Russian Journal of General Chemistry, Vol. 73, No. 4, 2003, pp. 511–518. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 4, 2003, pp. 545–552.
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Group Contributions to the Enthalpy Characteristics of Solutions of Formic and Acetic Acid Amides in Water–1,2-Propanediol Mixtures

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Received April 16, 2001

Abstract—Enthalpies of solution of formamide and of dimethyl and diethyl derivatives of formamide and acetamide in mixtures of water with 1,2-propanediol at 298.15 K were determined thermochemically. The contributions of hydrocarbon radicals and polar groups to the enthalpies of solution, vaporization, and solvation of the amides were determined. The influence exerted by the structure of molecules and the composition of mixtures on the enthalpy characteristics was considered.

This work continues a systematic study of solutions of formic and acetic acid amides in mixed solvents with hydrogen bond networks. The solvation of amides in mixtures of water with formamide and ethylene glycol was studied earlier [1, 2]. Owing to a larger size of the hydrocarbon radical and especially to the presence of a methyl group in its molecule, 1,2-propanediol is more hydrophobic than the abovementioned compounds. This is proved by the values of Gibbs pair interaction coefficients determined in [3]. The structure of aqueous solutions of diols is characterized by the presence of a hydrogen bond network [4]. However, different intensity of intermolecular interactions of diols of various structures with water determines structural features of these systems. Matsumoto *et al*. [5] assigned 1,2-propylene glycol to structure-making compounds exerting an effect similar to that of ethanol. The researchers' interest in solutions of amides in water and mixed solvents is determined by the possibility of using them for simulation of biomolecules. In this connection, we examined, on the one hand, the influence exerted by the nature, composition, and structural features of the solvent on the solvation of amide molecules, and, on the other, the interrelation between the structure of heterofunctional amide molecules and the enthalpies of their solvation. The features of the solvation of alkyl radicals and polar functional groups were also studied.

To this end, we have measured the enthalpies of solution of formamide, dimethylformamide (DMF), diethylformamide, *N*,*N*-dimethylacetamide, and *N*,*N*-diethylacetamide in mixtures of water with 1,2-propanediol in the entire range of their compositions. The measurements were carried out calorimetrically at 298.15 K. The experimental data obtained are given in Table 1.

Figure 1 shows the enthalpies of solvation ($\Delta_{\mathrm{solv}}H^0$) of the amides under study, calculated by formula (1) from the standard enthalpies of solution ($\Delta_{\mathrm{soln}}H^0$) and vaporization ($\Delta_{\mathrm{vap}}H$) given in Table 2.

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

Figure 1 shows that, in the entire range of compositions of the mixed solvent, the negative enthalpies of solvation of dialkylamides grow in the order DMF < diethylformamide < *N*,*N*-dimethylacetamide < *N*,*N*-diethylacetamide. Such an order can result, first, from strengthening of the solvophobic solvation of compounds with increasing size of a hydrocarbon radical [9] and, second, from increase in the base properties of the amides (the donor numbers of DMF, diethylformamide, *N*,*N*-dimethylacetamide, and *N*,*N*-diethylacetamide are 26.6, 31.0, 27.8, and 32.1 kcal/mol, respectively [10]). The negative enthalpy of solvation of the above amides in the previously studied systems water–formamide [1] and water–1,2-ethanediol [2] increases in the same order. Thus, the properties of dissolved amides exert a greater effect on their solvation than the nature of the solvent.

The effect of the mixture composition on the enthalpies of solvation of the compounds is reflected in the enthalpies of their transfer from water into the mixed solvent, which were calculated by formula (2). These data are presented in Fig. 2.

