ARTICLE

Determining the Gibbs Energies of Hydrogen-Bonding Interactions of Proton-Accepting Solutes in Aqueous Solutions from Thermodynamic Data at 298 K with Regard to the Hydrophobic Effect

Igor A. Sedov and Boris N. Solomonov*

Department of Chemistry, Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

ABSTRACT: Reaction rate and equilibrium constants in aqueous solutions are affected by the strength of hydrogen bonds formed between dissolved species and water molecules. Thermodynamic functions of hydrogen bonding with bulk water cannot be measured directly using spectroscopic methods, but the contribution of hydrogen-bonding processes to the thermodynamic functions of hydration may be determined using some model of aqueous solutions. We determined the Gibbs energies of hydrogen-bonding interactions in water for various simple proton-accepting organic molecules on the basis of two different models that allow the contributions of nonspecific van der Waals interactions and the hydrophobic effect to be quantified. It is shown that hydrogen bonding with bulk water may be stronger than with a single water molecule. The influence of solute structure on the Gibbs energy of hydrogen-bonding interactions is discussed.

■ INTRODUCTION

In aqueous solutions, hydrogen bonding of dissolved molecules with water greatly affects the properties of these molecules and in particular the thermodynamics and kinetics of important biochemical and industrial chemical processes.[1,2] Enzyme—substrate and receptor—agonist binding usually involves dehydration of the active sites of the participating molecules accompanied by breaking of the hydrogen bonds between these sites and water. If the reacting species in water undergo significant changes of solvent-accessible surface area and volume, another major influence on the reaction rate and equilibrium can be due to the hydrophobic effect. It is clear that both effects must be described quantitatively in order to allow their roles in biochemical and chemical processes to be understood. These effects also govern the solubilities of chemical species, including toxic and pollutant compounds.

Solute—solvent hydrogen bonding in liquid water has its peculiarities. Having two hydrogen atoms and two lone-pair electrons on the oxygen atom, water molecules in the bulk phase associate into large clusters with very complicated structures and dynamics. Both proton acceptors and donors can form complexes with these clusters upon dissolution. Spectroscopic (IR, NMR, microwave) methods have been successfully used to study hydrogen-bonded complexes with one or several molecules of water in inert and proton-accepting solvents, solid inert matrices, and supersonic molecular beams.[3] Unfortunately, they are not informative for dilute aqueous solutions.

The quantities that can provide us with information on the energetics of hydrogen bonding with bulk water are the thermodynamic functions of solvation or dissolution in an infinite amount of water. The magnitude of the contribution of hydrogen-bonding interactions to the thermodynamic functions of solvation in water and in other self-associated solvents is determined by at least two interrelated processes. One of these is hydrogen bonding between the solute and associates of solvent. The strength of such bonding may depend on the size of the

associate and is generally greater than that of well-studied complexes with a monomer of solvent because of cooperative effects.[4] Another process that accompanies solute—solvent hydrogen bonding is reorganization of solvent associates. The number of bonds that are reorganized is not the same in different systems: it is determined at least by the number of proton-accepting and -donating sites in both the solute and solvent molecules. The total contribution of these processes to the Gibbs energy of solvation is what we call the Gibbs specific-interaction energy of solute A in solvent S $[\Delta_{\mathrm{int(sp)}}G^{\mathrm{A/S}}]$,[5] which reflects the change in Gibbs energy during the transfer of solute from its non-hydrogen-bonded state in solution into the equilibrium mixture of solute—solvent complexes with various structures. The magnitude of $\Delta_{\mathrm{int(sp)}}G^{\mathrm{A/S}}$ determines the hydrogen-bonding-induced changes in solute reactivity.

The influence of the hydrophobic effect on chemical processes in water is usually shown by the examples of hydrophobically driven aggregation of surfactants into micelles and protein folding. There have also been several studies of hydrophobically accelerated Diels—Alder reactions.[6,7] To measure the hydrophobicities of different molecules, several scales have been suggested. We have considered them in our previous works.[8,9] We have also suggested a method to determine the contribution of the hydrophobic effect to the thermodynamic functions of hydration (solvation in water) for different solutes.

