# Gas Phase Cluster Formation of Sodium Chloride and Water: Monte Carlo Simulations

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Monte Carlo simulations of a system of 200 water and 24 NaCl molecules at 6 different densities in the range from 0.003 g/cm$^3$ to 0.999 g/cm$^3$ and $T = 125$ °C and 225 °C were performed to obtain some insight into cluster formation which should precede and determine the formation of aerosol structures and has possibly played some role in prebiotic atmosphere chemistry. Solute hydration occurs already at very low concentrations mainly in the form of hydrated molecules ("contact ion pairs"). At higher densities larger cluster structures are observed, leading rather continuously to the structure of the supersaturated 7.1 M NaCl solution at the same temperature. Radial distribution functions, coordination numbers and particle interaction energies are discussed with respect to the simulation parameters density and temperature.

## Introduction

The formation of gas phase clusters between ions and solvent molecules is a well known phenomenon and has been investigated by high-pressure [1–3] and low pressure [4] mass spectroscopy. For water vapour, molecular beam experiments have revealed the formation of clusters containing up to 180 molecules, with a maximal stability for $(H_2O)_{21}$ clusters [5, 6]. Above the ocean, aerosol particles, mainly consisting of water and sodium chloride are present with a maximum of particle density at about 500 m above sea level, and their concentration and size depends strongly on weather conditions: with clear weather and without wind, 10 µg/m$^3$ is the average value, increasing after a storm by a factor of 100 or more [7]. These aerosol particles are important factors in nucleation and cloud formation processes [8] and the reason for the observation of some atmospheric phenomena [9] and reactions [10].

In 1979, Woese published a most remarkable hypothesis on the occurrence of the first prebiotic biochemical reactions on the primitive earth [11]. According to this assumption, such reactions, leading to precursors of molecules essentially for the evolution of life, already occurred in the atmosphere, before earth cooled down to an extent to allow the condensation of water to a primordial ocean. The microstructures responsible for the reactions are supposed to be clusters and aerosol particles of water and mineral salts, in which the organic molecules formed in the atmosphere (e.g. amino acids) were captured and brought to reaction with each other ("salty-droplet-hypothesis").

The recent finding, that high sodium chloride concentrations can induce peptide condensation in the presence of copper ions in aqueous solution without any further condensation reagent [12, 13], has – besides being the so far simplest possible way to prebiotic peptides in aqueous solution – also given new actuality to Woese's hypothesis, as the same reaction might occur also in an aerosol, provided it would contain suitable structures held responsible for the salt-induced peptide condensation in solution [14]. It seemed of interest, therefore to investigate the possibility of NaCl/water cluster formation, especially of hydrated ion clusters, under conditions that could have been realized in the gas phase or aerosol state of a hot atmosphere.

Experimental investigations on such systems encounter serious technical problems. The advances of computational chemistry methods, especially simulation techniques, let however the application of Monte Carlo and Moleular Dynamics techniques seem a most promising approach to obtain structural information in detail. A simple MD simulation for the gas phase hydration of one NaCl molecule at 327 °C and 454 °C has been reported recently [15], showing the

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applicability of statistical methods for such systems. Within the context of questions raised here, however, lower temperatures and a larger ensemble of solvent and solute molecules seemed essential. We have decided, therefore to perform simulations of a highly concentrated NaCl/water system at varying conditions of density and lower temperatures.

## Method

The basic system for the Monte Carlo simulations presented here consisted of 200 water and 24 NaCl molecules (in the liquid state, this corresponds to a supersaturated 7.1 M sodium chloride solution). The interactions between species were described by well-tested potential functions obtained from literature (water-water: [16]; ion-water and ion-ion interactions from [17–21]).

The density was varied from 0.003 g/cm$^3$ to 0.999 g/cm$^3$, and for comparison a simulation of the supersaturated solution, previously presented for room temperature [16], was repeated for elevated temperature. All simulations were performed for two temperatures, 125 °C (near the boiling point of the solution) and 225 °C. Using the Metropolis sampling algorithm and periodic boundary conditions, 500 000 configurational steps were needed for equilibration, and a further million steps was used for sampling. For exponential terms, a cutoff of half of the periodic box length (liquid) or 10 Å (gas phase) was applied. For long range ion-ion interactions, a summation over two shells of neighbouring boxes (for numerical reasons starting from the outer sphere) was performed. No dielectric corrections for $\varepsilon$ of the surrounding were made, as most of the systems had very low densities, better represented by $\varepsilon = 1$.

