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# Self Assembly of Ionic Liquids at the Air/Water Interface

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## Abstract

Due to its special properties, the air/water interface is of interest in chemistry, physics and biology. Understanding phenomena at the interface is a challenging subject in both experimental and theoretical research. The behavior of ions at the air/water interface is of special interest since it is relevant for many surface chemical reactions. Ionic liquids are liquid organic salts that are generally composed of a bulky hydrophobic cationic partner and a smaller but generally multi-atomic and more hydrophilic anionic partner. The propensity of the constituent hydrophobic and hydrophilic ions of ionic liquids for the air/water interface raises many questions regarding the self-assembly of these ions and their interactions with water molecules. How do these ions interact with water? How do hydrogen-bonding networks of water change when ions have strong propensity to the surface? Are water-anion interactions stronger than water-cation or water-water interactions? How are those interactions affected at different concentrations of ionic liquids? How does the nature of these cations and anions influence surface properties and orientation of ions at the interface? How do ionic liquids make self-assemblies at the interface, and which are the dominant forces for this process? This minireview aims to answer these questions.

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## 1 Introduction

Ionic liquids are liquid organic salts composed of a bulky hydrophobic cationic partner and a smaller but generally multi-atomic anionic partner. Their large, asymmetric organic cations are generally quite flexible. This extreme conformational flexibility contributes to small lattice enthalpies and high entropies that favor the liquid state [1].

Due to their unique properties, ionic liquids are an attractive focus for research and industrial applications. The physical and chemical properties of ionic liquids, such as thermal stability, low vapor pressure at room temperature and phase change characteristics are of special interest [2]. Ionic liquids are used for many applications, such as electrochemical applications and electrochemical devices [3], catalysis [4], and task-specific applications [5]. The high hydrophobicity of the cationic components of ionic liquids confers unusual properties to the solutions of these compounds in water, leading to special applications in protein science, such as protein crystallization and protein extraction [6–17].

Hydrophobic ionic liquids strongly aggregate at the air/water interface. Hydrophobicity of ionic liquids can be increased by increasing the length of alkyl chain in which the alkyl chain – alkyl chain interactions is the key factor for aggregation at the air/water interface.

One of the key issues that will be discussed in this mini-review is the aggregation and self assembly of ionic liquids at the air/water interface for further applications in the areas of nanoparticles, protein stabilization, protein crystallization and colloid chemistry. As the interactions of cations and anions in pure and aqueous solutions of ionic liquids are important to understand their physicochemical properties thus first ion – ion interaction will be addressed then water – ions interactions will be discussed.

## 2 Ion – Ion Interactions in Ionic Liquids

To understand the physical and chemical properties (i.e., thermal stability, low vapor pressure and phase change characteristics) and transport properties (i.e., viscosity, ionic conductivity and diffusion coefficient) of ionic liquids we need to identify the structure and dynamics of ions in ionic liquids. At the molecular level, this will unveil liquid structures of the ionic liquid and

interactions among the ions. Vibrational spectroscopy and molecular dynamics simulations are suitable tools to study the molecular structure of ionic liquid and their interactions in the liquid phase. The nature and strength of the interactions in ionic liquids help to describe physicochemical properties. Knowing the interactions in ILs can bring new insights designing future task specific for ionic liquids.

Since ionic liquids consist of cations and anions thus electrostatic interaction is dominated by cations and anions. Due to their low melting points, however, it is logical to suggest that not only Coulomb force are important but also weak interactions such as hydrogen bonding and dispersion interactions. The nature of weak, non-covalent interactions between cations and anions is key in describing the physicochemical properties of pure and solutions of ionic liquids in molecular liquids.

Dong and co-workers by means of density functional theory (DFT) investigated the weak interactions such as hydrogen bonding in ionic liquids [19–22]. They have used 1, 3-dialkylimidazolium based ionic liquids with different counter ions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$  and  $\text{PF}_6^-$ . They revealed the nature of hydrogen bonds between cations and anions with particular geometric, energetic, electronic, and dynamic features which are different than conventional hydrogen bond [23].

