Models of Monovalent Ions Dissolved in Water

Lavinia L. PRUTEANU[1,2], Lorentz JÄNTSCHI[1,2,*,‡], Mihaela L. UNGUREŞAN[2], Sorana D. BOLBOACĂ[3,‡]

[1] Babeş-Bolyai University, Institute for Doctoral Studies, Kogălniceanu Street no. 1, 400084 Cluj-Napoca, Romania.

[2] Technical University of Cluj-Napoca, Department of Physics and Chemistry, Muncii Blvd. no. 103-105, 400641 Cluj-Napoca, Romania. E-mails: lavinia@chimie.utcluj.ro (LLP), lori@chimie.utcluj.ro (LJ), mihaela@chimie.utcluj.ro (MLU)

[3] Iuliu Haţieganu University of Medicine and Pharmacy, Department of Medical Informatics and Biostatistics, Louis Pasteur no. 6, 400349 Cluj-Napoca, Romania. E-mail: sbolboaca@umfcluj.ro

* Corresponding author: Phone: +4-0264401775, Technical University of Cluj-Napoca, Department of Physics and Chemistry, Muncii Blvd. no. 103-105, 400641 Cluj-Napoca, Romania; ‡ These authors equally contributed to the work.

Abstract

A computational study on water-ions clusters for six ions (NH_4^+, F^-, Cl^-, Li^+, Na^+, and K^+) is described. Restricted Hartree-Fock method with 6-31G* basis set was used to optimized the investigated water ion-clusters. Stable ion-water clusters proved to form with four ($NH_4^+ \cdot 4H_2O$ and $Li^+ \cdot 4H_2O$), five ($Cl^- \cdot 5H_2O$ and $Na^+ \cdot 5H_2O$) and respectively six water molecules ($F^- \cdot 6H_2O$ and $K^+ \cdot 6H_2O$). The arrangement of water molecule around investigated ions proved not symmetrical. Furthermore, the investigation of the stability of dodecahedron cages constructed with the investigated ions showed stable symmetry for $O_{12}N_8H_{50}$, $O_{12}Li_8H_{18}$, and $O_{15}K_5H_{29}$.

Keywords: ion-water cluster; monovalent ion; stabilization

Introduction

Structure of the water is a subject of theoretical physics [1], and differs significantly from gaseous state and solid state (ice) to liquid state (where is known the lack of geometrical symmetries which make more difficult the analysis) [2]. Fifteen phases of ice formed by two "close-packed" structures have been identified: hexagonal (at upper temperatures) [3] and cubic (at lower temperatures) [4-6]. The distances between atoms in ice proved to be either 100pm (d(O─H)) or 175pm (d(O…H)) [7]. The d(O─H) length of water was determined experimentally [8] and furthermore calculate at different levels of theories (Table 1 [8]), showing that the top 3 closest values are given by the following methods: M06-2X/6-31G*, HF/3-21G* and MP3/6-31G*.

Table 1. d(O─H) length in water: experimental vs. calculated [8]

Method	d(O─H) pm
Experimental	95.78
MP4/6-31G*	97.03
MP3/6-31G*	96.68
MP2/6-31G*	96.89
M06-2X/6-31G*	96.56
HF/6-31G*	94.73
HF/3-21G*	96.65
HF/STO-3G	98.92

Water clusters, hydrogen bounded assembly [9] (the simplest being the water dimer $(H_2O)_n$, where n=2), are important components of the atmospheric chemistry [10]. Different water clusters such as $(H_2O)_6$ (proved changes of

properties on different methods of temperature transition and density [11]); $(H_2O)_{20}$ as dodecahedron [12], edge-sharing pentagonal prisms, fused cubes, and face-sharing pentagonal prisms [13], etc. were identified and investigated.

Ion-water clusters $X[H_2O]_n$ (where X is the ion) properties have also been investigated. The importance of $(H_2O)_{20}$ surrounding monovalent cations have been demonstrated by infrared photodissociation spectroscopy and blackbody infrared radiative dissociation [14]. Global minimum were identified for $Na^+(H_2O)_{20}$, $Cl^-(H_2O)_{17}$, and $Na^+(H_2O)_{100}$ using PBHaT algorithm (a hybrid algorithm able to sample efficiently the partition function from the global minima to the liquid state) [15].

