

# Enthalpic pair-interaction coefficients of benzene, aniline and nitrobenzene with *N,N*-dimethylformamide and acetonitrile in water at 298.15 K

Andrey V. Kustov<sup>a,\*</sup>, Anastasiya V. Bekeneva<sup>b</sup>,  
Olga A. Antonova<sup>a</sup>, Valeriy P. Korolev<sup>a</sup>

<sup>a</sup> Thermochemical Laboratory, Institute of Solution Chemistry, Russian Academy of Sciences, 1 Academicheskaya Str., 153045 Ivanovo, Russia

<sup>b</sup> The Higher chemical college of Russian Academy of Sciences at Ivanovo State University of Chemistry and Technology,  
7 F. Engels Avenue, 153460 Ivanovo, Russia

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## Abstract

The enthalpies of benzene and nitrobenzene solution in the highly aqueous water–*N,N*-dimethylformamide and water–acetonitrile mixtures have been measured at 298.15 K calorimetrically and compared with the results reported earlier for aniline. The enthalpic coefficients ( $h_{xy}$ ) of the solute–organic cosolvent pair interaction in water were computed. The  $-\text{NO}_2$  and  $-\text{NH}_2$  group increments to the pair-interaction coefficients were estimated. It was found that the interaction of  $-\text{NO}_2$  and  $-\text{NH}_2$  groups with the aprotic cosolvent molecule in water differs strongly—for the former group the interaction is strongly thermochemically repulsive, but for the latter one it is attractive. The investigation of the solutes behaviour in highly diluted aqueous solutions indicated the extreme sensitivity of the aromatic solutes to the presence of cosolvent molecules in water that increases from aniline to nitrobenzene.

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## 1. Introduction

The importance of studying the aromatic compounds behaviour in solutions is dictated by the fact of their using in a wide range of applications [1–4]. The investigation of the energetics of interactions between simple aromatic solutes and their functional groups with cosolvent molecules in a highly diluted aqueous solution provides also useful information and

predictions on the properties of biologically active compounds [3,4].

We have recently reported the enthalpies of solution ( $\Delta H_{\text{sol}}^0$ ) of aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) in the mixtures of water with dimethylsulfoxide (DMSO), 1,4-dioxane (DO), acetone ( $\text{Me}_2\text{CO}$ ) [5], *N,N*-dimethylformamide (DMF) and acetonitrile (MeCN) [6]. The curves ( $\Delta H_{\text{sol}}^0$ ) vs. the mixed solvent composition ( $X$ ) were found to pass through the maximum at  $X = 0.07$ – $0.2$  mole fraction of an organic component, the height of which is defined to a great extent by peculiarities of phenyl radical solvation [5,6]. The analysis of the enthalpic coefficients of the aniline–aprotic cosolvent pair interaction in water indicated that a good

\* Corresponding author. Tel.: +7-932-327256;  
fax: +7-932-378509.

E-mail addresses: kustov@isuct.ru (A.V. Kustov),  
korolev@icti.ivanovo.su (V.P. Korolev).

correlation between the  $h_{xy}$  values and the enthalpies of aprotic solvent hydration ( $\Delta H_{\text{hyd}}^0$ ) is observed [6], the coefficients above increasing with the decrease of the  $\Delta H_{\text{hyd}}^0$  values.

In the present paper, we report the enthalpies of solution of benzene ( $\text{C}_6\text{H}_6$ ) and nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) in the water-rich region of the water–DMF and water–MeCN mixed solvents. The principal objective of this work is to obtain and compare experimental information on the energetics of interaction of simple aromatic solutes and their functional groups with cosolvent molecules in water.

