Thermochemistry of dissolution of aniline in mixtures of water with methanol and *tert*-butyl alcohol

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The enthalpies of dissolution ($\Delta H°_{sol}$) of aniline in mixtures of water with methanol and *tert*-butyl alcohol were determined in the whole concentration range of mixed solvents at 25 °C. Maxima of endothermicity were found in both systems at ~0.3 and ~0.06 molar fractions, respectively. The data obtained were compared with the thermochemical characteristics of the nonelectrolytes studied previously (dimethylsulfoxide, nitromethane, formamide, *etc.*). The conclusion was drawn that the behavior of aniline in water—alcohol mixtures is mainly determined by its proton-donating ability and solvation of the benzene ring. A comparison of acoustic data and spectral and thermodynamic characteristics showed that thermochemical data are the most sensitive indicator for energy and structural changes occurring upon variation of the composition of a mixed solvent.

Key words: dissolution enthalpy, transfer enthalpy, solvation enthalpy, universal and specific solvation, aniline, mixed solvent, water, methanol, *tert*-butyl alcohol, solvatochromic parameters.

Aniline as aromatic amine is a strong base. At the same time, it can be a proton donor in reactions with bases. In water-organic media, aniline can manifest both properties.

The dissolution enthalpies ($\Delta H°_{sol}$) of aniline[1] and nitromethane (NM)[2] in mixtures of water with hexamethylphosphotriamide (HMPA) have been determined. Similar measurements have been performed for acetonitrile (AN), propylene carbonate (PC), and NM in mixtures of water with *tert*-butyl alcohol.[3,4] In all systems indicated, the dependences $\Delta H°_{sol} = f(X)$ have pronounced maxima at the content of a nonaqueous component X = 0.05—0.07 molar fractions. The dissolution enthalpies of AN, PC, and NM in mixtures of water with methanol reach maximum values at X = 0.2—0.3 molar fractions of alcohol.[3,5] However, the dependences $\Delta H°_{sol} = f(X)$ do not always exhibit the extreme character: for example, the dissolution enthalpies of dimethylsulfoxide (DMSO) in the H_2O—MeOH and H_2O—Bu^{t}OH mixtures have no maxima; the exothermicity of dissolution of DMSO in both systems decreases continuously as the content of the nonaqueous component increases.[3,4] The same behavior is characteristic of HMPA in mixtures of water with methanol, ethylene glycol, or glycerol.[5,6]

Organic compounds can be conventionally classified by their electron donor-acceptor (EDA) ability into predominantly electron donors and predominantly electron acceptors.[5,7] From this viewpoint, DMSO and HMPA are predominantly electron donors, and AN, NM, and PC are predominantly electron acceptors (rather than H-donors). In the first case, the dependences $\Delta H°_{sol} = f(X)$ have no maxima, and in the second case, they do. Therefore, the thermochemical behavior of aniline (a strong electron donor in the H_2O—HMPA system) seems rather unusual, especially if it is taken into account that for such different (by EDA ability) nonelectrolytes as $PhNH_2$ and NM, the positions and heights of maxima on the curves of change of the dissolution enthalpies (relative to the value of the dissolution enthalpy in water) virtually coincide.[1,2] This suggests that solvation of aromatic compounds in water-organic solvents has specific features as compared to that of aliphatic derivatives. It is of interest to compare the data for two amines ($PhNH_2$ and $BuNH_2$) in two H bond-associated solvents, water and *n*-octanol.[8—11] In water the dissolution enthalpies are equal to 1.8 ($PhNH_2$) and −24.0 kJ mol^{-1} ($BuNH_2$), and in *n*-octanol they are 4.6 and −9.4 kJ mol^{-1}, respectively. These data illustrate the aforesaid well. Note that aniline is one of the few liquid nonelectrolytes whose dissolution enthalpy in water is positive.

In this work, we thermochemically studied solutions of aniline in H_2O—MeOH and H_2O—Bu^{t}OH mixtures (Table 1). These organic solvents were chosen because Bu^{t}OH is one of the most hydrophobic nonelectrolytes

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Table 1. Dissolution enthalpies (ΔH^m_{sol}/kJ mol^{-1}) of aniline in mixed water-alcohol solvents at 25 °C