The aim of our research was to investigate the bond angles and distances in ion-water clusters on stable states, defined as the equilibrium state for which adding water molecules change neither the distances in ion-water cluster nor angles between atoms in the cluster, for NH_4^+, F^-, Cl^-, Li^+, Na^+, and K^+. Further, by using the dodecahedron arrangement of water and ammonia molecules, the possible stable states as a preparative step to provide information about water + ammonia mixtures were explored.

Materials and Methods

In-silico computation study was conducted for six ions: NH_4^+, F^-, Cl^-, Li^+, Na^+, and K^+. The geometry optimization of water ion-clusters was performed using restricted Hartree-Fock (RHF) method (proposed in [16- 20]) with 6-31G* basis set (spin-valence basis set, proposed by Ditchfield et al. [21], Hehre et al. [22], and Hariharan and Pople [23]) in water (SM8 solvation model [24,25,26]). To obtain the stable ion-water cluster, the molecules of water were progressively added and the geometry was optimized to identify those ion-water clusters that are stable. The step-by-step procedure applied to obtain the most stable $X(H_2O)_n$ ion-clusters was as follows:

- Step 1: a number of water molecules were placed in the vicinity of the investigated ion
- Step 2: geometry optimization was conducted
- Step 3: other water molecules were added in the empty spaces in the vicinity of the investigated ion
- Step 2 and 3 were repeated till no changes were observed in the arrangement of the water molecules surrounding the investigated ion in the first layer
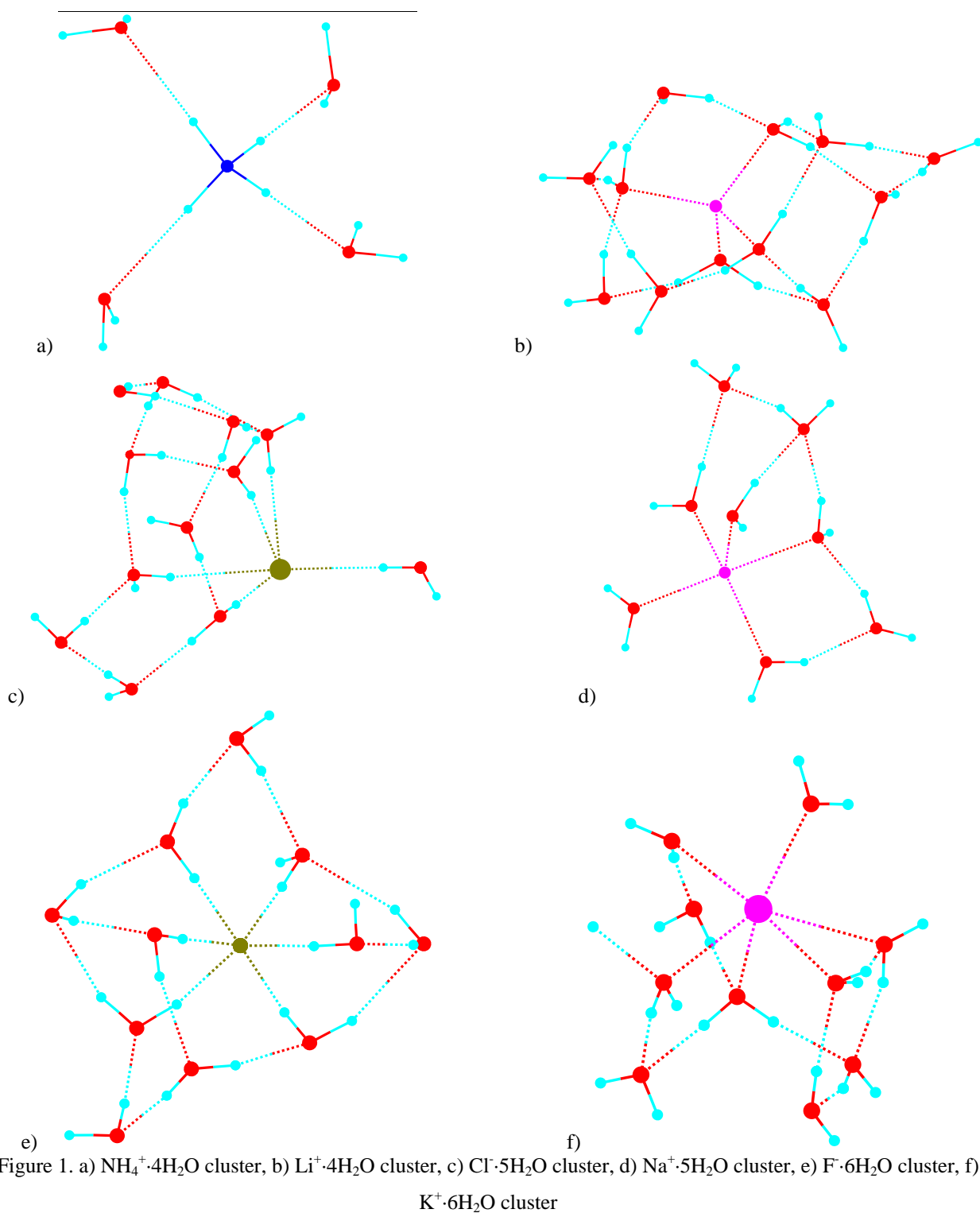
The above-described steps were applied for each investigated ion. Geometry optimization and calculations were performed with Spartan software (v. 10). For each ion-water cluster, distance between atoms (expressed in pm) and the angles between bonds (degree) were measured and collected.