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Table 1. Thermal effects ($\Delta_{soln}H^m$, kJ/mol) of solution of formamide (**I**), DMF (**II**), diethylformamide (**III**), *N*,*N*-dimethylacetamide (**IV**), and *N*,*N*-diethylacetamide (**V**) in mixed solvent water–1,2-propanediol 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_2 0.125					
491	3.79	256	–7.07	191	–5.73	176	–11.53	186	–10.17
972	3.75	487	–7.11	415	–5.77	372	–11.55	402	–10.09
				X_2 0.249					
580	2.29	255	–4.80	348	–2.90	285	–8.67	277	–6.63
1267	2.28	484	–4.79	562	–2.95	508	–8.64	474	–6.58
				X_2 0.499					
546	0.76	368	–2.94	257	–1.83	197	–6.08	242	–4.81
1003	0.79	669	–2.91	527	–1.85	422	–6.05	469	–4.80
				X_2 0.750					
500	0.26	295	–0.96	260	–0.45	316	–3.24	193	–3.01
1188	0.27	635	–0.97	516	–0.43	613	–3.24	440	–2.99
				X_2 0.900					
642	0.05	360	0.27	363	0.41	301	–1.97	243	–1.71
1102	0.05	733	0.24	683	0.43	586	–1.94	404	–1.68
				X_2 1.00					
630	–0.13	244	1.07	257	0.96	298	–0.91	171	–1.02
1227	–0.11	533	1.10	466	0.96	713	–0.98	448	–1.13

[a] *m* (mol/kg of a solvent) is the molal concentration of a solute; X_2 is the mole fraction of $C_3H_6(OH)_2$.

Table 2. Standard enthalpies of solution ($\Delta_{soln}H^0$, kJ/mol) and vaporization ($\Delta_{vap}H$, kJ/mol) of formamide, DMF, diethylformamide, *N*,*N*-dimethylacetamide, and *N*,*N*-diethylacetamide in mixed solvent water–1,2-propanediol at 298.15 K and electron-acceptor power of the mixtures (E_T^N)[a]

X_2	**I**	**II**	**III**	**IV**	**V**	E_T^N [6]
			$\Delta_{soln}H^0$			
0.00	1.97[b]	–15.22[b]	–17.97[b]	–21.42[b]	–24.08[b]	0.992
0.13	3.77 ± 0.02	–7.09 ± 0.02	–5.75 ± 0.02	–11.54 ± 0.01	–10.13 ± 0.04	0.855
0.25	2.29 ± 0.01	–4.80 ± 0.01	–2.92 ± 0.03	–8.65 ± 0.02	–6.61 ± 0.03	0.804
0.50	0.77 ± 0.02	–2.93 ± 0.02	–1.84 ± 0.01	–6.07 ± 0.02	–4.80 ± 0.01	0.760
0.75	0.26 ± 0.01	–0.97 ± 0.01	–0.44 ± 0.01	–3.24 ± 0.01	–3.00 ± 0.01	0.741
0.90	0.05 ± 0.01	0.25 ± 0.02	0.42 ± 0.01	–1.95 ± 0.02	–1.69 ± 0.02	0.734
1.00	–0.12 ± 0.01	1.09 ± 0.02	0.96 ± 0.01	–0.95 ± 0.03	–1.08 ± 0.05	0.730
			$\Delta_{vap}H$			
	60.13[c]	46.89[c]	50.32[c]	50.23[c]	54.11[c]	

[a] Numbering of compounds as in Table 1. [b] Data of [7]. [c] Data of [8].

