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Precipitation Reactions in Water Clusters

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The reactions of hydrated metal cations $Ag^+(H_2O)_n$, $n = 11-26$, and $Na^+(H_2O)_n$, $n = 12-28$, with HCl were studied by FT-ICR mass spectrometry. One observes an efficient fragmentation due both to collisions and to blackbody radiation, as well as ligand exchange reactions. The number of HCl molecules which can be stabilized in a cluster depends on the number of H_2O ligands. In the case of $Na^+(H_2O)_n$ clusters, 12 and 15 H_2O ligands are needed to "dissolve" 1 and 2 HCl molecules, respectively, results very similar to $H^+(H_2O)_n$. On the other hand, in the case of hydrated silver cations, only 4 and 7 H_2O molecules are necessary to stabilize 1 and 2 HCl molecules. The difference is due to the fact that many water ligands are needed to stabilize the HCl and NaCl species which are ionically dissolved, while much less water is needed in the case of hydrated Ag^+ cations, which form within the cluster a covalently bound AgCl. The observed behavior reflects the large difference in the solubility products of NaCl and AgCl and shows that an analogue to bulk precipitation reaction occurs on a molecular level in clusters.

1. Introduction

It is well-known that solvents can have a profound influence upon the course of chemical reactions. Water is by far the most common solvent, and aqueous chemistry is important not only in industry and technology but also in the environment around us. Spectroscopy, usually the major tool for learning about the species involved in a chemical reaction and their interactions, is blunted by the various mechanisms of line broadening, so that relatively little detailed information can be obtained from bulk aqueous solutions. We have recently shown that ionized water clusters can be viewed as simpler, tractable model systems,[1−5] whose studies can often provide at least some microscopic information about the reactant solvation and its effects.

Using a molecular beam cluster source constructed in our laboratory, we can generate ions, both positively and negatively charged, solvated by up to well over 100 water molecules, and investigate their stability and chemical reactions. Our studies have shown that such clusters which are exposed to the room temperature background infrared radiation in the ion trap of the FT-ICR mass spectrometer gradually fragment.[6] In this way, one can remove the solvent molecules one by one, and thus investigate the effect of solvation upon chemical reactions. In this way, we have for instance been able to show that HCl will dissolve ionically in finite clusters just like in bulk water,[1,2] redox or neutralization reactions leading to salts can take place,[3,4] and even organic base or acid catalyzed reactions proceed as they do in bulk.[5] Most of these reactions can be viewed as basically bimolecular processes, involving collisions of two reactants in the presence of the solvent, and it is perhaps not surprising to find such parallels between their course in bulk solutions and in the finite clusters.

When two ions of opposite charge encounter each other in an aqueous solution, the outcome depends strongly on their specific nature. Thus, in general when an Na^+ ion encounters a chloride, Cl^- anion, no real reaction will take place, and the ions will remain in the solution. On the other hand, if an Ag^+ cation is substituted for the Na^+, a "precipitation reaction" will take place, resulting in solid AgCl formation, and removing essentially all silver cations from the solution. The two salts, NaCl and AgCl, differ substantially in their solubility products. Solubility is, of course, essentially a bulk property. The question to be addressed experimentally in the present paper is whether this difference in bulk solubilities will also be reflected in the behavior of hydrated ions in the mass spectrometer, and if similar to macroscopic systems, insoluble salt precipitation takes place in finite water clusters.

As noted above, NaCl is a highly soluble salt with a solubility product of $K_S = 37.7$ mol^2 L^{-2}.[7] On the other hand, formation of silver halides in aqueous solutions in the presence of halide anions is perhaps the best known precipitation reaction extensively used in analytical chemistry, and silver chloride specifically has $K_S = 1.7 \times 10^{-10}$ mol^2 L^{-2}.[8] To investigate possible precipitation reactions in clusters, we generate $Ag^+(H_2O)_n$ and $Na^+(H_2O)_n$ cations with up to about 50 water ligands, react them with hydrochloric acid, and try to gain insight into their structure by allowing them to fragment and by removing the water ligands from the product ion cluster one by one.

