Solvation enthalpies of formamides and acetamides in a water—glycerol mixture. Additivity of thermochemical characteristics of solutions

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The solution enthalpies of formamide and *N*,*N*-dimethyl- and diethylamides of formic and acetic acids in a water—glycerol mixed solvent were measured and the solvation enthalpies were calculated. The enthalpy coefficients of amide—glycerol pair interactions in aqueous solution were calculated. The effect of the mixture composition and the structure and properties of solutes on the enthalpic characteristics were considered. The contributions of structural fragments of the amide molecules to the enthalpic characteristics of solutions were calculated in the framework of the proposed additive scheme. This made it possible to analyze the role of nonspecific and specific solvations of the amides in solution and predict the vaporization, solution, and solvation enthalpies and enthalpy coefficients of pair interactions of experimentally unstudied *N*-methylformamide, *N*-ethylformamide, *N*-methyl-*N*-ethylformamide, *N*-methylacetamide, *N*-ethylacetamide, and *N*-methyl-*N*-ethylacetamide in a water—glycerol mixture, as well as donor numbers for these amides.

Key words: solution enthalpy, solvation enthalpy, enthalpy coefficients of pair interactions, additivity of thermodynamic properties of solutions, formamides, acetamides, mixed solvents, water, glycerol.

An important problem of the solutions chemistry is to reveal an interrelation between the thermodynamic properties of solutions of organic substances and the composition of compounds and structures of their molecules. To solve this problem, it seems promising to develop the additive-group method. It is of special interest to produce the developed additive schemes for description of properties of substances, whose molecules consist of fragments of compounds of different classes. Such compounds are amides, whose molecules contain fragments of carboxylic acids and amines. Studies of solutions of amides in water and mixed solvents are urgent, because they can be used for simulation of fragments of biomolecules. Aqueous solutions of glycerol and amides have been studied in rather detail, including thermochemical measurements.[1—5] However, ternary systems water—glycerol—amide (in an infinitely dilute state) remain unstudied. These data make it possible to characterize (in the framework of the McMillan—Mayer theory[6]) the strength of amide—glycerol pair interactions in aqueous solutions. We continued to study solutions of amides in mixed solvents with hydrogen bond networks.[7—9] The purpose of this work is to determine the thermochemical characteristics of dissolution and solvation of amides and to study the additivity of contributions of nonpolar and polar groups to the thermochemical characteristics of solutions.

Experimental

Thermal solution effects ($\Delta_{sol}H^m$) were measured and standard solution enthalpies ($\Delta_{sol}H^\circ$) of formamide (FA), dimethylformamide (DMF), diethylformamide (DEF), *N*,*N*-dimethylacetamide (DMA), and *N*,*N*-diethylacetamide (DEA) were calculated by the calorimetric method in water—glycerol mixtures in a composition interval of 0—0.2 molar fraction of nonaqueous component. For a higher glycerol content, the viscosity of the mixtures increased strongly, which impeded to stir the solvent in a calorimetric vessel and decreased the reproducibility of results. Substances used in the work (FA (pure); DMF, DEF, DMA, DEA (all Aldrich)) were purified according to a previously described procedure.[7] Glycerol (pure) was purified by double fractional vacuum distillation at 353 K. The water content in organic solvents determined by titration with the Fischer reagent[10] was at most 0.03 wt.%.

Mixed solvents were prepared by the gravimetric method (accuracy of down to 0.001 molar fraction) using fresh-prepared bidistilled water (specific conductivity 10^{-3} S m^{-1}).

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Solution enthalpies were measured on a variable-temperature calorimeter with an isothermic shell, whose design is similar to that described earlier.[11] A thermoresistor (Karmanov´s design) placed into a titanium case filled with Wood´s alloy was used as a temperature sensor in the calorimeter. The design of the calorimeter and measuring circuit provided thermometric and thermal sensitivities of 10^{-5} °C and $2 \cdot 10^{-3}$ J, respectively, per mm of the detector scale. To measure thermal solution effects, a comparative method was used, according to which the system was calibrated with electric current after each experiment. The relative random measurement error was at most 0.6%. Arithmetic mean thermal solution effects, $\Delta_{sol}H^m$, were taken as standard solution enthalpies, because they are independent of molality, m, in the studied region of solute concentrations (Table 1). Our standard solution enthalpies of amides in water[7] agree well with published data.

