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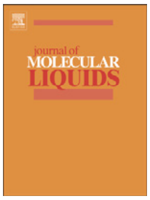

Understanding ionic liquids from theoretical methods

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ABSTRACT

We present a short overview of our results which have been obtained from theoretical investigations during the period of the SPP-1191 priority program. The liquid state of imidazolium-based ionic liquids and protic ionic liquids has been studied intensively in our group not only mainly from *ab initio* molecular dynamics simulations, but also from classical molecular dynamics simulations. Hydrogen bonds and intermolecular forces have also been examined by quantum chemical methods, and their influence on molecular and macroscopic properties is reviewed here. We have extended our investigations to the gas phase which has been studied from both classical and *ab initio* molecular dynamics simulations. More insights into water(-impurities) ionic liquid interactions have been gained, and mixtures of ionic liquids have been explored. The mechanism of reactions in ionic liquids and solute ionic liquid relationships as well as cation and anion effects — which is reflected in either an active or a passive role of the ionic liquid — have been considered.

1. Introduction

Due to the technical progress and the developments in theoretical chemistry over the last 20 years, computational methods have become a powerful tool in chemistry. Observed macroscopic properties have been assigned to functional parts of a molecule which facilitates a more task-related design of new compounds. Still, the interplay of nuclei and electrons is too complex for feasible black box methods treating systems larger than a few atoms until now. Therefore, a computational chemist should always choose an approach carefully and verify how the necessary approximations influence the results.

Ionic liquids are a special challenge for computational chemistry. High viscosity enforces the consideration of ionic liquids on a large simulation time scale. Furthermore, mainly due to the important role of cooperativity [1], the investigation including a reliable electronic structure is necessary to obtain trustworthy results. Unfortunately, required computational approaches are available only for medium sized systems. These approaches then possess the appropriate flexibility of the electronic structure for an accurate *ab initio* description of for example cooperativity. Additionally, dispersion forces lead to difficulties regarding the choice of a reliable approach for ionic liquids. Nevertheless, carefully selected computational approaches can allow predictions for ionic liquids or support many experimental findings and aid in exploring them. One example for the former is the nanoscale segregation of polar and nonpolar domains (also called microheterogeneity) in ionic liquids. These domains were found in coarse-grained models [2] and in fully atomistic molecular dynamics simulations [3] before they were reported by X-ray diffraction [4] or Raman-induced Kerr effect spectroscopy [5] studies. In addition to the prediction of the liquid structure, the calculation of thermodynamic data, like the gaseous enthalpy of formation, has been undertaken [6]. These two presented examples show that carefully selected computational approaches are powerful tools for the investigation of ionic liquids [7–14].

2. Pure ionic liquids and intermolecular forces

The liquid state of imidazolium-based ionic liquids (ILs) and protic ILs was studied intensively in our group. So far, we have learned that there are several subtle effects occurring in ionic liquid systems which again affect the macroscopic properties. From considering several studies in literature [15–53] and also from our own work [1,54–58], it is obvious that the different interactions, steric effects and other molecular influences — even if they are small — should be carefully taken into account while analyzing or tuning the properties of ionic liquids. Each of these effects can change the global characteristic of an ionic liquid — even if this occurs just slightly, but affections in a pronounced way by influencing its own environmental features have been observed as well. The effects might originate from different sources which can be grouped into three topics: 1. Molecular interactions like electrostatics,

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dispersion forces, hydrogen bonding features; 2. Structural influences like bulkiness, side-chain effects, charge concentration, and 3. Group contributions constituting features as hydrophobicity, lipophobicity, or molar mass. Therefore, starting from the picture of a common salt in which the organization is driven by purely electrostatic interactions providing a grid of favored ion positions, the ionic liquid may be considered as a disturbed salt system [54,55,57] or as a "melange" [59] of ions.

Monomethylammonium nitrate possesses directional hydrogen bonds similar to water [60]. However, a fast ion rattling in the cages of counter ions has been observed for the protic ionic liquid. This observation constitutes a similarity to imidazolium based ILs [25,56,61–63]. In contrast to protic ILs, hydrogen bonds in imidazolium based ILs have been observed to be scarcely directional [55,57,64]. It should be highlighted here, that the main interactions of the ions are obviously of Coulombic nature, and these again affect some of the well known criteria for hydrogen bonding like molecular or ionic structure, respectively, frequency shifts, charge transfer, and molecular orbital mixing [57]. Therefore, it is insufficient to apply only one method to identify hydrogen bonding in ILs, and the term *hydrogen bond* should be employed with care in IL systems [57,64]. Furthermore, detected hydrogen bonds seem to contribute in an important way to the macroscopic properties of the ionic liquid, as they can solidify the IL by stabilizing grid positions or fluidize the IL by stabilizing transition states between two positions of the electrostatically favored ionic grid [57]. For example, the substitution of the most acidic proton at C2 of 1,3-dialkylimidazolium based ionic liquids with a methyl group hinders the mobility of the anion around the imidazolium ring resulting in a lower activation barrier to reach the critical displacement for melting [55,57]. The methyl substitution decreases the mobility of the anion and therefore, these compounds possess an increased melting point [55,57]. *Ab initio* molecular dynamics simulations have revealed a faster hydrogen bond dynamics at the most acidic proton (H2) than the according dynamics at the H4 and H5 proton [65]. This is in contrast to expectations from static quantum chemistry calculations. These have inferred a superior directionality for the most acidic hydrogen atom (H2) of 1,3-dialkylimidazolium based ionic liquids as compared to the two other hydrogen atoms (H4, H5) at the imidazolium ring [27,32,55,57]. Only if directionality was neglected, the dynamics reflected the expected one from a geometrical analysis [65]. Overall, geometrical considerations on hydrogen-bond acceptor and donor distances have indicated rather weak hydrogen-bond situations in imidazolium based ionic liquids while a significant indication for hydrogen bonding has been observed if the net charge transfer via the acidic proton was selected as criteria [57].

