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Solvation and Enthalpy Coefficients of Interaction of Carboxylic Acid Amides with 1,2-Diols in Water

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Abstract — The enthalpies of solution of formamides, acetamides, and propionamides with various extents of N-substitution in aqueous solutions of propylene glycol and 1,2-butanediol (concentration ≤ 4 mol kg^{-1}) at 298.15 K were measured. The enthalpies of transfer of the amides from water to mixed aqueous-organic solvents were determined and discussed in combination with data on the enthalpies of transfer of amides from water to aqueous ethylene glycol solutions. The enthalpy coefficients of pair interactions of amides with 1,2-diols in water were calculated and used for evaluating the group components on the basis of the principle of group additivity of contributions. As the hydrophobic properties of polyfunctional nonelectrolytes are enhanced, the coefficients increase, which is due to the growth of the hydrophobic component of the interaction.

Revealing correlations between the structure of polyfunctional organic compounds and the thermodynamic characteristics of their nonelectrolyte mixtures, reflecting specific features of intermolecular interactions of the components, is an urgent problem of the modern chemistry of solutions [1, 2]. This work is a part of our studies of thermochemical properties of ternary aqueous systems containing carboxylic acid amides. One of our principal goals was to study specific features of interaction of polar and alkyl groups of amides differing in the degree of N-substitution with diols in water. The study was based on a thermochemical experiment. We measured the standard enthalpies of solution of primary, secondary, and tertiary amides of formic, acetic, and propionic acids in mixtures of water with propylene glycol (1,2-propanediol) and 1,2-butanediol at 298.15 K. From these data, we calculated the enthalpy coefficients of interaction of amides with diols, characterizing the enthalpy component of interaction of these compounds in water. We discuss our results in combination with previously obtained data for ternary aqueous systems whose nonaqueous components are amides and ethylene glycol [3].

The enthalpies of solutions of amides in aqueous solutions of diols at infinite dilution, determined in this work, are listed in Tables 1 and 2. The concentration dependences of the enthalpies of transfer of amides from water to aqueous solutions of propylene glycol, approximated by formulas (1) [5], are shown in Fig. 1.

$$\Delta H^0_{\mathrm{tr}} = \Delta H^0_{\mathrm{s}}(\mathrm{A,\ water–propylene\ glycol}) - \Delta H^0_{\mathrm{s}}(\mathrm{A,\ water}) = am + bm^2. \quad (1)$$

Here, ΔH^0_{s}(A, water–propylene glycol) and ΔH^0_{s}(A, water) are the standard enthalpies of solution of amides A in water–propylene glycol mixtures and in water, respectively; *a* and *b* are the approximation coefficients evaluated by the least-squares technique. The enthalpies of transfer were calculated using the standard enthalpies of solution of amides in water [4].

The enthalpies of transfer, equal to the differences between the enthalpies of solvation of substances in an aqueous-organic solvent and water, reflect how the solvation of amides varies with increasing concentration of the nonaqueous cosolvent, propylene glycol. Figure 1 shows that the solvation of all the amides becomes weaker with increasing concentration of this diol. It is commonly accepted now that the enthalpy of solvation is the sum of the enthalpy effects of the cavity formation in the solvent and of specific and nonspecific interactions between the solute and solvent molecules [1, 2]. It was shown previously that the major contribution to the enthalpy of hydration of amides is made by interaction of their polar groups with water [6, 7]. Addition of propylene glycol whose proton-donor power is lower than that of water [8] causes a regular decrease in the electron-acceptor

