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Thermochemistry of Aniline Solution in Binary Mixtures Water–Aprotic Solvent

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Abstract—Enthalpies of aniline solution in mixed solvents water–1,4-dioxane, water–acetone, and water–dimethyl sulfoxide at 25°C were determined within entire ranges of their compositions. The enthalpies of its solvation and transfer from water into mixed solvents, and also contributions of hydrocarbon radicals and functional groups to these quantities were calculated. Effects of composition and properties of the mixtures on the aniline thermochemical characteristics in solutions were considered.

A few published data [1–5] demonstrate that the solvation of aniline and its derivatives in mixed aqueous-organic solvents has specific features as compared to the solvation of aliphatic compounds. These features are attributable to the solvation of the phenyl radical and the amino group bound to it. The mixed solvents selected in this work are of doubtless interest for both practice and theory of solutions. Water–dimethyl sulfoxide mixtures are used in studies of electrolyte solutions and thermodynamics of proton-transfer reactions and in the determination of protolytic dissociation constants of poorly water-soluble compounds with further extrapolation to water. Water–1,4-dioxane $[(CH_2)_4O_2]$ mixtures are frequently used in studying relations between properties of solutions and dielectric constants and nature of solvents (dielectric constants of the mixtures vary from 78 to 2 with preservation of a high solvency). Insignificant difference in solvating powers of acetone and dioxane contrasts with essential difference in properties of mixtures of these solvents with water. We point out that the thermochemical data on the enthalpies of mixing suggest different nature of heterocomponent interactions in mixtures of water with dimethyl sulfoxide, acetone, and 1,4-dioxane. The enthalpy of mixing in the H_2O–Me_2SO system [6] is strongly negative in the entire range of the mixture compositions, whereas the enthalpies of mixing of water with Me_2CO [7] and $(CH_2)_4O_2$ [8] have S-shaped forms. According to the X-ray diffraction data [9], the mixtures H_2O–Me_2CO and H_2O–$(CH_2)_4O_2$ have a microheterogeneous structure.

Data on the enthalpies of aniline solution in mixtures of water with acetone and dimethyl sulfoxide in the range of mole fractions of the organic component up to 0.15 were obtained earlier [4].

However, other ranges of compositions of mixed solvents are of considerable interest. When the composition of an aqueous-organic mixture is varied, a change in the preferential mechanism of the donor–acceptor interaction aniline–solvent can be expected. Water is known to have pronounced acid properties. The aniline molecule, in turn, is characterized by strong electron-donor properties caused by the presence of a lone electron pair of the nitrogen atom, and by the capability for hydrogen bonding (acceptor properties) due to the presence of two amino group protons. In aqueous-organic mixtures aniline can exhibit both types of properties.

This work continues studies of aniline solvation in mixed solvents started from water–alcohol mixtures [5].

Figures 1a–1c show the enthalpies of aniline transfer ($\Delta_{tr}H^0$) from water into its mixtures with acetone, 1,4-dioxane, and dimethyl sulfoxide, which demonstrate the effect of the composition of a mixed solvent on the solvation ($\Delta_{solv}H^0$) of a solute.

$$\Delta_{tr}H^0(H_2O \rightarrow H_2O + S) = \Delta_{soln}H^0(H_2O + S) - \Delta_{soln}H^0(H_2O) = \Delta_{solv}H^0(H_2O + S) - \Delta_{solv}H^0(H_2O), \quad (1)$$

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

Here S denotes an organic cosolvent.

The initial data for the calculation are given in Tables 1 and 2. To reveal the dependence of the enthalpy characteristics of solvation on the structure and properties of solutes, we compared the data of this study with the thermochemical characteristics of solvation of the previously studied nonelectrolytes [6, 14–16].

