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How Many Waters Are Necessary To Dissolve a Rock Salt Molecule?

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It is textbook knowledge that in order to dissolve rock salt in liquid water at ambient conditions at least nine water molecules per salt molecule are needed. An obvious but until now unsolved question arises: How many water molecules are necessary to solvate a single sodium chloride molecule? In other words, what is the smallest water cluster in which a solvent separated Na^+/Cl^- ion pair becomes stabilized? The answer, based on accurate quantum chemical calculations, is that simple extrapolation from the liquid is quantitatively wrong and that the *hexamer* represents the smallest water species that dissolves the NaCl molecule.

1. Introduction

It belongs to our everyday experience to dissolve rock salt in water. On the molecular level, sodium chloride separates into Na^+ and Cl^- ions surrounded by water molecules.[1,2] From the saturation concentration it can be deduced that, on average, nine water molecules are necessary to solvate NaCl.[3] The question whether this number really represents the smallest water cluster capable of dissolving a NaCl molecule has puzzled researchers for a long time. Moreover, quantitative understanding of molecular processes connected with the onset of ionic solvation has very practical implications. For example, environmentally important photolytic formation of molecular chlorine in a reaction of ozone with airborne sea-salt microparticles in the marine boundary layer crucially depends on their degree of hydration.[4]

The development of supersonic jet nozzles has enabled routine experiments in molecular clusters; however, no small NaCl−water heteroclusters have been measured so far. While solvation in the liquid can be easily accomplished, it is very hard to prepare small $NaCl(H_2O)_n$ complexes by supersonic expansion into the vacuum due to a very low vapor pressure of rock salt. The only measurement of this type which has not been, however, designed to directly detect solvent separated ion pairs concerns sodium iodide (which evaporates more easily than NaCl) in water and other polar cluster solvents.[3]

On the theoretical side, simulations of clusters with up to ten water molecules employing empirical[5] or semiempirical[6] interaction potentials did not lead to location of a solvent separated Na^+/Cl^- ion pair. Thermodynamic calculations based on a continuum dielectric model[7] and utilizing results from liquid-state molecular dynamics simulations[8] have provided an estimate that NaCl solvation occurs for clusters with more than 12 water molecules.[9] This simple and elegant approach is based on the knowledge from the liquid phase, and its predictive power for small clusters can be at best qualitative. As the authors state: “More accurate predictions might be possible by detailed microscopic calculations”.[9] It is the goal of the present paper to meet this challenge and answer the question in the title.

2. Method

In our search for the smallest water cluster which can dissolve a sodium chloride molecule, we have started from simple energy considerations, taking into account only the major electrostatic interactions. From simulations in liquid water[10] we know that a contact Na^+/Cl^- ion pair occurs at an interionic distance of 2.8 Å, while the solvent separated pair corresponds to a distance of approximately 5 Å. From the NaCl ionic potential curve[11] it can be deduced that the salt molecule itself is destabilized by such a solvation by some 65 kcal/mol. This is compensated by interactions of the solvated ions with water molecules. Both experiment[12,13] and theory[14,15] agree that the first water molecule stabilizes Na^+ by 23 and Cl^- by 15 kcal/mol while the stabilization per solvent molecule by additional one to five waters drops to 10−20 kcal/mol for the former and to 10−15 kcal/mol for the latter ion. Finally, the stabilization of the contact ion pair (i.e., the undissolved NaCl molecule) in small water clusters reads 12−18 kcal/mol per water molecule.[6,16] To obtain a first estimate on the size of a water cluster at which NaCl solvation becomes at all possible we simply put the above numbers together both for the contact and solvent separated ion pairs. From these rough considerations it follows that an approximate energy balance between the solvent separated and contact ion pairs is reached at the size of the trimer, with water monomer and dimer strongly disfavoring NaCl solvation.