In our previous study,[10] the values of the specific-interaction Gibbs energies for a number of amines and pyridines in water were determined. When they were compared with the Gibbs

energies of 1:1 complexation with water, large discrepancies were found. Moreover, the difference between the two quantities was shown to be dependent on the solute structure. An important consequence of this result is that one cannot use the same parameters of solute hydrogen-bonding acidity or basicity for aqueous and nonaqueous solutions.

Here we consider aqueous solutions of some ketones, esters, nitriles, and nitro compounds in order to study the influence of solute structure on the energy of hydrogen-bonding processes in aqueous solutions.

■ METHODOLOGY

The main experimental quantity in the present work is the Gibbs energy of solvation, $\Delta_{solv}G^{A/S}$, which is the Gibbs energy of isothermal transfer of solute A from the gas phase to an infinitely dilute solution in solvent S. The standard states here and below are 298.15 K temperature, 0.1 MPa fugacity of gaseous A, and the hypothetical state of unit mole fraction for solutions.

Our approach is based on regarding the Gibbs energy of hydration (solvation in water) as the sum of three contributions, namely, nonspecific hydration $[\Delta_{solv(nonsp)}G^{A/H_2O}]$, the hydrophobic effect ($\Delta_{h.e.}G^A$), and the above-mentioned specific interactions term $[\Delta_{int(sp)}G^{A/H_2O}]$:

$$\Delta_{solv}G^{A/H_2O} = \Delta_{solv\ (nonsp)}G^{A/H_2O} + \Delta_{h.e}G^A + \Delta_{int(sp)}G^{A/H_2O} \tag{1}$$

The last term, $\Delta_{int(sp)}G^{A/H_2O}$, equals zero if solute A does not form hydrogen bonds with water and can be neglected if only a small fraction of molecules are involved in H complexation. For such compounds, we have shown[11] that there is a correlation between $\Delta_{h.e.}G^A$ and V_x^A, the characteristic molecular volume[12] of A:

$$\frac{\Delta_{h.e}G^A}{kJ\cdot mol^{-1}} = \frac{22.0 V_x^A}{10^2\cdot cm^3\cdot mol^{-1}} + 3.65$$

$$\left(n = 58, \frac{\sigma}{kJ\cdot mol^{-1}} = 1.09, r^2 = 0.9847\right) \tag{2}$$

V_x^A can be calculated using an additive scheme based on atomic contributions tabulated in ref 12. Since a linear dependence holds for compounds with various types of atoms, including noble gases, simple gases, and halogenated compounds, we suggested that $\Delta_{h.e.}G^A$ should follow the same correlation if a solute is able to form hydrogen bonds with water.

According to eq 1, it is necessary to know the Gibbs energy of nonspecific hydration, $\Delta_{solv(nonsp)}G^{A/H_2O}$, to determine the value of $\Delta_{int(sp)}G^{A/H_2O}$. The following equation, which was suggested in our previous works, can be used to calculate the Gibbs energy of nonspecific solvation, and in particular, the Gibbs energy of nonspecific hydration:

$$\Delta_{solv\ (nonsp)}G^{A/S} = \Delta_{solv}G^{A/S_0} + (\delta g^S - \delta g^{S_0})\cdot V_x^A$$
$$+ \left[a + b(\delta g^S)^{1/2}\right]\cdot \left[(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0})\right.$$
$$\left. - (\delta g^{S_R} - \delta g^{S_0})\cdot V_x^A\right] \tag{3}$$

in which

$$a = -\frac{(\delta g^{S_0})^{1/2}}{(\delta g^{S_R})^{1/2} - (\delta g^{S_0})^{1/2}}$$

$$b = \frac{1}{(\delta g^{S_R})^{1/2} - (\delta g^{S_0})^{1/2}}$$

Here $\Delta_{solv}G^{A/S_0}$ and $\Delta_{solv}G^{A/S_R}$ are the Gibbs energies of solvation of solute A in the standard solvents S_0 and S_R, respectively, δg^S, δg^{S_R}, δg^{S_0} are the relative Gibbs energies of cavity formation for the corresponding solvents, and V_x^A is above-mentioned characteristic molecular volume of A.

