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Thermochemistry of Aniline Solution in Isomeric Butyl Alcohols and Their Aqueous Solutions

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Abstract—The enthalpies of solution ($\Delta_s H^0$) of aniline in isomeric butyl alcohols and their aqueous solutions at 25°C were determined. The dissolution of aniline becomes more endothermic with increasing content of alcohol in aqueous solution. The enthalpy coefficients of pair interaction alcohol–aniline in aqueous solution were calculated. This interaction is enhanced in the order *tert*-butanol–*sec*-butanol–*iso*-butanol–*n*-butanol. The correlations of these characteristics with physicochemical properties of solvents were revealed.

This work continues our thermochemical studies of solvation and state of aniline ($PhNH_2$) in aqueous solutions of alcohols [1]. In particular, we have not considered previously the influence of the structure of isomeric alcohols on solvation of aniline in aqueous-alcoholic solvents. Since aniline is an aromatic amine, it can exhibit noticeable base properties. However, in interaction with stronger bases it acts as a proton donor. At the same time, aniline also shows hydrophobic properties due to the presence of the hydrophobic phenyl group. Thus, the behavior of aniline in a binary solvent should be fairly complex.

Therefore, we studied in this work the solvation of aniline in aqueous solutions of isomeric alcohols. We chose butyl alcohols: *n*-butanol (*n*-BuOH), *sec*-butanol (*s*-BuOH), *iso*-butanol (*i*-BuOH), and *tert*-butanol (*t*-BuOH). Butyl alcohols except *t*-BuOH are limitedly soluble in water; the limiting content of alcohol X is less than 5 mol %. In this work we studied the water-rich range of compositions. An interesting feature of this range is that the thermochemical characteristics of solution (solvation) of various substances pass through extrema due to a complex effect of various interparticle interactions in solutions.

Published data are available only on the enthalpies of solution of aniline in aqueous solutions of *t*-BuOH [1–3]. As for the other isomeric butyl alcohols, only the enthalpies of mixing of aniline with them were measured [4, 5].

In this work we determined by a thermochemical experiment the enthalpies of solution of aniline in mixtures of water with *n*-BuOH, *i*-BuOH, and *s*-BuOH, and also in neat alcohols (Table 1).

Table 1 shows that in aqueous solutions of *n*-BuOH at $X < 0.1$ mol %, *i*-BuOH at $X < 0.16$ mol %, and *s*-BuOH at $X < 0.1$ mol % the enthalpy of solution of aniline is independent of the alcohol concentration. The same is true for *t*-BuOH in its mixtures with

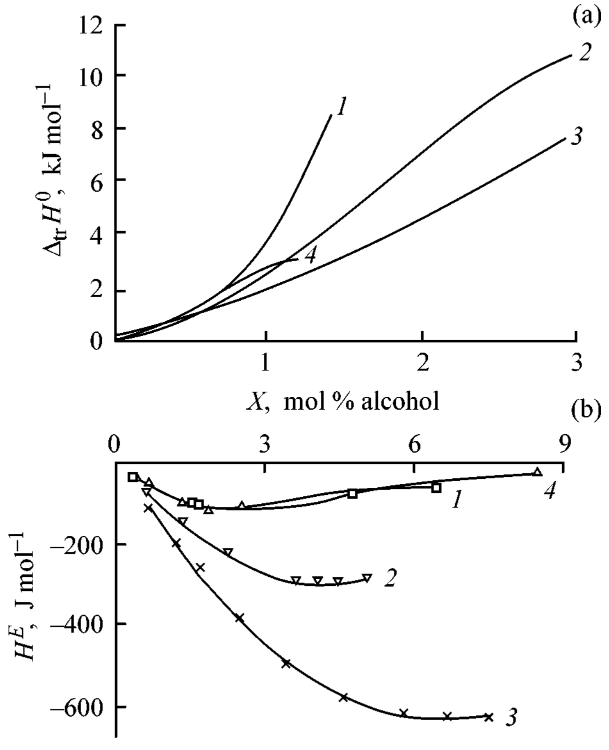

Fig. 1. Smoothed dependences (a) of the enthalpies of transfer of aniline from water to aqueous solutions of (*1*) *n*-BuOH, (*2*) *s*-BuOH, (*3*) *t*-BuOH [1], and (*4*) *i*-BuOH and (b) of the enthalpies of mixing of the corresponding alcohols with water at 26°C (data of [8]) on the alcohol content.