Investigations of small NaCl−water clusters are within the reach of accurate quantum chemical computational methods.[17] Knowledge gained on pure water clusters[18−20] and complexes with a sodium[14] or chlorine[15] ion indicates that a practically converged level of description in terms of structure geometries and even relative energetics is computationally feasible for up to about six water molecules. Building on this experience, we have optimized structures of $NaCl(H_2O)_n$ ($n = 3-6$) clusters using the second-order Möller−Plesset (MP2) perturbation method with Pople’s 6-31G basis set augmented by a standard polarization set on heavy atoms and by a standard diffuse set on Cl in order to correctly describe the anion.[21] Harmonic frequency analysis has been performed for stationary points (minima and saddles) at the same level of theory. This level is comparable to that previously successfully applied to the description of the smallest $NaCl(H_2O)_n$ ($n = 1-2$) clusters.[16] Energies of the stationary points have been then recalculated at the coupled cluster level with single and double excitations and perturbative triples (CCSD(T)) with the same basis, and using the MP2 method with a standard triple-ζ McLean−Chandler basis

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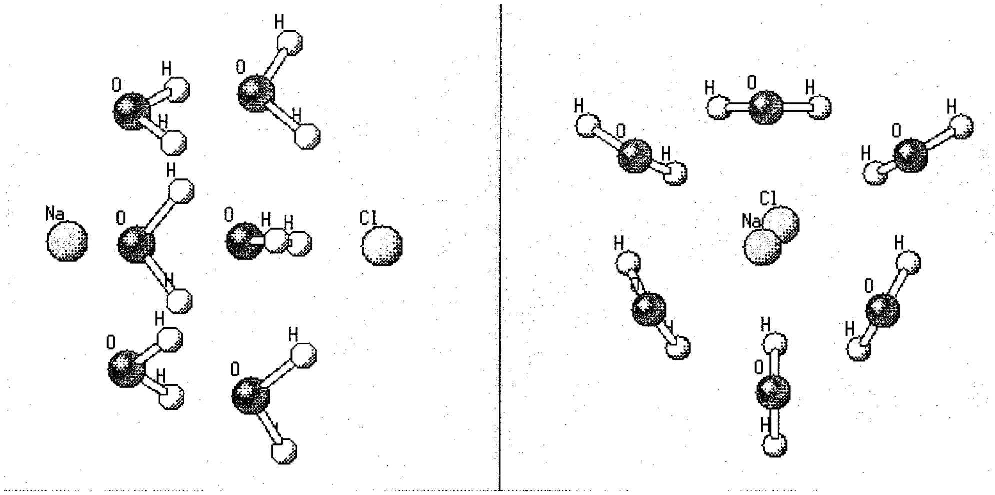

Figure 1. Side and top views on the geometry of the solvent separated Na$^+$/Cl$^-$ ion pair in water hexamer.

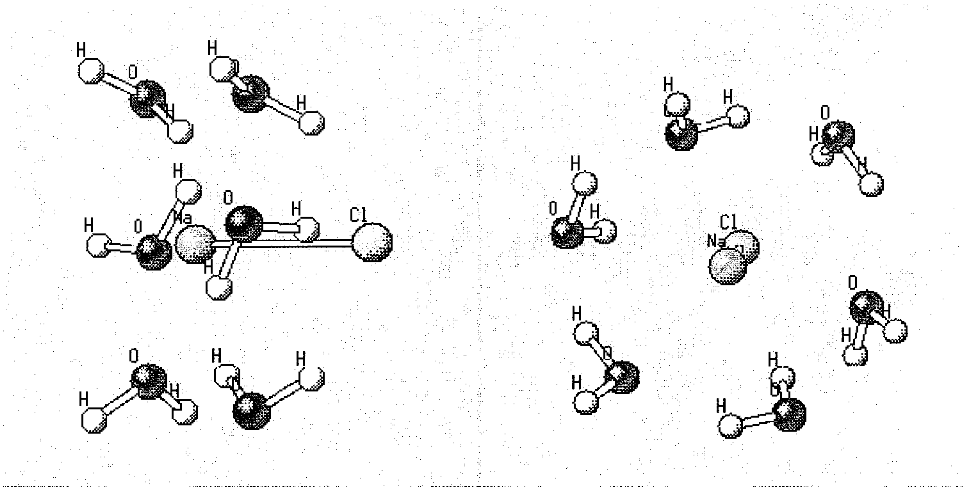

Figure 2. Side and top views on the geometry of the contact Na$^+$/Cl$^-$ ion pair in water hexamer.

set with two polarization functions on heavy atoms and one on hydrogens together with a diffuse set on chlorine.[21] In this way we have found that the relative energies are converged within ±1 kcal/mol. Moreover, the small effects of basis set extension and method improvement tend to cancel each other.

