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Thermodynamics of solvation and solvophobic effect in formamide

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ABSTRACT

Using semi-adiabatic calorimetry, we measured the enthalpies of solution for various low-polar compounds including alkanes, aromatic hydrocarbons and their halogenated derivatives in formamide at temperature of 298 K. For the same compounds, the values of limiting activity coefficients in formamide were determined using GC headspace analysis at 298 K, and Gibbs free energies of solution and solvation were calculated. Based on these data and the available literature values of the Gibbs free energy of solvation in formamide for a number of other low-polar solutes, a study of the solvophobic effect in this solvent is performed, and its resemblance to the hydrophobic effect in aqueous solutions is demonstrated. It is shown that the contribution of the solvophobic effect into the solvation Gibbs free energy in formamide is much higher than that in aliphatic alcohols, but lower than that in water. Like in water, the magnitude of this contribution for different solutes linearly increases with the solute molecular volume. Solvophobic effect also significantly affects the enthalpies of dissolution in formamide, causing them to be more negative in the case of alkanes and more positive in the case of arenes.

1. Introduction

Formamide $HCONH_2$ is an important solvent from both practical and theoretical points of view. Formamide finds its applications as a solvent in life science and technology and is promising for green organic synthesis. It is used in hybridization solutions for hybridization of nucleic acid duplexes [1] and as a component of cryoprotectant mixtures for vitrification of tissues [2]. In liquid formamide, its molecules form strong intermolecular hydrogen bonds [3]. Interest in the structural and energetic characteristics of these bonds shown by a number of researchers is due both to the fact that formamide is the simplest compound containing –CO–NH– fragment, which is present in peptides and proteins, and some analogy between hydrogen bond networks in formamide and liquid water [3–5]. Hydrogen bonds in water play a huge role in many natural phenomena and processes, and formamide is sometimes considered as an alternative solvent to water that is able to support life with some alternative biochemistry [6].

The similarity of formamide and water is quite obvious, if we consider the solubilities of various compounds. Non-polar substances have low solubility and high values of Gibbs free energy of dissolution in both solvents, while polar organic solutes and many inorganic salts are well soluble in water and formamide. Additionally, micelles can form in formamide solutions from the same amphiphilic surfactant molecules that form micelles in water, however, in formamide this process takes place at higher concentrations of surfactants [7].

2. Methodology

2.1. Solvophobic effect in formamide and thermodynamic functions of solution

An evident similarity in thermodynamic properties of aqueous solutions and solutions in formamide and in a number of other self-associated solvents led to introduction of the concept of solvophobic effects [8], by analogy with the hydrophobic effect. These effects influence thermodynamic and other properties of solutions in self-associated solvents. However, this concept remained fairly vague for a long time: no strict definition and no criterion to judge whether the solvophobic effect takes place in a certain system or not. In a recent paper [9], we proposed to recognize the presence of the solvophobic effects in solutions by considering the relationship between the Gibbs free energies and enthalpies of solvation. According to this approach and available experimental data, in formamide solutions the solvophobic effect is very strong, although weaker than in water. However, there is not enough literature values of the thermodynamic functions of solvation to quantify the solvophobic effect in formamide. Above all, the enthalpies of dissolution of low-polar compounds in formamide are unknown or unreliable.

Measurement of the enthalpy of dissolution of low-polar substances in formamide is difficult because of their low solubility, low dissolution rate, and high viscosity of solvent. Even under

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vigorous stirring, a long time (up to tens of minutes) is required for a complete dissolution. If the substance is volatile, it can evaporate from the cell during this time. Thus, such experiments require high stability of the baseline and the use of a sealed calorimetric cell. Even some of the few enthalpies of solution in formamide reported in literature are contradictory: for example, for dissolution of hexane different authors [10,11] have obtained the values of (12.4 and 5.2) $\text{kJ} \cdot \text{mol}^{-1}$.

The values of thermodynamic functions of solution are not only of theoretical interest in order to study different types of intermolecular interactions, but may also serve as the basis for development of predictive models to calculate various properties of solutions and mixtures, or design of separation and synthetic processes.

This work aims to partially fill the gap in experimental data on the enthalpies and Gibbs free energies of solution of low-polar molecules in formamide. Obtained results will help us to study and quantify the solvophobic effect in this important and interesting solvent.