water at $X < 0.6$ mol % [6]. The possibility of existence of such a composition region in aqueous solutions of alcohols was emphasized in [7].

Consider the behavior of the enthalpy characteristics of aniline solvation in mixtures of water with isomeric butyl alcohols. Figure 1 shows the smoothed dependences of the enthalpies of aniline transfer from water to aqueous butanol solutions. The enthalpies of transfer were calculated by the formula

$$\Delta_{tr}H^0 = \Delta_s H^0 - \Delta_s H^0_1, \tag{1}$$

where $\Delta_{tr}H^0$, $\Delta_s H^0$, and $\Delta_s H^0_1$ are the standard enthalpies of transfer of aniline from water to a water–alcohol mixture and of solution of aniline in a water–alcohol mixture and in water, respectively. With increasing content of alcohol in solution, the dissolution of aniline becomes more exothermic, and the differences between solvation of aniline in solutions of different alcohols become more pronounced.

The character of interactions in mixtures of water with isomeric butyl alcohols can be judged from their enthalpies of mixing [8]. In aqueous solutions of alcohols (in the examined composition range) the exothermicity of mixing increases depending on the nature of alcohol in the order *n*-BuOH ~ *i*-BuOH < *s*-BuOH < *t*-BuOH and also with increasing content of alcohol. With increasing concentration of alcohol the curves flatten out (Fig. 1). On the whole, to exothermic mixing of the components corresponds endothermic transfer of aniline. However, the sequence of alcohols for these two processes does not coincide (in principle, to the more exothermic mixing should correspond more endothermic transfer). Thus, generally the energy characteristics of formation of a mixed solvent determine the energy characteristics of aniline solution in them, but the character of solvation of aniline in mixed solvents essentially depends on the nature of the cosolvent.

Table 1. Enthalpy of solution ($\Delta_s H^m$, kJ mol^{-1}) of aniline in aqueous solutions of butyl alcohols at 25°C[a]

$m \times 10^2$	$\Delta_s H^m$	$m \times 10^2$	$\Delta_s H^m$	$m \times 10^2$	$\Delta_s H^m$
Water–*n*-BuOH		Water–*i*-BuOH		Water–*s*-BuOH	
X 0.00		X 0.10		X 0.01	
0.000	1.78	1.714	1.86	1.407	1.84
X 0.10		2.632	1.77	1.424	1.76
3.840	1.66		[1.82]		[1.80]
X 0.30		X 0.16		X 0.05	
2.309	2.40	2.901	1.86	1.833	1.66
X 0.50		2.744	1.75	1.856	1.69
2.396	2.62		[1.81]		[1.68]
2.803	2.67	X 0.30		X 0.10	
	[2.65]	3.503	2.06	1.649	1.81
X 0.70		X 0.50		1.780	1.90
2.168	3.49	2.416	2.65		[1.86]
2.804	3.59	2.422	2.74	X 0.30	
	[3.54]		[2.70]	1.616	2.55
X 0.90		X 0.70		1.743	2.48
2.971	4.78	2.729	3.58		[2.52]
3.422	4.83	3.917	3.71	X 0.50	
	[4.80]		[3.65]	1.098	2.50
X 1.10		X 0.80		1.438	2.64
2.860	6.25	1.767	3.89		[2.57]
5.639	6.33	2.174	3.88	X 1.00	
	[6.29]		[3.89]	1.228	4.06
X 1.20		X 0.90		1.336	4.12
3.336	7.32	1.249	4.36		[4.10]
3.570	7.34	1.474	4.20	X 2.00	
	[7.33]		[4.28]	1.573	8.95
X 1.31		X 1.00		1.574	9.02
3.554	9.48	2.282	4.41		[8.99]
3.608	9.43	2.315	4.31	X 3.00	
	[9.45]		[4.36]	2.058	12.75
X 1.40		X 1.20		2.844	12.65
2.810	10.09	1.682	4.86		[12.70]
3.703	10.11	X 100.00		X 100.00	
	[10.10]	2.819	4.57	4.322	3.99
X 100.00		2.838	4.59	9.164	4.12
2.580	2.95		[4.58]	14.789	4.13
2.706	2.97				[4.08]
	[2.96]				