The investigation of cations as components of dodecahedron arrangement of water was conducted by constructing dodecahedron cages for NH^+, Li^+, Na^+, and K^+ following the steps presented by Twarock et al. [27].

The mean of bond lengths were compared by ANOVA test at a significance level of 0.33% (adjusted $\alpha = 0.05$ by the number of comparisons being considered – in our case the number of investigated ions; $\alpha^* = 0.05/[6*(6-1)/2]$) followed by Bonferroni test whenever significant differences were observed. Friedman ANOVA test was applied to test the differences between angles in the investigated ion-water clusters. Statistical analysis was done with Statistica software (v. 8.).

Results and Discussion

The identified stable ion-water clusters proved to form with four ($NH_4^+ \cdot 4H_2O$ and $Li^+ \cdot 4H_2O$), five ($Cl^- \cdot 5H_2O$ and $Na^+ \cdot 5H_2O$) and respectively six water molecules ($F^- \cdot 6H_2O$ and $K^+ \cdot 6H_2O$). The stable ion-water clusters are presented in Figure 1. Note that the ion-water clusters presented in Fig. 1 are those naturally formed and without constrains since the *in silico* modeling was conducted in water.

Figure 1. a) $NH_4^+ \cdot 4H_2O$ cluster, b) $Li^+ \cdot 4H_2O$ cluster, c) $Cl^- \cdot 5H_2O$ cluster, d) $Na^+ \cdot 5H_2O$ cluster, e) $F^- \cdot 6H_2O$ cluster, f) $K^+ \cdot 6H_2O$ cluster

The first solved ion ($NH_4^+ \cdot 4H_2O$) was selected as a reference for reproducibility of the calculation and for the validation of the chosen method of analysis. The obtained results are in agreement with known data [28- 31].

As expected, since different ion-water clusters were investigated, the lengths of the bonds as well as the angles between bonds are different from one cluster to another (see Table 2 and 3).

Table 2. Bonds length and angles between bonds in Cl⁻·5H₂O cluster and in F⁻·6H₂O cluster