The parameter δg^S is assumed to reflect nonspecific interactions of solvent molecules with other (solvent and solute) molecules relative to those in hexadecane ($C_{16}H_{34}$). It is determined from the Gibbs energies of solvation of octane (C_8H_{18}) in solvent S and $C_{16}H_{34}$:

$$\delta g^S = \frac{\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}}{V_x^{C_8H_{18}}} \tag{4}$$

For the case of water, we also made a correction for the hydrophobicity of octane. The value of δg^{H_2O} was found to be $5.8\cdot 10^{-2}$ kJ·cm^{-3}. The standard solvents S_0 and S_R should be some solvents with different magnitudes of δg^S (so we cannot choose, for example, two alkane solvents), and they should not form H-bonds with solute A. Here we used hexadecane ($\delta g^S = 0$) as S_0 and benzene ($\delta g^S = 1.7\cdot 10^{-2}$ kJ·cm^{-3}) as S_R. Thus, eq 3 can be written in a simplified form as

$$\frac{\Delta_{solv\ (nonsp)}G^{A/H_2O}}{kJ\cdot mol^{-1}} = \frac{\Delta_{solv}G^{A/S_0}}{kJ\cdot mol^{-1}} + \frac{2.66 V_x^A}{10^2\cdot cm^3\cdot mol^{-1}}$$
$$+ \frac{1.86(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0})}{kJ\cdot mol^{-1}} \tag{3a}$$

■ RESULTS AND DISCUSSION

Using eqs 1, 2, and 3 along with literature data on the Gibbs energies of solvation (or gas−solvent distribution coefficients) of solutes A in water, hexadecane, and benzene, we calculated the values of $\Delta_{int(sp)}G^{A/H_2O}$ for various aliphatic and aromatic proton-accepting solutes (Table 1). None of these solutes is noticeably ionized nor covalently hydrated in water.

Calculated properties of hydrogen bonds are usually compared with data from spectroscopic experiments. Unfortunately, we cannot do this in the case of dilute aqueous solutions. First, it is impossible to determine the constant of complexation by varying the concentration of a solute at infinite dilution because the solvent has a constant activity and the ratio of intensities of absorption bands from bonded and nonbonded forms of the solute do not change with its concentration. Second, spectral signals that carry information on O−H···X hydrogen bonds in water are usually extremely broad and/or indistinguishable from the signals from hydrogen bonds between water molecules. Thus, there are no literature data on the thermodynamic functions of hydrogen bonding of the considered species with liquid water. Additionally, we cannot check their validity by comparing with the properties of 1:1 complexes with water, since the values

1439

dx.doi.org/10.1021/je1011532 |J. Chem. Eng. Data 2011, 56, 1438–1442

Table 1. Contributions of Hydrogen-Bonding Processes and the Hydrophobic Effect to the Gibbs Energy of Hydration of Various Solutes Along with Values of Supplementary Experimental Data[a] Used in the Calculations (at 298 K)

| solute (A)	V_x^A $10^2 \cdot cm^3 \cdot mol^{-1}$	$\Delta_{solv}G^{A/H_2O}$ $kJ \cdot mol^{-1}$	$\Delta_{solv}G^{A/S_0}$ $kJ \cdot mol^{-1}$	$\Delta_{solv}G^{A/S_R}$ $kJ \cdot mol^{-1}$	$\Delta_{h.e.}G^A$ $kJ \cdot mol^{-1}$	$\Delta_{int(sp)}G^{A/H_2O}$ $kJ \cdot mol^{-1}$	$\Delta_{HB}G^{A\cdots H_2O}$ $kJ \cdot mol^{-1}$
2-propanone	0.5470	2.0	1.4	−1.9	15.7	−10.4	−6.9
2-butanone	0.6879	2.9	−2.1	−4.7	18.8	−10.7	−6.7
2-pentanone	0.8288	3.8	−4.8	−7.6	21.9	−10.3	−6.9
2-hexanone	0.9697	4.1	−7.6	−10.1	25.0	−11.2	−6.9
2-heptanone	1.1106	5.6	−10.5	−12.6	28.1	−11.0	
2-octanone	1.2515	5.9	−13.3	−15.4[c]	31.2	−11.5	
acetophenone	1.0139	−1.3	−14.7	−16.6	26.0	−11.8	−7.1
acetonitrile	0.4042	1.6	1.1	−2.2[d]	12.5	−7.0	−6.0
benzonitrile	0.8711	0.3[b]	−12.1	−15.6[c]	22.8	−6.2	−5.8
nitromethane	0.4237	1.2	0.2	−4.9[e]	13.0	−3.7	−3.9
nitrobenzene	0.8906	0.7	−15.0	−17.8	23.2	−4.6	−4.0
methyl acetate	0.6057	4.6	−0.2	−2.9	17.0	−8.7	−5.4
ethyl acetate	0.7466	5.0	−2.6	−5.0	20.1	−10.0	−6.2
propyl acetate	0.8875	6.2	−5.4	−7.8	23.2	−9.4	
butyl acetate	1.0284	6.8	−8.3	−10.2	26.3	−10.3	
pentyl acetate	1.1693	7.6	−10.7	−13.4	29.4	−9.2	
methyl propanoate	0.7466	5.6[b]	−2.9[b]	−5.2[f]	20.1	−9.2	
methyl pentanoate	1.0284	7.2[b]	−8.6	−10.5	26.3	−9.8	
methyl hexanoate	1.1693	7.5[b]	−11.7	−13.1	29.4	−10.6	
methyl benzoate	1.0726	1.5[b]	−15.4	−17.5[g]	27.2	−9.3	−5.9
triethylamine						−21.5[h]	−9.5
pyridine						−11.7[h]	−8.8

