Physical properties and atmospheric reactivity of aqueous sea salt micro-aerosols

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Abstract

Aqueous sea salt micro-aerosols play an important role in the heterogenous chemistry of the lower marine troposphere both in polluted and in remote areas. In particular, reactions with gases such as ozone or OH radicals leading to the release of molecular chlorine have been intensely studied, both experimentally and theoretically. Moreover, thin layers of sea water deposited on Arctic ice packs have been discovered to be a major source of reactive bromine species which destroy the surface ozone layer during polar sunrise. There is increasing evidence that the air-water interface is of a key importance in these chemical processes. Despite this, little has been known about the structure and physical properties of aqueous sea salt aerosols at a detailed, molecular level. Here, we summarize results of classical molecular dynamics, Car-Parrinello molecular dynamics and *ab initio* quantum chemistry calculations on concentrated aqueous sodium chloride and bromide solutions confined to cluster and slab geometries. The main questions addressed by the simulations

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concern the onset of NaCl ionic solvation in water clusters, transition from clusters to slabs, structure of solvation layers and degree of ion pairing in concentrated solutions with confined geometries. A key result of the simulations is the observation that polarizable halogen anions (chloride and bromide) are present at the air-water interface of bulk solutions in amounts sufficient for the heterogenous atmospheric chemistry to take place. The calculations also reveal that bromide actually exhibits surfactant activity, i.e. its concentration at the interface is higher than in the bulk. This is an accord with the observed enhanced atmospheric reactivity of aqueous bromide compared to chloride and with SEM experiments on wetting and re-drying of NaCl/NaBr co-crystals.

I. INTRODUCTION

Despite a spectacular progress in our understanding of atmospheric chemistry [1,2] heterogenous processes involving rain or aqueous sea salt droplets, ice particles, and other aerosols are still in general poorly understood. The importance of including heterogenous chemistry into atmospheric modeling can be demonstrated on the spectacular failure of earlier computer models to predict the Antarctic ozone 'hole' due to the omission of heterogenous reactions occurring on polar stratospheric clouds [2]. Recently, a lot of attention has been directed to elucidation of the role of aqueous sea salt aerosols in processes leading to the release of chlorine into the lower marine troposphere [3–11]. While the (ozone destructive) role of chlorine in the stratosphere is notoriously known its tropospheric role is less well established.

Field measurements revealed chlorine concentrations in the lower marine troposphere up to 150 ppt [3], which are more than order of magnitude higher than predictions based on standard atmospheric models [12]. In the search for the hitherto unrecognized chlorine source aerosol chamber experiments have been performed [4,6]. In the experiment dry sea salt or NaCl microparticles have been humidified above the deliquscence point in the presence of ozone as polluting gas and UV radiation and, consequently, production of molecular chlorine has been observed.

Consequently, a chemical kinetic model has been suggested, involving the following four steps: i) ozone UV photolysis in the presence of water vapor leading to creation of OH radicals, either directly or via hydrogen peroxide, ii) uptake of OH into the aqueous sea salt (or rock salt) aerosol, iii) creation of a Cl^-...OH complex followed by creation of a Cl radical (by charge transfer to the naturally present hydronium cation) and, subsequently, Cl_2^-, iv) self-reaction of two Cl_2^- anions leading to formation of molecular chlorine, which diffuses and is eventually released from the aerosol. This kinetic model successfully reproduced the initial photochemical depletion of ozone, however, it underestimated the chlorine production by three orders of magnitude. The bottleneck turned out to be the charge transfer step due a too low natural concentration of hydronium cations in roughly pH-neutral aerosols. This model could provide the observed chlorine concentration only when unrealistic acidities of the aerosols were assumed.

Another example of the role of aqueous sea salt in a confined geometry in atmospheric processes has been discovered recently. Indeed, thin layers of sea water deposited on ice packs have been found to be a major source of reactive halogen species during polar sunrise. Sea spray carried by winds lands on polar ice leading to an accumulating interfacial concentration of chloride and bromide during the polar winter. At the polar sunrise, a vigorous outburst of photochemistry is observed, leading to an almost complete destruction of ozone in the boundary layer at the timescale of hours [13–15]. Bromide, released from the snow packs in the form of an oxide has been shown to play a key role in polar tropospheric ozone destruction.