3. Results and Discussion

The only stable low-lying structures we were able to locate for complexes with three to five water molecules correspond to contact Na$^+$/Cl$^-$ ion pairs, surrounded by hydrogen-bonded water molecules. Although the Na−Cl bond length is elongated by 0.1−0.3 Å compared to the isolated molecule, the water molecules are unable to separate the ions. The definition of ion solvation in clusters requires an existence of an “unpaired” state separated from the “paired” state by a potential barrier,[9] therefore, water clusters up to the pentamer do not solvate sodium chloride.

The above search indicates that a compact noncyclic water structure is needed for stabilization of the solvent separated ion pair. The smallest water cluster which prefers such geometries is the water hexamer.[18,22] Especially the prism structure with two interconnected three-membered rings on top of each other[18] is a good candidate for NaCl solvation. Dangling hydrogens of the first ring can stabilize the chloride anion on one side of the cluster, and at the same time, oxygens of the second ring can electrostatically bind the sodium cation on the other side. According to the energy balance considerations presented above, such a structure may support a solvent separated ion pair. Although the solvated ions strongly modify the structure of the water cluster, this turned out to be a successful first guess leading eventually to a fully optimized structure depicted in Figure 1. The two ions are separated by 4.43 Å and the water molecules in between form two three-membered rings 1.67 Å from each other. All the individual water dipoles are nearly perfectly aligned in the electric field of the solvent separated ion pair.

In addition to the above structure we have found a second low-lying minimum corresponding to a contact ion pair with a Na−Cl bond length of 2.66 Å (see Figure 2). The water molecules form again two three-membered rings, separated, however, only by 1.39 Å and much better connected by a hydrogen bond network. The unsolvated NaCl molecule has sodium pointing into and chlorine away from the water cluster. The solvent separated and contact ion pair minimal geometries are separated by a saddle point with an interionic distance of 3.61 Å and a water structure closer to that of the latter minimum. Finally, we note that for all three stationary points more compact staggered rather than eclipsed water rings are preferred (allowing for a smaller interionic separation) and these structures possess a C_3 axis, although symmetry constraints have not been enforced during geometry optimizations.

The most important information concerning the energetics is summarized in Table 1. On the electronic potential surface the solvent separated pair lies slightly below the contact ion pair, and these two minima are separated by a relatively high barrier

TABLE 1: Energies (in kcal/mol) of the Contact Na^+/Cl^- Ion Pair and the Saddle Point Relative to the Energy of the Solvent Separated Ion Pair in Water Hexamer at Different Levels of Theory, Together with the Zero-Point Energy (ΔZPE) Corrections and Relative Free Energies (Δ*G*) at Ambient Conditions[a]

	contact ion pair	saddle point	solvent separated ion pair
$\Delta E(\mathrm{MP2/6\text{-}31_{+\mathit{Cl}}G^*})$	0.71	4.94	0 [−1078.91045]
$\Delta E(\mathrm{MP2/6\text{-}311_{+\mathit{Cl}}G(2d,p)})$	1.79	4.30	0 [−1079.46108]
$\Delta E(\mathrm{CCSD(T)/6\text{-}31_{+\mathit{Cl}}G^*})$	0.14	4.54	0 [−1078.98594]
$\Delta E(\mathrm{MP2/6-31_{+\mathit{Cl}}G^*}) + \Delta\mathrm{ZPE}$	−0.32	3.26	0 [−1078.75461]
$\Delta G(\mathrm{MP2/6\text{-}31_{+\mathit{Cl}}G^*}$, 298.15 K, 1 atm)	−0.63	2.79	0 [−1078.79764]

[a] In brackets are absolute energies (in atomic units) of the solvent separated ion pair

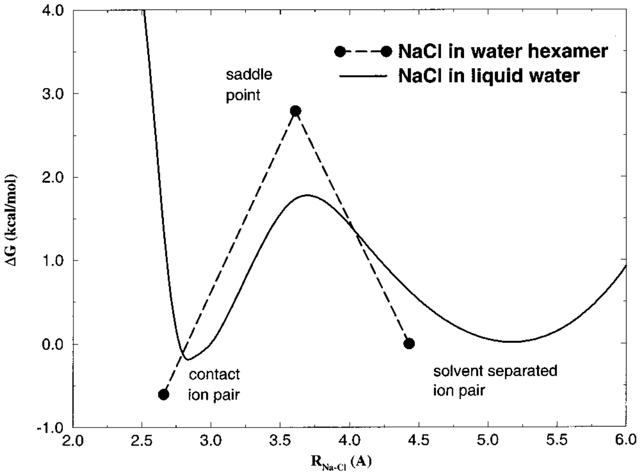

Figure 3. Free energy profile along the NaCl solvation path in water hexamer compared to the corresponding potential of mean force in the liquid (adopted from ref 10).

