the whole, the coefficients a_2 also obey expressions (16) and (17). These expressions can be used both for calculating the enthalpies of transfer of the amides under study in the whole range of compositions of the water–1,2-ethanediol mixture and for forecasting the $\Delta_{tr}H^0$ values for other alkylamides of carboxylic acids.

EXPERIMENTAL

Formamide, dimethylformamide, diethylformamide, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide were purified as described in [10]. Pure grade 1,2-ethanediol was purified by twofold fractional vacuum distillation at 353 K. The water content in organic solvents, as determined by Fischer titration [32], did not exceed 0.03 wt %.

Mixed solvents were prepared gravimetrically with an accuracy of 0.001 mole fraction, using freshly double-distilled water (electrical conductivity $10^{-5}\ \mathrm{S\ cm^{-1}}$).

The enthalpies of solution were measured on a variable-temperature calorimeter with an isothermal jacket. The arithmetic mean values of the thermal effects of solution ($\Delta_{soln}H^m$) were taken as the standard enthalpies of solution, because the $\Delta_{soln}H^m$ values are independent of m in the examined concentration ranges of the solutes (Table 1). It was shown [10] that our values of the standard enthalpies of solution of amides in water are in good agreement with published data.

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