Results and Discussion

The obtained data are given in Tables 1 and 2. Below we present the donor numbers (DN)[12] and standard vaporization enthalpies ($\Delta_{vap}H°$) of amides.[13,14]

$\Delta_{vap}H°$/kJ mol^{-1}	60.13	46.89	50.32	50.23	54.11	61.1
DN/kcal mol^{-1}	36.0	26.6	31.0	27.8	32.1	38.8

The standard solution enthalpies of hexamethylphosphotriamide (HMPA) in a water—glycerol mixture are also given in Table 2. These values for the mixed solvent compositions studied in the present work were calculated by square interpolation of the earlier obtained[15] values of $\Delta_{sol}H°$.

Analysis of published data showed[16,17] that the additive scheme is usually used for studying the solution and solvation enthalpies of compounds of a homological series

$$\Delta_{solv}H° = a_N + b_N N_C, \quad (1)$$

where $\Delta_{solv}H°$ is the solvation enthalpy, N_C is the number of carbon atoms in the radical of the compound, and a_N and b_N are fitting coefficients.

Equation (1) assumes the additivity of the methylene group contribution (coefficient b_N) to the property under study. Analysis of numerous data on the properties of

Table 1. Themal solution effects ($\Delta_{sol}H^m$/kJ mol^{-1}) of amides (FA, DMF, DEF, DMA, and DEA) in a water—glycerol mixture at 298.15 K

X_2 (m_2)	FA		DMF		DEF		DMA		DEA	
	m_3	$\Delta_{sol}H^m$	m_3	$\Delta_{sol}H^m$	m_3	$\Delta_{sol}H^m$	m_3	$\Delta_{sol}H^m$	m_3	$\Delta_{sol}H^m$
0.0089	0.0655	2.02	0.0363	−14.68	0.0214	−16.98	0.0262	−20.68	0.0151	−22.88
(0.5)	0.1229	2.05	0.0623	−14.65	0.0425	−16.93	0.0483	−20.60	0.0278	−22.80
0.0177	0.0712	2.14	0.0267	−13.87	0.0174	−15.57	0.0263	−19.91	0.0154	−21.10
(1.0)	0.1459	2.16	—	—	0.0353	−15.62	—	—	0.0306	−21.20
0.0348	0.0733	2.29	0.0330	−12.92	0.0243	−14.90	0.0190	−18.45	0.0162	−20.21
(2.0)	0.1362	2.28	0.0578	−12.92	0.0401	−14.88	—	—	0.0286	−20.30
0.0513	0.0435	2.41	0.0238	−12.09	0.0126	−13.51	0.0202	−17.38	0.0125	−18.98
(3.0)	0.0889	2.38	—	—	0.0295	−13.50	0.0443	−17.41	0.0300	−18.93
0.0593	0.0701	2.40	0.0209	−11.78	0.0166	−13.30	0.0195	−16.95	0.0136	−18.16
(3.5)	0.1149	2.39	0.0437	−11.68	0.0330	−13.20	0.0371	−17.09	0.0312	−18.26
0.1000	0.0514	2.67	0.0300	−10.17	0.0160	−10.70	0.0240	−15.26	0.0188	−15.60
0.2000	0.0485	2.06	0.0151	−7.63	0.0172	−7.19	0.0225	−11.94	0.0091	−11.59
	—	—	—	—	0.0371	−7.23	—	—	—	—

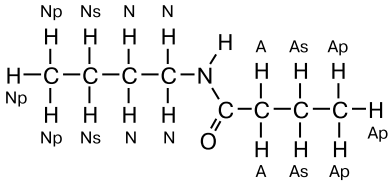
Note. X_2 and m_2 are the molar fraction and molality of glycerol in a binary mixed solvent, respectively; m_3 is the molal concentration of amide in a three-component solution.

Table 2. Standard solution enthalpies ($\Delta_{sol}H°$/kJ mol^{-1}) of amides in a water—glycerol mixture at 298.15 K and the arithmetic mean errors (s/kJ mol^{-1})