Distance		Angle			
d(Atom…Atom)	pm	(Atom…Atom)$_{d(Atom…Atom)}$	(°)	(Atom…Atom)$_{d(Atom…Atom)}$	(°)
Cl⁻·5H₂O cluster					
d(H…Cl)	265	(H…Cl)$_{281}$—(H…Cl)$_{307}$	67	(H…Cl)$_{274}$—(H…Cl)$_{281}$	96
d(H…Cl)	274	(H…Cl)$_{274}$—(H…Cl)$_{307}$	76	(H…Cl)$_{265}$—(H…Cl)$_{274}$	101
d(H…Cl)	281	(H…Cl)$_{281}$—(H…Cl)$_{284}$	82	(H…Cl)$_{265}$—(H…Cl)$_{284}$	129
d(H…Cl)	284	(H…Cl)$_{274}$—(H…Cl)$_{284}$	82	(H…Cl)$_{284}$—(H…Cl)$_{307}$	140
d(H…Cl)	307	(H…Cl)$_{265}$—(H…Cl)$_{307}$	89	(H…Cl)$_{265}$—(H…Cl)$_{281}$	146
F⁻·6H₂O cluster					
d(H…F)	179	(H…F)$_{179}$—(H…F)$_{184}$	77	(H…F)$_{184}$—(H…F)$_{185}$	89
d(H…F)	182	(H…F)$_{184}$—(H…F)$_{187}$	85	(H…F)$_{179}$—(H…F)$_{185}$	90
d(H…F)	183	(H…F)$_{182}$—(H…F)$_{183}$	85	(H…F)$_{183}$—(H…F)$_{187}$	93
d(H…F)	184	(H…F)$_{179}$—(H…F)$_{183}$	86	(H…F)$_{182}$—(H…F)$_{187}$	109
d(H…F)	185	(H…F)$_{185}$—(H…F)$_{187}$	87	(H…F)$_{179}$—(H…F)$_{187}$	162
d(H…F)	187	(H…F)$_{183}$—(H…F)$_{184}$	88	(H…F)$_{182}$—(H…F)$_{184}$	165
		(H…F)$_{179}$—(H…F)$_{182}$	89	(H…F)$_{183}$—(H…F)$_{185}$	177

The analysis of the other ion-water clusters showed that the arrangement of water molecule around investigated ions is not symmetrical even if sometimes (e.g. Fig. 1a) the symmetry is mimed. Additionally, adding more water after the bond directly related to the investigated ions led to clusters of water molecules highly unsymmetrical. It can be said that it is expected to see the molecular arrangement symmetry broken when more upper energy orbitals become available in the near range of the complete ones. Actually, it is hard to believe that at the solving of an ion in water, in diluted solutions, the arrangement of water molecules will follow the expected symmetry of the fundamental state of the ion *in vitro*. By using the obtained angles between bonds (see Table 2 for fluorine ion), a deviation from the ideal symmetrical square bi-pyramidal arrangement can be expressed as the standard deviation between obtained and expected (90° and 180°) angles is about 9°.

In the case of anions (Cl⁻ and F⁻) the bridge between water molecules and the ions are created by using the hydrogen's of the water. This fact is explained by the presence of the region rich in electrons surrounding the anions. Thus, the distances and the angles of the arrangement are given relative to these hydrogen atoms (see Table 2 for Cl⁻ and F⁻). The H…Cl⁻ distances in the Cl⁻·5H₂O cluster are closed by the values of H…Cl⁻ distance in the normal clathrate size where large angles orientation jumps are possible [32].

As can be observed for chlorine ion, the symmetry is totally broken due to the supplementary effect of the presence of free energy levels corresponding to the d-type orbitals (see Table 2). Other important remark is in regards of the number of water molecules surrounding the anion. Since the bonds are created via hydrogen atoms, it is expected that the electronegativity to play an important role to the ability to attract hydrogen atoms of the water molecules. Indeed, if fluorine was able to attract in the first layer 6 hydrogen atoms of water molecules, chlorine, with less electronegativity, attracted only 5 hydrogen atoms of water molecules. By calculating again the standard deviation between obtained and expected angles (here using the five vertices six faces platonic structure - 6×90°, 3×120°, 1×180°) the standard deviation becomes about twice (16°) compared to fluoride ion-water cluster.

For fluorine ion solved in water, the arrangement of the water molecules in the first layer surrounding F⁻ ion is, based on the angles, close to a square bi-pyramidal arrangement (see Table 2). In an ideal arrangement (when the hydrogen atoms are attracted with equal strengths, such in liquid HF), it is expected that the preferred arrangement to be a symmetrical square bi-pyramidal one. However, because of the difference on electronegativity between oxygen and fluorine, an unsymmetrical square bi-pyramidal arrangement of hydrogen atoms surrounding fluorine ion is observed. For cations, the situation is reversed and the bridge between water molecules and the cation is created through oxygen atoms. Due to this fact, also the situation of decreasing of the coordination number with the increasing of the atomic

number observed at anions (6 for F⁻, 5 for Cl⁻) is expected to be reversed (see Table 3). Indeed, lithium ion coordinates 4 oxygen atoms in the first layer surrounding the ion, sodium coordinates 5 and potassium coordinates 6 (see Table 3). In the terms of the deviation from the ideal platonic arrangements (with 4, 5 and 6 water molecules placed in the first layer surrounding the ions) the standard deviations for the case of cations is almost 7° for Li^+, 9° for Na^+ and 22° for K^+ (when again, the presence of the d-type orbitals disturbed significant the symmetry).

