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Solvation of Aniline in Mixtures of Water with *N*,*N*-Dimethylformamide and Acetonitrile

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Abstract—Thermal effects of aniline solution in water–*N*,*N*-dimethylformamide (DMF) and water–acetonitrile mixtures were measured at 25°C. In almost the whole range of compositions of the mixed solvents, the thermal effects are more positive in aqueous acetonitrile than in aqueous DMF. Particular attention was given to binary solvents with a very low content of the organic cosolvent. In the mixture with the mole fraction of DMF of 10^{-3}, the enthalpy of aniline solution is higher than in water by 5%, and in the mixture with the mole fraction of acetonitrile of 4×10^{-4}, even by 15%. Features of specific solvation of aniline and an aliphatic amine (n-BuNH$_2$) in the water–DMF mixture were discussed taking into account the acid–base properties of the mixtures. The coefficients of pair interactions aniline–organic solvent in water and aniline–water in the organic solvent were calculated using the McMillan–Mayer theory. These coefficients correlate with the enthalpies of hydration of aprotic solvent molecules.

Studies of the state of aromatic compounds in aqueous-organic solvents are urgent not only for applied chemistry, but also because of the fact that many of aromatic compounds are used as solvatochromic indicators for constructing empirical scales of the solvating power of solvents [1].

Mixtures of water with DMF and acetonitrile have been extensively studied. DMF and acetonitrile differ in the molecular shape and size, donor–acceptor power, and effect exerted on the water structure. The enthalpy of mixing of water with acetonitrile is positive in the whole composition range except mixtures with a very low CH_3CN content. This feature distinguishes acetonitrile from other aprotic solvents. The observed pattern means that mixing of H_2O with CH_3CN is controlled by the entropy component of the Gibbs energy. Mixing of water with DMF is exothermic, and the enthalpy factor favors mixing. Studies of mixtures of water with acetonitrile and DMF on molecular level were performed by computer simulation [2, 3]. A number of publications are available on the thermal properties of nonelectrolyte solutions in these mixtures. Rouw *et al*. [4–6] measured the enthalpies of solution of alkylamines [4, 5] and enthalpies of dilution of alcohols [6] in the water–DMF system. Data are also available on the enthalpies of solution of ethyl acetate in water–acetonitrile mixtures [7] and of aniline in mixtures of water with methanol, tert-butyl alcohol [8], acetone, dimethyl sulfoxide [9, 10], 1,4-dioxane [10], and hexamethylphosphoramide [11].

In this work, we measured the heats of solution of aniline in the systems water–DMF and water–acetonitrile. The results are listed in Tables 1 and 2.

Of particular interest are studies of mixtures dilute with respect to the organic component, in which the solute–cosolvent pair interactions prevail. For more convenient presentation of the results, we introduced the characteristics *Y* and *Z* defined as follows:

$$Y = [\Delta_s H^0(\text{mix.}) - \Delta_s H^0(H_2O)] \times 100/\Delta_s H^0(H_2O), \quad (1)$$

$$Z = [\Delta_s H^0(\text{mix.}) - \Delta_s H^0(H_2O)] \times 100/\Delta_s H^0(\text{mix.}), \quad (2)$$

where $\Delta_s H^0(\text{mix.})$ and $\Delta_s H^0(H_2O)$ are, respectively, the enthalpies of solution (kJ mol^{-1}) of aniline in a given binary solvent and in water; the quantities *Y* and X characterize the changes (%) in the enthalpy of solution in going from water to binary solvent (relative to water) and in going from binary solvent to water (relative to binary solvent), respectively.

The dependences *Y*(*X*) and *Z*(*X*) are plotted in Figs. 1a and 1b (*X* is the mole fraction; unless otherwise stated, X_1 refers to water, and X_2, to the nonaqueous cosolvent).

Figure 1a shows that even the first, very small amount of acetonitrile added to water (X_2 4×10^{-4}) increases the enthalpy of solution of aniline by 15% (0.3 kJ mol^{-1}), which considerably exceeds the experimental error. At equal content of DMF and acetonitrile (X_2 10^{-3}), the heat of aniline solution increases

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Table 1. Enthalpies of solution of aniline ($\Delta_s H^m$, kJ mol^{-1}) in mixtures of water with *N,N*-dimethylformamide at 25°C[a]