X_{MeOH}[a]	H_2O—MeOH		X_{Bu^tOH}[a]	H_2O—Bu^tOH	
	$m^b \cdot 10^4$	ΔH^m_{sol}[c]		$m^b \cdot 10^4$	ΔH^m_{sol}
0	136	1.81	0.0120	366	4.69
	138	1.76		735	4.51
	238	1.78			[4.60]
	263	1.75			
	441	1.79	0.0277	498	8.46
	706	1.78			
		[1.78]	0.0465	407	14.35
0.0060	301	2.01	0.0588	347	16.17
0.0089	174	2.22	0.0736	388	14.40
0.0227	278	2.68	0.1009	477	11.25
0.0535	251	4.43	0.2034	411	6.88
0.0715	146	5.34	0.2943	464	5.62
				923	5.54
0.0893	136	5.84			[5.58]
0.1313	141	7.20	0.4963	560	5.05
0.1950	988	8.56	0.7433	637	5.78
0.3391	454	7.78	0.8441	564	6.83
0.5219	271	3.52	0.8994	569	7.90
0.7260	767	0.74	0.9368	870	8.50
0.8636	147	−1.12	0.9878	187	10.54
				689	10.80
0.9014	149	−1.47			[10.67]
0.9267	120	−1.73	1.0000		11.20[d]
1.0000	79	−2.53			
	120	−2.51			
	257	−2.53			
	618	−2.52			
	1046	−2.50			
		[−2.52]			

[a] *X* is the content of the nonaqueous component of the solvent (molar fractions).

[b] *m*/mol kg^{-1} is molarity of the dissolved substance.

[c] The mean arithmetic values are presented in brackets.

[d] ΔH^m_{sol} of aniline at $X = 1.0000$ molar fractions of Bu^tOH was obtained by extrapolation.

by its action on water. In addition, it is the single alcohol of isomeric butyl alcohols that is indefinitely soluble in water. The H_2O—Bu^tOH system has been studied for many years by various methods, but no complete information has been obtained. The H_2O—MeOH system is a traditional object for studies, since methanol also possesses hydrophobic properties, although they are considerably less pronounced than in the case of Bu^tOH and HMPA. Both alcohols (methanol and *tert*-butyl alcohol) are characterized by the intermolecular H bond, which allows them to be classified as associated liquids. To get a complete pattern and reveal general tendencies, the results obtained in this work are given in comparison with the data for other electrolytes published previously.[2—7]

The solvation process and the state of aromatic compounds in water-organic mixtures are also of interest owing to the fact that studies of the solvatochromic characteristics of these solvents[12,13] have recently become much more numerous; in addition, solvatochromic indicators are aromatic compounds: nitrophenol, nitroaniline, and their derivatives. In particular, these studies have been performed recently[13] for the H_2O—Bu^tOH system.

Experimental

The following solvents were used: methanol (reagent grade), which was purified and dehydrated according to the standard procedure[14] by distillation with calcium methylate; Bu^tOH (analytical purity grade), which was slowly frozen, then the liquid fraction was removed, and the solid fraction was melted (the procedure was carried out twice); and aniline purified by triple vacuum distillation (according to GLC analysis, the water content was <0.5 wt.%). Aniline was stored not longer than 1 month in the dark.

The water content (according to the data of titration by the Fischer reagent[15]) was not greater than 0.04 and 0.15 wt.% for MeOH and Bu^tOH, respectively.

The water—alcohol mixtures were prepared by the gravimetric method with an accuracy to 0.0001 molar fractions using freshly prepared bidistilled water (specific electroconductivity $1 \cdot 10^{-5}$ Ohm^{-1} cm^{-1}).

The dissolution enthalpies were measured by a temperature-variable calorimeter with an isothermic shell. A glass ampoule containing 0.2 mL aniline was broken in a calorimetric vessel containing 60 mL of the solvent. Note that an ampoule-type calorimeter provides higher accuracy of measurements than a titration calorimeter.[16] The accuracy of maintenance of the temperature of the calorimeter shell was ±0.002 K. The instrument error of measurements was not higher than 0.5%, and reproducibility of results was not worse than 0.1%. Arithmetic mean values of heat effects of dissolution ΔH^m_{sol} were accepted as the standard values of dissolution enthalpies, since no dependence of ΔH^m_{sol} on the concentration of aniline was observed.

The values obtained for dissolution enthalpies (kJ mol^{-1}) of aniline in water, methanol, and *tert*-butyl alcohol agree with the literature data presented in parentheses: 1.78 (1.82±0.02),[1] (1.78);[8] −2.52 (−2.59±0.12);[11] and 10.67 (11.21±0.12),[11] respectively.