Table 3. Bonds length and angles between bonds in cations-water clusters: $NH_4^+ \cdot 4H_2O$, $Li^+ \cdot 4H_2O$, $Na^+ \cdot 5H_2O$, $K^+ \cdot 6H_2O$

Distance		Angles			
$d(Atom…Atom)$	pm	$(Atom…Atom)_{d(Atom…Atom)}$	(°)	$(Atom…Atom)_{d(Atom…Atom)}$	(°)
$NH_4^+ \cdot 4H_2O$ cluster					
$d(O{-}H)$	95	$(H{-}O)_{95}{-}(O{-}H)_{95}$	105		
$d(N{-}H)$	101	$(H{-}N)_{101}{-}(N{-}H)_{101}$	109		
$d(O…H)$	208	$(H{-}O)_{95}{-}(O…H)_{208}$	113		
$Li^+ \cdot 4H_2O$ cluster					
$d(Li…O)$	193	$(Li…O)_{193}{-}(Li…O)_{196}$	99	$(Li…O)_{193}{-}(Li…O)_{200}$	111
$d(Li…O)$	194	$(Li…O)_{194}{-}(Li…O)_{200}$	104	$(Li…O)_{194}{-}(Li…O)_{196}$	116
$d(Li…O)$	196	$(Li…O)_{196}{-}(Li…O)_{200}$	110	$(Li…O)_{193}{-}(Li…O)_{194}$	117
$d(Li…O)$	200				
$Na^+ \cdot 5H_2O$ cluster					
$d(Na…O)$	231	$(Na…O)_{234}{-}(Na…O)_{239}$	84	$(Na…O)_{234}{-}(Na…O)_{235}$	97
$d(Na…O)$	234	$(Na…O)_{236}{-}(Na…O)_{239}$	85	$(Na…O)_{231}{-}(Na…O)_{234}$	100
$d(Na…O)$	235	$(Na…O)_{231}{-}(Na…O)_{239}$	88	$(Na…O)_{234}{-}(Na…O)_{236}$	123
$d(Na…O)$	236	$(Na…O)_{231}{-}(Na…O)_{235}$	93	$(Na…O)_{231}{-}(Na…O)_{236}$	135
$d(Na…O)$	239	$(Na…O)_{235}{-}(Na…O)_{236}$	94	$(Na…O)_{231}{-}(Na…O)_{235}$	178
$K^+ \cdot 6H_2O$ cluster					
$d(O…K)$	278	$(O…K)_{285}{-}(O…K)_{293}$	58.1	$(O…K)_{278}{-}(O…K)_{284}$	94.4
$d(O…K)$	279	$(O…K)_{281}{-}(O…K)_{285}$	79.0	$(O…K)_{281}{-}(O…K)_{293}$	100.5
$d(O…K)$	281	$(O…K)_{284}{-}(O…K)_{293}$	79.1	$(O…K)_{279}{-}(O…K)_{284}$	121.6
$d(O…K)$	284	$(O…K)_{278}{-}(O…K)_{281}$	80.8	$(O…K)_{284}{-}(O…K)_{285}$	127.8
$d(O…K)$	285	$(O…K)_{281}{-}(O…K)_{284}$	81.3	$(O…K)_{278}{-}(O…K)_{285}$	128.8
$d(O…K)$	293	$(O…K)_{279}{-}(O…K)_{293}$	86.2	$(O…K)_{279}{-}(O…K)_{281}$	157.1
		$(O…K)_{279}{-}(O…K)_{285}$	86.3	$(O…K)_{278}{-}(O…K)_{293}$	173.0
		$(O…K)_{278}{-}(O…K)_{279}$	92.5		