[a] m (mol kg^{-1}) is the molality of the solute; X (mol %) is the mole fraction of the nonaqueous cosolvent. In brackets are given the average values of two–three measurements, taken as the standard enthalpies of solution ($\Delta_s H^0$).

Since the excess partial molar enthalpy of the mixture components shows how the energy of their interaction with the solution varies depending on the mixed solvent composition, this quantity can be compared with the enthalpy of transfer of aniline from water to the corresponding water–alcohol mixture. Thus, we can consider a correlation between the energy state of mixture components and solvation of aniline. The excess partial molar enthalpies of water (H^E_1) and aniline (H^E_2) were calculated by formulas (2) and (3), in which the enthalpies of mixing (H^E) of the components of the binary system, taken from [8], were approximated by the Redlich–Kister equation [9].

$$H^E_1 = H^E - X(dH^E/dX), \tag{2}$$

$$H^E_2 = H^E + (1 - X)(dH^E/dX). \tag{3}$$

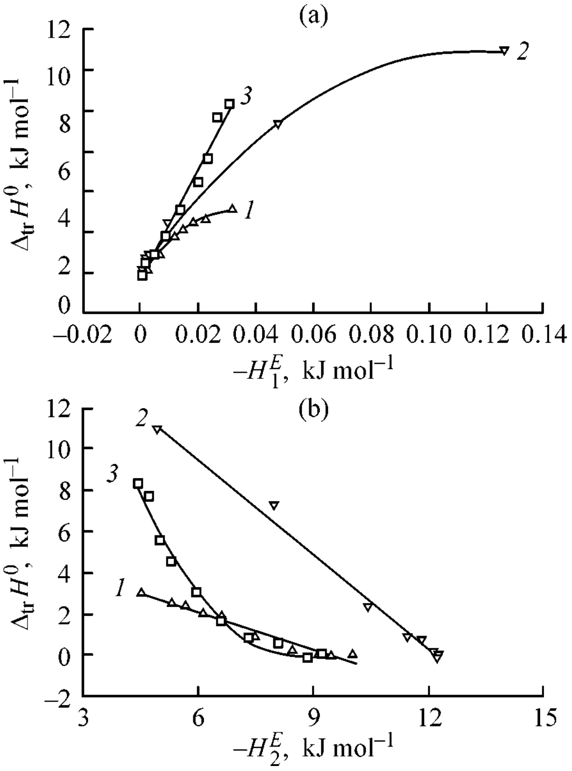

Fig. 2. Correlation of $\Delta_{tr}H^0$ of aniline with (a) H_1^E and (b) H_2^E of mixtures of water with (*1*) *i*-BuOH, (*2*) *s*-BuOH, and (*3*) *n*-BuOH.