X_2	FA		DMF		DEF		DMA		DEA		HMPA
	$\Delta_{sol}H°$	s	$\Delta_{sol}H°$	s	$\Delta_{sol}H°$	s	$\Delta_{sol}H°$	s	$\Delta_{sol}H°$	s	$\Delta_{sol}H°$
0.0089	2.03	0.01	−14.66	0.01	−16.96	0.02	−20.64	0.04	−22.84	0.04	−47.92
0.0177	2.15	0.01	−13.87	—	−15.59	0.03	−19.91	—	−21.15	0.05	−46.39
0.0348	2.29	0.01	−12.92	0.00	−14.89	0.01	−18.45	—	−20.26	0.05	−43.60
0.0513	2.39	0.02	−12.09	—	−13.51	0.01	−17.4	0.01	−18.95	0.03	−41.12
0.0593	2.39	0.01	−11.73	0.05	−13.25	0.05	−17.02	0.07	−18.21	0.05	−40.00
0.1000	2.67	—	−10.17	—	−10.7	—	−15.26	—	−15.6	—	−35.09
0.2000	2.06	—	−7.63	—	−7.21	0.02	−11.94	—	−11.59	—	−28.65

aqueous solutions of organic compounds showed[18] that Eq. (1) describes the $\Delta_{solv}H^\circ$ and $\Delta_{sol}H^\circ$ values for monofunctional compounds, beginning from the third member of the homological series, with an accuracy close to the experimental one. The solution enthalpies in water and hydration enthalpies of the first two members of the homological series deviate from the linear function (1). A similar effect is usually observed in nonaqueous media as well.[19,20] The enthalpy characteristics of solutions of polyfunctional compounds, especially heterofunctional, do not obey the additive equation (1).[18]

In this work, we used the previously proposed[9] additive scheme for quantitative description of the enthalpic characteristics of dissolution and solvation of amides. The scheme is based on the division of a molecule into structural units, according to which particular atoms can belong to two or several structural fragments.[21] The C—H bond was chosen as the main fragment of hydrocarbon radicals for two reasons. First, more detailed treatment (based on bonds instead of radicals) makes it possible to examine more substances without changing the number of structural units. Second, this approach allows one to avoid the use of fractional values for radical contributions, for example, in the formamide molecules (C—H fragment was accepted[22] as equivalent to 1/2 methylene group). The summation of the bond contributions gives the contributions of the corresponding hydrocarbon radicals. According to the known proposals,[21] the structural fragments were isolated taking into account their close environment. The basic scheme of isolation of structural fragments in monocarboxamide molecules with saturated hydrocarbon radicals of normal structure is shown below for *N*-butylbutyramide.



The NCO group and N—H bond were distinguished as functional fragments in the amide molecules. The isolation of the NH group makes it possible to explicitly take into account the degree of *N*-substitution in the amide molecules. Three types of C—H bonds were distinguished in hydrocarbon radicals: $(C—H)_{Np}$ and $(C—H)_{Ap}$ are the bonds of the primary C atoms in substituents at the N atom and in acyl, respectively (terminal fragments), $(C—H)_{Ns}$ and $(C—H)_{As}$ are the bonds of the secondary C atoms in substituents at the N atom and in acyl (chain fragments), and $(C—H)_N$ and $(C—H)_A$ are the bonds in the close environment of the functional group. The $(CH)_N$ and $(CH)_A$ fragments represent the C—H bonds formed by two C atoms closest to the heteroatom. This isolation is caused by the above-mentioned specific features of dissolution and solvation of the two first members of the homological series of compounds of different classes. The formamide molecules contain one $(CH)_A$ fragment. Since the formamide molecules consist of fragments of carboxylic acid and amines, it should specially be mentioned that the C—H bonds in the acyl radical and the substituents at the N atom are nonequivalent. The additive scheme of expansion of enthalpic characteristics of organic compounds can be presented by the following equation:

$$\Delta H^\circ = \Sigma m_j \Delta H^\circ(Y_j) + \Sigma n_i \Delta H^\circ(CH)_i, \qquad (2)$$

where m_j and n_i are the numbers of polar groups of the type j (Y_j) and structural CH fragments of the type i ($(CH)_i$), respectively, in the amide molecules, which are determined from their structure; ΔH° is the contribution of the fragment to the general property of the compound: to the standard solvation enthalpy ($\Delta_{solv}H^\circ$), solution enthalpy ($\Delta_{sol}H^\circ$), vaporization enthalpy ($\Delta_{vap}H^\circ$), and enthalpy coefficient of pair interactions (h_{xy}).