2.2. Available experimental thermodynamic data

Experimental enthalpies of solution of low polar solutes in formamide at infinite dilution are limited to results at 298 K obtained by Berling and Oloffson for hexane, heptane, cyclohexane, benzene, 1-chloropentane and 1,5-dichloropentane [10], by Krishnan and Friedman for hexane, heptane, benzene, toluene and ethylbenzene [11], and by Catalan et al. for benzene and toluene [12]. The values obtained in these works are summarized in table 1. Dissolution of several polar compounds in formamide has also been studied, including normal alcohols and water [10,11,13,14] nitrogen-containing heterocycles [12,15], and amides [16]. In all of these works, solution calorimetry techniques was used.

A little more data is available on the Gibbs free energies of solution in formamide and quantities that are directly related to it, such as limiting activity coefficients or Ostwald solubility coefficients or retention volumes. Most of them were measured by gas-liquid chromatography with formamide as a stationary phase. These data have been assembled and recalculated into the gas–liquid distribution constants at 298 K in a paper [17].

In many works where thermodynamic functions of solution of organic nonelectrolytes in formamide have been determined experimentally, the solvophobic effect has not been discussed. The exceptions are the paper of Berling and Oloffson [10], where the similarities and differences of thermodynamic properties of solutions in water and formamide have been discussed, and the work of Sjoberg et al. [18], who also compared the behavior of aqueous and formamide solutions of nonpolar compounds. In the first of these papers, it was concluded that in formamide the solvophobic effect has an enthalpic origin, while in water it arises mainly from a large loss of entropy. In a number of works [19,20], solvation properties of organic electrolytes with hydrophobic chains such as tetraalkylammonium salts in formamide were studied, and a comparison with the behavior of their aqueous solutions was made.

TABLE 1
Summary of experimental values of enthalpy of dissolution for low polar solutes in formamide at infinite dilution (T = 298 K).

Solute (A)	$\Delta_{soln}H^{A/FA}/(\text{kJ} \cdot \text{mol}^{-1})$
n-Hexane	12.36 [10], 5.15 [11]
n-Heptane	14.10 [10], 6.32 [11]
Cyclohexane	7.16 [10]
Benzene	4.63 [10], 4.69 [11], 4.85 [12]
Toluene	4.94 [11], 5.39 [12]
Ethylbenzene	5.94 [11]
1-Chloropentane	5.73 [10]
1,5-dichloropentane	5.78 [10]

There are also many studies of the process of micelle formation in formamide [8,21–24], which is considered as a result of solvophobic interactions or solvophobic effect. In these works thermodynamic functions of micellization and dissolution of surfactants in formamide were determined. However, no attempts to make a comparison with the properties of solutions of nonpolar solutes were made.

2.3. Our approach to analyze the solvophobic effects

On the qualitative level, no one doubts about the presence of solvophobic effect in formamide solutions. However, no quantitative characteristics of their impact on the thermodynamic properties of solutions have been given. We proposed [9] to determine the contribution of the solvophobic effect into the thermodynamic functions of solvation using the values of the Gibbs free energies and enthalpies of solvation at T = 298 K. Thermodynamic functions of solvation $\Delta_{solv}f^{A/S}(f = G, H)$ are functions of transfer of solute A from gas phase into solvent S. They are related to the excess thermodynamic functions of solution at infinite dilution $\Delta_{soln}f^{A/S}$ through equation

$$\Delta_{solv}f^{A/S} = \Delta_{soln}f^{A/S} - \Delta_{vap}f^{A} \tag{1}$$

where $\Delta_{vap}f^{A}$ is the corresponding thermodynamic function of vaporization of solute. The standard state for solutions is mole fraction-based and the standard pressure of gaseous solutes p° = 1 bar.