Radial density distribution functions (RDF) and their integrations were evaluated, together with the distribution of first-shell coordination numbers. Further important information could be obtained from particle interaction energies in the systems.

All simulations were performed at the CONVEX 220 computer of the University of Innsbruck by a newly written MC program [22]. Depending on system conditions and computing technique, one simulation of 1.5 million steps needed between 1000 and 4000 minutes. Simulations were done for 6 gas phase densities at each temperature and for the liquid, thus leading to total computational effort of approximately 700 hours.

## Results and Discussion

### *1. Radial Distribution Functions*

Figure 1 shows the O–O radial distribution functions' development with increasing density of the system and the corresponding integrations for $T = 125$ °C. The RDF for 0.003 g/cm$^3$ has not been included in this graph, as it is very similar to that for $d = 0.008$ g/cm$^3$. Comparison of the curves shows that even at low densities a large amount of the water molecules is associated at least to dimers. The degree of association increases to an average water-water coordination number of 4–5 at 0.999 g/cm$^3$. While at low densities the peak for associated neighbouring water still displays a shoulder or at least tailing up to 7–8 Å, this cannot be observed any more at the highest density, the curve at 0.999 g/cm$^3$ is already nearly identical to that of the liquid at the same temperature ($d = 1.220$ g/cm$^3$). For this reason, the RDF for the liquid was also not included in the graph. A general feature of this diagram is the continuously decreasing O–O distance with increasing density, from 3.05 Å to 2.95 Å.

Figure 2 displays the $Na^+$–O RDFs under the same conditions. It is obvious that cation hydration takes place already at the lowest density, leading to $Na^+(H_2O)_{2-3}$ clusters, where two of the water molecules are in most directly bound to the ion, and some other waters to these two, thus representing water dimers bound to the ion (or a rudimentary "second hydration

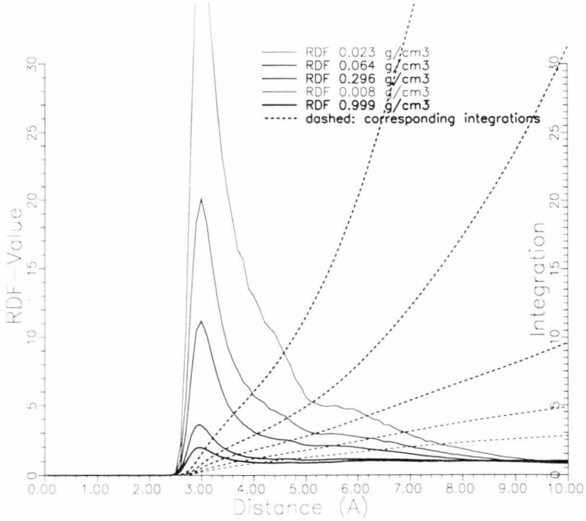

Fig. 1. Radial distribution functions for O···O distances in the gas phase system NaCl/$H_2O$ at various densities.

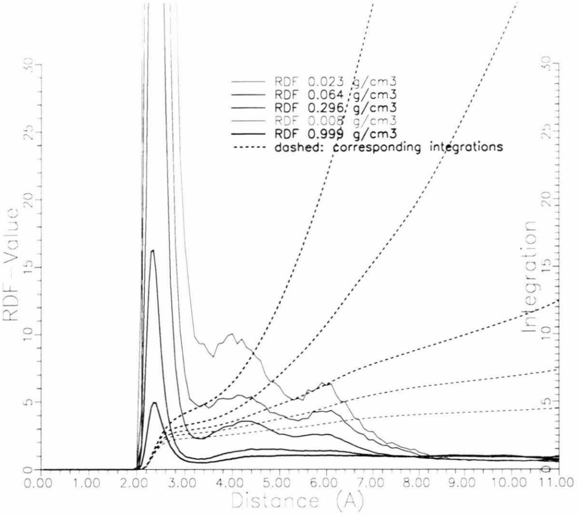

Fig. 2. Radial distribution functions for $Na^+ \cdots O$ distances in the gas phase system $NaCl/H_2O$ at various densities.

sphere"). With increasing density, the first shell solvation number increases to almost 6, whereas no secondary shell can be clearly distinguished after the density exceeds 0.3 $g/cm^3$.

