Chapter 2

Alkali halides – Solvation and Application
2.1. A First Principles Study towards the Minimum Number of Water Molecules required to Dissolve a single Potassium Chloride Molecule

2.1.1. Introduction

The theoretical studies on the effects of solvent on chemical phenomena have advanced recently with great interest, because solvation plays an important role in the most chemical processes. Alkali halides solvation is important in solution chemistry\textsuperscript{1-16} and poses a problem of elementary importance in which a polar solvent and an electrolyte is placed in contact to each other and the electronic and molecular structure of the electrolyte alters. Although it is clear that such a polar salt dissociates into solvated ions in aqueous solution but it is not clear how the system progresses from a polar gas molecule to the dissociated ions, as solvent molecules are added. It has been observed from the previous reports on the progression from gas phase to solvent-separated ion-pairs of sodium chloride and cesium fluoride that a cluster of six water molecules are necessary to dissociate such alkali halides.\textsuperscript{17,18} However, related studies involving the solvation phenomena of another important alkali halides, i.e., potassium chloride are scarce in the literature. Potassium chloride has a range of applications: it is very useful in fertilizers and occurs naturally as sylvite.\textsuperscript{19,20} It is also used in medicines, food processing and as a lethal weapon in judicial execution.\textsuperscript{19-21} Potassium chloride can act as a source of chloride ion. KCl is sometimes used in water as a completion fluid in petroleum and natural gas operations, and being an alternative to sodium chloride in household water softener units. KCl is also used as salt substitute, and it is commonly mixed with common salt NaCl to improve the taste.

From the book knowledge it has been observed that on an average, 15 water molecules are necessary to separate a single KCl molecule. The question whether this number really represents the smallest water cluster capable of dissolving a KCl molecule has baffled researchers for a long time. A decade back report on the association of a KCl molecule with water molecules using the attenuated total reflection (ATR) absorbance spectral studies had shown that pure KCl-solvated water exists as two close-bound ions (cation and anion), with a mean of five molecules of water forming a cluster: [K\textsuperscript{+}(H\textsubscript{2}O\textsubscript{5})\textsubscript{2}Cl\textsubscript{2}].\textsuperscript{22,23} ATR studies also determined that sodium chloride in water behaves in the same manner, forming a cluster containing a mean of five molecules of water: [Na\textsuperscript{+}(H\textsubscript{2}O\textsubscript{5})\textsubscript{2}Cl\textsubscript{2}].\textsuperscript{22,23} However, the geometrical arrangement of molecules in the cluster cannot be determined from the Infra Red measurements.

Recently, it has been observed that a specific arrangement of water clusters is required to dissociate sodium chloride and cesium fluoride using accurate quantum chemical methods.\textsuperscript{17,18}
For NaCl, a water hexamer in prismatic form was predicted to solvate the ion-pairs, whereas a cubic structure was observed for the dissociation of CsF molecule. From liquid water simulations studies it has been observed that a solvent separated pair for alkali halides corresponds to a distance of approximately 5.0 Å. The solvent separated ion-pair distance was found to be 4.4 Å for NaCl and 4.3 Å for CsF with a six water cluster using quantum chemical methods. In clusters with one salt molecule, the ions are always paired in the sense that both cations and anions are confined in a finite cluster environment which is different from the bulk. However, there is a definite difference between a half-dissociated contact ion-pair and a fully dissociated solvent separated pair as a function of the inter-ionic distance, wherein the ions closer than the barrier distance are considered as contact ion-pair. The elaborate discussion on half-dissociated (contact ion-pair) and fully dissociated (solvent separated pair) forms are given below.

In this section of the thesis we have investigated the minimum water cluster required to dissociate the potassium chloride molecule, i.e., the dissolution phenomena of KCl by water molecules. In this chapter, we have reported a systematic study of the effects of adding water molecules (up to six water molecules) on the molecular and electronic properties of KCl. The findings of this study not only answer the question concerning the onset of ionic solvation, but are also directly relevant to studies of reactivity of atmospheric sea-salt microparticles where hydrates have been reported to have key roles. This study involves the progressive dissolution process for KCl and is not intended to be relevant for the oligomeric form of this salt. The structures, energetics, and spectral properties of KCl with clusters of water molecules using the second-order Møller-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 Chloride to correctly describe the anion have been performed. Similar methods have been successfully applied to predict the description of sodium chloride-water clusters. Single point energies are performed with more accurate coupled cluster level with single and double and perturbative triple excitations (CCSD(T)) using the same basis set to determine the energetics. The separation of ions in clusters is more compact compared with the bulk environment; therefore, in the absence of the condensed phase, the ions are only partially surrounded by water molecules and the intermolecular geometry can differ from that of the bulk.

2.1.2. Computational Methods

The various equilibrium geometries of the dissociated and undissociated clusters-KCl(H$_2$O)$_n$=1-6, with different $n$ ($n =$ number of water molecules) in the cluster have been examined. Calculations were performed at the Møller-Plesset second-order perturbation theory (MP2)
and the CCSD(T)\textsuperscript{30,31} level of theory. We used Pople’s 6-31G basis set\textsuperscript{32} for oxygen, potassium, chlorine and hydrogen with augmented standard polarization set for heavy atoms. A standard diffuse set on chloride was incorporated in order to correctly describe the anion in both the second-order Møller-Plesset (MP2) perturbation method and CCSD(T) levels of theory. The geometries were optimized with the MP2 level of theory and a harmonic frequency analysis has been performed for stationary points to confirm minima and saddle points at the same level of theory. CCSD(T) results were obtained from single point calculations on the optimized geometries at the MP2 level. The zero-point (ZPE) uncorrected energies ($\Delta E_e$) and corrected ($\Delta E_o$) internal energies have been reported in conjunction with the enthalpies ($\Delta H_{298}$) and Gibbs free energies ($\Delta G_{298}$) at 298 K. For CCSD(T) energies, zero-point and thermal energy corrections were done with MP2/6-31+\textsubscript{G*} values. We have used CCSD(T) energies for comparison, which are generally known to be most realistic and the MP2 optimized geometries, unless otherwise stated. The vibrational frequencies are scaled using the scale factor 0.96 in the present discussion.\textsuperscript{33} All calculations were carried out employing the Gaussian 03 suite of programs.\textsuperscript{34}

2.1.3. Results and Discussions

2.1.3.1. Geometrical parameters of KCl and H\textsubscript{2}O

The geometrical parameters of KCl and H\textsubscript{2}O are given in Table 1. The calculated structural parameters at the MP2/6-31+\textsubscript{G*} and CCSD(T)/6-31+\textsubscript{G*} levels are in good agreement with each other and agree well with the experimental values. The MP2/6-31+\textsubscript{G*} optimized geometry of the KCl molecule is given in figure 1.

<table>
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<tr>
<th>Properties</th>
<th>MP2/(6-31+\textsubscript{G*})</th>
<th>CCSD(T)/(6-31+\textsubscript{G*})</th>
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<td>2.85</td>
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<td>$v_e$/cm$^{-1}$</td>
<td>272.01</td>
<td>262.58</td>
<td>281\textsuperscript{c}</td>
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</table>

\textsuperscript{a} Reference 35, \textsuperscript{b} Reference 36, \textsuperscript{c} Reference 37,38,39.
2.1.3.2. Definition of Half and Full dissociated geometries

In the study of the dissociation of KCl by water molecules, it is useful to define the dissociated structure of this alkali halide. In contrast to the bulk solution, in a cluster containing one salt molecule the ions are always paired in the sense that they are confined to a finite cluster environment. However, we can distinguish between a “paired” and an “unpaired” state if there is an existence of a potential barrier as a function of the inter-ionic distance, so that ions closer than the barrier distance are considered paired. Therefore, a dissociated or unpaired structure (at a minimum) is separated from the undissociated or paired structure (at a minimum) with a barrier between the two minima, which could be considered as a sufficient condition for the existence of a dissociated structure.\(^{17,40}\)

An alternative approach was described to define the undissociated, half-dissociated and dissociated structures based on the relative difference of distances from equilibrium gaseous alkali halide distance.\(^{18}\) By definition, the half-dissociated or contact ion-pair for Na\(^+\)/Cl\(^-\) occurs at an inter-ionic distance of \(\sim 2.8 \text{ Å}\), which is approximately the van der Waals contact distance for Na\(^+\) and Cl\(^-\) ions.\(^{24}\) The half-dissociated or contact ion-pair can be described as the situation where the inter-ionic distance of ions is larger than \(\sim 0.5 \text{ Å}\) compared to the gaseous state but less than \(\sim 0.1 \text{ Å}\). For a fully dissociated state, the inter-ionic distance should be larger than \(\sim 1.0 \text{ Å}\) compared to the gaseous state.