We used the fact that the Gibbs free energy and enthalpy of solvation for many compounds with different structures dissolved in various non-associated solvents are linearly correlated. For example, a correlation for 978 pairs composed from solutes and solvents of different polarity is $\Delta_{solv}G^{A/S} = 0.627\Delta_{solv}H^{A/S} + 16.3$ with σ = 1.6 $\text{kJ} \cdot \text{mol}^{-1}$, R^2 = 0.9768 [25]. The accuracy of correlations for solutes only from a certain class of compounds is much higher, although their slopes and intercepts can be a little different. For n-alkanes from methane to octane in 34 different solvents (101 system in total), there is a correlation $\Delta_{solv}G^{A/S} = 0.632\Delta_{solv}H^{A/S} + 15.6$ with a standard deviation σ = 0.75 $\text{kJ} \cdot \text{mol}^{-1}$ and a correlation coefficient R^2 = 0.9890 [9]. Data points for solutions in self-associated solvents deviate from these correlations, so that the Gibbs free energy of solvation is always higher than for a solution in non-associated solvent with the same enthalpy of solvation. We viewed these deviations as results of the solvophobic effect, which leads to a decrease in solubility. On a molecular level, this can be interpreted as an unusually high entropic cost of creating a cavity to accommodate a solute molecule in associated solvents. If so, the additional "solvophobic" Gibbs free energy should grow up with the solute size. We determined [9] the contribution of the solvophobic effect into the Gibbs free energy of solvation of various non-polar substances in aliphatic alcohols. It was found [9] that this contribution is linearly correlated with the characteristic molecular volume of a solute. A similar linear dependence on the characteristic molecular volume was observed when we considered the contribution of the hydrophobic effect into the Gibbs free energy of solvation in water [26]. Its slope is much larger than that for alcoholic solutions. The hydrophobic effect in water affects not only the Gibbs energy, but also the enthalpy of solvation, and leads to its decrease in the case of alkanes, while for arenes the contribution into the enthalpy due to the hydrophobic effect is positive [27]. The impact of the solvophobic effect on the enthalpy of solvation in alcohols seems to be small and comparable in magnitude with experimental uncertainties. In this paper, we quantitatively study the solvophobic effect in formamide using the same approach on the basis of measured and literature values of the thermodynamic functions of solvation.

3. Experimental

Formamide with purity >0.995 was purchased from Sigma–Aldrich. All the solutes were at least 0.99 pure grade from Acros organics, Sigma–Aldrich and Fluka (see table 2). The purity of substances was checked by gas chromatography and they were used without further purification.

3.1. Enthalpy of solution measurements

Enthalpies of dissolution were measured at $T = 298.15$ K using TAM III solution calorimeter. For liquid solutes, calorimetric titration method was used. In a typical experiment, 100 ml of formamide was placed in a glass calorimetric vessel equipped with a gold stirrer, a Joule heater and a thermistor. After about an hour of thermostatting and heater calibrations, 100 μl of solute was added by portions (5–20 μl) using an electronically operated microsyringe with a long gold cannula with its end immersed in calorimetric vessel. The heat effect of each addition was calculated from a calorimetric curve. Solid solute samples with a known mass were placed in sealed glass ampoules, which were then broken into a calorimetric vessel with 100 ml of formamide. The heat effect of breaking an empty ampoule was determined in a separate experiment, and subtracted from all heat effects measured in break experiments. Experiments with each solute were repeated 2–3 times using a fresh portion of solvent.

Since we determined the enthalpies of dissolution of poorly soluble volatile compounds, it was extremely important to take into account evaporation of the substance to a free volume of the calorimetric vessel. The vapor pressure $p^{A/S}$ of substance A over its infinitely diluted solution in solvent S is related by equation $p^{A/S} = p^A_{sat}\gamma^{A/S}_\infty x^{A/S}$ to the saturated vapor pressure of pure substance A p^A_{sat}, limiting activity coefficient of A dissolved in S $\gamma^{A/S}_\infty$, and the mole fraction of A $x^{A/S}$. Thus, the fraction of solute that evaporates after addition of a new small (such that the solution is still infinitely diluted) portion of solute equals

$$\varphi = 1/\left(1 + RT\nu_S/\left(p^A_{sat}\gamma^{A/S}_\infty V_{free}\right)\right) \tag{2}$$

where V_{free} is the volume of the free space in the calorimetric vessel, ν_S – number of moles of solvent in the vessel. The molar enthalpy obtained from calorimetric curves ΔH_{obs} is equal to the sum of heat effects of dissolution and evaporation of some part of solute:

$$\Delta H_{obs} = (1-\varphi)\Delta_{soln}H^{A/S} + \varphi\Delta_{vap}H^A \tag{3}$$

TABLE 2
List of compounds employed in the work and their purities.