$m \times 10^2$	$\Delta_s H^m$	$m \times 10^2$	$\Delta_s H^m$	$m \times 10^2$	$\Delta_s H^m$	$m \times 10^2$	$\Delta_s H^m$
X_2 0.0000		X_2 0.0143		X_2 0.1584		X_2 0.9020	
5.081	1.82	1.935	2.49	1.985	4.98	7.910	–10.49
11.96	1.84	X_2 0.0198		6.165	4.96	X_2 0.9403	
X_2 0.0008		2.863	2.64	11.72	4.97	6.060	–10.67
6.790	1.82	5.995	2.66	21.42	4.96	X_2 0.9737	
X_2 0.0010		X_2 0.0293		X_2 0.1848		4.696	–11.12
3.589	1.95	1.199	3.03	4.030	4.67	X_2 1.0000	
X_2 0.0018		6.077	3.05	X_2 0.2421		1.678	–11.22
2.099	2.01	X_2 0.0482		1.515	3.10	2.829	–11.32
X_2 0.0023		2.267	3.48	X_2 0.3396		3.795	–11.26
2.113	2.00	4.544	3.57	1.157	0.88	4.459	–11.16
X_2 0.0083		X_2 0.0708		3.276	1.13	4.544	–11.27
3.427	2.25	2.764	4.11	X_2 0.5833		5.038	–11.40
X_2 0.0132		7.759	4.13	5.390	–5.91	8.242	–11.26
2.045	2.31	X_2 0.1011		13.87	–5.86	9.566	–11.35
6.403	2.43	2.767	4.64	X_2 0.8002		13.94	–11.20
				8.266	–8.88	17.32	–11.26
				X_2 0.8822			
				6.114	–10.35		

[a] (X_2) Mole fraction of *N,N*-dimethylformamide; (m) molality, mol kg^{-1}; the determination error for the enthalpies of solution does not exceed 1.5% according to our estimate.

Table 2. Enthalpies of solution of aniline ($\Delta_s H^m$, kJ mol^{-1}) in mixtures of water with acetonitrile at 25°C[a]

X_2	m	$\Delta_s H^m$	X_2	m	$\Delta_s H^m$
0.0004	0.0224	2.11	0.1999	0.0479	3.20
0.0009	0.0226	2.55	0.3000	0.0577	1.86
0.0050	0.0196	2.93	0.4999	0.0600	1.38
0.0100	0.0074	3.40	0.5999	0.0137	0.97
0.0166	0.0247	3.86	0.6998	0.0656	0.82
0.0250	0.0339	4.49	0.7998	0.0314	0.27
0.0500	0.0359	6.03	0.9001	0.0661	0.04
0.0750	0.0397	6.40	0.9501	0.0373	0.24
0.1000	0.0423	5.95	1.0000	0.0766	0.15
0.1500	0.0437	4.44			

[a] (X_2) Mole fraction of acetonitrile and (m) molality, mol kg^{-1}.

relative to water by only 6% (0.1 kJ mol^{-1}) in the former case and by 40% (0.7 kJ mol^{-1}) in the latter case.

Let us compare the behavior of aniline in the whole range of compositions of the binary mixtures. Figure 2 shows that solvation of aniline in water–acetonitrile mixtures is less exothermic than in water–DMF mixtures. Since aniline exhibits both base and acid properties (Table 3), this feature of its behavior in the two systems should be discussed taking into account the

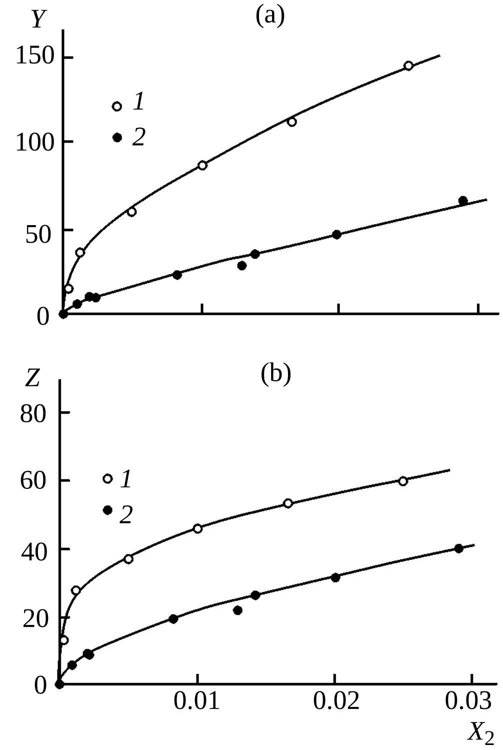

Fig. 1. Parameters (a) Y and (b) Z for solutions of aniline in mixtures of water with (*1*) acetonitrile and (*2*) DMF as functions of mixed solvent composition.