Table 1. Enthalpies of solution (ΔH_s^0, kJ mol^{-1}) of amides at infinite dilution in aqueous solutions of propylene glycol at 298.15 K

m_y, mol kg^{-1}	Formamide	Acetamide	Methylformamide	Methylacetamide	Dimethylformamide
0 [4]	1.97 ± 0.05	9.63 ± 0.07	–6.98 ± 0.07	–13.36 ± 0.04	–15.22 ± 0.06
0.5	2.30 ± 0.02	10.08 ± 0.01	–6.46 ± 0.03	–12.52 ± 0.04	–14.29 ± 0.02
1.0	2.65 ± 0.01	10.55 ± 0.06	–5.94 ± 0.09	–11.77 ± 0.01	–13.58 ± 0.07
1.5	2.83 ± 0.08	10.88 ± 0.07	–5.49 ± 0.02	–11.01 ± 0.05	–12.71 ± 0.06
2.0	3.19 ± 0.03	11.15 ± 0.01	–4.99 ± 0.09	–10.51 ± 0.07	–11.95 ± 0.01
2.5	3.33 ± 0.09	11.44 ± 0.03	–4.63 ± 0.05	–9.97 ± 0.05	–11.20 ± 0.07
3.0	3.52 ± 0.04	11.72 ± 0.06	–4.22 ± 0.01	–9.62 ± 0.03	–10.70 ± 0.05
4.0	3.68 ± 0.06	12.36 ± 0.06	–3.43 ± 0.05	–8.64 ± 0.01	–10.02 ± 0.02

m_y, mol kg^{-1}	Dimethylacetamide	Diethylformamide	Diethylacetamide	Dimethylpropionamide
0 [4]	–21.42 ± 0.04	–17.97 ± 0.04	–24.08 ± 0.11	–22.34 ± 0.05
0.5	–20.44 ± 0.03	–16.68 ± 0.05	–22.64 ± 0.08	–20.83 ± 0.01
1.0	–19.41 ± 0.04	–15.49 ± 0.01	–21.39 ± 0.06	–19.38 ± 0.01
1.5	–18.75 ± 0.02	–14.48 ± 0.06	–20.15 ± 0.08	–18.40 ± 0.06
2.0	–17.91 ± 0.05	–13.49 ± 0.05	–19.04 ± 0.01	–17.32 ± 0.04
2.5	–17.30 ± 0.02	–12.47 ± 0.04	–17.82 ± 0.01	–16.67 ± 0.08
3.0	–16.43 ± 0.01	–11.66 ± 0.09	–17.17 ± 0.02	–15.99 ± 0.04
4.0	–15.51 ± 0.10	–10.21 ± 0.09	–15.45 ± 0.02	–14.44 ± 0.01

Table 2. Enthalpies of solution (ΔH_s^0, kJ mol^{-1}) of amides at infinite dilution in aqueous solutions of 1,2-butanediol at 298.15 K

m_y, mol kg^{-1}	Formamide	Acetamide	Methylformamide	Methylacetamide	Dimethylformamide
0 [4]	1.97 ± 0.05	9.63 ± 0.07	–6.98 ± 0.07	–13.36 ± 0.04	–15.22 ± 0.06
0.5	2.45 ± 0.01	10.17 ± 0.01	–6.32 ± 0.02	–12.34 ± 0.06	–13.91 ± 0.01
1.0	2.75 ± 0.03	10.61 ± 0.02	–5.74 ± 0.01	–11.42 ± 0.01	–12.81 ± 0.08
1.5	3.20 ± 0.01	11.02 ± 0.04	–5.25 ± 0.05	–10.53 ± 0.06	–11.72 ± 0.05
2.0	3.44 ± 0.03	11.37 ± 0.06	–4.46 ± 0.06	–9.57 ± 0.01	–11.01 ± 0.03
2.5	3.49 ± 0.02	12.11 ± 0.08	–4.15 ± 0.02	–8.93 ± 0.06	–10.29 ± 0.01
3.0	3.82 ± 0.03	12.39 ± 0.03	–3.70 ± 0.02	–8.73 ± 0.01	–9.58 ± 0.08
4.0	3.68 ± 0.04	12.65 ± 0.07	–3.06 ± 0.07	–7.52 ± 0.01	–8.65 ± 0.04