In certain cases, the validity of this definition could be somewhat confusing. So another additional criterion can be applied to define the undissociated/dissociated structure by using K-Cl stretching frequency ($\nu_{\text{KCl}}$). If the K-Cl stretching characteristic exists, then the structure should be considered undissociated, whereas if it is not observed it would be considered dissociated. However, this $\nu_{\text{KCl}}$ mode is mostly coupled, so it is not clear whether it really reflects the K-Cl stretch in the presence of other coupling modes. Thus, if $\nu_{\text{KCl}}$ is strongly coupled with other vibrational modes, then it can be considered dissociated. In general, in the hydrated structure, if $\nu_{\text{KCl}} < \sim 100 \text{ cm}^{-1}$, then the K-Cl stretch mode shows a strong coupling with other modes involving water and can be termed as half dissociated and if $\nu_{\text{KCl}} < 50 \text{ cm}^{-1}$, then the K-Cl...
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2.1.3.3. Interactions of n = 1 to 6 water molecules with the KCl molecule

Interaction of 1 water molecule with the KCl molecule increases the distance to 3.07 Å from the original distance of 2.88 Å between the K⁺ and Cl⁻ ion (Figure 1 and Figure 2). This is a situation of undissociation as the distance is less than 0.5 Å than the gaseous state.

Figure 2. MP2/6-31+G* optimized geometry and important distances for KCl(H₂O)ₙ=1
[potassium : purple; chlorine : green; oxygen : red; hydrogen : white].

Two possibilities have been observed for the interaction of two water molecules with the KCl molecule. Figure 3 shows the geometries of the KCl(H₂O)ₙ=2 clusters. Geometry 2a is an undissociated structure as the K⁺–Cl distance is within 0.5 Å, while geometry 2b is observed to be half-dissociated where the K⁺–Cl distance lies between 0.5 Å – 1.0 Å larger than the gaseous KCl distance.

Figure 3. MP2/6-31+G* optimized geometries and important distances for various conformers of KCl(H₂O)ₙ=2 [potassium : purple; chlorine : green; oxygen : red; hydrogen : white].

MP2/6-31+G* optimized geometries 3b and 3c of the KCl(H₂O)ₙ=3 clusters is observed to be half-dissociated structures while 3a has been observed to be undissociated. Figure 4 shows three different structures of KCl(H₂O)ₙ=3 clusters. The most symmetrical geometry 3b shows the maximum distance between the K⁺–Cl (3.50 Å).
Figure 4. MP2/6-31+G∗ optimized geometries and important distances for various conformers of KCl(H₂O)ₙ = 3 [potassium : purple; chlorine : green; oxygen : red; hydrogen : white].

The most stable geometry of KCl(H₂O)ₙ = 4 (4c) showed an increase in K⁺-Cl distance of ~3.5 Å (Table 2 and Figure 5). The geometry 4d (prismatic structure) observed to have larger separation between the K⁺ and Cl⁻ ions (4.40 Å) is unstable by 10.0 kcal/mol than 4c in CCSD(T) level of theory (Figure 5 and Table 2). However, for n = 5, the K⁺-Cl distance is elongated only up to ~3.7 Å (Figure 6). The attenuated total reflection (ATR) absorbance spectrum of potassium chloride has been reported. The KCl molecule dissociates in water to form two non-absorbing ions: K⁺/Cl⁻. The spectrum obtained is the absorption of two entities: pure water and water strongly associated to the K⁺/Cl⁻ pair. The observation of water associated KCl indicates that the water molecules form clusters made up of a pair of closely bound ions and a mean of 5 molecules of water: [K⁺(H₂O)₅Cl⁻]. In the absence of any information regarding the geometrical arrangement of [K⁺(H₂O)₅Cl⁻] from ATR studies, a direct comparison cannot be made with the calculated results. The calculated water clusters of KCl(H₂O)ₙ = 1-6 also demonstrated that 5 water molecules associated with the pair of K⁺/Cl⁻ does not fulfill the criteria of fully dissociated KCl molecule, which is in qualitative agreement with the observed ATR experiments. The small second-order effect that appears in the ATR studies indicate that some minor interaction exists between the [K⁺(H₂O)₅Cl⁻] clusters and the surrounding water molecules. It has been suggested that the band due to a second order effect in the solution perturbs the band of surrounding water molecules. Furthermore, the slight second-order effect observed in the ATR spectrum indicates that the clusters are stabilized by weak interactions with surrounding water molecules.
Figure 5. MP2/6-31+G* optimized geometries and important distances for various conformers of KCl(H₂O)₄ [potassium : purple; chlorine : green; oxygen : red; hydrogen : white]. The dissociated structure is underlined.

Figure 6. MP2/6-31+G* optimized geometries and important distances for various conformers of KCl(H₂O)₅ [potassium : purple; chlorine : green; oxygen : red; hydrogen : white]. The structure of 6a (cube) involves separation of ions to K⁺(H₂O)₃ (C₃v) and Cl⁻(H₂O)₃ (C₃v). The distance between K⁺/Cl⁻ was found to be 4.97 Å (Figure 7). Six different geometries were observed with six water molecules. Two full dissociated (6a and 6c) and 4 half-dissociated structures (6b, 6d, 6e and 6f) have been observed. It has been observed from the calculated results that orientation of the water molecules is primarily important to dissolve an alkali halide in water.
The energetics of the different KCl(H₂O)ₙ=1-6 clusters at MP2/6-31+G(d) and CCSD(T)/6-31+G(d) level of theory are given in Table 2. Both level of theory are in coherence with each other except for one case in the six water molecules where in MP2 level the cubic geometry (6a) was more stable while in CCSD(T) the geometry 6f was stable. The water-water intermolecular bond distances (O–H) for the KCl(H₂O)ₙ=1-6 cluster are also given in Table 2. In general, the O–H distance increases with the size of the cluster from n = 2 to n = 4. However, for n = 2 and 3 there are no water-water interactions in their stable conformations. The intermolecular hydrogen bond distance is 1.75 Å for 2a and 2.04 Å for the stable cluster 4c. The hydrogen bonding distance increases further to 2.11 Å in 5a, however, in 6a it is relatively short (1.94 Å). The calculations show that K⋯O distance is marginally varied between 2.7 – 2.8 Å irrespective of the size of the cluster. The Cl⋯H distance varies between 2.11 Å to 2.26 Å in clusters n = 1 to 6, which suggests that these interactions are strong in nature.

The stretching modes of vibration observed for the K⋯Cl and K⋯O bonds are also given in Table 2. For gaseous KCl, the frequency of the stretch mode νKCl is 272 cm⁻¹. The geometries with undissociated KCl bond showed to have a K⋯Cl stretch mode of more than 100 cm⁻¹ while for half-dissociated and full dissociated geometries it was observed to be > 100 cm⁻¹ and > 50cm⁻¹ respectively except in the case of 4b and 5b geometries.
Table 2. Selected structural parameters for KCl(H$_2$O)$_n$ calculated at (MP2/6-31+G*) level of theory.

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<th>UHF</th>
<th>$\Delta E_0$ in kJ/mol</th>
<th>Coordination (KCl) n=H$_2$O</th>
<th>$r_{KCl}$ in Å</th>
<th>$r_{K-O}$ in Å</th>
<th>$r_{H-bonding}$ in Å</th>
<th>$\nu_{KCl}$ in cm$^{-1}$</th>
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</table>

\( \partial E_0 \) denotes the relative energy at the MP2/6-31+G* [CCSD(T)/ 6-31+G*] level. In "UHF", U, H, and F denote un-, half-, and full-dissociated state, respectively. \(^b\)Coordination (K/Cl) denotes the number of H\(_2\)O molecules co-ordinated with K\(^+\) and Cl\(^-\), where \(n\) is the number of H\(_2\)O molecules co-ordinated with K\(^+\) and Cl\(^-\).