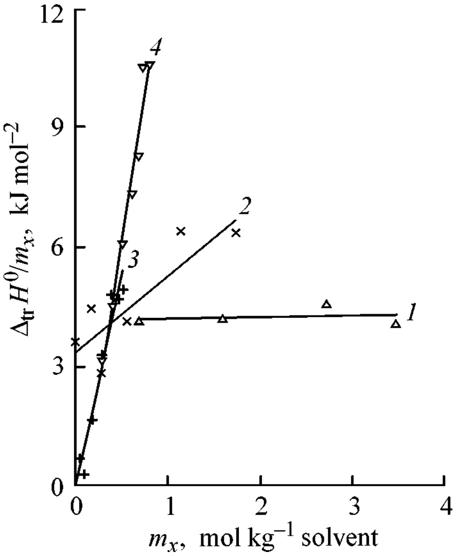

Fig. 3. $\Delta_{tr}H^0/m_x$ of aniline as a function of the molal concentration of aqueous solutions of alcohols: (*1*) *t*-BuOH, (*2*) *s*-BuOH, (*3*) *i*-BuOH, and (*4*) *n*-BuOH.

The correlations of the enthalpies of transfer of aniline from water to mixed solvents with H_1^E and H_2^E are shown in Fig. 2. It should be noted that to the increase in the negative value of H_1^E corresponds weakening of the aniline solvation. The sensitivity of aniline to the state of water increases in going from water–*i*-BuOH to water–*s*-BuOH and water–*n*-BuOH mixtures. The correlation of $\Delta_{tr}H^0$ with H_1^E in the water–*n*-BuOH mixtures is linear [Eq. (4)]:

$$\Delta_{tr}H^0 = -0.37 - 275.8H_1^E;\ r^2\ 0.974,\ s_f\ 0.51\ \mathrm{J\ mol^{-1}},\ n\ 9. \tag{4}$$

On the contrary, increase in the negative values of H_2^E corresponds to enhancement of aniline solvation, i.e., the stronger the interaction of alcohol with the mixed solvent, the more exothermic is the aniline solvation. This may be due to the fact that the molecules of the alcohol cosolvent affect the solvation of aniline by affecting the water–alcohol solution. As the alcohol concentration in solution is increased, the solvation of both alcohol (as a solute) and aniline is weakened, which suggests the enhancing effect of the cosolvent on the structure of the water–alcohol solution (hydrophobic hydration). The quantity $\Delta_{tr}H^0$ linearly correlates with H_2^E in the mixtures water–*i*-BuOH [Eq. (5)] and water–*s*-BuOH [Eq. (6)]:

$$\Delta_{tr}H^0 = 6.19 + 0.672H_2^E;\ r^2\ 0.980,\ s_f\ 0.17\ \mathrm{J\ mol^{-1}},\ n\ 9, \tag{5}$$

$$\Delta_{tr}H^0 = 18.85 + 1.548H_2^E;\ r^2\ 0.991,\ s_f\ 0.39\ \mathrm{J\ mol^{-1}},\ n\ 8. \tag{6}$$

Thus, solvation of aniline in aqueous solutions of isomeric butyl alcohols is probably determined by the state of water: Its bound state results in weakened solvation of aniline, and the alcohol cosolvent weakens solvation of aniline by affecting the structure of the solution.

Let us consider then the regular trends in variation of interparticle interactions in solutions, judging from the enthalpy coefficients of pair interactions [10]. The enthalpy coefficients of interaction of aniline with alcohols in their aqueous solutions were calculated in terms of the McMillan–Mayer theory [11] using Eq. (7) [12]:

$$\Delta_{tr}H^0/m_y = 2h_{xy} + 3h_{xyy}m_y + 3h_{xxy}m_x, \tag{7}$$

where m_y and m_x are the molal concentrations of alcohol and aniline, and h_{xy}, h_{xyy}, and h_{xxy} are the enthalpy coefficients of pair and ternary interactions of aniline (x) with alcohol (y). The coefficients h_{xy} and h_{xyy} were determined by the least-squares procedure, neglecting the last term of Eq. (7) because of the low concentration of aniline (Fig. 3). The calculated coefficients h_{xy} are listed in Table 2.