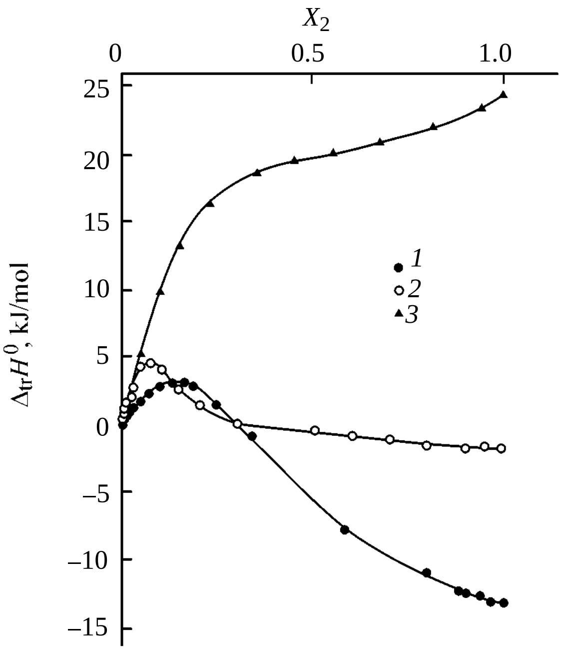

Fig. 2. Enthalpies of transfer of (*1, 2*) aniline and (*3*) *n*-butylamine from water and its mixtures with (*1, 3*) DMF and (*2*) acetonitrile.

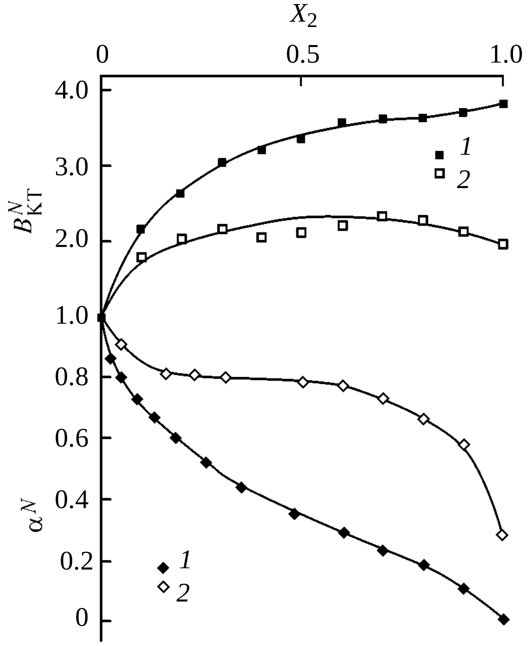

Fig. 3. Normalized basicity (B^N_{KT}) and acidity (α^N) parameters of mixtures of water with (*1*) DMF and (*2*) acetonitrile.

acid–base properties of the water–DMF and water–acetonitrile systems. Figure 3 illustrates variation of these parameters with the mixed solvent composition. For conveniency, the parameters α [12, 13] and B_{KT} [15] were normalized, namely, their values were divided by those for water. The trend in variation of the Kamlet–Taft parameter α shows that the acid properties of the binary mixtures weaken with increasing content of the nonaqueous component and that the acid properties of the water–DMF system are less pronounced than those of the water–acetonitrile system. If the composition dependence of the enthalpy of aniline transfer were governed by interactions of aniline as a base with the solvent as an acid, the enthalpy of aniline solution in aqueous DMF would be more positive than in aqueous acetonitrile (Figs. 1, 2). However, the actual pattern is opposite. This may be due to the lower basicity (B_{KT}) of the water–acetonitrile system compared to water–DMF (Fig. 3). The mutual arrangement of the curves in Figs. 1 and 2 is mainly determined by interactions of aniline as an acid with the solvent as a base. This is confirmed by comparison (Fig. 2) of the enthalpies of transfer of two amines, aromatic ($PhNH_2$) and aliphatic (n-$BuNH_2$), from water into its mixtures with DMF. It is known that aliphatic amines, being strong bases (Table 3), show virtually no acid properties. Therefore, it should be expected that the enthalpy of solution of *n*-butylamine in the system water–DMF will correlate with the acidity parameter of this system α. Figure 4 shows how the enthalpy of solution of *n*-butylamine (data of [5]) depends on the parameters *AN*, α, and E_T of the water–DMF mixture. The values of *AN* [16] were normalized similarly to α. The normalized Dimroth–Reichardt parameters E^N_T were taken from [15]. In the plot of $\Delta_sH^0 = f(AN)$, we can distinguish two linear portions corresponding to the X_2 ranges 0–0.25 and 0.35–1. Thus, the behavior of the aliphatic amine in the mixed solvent, in contrast to that of the aromatic amine, is governed by interactions of the amine as a base with the solvent as an acid.