m_y, mol kg^{-1}	Dimethylacetamide	Diethylformamide	Diethylacetamide	Dimethylpropionamide
0 [4]	–21.42 ± 0.04	–17.97 ± 0.04	–24.08 ± 0.11	–22.34 ± 0.05
0.5	–19.96 ± 0.02	–16.20 ± 0.07	–22.17 ± 0.01	–20.74 ± 0.08
1.0	–18.67 ± 0.05	–14.48 ± 0.01	–20.33 ± 0.07	–19.10 ± 0.03
1.5	–17.60 ± 0.03	–13.03 ± 0.08	–18.79 ± 0.02	–17.70 ± 0.09
2.0	–16.66 ± 0.03	–11.83 ± 0.06	–17.14 ± 0.05	–16.15 ± 0.04
2.5	–15.58 ± 0.04	–10.50 ± 0.01	–15.77 ± 0.01	–15.10 ± 0.05
3.0	–15.11 ± 0.08	–9.30 ± 0.03	–14.54 ± 0.11	–13.79 ± 0.03
4.0	–13.78 ± 0.06	–7.39 ± 0.01	–11.72 ± 0.08	–11.33 ± 0.07

power of binary solutions relative to pure water [9]. Most probably, this is one of the major factors responsible for weakened solvation of amides in mixtures of water with propylene glycol. The major component of nonspecific interaction of amides with water is hydrophobic hydration. According to Rouw and Somsen's estimates [10], the enthalpy of the structure-making effect of DMF alkyl fragments on water is about –16 kJ mol^{-1}, and in going to bulkier alkyl radicals in amide molecules the hydrophobic contribution to the enthalpy of hydration grows in the absolute value. Data on thermodynamic characteristics and dielectric permittivity of aqueous diol solutions [11], taking into account the concept of Goncharov *et al.* [12], show that propylene glycol in the examined composition range exerts a weak structure-breaking effect on water. This results in decreased absolute values of the effect of solvophobic solvation of amides in water–propylene glycol mixtures, compared to hydrophobic hydration in water, Moreover, a decrease in the contribution of the cavity mechanism of solvation [2] with increasing concentration of propylene glycol leads to the growth of the energy consumption for cavity formation in these solutions. Figure 1 shows that the enthalpies of transfer of amides depend on the degree of their N-substitution and grow in the order primary < secondary < tertiary amides. It is known that the hydrophobicity [1] and electron-donor power [13] of amides increase in the same direction. Apparently, the effect of the above factors responsible for weakening of solvation is the most pronounced with diethyl-substituted amides characterized by the strongest hydrophilic and hydrophobic properties and by the largest molar volume. For the same reasons, the enthalpies of transfer of acetamides, which contain an additional methyl group exerting an inductive effect on the carbonyl group, are always greater than the enthalpies of transfer of the corresponding formamides. The curve of $\Delta H^0_{\mathrm{tr}}(m)$ for dimethylpropionamide, which is a weaker electron donor than dimethylacetamide [14] but has a bulky acid residue, is located between the curves for dimethylformamide and dimethylacetamide.

The enthalpies of transfer of acetamides with various degrees of N-substitution from water to aqueous solutions of 1,2-diols are plotted in Fig. 2. For the sake of clarity, the curves for dimethylacetamide, which intersect with the corresponding curves for methylacetamide and diethylacetamide, are not shown. For acetamides with various degrees of N-substitution, ΔH^0_{s} tends to grow with increasing size of diol molecules. Presumably, this is primarily due to a regular decrease in the proton-donor power of mixed solvents water–1,2-diol, in view of the fact that aliphatic carboxamides are fairly strong proton acceptors [8]. It should be noted that addition to water of urea, which is a stronger proton donor than water, is characterized by negative values of ΔH^0_{tr} for carboxylic acid amides [4].

Data on the enthalpies of transfer allow estimation of the enthalpy coefficients bearing quantitative information on the energy characteristics of interaction of dissolved nonelectrolytes in water. According to the McMillan–Mayer theory [15], these coefficients are calculated by Eq. (2) [16]:

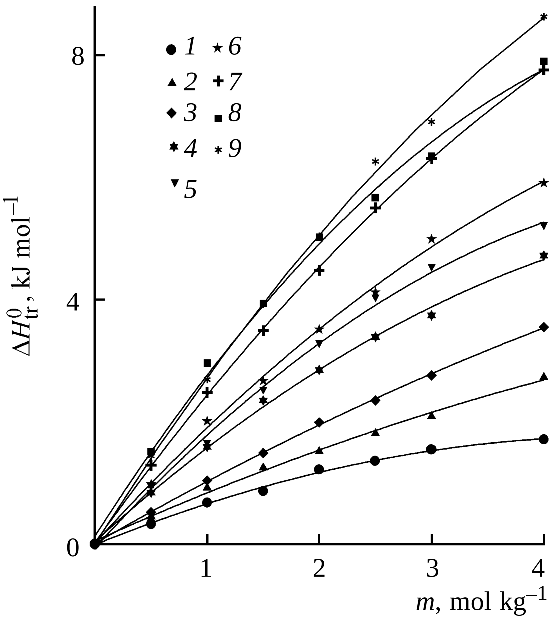

Fig. 1. Enthalpies of transfer of amides from water to water–propylene glycol mixed solvent at 298.15 K: (*1*) formamide, (*2*) acetamide, (*3*) methylformamide, (*4*) methylacetamide, (*5*) dimethylformamide, (*6*) dimethylacetamide, (*7*) diethylformamide, (*8*) dimethylpropionamide, and (*9*) diethylacetamide.

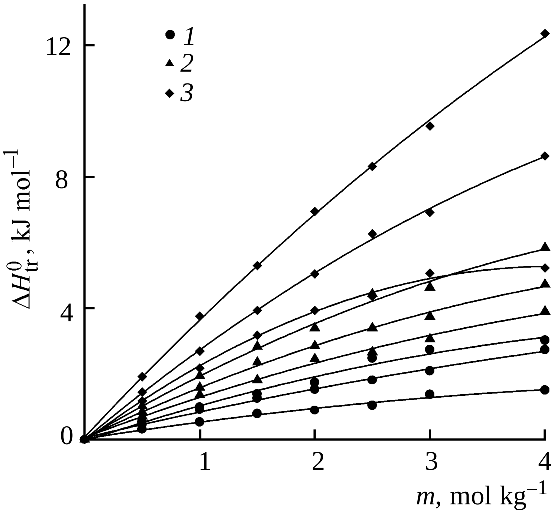

Fig. 2. Enthalpies of transfer of (*1*) acetamide, (*2*) methylacetamide, and (*3*) diethylacetamide from water to aqueous solutions of 1,2-diols: (lower curves) ethylene glycol, (middle curves) propylene glycol, and (upper curves) 1,2-butanediol.

Table 3. Enthalpy cpefficients of pair interactions of amides with 1,2-diols in water at 298.15 K, enthalpy and Gibbs coefficients of pair interactions of amides in water, parameters $(dB_{22}/dp)_T$ [cm^3 mol^{-1} bar^{-1}], and numbers of equivalent methylene groups in amides

Amide	Cosolute					Parameters	
	ethylene glycol h_{xy}, J kg mol^{-2}	propylene glycol h_{xy}, J kg mol^{-2}	1,2-butanediol, h_{xy}, J kg mol^{-2}	amide, h_{xx}, J kg mol^{-2}	amide, g_{xx}, J kg mol^{-2}	$(dB_{22}/dp)_T$	n_{CH_2}
Formamide	144(16) [3]	358(15)	497(24)	–115 [17]	–31 [17]	0.4	0.5
Acetamide	306(18) [3]	472(19)	538(32)	1 [17]	–145 [17]	–0.1	1.5
Methylformamide	416(28) [3]	537(7)	674(25)	272 [17]	–	–	2.0
Methylacetamide	731(26) [3]	875(18)	1057(30)	286 [18]	–400 [19]	–	3.0
Dimethylformamide	694(22) [3]	939(32)	1357(23)	737 [17]	–129 [17]	–1.8	3.5
Dimethylacetamide	1000(19) [3]	1033(30)	1513(27)	1081 [17]	–177 [17]	–4.9	4.5
Diethylformamide	1153(21) [3]	1319(16)	1845(11)	1767 [17]	–	–	5.5
Diethylacetamide	1251(24) [3]	1466(23)	1968(31)	2355 [17]	–	–	6.5
Dimethylpropionamide	1036(14) [3]	1587(46)	1663(28)	1797 [17]	–500 [17]	–	5.5

$$\Delta H^0_{\mathrm{tr}}/m_y = 2h_{xy} + 3h_{xyy}m_y + 3h_{xxy}m_x. \qquad (2)$$

