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Enthalpies of solution and enthalpies of solvation of organic solutes in ethylene glycol at 298.15 K: Prediction and analysis of intermolecular interaction contributions

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ABSTRACT

Ethylene glycol is one of the most usually used liquid media for realization of different industrial processes. In present work thermochemistry of solvation of inert gases and organic solutes in ethylene glycol was thoroughly studied using solution calorimetry technique. Enthalpies of solution of 28 organic solutes in ethylene glycol were measured for the first time. Acree and Abraham multi-parameter correlations were successfully applied for description of enthalpies of solvation of number of inert gases and organic compounds in ethylene glycol calculated on the basis of experimental and literature data. Enthalpies of solute-ethylene glycol hydrogen bonding for some ketones, esters, ethers, nitriles, monoatomic aliphatic alcohols, amines and etc. were determined. Linear correlation between enthalpies of solute-ethylene glycol and solute-methanol hydrogen bonding was observed.

1. Introduction

Ethylene glycol (ethanediol-1,2) is an organic compound which is widely used in industry. Ethylene glycol and its mixtures with water can be utilized as antifreeze, heat transfer agent or as a medium for micelle formation processes [1,2]. As to chemical synthesis, ethylene glycol is a precursor to polyester fibers and resins. Besides, ethylene glycol is used as a thermodynamic inhibitor of natural gas hydrates formation in pipelines [3].

Most of physical and chemical properties of ethylene glycol are attributed to intermolecular hydrogen bonds in bulk phase. As well as water, ethylene glycol molecules are capable of formation of spatial network of intermolecular H—O···H hydrogen bonds [4], which is one of reasons of poor solubility of non-polar solutes in ethylene glycol media. Relatively high viscosity causes additional obstacles to solubility measurements. Therefore, solvation processes in ethylene glycol are studied insufficiently full.

The aim of present work is examination of enthalpies of transfer of solute molecule from gas phase to infinitely diluted solution in ethylene glycol (solvation process). Enthalpies of solvation provide valuable information about solute-solvent intermolecular interactions. As an example, solvation enthalpies values are used to assess solvent influence on reaction kinetics and equilibria [5–7].

Since experimental measurement of solvation enthalpies in ethylene glycol is difficult for some solutes, a predictive solvation correlation should be ascertained. A multi-parameter correlations between solvation enthalpies and several solute properties were proposed earlier by Abraham et al. [8]. To date such correlations are available for number of solvents [8–27] including self-associated solvents: water [8], monoatomic aliphatic alcohols [8,15,16,18,19,23], acetic acid [26] and formamide [25]. Abraham multi-parameter correlations for enthalpy of solvation of noble gases and organic solutes are expressed by following equations:

$$\Delta_{solv}H^{A/EG} = c_{h,l} + e_{h,l} \cdot E + s_{h,l} \cdot S + a_{h,l} \cdot A + b_{h,l} \cdot B + l_{h,l} \cdot L \quad (1)$$

$$\Delta_{solv}H^{A/EG} = c_{h,v} + e_{h,v} \cdot E + s_{h,v} \cdot S + a_{h,v} \cdot A + b_{h,v} \cdot B + v_{h,v} \cdot V \quad (2)$$

Solute descriptors in Eqs. (1) and (2) represent ability of solute molecule to interact with solvent molecules in bulk liquid media. E descriptor refers to the excess molar refraction of solute; S is a dipolarity/polarizability solute parameter; A and B represent over-

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