



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.

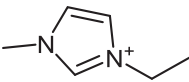

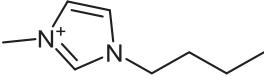
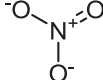
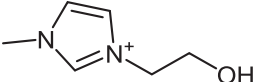
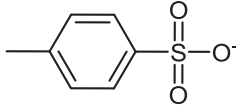
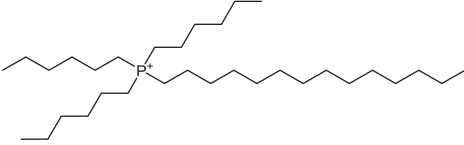
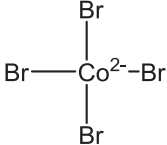
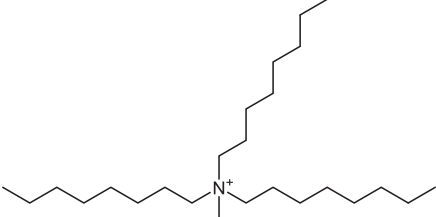
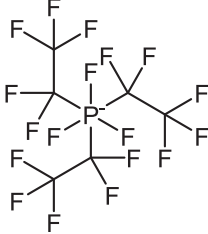
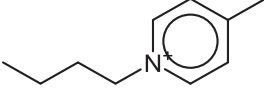
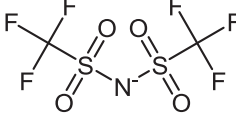
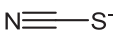

The solvophobic effects in such solvents as glycerol, formamide, ethylene glycol or water lead to remarkable patterns in thermodynamic functions of solvation [8–10]. High values of the Gibbs free energies of solvation of apolar molecules in these solvents are responsible for their low solubility, and 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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Table 1
The structures of some cations and anions constituting ionic liquids mentioned in the text.

Cation abbreviations	Cation structures	Anion abbreviations	Anion structures
[EMIM]		[BF ₄]	
[BMIM]		[NO ₃]	
[OH-C ₂ MIM]		[TOS]	
[P _{6,6,6,14}]		[CoBr ₄]	
[N _{1,8,8,8}]		[(C ₂ F ₅) ₃ PF ₃]	
[BMPY]		[NTf ₂]	
		[SCN]	
		[Cl]	

2. Methodology

In our previous works [8–11], we have analyzed the influence of the solvophobic effects on the thermodynamic functions of solvation from the gas phase into various non-ionic organic solvents. We used the Gibbs free energy of solvation $\Delta_{solv}G$ versus enthalpy of solvation $\Delta_{solv}H$ plots at a single (298 K) temperature as a tool to judge about the presence of the solvophobic effect and to estimate its relative strength. The data points for low polar solutes dissolved in many apolar and aprotic polar non-ionic solvents fall on the same straight line, while in protic solvents forming intermolecular hydrogen bonds the solvophobic effect causes the deviations of data points from this line. The equation of the mentioned line is $\Delta_{solv}G/(\text{kJ mol}^{-1}) = 0.632\Delta_{solv}H/(\text{kJ mol}^{-1}) + 15.6$ (1) if we average only the data for alkane solutes or $\Delta_{solv}G/(\text{kJ mol}^{-1}) = 0.627\Delta_{solv}H/(\text{kJ mol}^{-1}) + 16.3$ (2) if we average the data for different classes of organic compounds. In other words, in aprotic solvents the value of $\Delta_{solv}G$ can be high due to unfavorable van der Waals interactions, but the value of $\Delta_{solv}H$ will also be high according to the correlation (1). This correlation has some relation to the enthalpy-entropy compensation phenomena, and the values of $\Delta_{solv}S$ are also correlated with $\Delta_{solv}H$. However, the entropy cannot be directly measured experimentally, and its values are influenced by the

uncertainties of both Gibbs free energy and enthalpy. To reduce the influence of the errors, we always consider G-H plots and not S-H plots.

In self-associated protic solvents, the values of $\Delta_{solv}G$ are higher than could be expected from the values of $\Delta_{solv}H$ using the same equation (1). The magnitude of deviations $\Delta/(\text{kJ}\cdot\text{mol}^{-1}) = \Delta_{solv}G/(\text{kJ}\cdot\text{mol}^{-1}) - 0.632\Delta_{solv}H/(\text{kJ}\cdot\text{mol}^{-1}) - 15.6$ (3) decreases in a row water > glycerol > formamide, ethylene glycol > monohydric alcohols and can be considered as a measure of the relative strength of the solvophobic effect in various solvents. The values of Δ for a single solute in different solvents is usually growing up with the number of hydrogen bonds per unit volume of a solvent [12], evidencing the crucial role of solvent-solvent hydrogen bonding in the solvophobicity phenomenon.

Now we extend our consideration to ionic liquids on the basis of the reported experimental values of thermodynamic functions of solvation. In contrast with molecular solvents, self-assembly of amphiphiles and low solubility of apolar molecules are typical for both protic and aprotic ionic liquids. In aprotic ionic liquids, there are no intermolecular hydrogen bonds between ions. It is reasonable to suggest that Coulomb interactions between the ions that are disturbed by the solutes cause the solvophobic effects in that case.

A large amount of experimental values of limiting activity

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