Results and Discussion

The parameters characterizing the solvating ability of the compounds and sizes of molecules are presented in Table 2. The parameters obtained up to the present time for mixed H_2O—MeOH and H_2O—Bu^tOH solvents are shown in Fig. 1. The basicity (H-acceptor ability) of a mixture is reflected by the parameter β[13] (or B_{KT}[21]). The B_{KT} parameter of mixtures of water with methanol was determined using a pair of indicators: *p*-nitroaniline/*N*,*N*-diethyl-*p*-nitroaniline.[21] The β parameter for the H_2O—Bu^tOH system has been obtained recently from the solvatochromic characteristics of the *p*-nitrophenol/*p*-nitroanisole system.[13] The authors of Ref. 13 presented no β values for water and *tert*-butyl alcohol; therefore, the corresponding values were taken from Ref. 20 for the same pair of indicators (see Table 2). The E_T^N parameter (normalized E_T values) of the wa-

Table 2. Empirical parameters and physicochemical characteristics of compounds at 25 °C

Compound	E_T[17]	E[18]	B[18]	AN[19]	DN[19]	β[20]	B_{KT}[20]	ΔH_{vap} /kJ mol^{-1}	V_m /cm^3 mol^{-1}
HMPA	40.9	−0.2	234	10.6	38.8	0.97	1.00	65.0	175.7
Bu^{t}OH	43.9	5.15	—	27.1	>20	0.91	0.95	46.8	94.9
$PhNH_2$	44.3	6.15	210	28.8[a]	33.3[b]	—	—	56.8	91.2
DMSO	45.0	3.7	193	19.3	29.8	0.72	0.74	52.8	71.3
AN	45.6	5.21	101	18.9	14.1	—	—	33.3	52.9
NM	46.3	5.15	58	20.5	2.7	—	—	38.3	54.0
PC	46.6	—	—	18.3	15.1	—	—	49.8	85.2
MeOH	55.4	14.94	—	41.3	19.0	0.70	0.62	37.5	40.7
FA	56.6	14.59	—	39.8	24.0	—	—	60.1	39.9
H_2O	63.1	21.8	123	54.8	18.0	0.47	0.14	44.0	18.1

Note. E_T is the Dimroth—Reichardt parameter, E and B are the electrophilicity and nucleophilicity parameters, AN and DN are the acceptor and donor numbers.

[a] Determined from the linear dependence of AN on E in the series Bu^{t}OH, Pr^{i}OH, Pr^{n}OH, Bu^{n}OH, EtOH, and H_2O; the linear dependence of AN on E_T (Bu^{t}OH, Pr^{i}OH, EtOH, and MeOH) gives the value AN ($PhNH_2$) = 27.3.

[b] Determined[19] from the dependence of DN on B.

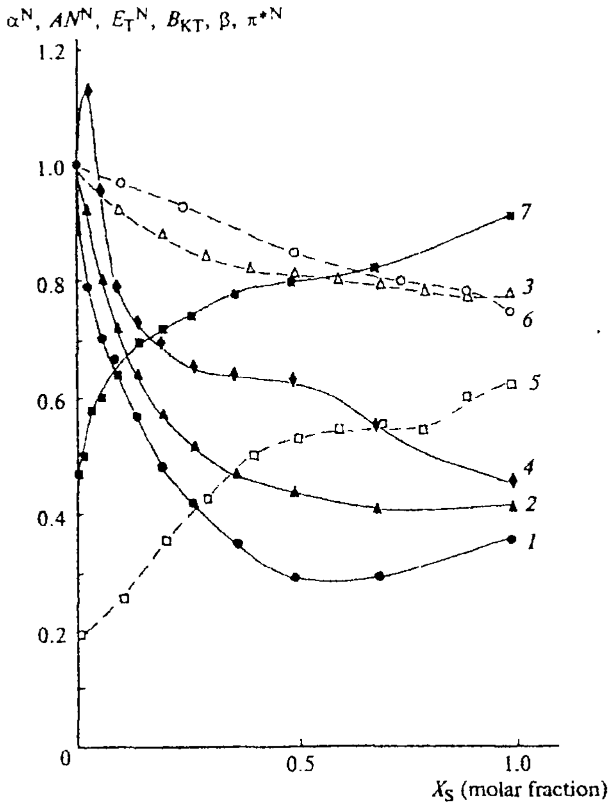

Fig. 1. Normalized parameters of the solvating ability of mixed solvents water—methanol (dotted line) and water—*tert*-butyl alcohol (solid line): α^N (*1*); E_T^N (*2*, *3*); π^{*N} (*4*); B_{KT} (*5*); AN^N (*6*); and β (*7*). S is methanol or *tert*-butanol.

ter—methanol system was determined previously,[21] and that for the water—*tert*-butyl alcohol system was calculated by us from spectral characteristics.[13] We found a good correlation between the E_T and E values (see Table 2) for 11 H bond-associated liquids (6 aliphatic alcohols, benzyl alcohol, 2-methoxyethanol, ethylene glycol, diethylene glycol, and water). It follows from this that the E_T^N parameter reflects mainly the electron-acceptor ability of the solvent.[21] Taking into account the solvatochromic equation (1), which is presented below and describes the interrelation between the α, E_T, and π^* parameters, we can say that the E_T^N parameter reflects the H-donor ability (α) with a fraction of the contribution from polarity/polarizability (π^*).