Compound	Manufacturer	Purity (mass fraction)
Formamide	Sigma–Aldrich	0.995
Hexane	Acros organics	0.99
Heptane	Acros organics	0.99
Octane	Acros organics	0.99
Cyclohexane	Acros organics	0.995
Benzene	Sigma–Aldrich	0.997
Toluene	Sigma–Aldrich	0.998
Ethylbenzene	Fluka	0.99
Fluorobenzene	Aldrich	0.99
Chlorobenzene	Sigma–Aldrich	0.995
Bromobenzene	Aldrich	0.995
1,2-dichlorobenzene	Sigma–Aldrich	0.99
Naphthalene	Aldrich	0.99
Biphenyl	Sigma–Aldrich	0.995

We calculated the values of $\Delta_{soln}H^{A/S}$ using literature values of $\Delta_{vap}H^A$ [28], p^A_{sat} [29], and literature [17] or measured as described below values of $\gamma^{A/S}_\infty$. V_{free} was determined using two methods: direct measurement using a digital caliper and measurement of the amount of heat absorbed when volatile alkane is added to 100 ml of water in the calorimetric vessel. Alkane is almost insoluble in water, thus, if we add enough alkane to saturate the vapor phase in the vessel, we observe the heat effect $Q = -\Delta H^A_{vap}p^A_{sat}V_{free}/(RT)$. From here one can calculate V_{free}. The results of both methods were in agreement.For each solute, an average value of enthalpy of dissolution was taken. The results are given in table 3.

3.2. Limiting activity coefficient measurements

Measurements of limiting activity coefficients were carried out by gas chromatographic head space analysis technique using PerkinElmer Clarus 580 chromatograph with Turbomatrix HS-16 headspace autosampler. Equilibrium vapor phase samples were automatically taken from thermostatted 22 ml vials containing 5 ml of solution or pure substance and transferred to the gas chromatograph. The vial thermostat was modified in order to conduct measurements at 298 K.

The values of limiting activity coefficients $\gamma^{A/S}_\infty$ can be calculated from the ratio of vapor pressures of solute A over its dilute solution in S and above pure A: $\gamma^{A/S}_\infty = p^{A/S}/(p^A_{sat}\cdot x^{A/S})$, where $x^{A/S}$ is the molar fraction of A in solution. The ratio $p^{A/S}/p^A_{sat}$ is equal to the ratio of areas of chromatographic peaks in experiments with the solution and with pure A. In our calculations we made a correction of initial concentration of solute on the quantity of evaporated solute. Measurements were conducted at three different concentrations of every solute in the range 0.1–1.5 vol% and repeated two times for each concentration. No significant concentration dependence of the activity coefficients was observed. An average value of the Gibbs free energy of solution $\Delta_{soln}G^{A/S} = RT\ln\gamma^{A/S}_\infty$ was taken. The Gibbs free energy of solvation is given by $\Delta_{solv}G^{A/S} = \Delta_{soln}G^{A/S} - RT\ln p^A_{sat}$. The values of p^A_{sat} were taken from EPA database [29]. Obtained results are given in table 4.

4. Discussion

4.1. Enthalpies of solution in formamide

When comparing the obtained values of the enthalpies of solution with the available published data (see table 1), we can note the following. While for relatively highly soluble benzene and toluene our results are in good agreement with the literature, for alkanes we observed significantly different results. Apparently, authors of the work [10] did not consider partial evaporation of alkanes, which gives a huge endothermic heat effect. Another point is that according to available data in various solvents including water and dimethylformamide, enthalpies of solution of hexane and cyclohexane differ by no more than 1 $\text{kJ}\cdot\text{mol}^{-1}$. In formamide, previously reported difference between them was more than 5 $\text{kJ}\cdot\text{mol}^{-1}$. From our measurements this difference is only 0.8 $\text{kJ}\cdot\text{mol}^{-1}$. The methylene group increment of the enthalpy of dissolution of alkanes in formamide is, according to our data, about 1.2 $\text{kJ}\cdot\text{mol}^{-1}$, which is consistent with the observed difference in solution enthalpies of toluene and ethylbenzene (1.1 $\text{kJ}\cdot\text{mol}^{-1}$) and with the reported methylene group increment of the enthalpy of dissolution of n-alkanols (1.0 $\text{kJ}\cdot\text{mol}^{-1}$) [10]. Enthalpies of solution of halobenzenes, naphthalene and biphenyl were determined in the present work for the first time.