[a] Experimental data were taken from ref 22 unless otherwise noted. [b] Value taken from ref 15. [c] Value taken from ref 17. [d] Value taken from ref 19. [e] Value taken from ref 18. [f] Value taken from ref 16. [g] Value estimated using eq 3. [h] Value taken from ref 10.

of $\Delta_{int(sp)}G^{A/H_2O}$ are greatly affected by cooperative effects and reorganization of hydrogen bonds between water molecules.

On the other hand, we can consider a different method to take into account the nonspecific effects during the process of hydration. Fuchs and Stephenson[13] suggested such a method for determining the contribution of hydrogen-bonding processes to solvation enthalpies. We applied their method to the Gibbs energies, relying on fact that the contribution of the hydrophobic effect given by eq 2 should be almost the same for solutes with similar values of the characteristic molecular volume.

For a solute A, we start by choosing a structurally similar model solute M that does not form hydrogen bonds with water and has a similar value of the hydrophobic-effect Gibbs energy. Next, we consider a set of solvents S_i with different values of the π^* solvent parameter of Kamlet, Abboud, and Taft.[14] Neither A nor M should form hydrogen bonds with these solvents. The value of $\Delta_{solv}G^{A/S_i} - \Delta_{solv}G^{M/S_i}$ is expected to be linearly dependent on π_i^*. The deviation of $\Delta_{solv}G^{A/H_2O} - \Delta_{solv}G^{M/H_2O}$ from this "non-hydrogen-bonding baseline" (NHBB) is supposed to be the Gibbs energy of specific interactions in water. The NHBB takes into account the influence of solute structure on the nonspecific solvation energy.

The following example illustrates the applicability of the NHBB method to aqueous solutions and its weak sensitivity to the choice of model compounds. Naphthalene (A) and heptane (M) have close values of V_x^A [(1.0854 and 1.0949)·10^2 cm^3·mol^{-1}, respectively]. Thus, the corresponding contributions of the hydrophobic effect to the Gibbs energy (eq 2) should
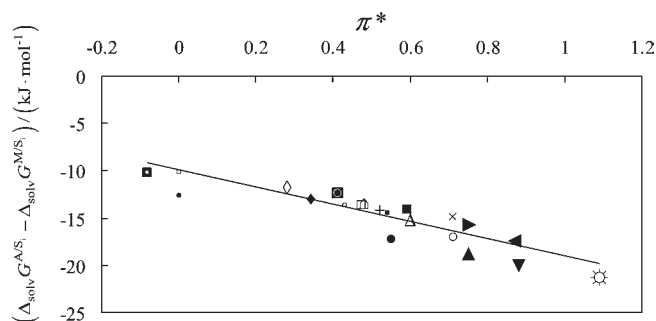
Figure 1. NHBB plot for naphthalene (A) modeled by heptane (M) in various solvents: large ●, 1,4-dioxane; large ○, 2-propanone; ▲, acetonitrile; large ■, benzene; large □, butanol; ◇, carbon tetrachloride; ×, chlorobenzene; small □, cyclohexane; right-pointing triangles, cyclohexanone; ▼, dimethylformamide; small ■, ethanol; ◻ heptane; small ●, hexadecane; ⬠ isopropyl alcohol; Δ, methanol; ◆, octanol; +, propanol; small ○, p-xylene; left-pointing triangles, pyridine; ■ with white circle, tert-butyl alcohol; ☼, water. The solid line is the NHBB linear correlation.