For \(n = 4\), the next low lying conformer (4d) is fully dissociated, which is higher in energy by 9.2 kJ /mol at MP2 level and 10.0 kJ/mol at CCSD(T) level than the global minimum half-dissociated structure (4c). In the case of \(n = 6\), the fully dissociated structure (6a) cube is relatively comparable in energy to the global minimum half-dissociated structure (6f) (Table 3). Another cluster formed with \(n = 6\), i.e., the 6c structure, can also be said to be a solvent separated form of KCl molecule. The distance between K\(^+\)/Cl\(^-\) was found to be 4.47 Å (Fig. 1). However, this structure is much higher in energy (41.6 kJ/mol) than the global minimum structure 6f at CCSD(T) level of theory. Furthermore, the dissociated and half-dissociated structures with six water cluster were found to be separated by a saddle point with an inter-ionic distance of 4.33...
Å. The saddle point is 2.9 kJ/mol higher than the half-dissociated structure 6f at CCSD(T) level (Figure 8). The water molecules in the distorted 6f cubic structure arranges to a more ordered cubic form in the transition state, which eventually leads to the 6a cubic structure. However, in the case of four water clusters, the saddle point was not observed between the half-dissociated 4c and fully-dissociated structure 4d. This study of solvation of a KCl molecule and the solvation studies performed with NaCl and CsF indicates that even numbers of water molecules can have a larger impact on separation of a salt molecule than that of odd water clusters.\textsuperscript{17,18}

![Figure 8](image.png)

**Figure 8.** MP2/6-31+G* optimized geometries and important distances for the saddle point between the half dissociated and full dissociated geometries of KCl(H\textsubscript{2}O)\textsubscript{n}=6 [potassium : purple; chlorine : green; oxygen : red; hydrogen : white].

The calculated results at CCSD/6-31+G* show that the K\textsuperscript{+}Cl distance of global minimum structures increases monotonically towards 3.0-3.5 Å as the cluster size increases from \(n = 2\) to 6 (Figure 9).

![Figure 9](image.png)

**Figure 9.** CCSD(T)/6-31+G* calculated K\textsuperscript{+}Cl distances of the lowest-energy undissociated and half-dissociated conformers.

The hydration energies calculated for these KCl(H\textsubscript{2}O)\textsubscript{n}=1-6 clusters show that the hydration is more exothermic with increasing number of water molecules (Table 3).
Table 3. MP2/6-31+G* and CCSD(T)/6-31+G* calculated hydration energies (kJ/mol) of various conformer of KCl(H₂O)ₙ=1-6.

<table>
<thead>
<tr>
<th>KCl(H₂O)ₙ=1-6</th>
<th>MP2</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>-ΔE₀</td>
<td>-ΔH</td>
</tr>
<tr>
<td>1</td>
<td>67.8</td>
<td>61.5</td>
</tr>
<tr>
<td>2a</td>
<td>123.1</td>
<td>110.1</td>
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<tr>
<td>2b</td>
<td>131.8</td>
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<tr>
<td>3a</td>
<td>174.5</td>
<td>154.5</td>
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<tr>
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<td>170.8</td>
<td>181.2</td>
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<tr>
<td>3c</td>
<td>185.4</td>
<td>164.5</td>
</tr>
<tr>
<td>4a</td>
<td>257.4</td>
<td>231.1</td>
</tr>
<tr>
<td>4b</td>
<td>229.4</td>
<td>202.2</td>
</tr>
<tr>
<td>4c</td>
<td>262.4</td>
<td>239.0</td>
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<td>4d</td>
<td>243.2</td>
<td>218.9</td>
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<td>233.6</td>
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<td>5c</td>
<td>322.7</td>
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</tr>
<tr>
<td>6a</td>
<td>378.4</td>
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<tr>
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<td>370.4</td>
<td>331.1</td>
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<tr>
<td>6c</td>
<td>333.6</td>
<td>283.8</td>
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<td>333.6</td>
</tr>
<tr>
<td>6e</td>
<td>372.9</td>
<td>333.6</td>
</tr>
<tr>
<td>6f</td>
<td>382.6</td>
<td>341.6</td>
</tr>
</tbody>
</table>

2.1.3.4. Vibrational Frequencies

Table 4 and Figure 9 give detailed descriptions of the selected OH stretch taking place in the different structures of KCl(H₂O)ₙ=1-6. The OH stretching frequencies are usually used to classify the various cluster structures.42 MP2/6-31+G* vibrational frequencies (scaled with 0.96) for the O⁻H stretch modes of the lowest-energy undissociated, half-dissociated, and fully dissociated structures (Table 4 and Figure 9) have been studied. The –O-H stretching frequencies obtained when oxygen co-ordinates with potassium ion and the hydrogen atom interacts with other water molecules ν[B] yields a range of ~3230-3630 cm⁻¹. The lower frequency values (3230-3490 cm⁻¹) corresponds to the interaction of one water molecule with the –OH coordinated with K⁺ ion, whereas, the relatively higher values (3490-3630 cm⁻¹) were observed for 2 water molecules.
The $\text{O-H}$ stretching frequencies $\nu[\text{U}]$ ($\sim 3280$-$3510 \text{ cm}^{-1}$) appears due to the interaction of oxygen atom with $\text{K}^+$ ion and the hydrogen interacting with $\text{Cl}^-$ ion (Figure 9). These frequencies coincide with the values observed in the $\nu[\text{B}]$ case and any meaningful assignment is difficult. The $\text{O-H}$ frequencies given in $\nu[I]$ ($\sim 3660$-$3840 \text{ cm}^{-1}$) are clearly distinguishable compared to other cases. In the case of $\nu[I]$, the water molecule associated with the $\text{K}^+$ ion involving a dangling hydrogen is in general $\sim 9$-$21 \text{ cm}^{-1}$ larger than the $\nu_s$($\nu$ scaled) associated with $\text{Cl}^-$. This spectral information would be useful for IR experiments to identify the subtle changes in the hydration environment for $\text{KCl(H}_2\text{O)}_{n=1-6}$.

Table 4. MP2/6-31+G* scaled frequencies (cm$^{-1}$) for the OH stretch modes of $\text{KCl(H}_2\text{O)}_{n=1-6}$ (scale factor 0.96)$^a$

<table>
<thead>
<tr>
<th>Conformers</th>
<th>O-H stretching frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3407, 3697.</td>
</tr>
<tr>
<td>2a</td>
<td>3294, 3679, 3700.</td>
</tr>
<tr>
<td>2b</td>
<td>3408(a), 3499(s), 3693(a), 3700(s).</td>
</tr>
<tr>
<td>3a</td>
<td>3417, 3480, 3679, 3687, 3708.</td>
</tr>
<tr>
<td>3b</td>
<td>3280(a), 3282(a), 3503(s), 3685(a), 3685(a), 3688(s).</td>
</tr>
<tr>
<td>3c</td>
<td>3372, 3452, 3541(s), 3626(a), 3673, 3677</td>
</tr>
<tr>
<td>4a</td>
<td>3244, 3339, 3469(s), 3516(s), 3587(s), 3604, 3676, 3682.</td>
</tr>
<tr>
<td>4b</td>
<td>3333(a), 3395(s), 3683(a), 3699(a), 3700(a).</td>
</tr>
<tr>
<td>4c</td>
<td>3525(s), 3621(a), 3681(a), 3682(s), 3694(a).</td>
</tr>
<tr>
<td>4d</td>
<td>3298, 3475, 3489, 3669(s), 3683(s).</td>
</tr>
<tr>
<td>5a</td>
<td>3490(a), 3510(s), 3620(a), 3628(a), 3678(a), 3685(a), 3686(s).</td>
</tr>
<tr>
<td>5b</td>
<td>3309, 3372, 3399, 3486, 3631, 3689, 3699, 3703, 3769.</td>
</tr>
<tr>
<td>5c</td>
<td>3275(a), 3314(s), 3326, 3496(s), 3568(a), 3679(a), 3680(s), 3694, 3710.</td>
</tr>
<tr>
<td>5d</td>
<td>3252, 3373, 3456, 3526, 3532(a), 3620(s), 3673, 3691, 3695</td>
</tr>
<tr>
<td>6a</td>
<td>3469(a), 3470(a), 3489(s), 3541(a), 3572, 3572, 3672(a), 3672(a), 3674(s).</td>
</tr>
<tr>
<td>6b</td>
<td>3397, 3413, 3433, 3490, 3497, 3620, 3630, 3682, 3685, 3694.</td>
</tr>
<tr>
<td>6c</td>
<td>3231, 3334, 3430, 3452, 3678, 3690, 3702(a), 3709(s).</td>
</tr>
<tr>
<td>6d</td>
<td>3303, 3321, 3325(a), 3364(s), 3437, 3682, 3684, 3698, 3705.</td>
</tr>
</tbody>
</table>
2.1.4. Conclusion