## 2. Experimental

Purification of the solvents was carried out as described previously [6]. Water was deionised and distilled twice. DMF (Fluka) was purified according to the following procedure: drying by  $\text{CuSO}_4 \rightarrow$  first vacuum distillation  $\rightarrow$  drying by 4 Å sieves  $\rightarrow$  second vacuum distillation. Acetonitrile (Purum) was dried by 3 Å sieves and distilled twice. The water content obtained by Karl Fischer titration for both solvents did not exceed 0.05 mass%. The enthalpies of DMF and MeCN solution in water at 298.15 K were  $-15.31 \pm 0.05$  and  $-1.50 \pm 0.06 \text{ kJ mol}^{-1}$ , respectively. These values are in good agreement with literature data being  $-15.27 \text{ kJ mol}^{-1}$  for DMF [7] and  $-1.44 \text{ kJ mol}^{-1}$  for MeCN [8].

Benzene (Chemapol, for UV spectroscopy) has been used as supplied. Nitrobenzene (Chemapol) was

frozen at 278 K, dried by 4 Å sieves and distilled under reduced pressure.

The measurements were carried out using a precise hermetic “isoperibol” ampoule calorimeter fitted with a 75 cm<sup>3</sup> titanium calorimetric vessel [9]. The calorimetric vessel was equipped with a calibrating heater, a titanium stirrer and a thermistor. A glass ampoule containing a solute was attached to a stirrer. The dissolution process was initiated by an ampoule crushing against the vessel bottom. The thermistor was connected with a precise resistance bridge and a recorder potentiometer. The enthalpy of solution was determined by a comparative method. The electrical calibration was carried out before and after each experiment. The apparatus was tested by measuring the enthalpies of solution of potassium chloride (KCl) in water and aniline in DMF at 298.15 K being  $17.25 \pm 0.03 \text{ kJ mol}^{-1}$  [10] and  $-11.28 \pm 0.05 \text{ kJ mol}^{-1}$  [6], respectively. The agreement between our and literature  $\Delta H_{\text{sol}}^0$  values ( $17.22 \text{ kJ mol}^{-1}$  for KCl [11] and  $-11.20 \text{ kJ mol}^{-1}$  for aniline [12]) was excellent.

## 3. Results

The experimental results in water are listed in Table 1. It should be noted that both solutes are slightly dissolved in water. The main period of a single experiment was approximately 20 min for benzene and 35 min for nitrobenzene. Thus, for the treatment of the experimental data Regnault–Pfaundler procedure was used [13,14]. The estimated precision of

Table 1

Experimental enthalpies of solution ( $\Delta H_{\text{sol}}^m$ ) and enthalpies of solution at infinite dilution ( $\Delta H_{\text{sol}}^0$ ) of benzene and nitrobenzene in water at 298.15 K

$\text{C}_6\text{H}_6$ ( $\Delta H_{\text{sol}}^0 = 2.05 \pm 0.06^a$ ; $2.08 \pm 0.04^b$ )			$\text{C}_6\text{H}_5\text{NO}_2$ ( $\Delta H_{\text{sol}}^0 = 3.96 \pm 0.11$ )		
$m \times 10^{2c}$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )	$m \times 10^2$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )	$m \times 10^2$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )
0.3512	2.03	0.1112	3.56	0.5100	4.12
0.3991	2.25	0.2244	4.21	0.5112	3.67
0.4953	2.04	0.2298	4.18	0.5803	4.09
0.5859	1.89	0.3241	3.90	0.5846	3.60
0.5890	2.14	0.4421	3.90	0.7411	4.41
0.8505	1.94				

<sup>a</sup> Errors represent 95% confidence limits.

<sup>b</sup> Value from Ref. [15].

<sup>c</sup> Moles of the solute per 1 kg of the solvent.

Table 2

Enthalpies of solution ( $\Delta H_{\text{sol}}^m = \Delta H_{\text{sol}}^0$ ) of benzene and nitrobenzene in the water–DMF mixtures at 298.15 K

C <sub>6</sub> H <sub>6</sub>			C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>		
$X_y \times 10^{2a}$	$m \times 10^{2a}$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )	$X_y \times 10^2$	$m \times 10^2$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )
2.473	0.7121	3.71	1.061	0.1566	4.92
4.011	0.9020	4.55	2.267	0.2616	6.89
4.699	1.534	4.79	3.192	0.2549	7.70
5.157	0.7993	4.97	5.162	0.3275	9.27
5.518	1.112	5.11	6.777	1.241	10.05
7.094	0.7582	6.09	10.14	0.4339	11.78
10.01	1.305	7.19			

<sup>a</sup> Mole fraction of DMF in a mixed solvent.