2. Experimental Details

The experiments were performed on a modified Spectrospin CMS47X mass spectrometer described in detail elsewhere.[9,10] Hydrated silver or sodium cations were produced by laser vaporization of a solid disk of the respective metal (Ag: Chempur, 99.995%+, Na: Merck, 99.8%+). The helium carrier gas (Messer Griesheim 4.6) at 10 bar backing pressure was seeded with 30 mbar of water vapor. The metal plasma was entrained in a pulse of the carrier gas, cooled by flowing through a confining channel and by subsequent supersonic expansion into high vacuum, resulting in formation of hydrated metal

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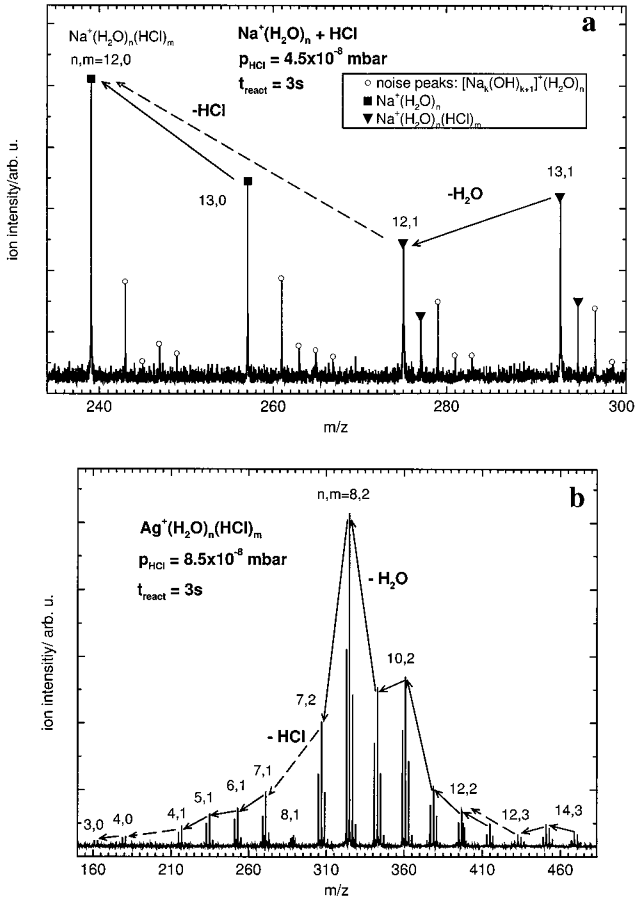

Figure 1. (a, top) Mass spectrum of the analogous reaction of hydrated sodium cations, $Na^+(H_2O)_n$, $n = 12-28$, after a reaction delay of 3 s at an HCl pressure of 4.5×10^{-8} mbar. The clusters have completely reacted with HCl and products $Na^+(H_2O)_n(HCl)$ have been formed. The dominant processes are blackbody radiation and collision-induced fragmentation, leading to the evaporation of either HCl or H_2O as shown by the arrows. Evaporation of an HCl molecule takes place at $n = 12$, as at this characteristic cluster size HCl recombines due to the lack of solvent molecules needed for ionic dissolution. Peaks labeled with circles belong to cluster ions $[Na_k(OH)_{k+1}]^+(H_2O)_n$, $k = 2,3$, that were also formed in the source and their reaction products. (b, bottom) Mass spectrum of the reaction of hydrated silver cations, $Ag^+(H_2O)_n$, $n = 11-26$, with HCl under the same conditions. The clusters are also saturated with HCl and the products have the composition $Ag^+(H_2O)_n(HCl)_m$. In this case, evaporation of an HCl molecule takes place at $n = 4$, $n = 7$, and $n = 12$.

cations. The ions were transferred through several stages of differential pumping into the high-field region of the superconducting magnet and stored inside the ICR cell at a background pressure of 6×10^{-10} mbar. The reactant gas HCl was introduced into the ultrahigh vacuum region via a needle valve at a pressure of typically 6×10^{-8} mbar. After varying delays, the ions remaining in the cell were excited, and the mass spectra of the reaction products identified.

