Solvation of amides of carboxylic acids in aqueous solutions of ethylene glycol

A. M. Zaichikov[a]* *and N. G. Manin*[b]

[a]*Ivanovo State University of Chemical Technology,*
7 prosp. F. Engel'sa, 153460 Ivanovo, Russian Federation.
Fax: +7 (093 2) 41 7995. E-mail: bushuev@icti.ivanovo.su
[b]*Institute of Solution Chemistry, Russian Academy of Sciences,*
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (093 2) 37 8507

Enthalpies of solution of amides of formic, acetic, and propionic acids with different degrees of *N*-substitution in aqueous solutions of ethylene glycol were measured at 298.15 K. The concentration of ethylene glycol did not exceed 4 mol kg^{-1}. The reasons for increasing endothermic values of the enthalpies characterizing the amide transfer from water to a mixed aqueous-organic solvent on going from primary to tertiary amides and from formamides to the corresponding acetamides are discussed. The enthalpic coefficients of pair interactions between amides and ethylene glycol in water were calculated. The endothermicity of the interaction of the alkyl groups of the amide molecules with ethylene glycol results in positive values of the coefficients. The coefficient values increase with the enhancement of the hydrophobic properties of hydrophilic non-electrolytes (urea, formamide, ethylene glycol) due to an increase in the contribution of the hydrophobic component and a decrease in the contribution from the interaction of the polar groups of amides to the total interaction.

Key words: amides, ethylene glycol, water, enthalpies of solvation and transfer, enthalpic pair-interaction coefficients.

The establishment of a relation of the structure of polyfunctional organic molecules to the thermodynamic properties of aqueous solutions containing these molecules is of fundamental importance in chemistry of solutions.[1,2] The most important parameters of such systems are the enthalpy of solvation and pairwise-interaction coefficients.[3,4] Based on the signs and relations of these values, a number of authors[2,5] introduced the classification of non-electrolytes that consists of three groups: hydrophobic ($g_{xx} < 0$ and $Ts_{xx} > h_{xx} > 0$), hydrophilic urea-like ($g_{xx} < 0$ and $h_{xx} < Ts_{xx} < 0$), and hydrophilic sucrose-like non-electrolytes ($g_{xx} > 0$ и $h_{xx} > Ts_{xx} > 0$). Here g_{xx} are Gibbs, h_{xx} are enthalpic, and Ts_{xx} are entropic pairwise-interaction coefficients. Except formamide, amides of aliphatic carboxylic acids are referred to the first group,[6] and ethylene glycol is in the third group.[7,8] Binary aqueous solutions of amides and ethylene glycol have been studied in detail.[1,2] However, published data on enthalpies of solvation of amides in water—ethylene glycol mixtures are lacking, and the pairwise-interaction coefficients for amide—ethylene glycol were determined only for some *N*-alkylamides.[9] The data are available for the tertiary aqueous systems containing amides and urea[10] or formamide,[11] whose molecules are hydrophilic and, according to the classification,[2,5] are assigned to the second group of non-electrolytes. The purpose of this work is the thermochemical study of the specific features of interaction of polar and alkyl groups of amides having different degrees of *N*-substitution with ethylene glycol in its aqueous solutions.

Experimental

Ethylene glycol (EG, pure grade) was twice distilled *in vacuo*, and medium fractions were taken. DMF (specially pure grade), diethylformamide (DEF, Fluka) and dimethylacetamide (DMA, Fluka), dimethylpropionamide (DMP, Aldrich), diethylacetamide (DEA, pure grade), *N*-methylformamide (NMF, Aldrich), and formamide (FA, pure grade) were purified according to a described procedure.[12] *N*-Methylacetamide (NMA, pure grade) was purified by double vacuum distillation, and the intermediate product was dried with molecular sieves 4 Å (Aldrich) at 323 K and used in the experiment as a supercooled liquid. Acetamide (AA, pure grade) was twice recrystallized from anhydrous MeOH and dried *in vacuo* for 72 h at ~20 °C. The water content in organic solvents determined by the Fischer method did not exceed 0.03%. The density and melting points of reagents corresponded to reference data.[13] Mixtures of H_2O with EG were prepared by the gravimetric method using freshly bidistilled water.

