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Inorganic Chemistry Article

Ionic Liquids from Car–Parrinello Simulations. 2. Structural Diffusion Leading to Large Anions in Chloraluminate Ionic Liquids

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We present Car–Parrinello molecular dynamics simulations of the liquid imidazolium chloride/$AlCl_3$ by inserting one pair of $[C_2C_1im]Cl$ into liquid $AlCl_3$, forming an acidic mixture. Two different starting conditions lead to two trajectories from which we harvest structural data. For both simulations, we find large anions within the equilibrium phase: In both trajectories at longer simulation time, the anion size converges to four monomer units, i.e., to $Al_4Cl_{13}^-$. The cluster size fluctuations indicate that Grotthus diffusion must play a role. We discuss one possible mechanism of such a reaction changing the anionic species. This process involves many steps of chlorine rattling, bond breaking, and bond forming. With the aid of the electron localization function, a probable rationale for the formation of larger anions is determined: Large anionic species are formed simply to account for the "lack of electrons" present in the acidic melt.

1. Introduction

Ionic liquids (ILs), or room-temperature molten salts that consist of inorganic anions and organic cations and that form a new class of solvents, are increasingly appearing in the literature because of their interesting properties in chemical and industrial applications: These liquids are alternatives to "more toxic" liquids, and their solvent properties can be adjusted to the particular problem by combining the right cation with the right anion.[1,2] A wealth of informative review articles on ILs are available.[3−7]

In this study we are interested in 1-ethyl-3-methylimidazolium ($[C_2C_1im]^+$) chloroaluminate based ILs, as discovered by Wilkes and co-workers.[8] Depending on the mole fraction of $AlCl_3$ in the mixture of $MCl-AlCl_3$ (where M is a suitable cation to obtain an IL or a molten salt), the Lewis acidity−basicity can be altered. Compositions containing an excess of Cl^- [i.e., $x(AlCl_3) < 0.5$] are called basic, and those where $x(AlCl_3) > 0.5$ are called acidic.[3−5,7] It is the general belief that such acidic liquids contain anionic species that are larger than $AlCl_4^-$, such as $Al_2Cl_7^-$ or $Al_3Cl_{10}^-$.[3−5,7] While sometimes it is discussed that only the $Al_2Cl_7^-$ anion is present, the larger trimeric anion could be shown to play a role, for example, by Raman IR spectroscopy studies.[9−11] Nevertheless, it is still a matter of debate how large the anionic species are and at which composition of $AlCl_3$ they occur. One decade ago Oye and co-workers brought up the interesting question of an even larger species, namely, the $Al_4Cl_{13}^-$ unit.[12] In a thorough investigation of the vapor pressure and by derivation of a thermodynamic model, the presence of a tetrameric species could be established together with neutral

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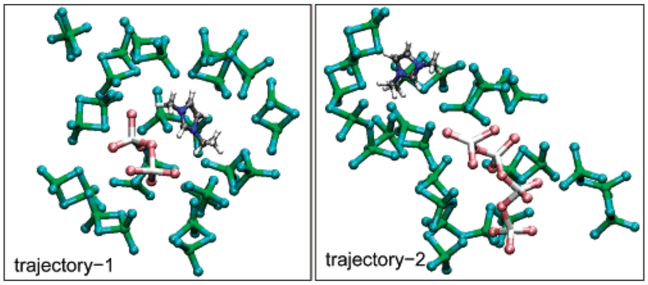

Figure 1. Starting configurations for the simulation of $[C_2C_1im]Cl$ solvated in $AlCl_3$. Left panel: trajectory-1. Right panel: trajectory-2.

Al_2Cl_6 dimers at high mole fractions of $AlCl_3$, i.e, in highly Lewis acidic mixtures.[12] The different mole fractions of $AlCl_3$ in ILs that are genuinely very complex are accompanied by numerous anions in equilibrium with each other.