3. Results and Discussion

Figure 1a shows the mass spectrum resulting from the reaction of a distribution of hydrated sodium cations $Na^+(H_2O)_n$, $n = 12-28$, with HCl hydrogen chloride. An advantage of the high-resolution FT-ICR experiment is that the elemental composition of each cluster can be unambiguously determined. One notes that after the relatively long 3 s reaction delay, aggregates of the $Na^+(H_2O)_n(HCl)_m$ composition have formed, with many clusters having exchanged one or more of their water ligands for HCl. It is also immediately evident that the number of HCl molecules m in the clusters is not random but depends on the cluster size. Thus, most clusters with $n \geq 16$ contain two HCl molecules, and clusters with 12−15 water molecules show characteristic chlorine isotopic doublets indicating the presence of one HCl, while clusters $n \leq 11$ are apparently not reacting with HCl at all.

The key to understanding these data is provided by our earlier, similar experiments with protonated water clusters.[1] In that study we have established that hydrochloric acid "dissolves" in $H^+(H_2O)_n$ clusters, and we obtained results almost identical to the present study: clusters with less than 10 water molecules did not dissolve any HCl molecules, those with $n \geq 10$ dissolved one and with $n \geq 13$ two HCl. We have explained these results in terms of ionic dissociation of the hydrochloric acid in the water cluster. For the ionic dissociation to proceed, the ligand water molecules have to stabilize not only the proton originally present in the cluster, but also the H^+ and Cl^- ions formed by the dissociation; apparently $\approx$10 solvent molecules represent the minimum for making the dissociation of one HCl energetically possible. Similarly, $\approx$13 water molecules are needed to dissolve ionically two hydrochloric acid molecules. Conversely, when the larger clusters $X^+(H_2O)_n(HCl)$ are allowed to fragment, when n reaches this 10 or 13 solvent molecules limit, the H^+ and Cl^- recombine, forming covalent HCl. Unlike H_2O, covalent HCl has only one proton with which to hydrogen bond, is bound weaker than the water ligands, and evaporates preferentially from the cluster. The similarity between these limiting values of n for solvated H^+ and Na^+ ions indicates that the specific nature of the central cation makes little difference, as far as the HCl dissociation is concerned.

In Figure 1b, similar data for $Ag^+(H_2O)_n$ ions are shown for comparison. Here an initial distribution with $n = 11-26$ was reacted with HCl for 3 s, and the mass spectrum of the resulting ion distribution was recorded. While qualitatively one can again observe the HCl dissolving in the larger hydrated clusters, quantitatively the limits discussed above for hydrated H^+ and Na^+ cations have shifted drastically. $Ag^+(H_2O)_n(HCl)_m$ cluster ions again form, but only $n \geq 4$ is now needed to dissolve one HCl, clusters with $n \geq 7$ dissolve two, and those with $n \geq 12$ dissolve three HCl molecules.

When the $Ag^+(H_2O)_n(HCl)_m$ are allowed to fragment, they again gradually lose water ligands until one of the above limiting values of n is reached. When this happens, a recombination of a proton and chloride anion within the cluster takes place, forming again a covalent HCl molecule, which evaporates instead. This stepwise fragmentation of the clusters is illustrated in Figure 1, with solid arrows denoting evaporation of H_2O, while evaporation of HCl is indicated by dashed arrows.