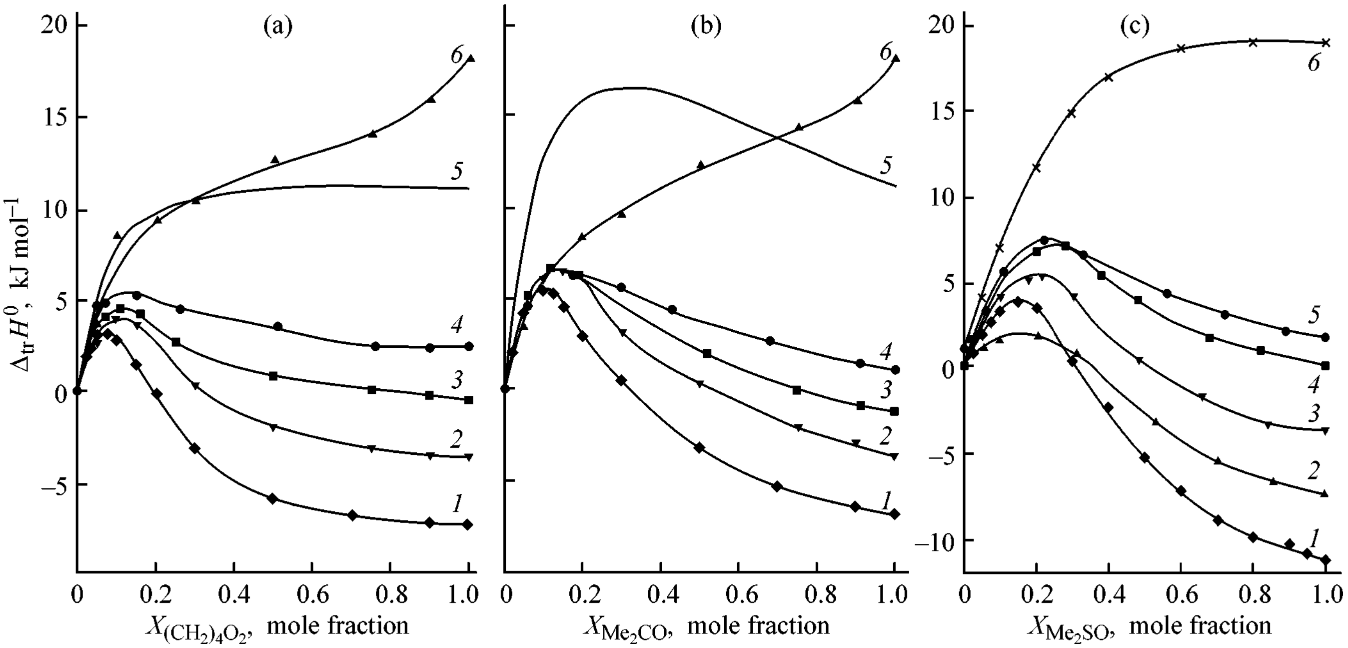

Fig. 1. Enthalpies of transfer of nonelectrolytes from water into its mixtures with (a) 1,4-dioxane, (b) acetone, and (c) dimethyl sulfoxide at 25°C as functions of compositions of the mixtures: (*1*) $PhNH_2$, (*2*) $MeNO_2$, (*3*) $C_3H_6CO_3$ (propylene carbonate), (*4*) MeCN, (*5*) C_2H_6, (*6*) Me_2SO, and (*7*) $HCONH_2$.

According to a classification accepted in [17, 18], acetonitrile, propylene carbonate ($C_3H_6CO_3$), nitromethane, and formamide are classed with predominantly electron-acceptor solvents ($\sigma/\xi < 1.442$), and dimethyl sulfoxide, with electron-donor solvents ($\sigma/\xi >$ 1.442). The maximum in the dependence $\Delta_{tr}H^0 = f(X_2)$ suggests that $PhNH_2$ in the solutions under consideration exhibits mainly acceptor properties although its reduced electron-donor power is $\sigma/\xi > 1.442$ (Table 2). Aniline in aqueous solutions exhibits the same prop-

Table 1. Thermal effects ($\Delta_{soln}H^m$, kJ mol^{-1}) of aniline solution in mixed solvents at 25°C

$H_2O–(CH_2)_4O_2$			$H_2O–Me_2CO$			$H_2O–Me_2SO$		
X_2	$m \times 10^4$	$\Delta_{soln}H^m$	X_2	$m \times 10^4$	$\Delta_{soln}H^m$	X_2	$m \times 10^4$	$\Delta_{soln}H^m$
0.025	201	3.75	0.025	448	3.92	0.025	449	2.65
0.035	218	4.04	0.050	145	5.97	0.050	597	3.74
0.050	488	4.82	0.100	457	7.40	0.075	396	4.51
0.075	464	4.94	0.125	459	7.19	0.100	544	5.12
0.100	741	4.57	0.150	526	6.43	0.150	550	5.70
0.150	588	3.32	0.200	1221	4.74	0.200	549	5.27
0.200	329	1.64	0.300	713	2.30	0.300	424	2.23
0.300	405	–1.36	0.500	532	–1.41	0.400	221	–0.57
0.500	596	–4.01	0.700	708	–3.51	0.500	457	–3.39
0.700	456	–4.95	0.900	600	–4.63	0.600	413	–5.34
0.900	495	–5.36	1.000	427	–4.98	0.703	346	–7.03
1.000	347	–5.41					390	–7.15
						0.799	581	–8.19
						0.900	402	–8.35
							469	–8.52
						0.950	598	–9.04
						1.000	324	–9.25
							413	–9.68