Formally, the enthalpy coefficient of pair interactions can be considered as a result of solvation of solutes with the solvent and of solute–solute interactions [14, 15] [Eq. (8)]:

$$h_{xy} = \text{æ}_{xy} - \text{æ}_{x\mathrm{S}} - \text{æ}_{y\mathrm{S}}, \tag{8}$$

where the term æ_{xy} corresponds to interaction between solvated species x and y, and $\text{æ}_{x\mathrm{S}}$ and $\text{æ}_{y\mathrm{S}}$, to interaction between the major solvent S and species x and y, respectively. Thus, from the thermochemical viewpoint, the following situations are possible:

(1) interactions between the solvent and solutes are strong (solutes are well solvated), and the quantity $(\text{æ}_{x\mathrm{S}} + \text{æ}_{y\mathrm{S}})$ is negative, whereas interactions between the solvated species x and y are weak (æ_{xy} is positive); then $h_{xy} > 0$;

(2) interactions between the solvent and solutes are weak (solutes are poorly solvated), and the quantity $(\text{æ}_{x\mathrm{S}} + \text{æ}_{y\mathrm{S}})$ is positive, whereas interactions between the solvated species x and y are strong (æ_{xy} is negative); then $h_{xy} < 0$.

Table 2 shows that the positive value of h_{xy} decreases in the order *t*-BuOH, *s*-BuOH, *i*-BuOH, and *n*-BuOH. The signs of h_{xy} show that in aqueous solutions of *t*-BuOH and *s*-BuOH hydration of aniline and alcohol molecules prevails over interaction of these molecules in the hydrated state (positive coefficient), whereas in aqueous solutions of *i*-BuOH and *n*-BuOH interaction of hydrated molecules of aniline and the cosolvent prevails over hydration (negative coefficient). If we assume constant contribution to the pair coefficient from interaction of aniline with water and take into account enhancement of alcohol hydration (values in kJ mol^{-1} [7]) in the order *i*-BuOH (–60.1), *n*-BuOH (–61.5), *s*-BuOH (–62.9), *t*-BuOH (–64.0), this will correspond to the growth of the positive value of h_{xy}, which suggests weakening of interactions of aniline with isomeric butyl alcohols in aqueous solutions in going from the primary to the secondary and then tertiary alcohol. In terms of this approach, the less negative coefficient h_{xy} of interactions aniline–*i*-BuOH, compared to aniline–*n*-BuOH, may be due to steric hindrance to interaction of hydrated aniline molecules with hydrated *i*-BuOH molecules.

Table 2 shows that to increase in the positive value of h_{xx} corresponds decrease in the positive value of h_{xy} in the order *t*-BuOH, *s*-BuOH, *i*-BuOH, *n*-BuOH. As noted in [7], increase in the size of the nonpolar substituent in the alcohol in aqueous solution results in that interaction occurs via hydrocarbon group (hydrophobic interaction) rather than via H bonding, which is responsible for the increase in the positive value of h_{xx}. Thus, decrease in h_{xy} correlating with increase in h_{xx} may be due to weakening of the hydrophobic interaction of aniline with alcohol molecules in water (which probably occurs as interaction of the phenyl ring of aniline with the hydrocarbon group of the cosolvent) and enhancement of the specific interactions aniline–alcohol via amino group.