The RDFs presented here also indicate that some characteristic features of cluster formation can be discussed better on the basis of a detailed first-shell coordination number statistics, as a second shell does not seem to be of major importance. Further structural results are presented therefore on the basis of coordination number distributions.

## 2. *Coordination Number Distributions*

As the structural transition from low to high density systems occurs rather smoothly, according to the previously discussed RDF's, it seemed sufficient to present in Table 1 only some characteristic cases, representing a low and a high density gas phase simulation, and to compare them with that for the liquid at the lower temperature. Due to elongated distances between particles in the gas phase, the first shell radii for $Na^+/H_2O$, $Cl^-/H_2O$ and $Na^+/Cl^-$ were taken at different values (in Å: 4.00, 4.00 and 4.50 for $d = 0.023$ $g/cm^3$, and 3.50, 4.00 and 4.00 for $d = 0.999$ $g/cm^3$ and liquid). For $Cl^-$ hydration, the determination of the minimum after the first peak is not unambiguous; therefore rather large hydration numbers result, the comparison, however, should reflect trends correctly.

Considering the data for $Na^+$ coordination by water in Table 1, a minimal average hydration (CN > 2) is even observed at very low density. At high gas phase density, average hydration number and distribution of probabilities become very similar to those of the liquid at the same temperature, with a maximum of probability for CN = 4. Closely related to these values is the direct binding of $Na^+$ to $Cl^-$ ions. At low density – although coordination numbers up to 3 are already observed – 60% of the sodium ions have one chloride as close neighbour, i.e. a large part of the clusters is made up of partially hydrated NaCl molecules. At higher density, CN's up to 4 are observed (more than in the liquid), and at the same time, the probability of CN = 0 is higher than for low density and liquid, indi-

Table 1. Percentual coordination number distribution and average coordination number (av. CN) for NaCl/water systems in gas phase and liquid at 2 temperatures (details for evaluation see text). NaW: $Na^+(H_2O)_n$-, ClW: $Cl^-(H_2O)_n$-, NaCl: $Na^+(Cl^-)_n$-coordination.

| | $T = 125$ °C | | | | | | | | | $T = 225$ °C | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $d = 0.023$ | | | $d = 0.999$ | | | liquid | | | $d = 0.023$ | | | $d = 0.999$ | | |
| | NaW | ClW | NaCl | NaW | ClW | NaCl | NaW | ClW | NaCl | NaW | ClW | NaCl | NaW | ClW | NaCl |
| 0: | 10.4 | 14.0 | 17.7 | 1.6 | 0.1 | 47.2 | 1.8 | 0.0 | 31.9 | 13.7 | 23.3 | 17.7 | 0.7 | 0.0 | 31.9 |
| 1: | 19.2 | 30.6 | 60.5 | 3.6 | 1.0 | 28.2 | 3.5 | 1.4 | 51.0 | 19.9 | 28.4 | 56.3 | 6.2 | 0.3 | 47.0 |
| 2: | 24.5 | 27.5 | 21.0 | 7.1 | 3.8 | 15.1 | 4.1 | 3.4 | 15.0 | 20.2 | 26.1 | 22.3 | 10.4 | 1.2 | 13.9 |
| 3: | 22.8 | 15.9 | 1.0 | 19.2 | 7.5 | 6.5 | 14.3 | 5.3 | 2.1 | 25.4 | 15.6 | 3.7 | 19.1 | 5.3 | 7.2 |
| 4: | 9.9 | 8.1 | – | 25.1 | 13.5 | 3.1 | 23.5 | 8.0 | – | 13.5 | 5.4 | – | 29.9 | 11.9 | – |
| 5: | 7.2 | 3.2 | – | 18.0 | 9.3 | – | 22.6 | 6.2 | – | 5.2 | 1.0 | – | 19.6 | 14.8 | – |
| 6: | 4.6 | 0.6 | – | 16.3 | 10.3 | – | 22.2 | 8.0 | – | 2.0 | 0.1 | – | 6.9 | 14.0 | – |
| 7: | 1.2 | – | – | 7.5 | 10.8 | – | 6.8 | 8.5 | – | 0.3 | – | – | 5.1 | 10.7 | – |
| 8: | 0.2 | – | – | 1.4 | 13.0 | – | 1.1 | 11.7 | – | – | – | – | 1.9 | 10.4 | – |
| 9: | – | – | – | 0.2 | 12.5 | – | 0.1 | 11.6 | – | – | – | – | 0.1 | 11.4 | – |
| av. CN: | 2.50 | 1.86 | 1.05 | 4.29 | 6.79 | 0.90 | 4.51 | 7.99 | 0.87 | 2.30 | 1.55 | 1.12 | 3.96 | 6.97 | 0.96 |