Recently, an extensive simulation study of 1-butyl-3-methylimidazolium ionic liquids with varying anions has revealed that larger and less coordinating anions increase the competition with the cation for the on-top conformation around the imidazolium ring [66]. Furthermore, aggregation of side chains — that means microheterogeneity [2–5,67–69] — is decreased by large and weakly coordinating anions. Additionally, the influence of fluorination of the cationic side chain has been investigated which promotes the on-top position of the anions as well as the aggregation of side chains [66].

Finally, we have focused on the general influence of intermolecular forces on dynamical and macroscopic properties. The comparison of potential energy surfaces obtained by symmetry-adapted perturbation theory (SAPT) calculations has revealed that dispersion effects play an important role for IL systems as compared to typical salts [54,55]. As a result, shallower energy potential surfaces for ILs have been received due to the mixing of intermolecular forces which allows the IL counter ions to change their respective distances more easily [54,55]. In summary, we can say that the more balanced the molecular features disturbing the ionic grid are, the more flat the potential energy landscape is which results in a more fluid system.

3. Methodological developments with respect to force fields and electronic structure

Important methodological knowledge has been collected, and developments with respect to force fields and density functional theory have been made. In order to carry out proper molecular dynamics (MD) simulations of such ionic systems, partial charges should be determined thoroughly [1,33,39,43,62]. Their values can have a great influence on the calculated structural and dynamical properties of ionic liquids [56,63]. We applied a standard RESP, i.e., restrained electrostatic potential fit, with different scaling factors which was proposed to approximate charge transfer between cations and anions in ILs [33,39,70]. Two further quantum chemical based charge sets have been employed, namely the shared electron number (SEN) charges [71] and the natural partial atomic (NPA) charges [72]. We showed that the standard set with a certain scaling factor (0.8) provides the best results, while both of the other sets failed at least for one of the investigated properties, see Fig. 1 for an illustration of obtained spatial distribution functions (SDF) [63]. Furthermore, we carried out MD simulations with different model charge systems in order to clarify the role of hydrogen bonds on the structure and dynamics of the ionic liquid [C_4C_1im][Br]. These results have been compared to experimental data [58]. The hydrogen bonding ability, represented by different atomic partial charges on the most acidic hydrogen atom and its connecting carbon atom, influences the structure and the dynamics differently depending on the degree of the alteration [58].

Currently, we are collaborating with the group of Padua and Costa Gomez as well as with the group of Fernandez on the development of force fields for ionic liquid interfaces. A force field has already been developed to study the interaction of graphene sheets or single-wall carbon nanotubes with ILs [73]. Graphene-based materials can be used as electrodes in high energy density supercapacitors due to their excellent mechanical and electrical properties [74–79]. We observed a strong adsorption layer composed of cations and anions close to the graphene surface. Interestingly, this strong adsorption of the IL resulted in a region of low density in the middle of a carbon nanotube with small diameter. Increasing the carbon nanotube diameter led to a region in the center for which the structure was similar to the one in the bulk.

Additionally, we have investigated the reliability of *ab initio* molecular dynamics simulations. These employ Kohn–Sham density functional theory [80,81] (KS-DFT) as an electronic structure method. Significant deviations for B3LYP calculations compared to experimental results have been reported in the literature [6,82]. One error might stem from the description of dispersion forces for which common density functionals fail [83–88]. Thus, specific interactions are not accurately represented, e.g., the aggregation of the alkyl chains resulting in a nanoscale segregation [2–5,67–69] or the π–π stacking of the imidazolium cations [89–92]. Therefore, we have investigated the reliability of KS-DFT in these IL systems for common density functionals as well as for recently proposed dispersion corrected methods [93,94]. While common KS-DFT functionals like B3LYP produced remarkable deviations, see Fig. 2 for an illustration, nearly all investigated dispersion corrected approaches proved results closely to the *ab initio* reference calculations [93,94]. Additionally, the self-interaction error of KS-DFT turned out to be only important at large ion distances and thus, negligible for solid and liquid state studies [94]. Recently, we have shown that neglecting dispersion forces in *ab initio* molecular dynamics simulations leads to an unrealistic faster diffusion of the anions than that of the cations which is in contradiction with experimental observations [95].

Nevertheless, the question arises if the feasible system size of *ab initio* molecular dynamics simulations is sufficient for convergence of electronic properties due to the important role of induction forces [1,54,55]. In cooperation with the groups of Holm, Berger, and Delle Site it has been shown that electronic properties like the dipole moment are converged if eight ion pairs are taken into account under periodic boundary conditions [96–98]. Therefore, dispersion corrected KS-DFT