Enthalpies of solution ($\Delta_s H$) were measured at 298.15 K in an multiampule-type microcalorimeter[14] with the isothermic shell and 50-cm^3 reaction vessel. The temperature of measurements was maintained with an accuracy of at least 0.002 K. The temperature sensitivity of the calorimeter was not lower than

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$5 \cdot 10^{-5}$ K. The enthalpies of solution were determined at concentrations of the solute <0.08 mol kg^{-1} of solvent. Since it was established that concentrations in solutions had no effect on the $\Delta_s H$ values, enthalpies of solution at infinite dilution ($\Delta_s H°$) were calculated as average values from three—four measurements.

Results and Discussion

The enthalpies of solution at infinite dilution of amides in aqueous solutions of ethylene glycol are presented in Table 1. Figure 1 presents the concentration plots of the enthalpies of transfer ($\Delta_{tr}H°$) of amides from water to aqueous solutions of ethylene glycol approximated by

$$\Delta_{tr}H°(H_2O \rightarrow H_2O + EG) = \\ = \Delta_s H°(H_2O + EG) - \Delta_s H°(H_2O) = am + bm^2, \quad (1)$$

where $\Delta_s H°(H_2O)$ and $\Delta_s H°(H_2O + EG)$ are the standard enthalpies of solution of amides in water and water—ethylene glycol mixtures, respectively; m is the molal concentration of EG; a and b are the approximation coefficients calculated by a least-squares method. Enthalpies of transfer reflect a change in solvation of amides when H_2O—EG mixtures are formed. Solvation of amides is reduced with an increase in the ethylene glycol concentration (see Fig. 1).

It is commonly accepted[1,2] that the enthalpy of solvation is the sum of enthalpy effects of cavity formation in the solvent and the specific and nonspecific interactions between the solute and solvent molecules. The main contribution to the enthalpy of hydration of *N,N*-disubstituted (tertiary) amides and hexamethylphosphorotriamide (HMPA) is made by the interaction of polar groups of amides with water,[16,17] which is accompanied by significant exothermic effects[18] because these polar groups form with water stronger hydrogen bonds than H bonds inherent in water.

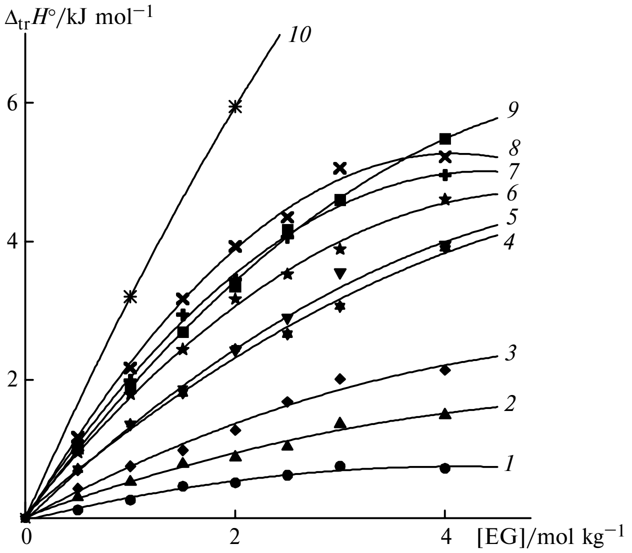

Fig. 1. Enthalpies of transfer of FA (*1*), AA (*2*), NMF (*3*), NMA (*4*), DMF (*5*), DMA (*6*), DEF (*7*), DEA (*8*), DMP (*9*), and HMPA[15] (*10*) from water to the mixed H_2O—EG solvent at 298.15 K.

Two hydrogen atoms participate in the formation of hydrogen bonds in the ethylene glycol molecule, however, its proton-donating capacity is lower, as a whole, than that of water.[19] That is why heteromolecular H bonds formed by protons of EG are less stable compared to H bonds of water protons. Accordingly, the proton-donating capacity of the mixed H_2O—EG solvent gradually decreases with an increase in the ethylene glycol concentration in water.[20] Correspondingly, the maximum decrease in the hydrophilic component of solvation in the H_2O—EG system is observed only for the amides, which are stronger electron-donors and form more stable hydrogen bonds with H_2O. Most probably, this is a main factor of the noticeable weakening of DEA and HMPA solvation compared to other amides (see Fig. 1).