Note: (*m*) Molal concentration, mol $PhNH_2$ per kg solvent.

Table 2. Physicochemical properties and empirical parameters of solvent polarity at 25°C

Solvent	V_W [11]	V_m [12]	$\Delta_{vap}H$	*DN* [11]	*AN* [13]	E_T^N [11]	σ/ξ
$PhNH_2$	56.38	91.2	56.8	35.3	28.8	44.3	1.48
Me_2CO	39.04	74.0	30.8	17.0	12.5	42.2	1.47
MeCN	28.37	52.9	33.3	14.1	18.9	46.0	1.41
Me_2SO	43.34	71.3	52.8	29.8	19.3	45.1	1.51
$(CH_2)_4O_2$	49.62	85.7	35.7	14.8	10.8	36.0	1.47
$MeNO_2$	30.47	54.0	38.3	2.7	20.5	46.2	1.33
$C_3H_6CO_3$	49.78	85.2	49.8	15.1	18.3	46.6	1.43
$HCONH_2$	26.23	39.9	60.1	24.0	39.8	56.6	1.36
H_2O	10.40	18.1	44.0	18.0	54.8	63.1	1.25

Note: Reduced electron-donor power σ/ξ was calculated from the quantities $\sigma = 8.83 + 0.04337DN$ and $\xi = 6.125 + 0.029AN$ [10]. *DN* and *AN* are the donor and acceptor numbers, respectively. Units: V_W and V_m, cm^3 mol^{-1}; $\Delta_{vap}H$, kJ mol^{-1}; *DN* and E_T^N, kcal mol^{-1}.

erties as nitromethane and propylene carbonate. These compounds have limited solubility and close positive values of $\Delta_{soln}H^0$ in water. The enthalpy of aniline transfer from water into a nonaqueous component is more negative than the enthalpies of transfer of MeCN, $C_3H_6CO_3$, and $MeNO_2$.

Figure 1 also shows the enthalpies of ethane transfer, as calculated from the data in [19], which characterize changes in the nonspecific solvation of compounds. This phenomenon in our work involves the processes of cavity formation in a solvent to accommodate a solute molecule, related effects of solvent reorganization, and also van der Waals interaction of the solute with the solvent. It is interesting that the enthalpies of solvation of a nonpolar ethane molecule in acetone (–8.7 kJ mol^{-1}) and 1,4-dioxane (–8.9 kJ mol^{-1}) are approximately equal [19]. At the same time, solvation of ethane in mixtures of acetone and 1,4-dioxane with water essentially differs. In [19, 20] the phenomenon that similarly solvating components make different contributions to the properties of a mixture with water is explained by considering changes in the cohesion energy density. The cohesion energy densities of pure and mixed solvents can be calculated by formulas (3) and (4), respectively, and the additive value for mixtures, by formula (5).

$$p = (\Delta_{vap}H - RT)/V, \quad (3)$$

$$p = (X_1\Delta_{vap}H_1 + X_2\Delta_{vap}H_2 - H^E - RT)/V, \quad (4)$$

$$p_{ad} = \varphi_1 p_1 + \varphi_2 p_2. \quad (5)$$

In expressions (3)–(5) $\Delta_{vap}H$ is the enthalpy of vaporization; H^E, the enthalpy of mixing of components; *V*, the molar volume of (3) pure or (4) mixed solvent; *X* and φ, the mole and volume fractions, respectively; subscripts 1 and 2 refer to water and organic component, respectively. In the calculation of the cohesion energy density we used the enthalpies of vaporization from [12], enthalpies of mixing from [6–8], and densities of solvents from [21–23].

