



Standard molar Gibbs free energy and enthalpy of solvation of low polar solutes in formamide derivatives at 298 K



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ABSTRACT

Novel experimental values of the limiting activity coefficients and standard molar enthalpies of solution in *N*-methylformamide at 298.15 K are reported and used to calculate the thermodynamic functions of solvation. We compare the plots of the standard molar Gibbs free energy against the standard molar enthalpy of solvation of low polar molecules in *N*-methylformamide, *N,N*-dimethylformamide, and formamide. The solvophobic effect is responsible for the deviations of the data points from the straight line corresponding to a correlation between thermodynamic functions of solvation in aprotic solvents. It is shown that the solvophobic effects are strong in formamide solutions, significantly weaker in *N*-methylformamide, and very weak in *N,N*-dimethylformamide, which coincides with the average number of intermolecular hydrogen bonds per unit volume of these solvents. Behavior of solutions in binary solvents composed of *N*-methylformamide or formamide mixed with water and ethylene glycol and a possibility to tune the solvophobic effect by changing the solvent composition are also considered.

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1. Introduction

Formamide (HCONH_2 , FA), *N*-methylformamide (HCONHCH_3 , NMF) and *N,N*-dimethylformamide ($\text{HCON}(\text{CH}_3)_2$, DMF) are highly polar solvents which have numerous practical applications. They are different by the hydrogen bonding ability and the liquid phase structure [1]. FA has one hydrogen bond accepting site (oxygen atom) and two acidic hydrogens. It forms a branched network of the hydrogen bonds consisting of cyclic dimers and linear chains [2,3]. There is an evidence that at least at high pressure C–H...O contacts play an important role in the structure of FA [4]. NMF has only one acidic hydrogen and the linear chain associates predominate in its liquid phase, as confirmed by means of neutron diffraction and EPSR and Monte Carlo simulations [5]. DMF has no sufficiently acidic hydrogen atoms and consists primarily of monomers, however, some authors prove the existence of weak C–H...O hydrogen bonds [6,7]. At the same time, strong dipole-dipole interactions in DMF lead to orientational ordering of the liquid phase [8].

Intermolecular hydrogen bonds have a strong influence on solvation properties. This influence is expressed in elevated values of the excess Gibbs free energy of dissolved apolar molecules,

decreased excess entropies and violation of the linear correlations between the standard entropy and enthalpy or between the standard Gibbs free energy and enthalpy of solvation that are typical for aprotic solvents [9,10]. Such behavior of hydrogen-bonded liquids is attributed to the so-called solvophobic effect. Due to these effects amide solvents are known to support amphiphile self-assembly [11]. We have previously studied the thermodynamic functions of solvation for a set of low polar compounds in FA [12] and concluded that the strong solvophobic effect affects both the entropy and enthalpy of solvation in this solvent. There was also an attempt to study the solvophobic effects in amides by comparison of the pressure derivatives of the second virial coefficients, but such method requires very precise and difficult to obtain experimental data [13].

In the present work, we experimentally determine the thermodynamic functions of solvation in NMF and compare them with those for solutions in FA and DMF. Thermodynamics of solvation in DMF has been studied rather extensively. Gas-DMF partition coefficients at 298 K for about 170 different solutes [14] and the enthalpies of solvation at 298 K for 159 solutes [15] were reported. For NMF, some data on gas-liquid partition were also obtained [14], but the calorimetric data are not available except for a few compounds at conditions far from infinite dilution and/or not at 298 K [16,17]. In this work we also determine the solvation properties of the mixtures of NMF and FA with two other hydrogen bonded

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liquids—ethylene glycol (EG) and water in order to understand how these properties change with the composition of a solvent mixture.

2. Experimental

2.1. Chemicals

N-methylformamide and formamide with purity grade >0.99 were purchased from Sigma-Aldrich. Ethylene glycol with purity 0.995 was from Acros Organics. All solutes were purchased from Sigma-Aldrich, Fluka, and Acros (purity >0.99). Their purity was confirmed in gas chromatographic experiments by the absence of peaks with the area more than 0.5% of the peak of the main substance in all the cases. All chemicals were used without further purification. Absence of significant amounts of water was checked by Karl Fisher titration [18] (Table 1).

2.2. Equipment and procedures

Limiting activity coefficients γ_∞ were determined using gas chromatographic headspace analysis as described in our previous papers [19,20]. The standard molar Gibbs free energy of solvation $\Delta_{\text{solv}}G^\circ$ was calculated using a formula

$$\Delta_{\text{solv}}G^\circ = RT \ln \left(\frac{\gamma_\infty p_{\text{solute}}}{p^\circ} \right) \quad (1)$$

where p_{solute} is the saturated vapor pressure of a solute, p° is the standard state pressure (1.00×10^5 Pa). The standard state for solutions is molar fractions-based. The standard state for the solutes are pure solutes in their most stable form, which is liquid for all the studied substances except naphthalene, for which the standard state is its solid state. The values of p_{solute} were taken from literature [21,22]. Obtained results are presented in Tables 2–3 along with the standard uncertainties $u(\gamma_\infty)$. For several aromatic solutes, the limiting activity coefficients were previously reported in literature [23] at temperatures 303.15–333.15 K, which allows to estimate the values at 298.15 K by extrapolation (fifth column of Table 2). We

have measured the values of γ_∞ directly at 298.15 K and found them in agreement with the results of extrapolation. In addition, several saturated hydrocarbons were studied previously at 298.15 K [24]. These results are smaller than our values (by 3–9%). At the same time, extrapolation to 298.15 K of the data from [23] for alkane solutes will lead to the value closer to our one in the case of *n*-heptane, but not in the case of *n*-hexane and *n*-octane.