To understand the quantitative differences between the fragmentation, stability, and structures of the $M^+(H_2O)_n(HCl)_m$ in the case of Na and Ag, it is instructive to consider the differences in the properties of NaCl and AgCl. Since the reactions in the cluster proceed at relatively low temperatures, one can in many cases neglect the small entropic contributions and concentrate the discussion upon enthalpies of the individual processes. Figure 2 summarizes the thermochemical data for the solvation and dissociation of the two species as Born−Haber cycles. When NaCl(g) comes in contact with water, the bonds between Na and Cl will break and the molecule will dissolve ionically forming Na^+ and Cl^- ions. While such ionic dissociation of NaCl in the gas phase would require 557 kJ/mol,[11] it will proceed spontaneously and exothermically in solution due to the large hydration energies of the ions and their stabilization.

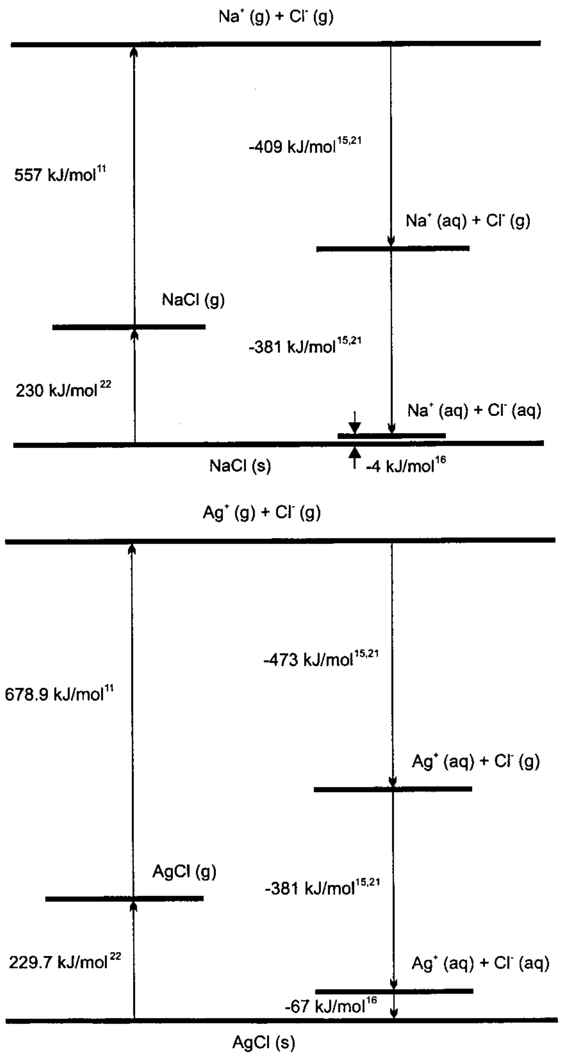

Figure 2. Born−Haber cycles of the dissolution process of NaCl and AgCl, respectively. The major difference between AgCl and NaCl is the difference in the energy needed for ionic dissociation, caused by the strong covalent character of AgCl. All other values are quite comparable. The sum of every cycle is not exactly zero because of the experimental errors.

The situation is quite different with silver chloride, which will not dissolve to any appreciable degree in water. Quite to the contrary, when solutions containing Ag^+ and Cl^- ions are brought into contact, AgCl precipitates out, even though in the gas phase the AgCl molecule is, with $D_0 = 311$ kJ/mol,[12] considerably weaker bound than NaCl with 408 kJ/mol.[12] Inorganic salts in solution do not dissociate into neutral atoms, but into ionic fragments, and the energy needed for ionic dissociation of AgCl in the gas phase, 678.9 kJ/mol,[11] is much higher than that of NaCl, 557 kJ/mol.[11] This in turn is due to the much higher ionization potential of silver atoms, 731 kJ/mol,[11] compared to 496 kJ/mol for sodium[11] and reflects also the higher covalent character of AgCl.[14] Even though the hydration energies of Ag^+ (473 kJ/mol)[15,21] and Na^+ (409 kJ/mol)[15,21] are comparable, in the case of silver chloride they cannot outweigh the much higher energy needed for ionic dissociation, as depicted in Figure 2. As a result, while the NaCl molecule will be in the larger water clusters dissociated into ions, the AgCl will be present in molecular form. The ability of much smaller $Ag^+(H_2O)_n$ clusters, down to $n = 4$, to accommodate one HCl molecule is due to the fact that the Ag^+ and Cl^- do not have to be individually stabilized by the solvent, but "precipitate" out of the solution as a diatomic AgCl molecule.