The types and number of isolated structural fragments in molecules of some monocarboxamides, their standard solution enthalpies in water taken from Refs 23 and 24, and the enthalpy coefficients of amide—amide pair interactions in water[22,25—28] are given in Table 3. The contributions of structural fragments to $\Delta_{sol}H^\circ$ were calculated by the solution of Eq. (1) using the multiple linear regression method taking into account the data in Table 3. The contribution of the NCO group was calculated as a free term in the regression equation. Small errors indicate that the proposed model adequately describes the experimental data for the primary, secondary, and tertiary amides with different degrees of substitution at the N atom. The C—C bonds, which were ignored in the additive scheme, are probably eclipsed and make no substantial contribution to the interaction between the solute and solvent. The use of the concept of equivalent methylene groups[22] and the known approach,[29] which differ basically from scheme (1), does not allow one to describe the enthalpic characteristics of amides with different degrees of substitution at the N atom in the single framework.

The solution enthalpies contain the contribution from intermolecular interactions in a condensed solute. Therefore, to analyze the enthalpic characteristics of different solutes, the use of solvation enthalpies are preferential. The latter can be calculated from experimental values of the standard solution and vaporization enthalpies

$$\Delta_{solv}H^\circ = \Delta_{sol}H^\circ - \Delta_{vap}H^\circ. \qquad (3)$$

Reliable calorimetric data on vaporization enthalpies are published for methyl- and ethylamides of formic and acetic acids and for hexamethylphosphotriamide only.[13,14] Therefore, the solvation enthalpies for these compounds are calculated and discussed (Fig. 1). From the viewpoint

Table 3. Amount of the isolated structural fragments in the monocarboxamide molecules, their contributions to the standard solution enthalpies in water ($\Delta_{sol}H^\circ$), and enthalpy coefficients of amide—amide pair interactions (h_{22}) in a water (1)—amide (2) system at 298.15 K

Amide	Fragment [contribution]								$\Delta_{sol}H^\circ$ /kJ mol^{-1}	h_{22} /J kg mol^{-2}
	$(CH)_{Np}$ [−0.64]	$(CH)_{Ns}$ [0.52]	$(CH)_N$ [−0.68]	$(CH)_{Ap}$ [−1.49]	$(CH)_{As}$ [−0.15]	$(CH)_A$ [−3.18]	(NH) [6.31]	CNO [−7.88]		
Formamide	0	0	0	0	0	1	2	1	1.97	−115.0
Dimethylformamide	0	0	6	0	0	1	0	1	−15.22	−737.0
Diethylformamide	0	0	10	0	0	1	0	1	−17.97	−1767.0
N,*N*-Dimethylacetamide	0	0	6	0	0	3	0	1	−21.42	−1081.0
N,*N*-Diethylacetamide	0	0	10	0	0	3	0	1	−24.08	−2355.0
N-Propylacetamide	3	0	4	0	0	3	1	1	−15.76	—
N-Butylacetamide	3	2	4	0	0	3	1	1	−14.72	—
N-Methylpropionamide	0	0	3	3	0	2	1	1	−14.87	—
N,*N*-Dimethylpropionamide	0	0	6	3	0	2	0	1	−22.34	−1797.0
N-Methylbutyramide	0	0	3	3	2	2	1	1	−16.02	—
N-Methylvaleramide	0	0	3	3	4	2	1	1	−15.02	—
N-Methylformamide	0	0	3	0	0	1	1	1	−7.00	−272.0
N-Methylacetamide	0	0	3	0	0	3	1	1	−13.36	−286.0
N-Ethylformamide	0	0	5	0	0	1	1	1	—	−350.0
N-Ethylacetamide	0	0	5	0	0	3	1	1	—	—
N-Methyl-*N*-ethylformamide	0	0	8	0	0	1	0	1	—	—
N-Methyl-*N*-ethylacetamide	0	0	8	0	0	3	0	1	—	—

Note. Regression parameters for description of $\Delta_{sol}H^\circ$: standard deviation of the function se = 0.41 kJ mol^{-1}, correlation coefficient R = 0.9994.

of the additive scheme used, a specific feature of their structure is that the molecules contain only structural hydrocarbon fragments of the close environment of the functional group. The contributions of structural fragments to the vaporization ($\Delta_{vap}H^\circ$) and hydration (Δ_hH°) enthalpies of amides are presented in Table 4. The contributions of the fragments to $\Delta_{vap}H^\circ$ of amides were calculated by the multiple linear regression method using Eq. (2) and the data in Tables 2 and 3. The contributions of the fragments to Δ_hH° of the amides were calculated by Eq. (3) and the data in Table 4. The contribution of the N_3PO group was calculated as the difference of $\Delta_{sol}H^\circ$, $\Delta_{solv}H^\circ$, or $\Delta_{vap}H^\circ$ for HMPA and the contribution of six hydrocarbon fragments $(CH)_N$.