In the light of the above findings a new model, where chloride ions at the air-water interface play a prominent role, has been suggested [6]. It was, however, somehow disturbing that the new model is in conflict with standard theories of simple electrolytes and their surfaces [16]. Indeed, it has been a generally accepted textbook knowledge (albeit not supported by any direct experimental evidence) that atomic ions are repelled from the air-water interface by the electrostatic image forces, therefore, the interfacial layer is effectively devoid of ions [16–18]. In contrast, photoelectron spectroscopy measurements [19–21] and molecular dynamics (MD) simulations [22–28] performed in the last decade indicate that polarizable atomic anions such as chloride, bromide, or iodide reside at the surface of water clusters with several to several tens of solvent molecules.

The main purpose of the present study has been to investigate theoretically aqueous solutions of simple electrolytes such as sodium chloride or bromide in confined geometries corresponding to cluster or slab arrangements. In order to validate the basic assumption of the new atmospheric model (i.e., that heavier halides are present at the air-water interface of aqueous sea salt aerosols) we have in particular investigated the composition and structure of the interfacial layer. At the same time we have also addressed by means of a pragmatic combination of *ab initio* calculations, Car-Parinello and classical MD simulations the following questions: i) how many solvent molecules are necessary for NaCl solvation in water clusters, ii) what structural changes accompany the transition from cluster to slab geometry of simple electrolytes, iii) what is the structure of solvation shells around ions at the interface compared to the bulk, iv) what is the degree of ion pairing in concentrated solutions with confined geometries and at what concentrations the linear Debye-Hückel regime is no more valid, and, finally, v) what is the role of minor substituents, such as bromide, in aqueous sea-salt particles.

II. SYSTEMS AND COMPUTATIONAL STRATEGIES

Typical sizes of aqueous sea salt aerosols range from 0.1 to 1 μm. The salt concentration in the aerosols is higher than that in sea water due to rapid water evaporation. As a matter of fact saturation is often reached or even exceeded, leading eventually to dry salt microparticles. In the present study we have investigated aqueous sodium chloride solutions (in some cases doped also with bromide) in confined geometries. The atmospheric micro-aerosols possess way too many particles too allow for a direct computational modeling at a molecular level. As a first step, we have investigated much smaller clusters, containing from six to several hundreds of water molecules. However, a much more realistic computational model with molecular resolution of the atmospheric reality corresponds to a slab geometry with two roughly planar air-water interfaces. Therefore, most of our simulations were performed for slabs covering the whole salt concentration range from infinite dilution all the way to saturation.

The basic computational strategy consists in performing extended MD simulations with the quality of the force field checked and validated by Car-Parrinello and *ab initio* quantum chemical calculations for smaller systems of the same composition. The use of a polarizable potential model turned out to be essential for any realistic predictions. We have employed the SPC/POL model of water [29] and accounted explicitly for polarizabilities of the solute ions [30,31]. MD simulations have been run at 300 K employing a time step of 1 fs. The OH bonds have been kept frozen using the SHAKE algorithm [32]. Typically, the systems have been equilibrated for 500 ps after which a relatively long sampling period of 0.5 - 1 ns followed. The slab condition has been realized by confining 864 water molecules and an appropriate number of ions into a box of $30\times30\times100$ Å. Periodic boundary conditions have been applied and the particle mesh Ewald method has been used to calculate the electrostatic energies and forces [33]. The van der Waals interactions and the real space part of the Ewald sum have been truncated at 12 Å. All the classical MD simulations have been performed using the Amber code [34].