also be almost the same. A plot of $\Delta_{solv}G^{A/S_i} - \Delta_{solv}G^{M/S_i}$ vs π_i^* is shown in Figure 1. Despite the great difference in the structure and properties of the two compounds (the value of $\Delta_{solv}G^{A/H_2O} - \Delta_{solv}G^{M/H_2O}$ is −21.2 kJ·mol^{-1}), a linear dependence holds for 21 solvents, including water and aliphatic alcohols, with $\sigma = 1.26$ kJ·mol^{-1}. Experimental data used here and below were taken from the literature.[15−19]
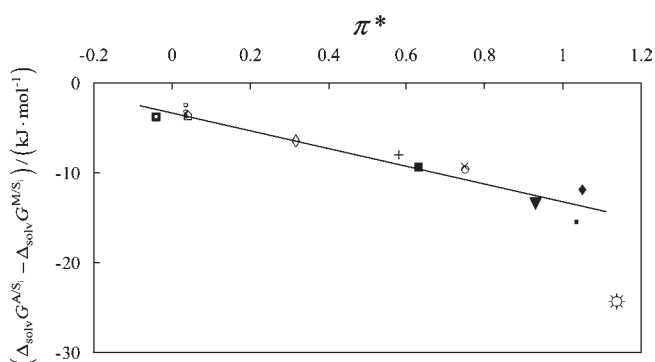
Figure 2. NHBB plot for 2-propanone modeled by propane in various solvents: large ○, 2-propanone; large ■, benzene; ◇, carbon tetrachloride; ×, chlorobenzene; small □, cyclohexane; small ○, decane; ▼, dimethylformamide; small ■, dimethyl sulfoxide; ◻ heptane; small ●, hexadecane; ⌂, hexane; ◆, nitrobenzene; +, toluene; ☼, water. The solid line is the NHBB linear correlation.

We used the NHBB method to determine the values of $\Delta_{int(sp)}G^{A/H_2O}$ for 2-propanone ($V_x^A = 0.5470$ cm^3 mol^{-1}·10^2; M = propane, $V_x^A = 0.5313 \cdot 10^2$ cm^3·mol^{-1}; $\Delta_{solv}G^{A/H_2O} - \Delta_{solv}G^{M/H_2O} = -24.2$ kJ·mol^{-1}), acetonitrile ($V_x^A = 0.4042 \cdot 10^2$ cm^3·mol^{-1}; M = ethane, $V_x^A = 0.3904 \cdot 10^2$ cm^3·mol^{-1}; $\Delta_{solv}G^{A/H_2O} - \Delta_{solv}G^{M/H_2O} = -23.8$ kJ·mol^{-1}), and triethylamine ($V_x^A = 1.0538 \cdot 10^2$ cm^3·mol^{-1}; M = heptane, $V_x^A = 1.0949 \cdot 10^2$ cm^3·mol^{-1}; $\Delta_{solv}G^{A/H_2O} - \Delta_{solv}G^{M/H_2O} = -23.8$ kJ·mol^{-1}). The following equations were obtained:

$$\frac{\Delta_{solv}G^{CH_3COCH_3/S_i} - \Delta_{solv}G^{C_3H_8/S_i}}{kJ \cdot mol^{-1}}$$

$$= -9.94\pi_i^* - 3.31 \qquad \left(\frac{\sigma}{kJ \cdot mol^{-1}} = 1.04, \, n = 13\right)$$

$$\frac{\Delta_{solv}G^{CH_3CN/S_i} - \Delta_{solv}G^{C_2H_6/S_i}}{kJ \cdot mol^{-1}}$$

$$= -10.87\pi_i^* - 6.17 \qquad \left(\frac{\sigma}{kJ \cdot mol^{-1}} = 1.53, \, n = 10\right)$$

$$\frac{\Delta_{solv}G^{(C_2H_5)_3N/S_i} - \Delta_{solv}G^{C_7H_{16}/S_i}}{kJ \cdot mol^{-1}}$$

$$= -3.04\pi_i^* + 0.86 \qquad \left(\frac{\sigma}{kJ \cdot mol^{-1}} = 0.57, \, n = 13\right)$$

Figure 2 shows the NHBB plot for the 2-propanone/propane pair.