The Kamlet—Taft parameter π^* reflects the ability of a solvent to nonspecific interactions. The values of parameter π^* for water—*tert*-butyl alcohol mixtures averaged by three solvatochromic indicators are presented in Ref. 13 cited above; however, the data for water and alcohol are scarce. Therefore, we calculated the π^* values for the H_2O—Bu^{t}OH system from the spectral characteristics of *p*-nitroanisole.[13,20]

The AN and α parameters reflect the H-donor ability of solvents. We used the literature[22] values of acceptor numbers of water—methanol mixtures. The α parameter of the H_2O—Bu^{t}OH system was calculated from the solvatochromic equation[13]

$$\alpha = (E_T - 11.5\pi^* - 31.2)/15.2. \qquad (1)$$

For clarification, the π^*, AN, and α parameters were normalized by division into the value of this parameter for water (see Fig. 1).

The transfer enthalpies (ΔH°_{tr}) calculated from the data in Table 1 for aniline and some nonelectrolytes studied previously from methanol and *tert*-butyl alcohol in their mixtures with water[3–6,23–27] are presented in Fig. 2. The transfer enthalpies reflect the influence of water additives to alcohols on solvation of organic substances. In the first approximation, the contribution

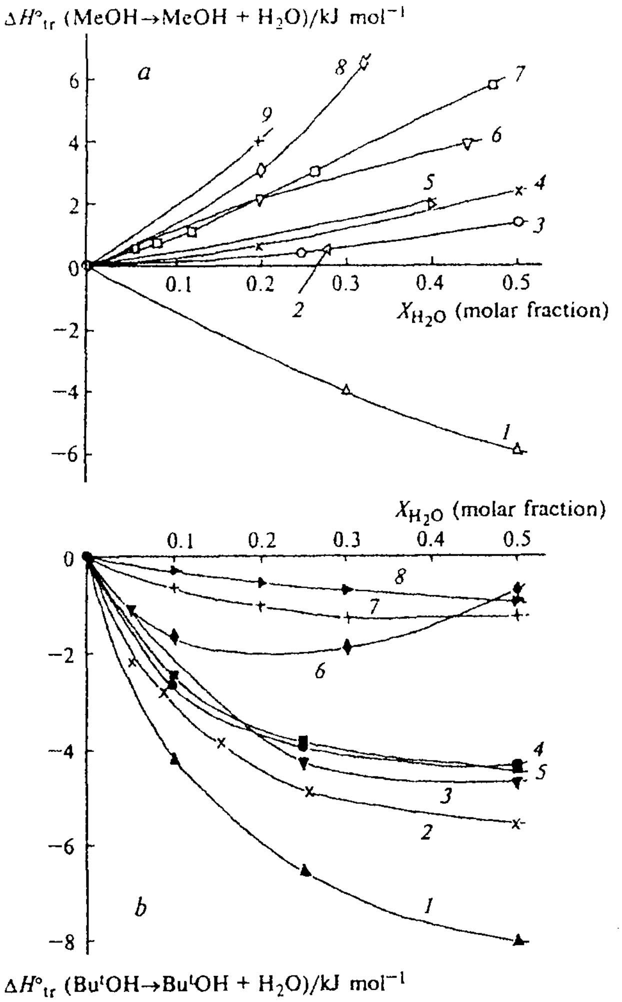

Fig. 2. Transfer enthalpies (ΔH°_{tr}) of nonelectrolytes from methanol (*a*) and *tert*-butyl alcohol (*b*) in their mixtures with water. *a*: DMSO (*1*), FA (*2*), AN (*3*), PC (*4*), carbamide (*5*), NM (*6*), $PhNH_2$ (*7*), heptane (*8*), and decane (*9*); *b*: DMSO (*1*), $PhNH_2$ (*2*), NM (*3*), AN (*4*), PC (*5*), FA (*6*), heptane (*7*), and decane (*8*).

corresponding to nonspecific (universal) solvation of polar molecules can be estimated from the enthalpy characteristics of alkanes. In the case of a methanol solution, we present additionally the dependences $\Delta H^\circ_{tr} = f(X)$ for two hydrophilic compounds with the NH_2 groups (of formamide and carbamide).

It is seen in Fig. 2 that the addition of water to methanol or *tert*-butyl alcohol has different effects on solvation of nonelectrolytes. In the $MeOH-H_2O$ system, only the solvation of DMSO is enhanced, whereas the solvation of other organic substances is weakened. When *tert*-butyl alcohol is diluted with water, the solvation of all nonelectrolytes is enhanced to some extent.