It is known that the enthalpy of dissolution of aromatic solutes in various solvents is linearly correlated with parameters representing their molecular volume [30]. In figure 1a, a correlation of

TABLE 3
Experimental values and uncertainties of enthalpies of solution in formamide, vaporization and solvation from the gas phase at $T = 298$ K.

Solute (A)	$\Delta_{soln}H^{A/FA}$/ (kJ · mol^{-1})	$\Delta_{vap}H^{A}$/(kJ · mol^{-1}) [28]	$\Delta_{solv}H^{A/FA}$/ (kJ · mol^{-1})
Hexane	8.1 ± 0.8	31.4	−23.3
Heptane	9.5 ± 0.6	36.6	−27.1
Octane	10.6 ± 0.5	41.6	−31.0
Cyclohexane	7.3 ± 0.6	33.1	−25.8
Benzene	4.54 ± 0.1	33.9	−29.4
Toluene	4.48 ± 0.1	38.0	−33.5
Ethylbenzene	5.60 ± 0.1	42.4	−36.8
Fluorobenzene	3.32 ± 0.1	34.5	−31.2
Chlorobenzene	3.63 ± 0.1	40.3	−36.7
Bromobenzene	4.54 ± 0.1	44.8	−40.3
Naphthalene	22.8 ± 1	72.3	−49.5
Biphenyl	25.3 ± 1	82.9	−57.6

TABLE 4
Experimental values and uncertainties of limiting activity coefficients and Gibbs free energies of solution and solvation in formamide at $T = 298$ K.

Solute (A)	$\gamma_{\infty}^{A/FA}$	$\Delta_{soln}G^{A/FA}$/ (kJ · mol^{-1})	$\Delta_{solv}G^{A/FA}$/ (kJ · mol^{-1})	$\Delta_{solv}G^{A/FA}$/ (kJ · mol^{-1}) [a]
Benzene	53 ± 3	9.8	4.7	4.7
Toluene	81 ± 4	10.9	2.8	3.4
Fluorobenzene	54 ± 3	9.9	4.3	
Chlorobenzene	94 ± 8	11.3	1.0	
Bromobenzene	107 ± 6	11.6	−1.3	
1,2-dichlorobenzene	159 ± 8	12.6	−3.1	
Naphthalene	533 ± 30	15.6	−6.9	
Biphenyl	1320 ± 70	17.8	−10.3	

[a] Calculated from Ostwald solubility coefficients given in Ref. [17].

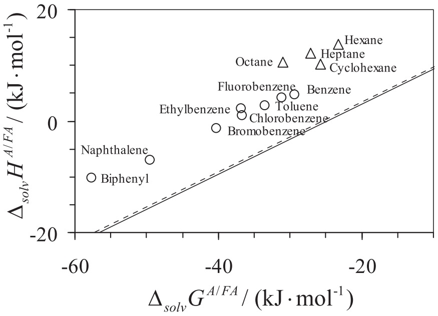

FIGURE 2. Gibbs free energies *vs* enthalpies of solvation of low-polar solutes in formamide. The solid line matches the linear equation of the correlation between Gibbs energies and enthalpies of solvation of alkanes in non-associated solvents and the dotted line matches the similar correlation for aromatic hydrocarbons.

enthalpies of solvation of non-alkylated aromatic hydrocarbons and their halogenated derivatives from table 3 with molar refractivity *MR*, which is calculated from refractive indices of compounds or atomic contributions [31], is shown. In figure 1b, the same enthalpies are plotted against another measure of molecular volume – characteristic volume V_x^A [32], which is also calculated using an additive scheme from atomic contributions. In both cases we observe a linear correlation. At the same time, alkanes do not follow this correlation: their enthalpies of solvation are less negative. The position of octane is marked with a triangle on both plots.

4.2. Gibbs free energy versus enthalpies of solvation for various solutes

In figure 2, the Gibbs free energies of solvation are plotted against the enthalpies of solvation of the same compounds in formamide. The graph also shows two lines that match the correlation between Gibbs energies and enthalpies of solvation of alkanes in non-associated solvents ($\Delta_{solv}G^{A/S} = 0.632\Delta_{solv}H^{A/S} + 15.6$, solid line) and a similar correlation for aromatic hydrocarbon solutes (dotted line). Deviations of data points from these lines in the direction of increased values of the Gibbs energies are due to the solvophobic effect.