Car-Parrinello MD simulations have been performed for a water hexamer containing a single chloride anion. The electronic equations of motion [35] have been integrated using a time step of 0.121 fs and a fictious electron mass of 800 a.u. The electronic structure has been computed with the gradient corrected BLYP exchange-correlation functional [36,37], treating the valence electrons explicitly, while the core electrons have been described using a pseudopotential [38].The cluster has been placed in a periodic cubic box with a box length of 13.2 Å and an energy cutoff of 70 Ry for the plane wave basis has been applied. Sampling has been based on 5 ps microcanonical trajectories corresponding to an average temperature of 250 K. Calculations have been performed using the CPMD program [39].

Quantum chemical *ab initio* calculations have been aimed at the investigation of NaCl ionic solvation in small clusters with up to six water molecules. Geometry optimizations have been performed at the MP2/6-31_{+Cl}G* level, while single point calculations for the allocated stationary points have been done at MP2/6-311_{+Cl}G(2d,p) and CCSD(T)/6-31_{+Cl}G* levels of theory. Zero point energy as well as entropy effect at ambient conditions have been accounted for within the harmonic oscillator/rigid rotor model. The Gaussian98 program [40] has been employed.

III. RESULTS AND DISCUSSION

A. NaCl Solvation in Small Water Clusters

An obvious question concerning salt solvation in confined aqueous systems is how many water molecules are necessary to dissolve a single rock salt molecule, i.e., to create a stable solvent-separated Na^+/Cl^- ion pair [41]. A direct extrapolation from the bulk saturated concentration leads to nine water molecules [42]. However, it is by no means obvious that such an extrapolation is justified since the molecular structure of small water clusters and the bulk differ significantly from each other. Calculations based on a continuum dielectric model and employing a potential of mean force between aqueous Na^+ and Cl^- from bulk liquid MD simulations predicted that at least twelve water molecules are necessary for ionic solvation of sodium chloride [41]. More recent electronic structure calculations on NaCl in water clusters with up to ten solvent molecules using the effective fragment potential method did not lead to location of a solvent separated ion pair [43], possibly since the relevant part of the potential energy landscape has not been explored in sufficient detail.

In our study, we have launched an extensive *ab initio* search of potential energy surfaces of clusters with up to six water molecules containing a single NaCl species with special emphasis on geometries corresponding to a possible solvent separated ion pair [44]. For clusters with five and less waters we have not been able to observe ionic solvation, the only stable structure corresponding to the contact ion pair, i.e., to an unsolvated NaCl molecule. However, for water hexamer we have allocated as stable minima both the contact and solvent separated ion pairs, the latter corresponding to ionic solvation. The two minima are roughly isoenergetic (within 2 kcal/mol) and separated by a relatively high barrier (3-5 kcal/mol).

Fig. 1 depicts the geometries of the three stationary points pertinent to NaCl solvation in water hexamer. The unsolvated NaCl molecule (the contact ion pair) is shown in Fig. 1a. The bond between sodium and chloride is well developed, although it is extended by some 10 % with respect to the gas phase (i.e. to 2.66 Å). The hydrogen bonded water structure is only moderately disturbed by the contact ion pair. The situation is very different for the almost isoenergetic solvent separated ion pair with Na-Cl distance of 4.43 Å (see Fig. 1c). Here, all six waters are strongly oriented in the electric field created by the two separated ions to the extend that virtually nothing is left from the water-water hydrogen bonding. Finally, the barrier separating the two stable minima corresponds to Na-Cl distance of 3.61 Å and water geometries closer to that of the contact ion pair structure (see Fig. 1b).

The principal result, i.e. the fact that only six waters are necessary for NaCl solvation, is not accidental. Indeed, water hexamer is the smallest water cluster which forms stable three-dimensional (non-cyclic) structures, which can then help in stabilizing a solvent separated Na^+/Cl^- ion pair. It is maybe not surprising that this result cannot be reached by simple extrapolation from the bulk. Finally, we can conclude, that ionic rock salt solvation occurs already at water cluster sizes much smaller than those pertinent to the atmosphere.