Recently, Idrissi and co-workers, by means of quantum chemical calculations, quantitatively investigated non-covalent interactions and they found strong hydrogen bonding between 1-butyl-3-methylimidazolium cations with different anions such as tetrafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, and bis (trifluoromethanesulfonyl) imide [24]. Umebayashi and co-workers revealed the closest ion–ion interaction in the ionic liquid by means of large angle X-ray scattering experiment and classical molecular dynamics (MD) simulations using the liquid structure of 1-ethyl-3-methylimidazolium tetrafluoroborate. Given the orientation of an anion around a cation, Umebayashi and co-worker found that the conformational changes upon ion–ion interactions in the ionic liquid depends on the conformational isomerism of the cation [25].

In another study, Umebayashi and co-worker observed nano-scale segregation of ionic liquid in liquid state using pure ethylammonium nitrate. They stated that the  $\text{C}(\text{C}_2\text{H}_5\text{NH}_3^+) \dots \text{O}(\text{NO}_3^-)$  interaction, which shows a peak at 3.4 Å, plays an important role in macroscopic properties of ionic liquids [26]. Due to the increasing importance of electrolyte content in lithium batteries, Umebayashi and co-workers also studied the solvation structure of many different ionic liquids in order to reveal the

liquids structure with [27–32] and without lithium ions [33–36]. For bis (trifluoromethanesulfonyl) amide [TFSA]<sup>−</sup> based ionic liquids composed of 1-ethyl-3- methylimidazolium and N-methyl-N-propylpyrrolidinium they found that the nearest neighboring cation-anion interaction in the imidazolium ionic liquid is slightly greater than in propylpyrrolidinium ionic liquids while solvation of Li<sup>+</sup> ion shows the cluster formations of [Li(TFSA)<sub>2</sub>]<sup>+</sup>. Also Watanab et al. investigated the solvation of lithium ion in oligo (ethylene glycol) dimethyl ethers as a model of polyethyleneoxide based polymer as potential electrolytes for lithium ion batteries. In the glyme–Li mixtures by measuring electrode potential of Li/Li<sup>+</sup> in different concentrations they found that at higher concentration of Li salt, the amount of free glyme affects the electrode reaction which lead to a drastic increase in the electrode potential and higher solvation of Li<sup>+</sup> ion [37]. This phenomena may have higher impact on the reactions at the electrode surface for lithium batteries which can improve the performance of such batteries. Moreover, they studied the effect of the solvent on the properties of complex and found that ion–dipole interactions and the chelate effect in the solutions are very important [38].

### 3 Ion – Water Interactions in Ionic Liquids

An interesting property of ionic liquids is their ability to solvate water which make them hygroscopic solvents a small amount of water can dramatically influence physical and chemical properties of them [39].

The presence of water can change the chemistry of some ionic liquids and they can be hydrolyzed. Water can also change the physical and electrochemical properties of ionic liquids, such as density, viscosity, surface tension and electrochemical window [40–43].

Both X-ray reflectometry and MD simulations showed the effect of water on the surface structure of 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonylimide in which a significant amount of water is adsorbed at the surface. MD simulations and X-ray reflectometry also showed special orientation of the butyl chain of cation at the surface [44].

Adding ionic liquids to water can decrease the surface tension as explained by applying Gibbs adsorption isotherm [45–47]. According to this theory increase of the surface tension by adding ions to the solution is related to the depletion of ions from the interfacial layer while the accumulation or surface propensity of ions to the air/solution interface decreases the surface tension of solution. Using MD simulations, Jungwirth et al. showed that small

non-polarizable are repelled from the surface while big polarizable ions show propensity to the air/electrolyte solution interface [48, 49].

Polarizable ions, such as bromide and iodide, have strong propensity to the air/water interface in which by increasing the polarizability the electrical field increases where the increase is nonlinear. Polarizability affects the water molecules in the first solvation shell. This effect causes the solvation shell to shrink at higher polarizability [50] which was introduced by Perera et al. in small clusters of chloride ion with 20 water molecules [51].

The driving force which causes ions to have propensity to the air/water interface differ from ions and molecules that have hydrophobic groups such as tetra-butyl ammonium ion in aqueous solution of tetra-butyl ammonium iodide. Using aqueous solution of tetrabutyl ammonium fluoride and iodide, Vrbka et al. showed that by applying polarizability, halides ions had different propensity to the air/water interface. Large iodide ions with high polarizability had strong surface propensity, while small, non-polarizable fluoride ions did not show any propensity to the air/water interface. The polarizability did not influence the propensity to the air/water interface for tetrabutyl ammonium cations as the most important driving force is hydrophobic forces [52].