cating a special tendency for both ion-ion and ion-water cluster formation at this density in the gas phase.

Summarizing these results, the main species found at low and high gas phase density and in the liquid can be characterized as $(H_2O)_{2-3}Na^+(Cl^-)_1$, $(H_2O)_{3-6}Na^+(Cl^-)_{1-0}$ and $(H_2O)_{4-6}Na^+(Cl^-)_1$, respectively.

The chloride ions bind water molecules less than $Na^+$, especially in the low density system. At high density, the coordination number increases considerably, and even more for the liquid. Due to the large radius of evaluation, this increase is surely due to water molecules shared with $Na^+$ ions close to $Cl^-$. CN = 5 seems to be unfavourable for chloride at higher densities, including the liquid state.

### Effect of Temperature

Raising the temperature by 100° leads to some well observable trends for ion coordination. Whereas the number of coordinated water molecules decreases by about 10%, $Na^+-Cl^-$ association increases. At low density, this increase favours higher coordination numbers, whereas at high density 1:1 associates become the main species. The unsymmetric coordination number distribution for chloride-water disappears at this temperature, but $Cl^-$ is still well surrounded by water molecules. In the MD simulation for a gas-phase hydrated NaCl molecule [15], the authors reported not to observe hydration of the chloride site of the molecule. This may well be an effect of the considerably higher temperatures employed in that study (> 320 °C), as the $Cl^-/H_2O$ interaction energies are strongly influenced by temperature (cf. next section). It could be partly due, however, also to the use of a nondissociable NaCl molecule immersed in water vapour in that MD simulation, as slightly elongated Na ··· Cl distances are increasingly favoured in the clusters at lower densities, according to our results.

A comparison of the results obtained for the liquid state as presented here with those for the same system at 25 °C [23] shows, that coordination numbers have decreased slightly for sodium/water (4.9 to 4.5), strongly for chloride/water (14 to 8) and remarkably for sodium/chloride (1.5 to 0.9). To a large extent, these effects can be attributed to temperature, but especially for $Na^+/Cl^-$ the long-range corrections employed in this work can be held partially responsible for the reduced ion/ion association. This is confirmed by some preliminary simulations of the same solution employing the Ewald summation method for long-range interactions of all types [22].

Table 2. Interaction energies of species in gas phase clusters (kcal/mole).