In fact, the cohesion energy densities of acetone and 1,4-dioxane are practically identical: 383 and 388 J cm^{-3}, respectively. At the same time, the deviation of cohesion energy density of the water–acetone mixture from an additive value ($\Delta p = p - p_{ad}$) is much greater than for the water–dioxane mixture. The enthalpies of solvation of aniline in 1,4-dioxane and acetone are close as is the case with nonpolar substances, whereas in the mixtures of these solvents with water the difference in $\Delta_{solv}H^0$ is as large as 4 kJ mol^{-1}. These facts suggest that the concentration dependences of the enthalpies of transfer of aniline, acetonitrile, propylene carbonate, and nitromethane molecules in the region of small content of a nonaqueous component ($X_2 < 0.3$) are determined mainly by changes in the nonspecific solvation, and in the region of its high content, by joint changes in the nonspecific and specific solvation (the specific solvation is due to the donor–acceptor interaction solute–solvent). Unlike these nonelectrolytes, weakening specific solvation of such bases as dimethyl sulfoxide in the region $X_2 > 0.5$ dominates over the contribution of the nonspecific solvation. The fact that a change in composition equally affects the solvation of the nonelectrolytes under study in the region prior to the endothermic maximum is the distinctive feature of water–acetone mixtures. The height of the maximum in mixtures of water with 1,4-dioxane and dimethyl sulfoxide correlates with the enthalpy of nonelectrolyte transfer from water into a nonaqueous component. In the region $X_2 > 0.4$, changes in the composition of a mixed solvent similarly intensify the solvation of electron acceptors (MeCN, $C_3H_6CO_3$, and $MeNO_2$).

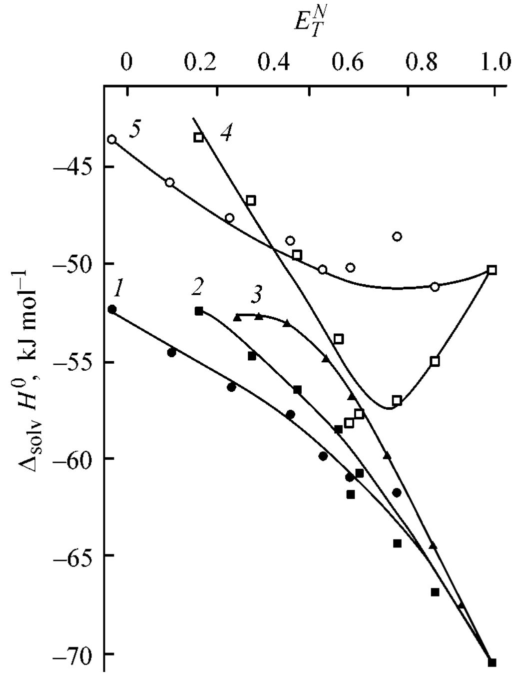

Fig. 2. Enthalpies of solvaiton of (*1–3*) Me_2SO and (*4*, *5*) sulfoxide group in mixtures of water with (*1*, *5*) 1,4-dioxane, (*2*, *4*) acetone, and (*3*) dimethyl sulfoxide as functions of the parameter E_T^N [24] of the mixtures at 25°C.

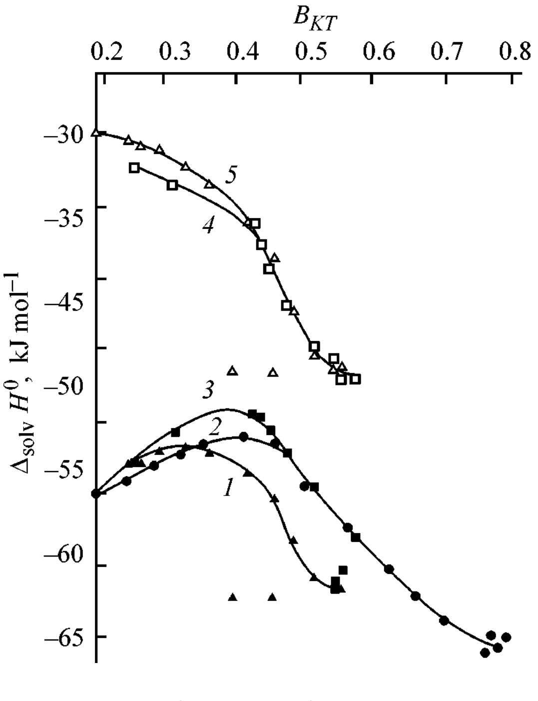

Fig. 3. Enthalpies of solvation of (*1–3*) $PhNH_2$ and (*4*, *5*) amino group in mixtures of water with (*1*, *5*) 1,4-dioxane, (*2*) dimethyl sulfoxide, and (*3*, *4*) acetone as functions of the parameter B_{KT} [25] of the mixtures at 25°C.