4.3. Solvophobic effect in formamide

Thermodynamic functions of solvation can be represented as the sum of contributions of non-specific effects that corresponds to a "normal" behavior of solvent and the solvophobic effect:

$$\Delta_{solv}G^{A/S} = \Delta_{solv(nonsp)}G^{A/S} + \Delta_{s.e.}G^{A/S}; \tag{4}$$

$$\Delta_{solv}H^{A/S} = \Delta_{solv(nonsp)}H^{A/S} + \Delta_{s.e.}H^{A/S}.$$

For non-associated solvents that follow the above discussed linear Gibbs energy – enthalpy relationship, $\Delta_{s.e.}G^{A/S} = \Delta_{s.e.}H^{A/S} = 0$. In self-associated solvents, solvophobic effect may contribute to both the entropic and enthalpic components of the Gibbs free energy of solvation. In our previous paper [9], we assumed that for the alkanes in monohydric alcohols the solvophobic effect enthalpy is small and can be neglected, so we were able to find the value of $\Delta_{s.e.}G^{A/S}$ of alkanes directly from the Gibbs energy – enthalpy of solvation plot: it equals the deviation of a data point from the line for non-associated solvents. There are no reasons to make such an assumption for formamide solutions. It should be noted that for alcoholic solutions data points for alkanes and aromatic hydrocarbons on the Gibbs energy – enthalpy of solvation plot lie on one straight line with sufficient accuracy, which is not observed in formamide, as well as in aqueous solutions. In latter ones, the hydrophobic effect seems to have a different influence on the enthalpies of solvation of aliphatic and aromatic compounds.

In the previous studies [9,33], we have shown that the values of the Gibbs free energies of solvation in non-associated solvents and non-specific parts of the Gibbs free energy of solvation in alcohols

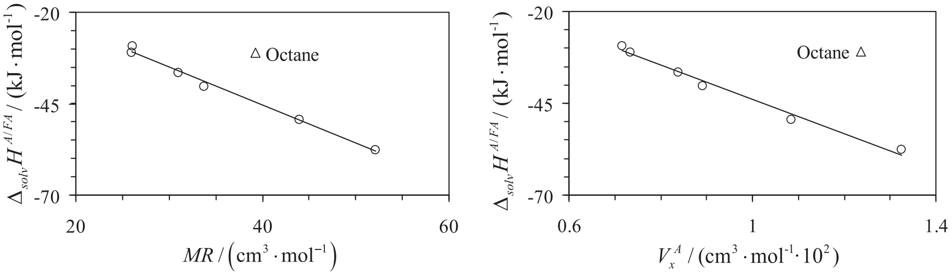

FIGURE 1. Correlation of enthalpies of solvation of non-alkylated aromatic hydrocarbons and their halogenated derivatives (benzene, fluorobenzene, chlorobenzene, bromobenzene, naphthalene, biphenyl, shown in circles) in formamide with (a) molar refractivity (b) characteristic molecular volume.

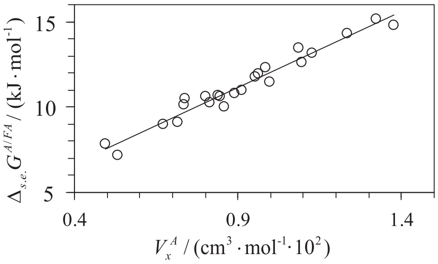

FIGURE 3. Correlation of the solvophobic effect Gibbs free energies in formamide with characteristic molecular volumes of solutes.

and water can be satisfactorily described using the following equation:

$$\Delta_{solv(nonsp)}G^{A/S} = \Delta_{solv}G^{A/S_0} + \left(\delta g^S - \delta g^{S_0}\right)^{1/2} \cdot V_x^A + \left[a + b\left(\delta g^S\right)\right] \cdot \left[\left(\Delta_{solv}G^{A/S_R} - \Delta_{solv}G^{A/S_0}\right) - \left(\delta g^{S_R} - \delta g^{S_0}\right) \cdot V_x^A\right]; \tag{5}$$

$$a = -\left(\delta g^{S_0}\right)^{1/2} \Big/ \left(\left(\delta g^{S_R}\right)^{1/2} - \left(\delta g^{S_0}\right)^{1/2}\right);$$

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

Here $\Delta_{solv}G^{A/S_0}$, $\Delta_{solv}G^{A/S_R}$ are the Gibbs free energies of solvation of solute *A* in the standard solvents S_0 and S_R, which should not form hydrogen bonds with the molecules of *A* (typically, S_0 is *n*-hexadecane and S_R can be, for example, benzene or dimethyl sulfoxide), and δg^S, δg^{S_R}, δg^{S_0} are solvent parameters reflecting nonspecific interactions of solvent molecules with other (solvent and solute) molecules.