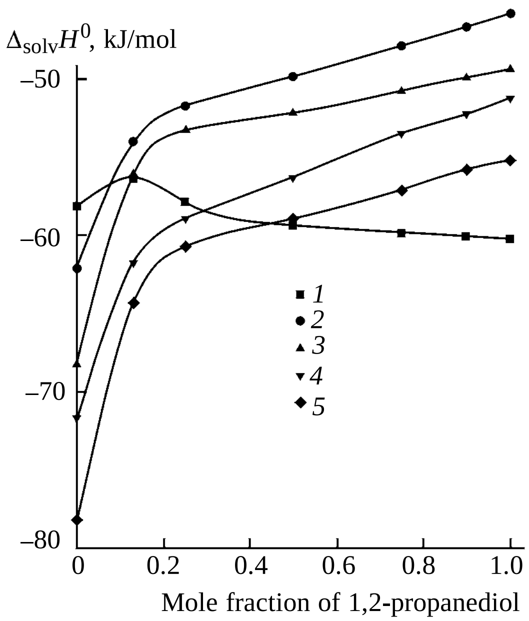


Fig. 1. Enthalpies of solvation of (*1*) formamide, (*2*) DMF, (*3*) diethylformamide, (*4*) *N,N*-dimethylacetamide, and (*5*) *N,N*-diethylacetamide in the mixed solvent water–1,2-propanediol at 298.15 K vs. composition of the mixture.

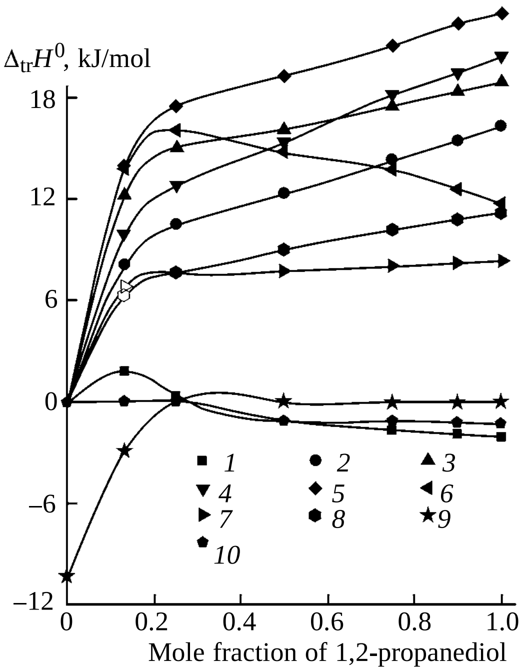


Fig. 2. Enthalpies of transfer of (*1*) formamide, (*2*) DMF, (*3*) diethylformamide, (*4*) *N,N*-dimethylacetamide, (*5*) *N,N*-diethylacetamide, (*6*) xenon, (*7*) ethylformamide, and (*8*) *N*-methylacetamide from water into the mixed solvent water–1,2-propanediol; partial molar excess enthalpies of (*9*) 1,2-propanediol and (*10*) water at 298.15 K, vs. composition of the mixture.

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

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

To account for the concentration dependences of the enthalpies of solvation of amides, we will consider the energy states of the components in the mixed solvent water–1,2-propanediol. The partial molar excess enthalpies of water (h_1) and 1,2-propanediol (h_2) as functions of the mixture composition are plotted in Fig. 2. From the integral enthalpies of mixing (H^E) [5], we calculated in [11] the quantities h_1 and h_2 by formulas (3) and (4).

$$h_1 = H^E - H_2(\partial H^E/\partial X_2), \quad (3)$$

$$h_2 = H^E + (1 - X_2)(\partial H^E/\partial X_2). \quad (4)$$

These values reflect the enthalpy component of the free energy of solution of components in a mixed solvent. It is seen that, as the concentration of $C_3H_6(OH)_2$ increases, the intensity of the intermolecular interaction of water with a binary mixture grows and the interaction of 1,2-propanediol with it weakens. It seems to result from binding of water molecules in strong heteroassociates.

The strong heteroassociation in the system H_2O–$C_3H_6(OH)_2$ seems to be a reason for the nonlinear reduction of the electrophilic properties of the mixed solvent occurring as the content of the diol grows. The E^N_T values for the mixed solvent, which characterize its electron-acceptor (H-donor) power [6], are given in Table 2. This parameter changes most considerably in the region of small additions of propylene glycol. Approximately a half of the total change in E^N_T occurs in the range of $C_3H_6(OH)_2$ mole fractions from 0 to 0.13. The decrease in the acid properties of the mixture causes weakening of specific solvation of the dissolved amides, as this solvation is due to the donor–acceptor interaction of amide as electron donor with the solvent as electron acceptor.