| Densities (g/cm$^3$) | $Na^+/H_2O$ | $Na^+/Na^+$ | $Na^+/Cl^-$ | $Cl^-/H_2O$ | $Cl^-/Cl^-$ |
|---|---|---|---|---|---|
| **125 °C** | | | | | |
| 0.003 | −63.88 | 123.3 | −218.9 | −6.14 | 126.7 |
| 0.008 | −64.72 | 196.3 | −308.3 | −6.05 | 201.0 |
| 0.023 | −70.15 | 279.5 | −397.9 | −2.38 | 273.3 |
| 0.064 | −83.01 | 381.7 | −500.1 | −3.02 | 372.2 |
| 0.296 | −103.8 | 600.6 | −725.1 | −12.8 | 586.6 |
| 0.999 | −142.4 | 831.6 | −955.9 | −68.2 | 844.9 |
| Liquid | −161.1 | 864.6 | −986.1 | −67.5 | 854.8 |
| **225 °C** | | | | | |
| 0.003 | −54.34 | 122.8 | −225.7 | −1.15 | 129.0 |
| 0.008 | −59.65 | 196.8 | −291.1 | −3.16 | 189.3 |
| 0.023 | −61.97 | 280.5 | −398.5 | −4.29 | 275.5 |
| 0.064 | −75.34 | 373.6 | −499.9 | −7.96 | 381.1 |
| 0.296 | −94.50 | 604.1 | −741.1 | −13.1 | 604.0 |
| 0.999 | −144.3 | 820.3 | −943.9 | −46.5 | 800.8 |

### *3. Species Interaction Energies*

Interaction energies between ions and of ions with water are summarized in Table 2. At 125 °C, a continuous increase of energies is observed for all cases except chloride-water, which decreases until $d = 0.023$ g/cm$^3$ and reaches a larger value only at high density. This supports the previous assumption that at low densities the main species are partly hydrated NaCl molecules ("contact ion pairs") with weaker affinity to water in the chloride part, whereas at higher densities ion cluster formation is favoured. At 225 °C, this effect disappears. Apparently, the NaCl molecules start to lose the water molecules at the chloride site and hydrated ion cluster formation is the energy-determining process at all densities, thus leading to the same continuous increase with density observed for all other species interactions. As mentioned above, this result can also explain that no chloride-part hydration was observed in [15].

Another effect observable only at 125 °C is, that at very low densities (0.003 and 0.008 g/cm$^3$) interaction of $Na^+$ and $Cl^-$ with water seems to remain rather constant – the species formed under such conditions seem to be quite stable towards further "dilution" of the gas phase.