It is known that the contributions of fragments depend on the scheme of division of molecules into fragments and have a relative value at the absolute value of the overall magnitude of the property. Nevertheless, the energetic equivalency of the distinguished C—H bonds and the achieved accuracy of description, which is close to the experimental one, make it possible to use the values of contributions of distinguished structural fragments for characterization of components of nonspecific and specific solvations of molecules. Let us assume that the change in Δ_hH° in the amide series is determined by a change in the nonspecific solvation of the molecules related to the contribution of the hydrocarbon radicals and in the specific solvation caused by the CNO and NH groups. The

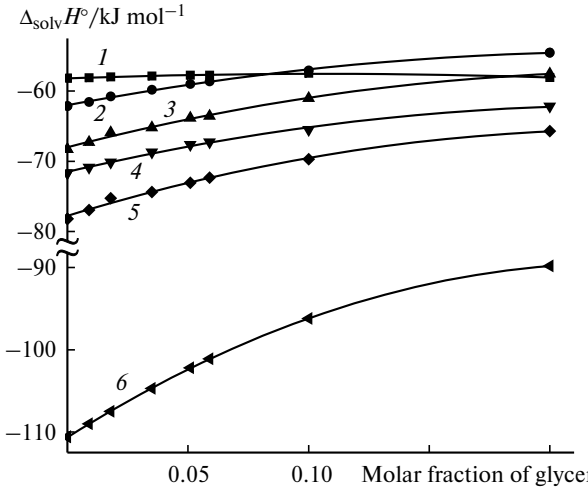


Fig. 1. Solvation enthalpies ($\Delta_{solv}H°$) of formamide (*1*), dimethylformamide (*2*), diethylformamide (*3*), *N*,*N*-dimethylacetamide (*4*), *N*,*N*-diethylacetamide (*5*), and hexamethylphosphotriamide (*6*) in a water—glycerol mixed solvent as functions of the mixed solvent composition at 298.15 K.

Table 4. Contributions of the structural fragments to the solution (in water) ($\Delta_{sol}H°$), vaporization ($\Delta_{vap}H°$), and hydration enthalpies ($\Delta_hH°$) and donor numbers of methyl- and ethylformamides, methyl- and ethylacetamides, and hexamethylphosphotriamide at 298.15 K

Fragment	Contribution to property			
	$\Delta_{sol}H°$ [a]	$\Delta_{vap}H°$ [b]	$\Delta_hH°$	DN [c]
	kJ mol^{-1}			/kcal mol^{-1}
$(CH)_N$	−0.68	0.91	−1.59	1.09
$(CH)_A$	−3.08	1.78	−4.86	0.57
NH	6.58	9.42	−2.84	7.95
NCO	−8.10	39.51	−47.61	19.53
N_3PO	−37.28	44.65	−81.93	19.2

[a] $R = 0.9999$, $se = 0.05$.
[b] $R = 0.9998$, $se = 0.23$.
[c] $R = 0.9999$, $se = 0.05$.

nonspecific hydration of compounds is known[30] to increase with an increase in the sizes of a hydrocarbon radical due to the enhancement of the van der Waals interaction and hydrophobic hydration. The negative contributions of the hydrocarbon fragments to $\Delta_hH°$ (see Table 4) reflect this regularity. Analysis of the obtained values shows that the changes in the composition of the acyl hydrocarbon radical exert much greater influence on the enthalpic characteristics of the amides than the changes in the composition of the hydrocarbon radicals of substituents at the N atom. The contribution of the $(CH)_A$ group to $\Delta_hH°$ threefold exceeds that of the $(CH)_N$ group.