Here, ΔH^0_{tr} is the enthalpy of transfer of amides from water to aqueous diol solutions; m_y and m_x are the molal concentrations of diols and amides; h_{xy}, h_{xyy}, and h_{xxy} are the enthalpy coefficients of pair and ternary interactions of amides (x) with diols (y). The coefficients h_{xy} and h_{xyy} were determined by the least-squares method neglecting the last term of Eq. (2) in view of low concentrations m_x. The calculation results are listed in Table 3. In parentheses are the standard errors of approximations (2).

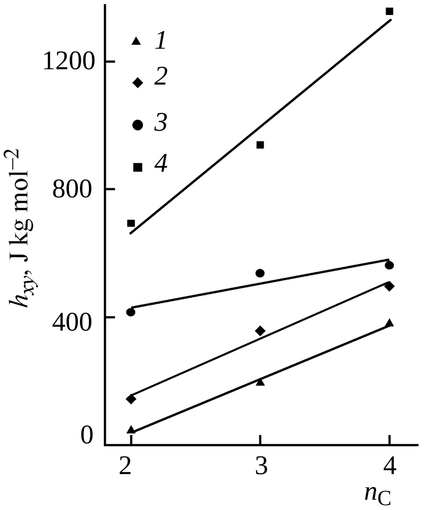

Fig. 3. Enthalpy coefficient of pair interactions h_{xy} as a function of the number of carbon atoms n_C in 1,2-diols: (*1*) urea, (*2*) formamide, (*3*) ethylene glycol, and (*4*) dimethylformamide.

We showed in [3] that, as the hydrophobicity of hydrophilic nonelectrolytes increases in the order urea < formamide < ethylene glycol, their enthalpy coefficients of pair interaction with carboxylic acid amides become more positive. This is due to the growth of the hydrophobic component of the interaction and decrease in the contribution from interaction of polar groups. The enthalpy coefficients of pair interactions of DMF and formamide with 1,2-diols, determined in this study, are plotted in Fig. 3 together with the published data for urea [20] and ethylene glycol [21]. It is seen that the coefficients h_{xy} for hydrophilic nonelectrolytes also increase in the order urea < formamide < ethylene glycol. Considering urea as a formamide derivative with the formyl proton substituted by the amino group, these data show that the heterotactic coefficients h_{xy} tend to grow with increasing hydrophobicity of amides in going from urea to DMF. In Table 3 we also give the derivative of the second virial coefficient with respect to pressure, $(dB_{22}/dp)_T$ [1], as one of the best hydrophobicity parameters. Also given are enthalpy coefficients of pair interactions of nonelectrolytes with each other (h_{xx}) and the Gibbs pair coefficients g_{xx} suggested in [1] as measures of the substance hydrophobicity. Previously, using the set of our and published data on the enthalpy coefficients of interaction of amides with electron-acceptor nonelectrolytes, we obtained an order of the relative hydrophobicity of amides: formamide < acetamide < methylformamide < dimethylformamide < dimethylacetamide < diethylformamide <

diethylacetamide [3, 4]. It shows that the hydrophobicity of N-substituted amides grows with increasing total size of alkyl groups (Table 3). This order is nicely consistent with the orders constructred on the basis of the parameters h_{xy}, $(dB_{22}/dp)_T$, and h_{xx} (Table 3), which confirms its reliability.