B. Water Clusters Saturated with NaCl

In a first attempt to bridge the gap between the single solvated NaCl molecule on one side and atmospheric micro-aerosols on the other side we have launched a series of studies of water clusters saturated with sodium chloride (salt:water number ratio of 1:9) containing 18 to 288 water molecules. For such systems rigorous quantum chemistry methods can no longer be applied since the cluster sizes are too large and the potential energy landscapes too complex. A remedy lies in employing empirical force fields within molecular dynamics simulations. It has been, however, demonstrated in earlier calculations, that simulations of aqueous ions are rather sensitive to the quality of the force field, namely to the use of polarizable potentials [22,26].

In our study, we have verified the force field against Car-Parinello simulations employing the BLYP density functional for chloride anion in/on water hexamer [45]. Among others, we have found a very good agreement for cluster geometries and chloride surface properties in particular between Car-Parrinello results and those obtained from classical MD with polarizable potentials. On the other hand, a non-polarizable force field yields results qualitatively different from those following from the Car-Parrinello simulations. Therefore, in all MD simulations discussed below we have employed a polarizable force field described in the previous section.

Our cluster results show that the polarizable chloride anion behaves very differently from the almost non-polarizable sodium cation. Indeed, while sodium ions are well solvated within the water clusters, chloride ions tend to spend a significant time at the air-water interface of the clusters. This observation is in accord with earlier simulations of a single chloride anion or sodium cation in medium sized water clusters [22]. It is also important to note that the propensity of chloride ions for the interface is strong for all cluster sizes under investigation.

In the view of possible atmospheric surface reactivity we have found it very useful to quantify the amount of the ions at the air-water interface by evaluating the averaged accessible surface of the two ionic species. There is a well established computational method for this based on rolling a spherical probe (of a diameter of 1.7 Åin our case) over the interface at each time step of the simulation [46]. Figures 2 and 3 show the accessible surfaces of the sodium and chloride ions along extended MD trajectories for a small cluster with 36 water molecules and a large cluster possessing 288 water molecules. In both cases chloride anions occupy a significant portion of the surface (about 12 %), while sodium is almost absent from the air-water interface. The propensities for the interface for the two anionic species differ by two orders of magnitude and the affinity of chloride to the surface is primarily due to its large value of polarizability. Indeed, by switching to a non-polarizable force field the chloride accessible surface drops dramatically, by a factor of three.

C. Aqueous slabs containing NaCl

As mentioned before, an appropriate computational model of atmospheric aqueous sea salt aerosols of a micrometer size is a slab containing a sufficient amount of water molecules in order to simulate faithfully both the bulk and the interface (864 waters in our case), and the appropriate amount of ionic solute species. Similarly as in the laboratory experiment [6] we have in the first study included only the dominant solute, i.e. sodium chloride. Other minor impurities such as bromide will be discussed in the next section. We have explored the whole range of salt concentrations from infinite dilution to saturation [47], the latter being close to the laboratory as well atmospheric conditions.

We have employed two methods how to quantify the abundance of the solvated ions in the water slabs. First, we have evaluated density profiles of sodium and chloride ions across the slab from the center to the surface by averaging over nanosecond MD simulations. Fig. 4 depicts such density profiles on the background of the density of water oxygens for three concentrations: "infinite dilution" (only one NaCl species), 1.2 M, and 6.1 M (saturation). In the whole concentration range a different behavior of the two ionic species is immediately imminent. While sodium cations are always fully solvated in the interior of the water slab, chloride anions penetrate significantly towards the air/water interface. The reason why the signal for low salt concentrations is more noisy turns out to be purely technical - there are simply less ions to sample over.

From the point of view of a possible atmospheric chemical reactivity of ions at the surface of aqueous sea salt micro-aerosols it is better to quantify the propensity to the interface by evaluating the accessible surface of the ions along the MD trajectory (as demonstrated for cluster systems in Figs. 2-3). Fig. 5 shows the dramatic, two orders of magnitude difference in accesible surfaces between Cl^- and Na^+. While at 6.1 M chloride occupies some 12 % of the surface (i.e. exhibits almost the same surface activity as an average water molecule) sodium is practically absent from the air water interface. Most of the difference between the two species can be attributed to the fact that chloride is a soft polarizable ion, while sodium is a hard non-polarizable ion. Indeed, MD simulations employing a non-polarizable force field show a threefold reduction of the propensity of chloride for the surface (see Fig. 5).

