Quantum Chemical Investigations on Solvated NaCl Adducts

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Ab initio MO calculations on solvated NaCl adducts are presented. They provide insight into effects to be expected upon oligomerisation of NaCl in aqueous solution or, vice versa, during the last step of the dissolution/solvation process in water. Extrapolation of the data obtained predict the minimal nucleation size for the formation of NaCl crystals to be represented by a $(NaCl)_{\sim 100}$ aggregate.

Introduction

In the past, quantum chemical investigations on the interaction of water molecules with ions have allowed to obtain numerous informations about geometry and hydration numbers of anions and cations [1 – 3]. For larger solvent molecules as ligands they have also predicted structure changes and rearrangements of the solvent in the field of these ions by chelate formation [4].

Potential curves for various solvated species such as $(H_2O)_3NaCl(H_2O)_3$, $(H_2O)_3Na^+(H_2O)Cl^-(H_2O)_3$, $Na^+(H_2O)_4Cl^-(H_2O)_4$ and $Na^+(H_2O)_4^{I}(H_2O)_2^{II}$-$Cl^-(H_2O)_4$ (II indicating the second solvation sphere), have been obtained recently, and the tendency of NaCl to dissociate in water into fully solvated ions is reproduced well by these potential curves [5]. They also indicate, that the association process of Na^+_{aq} and Cl^-_{aq} should start with a partial breakdown of the second solvation sphere of sodium, and that an intermediate formation of a "solvent-separated ion pair" is not to be expected but that the breakdown of the first solvation shell should occur rather simultaneously at cation and anion leading to the solvated molecule NaCl.

The process of aggregation of these solvated molecules to larger units and the comparison of these units with unsolvated lattice subunits is the subject of this work. Combination with the over-all potential curve obtained in the former calculations [5] and thermodynamic lattice data should then lead to an approximate reaction pathway for the association/dissociation reaction of NaCl in water.

Method

The ab initio MO-SCF procedure has been employed for all calculations, using well tested minimal (4s/2p for Na, 6s/3p for Cl) GLO basis sets [6, 7], and 2s/1p for oxygen in the water molecules [8]. These basis sets have been shown to give reliable series of relative bond energies and better absolute values than other minimal basis sets (e.g. STO3G) [8, 9].

The geometry of the water molecules has been kept constant throughout the calculations ($O-H = 0.957$ Å, $H-O-H = 104.5°$). The O-ion distances in hydrated cyclic $(NaCl)_2$, $(NaCl)_3$, $(NaCl)_4$, and NaCl itself have been optimized. The angles between the water molecules in these systems were optimized in the way illustrated in Fig. 1a – 1d, assuming C_{2v} and C_{3v} symmetry, respectively, in relation to the hydrated atom.

The NaCl distance in solvated and unsolvated NaCl-type lattice subunits was also optimized. The energy calculation for the monomer was also carried out using a more extended basis (10s, 6p(61111/411)+P for sodium and 12s, 8p(6111111/41111)+P for Cl^- ion; the exponents were taken from [10]). For the polarization functions of sodium and chloride the exponents 0.3 and 0.5 were chosen. The comparison (Table 2) shows, that the agreement of both results is very satisfactory for bond distance and energy at the optimized distance. Thus, the use of the minimal basis set seemed to provide sufficient accuracy for the treatment of larger units.

All calculations were performed at the CDC Cyber 74 computer of the University of Innsbruck. The program used is discussed detail in [11].

Results and Discussion

The hydration energies per water molecule for hydrated NaCl, cyclic $(NaCl)_2$, $(NaCl)_3$, and $(NaCl)_4$ are presented in Table 1.

