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Dedicated to Professor Mircea Diudea on the Occasion of His 65th Anniversary

MODELS OF MONOVALENT IONS DISSOLVED IN WATER

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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 optimize 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 molecules around the investigated ions proved not be symmetrical. Furthermore, the investigation of the stability of dodecahedral cages constructed with the investigated ions showed a 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 the lack of geometrical symmetry makes more difficult the analysis) [2]. Eighteen crystalline phases (where the oxygen atoms are in fixed positions relative to each other but the hydrogen atoms may or may not be disordered but obeying the “ice rules”) and three amorphous (non-crystalline) phases are known to date [3, 4].

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The crystalline phases formed by two “close-packed” structures have been identified: hexagonal (at upper temperatures) [5] and cubic (at lower temperatures) [6-8]. The distances between atoms in ice proved to be either 100pm (d(O─H)) or 175pm (d(O…H)) [9]. The d(O─H) length of water was determined experimentally [10] and furthermore calculate at different levels of theory (Table 1 [10]), showing that the top 3 closest values are given by the following methods: M06-2X/6-31G*, HF/3-21G* and MP3/6-31G*.

Water clusters, hydrogen bounded assembly [11] (the smallest water cluster being the water dimer $(H_2O)_2$), are important components of the atmospheric chemistry [12]. Different water clusters, such as $(H_2O)_6$ (function of the method, different temperature transition and density were reported [13]), dodecahedral $(H_2O)_{20}$ [14], edge-sharing pentagonal prisms, fused cubes, and face-sharing pentagonal prisms [15], etc. were identified and investigated.

Table 1. d(O─H) length in water: experimental vs. calculated [10]

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

Properties of Ion-water clusters $X[H_2O]_n$ (where X is the ion) have also been investigated. The importance of $(H_2O)_{20}$ surrounding monovalent cations has been demonstrated by infrared photo-dissociation spectroscopy and blackbody infrared radiative dissociation [16]. Global minima 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) [17].

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, possible stable states of water and ammonia mixtures were explored.

RESULTS AND DISCUSSION

Stable ion-water clusters have been 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 six water molecules ($F^- \cdot 6H_2O$ and $K^+ \cdot 6H_2O$), respectively. The stable ion-water clusters are presented in **Figure 1.** Note that these structures are without constrains since the *in silico* modelling was conducted in water.

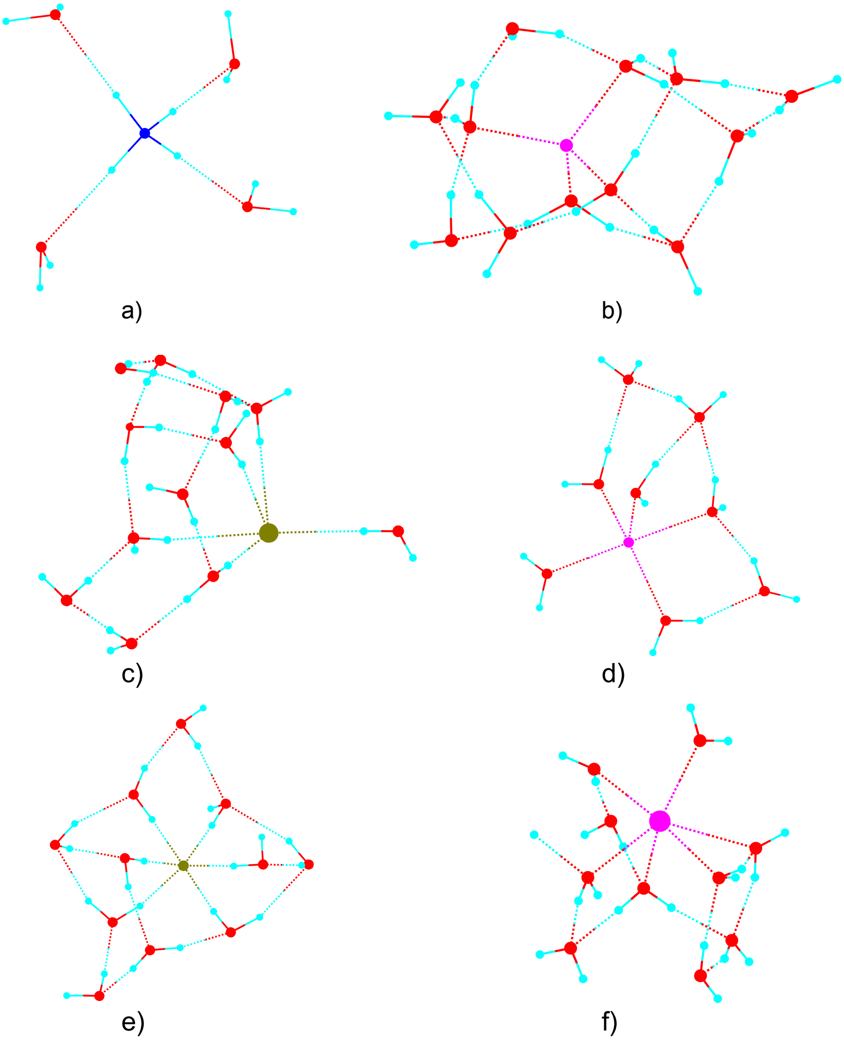
a) b) c) d) e) f)