Methanol solutions (see Fig. 2, *a*). An increase in the content of water weakens the universal solvation of molecules most likely due to an increase in the contribution of the formation of a cavity (endo-effect). The solvent becomes more structurized due to the intercomponent interaction. An increase in the size of molecules of a dissolved substance affects transfer enthalpies insignificantly, which is seen from a comparison of the data for nonpolar pentane and heptane or polar AN and PC with a close EDA ability and different sizes of the molecules (see Table 2).

Exothermicity of the transfer of DMSO from methanol to its mixtures with water can be explained only by enhancement of the specific interaction >S=O...H—O— favored by an increase in the electron-acceptor ability of the mixed solvent (*AN*). From this viewpoint, the behavior of aniline, which is even a stronger base than DMSO (see Table 2), is unusual. Aniline behaves in such a way as if the dilution of methanol with water has no effect on the specific solvation of this substance. This occurs because the acidity and basicity of the mixture (*AN* and B_{KT}) change in different directions (see Fig. 1). Although the >N...H—O— interaction is enhanced in a methanol solution as the water content increases, this effect is compensated by weakening of the >NH...O< interaction. The data for formamide and carbamide (see Fig. 2, *a*) confirm the aforesaid. However, it should be kept in mind that different functional groups of the molecules (>C=O and $-NH_2$) are specifically solvated in the case of amides. The participation in the interaction with a solvent of the benzene ring of aniline, which acts as both the electron donor and acceptor, cannot be ruled out.

Bu^tOH-H_2O system (see Fig. 2, *b*). This mixed solvent differs from the other mixtures of organic solvents with water studied to the present time by a unique specific feature: dilution of *tert*-butyl alcohol with water results in enhancement of solvation of nonpolar nonelectrolytes, for example, alkanes. The addition of water to methanol (see Fig. 2, *a*), ethanol and propanol,[25] acetone and 1,4-dioxane,[28] DMF,[29] and HMPA[30] exerts an opposite effect. It looks like the dilution of *tert*-butyl alcohol with water decreases the structurization of the solvent. As can be seen in Fig. 2, *b*, small water additives (to 0.1 molar fractions) are most efficient. The composition range X = 0.7—1.0 molar fractions of alcohol was not studied by spectrophotometry (see Fig. 1). It can be assumed that in this composition range, the ability of the solvent to nonspecific solvation increases (the π^* parameter increases). However, it can be stated that the dilution of *tert*-butyl alcohol with water enhances the universal solvation of molecules, and a change in their size has a minor effect. The basicity of the mixture β upon this dilution decreases as in the case of a methanol solution. At the same time, its acidity (based on the α parameter), unlike that of a methanol solution, also somewhat decreases. Thus, the addition of water to *tert*-butyl alcohol should result in a decrease in the ability of the solvent to specific solvation. Then it is clear why the dilution of alcohol with water differentiates considerably less organic compounds by their EDA ability in the case of Bu^tOH as compared to MeOH. For

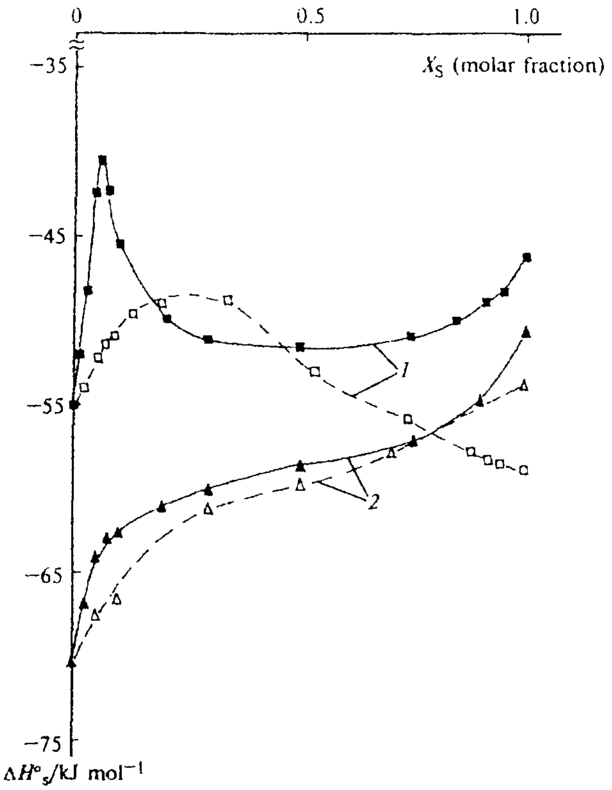

Fig. 3. Solvation enthalpies ($\Delta H°_s$) of aniline (*1*) and DMSO (*2*) in aqueous solutions of methanol (dotted line) and *tert*-butyl alcohol (solid line). S is methanol or *tert*-butyl alcohol.