The obtained values of $\Delta_{int(sp)}G^{A/H_2O}$ [(−10.1, −5.7, and −21.4) kJ·mol^{-1}, respectively] are in agreement with those calculated using our method (see Table 1). The origins of the uncertainties in both methods are the experimental errors in the Gibbs energies, deviations of single points from empirical correlations, and for the second method, errors in the values of π^*. They were determined from UV-spectroscopic studies of compounds that form no hydrogen bonds with a solvent. It is difficult to find compounds that are soluble and not H-bonded in water and other solvents with strong self-association. Thus, one

of the main drawbacks of the NHBB method is that the values of π^* for protic solvents and methods to determine them are still a subject of discussion. Additionally, it is not always possible to find a model compound that gives a linear correlation of $\Delta_{solv}G^{A/S_i} - \Delta_{solv}G^{M/S_i}$ with π_i^*.[20]

The results from Table 1 can be compared with values of $\Delta_{HB}G^{A\cdots H_2O}$, the Gibbs energies of formation of equimolar complexes A−H$_2$O, calculated from the complexation constants on the mole fraction scale of concentrations. Complexes with water are difficult to observe in inert solvent media, and we could only estimate their energies using, for example, the rather precise (standard deviation in the Gibbs energies = 0.5 kJ·mol^{-1} for a set of 1300 systems) correlation relationship for 1:1 complexes in tetrachloromethane medium obtained by Abraham et al.[21] These values are also given in Table 1.

On the basis of the values of $\Delta_{int(sp)}G^{A/H_2O}$, the proton-accepting power of solutes in water decreases in the following order: amines > pyridines > ketones > esters > nitriles, nitro compounds. This order is qualitatively the same as that for the decrease of $\Delta_{HB}G^{A\cdots H_2O}$. Neither $\Delta_{int(sp)}G^{A/H_2O}$ nor $\Delta_{HB}G^{A\cdots H_2O}$ changes significantly in homological rows when the carbon chain length is varied. The same result was obtained for aliphatic amines.[10]

Changing an aliphatic substituent on the proton-accepting functional group to an aromatic (phenyl) group did not lead to large changes in the hydrogen-bonding strength of the considered compounds, in terms of either $\Delta_{int(sp)}G^{A/H_2O}$ or $\Delta_{HB}G^{A\cdots H_2O}$. This fact can be used as an argument for the correctness of the obtained values. At the same time, the contribution of the hydrophobic effect differed greatly for the considered pairs.

The value of $\Delta_{int(sp)}G^{A/H_2O}$ is always more negative or nearly equal to that of $\Delta_{HB}G^{A\cdots H_2O}$. This means that hydrogen bonding with water is cooperative and that the enhancement of the H-bond strength due to bonding with polymer chains of water exceeds the cost of breaking water−water bonds. It should also be noted that ketones and esters can potentially form more than one hydrogen bond with liquid water.

■ CONCLUSIONS

We have observed some regularities in relations between solute structure and the magnitudes of the Gibbs energies of hydrogen-bonding processes. There is no single relationship between $\Delta_{HB}G^{A\cdots H_2O}$, the Gibbs energy of formation of equimolar complexes with water, and the values of $\Delta_{int(sp)}G^{A/H_2O}$. The difference between the two quantities is solute-dependent. This means that neither correlation relationships nor parameters of solute basicity obtained from data for equimolar complexes can be used to describe the thermodynamics of solvation in bulk water.

There is still much work to do in the development of a quantitative description of hydrogen-bonding processes in aqueous solutions and other self-associated solvents.

■ AUTHOR INFORMATION

Corresponding Author
*bsolomon@ksu.ru.

■ ACKNOWLEDGMENT

■ REFERENCES

(1) Akiya, N.; Savage, P. E. Roles of Water for Chemical Reactions in High-Temperature Water. *Chem. Rev.* **2002**, *102*, 2725–2750.