The effect of hydrophobic hydration is the most important component of nonspecific interaction of amides with water.[1,2] The enthalpy of structure-forming effect of the methyl group of *N*-alkylamides on water is approximately equal to −7 kJ mol^{-1}, and that of the

Table 1. Enthalpies of solution ($\Delta_s H°$) at infinite dilution of amides in aqueous solutions of ethylene glycol at 298.15 K

m_y /mol kg^{-1}	$\Delta_s H°$/kJ mol^{-1}								
	FA	AA	NMF	NMA	DMF	DMA	DEF	DEA	DMP
0	1.97±0.05	9.63±0.07	−6.98±0.07	−13.36±0.04	−15.22±0.06	−21.42±0.04	−17.97±0.04	−24.08±0.11	−22.34±0.05
0.5	2.09±0.04	9.94±0.10	−6.55±0.01	−12.65±0.01	−14.57±0.08	−20.47±0.05	−16.87±0.04	−22.91±0.05	−21.34±0.08
1.0	2.23±0.04	10.16±0.08	−6.23±0.03	−12.00±0.10	−13.88±0.06	−19.63±0.01	−15.98±0.08	−21.91±0.01	−20.44±0.05
1.5	2.43±0.06	10.42±0.03	−6.00±0.03	−11.55±0.01	−13.35±0.05	−18.98±0.03	−15.03±0.08	−20.91±0.03	−19.65±0.04
2.0	2.48±0.02	10.52±0.05	−5.71±0.04	−10.91±0.01	−12.81±0.01	−18.25±0.10	−14.52±0.02	−20.15±0.10	−18.99±0.10
2.5	2.59±0.01	10.67±0.08	−5.30±0.01	−10.70±0.05	−12.39±0.06	−17.89±0.05	−13.91±0.01	−19.73±0.05	−18.17±0.08
3.0	2.72±0.05	11.00±0.02	−4.97±0.02	−10.30±0.02	−11.69±0.06	−17.53±0.06	−13.38±0.06	−19.02±0.06	−17.74±0.05
4.0	2.69±0.05	11.13±0.02	−4.84±0.01	−9.46±0.03	−11.29±0.02	−16.81±0.03	−13.01±0.04	−18.86±0.03	−16.86±0.09

Note. The standard deviation of a single measurement is given as a measure of the error.

alkyl fragments of the DMA molecules is about −19 kJ mol^{-1}.[21,22] When the size of hydrocarbon radicals in amide molecules increases, the absolute value of the contribution of the hydrophobic solvation component to the enthalpy of hydration increases.[21] A new aqueous non-electrolyte network of hydrogen bonds is based on the initial water structure.[23] The data on dielectric permeability[24] show that the perturbation of the water structure becomes noticeable with the EG concentration. As a result, the effect of solvophobic solvation of amides decreases. It can be assumed that a decrease in the exothermic effect of hydrophobic hydration reflects, to a greatest extent, the solvation of HMPA and DEA with the largest alkyl radicals.

The perturbation of the water structure and a decrease in the role of the cavity mechanism of solvation[25] lead to an increase in the energy consumption needed to form cavities in the solvent present in the H_2O—EG mixtures. Correspondingly, the solvation of amides is reduced in the mixed H_2O—EG solvent. A comparison of the $\Delta_{tr}H^\circ(m)$ curves obtained for the FA—AA, NMF—NMA, DMF—DMA, and DEF—DEA pairs (see Fig. 1) shows that the weakening of solvation of primary, secondary, and tertiary formamides is lower than that of acetamides. Due to the additional methyl radical, which has an inductive effect on the carbonyl group, acetamides have stronger hydrophobic and hydrophilic properties than amides of formic acid.[1,16,19] In addition, due to a large molar volume, acetamides spend more energy than formamides to form a cavity in the solvent. Evidently, that is why a decrease in the solvation of formamides in the mixed H_2O—EG solvent is less pronounced than that of acetamides. The enthalpies of transfer of primary and secondary amides of both formic and acetic acids are lower than those for DMF and DMA because primary and *N*-monosubstituted amides have a lower basicity,[12] weaker hydrophobic properties, and a smaller molar volume than the corresponding *N*,*N*-dialkylamides.