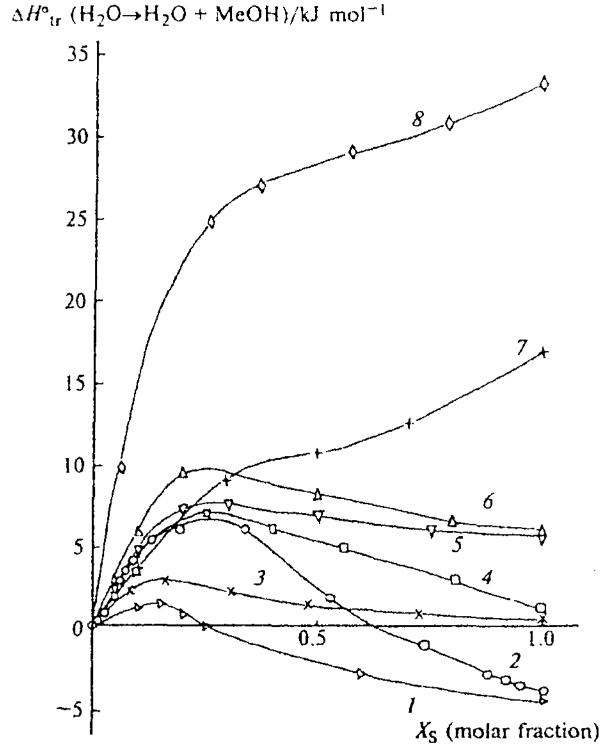

Fig. 4. Transfer enthalpies ($\Delta H°_{tr}$) of carbamide (*1*), $PhNH_2$ (*2*), FA (*3*), NM (*4*), AN (*5*), PC (*6*), DMSO (*7*), and HMPA (*8*) from water to an aqueous solution of methanol.

example, for the equimolar composition, the difference between the transfer enthalpies of AN, PC, and NM (on the one hand) and DMSO (on the other hand) is 8—11 kJ mol^{-1} in the MeOH—H_2O system and only 3.5 kJ mol^{-1} in the Bu^{t}OH—H_2O system. The corresponding difference for $PhNH_2$ and DMSO is equal to 12 kJ mol^{-1} (MeOH—H_2O) and 2.5 kJ mol^{-1} (Bu^{t}OH—H_2O). Perhaps, the electron-donor and electron-acceptor properties of the benzene ring of aniline are also manifested in this case.

A clear representation of specific features of solvation of two strong electron donors ($PhNH_2$ and DMSO) is given by enthalpies of their solvation shown in Fig. 3. Three composition regions with different solvating abilities of mixed solvents with respect to aniline are distinctly seen. At X = 0—0.15 and X = 0.45—1.0 molar fractions of the alcohol, methanol solutions possess a higher solvating ability. In the range of X = 0.15—0.45 molar fractions of the alcohol, butyl alcohol solutions possess a higher solvating ability.

Aqueous solutions. It is seen from the dependences presented in Fig. 4 that at X = 0—0.2 molar fractions of methanol, the changes related to the specific solvation of nonelectrolytes obviously play a secondary role. The transfer enthalpies of $PhNH_2$, DMSO, AN, and NM differ very slightly against substantial distinctions in the EDA ability of these compounds (see Table 2). Here weakening of universal solvation due to an increase in the endo-effect of formation of a cavity in the solvent is the main factor. The effects of specific solvation due to a decrease in the acidity of the mixture (E_T, *AN*, see Fig. 1) are probably overlapped somewhat by effects caused by an increase in its basicity (B_{KT}). At $X >$ 0.2 molar fractions of methanol, a decrease in the acidity of the solvent plays the main role in the case of DMSO, whereas in the case of $PhNH_2$, NM, and AN, an enhancement of universal solvation and an increase in the basicity of the medium are the main factors.

The transfer enthalpies of two hydrophilic substances (carbamide and formamide) are presented in Fig. 4. As can be seen in Table 2, formamide is a considerably stronger H-donor than aniline, and the amides indicated are more sensitive to a change in the basicity of the solvent. Therefore, in the case of amides, the height of the maximum decreases and its position is shifted to the region of lower methanol additives.