Enthalpy characteristics of solution of the third substance in a binary solvent can be used as a probe for the examination of mixed solvent properties. Selection of appropriate nonelectrolytes to be dissolved makes it possible to monitor changes in electron donor–acceptor properties of the mixture on variation of its composition. To reveal the possibility of using spectral acidity and basicity parameters of aqueous-organic mixtures for describing the enthalpy characteristics of solvation of nonelectrolytes, we compared in Figs. 2 and 3 such characteristics of the nonelectrolytes with the parameters of the aqueous-organic mixtures. It is evident (Fig. 2) that the solvation of Me_2SO regularly becomes more exothermic as the acidity E_T^N of the mixtures increases. The parameter B_{KT} (describing the basicity of a solvent) inadequately reflects changes in the enthalpies of solvation of $PhNH_2$ (Fig. 3), and also of MeCN, $C_3H_6CO_3$, and $MeNO_2$. It can be due to the fact that these nonelectrolytes exhibit amphiprotic properties in the systems studied. Furthermore, both the enthalpy of solvation and the solvatochromic parameter probably contain contributions from nonspecific interactions [25]. As pointed out above, the shape of the concentration dependence of the enthalpies of transfer of MeCN, $MeNO_2$, $C_3H_6CO_3$, and $PhNH_2$ is similar to that for ethane. The solvation of these molecules in the entire range of mixture compositions is intensified as van der Waals molar volume of the compounds increases (Table 2).

More detailed interpretation of changes in the enthalpies of solvation of nonelectrolytes in the mixed solvents under study can be given within the framework of the additive-group approach, which assumes that the enthalpy of solvation of a polar molecule is separated into the contributions of a hydrocarbon radical and a functional group (6).

$$\Delta_{solv}H^0(RY) = \Delta_{solv}H^0(R) + \Delta_{solv}H^0(Y). \quad (6)$$

The first term in Eq. (6) mainly characterizes nonspecific solvation of a molecule, and the second term, specific solvation. The enthalpy of solvation of a hydrocarbon radical was calculated by formulas (7) and (8) [19] from the enthalpies of solvation of alkanes in mixtures of water with 1,4-dioxane and acetone.

$$\Delta_{solv}H^0(R) = \varphi_1\Delta_{solv}H_1^0 + \varphi_2\Delta_{solv}H_2^0 + \Delta\Delta H^0, \quad (7)$$

$$\Delta\Delta H^0 = c\varphi_1\varphi_2. \quad (8)$$

Coefficients c (kJ mol^{-1}) for the mixtures H_2O–$(CH_2)_4O_2$ and H_2O–Me_2CO are 13.5 and 40.2 [19], respectively. The enthalpies of solvation of radicals in the components of the mixtures ($\Delta_{solv}H_1^0$ and $\Delta_{solv}H_2^0$) were calculated by formula (9).

$$\Delta_{solv}H^0 = a + bV_W(R). \quad (9)$$

The coefficients a (kJ mol^{-1}) and b (kJ cm^{-3}) for water, dioxane, and acetone are –12.5 and –0.274, 1.6 and –0.375, 1.4 and –0.376 [19], respectively. The van der Waals molar volumes V_W of hydrocarbon radicals of the molecules were calculated by adding volumes of all radicals entering into the composition of the molecules [11].

A correlation between $\Delta_{solv}H^0$ of the sulfoxide group and the acidity E_T^N of mixed solvents is given in Fig. 2. The enthalpies of solvation of the amino group as functions of the basicity B_{KT} are shown in Fig. 3 (similar relations were found for the groups CN, NO_2, and CO_3). Qualitative correlations for wide ranges of mixture compositions are observed, which is due to the fact that the contribution of the nonspecific solvation of molecules was found by calculating the enthalpy of solvation of their hydrocarbon radicals and setting it off from the enthalpy of solvation of the whole nonelectrolyte molecules. The nonlinear shape of the curves is due to the facts that the enthalpy of solvation of hydrocarbon radicals is described insufficiently adequately at a high water content in mixtures and that the simulation of a phenyl radical by an aliphatic radical of the corresponding size seems to be a too rough approximation. Different states (solvate environments) of the molecules under study and solvatochromic indicators in solution can be another reason. If the enthalpy of solution of a compound in a mixed solvent and its polarity parameter change in parallel or there is a linear correlation between them, it means that the compound under study and the solvatochromic indicator are preferentially solvated by the same component of a mixture or that their selective solvation is absent.