The puzzle of different anions and their transformation into each other have prompted us to carry out Car−Parrinello molecular dynamics (CPMD) simulations in which spontaneous events can occur.[13−15] In CPMD simulations, the electronic structure of the system is dynamically adjusted to the chemical events that occur in the system. Those simulations are computer time intensive because in each step of a long trajectory an expensive quantum chemical calculation has to be carried out. However, the high computational effort is well invested because CPMD calculations have a number of intrinsic advantages over either traditional quantum chemical or classical force-field-based methods.[13] We undertook dynamical CPMD simulations of one pair of $[C_2C_1im]Cl$ (1-methyl-3-ethylimidazolium chloride, emim chloride) in 30 $AlCl_3$ (i.e., modeling the acidic mixture).

This Article is structured as follows: First, we discuss the systems investigated. After this, we present the computational details. Next, we turn to the results with the main focus on the nature of the diverse anions. We will finish the Article with conclusions.

2. Systems Investigated

In this Article, we study one $[C_2C_1im]Cl$ pair solvated in 30 molecules of $AlCl_3$; see Figure 1. The initial geometry was taken from a sample of liquid $AlCl_3$ with 32 molecules, where we replaced one dimer with the $[C_2C_1im]^+$ cation. We calculated two trajectories, one where in the beginning we placed the ions in close proximity (denoted with traj-1 or trajectory-1; left panel of Figure 1) and one where we started from separated ions (abbreviated with traj-2 or trajectory-2; right panel of Figure 1). Within the equilibration phase of the simulations, large clusters form already. This is the reason why in Figure 1 there appear large anions instead of the anions Cl^- or $AlCl_4^-$.

Formerly, we could show that the pure $AlCl_3$ consists of the dimeric species but also of larger species.[16] Larger clusters with a size of up to nine monomer units were also observed, however only with low probability.

3. Computational Details

We performed the dynamical calculations with the CPMD code.[17] We used density functional theory with the generalized gradient approximation of Perdew−Burke−Ernzerhof (PBE)[18] as the exchange-correlation term in the Kohn−Sham equations, and we replaced the action of the core electrons on the valence orbitals with pseudopotentials; they are the same Troullier-Martins ones as in ref 16 for Al and Cl and of the Vanderbilt ultrasoft type[19] for the C, N, and H of $[C_2C_1im]^+$. In this way, we were able to retain the same cutoff energy of 25 Ry as that for the pure $AlCl_3$; in this case the saving of computer time is noticeable because only a few atoms (C, H, and N) bring in the extra terms due to charge augmentation, and the cutoff energy can be kept low (with norm-conserving pseudopotentials, one should use 60−70 Ry for a comparable accuracy). We sampled the Brillouin zone at the Γ point, employing periodic boundary conditions.

We did the simulations in the *NVT* ensemble, employing a Nosé-Hoover thermostat at a target temperature of 540 K (in order to keep $AlCl_3$ as a fluid) and a characteristic frequency of 595 cm^{-1}, a stretching mode of the $AlCl_3$ molecules. We propagated the velocity Verlet equations of motion with a time step of 6 atu = 0.145 fs, and the fictitious electron mass was set to 900 au. A cubic simulation cell with an edge length of 1.802 nm with 32 molecules of $AlCl_3$ gives the same density as the pure $AlCl_3$, 1.211 g/cm^3. We ran two trajectories employing CPMD: trajectory-1 is 38.0 ps long and trajectory-2 28.4 ps long.

In the analysis, we used a geometrical criterion to assign the connectivity between different molecular motifs in the liquid. Al and Cl atoms were defined to be bound if the distance between them is at most 1.5 times the bond length in the $AlCl_3$ monomer, leading to a cutoff radius of 276 pm. Two Al atoms were regarded as belonging to the same cluster if they are linked with at least one Cl atom bound to both Al atoms by the criterion given above.

4. Results

4.1. Size Evolution of the Anion Cluster. Figure 2 shows the evolution of the anionic cluster size (counting the number of Al atoms in an observed anion) with simulation time.