The intensive intercomponent interaction in the binary mixture should result in a decrease in the hydrophobic hydration of amides and in weakening of the nonspecific solvation of amides in the H_2O–$C_3H_6(OH)_2$ mixture. The latter conclusion is confirmed by the change in the enthalpies of transfer of xenon from water into the mixed solvent H_2O–

Table 3. Number of equivalent methylene groups, C–H bonds, and distinguished structural fragments in molecules of formamide, DMF, diethylformamide, *N*,*N*-dimethylacetamide, and *N*,*N*-diethylacetamide[a]

Parameter	**I**	**II**	**III**	**IV**	**V**
$N(CH_2)^b$	0.5	3.5	5.5	4.5	6.5
N(CH)	1	7	11	9	13
$m(CH)_N$	0	6	10	6	10
$n(CH)_C$	1	1	1	3	3
k(NH)	2	0	0	0	0
l(Y)	1	1	1	1	1

[a] Compound numbering as in Table 1. [b] Data of [15].

$C_3H_6(OH)_2$, which were calculated from the data of [12] and are presented in Fig. 2. The comparison of $\Delta_{tr}H^0$ for dialkylamides and xenon shows that the changes in the nonspecific and specific solvation act in the same direction in the region of low contents of the diol in a mixture, and in the region of high contents of the nonaqueous component they exert a competing effect on the solvation of amides.

The plots of the enthalpies of transfer of amides vs. solvent composition flatten out at the propanediol mole fraction in the mixture of ~0.25. The comparison of the $\Delta_{tr}H^0 = f(X_2)$ dependences for amides with the functions h_1 (h_2) = $f(X_2)$ shows that, at a higher content of propanediol, the partial molar excess enthalpies of the mixture components also change insignificantly.

More substantiated conclusions on the nature and intensity of interparticle interactions in solutions can be made from consideration of particular contributions to the interactions. In experimental studies of molecular solutions, it is appropriate to single out the contributions to the thermodynamic characteristics from a hydrocarbon radical and a functional group of an organic compound. Such approach is simultaneously the basis for the systematization of the experimental data.

The contributions of nonpolar and polar fragments of a molecule can be determined using one or another scheme of the additive-group approach. There are two fundamentally different approaches to the separation of molecules into structural units [13]. The first approach suggests that each nucleus belongs to only one structural unit, i.e., boundaries between structural units do not pass through nuclei. In the second method, it is admitted that certain nuclei can belong to two or several structural fragments, i.e., the boundaries between structural units can pass through nuclei. We used the second approach in this work. Proceeding from the structure of amide molecules, the number of experimentally determined enthalpy characteristics, and trends in their variation, we distinguished four structural fragments: the amide group O=C–N, the N–H group, the C–H group in a radical bound to the nitrogen atom, and the C–H group in the acid residue. Abramzon and Slavin [14] chose the C–H bond as a structural unit in the description of enthalpies of vaporization of organic compounds. In Table 3 the indicated groups are designated as Y, NH, $(CH)_N$, and $(CH)_C$, respectively. It is evident that two $(CH)_N$ or $(CH)_C$ groups form a methylene radical, and three such groups, a methyl radical. However, it should be noted that the fragments $(CH)_N$ and $(CH)_C$, the methylene groups $(CH_2)_N$ and $(CH_2)_C$ formed from them, and also the methyl radicals $(CH_3)_N$ and $(CH_3)_C$ located in the acyl group and bound to the nitrogen atom are nonequivalent.