We have explored the dissociation phenomenon of a KCl molecule in water using the Møller-Plesset second-order perturbation (MP2) and coupled cluster theory with single, double and perturbative triple excitations (CCSD(T)) levels of theory. The half-dissociated or paired structures were generated from the 2 water molecule cluster. We conclude that the formation of prismatic structure of KCl with 4 water molecules is sufficient to separate the cation and the anion (4.4 Å). This result reveals the smallest water cluster used to dissociate an alkali halide. The larger separation of K⁺ ion and Cl⁻ ion was achieved (4.97 Å) with 6 water cluster in a cubic structure as well. It appears that the separation of alkali halides with 6 water molecule is a magic number for such systems as the hexa-hydrated separated ion-pair was predicted for NaCl\textsuperscript{17} and CsF\textsuperscript{18}. The half dissociated or paired structures of KCl with 5 water molecules predicted by \textit{ab initio} calculations are in agreement with the attenuated total reflection (ATR) absorbance spectrum of KCl-solvated water, which shows the presence of clusters made up of a pair of closely bound ions and a mean of 5 molecules of water: [K⁺(H₂O)\textsubscript{5}Cl⁻].\textsuperscript{22,41} This study of the dissolution of KCl with water molecules not only shows the progression of ionic solvation but is also relevant to studies on the reactivity of atmospheric chemistry.\textsuperscript{47}
References


2.2. A computational study toward understanding the separation of ions of potassium chloride microcrystal in water

2.2.1. Introduction

Inorganic salts such as alkali halide solvation phenomena are of fundamental importance for theoretical, experimental and economic reasons. Though such solvation studies have been performed from decades but the association of the molecules in such solution is still not well understood.\textsuperscript{1-18} The sodium chloride dissolution, one of the most important alkali halides, has been studied at both molecular and crystal levels.\textsuperscript{19-26} Asada et al. performed Monte Carlo simulations on LiCl and NaCl in water to investigate the mechanism for the dissociation phenomenon of such salts.\textsuperscript{24} Ohtaki et al. studied the dissolution of an NaCl crystal with \{111\} and \{-1-1-1\} faces using molecular dynamics simulation and concluded that repulsive forces arising between the chloride ions and the water molecules pushes the chloride ion out from the crystal surface as they possess smaller hydration energy than the sodium ions.\textsuperscript{25} When an ionic crystal is dissolved in water, the surface of the crystal gets covered with water molecules and the cations and anions leave the surface of the crystal and disperses into the aqueous phase. The dissolution process involves a ‘contest’ between the ionic bonds and the hydration of these ions. In the case of molecular level dissolution a cluster of six water molecules is necessary to achieve the solvent-separated ion-pair of NaCl rather than the textbook known 9 water molecules.\textsuperscript{19} Furthermore, the dissolution of sodium chloride crystal in water studied by molecular dynamics simulations indicated that a chloride ion at the corner of the crystal dissolves first.\textsuperscript{22} A detailed description about the process involved behind the dissolution of the Na\textsuperscript{+} and Cl\textsuperscript{-} ions from the NaCl crystal surface have been discussed by Liu et al.\textsuperscript{23} But theoretical studies on the dissolution phenomenon of potassium chloride crystals are still scarce.\textsuperscript{27}

A detailed description of the dissolution of a single potassium chloride molecule have been discussed in previous reports,\textsuperscript{28} finding that orientations of the water molecules around the potassium chloride seems to be important in the dissociation phenomena. The separation of K\textsuperscript{+} and Cl\textsuperscript{-} ions with 4 water molecules adopt a prismatic structure with the K–Cl distance of 4.4 Å while the largest separation of K\textsuperscript{+} and Cl\textsuperscript{-} ions (4.97 Å) was achieved with 6 water molecules in a cubic structure.\textsuperscript{28} In this chapter, we have explored the dissolution of KCl microcrystal which will also be relevant towards the study of salts in water clusters in environmental chemistry, atmospheric chemistry and cloud physics.\textsuperscript{29-33}

From saturation concentration or textbook knowledge, it can be deduced that on average 15 water molecules are necessary to dissociate a single KCl molecule at 273 K (Scheme 1); but
previous theoretical studies by our group suggested that the dissolution of a single KCl molecule starts with only a mere 4 water molecules. In this section the number of water molecules needed to start the dissolution process of the KCl crystal have been investigated. The progressive solvation of the ions in a microcrystal lattice has also been discussed. The dissolution process can either start from the corner or from the edge of the microcrystal surface. Scheme 2 shows the possibility of the separation of KCl into K$^+$ and Cl$^-$ ions from the crystal lattice in the presence of water molecules.

Scheme 1. Scheme showing the number of water molecules needed to dissolve a KCl molecule at 273 K

Scheme 2. The separation of ions from the corner or the edge positions of the lattice. Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white.

The solvation process of the microcrystal (KCl)$_6$ {100} cluster using DFT calculations consisting of 0 to 15 water molecules have been examined here in a systematic way. Static quantum chemical calculations using Density Functional theory and Classical Molecular dynamics
simulations have been discussed in this section to understand the solvation phenomenon of the KCl crystal.

The DFT results suggest that 4 is the minimum number of water molecules required to initiate the departure of the Cl\(^-\) ions from the KCl microcrystal (\(K^{+}\cdots Cl^- = 5.19 \text{ Å}\)) and similar to the dissolution of a single potassium chloride molecule, six water molecules augment the situation (6.12 Å).\(^{28}\) A maximum increase of the \(K^{+}\cdots Cl^-\) distance to \(~8.0 \text{ Å}\) with 14 water molecules have been observed. The simultaneous removal of more than one chloride ions from different sites seem to be less effective in comparison to the removal of a single Cl\(^-\) ion from the KCl lattice.

The dissociation of ions from the crystal lattice with the solvent molecules occurs with a number of steps: first is the formation of a solvent shared ion-pair, where only one solvent molecule separates the two ions, 2\(^{nd}\), dissociation via solvent separated ion-pairs, where the ion-pairs are separated with more than one solvent molecule. However, a clear experimental distinction between these two stages is not easily made.\(^{34}\) The circumstances under which these thermodynamically distinct species can exist in the solution have been reviewed by Marcus.\(^{1}\)

The finite cluster environment towards the salt dissociation process vary from the dissolution in the bulk environment.\(^{35}\) The classical molecular dynamics simulation are performed to understand the solvation of the KCl crystal in the bulk with the GROMACS 3.3.2 using the GROMOS96 43a1 force field and TIP4P water solvation model. The KCl crystal consists of three most important planes, \{100\}; \{110\} and \{111\} (scheme 3). Molecular Dynamics calculations were performed to examine the dissolution of \{100\} surface of KCl, and also extended with the less stable surfaces \{110\} and \{111\}. The arrangements of the potassium and chloride ions in the three different surfaces are shown in scheme 3.