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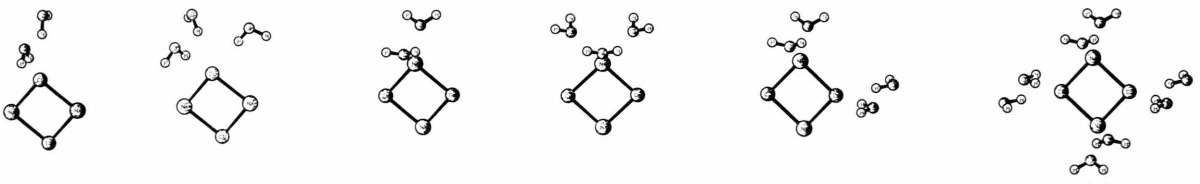
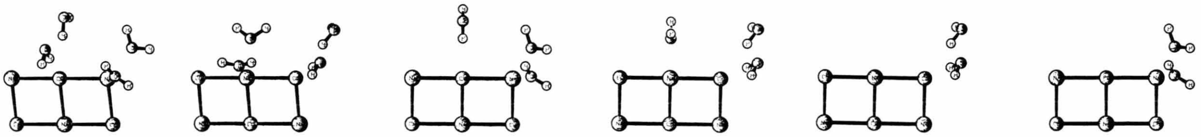


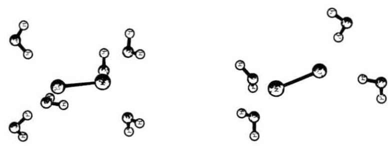
A1 A2 A3 A4 A5 A6

Fig. 1a system A. Hydrated cyclic $(NaCl)_2$. A1: O–Cl–O (Θ_2) = 78.0°; A2: O–Cl–O (Θ_2) = 74.0°; A3: O–Na–O (Θ_1) = 108.0°; A4: O–Na–O (Θ_1) = 87.5°; A5: O–Na–O (Θ_1) = 108.0°, O–Cl–O (Θ_2) = 78.0°; A6: O–Na–O (Θ_1) = 108.0°, O–Cl–O (Θ_2) = 78.0°.



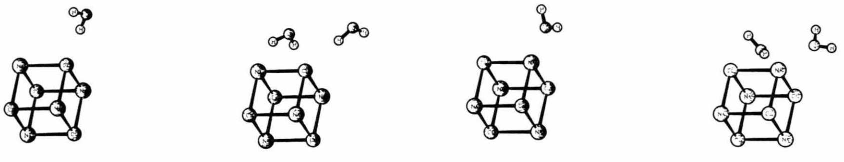
B1 B2 B3 B4 B5 B6

Fig. 1b system B. Hydrated cyclic $(NaCl)_3$. B1: O–Na–O (Θ_1) = 108.0°, O–Cl–O (Θ_2) = 78.0°; B2: O–Na–O (Θ_1) = 102.0°; O–Cl–O (Θ_2) = 78.0°; B3: O–Na–O (Θ_1) = 108.0°, †; B4: O–Cl–O (Θ_2) = 78.0°, ††; B5: O–Cl–O (Θ_2) = 78.0°; B6: O–Na–O (Θ_1) = 108.0°.



C1 C2

Fig. 1c system C. Hydrated NaCl. Cl: O–Na–O (Θ_1) = 102.9°, O–Cl–O (Θ_2) = 91.2°; C2: O–Na–O (Θ_1) = 108.0°, O–Cl–O (Θ_2) = 78.0°.



D1 D2 D3 D4

Fig. 1d system D. Hydrated $(NaCl)_4$. D1: *; D2: O–Na–O (Θ_1) = 88.0°; D3: *; D4: O–Cl–O (Θ_2) = 78.0°.

* The oxygen of the water molecule is situated in the prolongation of the space diagonal of the $(NaCl)_4$-cube.
† The water molecule lies in a plane perpendicular to the $(NaCl)_3$-plane with linear hydrogen bond.
†† The water molecule lies in a plane perpendicular to the $(NaCl)_3$-plane.

The hydration energy for cyclic $(NaCl)_2$, where Cl^- is coordinated with three water molecules, amounts to 84.1 kcal/mol. The hydration energy of the same system, Cl^- being coordinated with two molecules of water only, is 82.2 kcal/mol.