In Fig. 4, the enthalpy coefficients of interaction of propylene glycol and 1,2-butanediol with carboxylic acid amides are plotted vs. the number of equivalent methyl groups; data for ethylene glycol from [3] are also included. In compliance with [22], CH groups were considered equivalent to 0.5 methylene group, and CH_3 groups, to 1.5 methylene groups (Table 3). Ethylene glycol, according to its pair interaction coefficients (h_{xx} 415, g_{xx} 11 J kg mol^{-2} [23]; data for other 1,2-diols are also given in [23]), in terms of the approach developed in [24], exerts a hydrophilic effect on the water structure: $g_{xx} > 0$ and $h_{xx} > 0$. According to this classification, propylene glycol (h_{xx} 589, g_{xx} –126 J kg mol^{-2}) and all the amides studied in this work, except formamide (Table 3), are considered as hydrophobic nonelectrolytes: $g_{xx} < 0$ and $Ts_{xx} > h_{xx} > 0$. However, when the concentration scale in the McMillan–Mayer system [1] is used, propylene glycol together with ethylene glycol falls to the group of hydrophilic nonelectrolytes. This fact is apparently responsible for the similar behavior of the functions $h_{xy}(n_{CH_2})$ in aqueous solutions of these diols. It should be noted that, when both Lewis–Randall and McMillan–Mayer cocentration scales are used, 1,2-butanediol (h_{xx} 923, g_{xx} –217 J kg mol^{-2}) and its homologs with longer alkyl chains always fall into the group of hydrophobic structure-making nonelectrolytes [23].

The Gibbs pair coefficients show that intractions in aqueous solutions preferentially arise between the functional groups of nonelectrolytes exerting a similar effect on the water structure (hydrophobic–hydrophobic, hydrophilic–hydrophilic) [17]. Interactions between molecular fragments exerting different effects (hydrophobic–hydrophilic) are unfavorable [17]. Heterotactic coefficients given in Table 3 reflect interactions of amides exerting a hydrophobic effect on water (except formamide) with diols affecting the water structure differently. Enhancement of the hydrophobic properties of amides in going from formamide to diethylacetamide, and also in the series of diols ethylene glycol < propylene glycol < 1,2-butanediol is accompanied by a regular growth of the coefficients h_{xy} (Figs. 3, 4). Presumably, this reflects the general trend toward enhancement of interactions of nonaqueous components via alkyl radicals (hydrophobic interaction). This is also suggested by the enthalpy coefficients of pair interactions of DMF with *n*-alkanols in water [5]. However, in this case the obtained h_{xy} values are always more positive than in aqueous solutions of the corresponding diols, because monohydric alcohols are more hydrophobic.

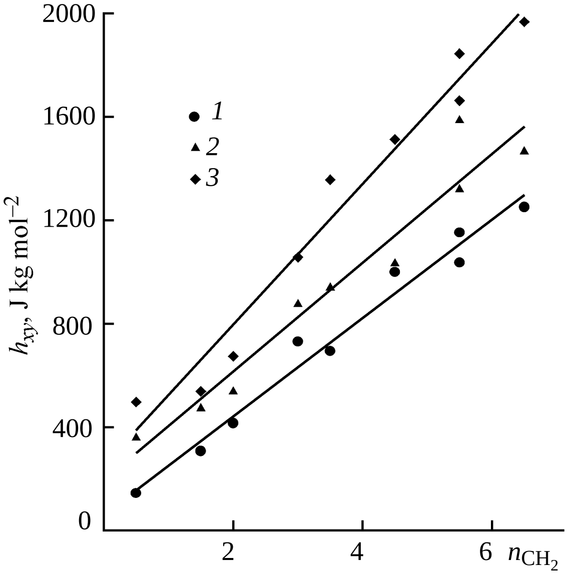

Fig. 4. Enthalpy coefficient of pair interactions h_{xy} as a function of the number of equivalent methylene groups in amides: (*1*) ethylene glycol, (*2*) propylene glycol, and (*3*) 1,2-butanediol.

The enthalpy coefficients of pair interactions of amides with diols have not been reported previously, except several h_{xy} values for interactions of ethylene glycol with primary amides [25]. The method of group additivity of contributions, suggested in this work, allows evaluation of the enthalpy components of h_{xy}:

$$h_{xy} = \Sigma n_i^x n_j^y H_{ij}. \quad (3)$$

Here n_i^x and n_j^Y are the numbers of groups of types i and j in molecules of amides (x) and diols (y), respectively; H_{ij} is the enthalpy contribution of interaction of these groups. A part of parameters H_{ij}, including those describing interaction of the methylene group with the amide group (AG) ($H_{CH_2–AG}$) and methylene group ($H_{CH_2–CH_2}$), have been reliably determined [22, 26]. The parameters $H_{AG–OH}$ and $H_{CH_2–OH}$ can be estimated on the basis of relationship (3) transformed into the following form:

$$\Delta h = h_{xy} - \Sigma n_i^x n_j^y H_{ij}^*, \quad (4)$$

where H_{ij}^* are the known interaction parameters. After cancellations and transformations, expression (4)