Grégoire et al. have recently reported results of resonance-enhanced two-photon photoionization spectroscopy experiments they have carried out with NaI−(solvent)$_n$ clusters (solvent = H_2O, NH_3, CH_3CN).[24] On the basis of the observed differences in the product cluster sizes, they proposed that charge separation into a Na^+/I^- ion pair does not occur for water clusters which contain as many as $n = 50$ molecules, whereas in ammonia and acetonitrile clusters it begins around a cluster size of $n = 9$ and $n = 6$, respectively, which seems to contradict our interpretation of a dissociatively solvated Na^+/Cl^- pair for $n > 12$. However, the additional proton in our study provides a considerably different environment from neutral clusters. Moreover, the possibility that the differences between water, ammonia, and acetonitrile reflect differences in the initial neutral cluster distribution rather than a different solvation behavior was not conclusively ruled out by Grégoire et al.

In comparing the behavior of the studied species in finite clusters with the bulk solution case, one has to consider the further stabilization of the solid salt by formation of crystal lattice. This stabilization energy for building the bulk NaCl(s) crystal from individual NaCl(g) molecules is 230 kJ/mol, and 229.7 kJ/mol[22] in the case of AgCl. This additional stabilization of course will further favor precipitation of AgCl(s) out of bulk solutions. It makes even the process of dissolving solid NaCl in water slightly endothermic, and this process was in fact in the past frequently used in the laboratory to generate low temperatures. The small positive enthalpy of the $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ process ($\Delta H_{hydr} = 4$ kJ/mol[16]) is near ambient temperature more than outweighed by the large and negative entropic contribution, resulting in a large negative value of the $\Delta G = \Delta H - T\,\Delta S$ of the dissolution process. The enthalpy of the $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ process, however, is too high ($\Delta H_{hydr} = 67$ kJ/mol[16]) to be outweighed by the entropic contribution which is comparable to that of NaCl.

In spite of the formation of molecular AgCl(aq) in the cluster, as water is gradually removed from the solvation shell, one finds that, as can be seen in Figure 1b, also here the last chlorine atom eventually leaves the cluster in the form of HCl(g), leaving behind an Ag^+ cation hydrated by the four remaining molecules of water. To understand this observation, one has to consider reaction 1:

$$AgCl(g) + H^+(g) \rightarrow Ag^+(g) + HCl(g) \qquad \Delta H = -715.7\ \text{kJ/mol}^{22} \quad (1)$$

In spite of this reaction being exothermic by more than 700 kJ/mol, it is, as discussed above, well-known that in aqueous solution the reaction essentially proceeds backward—upon addition of hydrochloric acid to a solution containing Ag^+, a silver chloride precipitate forms, with H^+ ions remaining in the solution. In order to understand this, it is instructive to explore the influence of solvent upon reaction 1, and consider the equilibrium 2 in the presence of n water ligands:

$$H^+(H_2O)_nAgCl \leftrightarrow Ag^+(H_2O)_nHCl \qquad (2)$$

As indicated by reaction 1, for $n = 0$ the equilibrium in the gas phase is entirely on the side of Ag^+ and HCl, reflecting the much lower ionization potential of silver atoms. The presence of molecules of solvent gradually shifts the equilibrium 2 in favor of $AgCl + H^+$, so that in bulk solution the AgCl precipitation is exothermic and proceeds essentially to completion. The main effect is the enormous hydration energy of the proton, which is stabilized in aqueous solution by 1091 kJ/mol.[15,21] Even though the stabilization energy of 473 kJ/mol[15,21] of the Ag^+ ions in water is also quite substantial, it is much smaller than that of the proton. While the difference in the ion stabilization energies, 658 kJ/mol, is still smaller than the exothermicity of reaction 1, this is in bulk solutions more than compensated by the lattice stabilization energy of AgCl (s). While the enthalpy of formation of a gaseous AgCl is +102.7 kJ/mol,[13] that of solid AgCl is −127 kJ/mol, indicating a large lattice stabilization energy ($\Delta H_{\text{lattice}}(\text{AgCl}) = 915.9$ kJ/mol, $\Delta H_{\text{lattice}}(\text{NaCl}) = 787.4$ kJ/mol[16]).

To understand the situation in finite clusters, one has to consider that also the solvation energy of the undissociated AgCl molecule is certainly not zero. The bond in AgCl is partially covalent, but still rather polar, and the water solvent has the effect of stabilizing polar structures. In the presence of a sufficient amount of water, that is for large n, the enthalpy of reaction 2 is positive, and the equilibrium (neglecting entropic effects at extreme dilutions) favors the side of undissociated AgCl. There is thus no problem of "nucleation" of the AgCl precipitation, and it proceeds efficiently even in relatively dilute solutions of Ag^+ ions. As the number of water ligands in a finite $H^+(H_2O)_nAgCl$ cluster is gradually reduced, the solvation energy of the AgCl molecule, and consequently also the enthalpy of reaction 2, is decreased. As shown by the experimental data, around $n = 4$ the enthalpy of reaction 2 approaches zero. The two limiting structures, $H^+(H_2O)_nAgCl$ and $Ag^+(H_2O)_nHCl$, become nearly isoenergetic, and the system becomes effectively bistable. A covalently bound, volatile HCl molecule may form, and evaporate from the cluster.

Support for this interpretation based on available thermochemical data can be found by examining the competing reactions 3 and 4:

$$(\text{Ag}-\text{Cl}-\text{H})^+(\text{H}_2\text{O})_4 \rightarrow \text{Ag}^+(\text{H}_2\text{O})_4 + \text{HCl} \qquad (3)$$

$$(\text{Ag}-\text{Cl}-\text{H})^+(\text{H}_2\text{O})_4 \rightarrow \text{H}^+(\text{H}_2\text{O})_4 + \text{AgCl} \qquad (4)$$

While no information is available about the reactant ion $(Ag-Cl-H)^+(H_2O)_4$, the right-hand side formation enthalpies were calculated to be $\Delta H_f(3) = 551$ kJ/mol and $\Delta H_f(4) = 631$ kJ/mol,[23] respectively, favoring HCl evaporation, as observed experimentally.

It would, of course, be quite interesting to gain some information about the detail of the structures of such clusters, and their change as a function of n. This could in principle be accomplished for instance by means of infrared photofragmentation spectroscopy. In an elegant study, Okumura and coworkers[25] recently observed a change in the core ion with increasing solvation as is known for a long time in atmospheric chemistry.[27,28] In $NO^+(H_2O)_n$ the change from NO^+ to H_3O^+ takes place at the same $n = 4$ value as is inferred from the data in our study for Ag^+ to H_3O^+. They obtained similar results for $NO_2{}^+(H_2O)_n$[26] as well.

Alternatively, one can gain some insight by ab initio theory. Some preliminary calculations we have done using the hybrid DFT B3LYP method[18] implemented in the Gaussian94 program package,[19] with 6-311++G(3d,3pd)/SECP wave functions,[20] yielded for the enthalpy of reaction 1 a value of 698 kJ/mol, in good agreement with the known thermochemistry. The optimized geometry of the $AgClH^+$ complex obtained at the same level of theory confirmed that its structure is consistent with an Ag^+ ion solvated by an HCl molecule ($AgClH^+$: $r_{AgCl} = 2.54$ Å, $r_{ClH} = 1.29$ Å, $\angle(AgClH) = 101.3°$; HCl: $r_{ClH} = 1.28$ Å; AgCl: $r_{AgCl} = 2.33$ Å). Calculations of the species in (2) would, however, be quite time-consuming, since a large number of competing isomers would have to be considered.