toward solvation of nearly 5 kcal/mol. The energy profile along the solvation reaction path results from a subtle balance between different (primarily electrostatic) forces. The solvent separated ion pair loses on the interionic interaction and on the water−water hydrogen bonding, the residual value of which (calculated as the difference between the energy of water hexamer in the geometry of the complex and six isolated water molecules) is only 3 kcal/mol. This is, however, compensated by a strong gain in ion−water interactions. The situation is exactly reversed for the contact ion pair where the water−water hydrogen bonding reaches 37 kcal/mol. This value is very close to the interaction energy of 40 kcal/mol of the prism form of the pure water hexamer.[18]

Accounting for the zero-point vibrational energy differences, the solvent separated and contact ion pairs become practically isoenergetic and the barrier between them is lowered by more than 1 kcal/mol (see Table 1). The table also shows relative free energies calculated at ambient conditions within the harmonic approximation. The temperature effect is slightly in favor of the contact ion pair; however, in agreement with ref 9 we have found that the relative entropy contribution in small clusters with confined volumes is only minor.The free energies are compared in Figure 3 to the potential of mean force along a path connecting the two ion pairs in liquid water.[10] We see quantitative differences between the cluster and the bulk. Primarily, the barrier is significantly higher in the cluster. Also, compared to the liquid both minima are shifted toward shorter interionic distances, indicating that the cluster represents a more compact environment. Therefore, the situation in the condensed phase cannot be directly extrapolated to clusters, and predictions based on simulations in the liquid[9] turn out to be quantitatively wrong. Structurally, this is due to the fact that in small clusters the ions are only partially surrounded by water molecules the intermolecular geometry of which, moreover, significantly differs from that in the bulk.

The reported existence of a stable solvent separated Na^+/Cl^- ion pair in water hexamer contrasts not only extrapolations from the liquid,[3,9] which have been discussed above, but also the result of a recent semiempirical cluster study using effective fragment potentials.[6] While the authors of ref 6 found as the most stable structure a contact ion pair, the geometry of which is similar to that depicted in Figure 2, they were not successful in locating solvated NaCl. We conclude that it is a solid fact at the present level of description, which is practically converged (and significantly more advanced than that applied in ref 6), that the solvated structure is a *true* minimum separated from the nearly isoenergetic contact ion pair by a first-order saddle point, thus fulfilling the requirements for cluster solvation.[9]

4. Conclusions

It has been shown in this paper that *six* water molecules are needed to dissolve a rock salt molecule. This result is not accidental—hexamer is the smallest water cluster which forms a balanced three-dimensional noncyclic structure which can stabilize a solvent separated Na^+/Cl^- ion pair. Such conclusion, however, cannot be reached by extrapolation from the liquid, which strongly overestimates the minimal size of the cluster. Computationally, the answer can only be obtained by descending to the microscopic level using accurate quantum chemical calculations. The finding that as little as six water molecules dissolve NaCl not only answers the old question concerning the onset of ionic solvation but is also directly relevant to studies of reactivity of atmospheric sea-salt microparticles, where the key role of hydrates has been discovered recently.[4,23−24] To come closer to these atmospheric microbrines we are currently pursuing a combined quantum chemical and molecular dynamics study of much larger highly concentrated saltwater clusters. The goal is to study the cluster size effect on the competition between full and surface solvation and on the formation of ion pairs. Finally, we note that in order to measure cluster solvated sodium chloride it is important to build the experimental setup in a way that allows the NaCl molecule to overcome the relatively high barrier on the path toward the solvent separated ion pair. Rather than trying to place a NaCl molecule on water hexamer, a better strategy might be to gently merge $Na^+(H_2O)_3$ and $Cl^-(H_2O)_3$ cluster ions, which can be relatively easily prepared.[12,13]

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