Table 3

Enthalpies of solution ( $\Delta H_{\text{sol}}^m = \Delta H_{\text{sol}}^0$ ) of benzene and nitrobenzene in the water–MeCN mixtures at 298.15 K

C <sub>6</sub> H <sub>6</sub>			C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>		
$X_y \times 10^{2a}$	$m \times 10^{2a}$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )	$X_y \times 10^2$	$m \times 10^2$ (mol kg <sup>-1</sup> )	$\Delta H_{\text{sol}}^m$ (kJ mol <sup>-1</sup> )
0.4997	0.4215	3.69	0.0990	0.1211	3.98
1.001	0.6312	5.23	0.250	0.1198	4.80
2.500	1.544	7.43	0.500	0.2118	6.30
5.000	1.937	9.67	1.001	0.5210	6.88
7.011	1.444	10.11	2.000	2.214	10.33
10.01	2.033	10.75	3.002	2.225	11.90
			4.498	0.8305	13.56
			5.500	0.9440	15.24
			6.000	0.6123	15.64

<sup>a</sup> Mole fraction of MeCN in a mixed solvent.

the  $\Delta H_{\text{sol}}^m$  values in water is  $\pm 5\%$ . In the water-rich region of the mixed solvents, both solutes were dissolved better and the overall experimental uncertainty of the  $\Delta H_{\text{sol}}^m$  values is estimated to be within 2%.

It can be seen from Table 1 that the experimental enthalpies of solution of benzene and nitrobenzene ( $\Delta H_{\text{sol}}^m$ ) in water do not depend on the solute molality. Thus, the enthalpies of non-electrolytes solution at infinite dilution, i.e. the standard enthalpies of solution ( $\Delta H_{\text{sol}}^0$ ) have been calculated as average values in the range of the experimental results. Table 1 shows a good agreement between our and literature data [15] for benzene. The  $\Delta H_{\text{sol}}^m = \Delta H_{\text{sol}}^0$  values in the mixtures of water with DMF and MeCN representing the results of a single experiment are given in Tables 2 and 3.

#### 4. Discussion

It is known that the solute behaviour in the region of the low cosolvent content is defined by the

solute–cosolvent pair interactions [3], the energetics of which can be studied using McMillan–Mayer theory [16]. This formalism allows to connect the solution properties at different activities and represent the excess thermodynamic properties of a diluted solution in terms of virial expansion [3]. According to Somsen and co-workers [17,18] for the enthalpy of solution  $\Delta H_{\text{sol}}^0$  of any solute ( $x$ ) in a mixture ( $S + y$ ) of a solvent ( $S$ ) and a cosolvent ( $y$ ) at low  $X_y$  values one can write:

$$\Delta H_{\text{sol}}^0(x \text{ in } S + y) = A_0 + A_1 X_y + A_2 X_y^2 \quad (1)$$

where  $X_y$  is a cosolvent mole fraction. The  $A_1$  coefficient is connected with the enthalpic coefficient  $h_{xy}$  of the solute–cosolvent pair interaction by a simple relationship [17]:

$$A_1 = \frac{2h_{xy}}{M_S} \quad (2)$$

where  $M_S$  is molar mass of a solvent (water).