(2) *Organic Reactions in Water*; Lindström, U. M., Ed.; Blackwell: Oxford, U.K., 2007.

(3) Maréchal, Y. *The Hydrogen Bond and the Water Molecule*; Elsevier: Amsterdam, 2007.

(4) Maes, G.; Smets, J. Hydrogen bond cooperativity: A quantitative study using matrix-isolation FT-IR spectroscopy. *J. Phys. Chem.* **1993**, *97*, 1818–1825.

(5) Sedov, I. A.; Solomonov, B. N. A method to determine the Gibbs energy of specific interactions in solutions. Hydrogen bonding of proton donating solutes in basic solvents. *Fluid Phase Equilib.* **2009**, *276*, 108–115.

(6) Butler, R. N.; Coyne, A. G. Water: Nature's Reaction Enforcer—Comparative Effects for Organic Synthesis "In-Water" and "On-Water. *Chem. Rev.* **2010**, *110*, 6302–6337.

(7) Pirrung, M. C. Acceleration of Organic Reactions through Aqueous Solvent Effects. *Chem—Eur. J.* **2006**, *12*, 1312–1317.

(8) Solomonov, B. N.; Sedov, I. A. Quantitative description of the hydrophobic effect: The enthalpic contribution. *J. Phys. Chem. B* **2006**, *110*, 9298–9303.

(9) Solomonov, B. N.; Sedov, I. A. The hydrophobic effect Gibbs energy. *J. Mol. Liq.* **2008**, *139*, 89–97.

(10) Solomonov, B. N.; Sedov, I. A.; Akhmadiyarov, A. A. Gibbs energy of cooperative hydrogen-bonding interactions in aqueous solutions of amines and pyridines. *J. Phys. Org. Chem.* **2009**.

(11) Sedov, I. A.; Solomonov, B. N. Relation between the characteristic molecular volume and hydrophobicity of nonpolar molecules. *J. Chem. Thermodyn.* **2010**, *42*, 1126–1130.

(12) Abraham, M. H.; McGowan, J. C. The use of characteristic volumes to measure cavity terms in reversed phase liquid chromatography. *Chromatographia* **1987**, *23*, 243–246.

(13) Stephenson, W. K.; Fuchs, R. Enthlpies of hydrogen bond formation of 1-octanol with aprotic organic solvents. A comparison of the solvation enthalpy, pure base, and non-hydrogen-bonding baseline methods. *Can. J. Chem.* **1985**, *63*, 342–348.

(14) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. The solvatochromic comparison method. 6. The π^* scale of solvent polarities. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038.

(15) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. S. Hydrogen bonding. Part 34. The factors that influence the solubility of gases and vapours in water at 298 K, and a new method for its determination. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1777–1791.

(16) Li, J.; Zhu, T.; Hawkins, G. D.; Winget, P.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. Extension of the platform of applicability of the SM5.42R universal solvation model. *Theor. Chem. Acc.* **1999**, *103*, 9–63.

(17) Smirnov, S. A. Ph.D. Thesis, Kazan State University, Kazan, Russia, 1990.

(18) Rohrschneider, L. Solvent characterization by gas−liquid partition coefficients of selected solutes. *Anal. Chem.* **1973**, *45*, 1241–1247.

(19) Thomas, E. R.; Newman, B. A.; Long, T. C.; Wood, D. A.; Eckert, C. A. Limiting activity coefficients of nonpolar and polar solutes in both volatile and nonvolatile solvents by gas chromatography. *J. Chem. Eng. Data* **1982**, *27*, 399–405.

(20) Borisover, M. D.; Solomonov, B. N.; Breus, V. A.; Gorbachuk, V. V.; Konovalov, A. I. Comparative-Analysis of Methods for the Determination of Enthalpy of Solute Specific Interaction with Solvent. *Zh. Obshch. Khim.* **1988**, *58*, 249–260.

(21) Abraham, M. H. Scales of solute hydrogen-bonding: Their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.* **1993**, *22*, 73–83.

(22) Katritzky, A. R.; Tulp, I.; Fara, D. C.; Lauria, A.; Maran, U.; Acree, W. E. A General Treatment of Solubility. 3. Principal Component Analysis (PCA) of the Solubilities of Diverse Solutes in Diverse Solvents. *J. Chem. Inf. Model.* **2005**, *45*, 913–923.