The enthalpies of vaporization and solution of formamides and acetamides under study were approximated by expression (5).

$$\Delta H^0 = m\Delta H^0(CH)_N + n\Delta H^0(CH)_C + k\Delta H^0(NH) + l\Delta H^0(Y). \qquad (5)$$

Here, $\Delta H^0 = \Delta_{soln}H^0$, $\Delta_{vap}H$, $\Delta_{tr}H^0$; *m*, *n*, *k*, and *l* are the numbers of the corresponding groups in the molecule, which are given in Table 3. The contributions of the distinguished structural units into $\Delta_{vap}H$ and $\Delta_{soln}H^0$ of amides were calculated by the multiple linear regression method. The data obtained are given in Table 4. Small inaccuracies and the high correlation coefficient show that the suggested model adequately describes the experimental data. The C–C bonds, which were not taken into account in the calculation, seem to be shielded, and their solvation can be neglected. The data on the enthalpies of solution in water of others alkylformamides and alkylacetamides with different degrees of N-substitution also well fit in the suggested scheme of separation of structural fragments. The average increment of the NH group into $\Delta_{soln}H^0$ in water for formamide, methylformamide, ethylformamide, and *N*-methylacetamide is 6.27±0.20 kJ/mol. The value of $\Delta_{soln}H^0(CH)_C$ for formamide, DMF, diethylformamide, *N*,*N*-dimethylacetamide, *N*,*N*-diethylacetamide, methylformamide, and *N*-methylacetamide is –3.12±0.08 kJ/mol. In the calculations we used the standard enthalpies of solution of methylformamide, ethylformamide, and *N*-methylacetamide of –7.00 [5], –9.65 [5], and –13.36 kJ/mol [5], respectively.

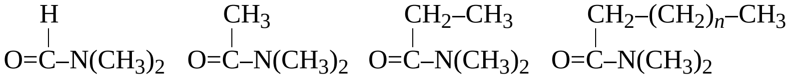
However, the enthalpies of solution and vaporization of *N*,*N*-dimethylpropionamide do not fit in the

Table 4. Increments of structural fragments of amide molecules to the enthalpy of their vaporization and solution in the mixed solvent water–1,2-propanediol at 298.15 K[a]

X_2	φ_2	$(CH)_N$	$(CH)_C$	NH	Y
0.00	0.00	–0.68 ± 0.01	–3.08 ± 0.02	6.58 ± 0.05	–8.11 ± 0.05
0.13	0.37	0.34 ± 0.01	–2.21 ± 0.02	6.47 ± 0.04	–6.97 ± 0.03
0.25	0.58	0.49 ± 0.02	–1.88 ± 0.04	5.03 ± 0.10	–5.90 ± 0.09
0.50	0.80	0.29 ± 0.02	–1.52 ± 0.04	2.75 ± 0.10	–3.20 ± 0.08
0.75	0.92	0.10 ± 0.04	–1.21 ± 0.07	0.87 ± 0.17	–0.26 ± 0.14
0.90	0.97	0.05 ± 0.01	–1.08 ± 0.02	0.07 ± 0.05	0.99 ± 0.05
1.00	1.00	–0.03 ± 0.01	–1.02 ± 0.01	–0.70 ± 0.01	2.30 ± 0.01
$\Delta_{vap}H$		0.91 ± 0.05	1.78 ± 0.11	9.42 ± 0.26	39.51 ± 0.23

[a] φ_2 is the volume fraction of $C_3H_6(OH)_2$ calculated by the formula $\varphi_2 = X_2V_2/(X_{V1} + X_{V2})$. The molar volumes of water (V_1) and 1,2-propanediol (V_2) are 18.07 and 73.7 cm^3/mol, respectively [16].

