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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.

1. Introduction

Formamide ($HCONH_2$, FA), *N*-methylformamide ($HCONHCH_3$, NMF) and *N*,*N*-dimethylformamide ($HCON(CH_3)_2$, 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 ofdissolved 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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