According to the additive scheme and results of calculation, the contribution of the electron-donor NCO group to the hydration enthalpy of amides is approximately the same. Differences in the solvation of the primary, secondary, and tertiary amides are determined by the contribution of the N—H bonds. The contribution of the NCO group caused by the amide—solvent donor-acceptor interaction constitutes the most part of $\Delta_hH°$. For instance, for DEA this is 60%. The electron-donor ability of amides is usually characterized in literature by donor numbers. Their values for FA, DMF, DEF, DMA, and DEA are given above. It is seen that the donor numbers increase more strongly on going from the *N*-methyl- to *N*-ethyl-substituted derivatives than on going from formamides to acetamides. The difference in the donor numbers of the amides is caused by two factors. First, the electron density on the oxygen atom changes due to the induction effects of substituents. Second, nonspecific solvation makes a contribution, because the donor numbers are the enthalpies of interaction of the dichloroethane-solvated amide molecules with $SbCl_5$.[31] The additive scheme used makes it possible to describe with high accuracy and, hence, to efficiently take into account the overall effect of these factors. The contributions of the isolated fragments to DN are presented in Table 4. Using the obtained contribution of the $(CH)_N$ fragment and the donor number of HMPA (see above), we calculated the contribution of the N_3PO group to DN (see Table 4). It is seen that the resulting value is approximately equal to the corresponding contribution of the NCO group. This result agrees with previous conclusions[32,33] that oxygen atoms are the centers of negative charge in carboxamides and hexamethylphosphotriamide. The contributions of the isolated groups to DN (see Table 4) and the group composition of the molecules (see Table 3) made it possible to calculate the donor numbers of *N*-methylformamide (MF), *N*-methylacetamide (MA), *N*-ethylformamide (EF), *N*-ethylacetamide (EA), *N*-methyl-*N*-ethylformamide (MEF), and *N*-methyl-*N*-ethylacetamide (MEA), being 31.3, 32.5, 33.5, 34.6, 28.8, and 30.0 kcal mol^{-1}, respectively.

The increment of the NH group in $\Delta_hH°$ has a low negative value, and its absolute value is inferior to the positive contribution of this group to the intermolecular interaction in neat liquid amides (to $\Delta_{vap}H°$) (see Table 4). This results in a positive contribution of the NH group to $\Delta_{sol}H°$ and is a formal reason for endothermicity of dissolution of primary amides in water. The observed contributions to $\Delta_{sol}H°$ and $\Delta_hH°$ can physically be substantiated by the conclusion about destabilization of the aqueous environment near the NH_2 groups of formamide and urea. This conclusion has been drawn previously[34,35] as a result of the study of the dielectric permeability of their aqueous solutions and the absorption of millimeter-range electromagnetic radiation.

The contribution of the distinguished structural groups to the solution and solvation enthalpies of the amides

Table 5. Contributions of the structural fragments to the solution ($\Delta_{sol}H°$) and solvation ($\Delta_{solv}H°$) enthalpies of methyl- and ethylformamides and methyl- and ethylacetamides in a water—glycerol mixed solvent at 298.15 K

X_2	$\Delta_{sol}H°$/kJ mol^{-1}						$\Delta_{solv}H°$/kJ mol^{-1}			
	CNO	$(CH)_N$	$(CH)_A$	(NH)	*se*	*R*	CNO	$(CH)_N$	$(CH)_A$	(NH)
0.009	−8.35	−0.56	−2.97	6.67	0.05	0.9999	−47.86	−1.47	−4.75	−2.75
0.018	−8.87	−0.37	−2.90	6.96	0.24	0.9999	−48.38	−1.28	−4.68	−2.46
0.035	−7.40	−0.47	−2.72	6.21	0.07	0.9999	−46.91	−1.38	−4.50	−3.21
0.051	−7.14	−0.37	−2.69	6.11	0.07	0.9999	−46.65	−1.28	−4.47	−3.31
0.059	−7.22	−0.34	−2.56	6.09	0.17	0.9999	−46.73	−1.25	−4.34	−3.33
0.100	−7.06	−0.11	−2.50	6.11	0.09	0.9999	−46.57	−1.02	−4.28	−3.31
0.200	−6.02	0.10	−2.17	5.13	0.03	0.9999	−45.53	−0.81	−3.95	−4.29

under study in a water—glycerol mixed solvent are given in Table 5. The contributions of the fragments to $\Delta_{sol}H°$ were calculated by the multiple linear regression method using Eq. (2) and the data in Tables 2 and 3. It is seen that the proposed additive scheme makes it possible to describe with high accuracy the experimental data on $\Delta_{sol}H°$ of the amides in both water and mixed solvent. The contributions of the fragments to $\Delta_{solv}H°$ were calculated by Eq. (3) and the data in Tables 4 and 5.

The solvation enthalpies of amides in a water—glycerol mixed solvent calculated by Eq. (3) and the data in Tables 2 and 3 are shown in Fig. 1. It is seen that in the studied composition interval the change in $\Delta_{solv}H°$ in the series of amides is similar to the change in their $\Delta_hH°$ and can be explained, probably, by the same factors. Formamide is exception.