Taking a look at the development of the cluster size, we find two regions in the simulation trajectory-15 where both ions are close together, one with a cluster size of two (first 16 ps) and one with a cluster size of four (last 15 ps), which is accompanied by fluctuations to a trimer and seldomly to

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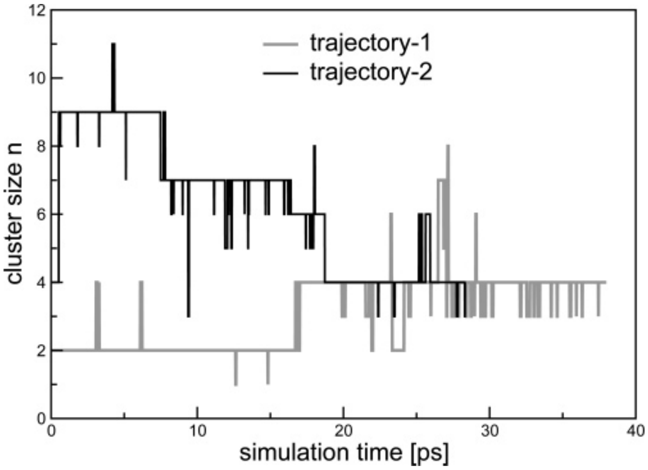

Figure 2. Evolution of the cluster size (counting the number of Al atoms in an observed anion) for both trajectories.

even larger clusters (see the gray line in Figure 2). In trajectory-2 (see the black line in Figure 2), we find that larger clusters of up to nine units are stable for about 10 ps, and after this, a cluster size of approximately seven is populated for 10 ps. In the last time region of trajectory-2, the average size of the cluster is like that for trajectory-1 about four. Thus, the major cluster size of the anion in simulations of this kind is four ($Al_4Cl_{13}^-$). Experimentally the accepted picture is that of $Al_2Cl_7^-$, and since the seminal work of Dymek and co-workers, $Al_3Cl_{10}^-$ is proven to play a role at mole fractions of $AlCl_3$ being larger than 0.5.[9] Earlier studies also indicated this trimeric anion.[20−22] However, from a thermodynamic model, Oye et al. were able also to show that in very high regions of $x(AlCl_3)$ tetrameric anions next to increasing amounts of the neutral dimeric species are present, which is in agreement with our observations.[12] Although our main cluster species contains four units, we also see fluctuations to other cluster sizes, which is in agreement with the requirement that the anions must be in equilibrium with each other.

4.2. Possible Mechanism of Structural Diffusion. The changes of the cluster size along time evolution can be understood under the assumption of structural diffusion. Structural or Grotthus diffusion was termed in liquid water, and it is a process of concerted bond breaking and forming. It allows the proton in water to migrate very fast and to react to different ionic species.[23]

In Figure 3, we show characteristic Al−Cl distances in picometers that illustrate one mechanism for such a Grotthus-like process, namely, the reaction from a dimeric anion plus a neutral dimer to a tetrameric anion. We observe that the bridged chlorine (Cl^b) of the dimeric anion rattles between the two Al atoms (see the red line with filled dots and the black line with open dots in Figure 3). This movement is mainly such that the distance to Al^I is short when the distance to Al^{II} is long and vice versa. The reaction includes several complicated steps: The terminal chlorine (Cl^t) attached to Al^{II} (green line with filled squares) vibrates in phase with the Cl^b-Al^I distance (the black line at time step 47); i.e., the $Al^{II}-Cl^t$ distance is long when the Cl^b-Al^{II} distance is short. At the instance where the distance between Cl^b and Al^{II} [$r(Cl^b-Al^{II})$] is smallest (time step 48) and Cl^t exhibits a maximum distance to Al^{II}, a neutral dimeric unit approaches and forms a covalent bond (see the blue line with stars indicating the Cl^t-Al^{III} distance in Figure 3). The approach from 400 to 200 pm takes 6 fs. It appears as if a (pseudo) $AlCl_4^-$ provides electron pairs for the electron-deficiency compound Al_2Cl_6.