The values of $\Delta_{tr}H^0(H_2O \rightarrow H_2O + S)$ of aniline for the mixtures of water with four aprotic solvents and two alcohols as functions of volume fractions of the components are given in Fig. 4. When the compositions of mixtures are expressed in such a manner, the position of the maximum in the endothermic effect of solution shifts toward smaller content of the nonaqueous component in the series H_2O–Me_2SO (φ_2 ~0.4), H_2O–Me_2CO and H_2O–$(Me_2N)_3PO$ (φ_2 ~0.3), H_2O–$(CH_2)_4O_2$ (φ_2 ~0.25). Probably there is no simple relation between the height of a maximum and the property of a solvent added to water. The addition of water to aprotic solvents weakens aniline solvation to the same extent as its addition to methanol [5]. Only the addition of water to *tert*-butyl alcohol is accompanied by strengthening of $PhNH_2$ solvation [5].

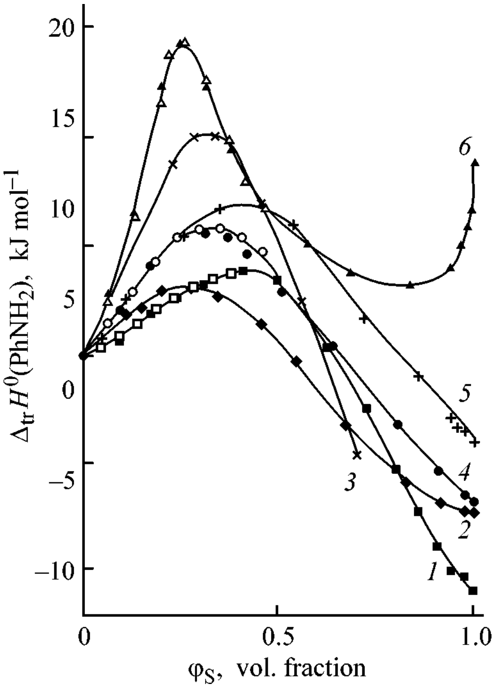

Fig. 4. Enthalpies of $PhNH_2$ transfer from water into its mixtures with (*1*) dimethyl sulfoxide, (*2*) 1,4-dioxane, (*3*) hexamethylphosphoramide [3], (*4*) acetone, (*5*) methanol [5], and (*6*) 2-methyl-2-propanol [5] as functions of the composition of mixtures at 25°C. Light symbols for (*1, 4, 6*) denote published data [4].

It is possible to judge the intensity of interparticle interactions in solutions on the basis of the enthalpy coefficients of pair, triple, and other interactions. The enthalpy coefficients of pair interactions (h_{23}) calculated within the framework of the McMillan–Mayer theory [26] are given in Table 3. The intensity of aniline interaction with organic components in aqueous solutions decreases in the series t-BuOH > $(Me_2N)_3PO$ > Me_2CO > $(CH_2)_4O_2$ > MeOH > Me_2SO. According to [3], extremely high values of h_{23} for t-BuOH and $(Me_2N)_3PO$ point to a strong hydrophobic interaction of aniline with them. The coefficients h_{23} for nonaqueous solutions show that in *tert*-butanol aniline interacts more strongly with water and in the remaining cases, with organic solvents, the strongest interaction taking place with Me_2SO. A clear linear correlation between h_{23} values in aqueous [$h_{23}(H_2O)$] and nonaqueous [$h_{23}(S)$] solutions was found for five systems under study [Eq. (10)].

$$h_{23}(H_2O) = (820 \pm 141) - (2.776 \pm 0.113)h_{23}(S); \quad (10)$$
$$s\ 141,\ R^2\ 0.9927.$$

Table 3. Enthalpy coefficients of pair interactions (h_{23}, kJ kg mol^{-2}) in aqueous and nonaqueous solutions at 25°C