The mean of bond lengths proved significantly different between investigated ion-water clusters (ANOVA test: p-value = $2.71 \cdot 10^{-10}$). The post-hoc Bonferroni test identified significant differences in regards or bond lengths for the following pairs of clusters (the differences were considered significant according with the adjusted significance level of 0.3333%):

- The mean of bond lengths on $NH_4^+ \cdot 4H_2O$ cluster proved significantly smaller compared to the one observed on $Cl^- \cdot 5H_2O$ cluster (p=$1.07 \cdot 10^{-8}$), $Na^+ \cdot 5H_2O$ cluster ($8.74 \cdot 10^{-6}$), and respectively $K^+ \cdot 6H_2O$ cluster ($5.00 \cdot 10^{-9}$).

- The mean of bond lengths on $Li^+ \cdot 4H_2O$ cluster proved significantly smaller compared to the one on $Cl^- \cdot 5H_2O$ cluster (p=$2.34 \cdot 10^{-5}$), and $K^+ \cdot 6H_2O$ cluster ($1.60 \cdot 10^{-5}$)

- The mean of bond lengths on $Cl^- \cdot 5H_2O$ cluster proved significantly higher compared to the one on $F^- \cdot 6H_2O$ cluster (p=$5.06 \cdot 10^{-7}$)

- The mean of bond lengths on $F^- \cdot 6H_2O$ cluster proved significantly smaller compared to the one observed on $K^+ \cdot 6H_2O$ cluster (p=$1.80 \cdot 10^{-7}$)

The analysis of the angles presented in Table 2 and 3 led to the following:

- As expected, the smallest angle between bonds is observed on a cluster with 6 water molecules, $K^+ \cdot 6H_2O$ cluster (angle=58.1°). The minimum value of the angles between pairs of bonds varied from 58.1° ($K^+ \cdot 6H_2O$ cluster) to 105° ($NH_4^+ \cdot 4H_2O$ cluster). The maximum value of the angle is of 178° and belongs to $Na^+ \cdot 5H_2O$ cluster. The range defined as the difference between maximum and minimum, as expected, increased as the number of water

molecules increased (is equal 8° for $NH_4^+ \cdot 4H_2O$ cluster and 114.9° for $K^+ \cdot 6H_2O$ cluster).

- No significant differences were identified when the angles between bonds were investigated (Friedman ANOVA statistic=4.27 p=0.5119).

The bonds and angles as obtained in the simulation study seem to be natural formation of bonds in water environment. The obtained results could be used to explain the solvation effects. Burnham et al. [15] showed temperature-dependent solvation of Na^+, Cl^-, and H^+ ions in water clusters and identified the global minimum for $Na^+(H_2O)_{20}$ and $Cl^-(H_2O)_{17}$. Nevertheless, Burnham et al. [15] had a different purpose of the study, namely to identify the optimal size of the water cluster surrounding the ions, since in our case, the arrangement of the water molecules in the first layer was the main point of interest. Cui et al. [33] proved by a computational study (B3LYP and BP86 methods with 6-311++G** basis set) that the symmetry of potential high-energy density materials $HB(N_5)_3X$ (X = Li, Na, K, and Rb) is a local minima on the potential energy surface.

Our results correspond to 'infinite dilution', e.g. no other ions are in the vicinity. It is expected that bonds lengths and angles between bonds to change when other ions by the same type exists in the vicinity, while it is also expected that the symmetry to be reconstructed.

Dodecahedron cages were constructed following the methods described in the specialty literature [33] for each investigated cation (NH^+, Li^+, Na^+, and K^+) and the obtained structures are presented in Figure 2.