Figure 1. Ion-water clusters: 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 the known data [18-21]. 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 **Tables 2** and **3**).

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. Additional more water, added on the direction of some cluster bonds led to clusters of water molecules highly unsymmetrical.

One can be said that the expected molecular arrangement symmetry broken when higher energy orbitals become available in the studied ion. Actually, it is hard to believe that, in diluted solutions, the arrangement of water molecules will follow the expected symmetry of the fundamental state of the *in vitro* ion. By using the calculated bond angles (see, e.g., **Table 2**, for fluoride ion), a deviation from the ideal symmetrical of square bi-pyramidal arrangement can be recorded (the standard deviation between expected (90° and 180°) and obtained angles is about 9°).

Table 2. Bond lengths and bond angles in $Cl^- \cdot 5H_2O$ cluster and in $F^- \cdot 6H_2O$ cluster

Distance		**Angle**			
d(Atom…Atom)	pm	(Atom…Atom)$_{d(Atom…Atom)}$	(°)	(Atom…Atom)$_{d(Atom…Atom)}$	(°)
		$Cl^- \cdot 5H_2O$ 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
		$F^- \cdot 6H_2O$ 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

In case of anions (Cl^- and F^-), bridges are created between water molecules and the ions by means of “hydrogen bonds” HB. This fact is explained by the presence of a rich electron region surrounding the anions.

Thus, the distances and the angles of the arrangements are given relative to hydrogen atoms involved in HB (see **Table 2** for Cl^- and F^-). The H…Cl^- distances in $Cl^-\cdot 5H_2O$ cluster are close to the values of H…Cl^- distance in the normal clathrate [22].

In case of chlorine ion, the symmetry is totally broken, maybe due to the effect of chlorine d-type orbitals (see Table 2). Other important remark is in regard 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 in the ability of HB creation. Indeed, if fluorine was able to attract in the first layer 6 hydrogen atoms of water molecules, chlorine, with less electronegativity, is able to form only 5 HB with the water molecules. By recalculating the standard deviation between the obtained and expected angles (in five- and six-fold regular faces: 6×90°, 3×120°, 1×180°) the standard deviation becomes about twice (16°) compared to the fluoride ion-water cluster.

For the fluoride ion solved in water, the arrangement of 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 in 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, the ion electronegativity is expected to work in a reversed way, compared to the case of anions (6 for F^-, 5 for Cl^-). Indeed, lithium ion coordinates 4 oxygen atoms in the first layer surrounding it, sodium coordinates 5 while potassium coordinates 6 (**Table 3**).

Table 3. Bond lengths and bond angles 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				

Distance		**Angles**			
d(Atom…Atom)	pm	(Atom…Atom)$_{\text{d(Atom…Atom)}}$	(°)	(Atom…Atom)$_{\text{d(Atom…Atom)}}$	(°)
		$Na^+\cdot 5H_2O$ 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		

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^+ (again, the presence of the d-type orbitals disturbed significant the symmetry).