System	h_{23}
H_2O(1)–*t*-BuOH(2)–$PhNH_2$(3)	3727 ± 49 [5]
H_2O(1)–$(Me_2N)_3PO$(2)–$PhNH_2$(3)	3320 [3]
H_2O(1)–Me_2CO(2)–$PhNH_2$(3)	774 ± 32[a]
H_2O(1)–$(CH_2)_4O_2$(2)–$PhNH_2$(3)	722 ± 134
H_2O(1)–MeOH(2)–$PhNH_2$(3)	505 ± 15 [5]
H_2O(1)–Me_2SO(2)–$PhNH_2$(3)	264 ± 38[a]
Me_2SO(1)–H_2O(2)–$PhNH_2$(3)	170 ± 7
MeOH(1)–H_2O(2)–$PhNH_2$(3)	147 ± 9 [5]
Me_2CO(1)–H_2O(2)–$PhNH_2$(3)	97 ± 3
$(CH_2)_4O_2$(1)–H_2O(2)–$PhNH_2$(3)	37 ± 9
t-BuOH(1)–H_2O(2)–$PhNH_2$(3)	–1280 ± 142 [5]

[a] Our own and published [4] data were used for the calculation.

In conclusion we emphasize the following results of our study. The maximum in the dependence $\Delta_{tr}H^0 = f(X_2)$ suggests that $PhNH_2$ exhibits mainly electron-acceptor properties in the solutions under study. The concentration dependences of the enthalpies of transfer of aniline molecules in the region of low content of a nonaqueous component ($X_2 < 0.3$) are determined mainly by a change in nonspecific solvation, and in the region of its higher content, by a joint change in the nonspecific and specific solvation. The simulation of the phenyl radical in aniline by an aliphatic radical of the appropriate size seems to be too rough approximation.

EXPERIMENTAL

The following solvents were used: 1,4-dioxane and acetone of analytically pure grade, purified and dehydrated according to [27]; dimethyl sulfoxide of chemically pure grade, which was frozen (80 vol %), a liquid fraction was decanted, and a solid was melted and subjected to fractional distillation [28]. The procedure was repeated, and a medium fraction with the electrical conductivity of 5×10^{-7} S cm^{-1} at 25°C was used in the work; aniline was purified by threefold vacuum distillation (according to the GLC data, the water content was less than 0.5 wt %). Aniline was stored for no more than a month in the dark.

The water content in organic solvents was controlled by Fischer titration [29]. It did not exceed (wt %) 0.08 in 1,4-dioxane, 0.07 in acetone, and 0.05 in dimethyl sulfoxide.

Mixed solvents were prepared by the gravimetric method accurate to 0.001 mole fraction using freshly double-distilled water (specific electrical conductivity 10^{-5} S cm^{-1}).

The enthalpies of solution were measured on a variable-temperature calorimeter with an isothermal jacket at aniline concentrations in solution less than 0.6 mol kg^{-1}. In this region $\Delta_{soln}H^m$ is independent of the concentration of a nonelectrolyte [5, 30]. In this connection we accepted experimental heats of solution ($\Delta_{soln}H^m$) (in certain cases their mean arithmetic values) as the standard enthalpies of solution ($\Delta_{soln}H^0$).

The resulting standard enthalpies of aniline solution ($\Delta_{soln}H^0$, kJ mol^{-1}) in water {1.88 (our data) [5], 1.82 ± 0.02 [3], 1.9 [4], and 1.78 kJ mol^{-1} [30]} and in mixed solvents nicely agree with published data. The values for the system water–*tert*-butanol, which we obtained earlier [5], are given because such a comparison was not carried out in [5]. The enthalpies of aniline solution significantly (by 8%) differ only for the water–acetone mixture at acetone mole fractions in the range 0.12–0.15. Our experimental value of $\Delta_{soln}H^0$ of aniline in dimethyl sulfoxide (–9.47 kJ mol^{-1}) differs from the value (–10.88 ± 0.13 kJ mol^{-1}) obtained in [31].