6 O-H in & 6 O-H out

d(Li,O) = 179±1 pm

$O_2N_8H_{50}$; stable

$O_{14}Na_6H_{22}$; instable

$O_{12}Li_8H_{18}$; stable

$O_{15}K_5H_{29}$; stable

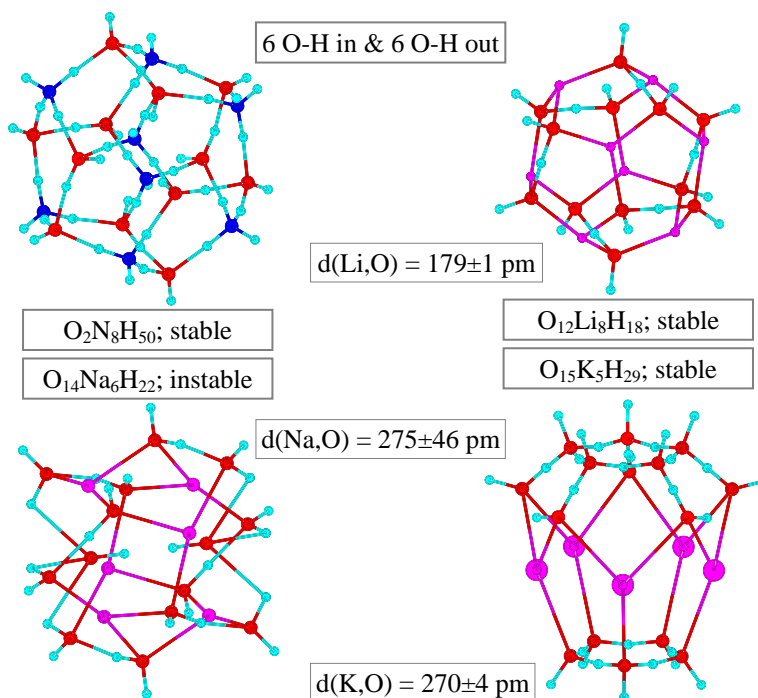d(Na,O) = 275±46 pm

d(K,O) = 270±4 pm

Figure 2. Dodecahedron clusters for NH^+, Li^+, Na^+, and K^+ cations

The symmetry of the structures is stabilized in all four cases as can be observed from Fig. 2. As it can be observed, the $O_{14}Na_6H_{22}$ structure is similar with the $Na^+(H_2O)_{20}$ complex described by Burnham et al. [15]. A special case is observed for ammonia ($O_{12}N_8H_{50}$) for which six O─H stabilized in the cluster and six O─H stabilized out in the stable symmetrical structure (see Fig. 2). This behavior is in some way expected since it is known that monovalent ions do not affect the water hydrogen-bonding network while a multivalent ion does affect it [34].

The formation and/or stability of the dodecahedron clusters at the solvation in water were furthermore investigated using the ammonia. Several arrangements for $O_xN_{20-x}H_{50}$ (Fig. 3) were investigated and the results are presented in Table 4.

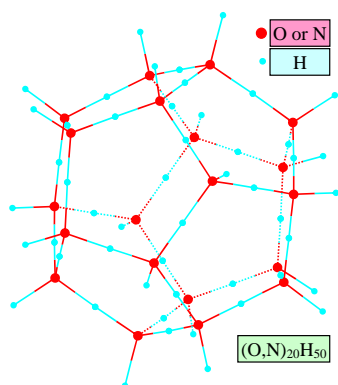Figure 3. General pattern for $O_xN_{20-x}H_{50}$