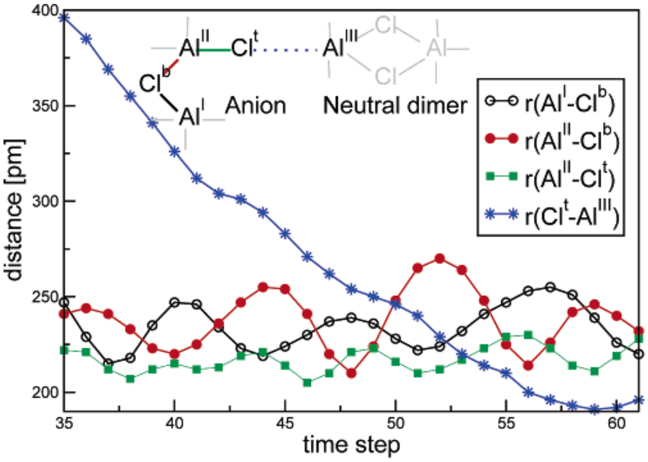

Figure 3. Al−Cl distances (in pm) illustrating the structural diffusion. The distances marked in black, red, and green belong to the dimeric anion (<16 ps), and the blue line marks the approach of a neutral dimer to form the tetrameric species. One time step is 1.45 fs long.

Structural diffusion in ILs was inferred and observed previously by experiment and theory. For example, Seifert and co-workers obtained a structural diffusion mechanism for an excess proton in imidazolium chains.[24] Furthermore, Grotthus diffusion for anions in ILs was discussed previously at the experimental data of conductance and viscosity.[25,26] In $AlBr_3$/TMSuBr (trialkylsulfonium bromide) as compared to HBr/TMSuBr, the authors obtained a 7-fold decrease in viscosity but a 24-fold increase in conductance.[25,26] The viscosity change is ascribed to the different ion sizes, while the conductance change is explained by a Grotthus mechanism for the Br^- exchange.[25,26]

4.3. Interpretation of Lewis Acidity with the Electron Localization Function. In order to shed light on the Lewis acidic properties, we calculated the electron localization function (ELF) at anions that were extracted from the CPMD simulations and at smaller anions like Cl^-. Typical species found in the simulations together with the calculated ELF are displayed in Figure 4.

For the sake of comparison, we added Cl^- and $AlCl_4^-$, which we obtained from geometry optimization. ELF is shown for the isosurface value 0.88 (blue spheres). Please

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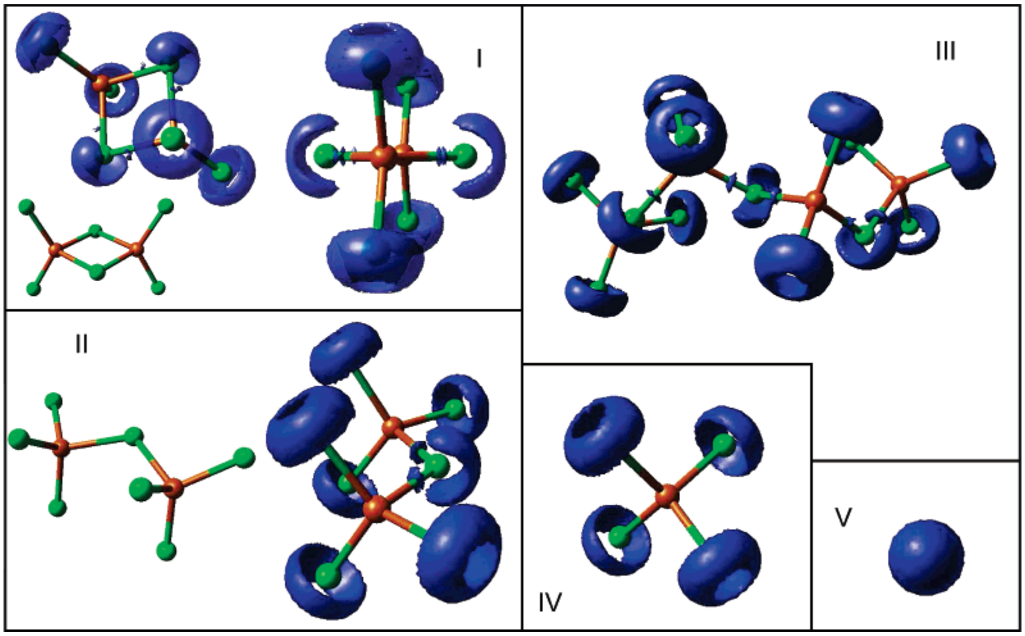