above correlation. The calculated value of $\Delta_{soln}H^0$ (–27.6 kJ/mol) is appreciably more negative than the experimental value (–22.34 kJ/mol [5]). Apparently, as the size of the hydrocarbon radical of molecules increases, there appear groups differing in the energy and geometric parameters from those considered for the amides under study. Nonmonotonic variation of the enthalpy characteristics is typical for organic compounds of various homologous series and is especially pronounced in the case of their aqueous solutions. The increase in the number of carbon atoms in an alkyl radical (N_C) to N_C 2–3 introduces the exothermic contribution to the enthalpy of solution in H_2O for alcohols [17, 18], amines [18, 19], ethers [20], carboxylic acids [18], ketones [21, 22], etc., whereas further introduction of methylene groups has an opposite effect. Belousov and Panov [23] explained such a dependence by the competitive effect of the hydrophobic hydration and specific features of dissolution of particles of various size in water. The prevalence of the hydrophobic hydration in the dissolution of the first homologs is due to the fact that small particles can be arranged in cavities in the water structure. Thus, the additivity of the contributions of methylene groups to the enthalpies of solution of organic compounds in water is obeyed starting from the third or fourth member of a homologous series. The observed course of the $\Delta_{soln}H^0 = f(N_C)$ plots is not unexpected and can be explained on the basis of the additivity of higher-order groups. Proceeding from the structures of molecules of organic compounds, we can distinguish (taking into account the nearest surrounding) the following structural fragments: $CH_3(C)$, $CH_2(C)_2$, $CH(C)_3$, $C(C)_4$, $CH_3(Y)$, $CH_2(Y)(C)$, $CH(Y)\cdot(C)_2$, $C(Y)(C)_3$, and Y(C). Here the kind and number of atoms in the first surrounding of the corresponding structural unit are indicated in parentheses. The character Y indicates a functional group, e.g., OH, Cl, NO_2, COOH, etc. The homologous series of *N*,*N*-dimethylalkylamides looks as follows.



$$O{=}\overset{\overset{H}{|}}{C}{-}N(CH_3)_2 \quad O{=}\overset{\overset{CH_3}{|}}{C}{-}N(CH_3)_2 \quad O{=}\overset{\overset{CH_2-CH_3}{|}}{C}{-}N(CH_3)_2 \quad O{=}\overset{\overset{CH_2-(CH_2)_n-CH_3}{|}}{C}{-}N(CH_3)_2$$

The size of the hydrocarbon radical in these amides grows as various groups appear in their molecules in the following order: $(Y)CH_3$, $(Y)CH_2(C)$, $(C)CH_3$, and $(C)_2CH_2$. The homologs of other classes of organic compounds are formed similarly. It is reasonable to suggest that the contributions of these groups to the enthalpy of solution will be different. Starting from the third member of the homologous series, the hydrocarbon radical becomes longer owing to the addition of the $CH_2(C)_2$ group only. This is the moment from which a monotonic change in the enthalpy of solution along homologous series of hydrocarbons and their monofunctional derivatives should be expected. The aforesaid suggests that the enthalpies of solution of *N*-propyl derivatives of alkylamides will probably be more positive than $\Delta_{soln}H^0$ of ethyl derivatives of alkylamides.

The enthalpies of solvation of structural units of amide molecules [O=C–N, N–H, $(CH)_N$, and $(CH)_C$]

Table 5. Increments of structural fragments of amide molecules to the enthalpy of their solvation in the mixed solvent water–1,2-propanediol at 298.15 K

X_2	$(CH)_N$	$(CH)_C$	NH	Y
0.00	–1.59	–4.86	–2.84	–47.62
0.13	–0.57	–3.99	–2.95	–46.48
0.25	–0.42	–3.66	–4.39	–45.41
0.50	–0.62	–3.30	–6.67	–42.71
0.75	–0.81	–2.99	–8.55	–39.77
0.90	–0.86	–2.86	–9.35	–38.52
1.00	–0.94	–2.80	–10.12	–37.21