In the case of three and two water molecules coordinated at one Na atom of cyclic $(NaCl)_2$, the corresponding energies are 98.3 and 94.0 kcal/mol, respectively. This indicates, that hydrated cyclic $(NaCl)_2$ should not carry more than two water molecules at Cl and, probably, also at the Na atom.

Thus one can suggest the possible first step of aggregation of solvated NaCl molecules (carrying 6 water molecules) to be a partial breakdown of the

Table I. Ab initio energies of hydrated NaCl, $(NaCl)_2$, $(NaCl)_3$, $(NaCl)_4$.

System	Number of H_2O	Optimized distance (Å)	Optimized O-Ion distance (Å)		Optimized angle		Hydration energy/H_2O	Hydration energy
		R (Na–Cl)	R (Na–O)	R (Cl–O)	Θ_1	Θ_2	(kcal/mol)	(kcal/mol)
A_1	2	2.49	–	3.19	–	78.0	41.1	82.2
A_2	3	2.50	–	3.25	–	74.0	28.0	84.1
A_3	2	2.49	2.20	–	108.0	–	47.0	94.0
A_4	3	2.50	2.22	–	87.5	–	32.8	98.3
A_5	4	2.50	2.20	3.19	108.0	78.0	28.0	112.1
A_6	8	2.52	2.20	3.19	108.0	78.0	20.0	160.0
B_1	4	2.52	2.20	3.19	108.0	78.0	41.3	165.3
B_2	4	2.52	2.20	3.19	102.0	78.0	40.1	160.4
B_3	3	2.52	2.20	3.17	108.0	†	52.5	157.4
B_4	3	2.52	2.20	3.19	††	78.0	48.0	144.0
B_5	2	2.52	–	3.19	–	78.0	67.4	134.8
B_6	2	2.52	2.20	–	108.0	–	74.1	148.1
C_1	6	2.46	2.20	3.19	102.9	91.2	12.4	74.5
C_2	4	2.41	2.18	3.17	108.0	78.0	13.3	53.3
D_1	1	2.55	2.20	–	*	–	216.9	216.9
D_2	2	2.55	2.21	–	88.0	–	112.4	224.8
D_3	1	2.55	–	3.19	–	*	210.8	210.8
D_4	2	2.55	–	3.23	–	78.0	107.9	215.7

A Hydrated cyclic $(NaCl)_2$ (these structures (A_1–A_6) are shown in Fig. 1 a).
B Hydrated cyclic $(NaCl)_3$ (these structures (B_1–B_6) are shown in Fig. 1 b).
C Hydrated NaCl (these structures (C_1, C_2) are shown in Fig. 1 c).
D Hydrated $(NaCl)_4$ (these structures (D_1–D_4) are shown in Fig. 1 d).
† The water molecule lies in a plane perpendicular to the $(NaCl)_3$-plane (with linear hydrogen bond).
†† The water molecule lies in a plane perpendicular to the $(NaCl)_3$-plane.
* The oxygen of water molecule is situated in the prolongation of the space diagonal of the $(NaCl)_4$-cube.

Table 2. Ab initio energies, optimized distance and charges for subunits of the NaCl ionic lattice. Ab initio energies calculated at the experimental NaCl lattice distance (2.81 Å) and calculated ionic charges.

System	Optimized distance (Å)	Association energy (kcal/mol) ($nNa^+ + nCl^- \rightarrow nNaCl$)	Charge	Association energy (kcal/mol) ($nNa^+ + nCl^- \rightarrow nNaCl$)	Charge
	2.35 2.36[a] 2.38[b]	−136.8 −130.0[a] −136.7[b]	0.961 0.837[b]	−121.6 −127.6[b]	0.985 0.847[b]
	2.46	−170.0	0.950	−157.5	0.976
	2.51	−170.1	0.948	−159.2	0.972
	2.51	−172.9	0.946	−162.4	0.971
	2.49	−176.6	0.949	−164.9	0.973
	2.51	−181.1	0.948	−169.7	0.972
	2.54	−187.5	0.943	−177.6	0.968
Experimental data (Crystal)	2.81[c]	−187.0[c]	–	−187.0	–

[a] Value taken from Ref. [13, 14].
[b] Value calculated with extended basis set.
[c] Ref. [12].

solvation sphere at all four ions, leading to hydrated $(NaCl)_2$, where the Cl and Na atoms are coordinated with $2\,H_2O$ each.