The mean of bond lengths proved significantly different among the investigated ion-water clusters (ANOVA test: p-value = $2.71\cdot10^{-10}$). The post-hoc Bonferroni test identified significant differences in regards of bond lengths for the following pairs of clusters (the differences were considered significant according to the adjusted significance level of 0.3333%):

- The mean of bond lengths in $NH_4^+\cdot4H_2O$ cluster was significantly smaller compared to the one observed in $Cl^-\cdot5H_2O$ cluster ($p=1.07\cdot10^{-8}$), $Na^+\cdot5H_2O$ cluster ($8.74\cdot10^{-6}$), and respectively $K^+\cdot6H_2O$ cluster ($5.00\cdot10^{-9}$).
- The mean of bond lengths in $Li^+\cdot4H_2O$ cluster was significantly smaller compared to the one in $Cl^-\cdot5H_2O$ cluster ($p=2.34\cdot10^{-5}$), and $K^+\cdot6H_2O$ cluster ($1.60\cdot10^{-5}$)
- The mean of bond lengths in $Cl^-\cdot5H_2O$ cluster was significantly higher compared to the one in $F^-\cdot6H_2O$ cluster ($p=5.06\cdot10^{-7}$)
- The mean of bond lengths on $F^-\cdot6H_2O$ cluster was significantly smaller compared to the one observed on $K^+\cdot6H_2O$ cluster ($p=1.80\cdot10^{-7}$)

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

- 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 bond angles 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 is found in $Na^+\cdot 5H_2O$ cluster. The range defined as the difference between maximum and minimum 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), as expected.
- No significant differences were found when the bond angles inside a cluster were investigated (Friedman ANOVA statistic=4.27 p=0.5119).

The bonds and angles, as obtained in the actual simulation study, seem to be natural formation of bonds in the water environment. The obtained results could be used to explain the solvation effects. Burnham et al. [17] reported temperature-dependent solvation of Na^+, Cl^-, and H^+ ions in water clusters and identified the global minimum for $Na^+(H_20)_{20}$ and $Cl^-(H_2O)_{17}$. Burnham et al. [17] tried to identify the optimal size of the water cluster surrounding the ions. Cui et al. [23] proved, by a computational study (B3LYP and BP86 methods with 6-311++G** basis set), that the symmetry of materials $HB(N_5)_3X$ (X = Li, Na, K, and Rb) is related to local minima on the potential energy surface.

Nevertheless, our study was focused on the arrangement of water molecules in the first layer around the ions. 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 (of the same type) exists in the vicinity, while it is also expected that the symmetry to be preserved.

Dodecahedral cages were constructed following the methods described in the literature [23] for each of the investigated cation (NH^+, Li^+, Na^+, and K^+) and the obtained structures are presented in Figure 2.

The symmetry of the structures was stabilized in all four cases, as can be observed from Figure 2. The structure of $O_{14}Na_6H_{22}$ is similar to that of $Na^+(H_2O)_{20}$ complex described by Burnham et al. [17]. A special case was observed in ammonia cluster ($O_{12}N_8H_{50}$) for which six O—H stabilized inside the cluster and six O—H stabilized outside, in the stable symmetrical structure (**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 [24].

The formation and/or stability of the dodecahedral clusters by hydration were further investigated in case of ammonia. Several arrangements for $O_xN_{20-x}H_{50}$ (**Fig. 3**) were investigated and the results are listed in **Table 4**.