Table 4

Enthalpic coefficients ( $h_{xy}$ , J kg mol<sup>-2</sup>) of the aromatic solute pair interaction with DMF or MeCN in water

<i>x</i>	S–water				
	y–DMF	y–MeCN	y–DMSO	y–Me <sub>2</sub> CO	y–DO
C <sub>6</sub> H <sub>6</sub>	579 ± 40	1916 ± 225	1198 ± 110 <sup>a</sup>	1315 ± 250 <sup>a</sup>	1287 ± 260 <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	432 ± 26 <sup>b</sup>	1034 ± 160 <sup>b</sup>	256 ± 38 <sup>b</sup>	942 ± 109 <sup>b</sup>	793 ± 70 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1186 ± 101	3032 ± 295	–	–	–
–NO <sub>2</sub>	607 ± 109	1116 ± 371	–	–	–
–NH <sub>2</sub>	–147 ± 48	–882 ± 276	–942 ± 116	–373 ± 273	–494 ± 270

<sup>a</sup> Calculated from the data in Ref. [20].<sup>b</sup> Values from Ref. [6].

The results of the Eqs. (1) and (2) application to the aqueous systems studied are given in Table 4. The  $h_{xy}$  values are seen to be positive indicating that the aromatic solute–cosolvent interaction is repulsive in a thermochemical sense [19]. As can be seen from Table 4, the coefficients above depend greatly on functional group nature. Therefore, it is important to estimate the –NH<sub>2</sub> and –NO<sub>2</sub> group increments to the  $h_{xy}$  values. In the first approximation, they can be calculated as follows:

$$h_{xy}(-\text{NH}_2) = h_{xy}(\text{C}_6\text{H}_5\text{NH}_2) - h_{xy}(\text{C}_6\text{H}_6) \quad (3)$$

$$h_{xy}(-\text{NO}_2) = h_{xy}(\text{C}_6\text{H}_5\text{NO}_2) - h_{xy}(\text{C}_6\text{H}_6) \quad (4)$$

Table 4 shows that the coefficients of the –NH<sub>2</sub> and –NO<sub>2</sub> group have different signs. It indicates that the –NO<sub>2</sub> group–aprotic cosolvent interaction is strongly thermochemically repulsive, whereas the –NH<sub>2</sub> group–cosolvent interaction is attractive. It is obvious that such attraction between aromatic aminogroup and dipolar aprotic solvent molecules in a highly diluted solution is sufficiently surprising especially for MeCN. This result prompted us to investigate the aminogroup behaviour in other aqueous systems.

Recently [20], we have reported the enthalpies of solution of benzene in the mixtures of water with Me<sub>2</sub>CO, DO and DMSO. Sufficient density of the experimental points in the water-rich region allows us to calculate in this work the benzene–aprotic cosolvent pair-interaction coefficients which are given in Table 4. Comparing the  $h_{xy}$  values obtained with those for aniline [6], one can evaluate according to Eq. (3) corresponding the –NH<sub>2</sub> group increments. It can be seen from Table 4 that the –NH<sub>2</sub> group behaviour in the systems studied is identical, i.e. its interaction with

the aprotic cosolvents in water is thermochemically attractive. A possible explanation of the results obtained is that cosolvent molecules are preferably oriented to –NH<sub>2</sub> group by their polar groups rather than non-polar –CH<sub>3</sub> or –CH<sub>2</sub> groups. Therefore, one can expect the short-range solute–cosolvent specific interaction in a highly diluted aqueous solution. However, the large variation of the coefficients above indicates that such explanation is likely to be simplified. In fact, it is hard to believe that molecular nature of the –NH<sub>2</sub> group interaction with DMF and DMSO in water should greatly differ (see the pair-interaction coefficients given in Table 4), because both aprotic solvents have close molar volumes, H-acceptor and H-donor ability [21]. On the contrary, the  $h_{xy}$  values are almost identical for the cosolvents with different H-acceptor properties such as MeCN and DMSO [21].