Scheme 3: The arrangement of potassium and chloride ions on the \{100\}, \{110\} and \{111\} planes of the KCl crystal [green: chloride; purple: potassium]

Formation of ions as well as ion pairs is observed during the MD simulation. The formation of ion-pairs shows an agreement to the study of dissolution of sodium chloride in water using Flicker Noise Spectroscopy (FNS).\(^{36}\) The top layer of the KCl crystal lattice seems to dissolve,
while the other layers remain intact in the crystal lattice. The dissolution of \{110\} and \{111\} surfaces of KCl crystal is much faster compared to the stable \{100\} surface as it is known from the surface energy calculations that \{100\} plane of alkali halides is more stable compared to other planes such as \{110\} and \{111\}.\textsuperscript{37-41} The MSD calculations also supports the stability of the \{100\} plane compared to other planes.

2.2.2. Computational Methods

2.2.2.1. DFT calculations

DFT calculations were performed with \{100\} \((\text{KCl})_6(\text{H}_2\text{O})_n\) \([n = 0 \text{ to } 15]\) cluster using the generalized gradient approximations (GGA’s) which includes density gradients\textsuperscript{42-49} along with the functional PW91\textsuperscript{43} employing the density functional program DMO\textsuperscript{3} in Materials Studio (version 4.1.2) of Accelrys Inc., the electronic wave functions were expanded in atom-centered basis functions defined on a dense numerical grid.\textsuperscript{50-53} We used the double numerical basis set DND which is comparable with 6-31G* basis set. Single point calculations at Becke’s three parameter exchange functional with the correlation functional of Lee, Yang and Parr with 6-311+G (2d,p)\textsuperscript{22,54-56} level of theory are performed on the GGA/PW91/DND optimized geometries using the following equation (Eq. 1) as performed by Yamabe et al.\textsuperscript{22} with Gaussian 09, Revision B.01.\textsuperscript{57} The KCl \{100\} microcrystal for the DFT calculations was prepared using X-ray crystal structure data (Figure 1).

\[
\text{B.E. (\Delta E)} = [E \{(\text{KCl})_6(\text{H}_2\text{O})_n\} - E(\text{water}) + E \text{ of the most stable } \{(\text{KCl})_6(\text{H}_2\text{O})_{n-1}\}] \quad \text{Eq.1}
\]

To examine the effect of entropic contributions to the dissolution process of KCl with water clusters, additional free energy calculations were performed using B3LYP/6-311+G(2d,p)//GGA/PW91/DND level of theory for \([(\text{KCl})_6(\text{H}_2\text{O})_n]_{n=1-6}\) for representative cases.

2.2.2.2. Molecular Dynamics Calculations

Molecular dynamics calculations are performed with GROMACS 3.3.2\textsuperscript{59} using GROMOS96 43a1 force field.\textsuperscript{60} The simulation super cell of the \{100\} plane consists of 108 K\textsuperscript{+} and 108 Cl\textsuperscript{-} ions in a cubic box surrounded by 3248 water molecules. The \{110\} and \{111\} KCl crystals consists of 210 (105 K\textsuperscript{+} ions and 105 Cl\textsuperscript{-} ions) and 240 (120 K\textsuperscript{+} ions and 120 Cl\textsuperscript{-} ions) atoms, respectively. Similarly, water molecules are placed around the \{110\} and \{111\} crystal planes (3249 water molecules surrounding \{110\} and 3238 water molecules surrounding \{111\} planes). The water-water interaction is described by the TIP4P solvation model\textsuperscript{61-63} available in GROMACS 3.3.2.\textsuperscript{59} The initial cubic simulation boxes for the \{100\}, \{110\} and \{111\} planes of the KCl microcrystal lattice were generated with linear dimensions of 47.236 Å, 47.216 Å and 47.447 Å respectively. In all cases, an initial minimization of 100ps was followed by an equilibration at 300K for a period of 200ps. Harmonic restraints on the KCl crystal coordinates
are used during the equilibration procedure. The KCl \{111\} plane is electrostatically highly polar\textsuperscript{64-66} and hence the ions get scattered during initial minimization step. Therefore, the ions were kept fixed in all directions during the initial minimization; however the constraints were removed during the equilibration process. The simulation was performed with the NPT ensemble. The isothermal isobaric simulation (i.e. NPT ensemble dynamics) protocol comprises three major steps: (1) energy minimization of the KCl crystal in bulk water, (2) equilibration run at a desired temperature with harmonic restraints on the KCl crystals and (3) the full molecular dynamics run or production run. The temperature was set to 300 K and at a pressure of 1 atm. Temperature and pressure are kept constant with the coupling constants of 0.1 and 0.5ps, respectively by the Berendsen scheme.\textsuperscript{67} A periodic boundary condition is applied. The time step used in the simulations was 0.5 fs and the total time for the molecular dynamics run was 2.5 ns. For electrostatic interactions, we used the particle-mesh Ewald method.\textsuperscript{68,69} For potassium and chloride ions, the parameters are taken from the originally developed and supplied within the GROMACS software.\textsuperscript{60,70,71} Mean Square Displacement was calculated from the GROMACS 3.3.2 software, as described in earlier studies.\textsuperscript{72,73,74} The KCl crystal structure with the \{100\}, \{110\} and \{111\} surfaces for the MD simulations were also prepared using the X-ray crystal structure data (Figure 11).\textsuperscript{58}

2.2.3. Results and Discussions

2.2.3.1. Geometrical parameters of KCl and H\textsubscript{2}O

The calculated geometrical parameters of K\textsuperscript{+}…H\textsubscript{2}O and Cl\textsuperscript{-}…H\textsubscript{2}O with GGA/PW91/DND and B3LYP/6-311+G(2d,p) levels of theory are given in table 1. The O–H distance and the \textdegree\textsubscript{HOH} angle are also provided in table 1 to compare the computational methods with the available experimental data. The energies calculated using B3LYP/6-311+G(2d,p) are found to be in better agreement with the available experimental results (Table 1). To minimize the computational cost, the single point calculations are performed with B3LYP/6-311+G(2d,p) on GGA/PW91/DND optimized geometries which also provided the similar energetics to those obtained with B3LYP/6-311+G(2d,p) optimized results (Table 1). Additionally, the interactions of K\textsuperscript{+} ion and Cl\textsuperscript{-} ion with water molecules were also calculated with the GROMOS96 43a1 force field with GROMACS 3.3.2 software as MD simulations are performed with this method.\textsuperscript{57,58} The interactive distances between the water molecule and K\textsuperscript{+} ; Cl\textsuperscript{-} ions are found to be comparable with the B3LYP optimized geometries (Table 1). The interaction of separated ions with the water molecule provides a direct comparison of the experimental data with the computational methods used in this study, which however is not available for KCl\textsuperscript{-}H\textsubscript{2}O cluster.
Table 1. Calculated and experimental structural parameters along with energies for the interaction of KCl with water are given.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Optimized at GGA/PW91/DND</th>
<th>Single point calculations at B3LYP/6-311+G(2d,p) with GGA/PW91/DND geometries.</th>
<th>Optimized at B3LYP/6-311+G(2d,p)</th>
<th>Minimized with GROMOS Force Field</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(\text{OH})</td>
<td>0.977 Å</td>
<td>0.977 Å</td>
<td>0.963 Å</td>
<td>1.00 Å</td>
<td>0.957 Å^b</td>
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<tr>
<td>(\angle\text{HOH})</td>
<td>103.409°</td>
<td>103.409°</td>
<td>105.228°</td>
<td>105.00°</td>
<td>104.5°^31,b,/&gt;</td>
</tr>
<tr>
<td>r(\text{K}^+\cdots\text{OH}_2)</td>
<td>2.699 Å</td>
<td>2.699 Å</td>
<td>2.62 Å</td>
<td>2.61 Å</td>
<td>----</td>
</tr>
<tr>
<td>r(\text{Cl}^-\cdots\text{HOH})</td>
<td>2.052 Å</td>
<td>2.052 Å</td>
<td>2.16 Å</td>
<td>2.13 Å</td>
<td>----</td>
</tr>
<tr>
<td>B.E. ((\text{K}^+\cdots\text{OH}_2))</td>
<td>21.66 kcal/mol</td>
<td>18.24 kcal/mol</td>
<td>18.08</td>
<td>----</td>
<td>17.9 kcal/mol^b</td>
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<tr>
<td>B.E. ((\text{Cl}^-\cdots\text{HOH}))</td>
<td>24.71 kcal/mol</td>
<td>12.83 kcal/mol</td>
<td>14.7</td>
<td>----</td>
<td>14.9 kcal/mol^3u</td>
</tr>
</tbody>
</table>