The influence of the mixed solvent composition on the solvation enthalpies of the compounds is reflected by their transfer enthalpies. The concentration relations of the transfer enthalpies ($\Delta_{tr}H°$) of the amides from water to a water—glycerol mixed solvent were calculated by the equation

$$\Delta_{tr}H° = \Delta_{solv}H° - \Delta_{solv}H°_1 = \Delta_{sol}H° - \Delta_{sol}H°_1, \qquad (4)$$

and are shown in Fig. 2. Subscript 1 designates the thermochemical characteristic of an aqueous solution.

The plots of the contributions of the isolated groups to the transfer enthalpies of amides *vs.* mixed solvent composition are presented in Fig. 3. These values were calculated by Eq. (4) using the increments of the corresponding structural fragments in the solution enthalpies (see Table 5).

A comparison of the change in the contributions of the structural fragments (see Fig. 3) with the transfer enthalpies of the amide molecules (see Fig. 2) indicates that the solvation energetics of disubstituted amides weakens due to a decrease in the specific interaction of the amide group with the solvent and in the nonspecific solvation of hydrocarbon radicals. The shape of the plot of the transfer enthalpies of formamide in the water-rich area is determined by the same factors. Further, the predominant effect on $\Delta_{tr}H°$ is made by a change in the contribution of

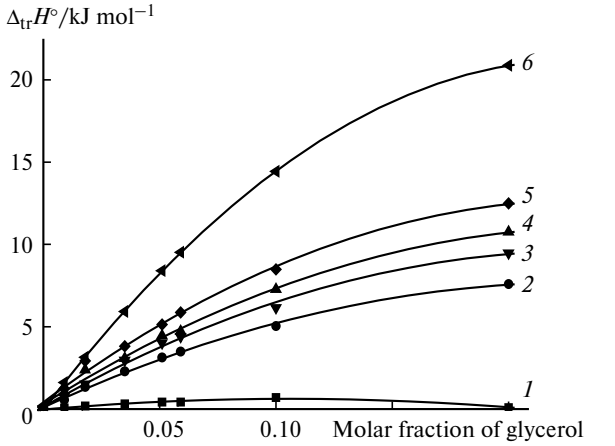


Fig. 2. Transfer enthalpies ($\Delta_{tr}H°$) of formamide (*1*), dimethylformamide (*2*), *N*,*N*-dimethylacetamide (*3*), diethylformamide (*4*), *N*,*N*-diethylacetamide (*5*), and hexamethylphosphotriamide (*6*) from water to a water—glycerol mixed solvent as functions of the mixed solvent composition at 298.15 K.

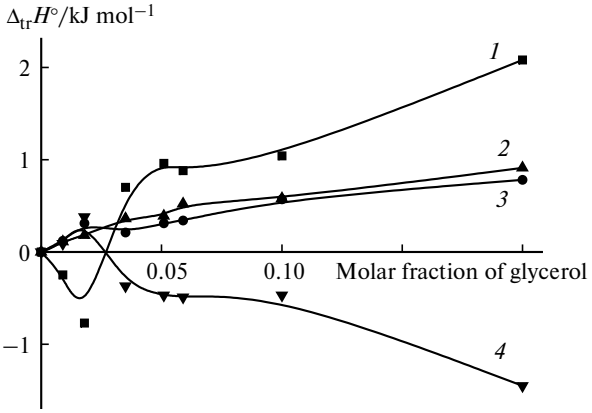


Fig. 3. Contributions of different structural fragments NCO (*1*), $(CH)_A$ (*2*), $(CH)_N$ (*3*), and NH (*4*) to the transfer enthalpies ($\Delta_{tr}H°$) of amides as functions of the water—glycerol solvent composition at 298.15 K.

Table 6. Enthalpy coefficients (h) of heterotactic pair and triple interactions in water (1)—glycerol (2)—amide (3) systems at 298.15 K

Amide	h_{23} /J kg mol^{-2}	h_{223} /J kg^2 mol^{-3}	*se* /J mol^{-1}	R
FA	99.4	−7.0	10	0.9995
DMF	686.1	−36.0	70	0.9991
DEF	1112.7	−84.5	270	0.9915
DMA	851.7	−41.5	60	0.9995
DEA	1348.7	−102.8	350	0.9900
HMPA	1648.4	−54.8	10	0.9999

two NH groups. A decrease in the contribution of aqueous environment destabilization with an increase in the glycerol concentration in a mixed solvent increases the exothermicity of solvation of the NH group and primary amide molecules. The increments of the structural fragments (see Table 5) and their number (see Table 3) make it possible to calculate (using Eq. (2)) the enthalpic characteristics of dissolution, solvation, and transfer of MF, MA, EF, EA, MEF, and MEA.