Based on the known theoretical concepts[3] and data on enthalpies of transfer, we can estimate the enthalpic coefficients using the following equation[4]:

$$\Delta_{tr}H^\circ m_y{}^{-1} = 2h_{xy} + 3h_{xyy}m_y + 3h_{xxy}m_x + \ldots , \qquad (2)$$

where $\Delta_{tr}H^\circ$ is the enthalpy of transfer of amides from water to EG solutions; m_x and m_y are the molal concentrations of amides and EG, respectively; h_{xy}, h_{xxy}, and h_{xyy} are the enthalpic coefficients of pair and triple interactions of amides (x) with EG (y).

The h_{xy} coefficients were determined by a least-squares method neglecting the last term in Eq. (2) because of low concentrations m_x (Table 2). The found enthalpic pairwise-interaction coefficients of NMF and NMA with EG in water agree well with the h_{xy} values calculated from the data on enthalpies of dilution.[9]

Table 2. Enthalpic pairwise-interaction coefficients (h_{xy}) of amides with hydrophilic non-electrolytes in aqueous solutions of EG, FA and urea at 298.15 K and the number of equivalent methylene groups of amides (*n*)

Amide	h_{xy}/J kg mol^{-2}			n_{CH_2}
	EG	FA[a]	Urea[b]	
FA	144 (16)	−126 (8)	−261 (6)	0.5
AA	306 (18)	59 (10)	−142 (4)	1.5
NMF	416 (28)	134 (16)	−132 (2)	2.0
NMA	731 (26)	418 (14)	15 (6)	3.0
DMF	694 (22)	289 (10)	−155 (9)	3.5
DMA	1000 (19)	551 (18)	−70 (8)	4.5
DEF	1153 (21)	602 (13)	36 (11)	5.5
DEA	1251 (24)	753 (17)	135 (10)	6.5
DMP	1036 (14)	556 (12)	—	5.5

Note. Standard errors of the free term of linear approximation are presented in parentheses.

[a] Ref. 11.

[b] Ref. 10.

Let us analyze the enthalpic pairwise-interaction coefficients of amides with non-electrolytes (h_{xy}) as a function of the number of equivalent CH_2 groups (n_{CH_2}) in alkyl radicals of amides[10]:

$$h_{xy} = n_{CH_2}H_{CH_2-y} + H_{A\Gamma-y}. \qquad (3)$$

The slope of the straight lines characterizes the interaction of the methylene group of amides with the non-electrolyte molecule (y) in an aqueous medium, whereas the intersept with the ordinate reflects the averaged extent of the interaction of the polar amide groups with the non-electrolyte molecule. Following earlier data,[9] we assume CH = 0.5CH_2 and CH_3 = 1.5CH_2 (Table 3). The plots of the h_{xy} coefficients *vs.* number of equivalent methylene groups of

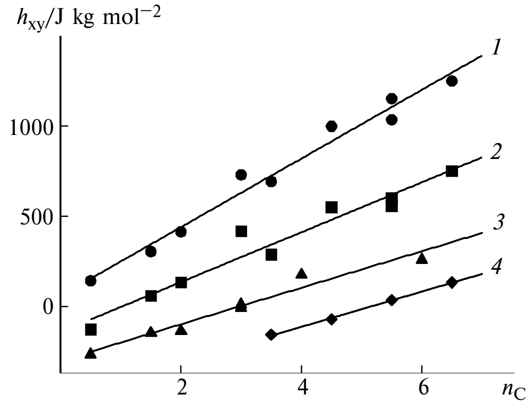

Fig. 2. Plots of the enthalpic pairwise-interaction coefficients (h_{xy}) *vs.* number of equivalent methylene groups (n_{CH_2}) for various systems: *1*, amide—EG (h_{xy} = 190.2n_{CH_2} + 61.2); *2*, amide—FA (h_{xy} = 138.4n_{CH_2} − 135.7); *3*, secondary (primary) amide—urea (h_{xy} = 101n_{CH_2} − 296);[10] *4*, tertiary amide—urea (h_{xy} = 101n_{CH_2} − 517).[10] The correlations relating the enthalpic pairwise-interaction coefficients to the number of methylene groups are presented in parentheses.

amides are presented in Fig. 2. One line comprises the pair-interaction coefficients of primary and secondary amides with urea, while another group groups together the corresponding coefficients for tertiary amides.[10] The different behavior of the amides is likely reasoned by an enhanced proton-donating capacity of urea, whose molecules are sensitive to different proton-donating properties of polar amide groups with varying the degree of substitution of the N atom. These differences are leveled in aqueous solutions of FA and EG.[11,19] The interaction of substituted and unsubstituted amide groups with nonelectrolytes can usually be presented by one parameter due to insignificant differences in the strength of the interaction.[26] Therefore, on approximating the h_{xy} values in aqueous solutions of FA and EG data for tertiary amide groups were also included.