Ions containing carboxylate group have been used as an anion in ionic liquids. Hydrophobic groups, such as  $\text{CH}_3$  in acetate ion, can show strong propensity to the air/water interface [53]. It has been shown that acetate ion in magnesium acetate aqueous solutions has propensity to the air/solution interface and it makes contact ion pair with magnesium ion [54].

Since hydrophobic forces are the most important force on solvation of surfactants at the air/water interface we observed, using MD simulations, that the presence of methyl groups on benzene dicarboxylate dianion causes a strong surfactant activity at the air/water interface. The three isomers, however, showed no surface propensity neither by non-polarizable nor polarizable force fields. Also benzene dicarboxylate dianion at the water/vapor interface have preferential orientation by the charged carboxylic groups anchored to the aqueous phase and the hydrophobic benzene ring and methyl groups pointing out from the solution interface towards the vapor phase [55].

The addition of salt to an aqueous solution of surfactant can increase the surface propensity of surfactants. Petrov et al. studied the addition of potassium halide salt to the aqueous solution of ionic and zwitterion surfactants by means of MD simulations and infrared-visible sum frequency generation (IR-vis SFG). They revealed that adding KF had a small effect on the surface propensity to the interface to both for ionic and zwitterion surfactants. Adding

KBr, however, had a strong effect on the interface since bromide ions have a strong affinity to the interface [56].

In the case of ionic liquids, there are strong electrostatic interactions between cations and anions and causes surface polarization, which can be changed by water molecules. Water molecules not only dramatically influence the surface properties of ionic liquids but also alter the bulk properties of solutions. Thus, addition of ionic liquids to water can influence both bulk and interfacial properties of aqueous solutions of ionic liquids. Many experimental and theoretical studies have been done in order to reveal the bulk and surface properties of pure and aqueous solution of ionic liquids [57–68]. Due to the hygroscopic property of ILs a small amount of water can be found that can influence the surface, interfacial and bulk properties of them [69–74].

The interfacial properties of ILs water mixture was investigated by Bowers and co-workers to identify the role of alkyl chain length and anion on the aggregation in aqueous solutions by using experimental techniques such as surface tension, conductivity, and small-angle neutron scattering [75]. Aggregation and strongly structured ionic liquids at the water surface make the surface tension of aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF<sub>4</sub>] anomalously with bulk concentration of ionic liquid [67]. We investigated the interfacial structure of aqueous solutions of [BMIM][BF<sub>4</sub>] at different concentrations to understand the anomalous dependence of the surface tension. We observed that the anomalous dependence of the surface tension is related to the surface propensity of cations to the air/water interface at low concentrations until saturation and after that increase of cations in bulk observed. This causes the moderate increase of surface tension according to the Gibbs adsorption isotherm. Moreover, MD simulations revealed that the adsorbed cations at the air/water interface have favored structures in which the hydrophobic butyl chains, pointing towards the air, and methylimidazolium ring are solvated in the aqueous phase [47].

These findings are also supported by sum frequency generation spectroscopy measurements performed by Baldelli et al.. The SFG measurements showed that the cation was oriented with the imidazolium ring parallel to the surface plane with a tilt angle  $\geq 70^\circ$  for pure ionic liquid and no noticeable change occurred by increasing the water concentration. They also showed that the butyl chain is pointing out towards the gas phase with a methyl group tilt angle of  $54 \pm 2^\circ$  for pure ionic liquid and for a mixture this angle becomes  $46 \pm 4^\circ$  [60].

In order to understand the interaction of water with cations and anions of ILs, quantum chemical calculations at the density functional theory (DFT) have been done for a series of hydrophobic and hydrophilic ionic liquids. Wang and co-workers revealed that anions have stronger interaction with water than cations and the ion-pair water interaction is the weakest interaction in the interaction of ionic liquids with water [61].

Wipff and co-workers have studied the interface of imidazolium based ionic liquids with different length of alkyl chain by employing an all-atom force field with a reduced electrostatic interaction of ions. They revealed that the orientation of the alkyl chain is related to the length of alkyl chain in which the octyl chain preferentially oriented towards the gas phase whereas butyl chain has no preferential orientation at water ionic liquid interface [59, 76].

