



# Thermodynamic description of the solvophobic effect in ionic liquids



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## ABSTRACT

The solvophobic effect is a driving force for self-assembly processes that acts in protic molecular organic solvents as well as in both protic and aprotic ionic liquids. It is known to reduce the solubility of apolar compounds and influence the magnitudes of thermodynamic functions of solvation in molecular solvents. In ionic liquids, thermodynamic aspects of the solvophobic effects have not yet been carefully considered. By comparing the relations between the Gibbs free energy and enthalpy of solvation of different compounds, we show that the solvophobic effect in aprotic ionic liquids can be even stronger than in organic solvents forming a network of intermolecular hydrogen bonds, such as formamide and ethylene glycol. The strength of the solvophobic effect expressed in terms of energy contributions is correlated with the average number of ions per unit volume, which is inversely proportional to the molar volume of the liquid. It is shown that the solvophobic effects become stronger when we change the cation or anion of the ionic liquid with another of a smaller size, and can be extremely weak when the cation contains long alkyl chains, but they are a general phenomenon for all ionic liquids.

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## 1. Introduction

The solvophobic effects in ionic liquids have recently attracted attention of researchers [1,2]. Like in molecular solvents, the solvophobic effects support self-assembly of amphiphilic compounds into micelles, vesicles, bilayers, and microemulsions. It was shown that such processes can also go in many different ionic liquids [3,4].

Ionic liquids as self-assembly media are interesting from the practical point of view. They can be used for the synthesis of nanostructures in a non-aqueous environment. The properties of ionic liquids can be tuned by variation of the cation or anion. This may allow to change the properties of synthesized objects, rates and selectivities of the chemical processes.

In syntheses through supramolecular self-assembly, we need to control the strength of the solvophobic effect by choosing one or another ionic liquid or their mixture. It is important to understand how it depends on the nature of the cation and anion of the ionic liquid.

A number of approaches have been suggested to measure or compare the power of solvophobic effects in non-ionic solvents. The comparison can be made either by direct observation of solvophobic-driven processes, such as micelle formation or

recently reported [5] solvent-induced conformational changes of synthetic molecular balances, or through introduction of a scale of the solvent parameters reflecting the strength of these effects. In particular, Gordon parameter [4,6] and cohesive energy density [5,7] were suggested to be the quantitative solvent descriptors of the solvophobic effect.

The solvophobic effects in such solvents as glycerol, formamide, ethylene glycol or water lead to remarkable patterns in thermodynamic functions of solvation [8–10]. High values of the Gibbs free energies of solvation of apolar molecules in these solvents are responsible for their low solubility, and the entropies of solvation are lower than in other solvents.

In many of the ionic liquids, hydrocarbons and especially alkanes are also poorly soluble. In the present work, we focus on thermodynamic aspects of the solvophobic effects in ionic liquids. Thermodynamic properties of solutions of various compounds in ionic liquids are a subject of a large and growing number of experimental studies right now. Applications have been proposed for ionic liquids in extraction, extractive distillation and separation processes. The knowledge of gas-liquid distribution properties like activity coefficients is valuable in the calculation of vapor/liquid equilibria for reaction or separation systems. The liquids with the strong solvophobic effect exhibit a good selectivity in alkane/alkene and alkane/aromatic hydrocarbon separations. From a more fundamental perspective, these data provide a reliable way to study the intermolecular interactions involved in the process of solvation.

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