4. Conclusion

The reaction of both hydrated silver cations $Ag^+(H_2O)_n$, $n = 11-26$, and hydrated sodium cations, $Na^+(H_2O)_n$, $n = 12-28$, with HCl hydrogen chloride was studied by FT-ICR mass spectrometry. The observed ligand exchange reactions are accompanied by blackbody radiation and collision-induced fragmentation. The number of HCl molecules which can be stabilized in a cluster is critically dependent on the number of H_2O molecules present. In the case of the hydrated silver cation, four H_2O molecules are necessary to stabilize one HCl, seven to stabilize two, and 12 to stabilize three HCl molecules. In the hydrated sodium clusters, the corresponding numbers are 12 and 15 H_2O molecules for one and two molecules of HCl, respectively. Comparison with previous results on protonated water clusters shows that the hydrated sodium clusters behave like a hydrated proton cluster, in which the HCl molecules are presumably ionically dissolved, while in the hydrated silver cations a covalently bound AgCl embedded in a protonated water cluster is formed. To stabilize these species, only a few water molecules are necessary, while the ionic dissolution in the case of hydrated sodium cations requires a significantly larger number of water molecules. The observed characteristic cluster sizes for HCl intake correspond to the large difference in the solubility product of NaCl and AgCl. The results show that classic precipitation reactions indeed have counterparts on a molecular level in clusters.

One can, of course, not carry the comparison of the reactions proceeding in the relatively small water clusters with reactions in bulk solution too far, and one has to realize the differences between the two processes. The main difference in the case of salt formation is the fact that in the bulk solution precipitation solid, macroscopic AgCl crystals grow, while in the cluster a single AgCl molecule is formed. The bulk reaction is thus further promoted by the lattice energy, which is for many substances quite considerable. In the present case, the enthalpy of formation of gaseous AgCl, +102.7 kJ/mol,[13] is appreciably higher than that of solid AgCl, −127 kJ/mol.[11] The AgCl molecule is not formed isolated in the gas phase, but solvated by molecular water ligands, and since the bond is quite polar, the solvation energy will not be negligible. In spite of the above-mentioned considerable differences between reactions in bulk and in finite clusters, it is interesting that one can clearly see parallels, and the limited solubility of AgCl in aqueous solutions is clearly reflected in the behavior of Ag^+ and Cl^- ions in water clusters. Studies of such finite, relatively simple systems thus provide interesting insights and can eventually lead to a better microscopic understanding of the mechanisms and energetics of bulk solution reactions.

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(21) The present calculated values rely on the established value of $\Delta H_{\mathrm{aq}}(\mathrm{H}^+) = 1090$ kJ/mol while recently a new value, $\Delta H_{\mathrm{aq}}(\mathrm{H}^+) = 1150.1 \pm 0.9$ kJ/mol, was determined (Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R. *J. Phys. Chem. A* **1998**, *102*, 7787). Any of our conclusions is, however, not affected by this numerical shift.

(22) These ΔH values were calculated by subtracting the values for the heat of formation of the reactants from that of the products. The heat of formation values were taken from refs 13 and 16, respectively.

(23) These ΔH values were calculated by adding the ΔH values of the association reactions $\mathrm{E}^+(\mathrm{H_2O})_n + \mathrm{L} \rightarrow \mathrm{E}^+(\mathrm{H_2O})_{n+1}$, E = Ag, H, taken from ref 17 to the heat of formation values for the unsolvated ions (taken from ref 13).

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