When hydrophobic ions of ionic liquids or surfactants adsorbed at the air/water, they produce a film. This film is highly concentrated and organized even at very low bulk concentration of surfactants or ionic liquids. The high concentrated film at air/water can give us valuable information about the surface structures and properties at the molecular level for ion-ion, water-ion, and water-water interactions also their ion distributions and structures. Understanding the structure and dynamics of ions at the air-water interface and their effect on properties of electrolyte solutions can give valuable information for biomolecular sciences such as studying peptides, proteins, lipids and colloidal particles.

Due to the fact that hydrophobicity of cations and anions of ionic liquids can be changed e.g. by increasing the length of alkyl chain thus propensity to the air/water interface and their self-organization and aggregation in aqueous solutions can be modified. This property makes them interesting for colloid and interface science. As many ionic liquids are environmentally friendly solvents and have biodegradable properties, thus applications of them for biodegradable materials is highly considered [77-79].

Goodchild et al. by means of conductivity, surface tension measurements and small angle neutron scattering studied the aggregation of alkyl-3-methyl-imidazolium with different counter ions in water and revealed that for alkyl chain greater than six aggregation observed.

In another study, Kumar and co-workers synthesized several ether-functionalized ionic liquids and investigated the physicochemical properties by several experimental techniques such as surface tension, conductivity and fluorescence techniques. They found that ionic liquids with short alkyl chain have lower critical aggregation concentration values than their

conventional ionic liquids [81]. Self aggregation of the ionic liquids, i.e., 1-butyl-3-methylimidazolium chloride, 3-methyl-1-octylimidazolium chloride, 1-butyl-3-methylimidazolium tetrafluoroborate, N-butyl-3-methylpyridinium chloride, in aqueous solution has also been investigated by Kumar and co-workers by means of  $^1\text{H}$  nuclear magnetic resonance (NMR) and steady-state fluorescence spectroscopy [82]. Moreover, self-aggregation behavior of imidazolium based ionic liquids by Zheng et al., Bowers et al. and Gomes et al. [83–85].

As the surfactant properties of ionic liquids can be changed, they become better candidates than conventional surfactants for protein applications [86–88]. The aggregation and self-assembly of ionic liquids can be employed in developing new materials for drug delivery or biochemical engineering. There are some compounds which are responsive to the pH and able to form micelle. Wang et al. have synthesized a series of pH responsive ILs which could make vesicles without any additives with reversible transition between spherical micelles and vesicles by changing the pH of solution. They suggested that the transition in self-assembly is driven by hydrophilicity/hydrophobicity of anions [89].

Self-assembly of ionic liquids derivatives at air/water interface for photochemical applications studied by using carbazole tailed methylimidazolium based ionic liquids for micelle formation in aqueous solutions [90] and interaction of gelatin as natural polymer with ionic liquids for future applications in pharmaceutical and other industries. Moreover, amino acid ionic liquid surfactants in aqueous solution have been used for self-aggregation and self-assembly due to their higher water solubility and biodegradability [92].

#### **4 Future Perspective**

Due to unique properties, ionic liquids have been used for many applications such as catalysis, extraction, energy storage, and environmentally friendly solvents for synthesis. Since the solubility of many drugs in water is limited, a promising application of ionic liquids is for drug delivery. To set forth its application, a true understanding is needed of the molecular interactions of ionic liquids, active pharmaceutical ingredients in water, and their physicochemical properties (such self-assembly and aggregation at air/water interface).

Many different functionalized ionic liquids will be used for antimicrobial activity in aqueous solution for specific interactions with biomolecules. Thus, understanding the surface activity and aggregation property of ILs in the aqueous solutions must be fully studied. Moreover, structural and dynamical

properties of ILs at surfaces and in particular air/water interface and aggregation must be understood in order to develop new task specific ionic liquids. Task specific ionic liquids can be used in many applications, such as drug delivery, protein stabilization, protein crystallization, DNA stabilization.

Another future application of ILs will be in colloidal and polymer industry in which smart separation based on magnetic responsive ILs will be used for separation at air/water interface by applying external magnetic field.

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## **Biography**



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