An important question with respect to the atmospheric reactivity, but having also broader consequences for our understanding of concentrated salt solutions, is what is the degree of ion pairing. In other words, what is the ration between solvated and unsolvated NaCl species at a given concentration, and how does this ratio differ at the surface from the bulk value. Fig. 6 shows the percentage of chloride anions paired with sodium cations along 500 ps MD trajectories for concentrations of 1.2 M and 6.1 M (saturation). We see that at 1.2 M the degree of ion pairing is low, reaching about 5 % both in the bulk and at the air/water interface (Fig. 6a). At this concentration the aqueous solution dominantly contains separated solvated ions, in accord with the Debye-Hückel model of strong electrolytes. However, the situation is dramatically different when the concentration approaches saturation. At 6.1 M, three out of four chloride anions are paired with Na^+ in the bulk of the solution (see Fig. 6b). Interestingly, ion pairing of chloride drops to 54 % at the interface, a clear consequence of the much lower concentration of sodium cations in the interfacial layer.

Another structural question concerns the solvation number, i.e. the number of waters in the first solvation shell, for chloride in the bulk vs. at the interface as a function of salt concentration. At infinite dilution the number of water molecules in the immediate vicinity of a bulk solvated chloride anion amounts roughly to six. We see from Fig. 7a that already at 1.2 M concentration the chloride solvation number drops to 5.5. At saturation the solvation number further decreases to 4.5 (see Fig. 7b). As expected, the solvation number for chloride at the interface is always smaller than in the bulk. However, the difference is rather small, indicating that even in the vicinity of the surface chloride anions form an almost complete water solvation shell. There is also a clear connection between solvation numbers and the degree of ion pairing - upon pairing of chloride, water molecules in the first solvation shell are being replaced by sodium cations.

D. Aqueous slabs with a mixture of NaCl and NaBr

Sodium chloride is the dominant solute contained in sea water and aqueous sea salt aerosols. However, also other solvated species exhibit important atmospheric reactivity. Among these, bromide anions, the natural concentration ratio of which with respect to chloride equals to 1:650, play a prominent role. For example, it has been discovered recently, that the destruction of the surface layer of ozone in the Arctic during polar sunrise is due to bromine chemistry [13–15]. Interestingly, it seems that, relative to chlorine, bromine reactivity is enhanced more than would follow from the direct comparison of the relevant rate constants. Since our previous results suggested that ionic polarizability is responsible for the propensity for the surface, we have speculated that bromide relative (with respect to chloride) and absolute concentration at the air/water interface could be enhanced due to its larger value of polarizability.

In order to mimic the atmospherically relevant situation we have taken an aqueous slab saturated with NaCl from our previous simulations and "transmuted" one of the chlorides into bromide. We have actually performed two simulations, one with initial position of the bromide anion at the interface and another with bromide initially near the center of the slab. Results of these two simulations, i.e. the time evolution of the distance of bromide from the center of the slab, are presented in Fig. 8. The emerging picture is quite clear. If bromide is initially placed at the interface, it tends to stay there, while bulk solvated bromide finds its way to the surface within 500 ps. Bromide and chloride differ only marginally in their values of the ionic radii, however, bromide is significantly more polarizable (soft). It is obviously the difference in polarizabilities and the related energy gain from asymmetric solvation, which drives bromide to the interface.