Figure 1. The KCl microcrystal taken for the DFT calculations. All distances are given in Å. [Potassium - purple; Chlorine – green]

2.2.3.2. DFT Calculations

2.2.3.2a. Solvation of KCl microcrystal with 1-6 water molecules

The approach of a single water molecule to the \((\text{KCl})_6\) microcrystal is considered gives three different isomeric structures (Figure 2). The relative interaction energies calculated with B3LYP/6-311+G(2d,p)/GGA/PW91/DND using Eq. 1 suggest that 2a is more stable than 2b and 2c by 4.0 kcal/mol and 2.8 kcal/mol, respectively (Figure 2). In 2a, the water molecule interacts with \(\text{K}^+\) and \(\text{Cl}^-\) ions at the corner of the \((\text{KCl})_6\) microcrystal. The calculated structure 2b showed the interaction of the water molecule with a single \(\text{K}^+\) ion at the corner of the microcrystal, whereas, in 2c, the water molecule sits in the edge of the surface, weakly interacting with a \(\text{K}^+\) ion and forming a strong hydrogen bond with the neighboring \(\text{Cl}^-\) ion (Figure 2). This approach of single water molecule towards the \((\text{KCl})_6\) microcrystal does not
affect the K-Cl distance significantly. The largest separation of K$^+$ and Cl$^-$ ions (3.35 Å) is observed with 2c.

![Diagrams showing geometries and binding energies](image)

Figure 2. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies ($\Delta E$) of (KCl)$_6$(H$_2$O)$_2$ are given in kcal/mol. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].

Four different geometries of KCl microcrystal interacting with two water molecules were observed. The geometries of (KCl)$_6$(H$_2$O)$_2$ are shown in figure 3. Two water molecules interacting with two different K$^+$–Cl$^-$ on the microcrystal showed marginal separation of the K-Cl distances (3a). In the geometry 3b, where two water molecules interact with the same Cl$^-$ ion but with two different K$^+$ ion at the corner and the edge showed the largest separation of K-Cl distance (3.65 Å) in the edge K-Cl (Figure 3). The isomers 3c and 3d, where the water molecules interact with a same K$^+$ ion but with different Cl$^-$ ion at the corner and the edge respectively showed very less perturbation in the K$^+$–Cl$^-$ distance.
Figure 3. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (ΔE) of (KCl)$_6$(H$_2$O)$_2$ are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].

The interaction of three water molecules with the (KCl)$_6$ microcrystal showed five different solvated structures of (KCl)$_6$(H$_2$O)$_3$ (Figure 4). In geometry 4a, all the three water molecules interact with a single potassium ion at the corner site of the microcrystal (Figure 4). This structure suggests an elongation of three pairs of K-Cl distance to ~3.42 Å from the initial KCl crystal distance of 3.13 Å. The more unstable Isomer 4b is significant in terms of the separation of the K$^+$…Cl$^-$.. In this case, the water molecules approach from the different sites of the (KCl)$_6$ crystal and the K-Cl distance in the crystal lattice K$_4$-Cl$_{10}$, K$_3$-Cl$_{10}$ and K$_4$-Cl$_7$ are elongated by more than 4.5 Å (Figure 4). Therefore, the increase in the K-Cl distance is ~1.37Å compared to the unhydrated KCl microcrystal. These ion-pairs separated with water molecules can be considered as solvent shared ion pair as only one water molecule sits between the K$^+$ and Cl$^-$ ions. The similar approach of 3 water molecules at the corner of KCl microcrystal does not show any significant separation of ions (3.42 Å) (4c, Figure 4). The isomers 4c and 4d interact with different K$^+$ ions on the same plane of the crystal at both the edge and the corner but does not show much significant separation of K$^+$…Cl$^-$ (Figure 4).
Figure 4. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (ΔE) of (KCl)$_6$(H$_2$O)$_3$ are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].

Six isomeric structures of (KCl)$_6$(H$_2$O)$_4$ are calculated for the interaction of 4 water molecules with the microcrystal. In the calculated geometry 5a, 4 water molecules approach the same face of KCl microcrystal and the water molecules are hydrogen bonded to each other (Figure 5). This arrangement of water molecules seem to provide the overall stability of the structure, but the separation of K$^+$ and Cl$^-$ ions are marginally higher compared to the unhydrated KCl microcrystal. In the case of 5b, the approach 4 water molecules from 3 different sites of the KCl microcrystal lattice was observed and the water molecules interacted two edge chloride ions, showing a significant movement of the Cl$^-$ ions (Figure 5). The K$_4$-Cl$_{10}$ and K$_3$-Cl$_{10}$ distances increase to ~5.0 Å where as K$_2$-Cl$_{10}$ and K$_4$-Cl$_7$ distances elongate to over 4.0 Å (Figure 5). Similar approach of water molecules at the corner of the microcrystal gave the most stable structure with 4 water molecules, however, no significant changes are observed in the K-Cl distance (5c, Figure 5). The other calculated geometries, where the water molecules interact to
the potassium and chloride ions in a single plane (5f) or dual planes (5d and 5e) does not show any significant separation between the \( K^+ \) and \( Cl^- \) ions (Figure 5).

![Diagram](image)

\[ \Delta E = -7.4 \]
\[ \Delta E = -2.9 \]
\[ \Delta E = -9.9 \]

\[ \Delta E = -7.0 \]
\[ \Delta E = -5.4 \]
\[ \Delta E = -6.2 \]

Figure 5. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies \( (\Delta E) \) of \( (KCl)_6(H_2O)_4 \) are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].

5 isomeric structures have been calculated for the interaction of five water molecules with the \( (KCl)_6 \) microcrystal. The isomeric structure 6a is observed to be the most stable geometry (Figure 6). In this geometry, 4 water molecules are hydrogen bonded to each other and interact the microcrystal at one surface and another water molecule interacting from another side. Interaction of 5 water molecules from the same surface mostly at the corner sites showed a clear departure of a corner \( Cl^- \) ion from the two neighbouring potassium ions (\( K_4 \) and \( K_2 \)) with distance of 5.0 Å and 4.1 Å respectively (6b, Figure 6). The longest K-Cl distance was achieved when all the 5 water molecules interacted to a single \( Cl^- \) ion at the edge position (6c, Figure 6). This chloride ion (\( Cl_7 \)) is moved far away from the crystal lattice and the distances from the four neighboring potassium ions \( K_3, K_4, K_5 \) and \( K_6 \) being 5.87 Å, 4.45 Å, 4.38 Å and 4.35 Å.
respectively.\textsuperscript{1,34} A different approach of 5 water molecules at the edge and the corner positions (6d and 6e, Figure 6) didn’t show much perturbations in the K-Cl distances, only an edge K-Cl distance for geometry 6d and a corner K-Cl distance for geometry 6e was observed to be above 4 Å (Figure 6).

![Diagram](image1)

\begin{align*}
\Delta E &= -11.3 \\
\Delta E &= -7.2 \\
\Delta E &= -5.3 \\
\Delta E &= -5.1 \\
\Delta E &= -8.3
\end{align*}

Figure 6. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (E) of (KCl)\textsubscript{6}(H\textsubscript{2}O)\textsubscript{5} are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium – purple; Chlorine – green; Oxygen – red; Hydrogen – white].

The highest separation of K\textsuperscript{+} and Cl\textsuperscript{−} is found to be 6.12 Å with 6 water molecules (7a, Figure 7) though it is energetically 2.9 kcal/mol less favourable than 7b where the water molecules interact to the same surface. For the geometry 7a, the chloride ion (Cl\textsubscript{10}) is hydrogen bonded with five water molecules and the sixth water molecule assists through bridging for better interaction. It appears that the 6\textsuperscript{th} water molecule catalyzes the separation of ions in this case.
The other separated distances of the Cl\(^{-}\) ion from the potassium ions K\(_1\), K\(_2\) and K\(_3\) are 4.90 Å, 4.16 Å and 4.50 Å, respectively. In geometry 7c, the water molecules interact to different K\(^+\) ions at the corner as well as the edge sites, where as 7d shows the water molecules interacting at one corner K\(^+\) ion. Only two K\(^+\)--\text{Cl}\(^{-}\) distances are observed to have elongated more than 3.5 Å in both the cases (Figure 7). In the 7e and 7f geometries, the water molecules interact to a single plane and two planes respectively. Single plane interaction resulted in a single K\(^+\)--\text{Cl}\(^{-}\) elongation, while two plane interactions showed three K\(^+\)--\text{Cl}\(^{-}\) to elongate over 4.0 Å (Figure 7).

\[\Delta E = \begin{array}{l}
-6.0 \\
-8.9
\end{array}\]
Figure 7. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies ($\Delta E$) of (KCl)$_6$(H$_2$O)$_n$ are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].