Parameter δg^S is determined from the Gibbs energy of solvation of *n*-octane in solvent *S*, taking into account the Gibbs solvophobic effect energy $\Delta_{s.e.}G^{C_8H_{18}/S}$, if the solvent *S* is self-associated:

$$\delta g^S = \left(\Delta_{solv}G^{C_8H_{18}/S} - \Delta_{s.e.}G^{C_8H_{18}/S} - \Delta_{solv}G^{C_8H_{18}/C_{16}H_{34}}\right) \Big/ V_x^{C_8H_{18}} \tag{6}$$

(C_8H_{18} = *n*-octane, $C_{16}H_{34}$ = *n*-hexadecane).

TABLE 6

Enthalpies of the solvophobic effect in formamide and water at *T* = 298 K.

Solute	$\Delta_{s.e.}H^{A/FA}$/(kJ · mol^{-1})	$\Delta_{s.e.}H^{A/H_2O}$/(kJ · mol^{-1}) [27]
Hexane	−1.7	−9.4
Heptane	−1.7	−10.1
Octane	−0.5	−9.9
Cyclohexane	−0.6	−7.7
Benzene	2.3	1.3
Toluene	2.6	
Ethylbenzene	2.4	
Fluorobenzene	2.8	
Chlorobenzene	3.3	
Bromobenzene	3.6	
Naphthalene	7.4	8.2
Biphenyl	7.3	9.9
1,2-dichlorobenzene	4.6	

Using the above equations and some experimental data we can calculate the solvophobic effect contributions into the Gibbs free energies of solvation of different compounds, if only we know the value of δg^{FA} (FA = formamide). To find it using equation (6) one must make assumptions about the value of $\Delta_{s.e.}G^{C_8H_{18}/FA}$, which is difficult as mentioned above.

There were suggested many parameters describing the strength of various types of intermolecular interactions of solvent molecules with dissolved molecules. The Gibbs free energies of solvation of apolar solutes were correlated with various solvatochromic polarity scales [34,35]. The succession of solvents in many scales is similar, and our δg^S scale of solvent non-specific interactions power resembles the π^* polarity scale. The π^* value for hexadecane is about zero, as well as its δg^S value. Despite these two parameters are not directly correlated, we suggested that the ratio of π^* values for formamide (0.97) [36] and water (1.09), which equals 0.89, can be an estimate for the ratio of δg^S values for the same solvents. Since δg^S for water was found to be $5.75 \cdot 10^{-2}$ kJ · cm^{-3}, $\delta g^{FA} \approx 5.1 \cdot 10^{-2}$ kJ · cm^{-3}.

As mentioned above, the values of $\Delta_{s.e.}G^{A/S}$ for various solutes *A* in aqueous and alcoholic solutions have been shown [9,26] to correlate linearly with the characteristic volume of a solute molecule V_x^A. We calculated the values of $\Delta_{s.e.}G^{A/FA}$ using experimental Gibbs

TABLE 5

Gibbs free energies of the solvophobic effect in formamide at *T* = 298 K and thermodynamic data used in their calculation by equations (4) and (5).