All heterotactic pair-interaction coefficients calculated in this work are positive and increase with the number of alkyl groups in amides. The positive values of the h_{xy} coefficients in H_2O—EG mixtures are mainly due to the endothermic nature of interaction between hydrocarbon groups of amide molecules and a EG molecule (see Fig. 2, Table 2). The enthalpic component of interaction of the alkyl groups of amides with the methylene radicals of EG in water (hydrophobic interaction) is positive. The interaction of the hydrocarbon groups in water with the hydroxyl groups of alcohols is accompanied by the endothermic effect.[6] Heat absorption is related to the release of water from the hydration sphere of the alkyl radicals of amides induced by contact between heterotype solvate shells of the fragments of the amide and EG molecules in an aqueous medium. The contribution from the interaction of the amide groups with EG to the h_{xy} coefficients is close to zero. Evidently, the exothermic effect of formation of heteromolecular hydrogen bonds between the carbonyl oxygen of amides and hydroxyl protons is compensated by the positive enthalpic effect of interaction of the methylene groups of EG with the polar groups of amides.[6]

The published data on the enthalpic and Gibbs amide—amide pair-interaction coefficients are presented in Table 3. The hydrophobic interaction of water-dissolved substances is characterized by relations $g_{xx} < 0$ and $Ts_{xx} > h_{xx} > 0$.[2] As the size of the alkyl radical increases, g_{xx} become more negative and the h_{xx} coefficients become more positive (see data in Refs. 10, 26, 27). The negative g_{xx} values and positive h_{xx} values of secondary amides and acetamide indicate that they also interact in aqueous solutions through hydrocarbon radicals. The interrelation of effects of hydrophobic hydration and hydrophobic interaction results in a parallel change in the enthalpy of hydration of amides and h_{xx} coefficients.[11] With an increase in the exothermic values of enthalpies of hydration of amides, the heterotactic enthalpic coefficients h_{xy} become more positive[31]; this tendency is retained for aqueous solutions of EG (Fig. 3). The enthalpies of hydration were calculated using the enthalpies of solution (see Table 1) and vaporization of amides[32] existing at 298.15 K in the liquid state. The data in Fig. 3 indicate that the amide—ethylene glycol interaction coefficients in aqueous solutions depend on the energy of desolvation of molecules, which increases, as the increasing the size of the alkyl chain promotes the hydration of amide. The correlation between the h_{xx} and h_{xy} coefficients and enthalpies of hydration of amides is confirmed by the results in Fig. 4. The h_{xy} coefficients increase with the number of alkyl groups and, correspondingly, with the enhancement of the hydrophobic properties of amides. The parallel change in the h_{xy} and h_{xx} coefficients and dB_{22}/dp derivative shows that the h_{xy} value can serve as a criterion for the relative hydrophobicity of amides.[1,11,30] Based on the available data on h_{xy} in the H_2O—EG mixtures, relative hydrophobicity of amides of aliphatic carboxylic acids increase in the order: FA < AA < NMF < DMF < DMA < DEF < DEA, which coincides with published data.[11] The same sequence can be obtained if the pairwise coefficients h_{xx} (see Table 3) are used as a criterion of hydrophobicity.[1]

Table 3. Enthalpic (h_{xx}) and Gibbs (g_{xx}) pairwise-interaction coefficients of non-electrolytes in water and the derivative of the second virial coefficient with respect to pressure $(dB_{22}/dp)_T$

Compound	h_{xx}	g_{xx}	$(dB_{22}/dp)_T \cdot 10^2$ * /cm^3 mol^{-1} bar^{-1}
	J kg mol^{-2}		
EG	362 [9]	15 [7]	—
FA	−115 [27]	−31 [26]	0.4
Urea	−350 [9]	−106 [7]	0.4
AA	12 [28]	−145 [28]	−0.1
NMF	272 [9]	—	—
NMA	286 [29]	−400 [7]	—
DMF	737 [27]	−129 [26]	−1.8
DMA	1081 [26]	−177 [26]	−4.9
DEF	1767 [10]	—	—
DEA	2355 [10]	—	—
DMP	1797 [26]	−500 [26]	—
HMPA	5160 [30]	—	−31.0

* Ref. 1.