It is known that the enthalpic pair-interaction coefficient is related to a temperature derivative of the integral of the mean force potential  $W_{xy}(r, \Omega)$  occurring between the solute and cosolvent molecules in a highly diluted solution [3,22]. Here  $r$  represents the  $x$ – $y$  intermolecular distance, and  $\Omega$  is the orientational contribution [22]. The latter contribution appears to be important in our systems and responsible to some extent for the difference in the –NH<sub>2</sub> group behaviour pointed out above. Moreover, it should be noted that negative  $h_{xy}$  values can result from the contribution of not only the contact, but also the solvent separated configurations if an appropriate minimum of the  $W_{xy}(r, \Omega)$  function lies in the region of the negative energy values [3]. Therefore, the explanation taking into account only the –NH<sub>2</sub> group–cosolvent contact specific interaction in a highly diluted aqueous solution is unlikely to be unique. The investigation of the

temperature dependence of the  $h_{xy}$  values for benzene and aniline would be useful from our point of view for understanding this problem.

Turning now to the  $h_{xy}$  values for benzene, aniline and nitrobenzene, we can make from the analysis of Table 4 one interesting observation. It is obvious that a larger  $h_{xy}$  value will cause the difference between the enthalpy of solution of a solute in a binary mixture ( $S + y$ ) and a pure solvent ( $S$ ) at a lower cosolvent mole fraction. Comparing the coefficients in the water–DMF and water–MeCN systems, we should expect that the difference pointed out above should be observed in the latter system at a much lower cosolvent mole fraction.

Recently [10,23,24], we have found the extreme sensitivity of hydrophobic solutes to the presence of a small amount of an organic cosolvent in water. In particular, it was shown that the identical values of the enthalpies of tetraalkylammonium bromides transfer ( $\Delta H_{tr}^0 = 0.5 \text{ kJ mol}^{-1}$ ) from water to water–hexamethyl phosphoric triamide (HMPT) mixed solvent are observed at a very small HMPT mole fraction. The HMPT–water mole ratios (one cosolvent mole per corresponding number of water moles in the mixture) for the mole fractions obtained were found to decrease linearly with increasing the tetraalkylammonium ion size [10,24]. In this paper, we performed an analogous procedure for the aromatic solutes in the water–DMF and water–MeCN systems. The cosolvent mole fraction  $X_y$  for  $\Delta H_{tr}^0 = 0.5 \text{ kJ mol}^{-1}$  were computed from the  $h_{xy}$  values given in Table 4 according the following relationship:

$$\Delta H_{tr}^0(x \text{ from } S \text{ to } S + y) = \Delta H_{sol}^0(S + y) - \Delta H_{sol}^0(S) = \frac{2h_{xy}X_y}{M_S} \quad (5)$$

Table 5 illustrates the expected trend—the mole ratios are sufficiently low and decrease in both systems

Table 5

Mole fractions of the aprotic cosolvent ( $X_y$ ) and cosolvent–water mole ratios (one cosolvent mole per corresponding number of water moles) for  $\Delta H_{tr}^0 = 0.5 \text{ kJ mol}^{-1}$

X	DMF:water	MeCN:water
C <sub>6</sub> H <sub>6</sub>	$X_y = 0.00778$ , 1:128	$X_y = 0.00235$ , 1: 425
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$X_y = 0.01043$ , 1:95	$X_y = 0.00436$ , 1:228
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	$X_y = 0.00380$ , 1:262	$X_y = 0.00149$ , 1:670

from aniline to nitrobenzene. The previous studies [10,23,24] indicated that the solute hydrophobicity increase strongly diminishes cosolvent–water ratios. Thus, the –NO<sub>2</sub> group behaviour in water appears to be rather hydrophobic than hydrophilic because its introduction into the benzene ring significantly decreases the cosolvent–water ratios in both the systems. It should be noted that this phenomenon is expressed stronger in the water–MeCN system.

It is interesting to note that the water mole numbers in the ratios obtained almost in all systems are more than sufficient to form hydration shells around both solute and cosolvent molecules. Therefore, the extreme sensitivity of the aromatic solutes to the presence of DMF and especially MeCN molecules in water can be explained as the result of significant overlapping the solute and aprotic cosolvent hydration cospheres, both of which appear to include a large number of water molecules. It allows to draw a conclusion that correct computer simulations of such heterotactic interactions require using a cubic with periodic boundary conditions in which cosolvent–water ratios should be lower than those given in Table 5.