Table 2. Enthalpy coefficients of pair interactions alcohol–alcohol [13] (h_{xx}, J kg mol^{-2}) and aniline–alcohol (h_{xy}, J kg mol^{-2}) in aqueous solution

Solute (*y*)–cosolvent (*x*)	h_{xx}	h_{xy}
Aniline–*n*-BuOH	1172	–698 ± 280
Aniline–*s*-BuOH	916	1694 ± 404
Aniline–*i*-BuOH	1000	–56 ± 227
Aniline–*t*-BuOH	656	2101 ± 137

The enthalpies of solution of aniline and coefficient h_{xy} linearly correlate (r^2 0.985, s_f 0.6 kJ mol^{-1}; r^2 0.802, s_f 600 J kg mol^{-2}, respectively) with the acidity (E_T) of the corresponding alcohols (Fig. 4): In infinitely dilute aqueous solutions of isomeric butanols, with increasing acidity of butanol the dissolution of aniline becomes less endothermic, and aniline–alcohol interactions are enhanced. This fact suggests a certain contribution of specific interactions to aniline–alcohol interactions in aqueous solution.

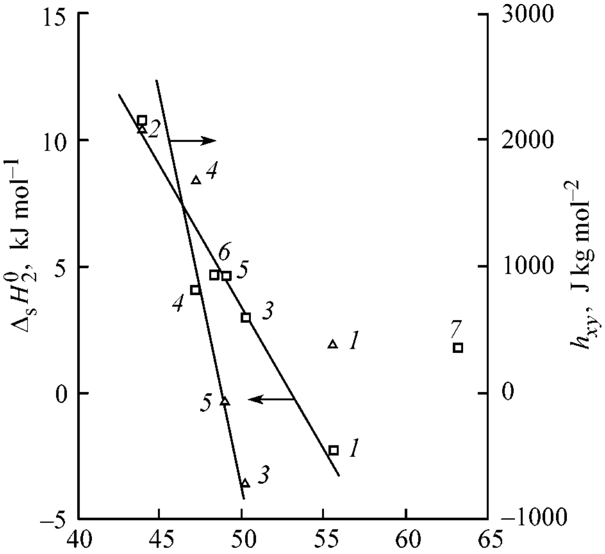

Fig. 4. Correlation of the enthalpy of solution of aniline and enthalpy coefficient h_{xy} with solvent properties: (*1*) MeOH [1], (*2*) *t*-BuOH [1], (*3*) *n*-BuOH, (*4*) *s*-BuOH, (*5*) *i*-BuOH, (*6*) *n*-OcOH [2], and (*7*) H_2O.

Table 3. Empirical parameters and physicochemical characteristics of compounds at 25°C [16]

Parameter[a]	$PhNH_2$	*t*-BuOH	*s*-BuOH	*i*-BuOH	*n*-OcOH	*n*-BuOH	MeOH	H_2O
E_T^b	44.3	43.9	47.1	49.0	48.3	50.2	55.4	63.1
$B \times 100$	98.9	70.0	68.5	65.6	67.7	66.0	62.3	44.5
$\Delta_{vap}H^c$	56.8	46.8	49.7[d]	51.2[d]	72.0[d]	52.5[d]	37.5	44.0
V_n^c	91.2	94.9	92.3[d]	92.9[d]	158.4[d]	92.0[d]	40.7	18.1

[a] E_T is the Dimroth–Reichardt parameter [determined from the shift in the UV spectrum of the absorption band of the indicator, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenoxide, in solution of the corresponding acceptor], expressed in kcal mol^{-1}; *B* is the nucleophilicity parameter (determined from the shift in the IR spectrum of the phenol OH band in CCl_4 solution in the presence of the excess of the corresponding donor), expressed in kcal mol^{-1}. Dimensions: V_n, cm^3 mol^{-1}; $\Delta_{vap}H$, kJ mol^{-1}. [b] [17]. [c] [1]. [d] [18].

Water as solvent does not fit in this correlation. It should be noted that the interaction of aniline with butanols strongly depends on the position of the OH group (at tertiary, secondary, or primary carbon atom): In this order, the aniline–alcohol interactions in water are enhanced.