REFERENCES

1. Chebib, par H., Jambon, C., and Merlin, J., *J. Chim. Phys. Phys.-Chim. Biol.*, 1982, vol. 79, no. 2, pp. 157–160.
2. Chebib, par H., Jambon C., and Merlin, J., *J. Chim. Phys. Phys.-Chim. Biol.*, 1982, vol. 79, no. 3, pp. 259–264.
3. Taniewska-Osinska, S. and Jozwiak, M., *J. Chem. Thermodyn.*, 1986, vol. 18, no. 4, pp. 339–349.
4. Gillet, H., *Can. J. Chem.*, 1990, vol. 68, pp. 655–665.
5. Manin, N.G., Antonova, O.A., Kustov, A.V., and Korolev, V.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 12, pp. 2471–2477.
6. Clever, H.L. and Pigott, S.P., *J. Chem. Thermodyn.*, 1971, vol. 3, no. 2, pp. 221–225.
7. French, H.T., *J. Chem. Thermodyn.*, 1989, vol. 21, no. 8, pp. 801–809.
8. Nakayama, H. and Shinoda, K., *J. Chem. Thermodyn.*, 1971, vol. 3, no. 3, pp. 401–407.
9. Korsunskii, V.I. and Naberukhin, Yu.I., *Zh. Strukt. Khim.*, 1977, vol. 18, no. 3, pp. 587–603.
10. Notoya, R. and Matsuda, A., *J. Am. Chem. Soc.*, 1985, vol. 107, no. 13, pp. 3922–3933.
11. Bondi, A., *J. Phys. Chem.*, 1964, vol. 68, no. 3, pp. 441–451.
12. Marcus, Y., *Ion Solvation*, New York: Wiley, 1985.

13. Kamlet, M.J., Abboud, J.L., and Taft, R.W., *Prog. Phys. Org. Chem.*, 1981, vol. 13, pp. 485–630.
14. Kropotova, N.Yu., Kulikov, M.V., Slyusar, V.P., and Korolev, V.P., Available from VINITI, 1997, Moscow, no. 1664-V97.
15. Kulikov, M.V., Antonova, O.A., Slyusar, V.P., and Korolev, V.P., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1995, no. 9, pp. 1747–1751.
16. Vandyshev, V.N., Korolyov, V.P., and Krestov, G.A., *Thermochim. Acta.*, 1990, vol. 169, pp. 57–67.
17. Batov, D.V., Vandyshev, V.N., Antonova, O.A., and Korolev, V.P., in *Termodinamika rastvorov neelektrolitov* (Thermodynamics of Nonelectrolyte Solutions), Ivanovo: Inst. Khimii Nevodnykh Rastvorov Ross. Akad. Nauk, 1989, pp. 13–20.
18. Korolyov, V.P., Batov, D.V., and Krestov G.A., *Thermochim. Acta*, 1990, vol. 169, pp. 69–80.
19. Kulikov, M.V., Kropotova, N.Yu., and Korolev, V.P., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 12, pp. 1953–1958.
20. Korolev, V.P., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 2, pp. 188–195.
21. Ogiwara, K. and Funayama, H., *Res. Repts. Akita Techn. Coll.*, 1980, no. 15, pp. 63–65.
22. Pruett, D.J. and Felker, L.K., *J. Chem. Eng. Data*, 1985, vol. 30, no. 4, pp. 452–455.
23. Schott, H., *J. Chem. Eng. Data*, 1961, vol. 6, no. 1, pp. 19–20.
24. Bosch, E. and Roses, M., *J. Chem. Soc., Faraday Trans.*, 1992, vol. 88, no. 24, pp. 3541–3546.
25. Krygowski, T.M., Wrona, P.K., and Zielkowska, U., *Tetrahedron*, 1985, vol. 41, no. 20, pp. 4519–4527.
26. McMillan, W.G. and Mayer, J.E., *J. Chem. Phys.*, 1945, vol. 13, pp. 276–288.
27. *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, New York: Wiley–Interscience, 1972.
28. Martin, D. and Hauthal, N.G., *Dimethylsulfoxid*, Berlin: Akademie, 1971.
29. Klimova, V.A., *Osnovnye mikrometody analiza organicheskikh soedinenii* (Basic Micromethods of Organic Microanalysis), Moscow: Khimiya, 1967.
30. Belousov, V.P. and Panov, M.Yu., *Termodinamika vodnykh rastvorov neelektrolitov* (Thermodynamics of Aqueous Solutions of Nonelectrolytes), Leningrad: Khimiya, 1983.
31. Stephenson, W.K. and Fuchs, R., *Can. J. Chem.*, 1985, vol. 63, no. 12, pp. 2540–2544.