The relative free energy calculations of [KCl]$_6$(H$_2$O)$_{n=1}$ clusters are given in Table 2. It has been the free energies calculated for these clusters shows similar energetic preferences like the electronic energies. The representative cases of the relative free energy calculations of [KCl]$_6$(H$_2$O)$_{n=2-6}$ clusters are given in tables 3-7 respectively.

Table 2. The relative free energies of [(KCl)$_6$(H$_2$O)$_{n=1}$] clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Free Energy in kcal/mol</td>
<td>0.0</td>
<td>1.7</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 3. The relative free energies of [(KCl)$_6$(H$_2$O)$_{n=2}$] clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>3a</th>
<th>3b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Free Energy in kcal/mol</td>
<td>1.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 4. The relative free energies of [(KCl)$_6$(H$_2$O)$_{n=3}$] clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>4a</th>
<th>4b</th>
<th>4c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Free Energy in kcal/mol</td>
<td>2.9</td>
<td>8.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 5. The relative free energies of [(KCl)$_6$(H$_2$O)$_{n=4}$] clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>5a</th>
<th>5b</th>
<th>5c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Free Energy in kcal/mol</td>
<td>6.4</td>
<td>9.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 6. The relative free energies of [(KCl)$_6$(H$_2$O)$_{n=5}$] clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>6a</th>
<th>6b</th>
<th>6c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Free Energy in kcal/mol</td>
<td>0.0</td>
<td>2.6</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 7. The relative free energies of [(KCl)$_6$(H$_2$O)$_{n=6}$] clusters.
2.2.3.2b. Solvation of KCl microcrystal with 7-15 water molecules

To examine the influence of more number of water molecules on the separation of ions in KCl microcrystal, interactions upto 15 water molecules have been calculated. Solvent shared ion pairs are observed with 7, 8 and 9 water clusters upon interaction with the KCl microcrystal lattice. The K-Cl distance increases with increasing number of water molecules. It has been observed that the edge K\(^+\)–Cl\(^-\) gives the maximum separation for 7, 8 and 9 water molecules. A maximum separation of 7.10 Å for the Cl\(^-\) ion from the edge K\(^+\) ion of the lattice have been observed with 9 water molecules (8c, Figure 8).

![Figure 8. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (\(\Delta E\)) of (KCl\(_6\)(H_2O))\(_7\), (KCl\(_6\)(H_2O))\(_8\), (KCl\(_6\)(H_2O))\(_9\) are given in kcal. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white]. The addition of a 10\(^{th}\) water molecule leads to the further separation of K\(^+\) and Cl\(^-\) ions (7.50 Å) in the microcrystal lattice of KCl (9a, Figure 9). As described above that a cluster of at least 4 water molecules around the K\(^+\) and Cl\(^-\) ions (5b) initiate the separation of the K\(^+\)–Cl\(^-\) (Figure 5) and 6 water molecules augment the situation (7a, Figure 7). Therefore, in the case of 10 water molecules interactions, there is another possibility that two water clusters of 4 and 6 water molecules can approach at two different sites of the microcrystal lattice (scheme 4). The clusters of 4 and 6 water molecules can be placed either near the edge Cl\(^-\) ions at the diagonal positions in the crystal lattice in one case (a, Scheme 4) or in another situation in the edge and
a corner Cl’ ion (b, Scheme 4). However the separation of the ions from the KCl crystal lattice were observed to be 6.29 Å in 9b and 6.79 Å in 9c respectively, which is smaller than that of 9a (Figure 9). In all the three situations the ions from the edge sites are observed to separate out but no such separations are observed for the corner Cl’ ions. The B3LYP/6-311+G(2d,p) calculated energies using Eq. 1 suggests that the separation of ions is more preferred in 9a compared to 9b and 9c.

![Scheme 4](image)

Scheme 4. The two possible approach of 4 and 6 water clusters towards the KCl microcrystal (a) on two diagonal edge chloride ions and (b) one edge and another corner chloride ion.

![Figure 9](image)

Figure 9. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (ΔE) of (KCl)₆(H₂O)₁₀ are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].
Furthermore, two possibilities of attack with one cluster or two clusters are possible for a larger number of water molecules. But it has always been observed that the single water cluster is more effective in terms of separation between the K-Cl. The K-Cl distances for the interaction of 11 water molecules as one cluster was observed to be 7.62 Å, but a different orientation with two water clusters, the distance was observed to be 6.89 Å (10a, 10b Figure 10). The single cluster interaction was observed to be better in energetics too. Departure of the Cl ions from the edge of the lattice was observed with \( n = 12 \) water molecules with a KCl distance of \( \sim 6.6 \) Å. The other orientations with two clusters showed much less distance of only 5.4 Å (10c, 10d Figure 10). The separation of the Cl ion from the edge potassium ions was found to be much higher in the case of 13 water molecules for both single and dual cluster interactions (10e, 10f Figure 10). Similarly like 11 water molecules the interactions through single cluster is energetically more applicable. The separation of Cl ions from the microcrystal lattice edge site, is found to be largest with 14 water molecules with a distance of 8.08 Å between the K\(^+\) and Cl\(^-\) ions (11a, Figure 11). Similar separation are observed between the K\(^+\) and Cl\(^-\) ions of the edge positions of the microcrystal lattice with 15 water molecules (11b, Figure 11). The hydrated forms of these KCl microcrystals showed the separation of more polarizable Cl\(^-\) ions from the lattice,\(^{79}\) whereas, the K\(^+\) ions are less perturbed on the lattice sites.

The separation of Cl\(^-\) ion from the crystal lattice was also observed with the dissolution process of NaCl.\(^{23}\) The metadynamics study of Liu et al. using PBE exchange–correlation functional incorporated in the CP2K/Quickstep package showed that the first step of the dissolution of the NaCl starts with an elongation of the corner Cl\(^-\) ion from the lattice, whereas, the Na\(^+\) ions resides in the crystal lattice. The metadynamics study further showed that Na\(^+\) in the form of adatom-like configuration is the second ion to be separated from the NaCl lattice. Thus, this study revealed that the electrical neutrality is conserved in the dissolution of NaCl.

The DFT calculations performed at B3LYP/6-311+G(2d,p)//GGA/PW91/DND level of theory showed a clear departure of Cl\(^-\) ion from the KCl crystal lattice. The DFT calculations are performed with water clusters and hence in contrast to the metadynamics calculations for NaCl crystals in bulk water,\(^{23}\) the complete dissolution of ions from the KCl lattice was not observed. Interestingly, the use of water clusters show the initiation of separation of Cl\(^-\) ion from the KCl crystal lattice with 4 water molecules, whereas, such information is not easy to attain with other approach. The separations of Cl\(^-\) ions from the KCl crystal through water clusters is more prominent from the edge of the lattice, which however, was observed from the corner site of NaCl crystal.\(^{23}\) Furthermore, the elongated Cl\(^-\) ion is coordinated with 5 water molecules in most of the cases of \([(\text{KCl})_6(\text{H}_2\text{O})_n = 1-15]\), which was also observed in the NaCl metadynamics study.\(^{23}\)
ΔE = -2.4

10a

ΔE = -1.1

10b

ΔE = 0.5

10c

11 water

ΔE = 0.1

10d

12 water

ΔE = 2.4

10a
ΔE = -6.8

13 water

Figure 10. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (ΔE) of (KCl)$_6$($\text{H}_2\text{O})_{11-13}$ are given in kcal/mol. Binding energies are calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white].