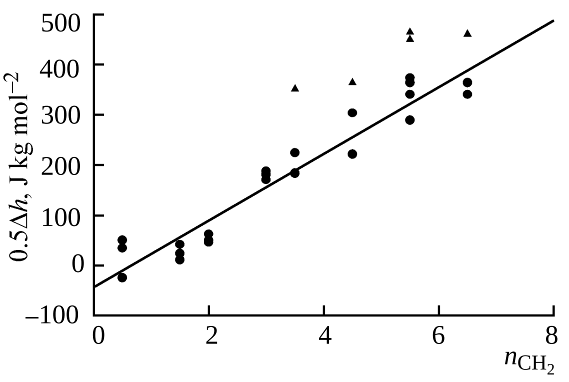

Fig. 5. Difference between the enthalpy components of the coefficients of pair interactions (5) as a function of the number of equivalent methylene groups in amides (parameters corresponding to coefficients of interaction of tertiary amides with 1,2-butanediol are given as triangles).

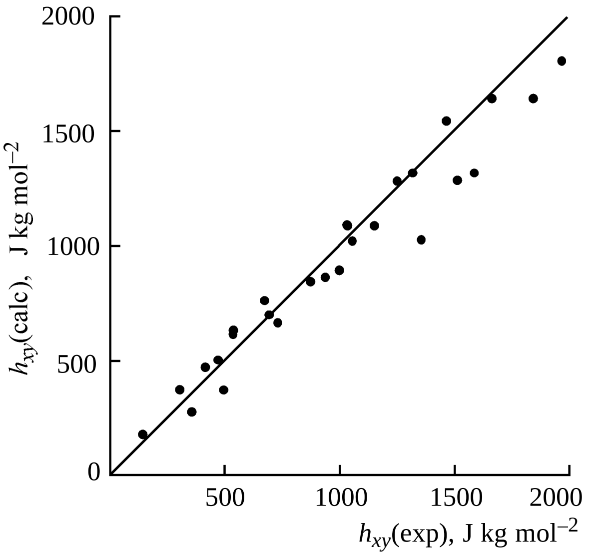

Fig. 6. Correlation between the experimental interaction coefficients h_{xy}(exp) and those calculated by additive scheme (3), h_{xy}(calc).

acquires the following explicit form:

$$0.5\Delta h = H_{\mathrm{AG-OH}} + n^{x}_{\mathrm{CH_2}} H_{\mathrm{CH_2-OH}}. \qquad (5)$$

The parameters Δh were calculated using the value $H_{\mathrm{CH_2-CH_2}}$ 32.7 J kg mol^{-2} [22] and the parametrers $H_{\mathrm{CH_2-AG}}$, which were taken equal to 80 J kg mol^{-2} for primary and secondary amides [22] and 49 J kg mol^{-2} for tertiary amides [26]. The initial separate approximation of data for tertiary amides and amides with a lesser degree of N-substitution showed that the parameters $H_{\mathrm{AG-OH}}$ and $H_{\mathrm{CH_2-OH}}$ determined for both groups virtually coincide. This allowed unified treatment of all the data obtained using relationship (5). Figure 5 shows the results of this treatment; the calculated enthalpy coefficients of interactions are $H_{\mathrm{CH_2-OH}}$ 66.4(4.3) and $H_{\mathrm{AG-OH}}$ −42.6(35.8) J kg mol^{-2} (in parentheses are the standard deviations). The enthalpy coefficients of interaction of tertiary amides with 1,2-butanediol, shown in the figure as triangles and lying out of the correlation, were not included in the approximation.