calculated by formula (1) using data of Table 4 are listed in Table 5. As the enthalpy of solution is the sum of the enthalpies of solvation and vaporization of a solute [Eq. (1)], the nonmonotonic variation of the enthalpy characteristics is due to specific features of either solute–solvent interactions or interparticle interactions in the condensed solute. For the majority of classes of organic compounds, the enthalpies of vaporization are additive within the limits of errors for the entire homologous series, i.e., the groups $CH_2(Y)(C)$ and $CH_2(C)_2$, or $CH_3(Y)$ and $CH_3(C)$ are approximately equivalent from the viewpoint of energy. Therefore, the nonmonotonic variation of $\Delta_{soln}H^0$ is more probably due to the features of intermolecular interactions in solution. Namely, the interactions through a solvent between the groups that are not directly bound to each other seem to be significant. Another explanation for this effect suggests that the change in the solvent–solvent interactions caused by introduction of solute molecules contributes to the enthalpies of solvation of structural fragments. It is approriate to note here that the largest differences in the contributions of nonpolar groups take place in aqueous solution (Table 5). As the content of a nonaqueous component increases, the contributions of the $(CH)_N$ and $(CH)_C$ groups become more equivalent. The difference in enthalpies of their hydration is 3.3 kJ/mol, whereas the difference in $\Delta_{solv}H^0$ in 1,2-propanediol is only 1.8 kJ/mol, and the difference in the enthalpies of vaporization, which can be considered as the enthalpies of the self-solvation of the $(CH)_N$ and $(CH)_C$ groups, is only –0.9 kJ/mol. Savage and Wood [15] have advanced the approach which considers the additivity of contributions of nonpolar groups to the coefficients of pair interactions taking into account the number of equivalent methylene radicals. Our results show that this approach is mainly applicable to nonaqueous solutions.

Let us consider the contributions of polar groups to the enthalpy of solvation of formic and acetic acid amides. It is seen that the increment of the NH group to the intermolecular interaction in pure liquid amides (Table 4) exceeds the contribution of this group to the enthalpy of solvation of amides in water-rich mixed solvents (Table 5). It is the main reason for the endothermicity of the dissolution of primary amides in water. Positive $\Delta_{soln}H^0$ values are characteristic also of primary aromatic amines. The value of $\Delta_{soln}H^0$ for aniline in H_2O was found to be 1.82 and 1.88 kJ/mol in [24] and [25], respectively. Presumably, the endothermicity of the dissolution of primary amines results from the structure-breaking effect of their electron-acceptor groups on water. It is probable that the nitro group acts similarly. The value of $\Delta_{soln}H^0$ for nitromethane (CH_3NO_2) in water is 3.23 kJ/mol [26]. The conclusion that the water environment around NH_2 groups of formamide and urea is destabilized was made in [27, 28] on the basis of studying permittivity of their aqueous solutions and absorption of millimeter-wave electromagnetic radiation by these solutions. The decrease in the solvent contribution to the destabilization results in an increase in the exothermicity of the NH group solvation with increasing content of the nonaqueous component in a mixture. The change in the increment of the NH group makes the major contribution to the strengthening of the formamide solvation in the range of compositions to the right of the endothermic maximum (Fig. 2).

The amide group makes a considerable exothermic contribution to the enthalpies of solvation and solution of amides, because it is capable of donor–acceptor interaction with a solvent (Table 5). Its value strongly depends on the composition of a mixed solvent and decreases in the absolute value with increasing diol content, owing to weakening of the electron-acceptor power of the mixture (Table 2).

Figure 3 shows the enthalpies of transfer of polar and nonpolar structural units of molecules of formamides and acetamides from water into a mixed solvent as functions of its composition expressed in volume fraction of the nonaqueous component. The values of $\Delta_{tr}H^0$ were calculated by formula (2) using the data of Table 4. The values of $\Delta_{tr}H^0$ for hydrocarbon radicals and amide group are positive and determine the shape of the concentration dependence for N,N-substituted alkylamides (Fig. 2). The enthalpies of NH group transfer have the opposite sign. The isotherms presented in Fig. 3 are satisfactorily described by polynomial functions of the diol volume fraction in the mixture. The coefficients of the polynomials and regression parameters are given in Table 6. We have calculated the enthalpies of transfer of the amides under study, using the correlations

