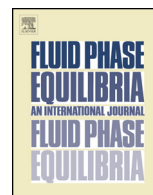




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ABSTRACT

Relationships between the Gibbs free energy and enthalpy of solvation of *tert*-butyl chloride in various protic solvents are considered in order to compare the strength of the solvophobic effects from solvent to solvent. The values of thermodynamic functions of solvation are determined experimentally using titration calorimetry and gas chromatographic headspace analysis techniques. Positions of the data points on the ΔG vs ΔH plot indicate that the solvophobic effects take place in various mono- and dihydric alcohols, acetic acid, and acid amides. The excess positive contribution into free energy of solvation of *tert*-butyl chloride in self-associated solvents is used to characterize their strength quantitatively. It is shown that the solvophobic effects are stronger when the concentration of the hydrogen bonds in a solvent is larger.

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1. Introduction

The solvophobic effects is a term used to describe a more general phenomenon than the hydrophobic effect in water. These effects take place in various solvents, the molecules of which can form hydrogen bonds with each other. Examples of such solvents are polyhydric and monohydric alcohols, formamide, hydrazine etc. The typical manifestations of the solvophobic effects are low solubility of apolar solutes, low entropy and large heat capacity change upon dissolution, micellization of amphiphilic compounds.

In our earlier works [1–4], we investigated the impact of these effects on the thermodynamic functions of solvation in various solvents. We have shown that the relationship of magnitudes of the Gibbs free energy and enthalpy of solvation is useful for qualitative identification and quantitative description of the solvophobic effects. Experimental values of thermodynamic functions are necessary for such analysis. Since, alkanes are the least polar organic molecules and cannot form hydrogen bonds with other species, we have studied them in the first place. However, it is very difficult to measure accurately the enthalpies of solution and activity coefficients of alkanes in many of self-associated solvents due to their poor solubility. Short chain alkanes are better soluble, but at the same time they are more volatile, which also leads to huge uncertainties of calorimetric experiments.

Monohalogenated alkanes are also low polar compounds that are not likely to form hydrogen bonds, but have significantly lower volatility than alkanes and therefore are more convenient to study calorimetrically. Thus, in the present work we decided to consider the relationship between the Gibbs free energy and enthalpy of solvation of a haloalkane in order to judge about the relative strength of the solvophobic effects in various solvents. We have chosen 2-chloro-2-methylpropane (*tert*-butyl chloride) as a probe of the solvophobic effect because of greater stability of chlorinated compounds in comparison with brominated and especially iodinated, low number of carbons in a molecule, and availability of experimental calorimetric data for this particular solute in a number of solvents. *tert*-Butyl chloride is a model compound to study the nucleophilic substitution reactions. The influence of solvent on their rate was a subject of several studies [5–7], for which the values of excess thermodynamic functions in dilute solutions were determined. The enthalpies of solution of *tert*-butyl chloride have been reported in the works of Albuquerque et al. [8] along with several other monohalogenated hydrocarbons (2-bromo-2-methylpropane, 2-chloro-2-methylbutane, and 3-chloro-3-methylpentane) in mono- and dihydric aliphatic alcohols. We compare their values with our own experimental data for the same systems.

2. Experimental

tert-Butyl chloride was distilled over P_2O_5 according to the recommendations given in [9]. Methanol, ethanol, propane-2-ol and hydrocarbons were purified by standard methods [9].

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