The dependences of the transfer enthalpies of organic substances (except for DMSO) on the composition of the mixture in the H_2O—Bu^{t}OH system (Fig. 5), as in the H_2O—MeOH system (see Fig. 4), have an extreme character. The positions of maxima on these

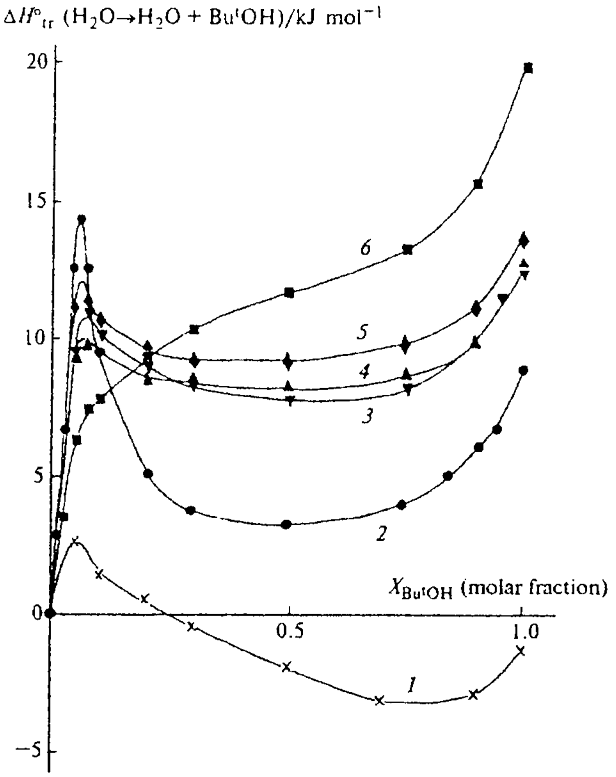

Fig. 5. Transfer enthalpies (ΔH°_{tr}) of FA (*1*), $PhNH_2$ (*2*), NM (*3*), AN (*4*), PC (*5*), and DMSO (*6*) from water to an aqueous solution of *tert*-butyl alcohol.

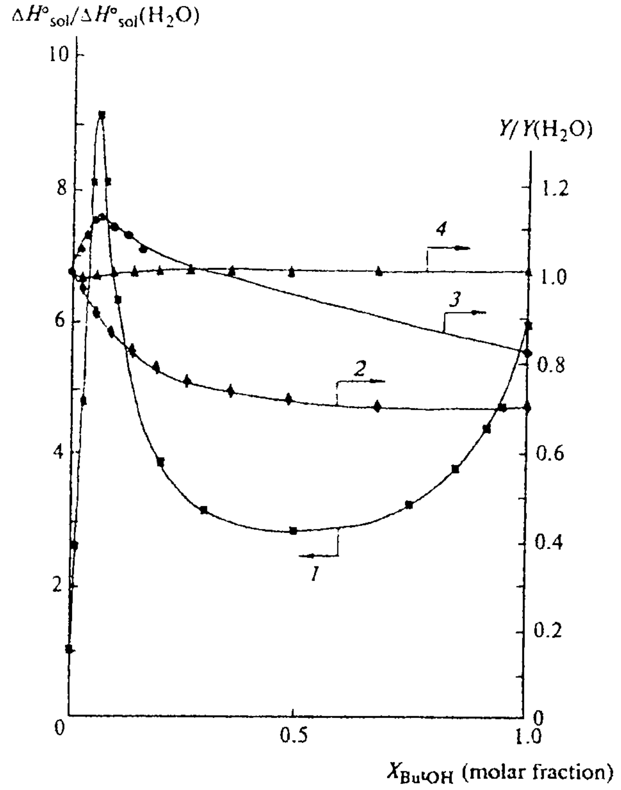

Fig. 6. Relative characteristics in the water—*tert*-butyl alcohol system: *1*, dissolution enthalpy of aniline; *2*, ν_{max} of absorption of Dimroth's betaine; *3*, hypersound velocity; and *4*, ν_{max} of absorption of *p*-nitrophenol.

dependences ($X \approx 0.06$ molar fractions of Bu^{t}OH) are probably independent of the nature of the nonelectrolyte. Aniline in the H_2O—Bu^{t}OH system is sensitive to changes in the solvent. The change in the π^* parameter (see Fig. 2) in the region of low alcohol additives indicates, however, an increase in the "polarity" of the solvent and, hence, an increase in its ability to nonspecific solvation. It follows from the thermochemical data that the solvation of the substances is weakened. This contradiction can be eliminated if one takes into account the fact that an increase in "polarity" of the solvent can result in an increase in energy expenditures to the formation of a cavity during solvation of molecules. It is also seen in Fig. 1 that minor additives of Bu^{t}OH to water shows up as an especially sharp decrease in the acidity of the solvent. This factor, acting in the same direction with the contribution from the formation of the cavity, is responsible for an increase in the endothermicity of nonelectrolyte transfer up to the maximum point.

It is most likely that thermochemical data are the most sensitive indicator for effects related to the rearrangement of the structure in a water-organic solvent. It follows from Fig. 6 that the dissolution enthalpy of aniline in the H_2O—Bu^{t}OH mixture in the maximum point relative to water increases by 9 times, the hypersound velocity increases[31] by 10%, and the ν_{max} value of *p*-nitroanisole decreases by 1%. The corresponding value of the π^* parameter increases by 13% (see Fig. 1). Such an indicator as Dimroth's betaine (the E_T parameter is determined on the basis of this reagent) is insensitive to structural and energy changes in an aqueous solution of alcohol (see Figs. 1 and 6).