Since both the solute (aniline) and the solvents (alcohols, water) can show both proton-donor and proton-acceptor properties (Table 3), it was necessary to estimate what property of aniline is manifested in these solvents. To do this, we constructed a two-parameter correlation (9) of the enthalpy of solution of aniline ($\Delta_s H^0$) with the acid and base properties of solvents:

$$\Delta_s H^0 = 158.6 - 1.777E_T - 1.01(B \times 100);\ r^2\ 0.986,\quad s_f\ 0.6\ \text{kJ mol}^{-1},\ n\ 6. \tag{9}$$

This correlation, along with alcohols, includes also water. However, further analysis showed that the correlation is improved by taking into account the solvent structurization, as alcohols and water are structurized solvents. The structurization can be characterized by the cohesion energy density of these solvents *p*: $p = (\Delta_{vap}H - RT)/V_n$, where $\Delta_{vap}H$ and V_n are, respectively, the enthalpy of vaporization and the molar volume of the solvent (Table 3).

$$\Delta_s H^0 = 110.85 - 1.621E_T - 0.45(B \times 100) + 0.058(p \times 100);\quad r^2\ 0.999,\ s_f\ 0.25\ \text{kJ mol}^{-1},\ n\ 6. \tag{10}$$

Relation (10) adequately describes the enthalpies of solution of aniline in six solvents: water, methanol (MeOH), *n*-BuOH, *t*-BuOH, *i*-BuOH, and octanol (*n*-OcOH). Inclusion of *s*-BuOH in correlations (9) and (10) considerably deteriorates them [e.g., for (10) r^2 0.956, s_f 1.14 kJ mol^{-1}). The mutual correlation of parameters for this group of solvents is low: r^2 is 0.872 for the correlation $B \times 100$–E_T, 0.796 for $p \times 100$–E_T, and 0.977 for $p \times 100$–$B \times 100$. The negative coefficients at the parameters of acidity (E_T) and basicity (*B*) of three-parameter equation (1) show that aniline with respect to alcohols and water behaves as an amphiprotic substance; however, it is more sensitive to acid properties of the medium, as the coefficient at E_T is by a factor of almost 4 higher than that at *B*. From Eq. (10) also follows that the solvation of aniline is weakened as the structurization of the solvent (parameter *p*) increases.

Thus, with respect to both alcohols in aqueous solutions and neat alcohols aniline behaves to a greater extent as an H acceptor. Presumably, interaction of aniline with an alcohol molecule occurs via the nitrogen atom of the aniline amino group and the OH proton of alcohol.

EXPERIMENTAL

n-BuOH, *i*-BuOH, and *s*-BuOH (all pure grade) were purified by single vacuum distillation at about 10^3 Pa, with collection of the middle fraction [19]; aniline was purified by triple vacuum distillation (the moisture content, as determined by chromatographic analysis, was less than 0.5 wt %). Aniline was stored in the dark for no more than a month.

The moisture content of alcohols was determined by Fischer titration [20]; it did not exceed 0.06 wt % in *n*-BuOH and *i*-BuOH and 0.08 wt % in *s*-BuOH.

Water–alcohol mixtures were prepared gravimetrically with an accuracy of 0.01 mol % using freshly double-distilled water (specific conductivity $1 \times 10^{-5}\ \Omega^{-1}\ \text{cm}^{-1}$).

The enthalpies of solution were measured at 25°C in a variable-temperature calorimeter with an isothermal jacket; the volume of the reaction vessel was

50 ml. The calorimetric device and type of the calorimeter are described in [1, 21, 22]. The weight of solute samples was within 0.15–0.2 g; the weighing accuracy was 5×10^{-5} g. The determination error did not exceed 0.6%. As standard enthalpies of solution ($\Delta_s H^0$) were taken the arithmetic mean values of the thermal effects of solution ($\Delta_s H^m$), since variation of $\Delta_s H^m$ of aniline with its concentration is within the experimental error (Table 1).

The measured enthalpy of aniline solution in water (1.78 kJ mol^{-1}) agrees with published data (kJ mol^{-1}): 1.82 ± 0.02 [23], 1.78 [7].

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