Figure 4. ELF for different units in blue. I: Al_2Cl_6. II: $Al_2Cl_7^-$. III: $Al_4Cl_{13}^-$. IV: $AlCl_4^-$. V: Cl^-. Green atoms: Cl. Orange atoms: Al.

note that ELF is not an observable but only a concept, such as, for example, the oxidation state. However, these concepts have proven to be very useful for chemists. Roughly speaking, ELF decomposes the electron density into sections of space that correspond to electron pairs. ELF is a function of real space, and high values of ELF indicate high probabilities of electron pairs, i.e., a higher localization of the electron pairs. In Figure 4, we immediately recognize that Cl^- (V) is a Lewis base and $Al_2Cl_7^-$ (II) as well as Al_2Cl_6 (I) are both Lewis acids because Cl^- displays a full sphere, while the dimers exhibit at the Cl^t atoms also full-doughnut-shaped spheres but at the Cl^b atoms half-moon-shaped spheres. It is obvious that due to the half-moon-shaped spheres electron pairs can be accepted at these sites as opposed to the doughnut-shaped spheres. $AlCl_4^-$ (IV) fits this picture because the four Cl^t atoms also are enclosed by the full-doughnut-formed sphere. Note that the anionic dimer is connected via shared corners and the neutral dimer via shared edges; this is displayed in the inlet of panels I and II of Figure 4. Because in the neutral dimer two half-moons are found, i.e., one half-moon per monomer unit, and in the anionic dimer there are 0.5 half-moons per unit, it is clear that either the neutral dimer and/or larger anions (for example, 0.75 half-moons per unit in the tetramer) must play a role. These species are formed simply to account for the "lack of electrons" present in the acidic melt. A smaller anion with Lewis base character would immediately be captured by a neutral Al_2Cl_6 according to this picture.

5. Conclusions

In this work, we have presented the first CPMD simulations on ILs built from chloraluminates and imidazolium chloride. Because the Lewis acidity−basicity properties of these liquids can be changed by the right choice of composition and because in the acidic mixture the size of the anions is still a matter of debate in the literature, we chose to simulate such an acidic liquid by solvating one pair of $[C_2C_1$-im]Cl within liquid $AlCl_3$. Starting from both close and distant ions, the anion size converges to four monomer units along the simulations. This nicely agrees with experimental observations of an anion as large as four monomer units, i.e., $Al_4Cl_{13}^-$.[12] What is also visible in the time evolution of both trajectories is that the anion size fluctuates, such that it can be assumed that numerous anion sizes are in equilibrium with each other, which infers that Grotthus diffusion must play a role. In our simulation, we chose an example that serves as one possible mechanism of such a transformation between different anionic species. In general, it should be noted that this process involves many steps of chlorine rattling, bond breaking, and bond forming similar to the structural diffusion process of the proton in water.[23] With the aid of the ELF, one rationale for the formation of larger anions could be determined. Large anionic species are formed simply to account for the "lack of electrons" present in the acidic melt. A smaller anion with Lewis base character would immediately be captured by the electron-deficiency compound Al_2Cl_6 according to the picture that is provided by the ELF.

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