Enthalpies of solution at infinite dilution at temperature $T=298.15$ K and pressure $p=0.1$ MPa have been determined using an isoperibolic solution calorimeter. The experimental procedures were essentially similar to those in our previous works [12,27]. For liquid solutes, semi-adiabatic titration method was used. The calorimetric vessel was filled with a solvent and thermostated for 90–120 min. Heater calibrations were done to determine the calorimeter constant, then 50–100 μl of solute was added from an electronically operated microsyringe in 5–15 μl portions. The experiments were repeated 2–3 times with a new portion of solvent for each solute. Naphthalene, the only solid solute, was placed in sealed glass ampoules, which were then broken inside a calorimetric vessel (the same one used for titration experiments) with the solvent. This experiment was repeated 4 times.

The heat effect was determined from a calorimetric curve for each addition of a solute, and all the values were averaged to give the observed enthalpy of solution ΔH_{obs} . ΔH_{obs} is equal to the sum of heat effects of dissolution and evaporation of a part of solute into a free space of a calorimetric cell:

$$\Delta H_{\text{obs}} = (1 - \varphi)\Delta_{\text{soln}}H^\circ + \varphi\Delta_{\text{vap}}H^\circ \quad (2)$$

where $\Delta_{\text{soln}}H^\circ$ is the standard molar enthalpy of solution, $\Delta_{\text{vap}}H^\circ$ is the standard molar enthalpy of vaporization of a solute at 298.15 K, φ is the molar fraction of solute in the vapor phase that can be calculated by equation

$$\varphi = \frac{1}{(1 + RT\nu_S / (p_{\text{solute}}\gamma_\infty V_{\text{free}}))} \quad (3)$$

here V_{free} is the volume of the free space in the calorimetric vessel, ν_S is the number of moles of solvent in the vessel. The

Table 1
Source and purity of the chemicals.

Chemical name	CAS number	MW	Source	Mass fraction purity stated by supplier	Mass fraction of water measured by authors
Formamide	75-12-7	45.04	Sigma-Aldrich	0.99	0.00107
<i>N</i> -Methylformamide	123-39-7	59.07	Sigma-Aldrich	0.99	0.00079
Ethylene glycol	107-21-1	62.07	Acros Organics	0.995	0.00121
<i>n</i> -Hexane	110-54-3	86.18	Sigma-Aldrich	0.99	0.00012
<i>n</i> -Heptane	142-82-5	100.20	Acros Organics	0.99	0.00011
<i>n</i> -Octane	111-65-9	114.23	Sigma-Aldrich	0.99	0.00023
<i>n</i> -Nonane	111-84-2	128.26	Acros Organics	0.99	0.00015
<i>n</i> -Decane	124-18-5	142.28	Acros Organics	0.99	0.00011
<i>n</i> -Undecane	1120-21-4	156.31	Acros Organics	0.99	0.00023
Cyclohexane	110-82-7	84.16	Acros Organics	0.995	0.00044
Cyclooctane	292-64-8	112.21	Sigma-Aldrich	0.99	0.00025
Cyclohexene	110-83-8	82.14	Acros Organics	0.99	0.00047
1,7-Octadiene	3710-30-3	110.20	Acros Organics	0.99	0.00060
(<i>RS</i>)-4-vinyl-1-cyclohexene	100-40-3	108.18	Fluka	0.995	0.00038
Benzene	71-43-2	78.11	Sigma-Aldrich	0.99	0.00043
Toluene	108-88-3	92.14	Sigma-Aldrich	0.998	0.00013
Ethylbenzene	100-41-4	106.17	Fluka	0.99	0.00050
<i>o</i> -Xylene	95-47-6	106.17	Sigma-Aldrich	0.99	0.00040
<i>m</i> -Xylene	108-38-3	106.17	Sigma-Aldrich	0.99	0.00031
<i>p</i> -Xylene	106-42-3	106.17	Sigma-Aldrich	0.99	0.00044
<i>p</i> -Cymene	99-87-6	134.22	Acros Organics	0.99	0.00030
Fluorobenzene	462-06-6	96.10	Acros Organics	0.99	0.00052
Chlorobenzene	108-90-7	112.56	Acros Organics	0.996	0.00047
Bromobenzene	108-86-1	157.01	Acros Organics	0.99	0.00061
Naphthalene	91-20-3	128.17	Acros Organics	0.99	–
Water	7732-18-5	18.02	deionized, Millipore	–	–

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