The positive value of $H_{\mathrm{CH_2-OH}}$ obtained in this work virtually coincides with the value calculated from the enthalpy coefficients of pair interactions of polyols in water [27]. The calculation shows that hydrocarbon radicals of amides interact with hydroxy groups of diols in water with an endoeffect. This is consistent with the previously found relationship [17] that interaction of the $\mathrm{CH_2}$ group with any polar group is characterized by the increment $H_{\mathrm{CH_2}-j} > 0$. The endothermicity of this interaction in the systems under consideration may be due to dehydration of different solvation shells upon approach of the corresponding fragments of amide and dihydric alcohol molecules. The increment $H_{\mathrm{AG-OH}}$ is negative, indicating that the interactions of amide and hydroxy groups is exothermic. This is apparently due to the fact that the direct interaction of these polar molecular fragments is more exothermic than their dehydration. Analysis of the enthalpy coefficients h_{xy} showed that, since the difference in the strength of interactions involving substituted and unsubstituted amide groups is insignificant, it is, as a rule, sufficient to describe their interaction with various functional groups of nonelectrolytes by a single parameter [28]. Estimation of the parameters $H_{\mathrm{AG-OH}}$ made in this work confirms this conclusion.

Thus, it follows from (3) the growth of h_{xy} in the series ethylene glycol < propylene glycol < 1,2-butanediol, and also in going from formamide to diethylacetamide, is due to an increase in the enthalpy component of interaction via alkyl radicals (hydrophobic interaction). On the other hand, estimations of H_{ij} show that a comparable contribution to h_{xy} is made by interaction of alkyl groups of amides with hydroxy groups of diols. At the same time, the contributions from interaction of amide groups with hydrocarbon and hydroxy groups of diols are smaller in the absolute value. Having opposite signs, they virtually compensate each other and have no noticeable effect on h_{xy}. Figure 6 shows a correlation between the experimental coefficients h_{xy} (Table 3) and those calculated by additive scheme (3). On the whole, these values are in reasonable agreement. However, the pair coefficients of interaction of 1,2-butanediol with tertiary amides systematically differ from those calculated by the additive scheme. Such a difference between h_{xy}(calc) and h_{xy}(exp) is probably due to specific preferential orientations of the interacting components [1]. This trend may be more pronounced when considering interactions of amides with 1,2-diols containing a longer alkyl chain.

EXPERIMENTAL

Propylene glycol (purre grade) and 1,2-butanediol (Aldrich) were double-distilled in a vacuum with collection of the middle fractions. DMF (ultrapure grade), diethylformamide (Fluka), dimethylpropionamide (Aldrich), dimethylacetamide (Fluka), diethylacetamide (pure grade), and methylformamide (Aldrich) were double-distilled in a vacuum, with intermediate drying over 4 Å molecular sieves (Aldrich). Methylacetamide (pure grade) was double-distilled in a vacuum with intermediate drying over the same sieves at 323 K; it was used in the experiment as a supercooled liquid. Formamide (pure grade) was purified by freezing, vacuum distillation, and drying over 3 Å molecular sieves (Aldrich). Acetamide (analytically pure grade) was recrystallized two times from anhydrous methanol and dried in a vacuum for 72 h at room temperature. The water content in the organic solvents, determined by Fischer titration, did not exceed 0.03 wt %, and the physicochemical characteristics of the chemicals (melting point, density) agreed with the reference data [29]. Water–diol mixtures were prepared gravimetrically using freshly double-distilled water.

The enthalpies of solution (ΔH_s) were measured at 298.15 K in an ampule-type calorimeter with an isothermal jacket; the volume of the reaction vessel was 50 cm^3. The device is described in detail in [30]. The calorimeter accuracy was checked previously by measuring the enthalpies of solution of carboxylic acid amides in water. The standard enthalpies of solution (ΔH_s^0) determined by us agreed with the most reliable reference data [4]. The enthalpies of solution were measured at solute concentrations less than 0.08 mol kg^{-1}. In this range, ΔH_s was found to be independent of the solute concentration; therefore, the enthalpies of solution at infinite dilution (ΔH_s^0) were calculated as mean values of 3–4 measurements. The standard deviation of a single measurement is given as the experimental error.

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