Solute	V_x^A/(cm^3 · mol^{-1} · 10^2)	$\Delta_{solv}G^{A/FA}$/(kJ · mol^{-1})	$\Delta_{solv}G^{A/C_{16}H_{34}}$/(kJ · mol^{-1})[a]	$\Delta_{solv}G^{A/DMSO}$/(kJ · mol^{-1})[a]	$\Delta_{s.e.}G^{A/FA}$/(kJ · mol^{-1})
Propane	0.5313	16.7	5.0	13.0	7.2
Butane	0.6722	15.4	1.8	10.3	9.0
Pentane	0.8131	14.1	−1.3	8.3	10.3
Hexane	0.9540	13.7	−4.2	7.3	11.7
Heptane	1.0949	12.2	−7.1	5.5	12.6
Octane	1.2358	10.6	−10.0	2.5	14.3
Nonane	1.3767	9.0	−12.9	1.1	14.8
Cyclohexane	0.8454	10.3	−5.9	4.4	10.6
Methylcyclohexane	0.9863	10.0	−7.5	2.7	12.3
Ethylcyclohexane	1.1272	8.4	−10.5	0.9	13.1
Methylene chloride	0.4943	4.8	−0.5	−2.7	7.8
Carbon tetrachloride	0.7391	6.9	−5.1	−0.9	10.5
Hex-1-ene	0.9110	12.1	−3.7	5.8	11.0
Cyclohexene	0.8024	8.1	−6.2	1.4	10.6
Benzene	0.7164	4.7	−4.9	−2.1	9.1
Toluene	0.8573	2.8	−8.0	−4.4	10.0
Ethylbenzene	0.9982	2.3	−10.6	−5.6	11.5
Fluorobenzene	0.7341	4.3	−5.9	−3.7	10.1
Chlorobenzene	0.8388	1.0	−9.9	−7.1	10.7
Bromobenzene	0.8914	−1.3	−12.1	−9.5	10.8
1,2-dichlorobenzene	0.9612	−3.1	−14.8	−12.3	12.0
Naphthalene	1.0854	−6.9	−19.5	−17.6	13.4
Biphenyl	1.3242	−10.3	−23.3	−22.4	15.1

[a] Calculated from the data given in reference [37].

free energies of solvation in formamide (table 4 and reference [17]). We also obtained a linear correlation with V_x^A (figure 3):

$$\Delta_{s.e.}G^{A/FA}/(\mathrm{kJ}\cdot\mathrm{mol}^{-1}) = (8.88 \pm 0.44)V_x^A/(\mathrm{cm}^3\cdot\mathrm{mol}^{-1}\cdot 10^2) + (3.23 \pm 0.41) \quad (7)$$

$n = 23$, $\sigma = 0.43$ kJ · mol^{-1}, $R^2 = 0.9516$.

Calculated values of the Gibbs free energies of the solvophobic effect in formamide, as well as the data used in their calculation are given in table 5. The magnitude of δg^{FA} we used is, of course, approximate. However, changing it has relatively small effect on the values of solvophobic effect Gibbs free energies. If we change the value of δg^{FA} in a wide range from ($4.6 \cdot 10^{-2}$ to $5.6 \cdot 10^{-2}$) kJ · cm^{-3}, a linear correlation of $\Delta_{s.e.}G^{A/FA}$ with V_x^A holds, and its slope and intercept stay in the range of their uncertainties in equation (7) (0.44 and 0.41, respectively).

Now, if we plot the values of $\Delta_{solv(nonsp)}G^{A/FA}$ against the values of $\Delta_{solv}H^{A/FA}$, the deviations from the line will reflect the contribution of the solvophobic effect into the enthalpies of solvation. Obtained values of $\Delta_{s.e.}H^{A/S}$ are given in table 6. In another column of table 6, the values of the enthalpies of the hydrophobic effect in aqueous solutions [27] for the same compounds are given. These results show that in solutions of low-polar molecules in formamide we observe the same trends of thermodynamics of the solvophobic effect as in water: negative values for saturated hydrocarbons and positive for aromatic hydrocarbons. The absolute values are, however, smaller than in water, especially in the case of alkanes.

5. Conclusion

We reported a number of new experimental values of enthalpies of solution and limiting activity coefficients for low polar substances in formamide at temperature of 298 K, which is a step forward in the study of the thermodynamic properties of solutions in formamide.

Analysis of the obtained and existing literature data showed that the solvophobic effect in formamide and the hydrophobic effect in aqueous solutions have a similar influence on the thermodynamic functions of solvation. The Gibbs energies of solution of all solutes in both solvents are increased to the extent depending on solute volume. However, the hydrophobic effect causes a larger increase of the Gibbs energy, larger decrease in solubility of low-polar compounds and a stronger destabilization of the contact between an apolar surface and solvent, which leads, in particular, to lower values of surfactant CMCs in aqueous solutions than in formamide. The obtained quantitative parameters of the solvophobic effect in formamide can be used to assess the contributions of the Gibbs free energies of hydrogen bonding of various dissolved molecules with the bulk phase of formamide, as it was done previously for aqueous and alcoholic solutions [38,39].

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