Table 3. Acidity (α, *AN*, E_T) and basicity (*DN*, B_{KT}) parameters of compounds[a]

Compound	α [12, 13]	*AN* [14]	E_T [14]	*DN* [14]	B_{KT} [15]
n-$BuNH_2$	–	–	38.4	47.0	–
$PhNH_2$	–	28.8	44.3	33.0[b]	–
DMF	0	16.0	43.8	26.6	0.72
CH_3CN	0.31	18.9	46.0	14.1	0.57
H_2O	1.13	54.8	53.1	18.0	0.14

[a] (E_T) Dimroth–Reichardt parameter, kcal mol^{-1}; (*DN*) Gutmann donor number, kcal mol^{-1}. [b] Data of [8].

It is interesting to specially consider the mixtures rich in the organic component, because in such mixtures it is possible to compare the data for polar compounds (amines) with those for the nonpolar *n*-butane, calculated by appropriate equations from [17, 18]. Figure 5 shows how addition of water to DMF and acetonitrile affects the enthalpies of solvation of the solutes. It is seen that addition of water to DMF and acetonitrile weakens solvation of both aniline and *n*-butane; with aniline, this trend is more pronounced. *n*-Butylamine behaves quite differently: Its solvation becomes stronger, which is due to the contribution from interactions of the amine as a base with water as an acid. In the acetonitrile–water system, solvation of *n*-butane is weakened to a considerably greater extent than solvation of aniline.

Table 3 shows that DMF is a considerably stronger electron donor (base) than acetonitrile. Therefore, it forms stronger hydrogen bonds with water. At the same time, it is not quite clear why the enthalpy of *n*-butane solution in $CH_3CN–H_2O$ is more positive than in $DMF–H_2O$ (Fig. 5). The results obtained for aniline are easier to explain. In this case, it should be considered how addition of water affects the acid–base properties of solvents. Data of [12, 13] and Fig. 3 show that, as the mole fraction of water is increased from 0 to 0.2, the acidity α of DMF–water mixtures increases by 0.2 unit, and that of $CH_3CN–H_2O$ mixtures, by 0.44 unit, i.e., the effect is stronger by a factor of 2. Therefore, with increasing water content, interactions of aniline as a base with the solvent as an acid should increase to a greater extent in $CH_3CN–H_2O$ mixtures. Variation of the basicity of the mixtures (Fig. 3) produces a similar effect. Thus, we can make fairly substantiated conclusions about relative contributions from nonspecific solvation of aniline and its specific interactions with the solvent in nonaqueous solvents. At X_1 0–0.2, in acetonitrile solution, the contributions from nonspecific solvation and specific interactions virtually fully compensate each other, so that the enthalpy of aniline transfer becomes independent of the composition. In the DMF solution, the enthalpy of solution becomes more positive owing to prevalence of the contributions from nonspecific solvation and certain decrease in the solvent basicity.

Let us consider the aniline behavior in dilute solutions using the formally rigorous McMillan–Mayer theory. The enthalpy coefficients of pair interactions h_{23} in the systems water (1)–organic solvent (2)–aniline (3) and organic solvent (1)–water (2)–aniline (3) in dilute solutions with respect to component 2 were calculated by Eqs. (3) and (4) suggested in [6]:

$$\Delta_s H^0 = a_0 + a_1 X_2 + a_2 X_2^2, \quad (3)$$

$$h_{23} = 0.5 a_1 M_1, \quad (4)$$

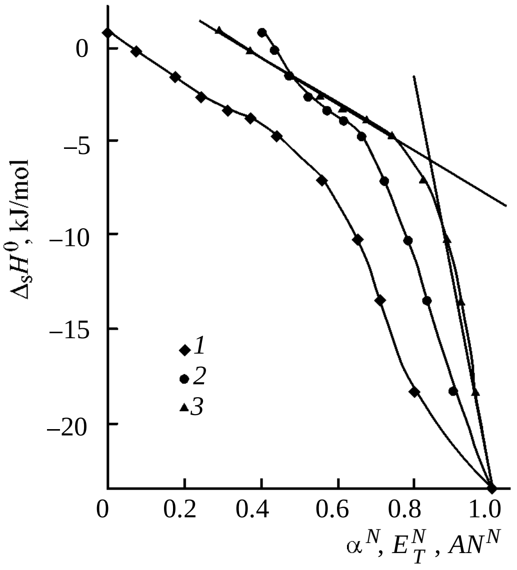

Fig. 4. Plots of the enthalpy of *n*-butylamine solution in water–DMF mixtures vs. normalized acidity parameters (*1*) α^N, (*2*) E_T^N, and (*3*) AN^N of the mixed solvent.

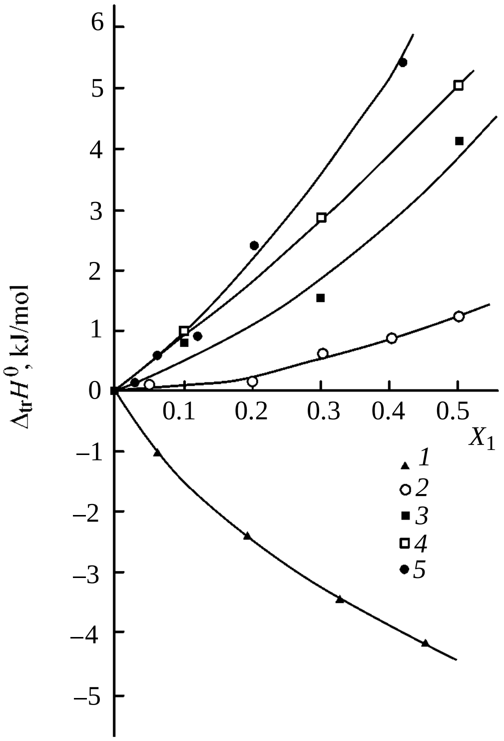

Fig. 5. Enthalpies of transfer of (*1*) *n*-butylamine, (*2, 5*) aniline, and (*3, 4*) butane from (*1, 3, 5*) DMF and (*2, 4*) acetonitrile into their mixtures with water.

Table 4. Enthalpy coefficients of pair interactions (h_{23}, J kg mol^{-2}) in systems I [water (1)–organic solvent (2)–aniline (3)] and II [organic solvent (1)–water (2)–aniline (3)] at 25°C

Organic solvent	System I	System II
$HCON(CH_3)_2$	432 ± 26	292 ± 43
CH_3CN	1034 ± 160	27 ± 10
$(CH_3)_2SO$	256 ± 38	170 ± 8
$(CH_3)_2CO$	942 ± 109	97 ± 3
$O(CH_2CH_2)_2O$	793 ± 70	38 ± 9
$[(CH_3)_2N]_3PO$	3861 ± 49	—
CH_3OH	505 ± 15	147 ± 9

where M_1 is the molecular weight of solvent (1). The enthalpy coefficients of pair interactions of aniline, determined in this work for the systems with DMF and acetonitrile and calculated from data of [8, 10] for several other systems, are compared in Table 4. It is seen that, both in water and in nonaqueous solvent, the values of h_{23} are positive and comparable. Only in the system with the strongly hydrophobic [19] HMPA h_{23} in water is several times higher than in the other systems. The lowest coefficient is observed with dimethyl sulfoxide (DMSO), which is less hydrophobic than the other nonaqueous cosolvents under consideration [19]. The other substances occupy intermediate positions, and it is difficult to rank them with respect to hydrophobicity on the basis of the h_{23} values.

The high value of h_{23} for acetonitrile seems to be surprising. For example, it is approximately twice that for methanol. This difference is apparently due both to interaction of aniline with the OH and CN groups in aqueous solution and to specific features of hydration of these groups. For interaction with water in methanol and acetonitrile, the h_{23} values also differ, but here, vice versa, the coefficient is somewhat higher for methanol (Table 4). Thus, in aqueous solution, replacement of the CN group by OH causes h_{23} to sharply decrease, whereas in nonaqueous solution h_{23}, on the contrary, somewhat increases. Therefore, it is reasonable to suggest that the observed difference between the h_{23} values for methanol and acetonitrile in water is largely associated with the differences in the energy of hydration of functional groups in the molecules of the nonaqueous cosolvents.