## References

- [1] M.J. Kamlet, J.L. Abboud, R.W. Taft, *Prog. Phys. Org. Chem.* 13 (1983) 485.
- [2] C. Reihardt, *Chem. Rev.* 94 (1994) 2319.
- [3] Yu.M. Kessler, A.L. Zaitsev, *Solvophobic Effects: Opinions and Facts*, Ellis Horwood, Chichester, UK, 1994 (Chapter 5).
- [4] B.D. Berezin, M.B. Berezine, *Molecule extracoordination on metalloporphyrins as one of the factors of the catalytic and enzyme activity of porphyrins*, in: A.M. Kutepov (Ed.), *Biological Active Compounds in Solutions, Structure, Thermodynamics and Reactivity*, Nauka, Moscow, 2001 (Chapter 5).
- [5] D.V. Batov, O.A. Antonova, V.P. Korolev, *Russ. J. Gen. Chem.* 71 (2001) 736.
- [6] A.V. Kustov, A.V. Bekeneva, O.A. Antonova, V.P. Korolev, *Russ. J. Gen. Chem.* 72 (2002) 981.
- [7] A. Rouw, G. Somsen, *J. Chem. Soc., Faraday Trans. II* 78 (1982) 3397.
- [8] M.V. Kulikov, O.A. Antonova, V.P. Slusar, V.P. Korolev, *Russ. Chem. Bull.* 44 (1995) 1747.
- [9] V.P. Belousov, S.G. Shutin, *Calorimetry of mixing*, in: G.A. Krestov (Ed.), *Experimental Methods of Solution Chemistry: Spectroscopy and Calorimetry*, Nauka, Moscow, 1995, pp. 305–306.
- [10] A.V. Kustov, Ph.D. Dissertation, Ivanovo State University of Chemistry and Technology, October 2000, pp. 81–83.

- [11] V.B. Parker, Thermal properties of uni-univalent electrolytes, Nat. Stand. Ref. Data Ser. Nat. Bur. Stand (US) 2 (1965) 66.
- [12] W.K. Stephenson, R. Fuchs, Can. J. Chem. 63 (1985) 2540.
- [13] V.P. Kolesov, The Basis of Thermochemistry, Moscow State University, 1996, pp. 138–143.
- [14] I. Wadso, The LKB Instrum. J. 13 (1966) 33–39.
- [15] D. Berling, G. Olofsson, J. Solution Chem. 23 (1994) 911.
- [16] W.G. McMillan, J.E. Mayer, J. Chem. Phys. 13 (1945) 276.
- [17] W.J.M. Heuvelsland, C. de Visser, G. Somsen, J. Chem. Soc., Faraday Trans. I 77 (1981) 1191.
- [18] M. Bloemendal, A.S. Rouw, G. Somsen, J. Chem. Soc., Faraday Trans. I 82 (1986) 53.
- [19] J. Fernandez, M.N. Garcia-Lisbona, T.H. Lilley, H. Linsdell, J. Chem. Soc., Faraday Trans. 93 (1997) 407.
- [20] D.V. Batov, O.A. Antonova, V.P. Korolev, Russ. J. Gen. Chem. (71) (2001) 1289.
- [21] K. Burger, Solvation, Ionic and Complex Formation Reactions in Non-aqueous Solvents, Akad. Kiado, Budapest, Hungary, 1983 (Chapter 4).
- [22] F. Franks, Pure Appl. Chem. 59 (1987) 1189.
- [23] A.V. Kustov, V.I. Savelèv, V.P. Korolev, Russ. J. Phys. Chem. 76 (2002) 205.
- [24] A.V. Kustov, V.I. Savelèv, V.P. Korolev, in: Proceedings of the VIII International Conference on Solvation and Complex Formation in Solutions, Ivanovo, 2001, p. 41 (Abstr.).