Returning to the analysis of thermochemical data, note the very interesting results obtained for solutions of benzene in mixtures of water with isopropanol.[32] On going from water to the mixture with 0.08 molar fractions of alcohol, the dissolution enthalpy of benzene increases from 3 to 27 kJ mol^{-1}. A further increase in the alcohol content to 0.2 molar fractions results in a decrease in the enthalpy to 12 kJ mol^{-1}. This behavior of the $\Delta H^\circ_{sol} = f(X)$ dependence can be explained[32] by the microheterogeneous nature of the mixed solvent. It is noteworthy that the positions of maxima at $X = 0.06$ molar fractions of Bu^{t}OH for aniline and at $X = 0.08$ molar fractions of Pr^{i}OH for benzene almost coincide if a volume content of alcohol of 0.25 and 0.27 vol.%, respectively, is used. This indicates the substantial role of the benzene ring in the formation of the dependences considered.

The transfer enthalpies of aniline from water to three water-organic solvents are presented in Fig. 7. A com-

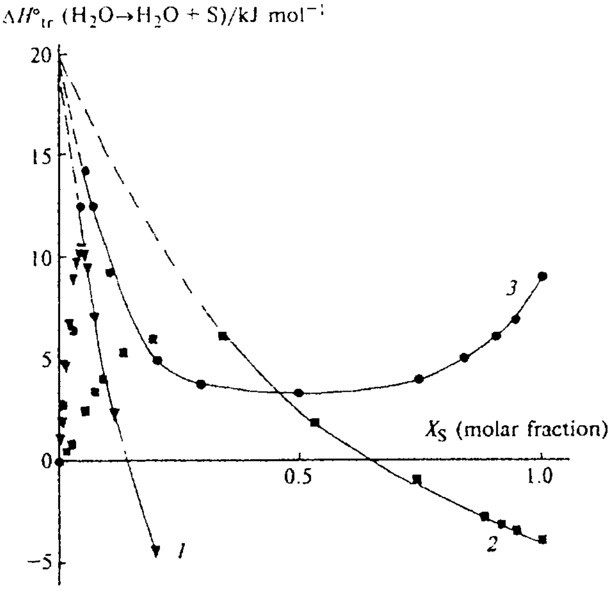

Fig. 7. Transfer enthalpies of aniline from water in H_2O-S mixtures, where S is HMPA (*1*), MeOH (*2*), and Bu^{t}OH (*3*).

parison of the two most hydrophobic compounds (HMPA and Bu^{t}OH) shows that the maxima of transfer enthalpies of aniline correspond to the same composition of ~0.05—0.06 molar fractions of the organic component. In the case of Bu^{t}OH, the maximum is considerably higher. At the same time, the height of the maximum for NM is approximately the same[2] in both systems: 10—12 kJ mol^{-1}. Note that *tert*-butyl alcohol is close in basicity to HMPA (in the β or B_{KT} scale) (see Table 2). Extrapolation of the smooth regions of the dependences to the zero content of the organic solvent gives the same value: ~20 kJ mol^{-1}. This value corresponds to the energy of the H bond. The regions of the dependences presented in Fig. 7 as dotted lines show a change in solvation of aniline when the organic component is added to water in the hypothetical state in which the three-dimensional network of H bonds is distorted. It can be assumed that the unique specific features of water due to the spatial network of H bonds are retained to some extent at $X < 0.35$ molar fractions of MeOH, $X < 0.075$ molar fractions of Bu^{t}OH, and $X < 0.06$ molar fractions of HMPA.

Interparticle interactions in solutions can be discussed on the basis of such characteristics as enthalpy coefficients of double, triple, and other interactions.[33] The enthalpy coefficients of double interactions calculated in terms of the McMillan—Mayer theory[34] have the following values (J kg mol^{-2}): 505±15, 3517±374, and 3727±49 in aqueous solutions of aniline—MeOH, aniline—Bu^{t}OH, and aniline—HMPA, respectively; 147±9 and −1280±142 in methanol and *tert*-butyl alcohol solutions of aniline—water, respectively. It follows from this that in an aqueous solution, the interaction between molecules of the dissolved substance (aniline) with the co-solvent (MeOH, Bu^{t}OH, and HMPA) is less preferable than that with the main solvent (water). This tendency is most pronounced for such hydrophobic substances as Bu^{t}OH and HMPA. In methanol solutions, the more preferable interaction of aniline with the main solvent (methanol) rather than with water is observed. In solutions of Bu^{t}OH, the interaction of aniline with water is more preferable than that of aniline with *tert*-butyl alcohol.

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