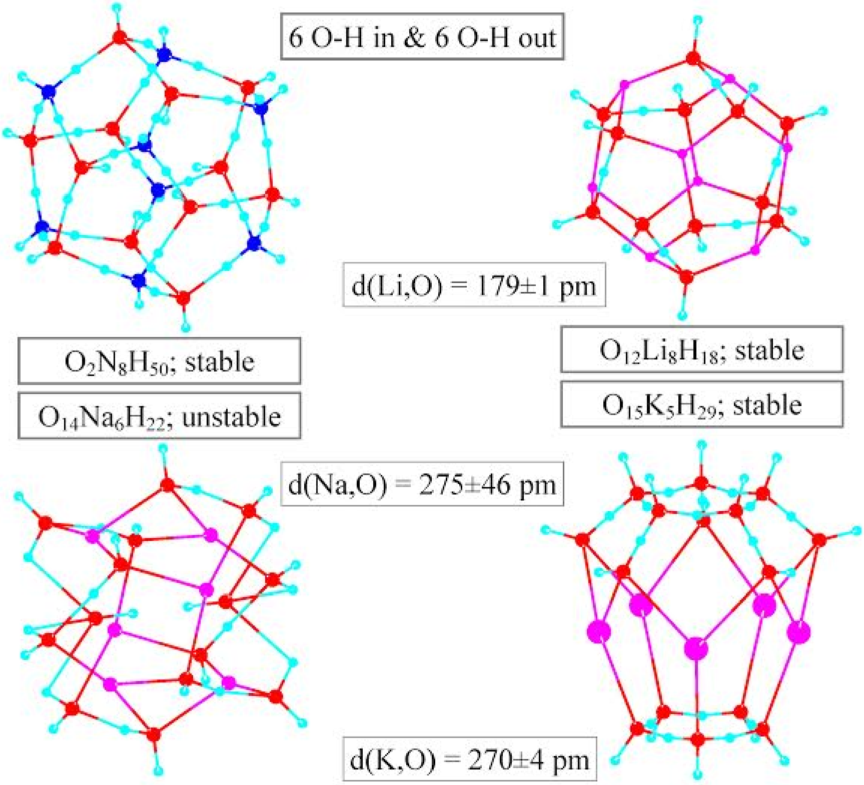

Figure 2. Dodecahedral clusters of NH^+, Li^+, Na^+, and K^+ cations

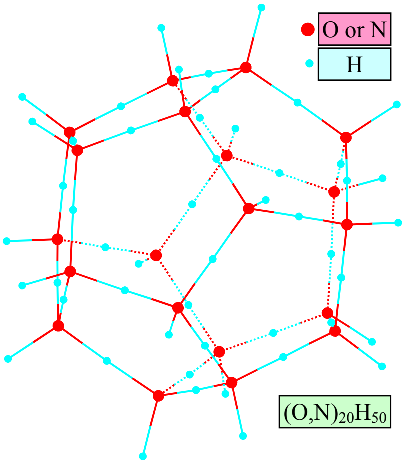

Figure 3. General pattern for $O_xN_{20-x}H_{50}$

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

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 preserve a certain level of symmetry (see Figure 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, at a choice level of symmetry (associated with a supplementary stabilization of the aggregate). Several calculations were done for different arrangements for $O_xN_{20\text{-}x}H_{50}$ and the obtained results are listed in Table 4, as follows: the ratio H_2O/NH_3 per cluster, 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 involved water molecules ($[^+/^-]/H_2O$ column), the reaction leading to the formation of the cluster (column 'Reaction of formation' which is also a checking key for the previous calculations) as well as the ratio O/N (nitrogen/oxygen) atoms corresponding to the arrangement of water and ammonia.

The bond angles in the studied ion-water clusters were successfully obtained; the clustering with a 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} [25], $(C_5H_5N)_n$ $(H_2O)_m$ (n=1~2, m=1~4) [26], methyl tert-butyl ether (MTBE)-water clusters [27], $H^+(NH_3)$(pyridine) $(H_2O)_n$, $H^+(NH_3)(\text{pyridine})_2(H_2O)_n$ (n= 18, 20, and 27) [28], $H^+(NH_3)_5(H_2O)_{20}$ (tetrahedral ammonium core encapsulated in a dodecahedral $(H_2O)_{20}$ structure, found in clathrates) [29].

A series of important results regarding the symmetry broken at solvation, due to high energy orbitals in some monovalent ions, were obtained in this study. Distribution of clusters in different solutions of water and ammonia, at different concentrations and temperatures, can be further conducted starting with these results.

CONCLUSIONS

Our study has shown that there is a significant difference among the congeneric ions in the tendency of clustering with water; at infinite dilution, and in the absence of other ions, the arrangements show, in general, a broken symmetry. In the presence of other ions (in concentrated solutions) dodecahedral clusters containing 8 atoms of lithium (Li) and four atoms of potassium (K) are symmetric and stable while dodecahedral clusters containing 6 atoms of sodium are unstable while the symmetry is broken.

MATERIALS AND METHODS

In-silico computational 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 [30-34]) with 6-31G* basis set (spin-valence basis set, proposed by Ditchfield et al. [35], Hehre et al. [36], and Hariharan and Pople [37]) in water (SM8 solvation model [38-40]). 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 by Spartan software (v. 10). For each ion-water cluster, distance between atoms (expressed in pm) and the bond angles were collected.

The investigation of cations as components of a dodecahedral arrangement of water was conducted by building dodecahedron cages by NH^+, Li^+, Na^+, and K^+ following the steps presented by Twarock et al. [41].

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

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