Table 4. Arrangements for $O_xN_{20-x}H_{50}$

No.	Cluster	H_2O	NH_3	H_3O^+	HO^-	$[^+/^-]/H_2O$	Reaction of formation	N/(N+O) %
0	O_0N_{20}	0	20	10	0	+(10)/(0+10)	$20NH_3 + 10H_2O \rightarrow O_0N_{20}H_{50} + 10H_3O^+$	18/28=100
1	O_2N_{18}	2	18	8	0	+(8)/(2+8)	$18NH_3 + 10H_2O \rightarrow O_2N_{18}H_{50} + 8H_3O^+$	18/28=64.3
2	O_4N_{16}	4	16	6	0	+(6)/(6+4)	$16NH_3 + 10H_2O \rightarrow O_4N_{16}H_{50} + 6H_3O^+$	16/26=61.5
3	O_5N_{15}	5	15	5	0	+(5)/(5+5)	$15NH_3 + 10H_2O \rightarrow O_5N_{15}H_{50} + 5H_3O^+$	15/25=60.0
4	O_6N_{14}	6	14	4	0	+(4)/(4+6)	$14NH_3 + 10H_2O \rightarrow O_6N_{14}H_{50} + 4H_3O^+$	14/24=58.3
5	O_8N_{12}	8	12	2	0	+(2)/(2+8)	$12NH_3 + 10H_2O \rightarrow O_8N_{12}H_{50} + 2H_3O^+$	12/22=54.5
6	$O_{10}N_{10}$	10	10	0	0	(0)/(0+10)	$10NH_3 + 10H_2O \rightarrow O_{10}N_{10}H_{50}$	10/20=50.0
7	$O_{12}N_8$	12	8	0	2	-(2)/(2+12)	$8NH_3 + 14H_2O \rightarrow O_{12}N_8H_{50} + 2HO^-$	8/22=36.4
8	$O_{14}N_6$	14	6	0	4	-(4)/(4+14)	$6NH_3 + 18H_2O \rightarrow O_{14}N_6H_{50} + 4HO^-$	6/24=25.0
9	$O_{15}N_5$	15	5	0	5	-(5)/(5+15)	$5NH_3 + 20H_2O \rightarrow O_{15}N_5H_{50} + 5HO^-$	5/25=20.0
10	$O_{16}N_4$	16	4	0	6	-(6)/(6+16)	$4NH_3 + 22H_2O \rightarrow O_{16}N_4H_{50} + 6HO^-$	4/26=15.4
11	$O_{18}N_2$	18	2	0	8	-(8)/(8+18)	$2NH_3 + 26H_2O \rightarrow O_{18}N_2H_{50} + 8HO^-$	2/28=07.1
12	$O_{20}N_0$	20	0	0	10	-(10)/(10+20)	$0NH_3 + 30H_2O \rightarrow O_{20}N_0H_{50} + 10HO^-$	0/30=0.00

Not all random arrangements of ammonia and water molecules may keep a certain level of the symmetry of the arrangement as can be observed from Fig. 3. Six different patterns of alternating water and ammonia, and therefore eleven different arrangements of placing water and ammonia in these patterns (see Table 4) can be observed if arrangements with certain level of symmetry (associated with a supplementary stabilization of the aggregate) are of interest. Several calculations were done for different arrangements for $O_xN_{20-x}H_{50}$ and the obtained results are presented in Table 4. Table 4 contains: the ratio between water and ammonia per cluster (H_2O and NH_3) as well as the number of hydronium (H_3O^+ column) and hydroxide (HO^- column) ions created (released) due to the formation of the cluster, the ratio of the released charge per total number of implied water molecules ($[^+/^-]/H_2O$ column), the reaction which lead to the formation of the cluster (column 'Reaction of formation' which is also the verification key for the previous calculations) as well as the ratio between nitrogen and oxygen atoms corresponding to the arrangement in full in the entire mixture of water and ammonia.

The angles between bonds in ion-water clusters of the investigated ions were successfully obtained and the clustering with certain number of water molecules could explain the dissolution of investigated ions in water. 'Certain number' of molecules also named 'magic number clusters' were investigated on Li_nNa_{8-n}, Na_nK_{8-n}, and K_nLi_{8-n} [35], $(C_5H_5N)_n$ $(H_2O)_m$ (n=1~2, m=1~4) [36], methyl tert-butyl ether (MTBE) - water clusters [37], $H^+(NH_3)(pyridine)(H_2O)_n$, $H^+(NH_3)(pyridine)_2(H_2O)_n$ (n = 18, 20, and 27) [38], $H^+(NH_3)_5(H_2O)_{20}$ (tetrahedral ammonium core encapsulated in a dodecahedral $(H_2O)_{20}$ structure, found in clathrates) [39].

A series of important results in regards of symmetry broken effects at energy levels of some monovalent ions at solvation due to the presence of water molecules were obtained in this study. Further studies to estimation the distribution of clusters in different solutions of water and ammonia at different concentrations and temperatures can be conducted starting with the obtained results. However, this experiment that involves twelve equations of formation of

ammonia in water and water dissociation, need many experimental data, and was beyond the aim of this study.

Conclusions

Our study showed that there is a significant difference among congener ions in the tendency of arrangement at equilibrium as result of interaction with the water molecules (here SM8 model was used), and, under the absence of other ions (at infinite dilution) the arrangement is, in general, with symmetry broken. In the presence of other ions (in concentrated solutions) dodecahedron clusters containing 8 atoms of lithium (Li) and four atoms of potassium (K) are symmetric and stable while dodecahedron clusters containing 6 atoms of sodium are unstable while the symmetry is broken.

Acknowledgements

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