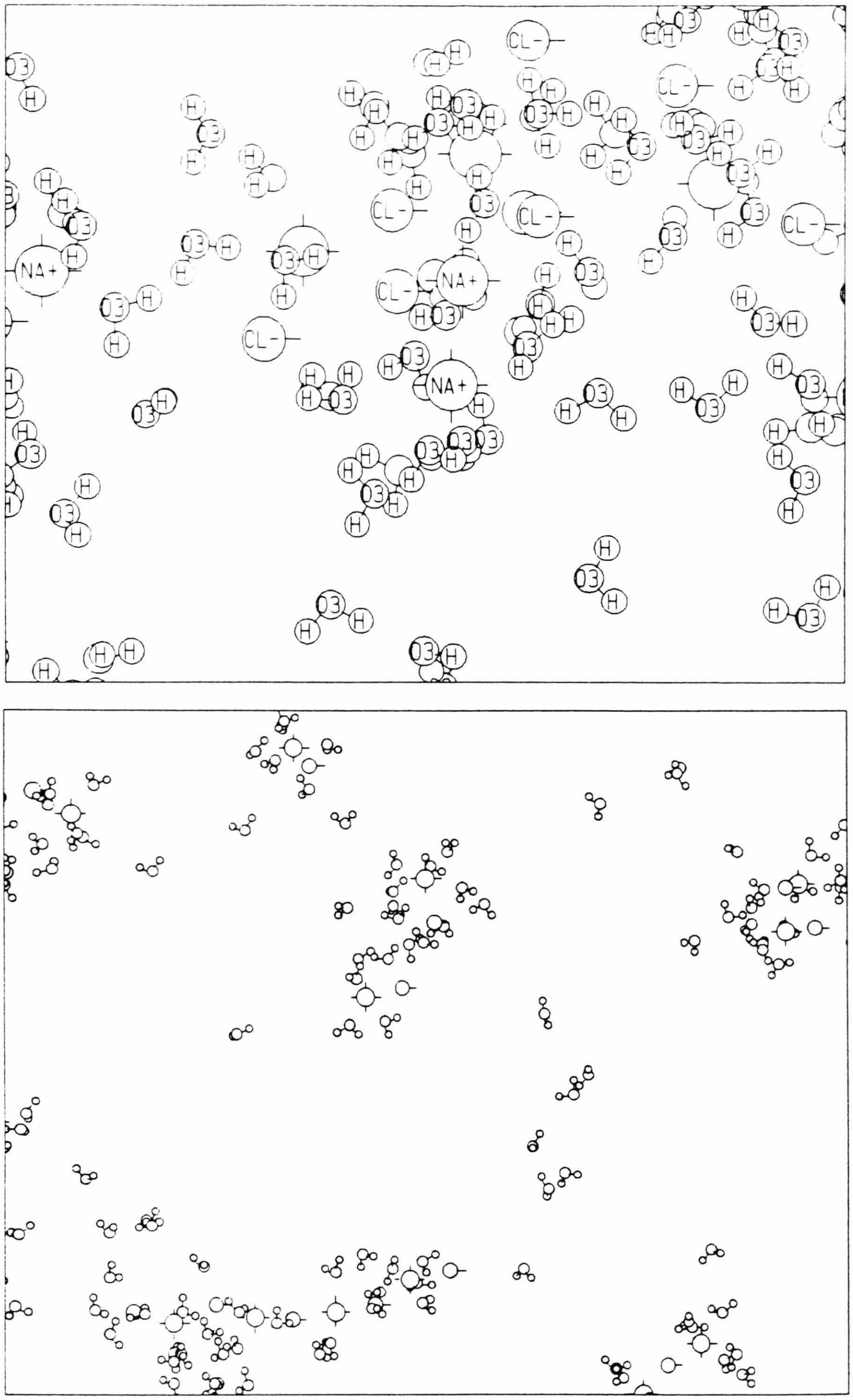

Fig. 3. "Snapshot" pictures of the gas phase system NaCl/$H_2O$ at 125 °C and the densities 0.296 (upper) and 0.023 g/cm$^3$ (lower part). In the lower figure, the ions can be recognized easily by their representation by larger circles (–O– for Na$^+$, O– for Cl$^-$). In the upper picture, approximately 31% of the elementary box are visible (12.5 × 8.0 × 18.7 Å), in the lower one 40% (14.3 × 11.6 × 18.7 Å).

Increase of temperature seems, at a first glance, to lower all interaction energies. Some deviations from this general feature seem to be noticeable, however: the increased $Na^+/Cl^-$ interaction at the lowest density (formation of more NaCl molecules), the energies almost identical to those at 125 °C for all ion-ion interactions at $d = 0.023$ g/cm$^3$ (compensation of lost ion hydration energy by ion-ion interactions), and the slightly higher contribution by sodium/water interactions at $d = 0.999$ g/cm$^3$, which may be related to a move of chloride hydration waters to sodium ions (in the same system, temperature reduces the chloride-water interaction by 1/3 of the value at 125 °C).

In order to illustrate the structures prevailing in the gas phase at lower and higher densities, "snapshot" pictures have been produced for two characteristic system configurations (Figure 3). These pictures demonstrate, that ion clusters are dominating in both cases as structural entities, at low density linearly associated clusters seem to be more favoured. Only a few isolated $H_2O$ molecules are observed, mostly they are associated as dimers, if they are not part of a ion hydration structure.

## Conclusions

As general result from the data reported in this study it can be concluded, that at moderate temperatures the gas phase system $NaCl/H_2O$ forms hydrated ion clusters even at very low density. At higher densities these clusters become more and more extended, smoothly leading to the structure of the condensed phase. The gas phase clusters provide structural entities and properties as required for the salt-induced peptide condensation in concentrated NaCl solutions reaction [13, 14]. If amino acids and copper ions were also present, this reaction may have occurred therefore also in a prebiotic atmosphere at a stage of evolution, where water could not yet condense on the earth's surface as postulated by Woese [11]. Besides this, the data presented here also seem to confirm the important role of NaCl in the formation of aerosols and in nucleation/cloud formation processes above today's oceans [8] and to provide some insight into microscopic structures involved in these processes.

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