The results for the optimized solvated subunits of NaCl, cyclic $(NaCl)_2$, $(NaCl)_3$, and $(NaCl)_4$ indicate that the water interacts strongly with these species solvating them with an increasing hydration energy per mole, which seems to reach a limiting value approximately at the tetramer.

Considering the case of larger crystals, the ratio between solvated molecules at the surface and molecules inside the crystal becomes smaller. The extrapolation of the surface solvation energy, using the energy values obtained for the tetrameric subunits, leads to the total hydration energies for larger crystals as given in Fig. 2, curve a, assuming that every Na and Cl atom at the surface of the $(NaCl)_n$ species is coordinated to two water molecules.

The stabilization energies, geometries and charges for some unsolvated subunits of NaCl-type ionic crystals are listed in Table 2.

The comparison of the optimized distances with the experimental [12] lattice distance shows that the latter is considerably larger. Therefore, the stabilization energies for the geometry optimized oligomers are higher than the corresponding values at the experimental distance, and the bonds in the units with the optimized distances prove to be less ionic. These small subunits with their smaller distances and higher energies reflect well the experimentally shown phenomena of higher surface energies and shortened bonds near the surface.

The energy data for several structures as given in Table 2, show that the formation of cubic subunits is clearly favoured over planar structures, even for the smallest subunit of $(NaCl)_4$. The association energy value for this cube calculated at the experimental distance is still 10 kcal below the experimental lattice energy, which seems to be a quite reasonable. For the optimized distance, which might be compared with a "surface corner" of a NaCl crystal, the full lattice energy is almost reached.

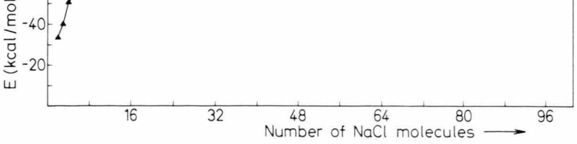


Fig. 2. Comparison between energies for surface hydration (curve a) and lattice (curve b).

Based on the data for the optimized subunit, an electrostatic approach was employed in order to obtain approximate stabilization energies for larger crystal subunits. Using the optimized distances and varying the atomic charges in the subunits, the electrostatic energy was fitted to the quantum chemical energy data calculated for the smaller oligomers.

The energy of larger unsolvated crystals was then extrapolated by a simple electrostatic calculation using these optimized charges, being $+0.993$ and -0.993, respectively, and 2.54 Å as interionic distance. These energies, up to the $(NaCl)_{96}$ crystal, are also given in Fig. 2 (curve b). The figure shows a crossing of both the solvation and the lattice curve, corresponding to a number of approximately 60 NaCl molecules. At this point, the total hydration energy of crystal subunits should not exceed any more the stabilization energy acquired by the ion interaction inside the crystal.

One can estimate, therefore, that the minimal size of a microcrystal required for the formation of larger crystals is a subunit consisting of at least 60 NaCl molecules, corresponding to a cube with edges of approximately 8 Å. The size, where the level of maximal solvation energy is surpassed by the lattice energy, is reached at about 100 NaCl molecules, corresponding to a cube of about 9–10 Å edge length. From that point on, growing of the crystal should be energetically favoured over redissolution.

This state of aggregation corresponds, therefore, to the minimal nucleation size for $(NaCl)_s$ formation from aqueous solution. For comparison, the experimental determination of homogeneous nucleation of ice in distilled water [15], shows that the critical cluster size in this case is about $(12\ \text{Å})^3$. The data thus obtained provide insight only into reaction energies. The probability of formation of this necessary minimal cluster size dependent on the concentration of the solution cannot be predicted by our data.

Acknowledgement

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