For the three-component systems (solvent (1)—solvent (2)—solute (3)) in a region of low solvent (2) additives, the concentration relations of $\Delta_{tr}H^\circ$ are mainly determined by the coefficients of pair interactions of components (2) and (3).[30] They bear quantitative information on the energetics of interaction between solvated molecules. The enthalpy coefficients of the interaction of amides with glycerol in an aqueous solution in the framework of the McMillan—Mayer theory[36] were calculated by the equation[37]

$$\Delta_{tr}H^\circ = 2h_{23}m_2 + 3h_{223}m_2^2 + 3h_{233}m_2m_3, \qquad (5)$$

neglecting the last term in the right part and taking into account the low concentration of amides. In Eq. (5), h_{23}, h_{223}, and h_{233} are the enthalpy coefficients of pair and triple interactions of the components; m_2 and m_3 are the molalities of glycerol in a mixed solvent and of amide in a solution, respectively. The data in an interval of 0—3.5 m were used for calculation.

The results of calculation are given in Table 6. It is seen that the coefficients of amide—glycerol pair interactions are positive and increase with an elongation of the alkyl radicals in the amides. To analyze the contributions of nonspecific and specific interactions to the h_{23} value, we used the proposed additive scheme. The contributions of the isolated fragments to the coefficients of pair interactions calculated by the multiple regression analysis of the data in Tables 3 and 6 using Eq. (2) are given in Table 7 along with the results of expansion of the enthalpy coefficients of amide—amide interactions in water from Table 3. We excluded from the analysis the data for MA and EF, which do not obey the most part of correlations.[24] A comparison of the data in Tables 6 and 7 shows that the positive values of the h_{23} and h_{22} coefficients are caused by contributions from the hydrocarbon fragments and NH group. The endothermicity of interaction of the hydrated hydrocarbon groups of the amide molecules with the hydrated glycerol and amide molecules agree with earlier conclusions[28,38]: the interaction of the CH_2 group in water with any polar group is accompanied by an endotherm. The process is endothermic, most probably, due to the desolvation of alkyl radicals when different solvate shells of interacting particles bring together in an aqueous medium.

Table 7. Contributions of structural fragments to the enthalpy coefficients of pair interactions amide—glycerol (h_{23}) in a water (1)—glycerol (2)—amide (3) system and amide—amide (h_{22}) in a water (1)—amide (2) system at 298.15 K

Fragment	h_{23} [a]	h_{22} [b]
	J kg mol^{-2}	
$(CH)_N$	115.0	288.4
$(CH)_A$	100.4	233.7
$(CH)_{Ap}$	—	296.5
NH	61.7	469.2
NCO	−124.5	−1290

[a] $R = 0.9993$. $se = 30.0$.
[b] $R = 0.9985$. $se = 86.0$.

The contributions of the hydrocarbon fragments $(CH)_N$ and $(CH)_A$ to h_{23} and of the $(CH)_N$, $(CH)_A$, and $(CH)_{Ap}$ fragments to h_{22} have close values (see Table 7). Due to this, the concept of equivalent methylene groups[22] can be used to analyze the influence of the composition and structure of amide molecules on their enthalpy coefficients of pair interaction. The contributions of the $(CH)_N$, $(CH)_A$, and $(CH)_{Ap}$ fragments to the solvation (hydration) and solution enthalpies (see Table 4) differ substantially, which indicates that this approach[22] is inappropriate for interpretation of $\Delta_{solv}H^\circ$ and $\Delta_{sol}H^\circ$.

The NH group makes a considerable positive contribution to h_{23} and h_{22}. As already mentioned, the positive

contribution of this group can be caused by the destabilization of its aqueous environment.

The negative contribution of the NCO group to h_{23} of an amide molecule is determined by the formation of hydrogen bonds between this group and the glycerol molecules.

In conclusion, it should be emphasized that the application of the new additive scheme to the enthalpic characteristics of amide solutions made it possible to analyze quantitatively the role of nonspecific and specific solvations in solutions and to predict the vaporization, solution, and solvation enthalpies and the enthalpy coefficients of pair interactions of experimentally unstudied *N*-methylformamide, *N*-ethylformamide, *N*-methyl-*N*-ethylformamide, *N*-methylacetamide, *N*-ethylacetamide, and *N*-methyl-*N*-ethylacetamide in a water—glycerol mixture, as well as donor numbers of these amides.

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