Table 6. Coefficients of polynomials $\Delta_{tr}H^0 = a_1\varphi + a_2\varphi^2 + a_3\varphi^3$ describing the dependences of the increments of structural fragments to the enthalpies of transfer of amides from water into a mixed solvent water–1,2-propanediol at 298.15 K[a]

Parameter[a]	$(CH)_N$	$(CH)_C$	NH	Y
a_1	3.89	2.04	3.69	7.31
a_2	–3.26	–	–10.75	–18.99
a_3	–	–		21.88
s	0.04	0.06	0.14	0.16
R^2	0.9924	0.9950	0.9998	0.9996

[a] s is the standard deviation (kJ/mol), and R is the correlation coefficient.

obtained and expression (5). The inaccuracy of the calculation was 0.1 kJ/mol for formamide, 0.2 kJ/mol for DMF, 0.3 kJ/mol for diethylformamide and *N,N*-dimethylacetamide, and 0.5 kJ/mol for *N,N*-diethylacetamide. The relationships obtained also allow us to forecast the enthalpies of transfer of other N-substituted alkylamides into water–1,2-propanediol mixtures within the entire area of compositions. The calculated isotherms $\Delta_{tr}H^0$ for ethylformamide and *N*-methylacetamide are shown in Fig. 2.

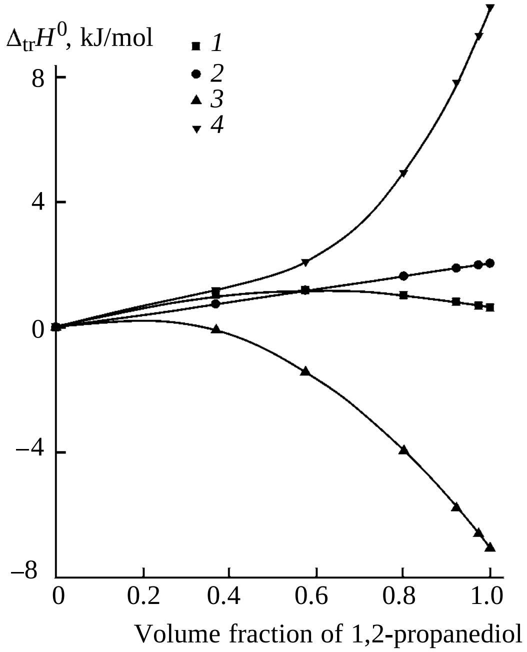


Fig. 3. Enthalpies of transfer of selected structural fragments of amide molecules [(*1*) $(CH)_N$, (*2*) $(CH)_C$, (*3*) NH, and (*4*) Y] from water into a mixed solvent water–1,2-propanediol at 298.15 K vs. mixture composition.

EXPERIMENTAL

The purification of formamide, dimethylformamide, diethylformamide, *N,N*-dimethylacetamide, and *N,N*-diethylacetamide was described in detail eslewhere [7]. Pure grade 1,2-propanediol was subjected to twofold vacuum fractional distillation at 353 K. The water content in organic solvents, determined by Fischer titration [29], did not exceed 0.03 wt%.

Mixed solvents were prepared gravimetrically with an accuracy of 0.001 (mole fraction) from freshly prepared double-distilled water (electrical conductivity 10^{-5} S/cm).

Enthalpies of solution were measured on a variable-temperature calorimeter with an isothermal jacket. The arithmetic mean values of the heat effects of solution ($\Delta_{soln}H^m$) were taken as the standard enthalpies of solution, because we have not found any dependence of $\Delta_{soln}H^m$ on the concentrations of amides (Table 1). In [7] we determined the standard enthalpies of solution of the compounds in water, which were well consistent with the published data.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 99-03-32414a).

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