In order to obtain better statistics and to quantify the difference between surface propensities of the two halides we have performed two sets of simulations, first for a slab doped with 0.6 M of NaCl and 0.6 M of NaBr, and second for a more concentrated slab with 3 M of sodium chloride and 3 M of sodium bromide. Fig. 9 shows representative snapshots (top views) of the surfaces of the slabs from the two simulations. Qualitatively, the emerging picture is clear already from these snapshots. Namely, both halides exhibit propensity for the interface, however, that of the more polarizable bromide ion is much stronger. Quantitative analysis shows that bromide is actually a surfactant, it's interfacial concentration being roughly twice the bulk value [48]. At lower concentrations of the salt mixture a linear regime prevails, i.e. the ionic interfacial concentrations are roughly the same as one would obtain from separate simulations of single salt (NaCl or NaBr) solutions at the appropriate concentration. However, the simulation of the highly concentrated slab shows non-linear effects, namely that bromide further replaces chloride at the interface and it's surface concentration exceeds three times that in the bulk. Also, due to a significant accumulation of negative charges at the interface, a larger amount of sodium cations is dragged towards the surface than in the low concentration solution.

Finally, Fig. 10 shows the accessible surfaces of the three ionic species along the MD trajectory for the concentrated mixed solution. We see again that bromide is a clear winner occupying more than 30 % of the air/water interface. In contrast, chloride covers less than 5 % and sodium cations less than 1 % of the surface area. The high absolute and relative (to chloride) propensity of bromide for the interface is in accord with recent SEM experiments, which show strongly increased surface concentration of sodium bromide upon wetting and re-drying of NaCl/NaBr co-crystals [49].

IV. CONCLUSIONS

The principal result of the present computational study is that the propensity for the air/water interface of polarizable ions (such as heavier halides) confirmed both experimentally and theoretically for aqueous clusters pertains also to surfaces of extended salt solutions in the whole concentration range. The determining factor is the value of the polarizability of the solvated ion - the larger the polarizability, the more the ion can profit from asymmetric solvation at the air/water interface. Our findings, which are indirectly supported by several experiments [7,6], contradict the standard Onsager model of the surface of simple electrolytes [16], which has been developed for solvated point charges and does not take polarization effects into account.

Quantification of the propensity of chloride anions for the surface of concentrated bulk salt solutions allowed to suggest a new kinetic model of photochemical reactivity of salt aerosols in the presence of ozone leading to a release of molecular chlorine [6]. Predictions based on this model, which involves heterogenous processes at the air/water interface of the aerosol, are in quantitative accord both with laboratory and field measurements [6,50,51]. Present simulations of mixed NaCl/NaBr aqueous solutions, which show a strongly enhanced interfacial propensity of bromide compared to chloride, have also direct implications for ozone destructing bromine chemistry above Arctic snow packs during polar sunrise [52].

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FIGURE CAPTIONS

Figure 1. Optimized structures of the $NaCl(H_2O)_6$ cluster. a) Contact Na^+/Cl^- ion pair, b) saddle point, i.e. the barrier between the contact and solvent separated ion pairs, and c) solvent separated ion pair corresponding to ionic solvation. O - red, H - white, Na^+ - brown, and Cl^- - yellow.

Figure 2. Accesible surface of the chloride anion compared to that of sodium cation for the $(NaCl)_4(H_2O)_{32}$ cluster.

Figure 3. Accesible surface of the chloride anion compared to that of sodium cation for the $(NaCl)_{32}(H_2O)_{28}$ cluster.

Figure 4. Density profiles of chloride anions, sodium cations, and water oxygens in a water slab with NaCl at a) infinite dilution, b) 1.2 M, and c) 6.1 M (saturation).

Figure 5. Accesible surface of the chloride anion compared to that of sodium cation for a water slab saturated with NaCl. Comparison between results using a polarizable (thick lines) and non-polarizable (thin lines) force fields.

Figure 6. Degree of ion pairing of chloride anions with sodium cations in a water slab with NaCl at a) 1.2 M and b) 6.1 M (saturation).

Figure 7. Aqueous chloride solvation numbers in a water slab with NaCl at a) 1.2 M and b) 6.1 M (saturation).

Figure 8. Time evolution of the position of a bromide anion in a water slab saturated with NaCl, placed initially at the surface or near the center of the slab.

Figure 9. Top views at representative snapshots from MD simulations of mixed NaBr/NaCl aqueous slabs at two different concentrations.

Figure 10. Accesible surfaces of bromide and chloride anions, and sodium cations for a mixed aqueous slab containing 3 M of NaBr and 3 M of NaCl.