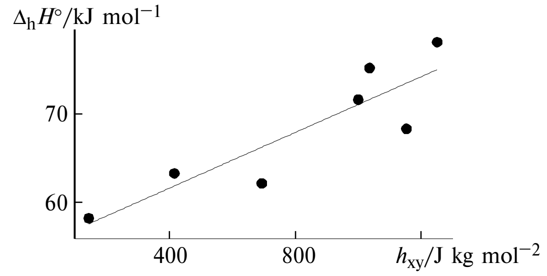

Fig. 3. Plot of the enthalpies of hydration of amides *vs.* enthalpic pairwise-interaction coefficients for ethylene glycol in water at 298.15 K.

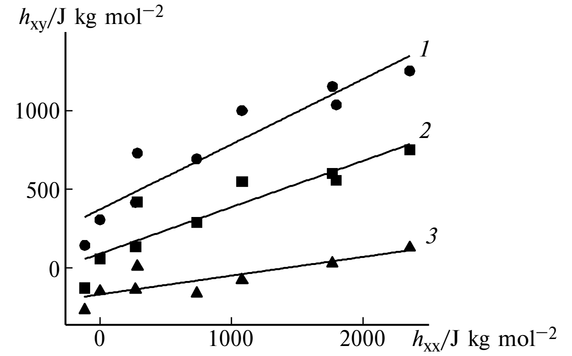

Fig. 4. Plots of the enthalpic amide—amide pairwise-interaction coefficients *vs.* interaction coefficients of amides with ethylene glycol (*1*), formamide (*2*), and urea (*3*).

An increase in the number of alkyl groups in molecules of co-dissolved hydrophilic non-electrolytes results in an increase in the h_{xy} values (see Fig. 4, Table 2) and a decrease in the hydrophobicity in the series EG > FA > urea. If the ratio of donor numbers to the number of hydrophobic groups is used to characterize the degree of hydrophilicity of non-electrolytes,[33] the hydrophilicity should enhance in the series: EG < FA < urea. Urea and FA are characterized by the hydrophilic properties, and EG occupies an intermediate position between non-electrolytes with hydrophilic and hydrophobic properties.

The data on Gibbs pair-interaction coefficients of EG in water (see Table 3) and published data[8] (g_{xx} = 11 J kg mol^{-2}) show that the pair association of EG molecules is thermodynamically unstable ($g_{xx} > 0$). The self-association of EG is prevented by the formation of numerous heterocomponent hydrogen bonds with water.[2] The heterotactic pair-interaction coefficients reflect the interaction of amides with hydrophilic non-electrolytes. According to analysis of increments of the contributions to the Gibbs pair coefficients,[6] the groups having the same effect on the water structure interact more favorably in aqueous solutions. The enhancement of the hydrophobic properties in the series urea < FA < EG is accompanied by the consecutive increase in the h_{xy} coefficients (see Fig. 4). This probably indicates that the nonaqueous components interact with each other mainly through the alkyl radicals. The enthalpic pair-interaction coefficients of DMF with aliphatic alcohols in water[34] confirm this assumption.

Thus, the concentration plots of the enthalpies of transfer of amides of aliphatic carboxylic acids from water to aqueous solutions of EG in the series FA < AA < NMF < NMA < DMFA < DMA < DMP < DEF < DEA reflect the sequence of increasing endothermic effect. The enthalpies of transfer increase on going from primary to tertiary amides and from formamides to the corresponding acetamides. These changes are mainly due to a decrease in the hydrophilic and hydrophobic components of amide solvation and an increase in the energy consumption needed to form a cavity in the mixed H_2O—EG solvent.

The positive values of heterotactic h_{xy} coefficients in aqueous solutions of EG calculated by the enthalpies of transfer are mainly due to the endothermicity of interaction of hydrocarbon groups of amide molecules with ethylene glycol. The contribution of interaction of the amide groups with EG to the h_{xy} values is close to zero due to the almost complete compensation of opposite effect of EG interaction with the methylene and hydroxyl groups. The enhancement of the hydrophobic properties of hydrophilic non-electrolytes in the series urea < FA < EG increases the h_{xy} values in this series, which is the result of an increase in the hydrophobic component of the amide—non-electrolyte interaction and a decrease in the exothermic effects of interaction of the amide and polar groups.

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