Since pair interaction solute–cosolvent in solution is accompanied by partial overlapping of their hydration spheres and displacement of a certain number of molecules to the bulk of the solvent, the solute–solvent interaction will become appreciably weaker. Therefore, a correlation should be expected between the enthalpies of solute–solvent interactions and coefficients of pair interactions. These quantities cannot be determined without making simplifying assumptions; however, as a first approximation, we can use the enthalpies of solvation. Equation (5) shows that the h_{23} values for the system aniline–aprotic solvent in water do correlate with the enthalpies of hydration [20] of acetonitrile, acetone, 1,4-dioxane, DMF, and DMSO:

$$h_{23} = 1799 + 21.7\Delta_{\mathrm{solv}}H^0;\ R\ 0.9995,\ S\ \mathrm{J\ kg^{-1}mol^{-2}}. \quad (5)$$

Methanol (associated solvent) and HMPA (strongly hydrophobic substance) lie out of this dependence. It follows from Eq. (5) that, as the hydration of the organic cosolvent is enhanced, the coefficient h_{23} decreases. Since in hydration of these substances the major contribution to formation of hydration shells is made by specific interactions (hydrogen bonding with water), overlapping of the hydration spheres will be accompanied by cleavage or weakening of some of the hydrogen bonds, which, under equal other conditions, is energetically unfavorable. In the case of acetonitrile, whose hydration shell is less stable than that of DMF or DMSO, the hydration spheres overlap more readily, and therefore the coefficient h_{23} is considerably larger than in water. The very large positive value of h_{23} in the case of HMPA is probably due to a contribution from interactions of the HMPA methyl groups with the benzene core in aqueous solution. Such a conclusion is supported the fact that the contribution from interaction of a CH_2 group of tetraalkylammonium ions with HMPA in aqueous solution to the enthalpy coefficient of pair interaction is as large as 663 ± 109 J kg mol^{-2} [21]. Therefore, it is reasonable to assume the following molecular pattern of pair interaction aniline–HMPA, responsible for very high h_{23}. For solute molecules in water, the most stable state will, apparently, be that in which their polar groups are incorporated into the network of hydrogen bonds in water (strong specific interactions) and the nonpolar groups are arranged in network voids. In this case, the nonpolar groups of solute molecules can occur as contact or solvent-separated molecular pairs, which suggests existence of certain preferred distances between them.

EXPERIMENTAL

The enthalpies of solution were measured on a hermetically sealed variable-temperature ampule calorimeter with an isothermal jacket. The thermometric and thermal sensitivities of the device were 5×10^{-6} deg and 5×10^{-3} J, respectively, per millimeter of the recorder scale [22]. The device error did not exceed

0.6%. The thermal effect of solution was determined by the comparative procedure. The thermal value of the calorimeter for the initial state of the system was determined electrically.

The chemicals used were purified by standard procedures [8, 23, 24]. Pure grade aniline was kept for 72 h over KOH and then distilled three times in a vacuum (60°C), with collection of the middle fraction (~60% by volume). Chemically pure grade dimethylformamide was purified by the following scheme: drying over anhydrous copper(II) sulfate–vacuum distillation–drying over 3 Å molecular sieves–vacuum distillation (30°C). Chemically pure grade acetonitrile was dried for 48 h over P_4O_{10}, decanted, refluxed for 2 h over freshly calcined potassium carbonate, and distilled. The moisture content in organic solvents, determined by Fischer titration, did not exceed 0.03%. Water was double-distilled; its conductivity was 1×10^{-6} S cm^{-1}. The enthalpy of solution of DMF in water at infinite dilution was -15.31 ± 0.05 kJ mol^{-1}, which excellently agrees with the reference value of -15.27 kJ mol^{-1} [25].

Table 1 shows that in pure DMF and mixed aqueous-organic solvent at a DMF content X_2 0.1584 the enthalpy of aniline solution is independent of the solute concentration. Therefore, we assumed that in the systems under consideration the standard enthalpies of solution can be calculated as average values in the series of integral heats of solution. However, in most cases we restricted ourselves to a single measurement, which allowed us to examine a large set of compositions of the mixed solvent. In this case, we assumed that $\Delta_s H^0 = \Delta_s H^m$.

The enthalpies of solution of aniline at infinite dilution in water and DMF, determined in our work, are 1.83 ± 0.01 and -11.28 ± 0.05 kJ mol^{-1}, respectively. These values are in excellent agreement with published data: 1.82 ± 0.02 [11] and -11.08 ± 0.4 [26] or -11.20 ± 0.33 kJ mol^{-1} [27], respectively.

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