ΔE = -2.8

14 water

Figure 11. B3LYP/6-311+G(2d,p)//GGA/PW91/DND calculated geometries and binding energies (ΔE) of (KCl)$_6$($\text{H}_2\text{O})_{14}$ and (KCl)$_6$($\text{H}_2\text{O})_{15}$ are given in kcal/mol. Binding energies are
calculated with Eq. 1. All distances are given in Å [Potassium - purple; Chlorine – green; Oxygen – red; Hydrogen – white.

As stated above, on average 15 water molecules are necessary to dissociate a single KCl molecule at 273 K at saturation concentration (Scheme 1) and the DFT calculations also showed a well separated \( K^+ \) and \( \text{Cl}^- \) ions in microcrystal lattice with ~15 water molecules, however, the complete dissolution of such lattice may require more number of water molecules.

To examine the dissolution of KCl microcrystal, classical molecular dynamics simulations are performed. The DFT studies also showed the formation of solvent-shared ion pairs (with water clusters containing 3-9 water molecules) and solvent separated ions (with water clusters of 10-15 water molecules) while interacting with different clusters of water molecules.

2.2.3.3. Molecular Dynamics Simulation

DFT calculations are static in nature, and thus dynamic study of separation of ions will shed further light on the dissolution of KCl microcrystal. The complete dissolution of the ions from the KCl microcrystal lattice in the bulk solution can only be observed with a quite long Molecular Dynamics simulation. To examine the dynamical profiles of the KCl crystal with larger number of water molecules, we have performed classical NPT MD with GROMOS96 43a1 force field with the GROMACS 3.3.2 program.\(^{58,59}\) The molecular dynamics calculations have been performed with a \{100\} plane of the (KCl) crystal with explicit water molecules using TIP4P solvation model. The \{110\} and \{111\} planes of KCl crystal are also taken for the MD simulation (Figure 12). The unstable planes \{110\} and \{111\} of alkali halides can be grown with the habit modifications of salt crystals.\(^{63-65,80-84}\)

![Figure 12. The initial structures of the KCl crystals for the MD calculations (a) \{100\} plane; (b) \{110\} plane and (c) \{111\} plane generated from the crystal structure of KCl. The water molecules are shown in light gray.](image)

To examine the dissolution of KCl microcrystal, classical molecular dynamics simulations are performed. The DFT studies also showed the formation of solvent-shared ion pairs (with water clusters containing 3-9 water molecules) and solvent separated ions (with water clusters of 10-15 water molecules) while interacting with different clusters of water molecules.
molecules are shown surrounding the different planes of the crystals [green: chloride; purple: potassium; red: oxygen and black: hydrogen].

2.2.3.3a. KCl {100} surface

The Cl\(^-\) and K\(^+\) ions seem to separate from the crystal lattice from the different corners of the crystal (a, Figure 13). We have also noticed that the MM approach does not show a clear preference of Cl\(^-\) ion dissolution from the crystal lattice in contrast to the DFT calculations. This difference seems to arise due to the fact that MM force fields does not account for the polarization difference between the ions as observed by Liu et al.\(^{23}\) At slightly longer time steps (~653ps), the well separated ion-pair and a solvated K\(^+\) ion is observed (b, Figure 13 and Figure 14). The departures of ions are observed from the different sides of the crystal during the simulations of the {100} plane, however, such ions reabsorb in the lattice at longer time scales. At the completion of the MD run, the dissolved ions separate out only from the top layer of the KCl crystal lattice (c, Figure 13). The formation of solvated K\(^+\) ion interacting with 6 water molecules and K\(^+\)-Cl\(^-\) ion pair was observed at different stages of the MD simulation (Figure 14).

Figure 13. Snapshots at (a) 50ps, (b) 653ps and (c) 2.5ns for the molecular dynamics study of {100} plane with (KCl)\(_{216}\) and 3248 water molecules are given here. The separating K\(^+\) and Cl\(^-\) ions at 50ps are indicated by circles. The water molecules as point structures are shown.
surrounding the {100} plane of the KCl crystal [green: chloride; purple: potassium; red: oxygen and black: hydrogen].

Figure 14. (a) The orientations of water molecules around the K⁺ ion separated from the {100} plane of the KCl microcrystal lattice (b) The orientations of water molecules around the ion-pair separated from the {100} plane of the KCl microcrystal lattice at 653ps (purple: potassium ion, blue: interacting water molecules; red: oxygen; black: hydrogen).

2.2.3.3b. KCl {110} surface

In the case of the less stable {110} plane of KCl, the ion-pair initiates to separate from the edge of the lattice (a, Figure 15). At longer time steps, the ions separate from multiple sites of the {110} plane and the separation the ions is more distinct compared to the {100} plane (b and c, Figure 15). This result suggests that the unstable {110} plane dissolve much faster than the corresponding {100} plane, which supports the surface energy data of alkali halides.37-41

According to classical MD simulations by Shinto et al. for the dissolution study of NaCl {001} and {011} surfaces, no ion is dissolved from the surfaces within 10 ps85 and our study very aptly showed similar observations for KCl crystal as the dissolution process of the {100} and {110} planes of KCl started after 10 ps.
2.2.3.3c. KCl {111} surface

The dissolution of the KCl {111} plane was observed to be the fastest of the three planes suggesting it to be the most unstable one. The separation of 3 Cl\textsuperscript{-} ions from corner and edge of the crystal lattice during initial MD steps (a, Figure 16) was observed. At ~3ps, potassium ions started to separate out from the crystal lattice (b, Figure 16). This observation is very similar to the dissolution of {111} plane of NaCl as noticed by Ohtaki et al.\textsuperscript{25} Moreover, the ions separate out in a random fashion from the lattice at longer time steps (c, Figure 16).

Figure 15. Snapshots at (a) 12ps; (b) 1000ps and (c) 2.5ns for the molecular dynamics study of {110} plane of (KCl\textsubscript{210} microcrystal with 3249 water molecules are given here [green: chloride; purple: potassium; red: oxygen and black: hydrogen].
2.2.3.3d. MSD analysis

The mean square displacement (MSD) calculations performed using the GROMACS 3.3.2 software for the different planes of KCl showed that the displacements of the ions from their initial positions with time are relatively lower for \{100\} than \{110\} and \{111\} plane (Figure 17). This indicates that the \{110\} and \{111\} plane solvates much faster than the \{100\} plane.

Figure 16. Snapshots at (a) 1ps; (b) 3ps and (c) 2.5ns for the molecular dynamics study of \{111\} plane of (KCl)$_{240}$ microcrystal with 3238 water molecules are given here [green: chloride; purple: potassium; red: oxygen and black: hydrogen].
2.2.4. Conclusion

In this part of the thesis, we have investigated the solubility and dissociation phenomenon of (KCl)$_6$ microcrystal in the presence of 1 to 15 water molecules computationally using DFT calculations. Molecular dynamics simulations with GROMACS force field have been carried out to investigate the solvation process in the bulk water for the different planes of the KCl crystal [(100), (110) and (111)]. It was observed from the DFT calculations that the initial dissolution occurs with the separation of the Cl$^-$ ions from the crystal lattice. This observation is similar to the studies performed with NaCl crystals using \textit{ab initio} MD. The departure of Cl$^-$ has been found to be more significant from the edge of the KCl microcrystal. A minimum of four water molecules are necessary to initiate the separation of the ions from KCl microcrystal as observed for single KCl solvation. The simultaneous removal of more than one Cl$^-$ ions seems to be less effective in comparison to the removal of a single Cl$^-$ ion from the KCl surface. The DFT calculations reveal that solvent shared ion pairs are formed with 3 to 9 water clusters, whereas solvent separated ion-pairs are observed with 10-15 water clusters in the hydration process of KCl microcrystal. Classical molecular dynamics calculations, performed with the stable (100) surface containing a cluster of 108 K$^+$ and 108 Cl$^-$ ions revealed that both ions seem to separate from corner sites of the crystal lattice in the initial stages of the simulation process and solvation of ions occurred from a single layer, while other layers remain intact. The polarizability of ions accounts for the preference for the separation of Cl$^-$ ions from the crystal lattice in DFT studies, which is lacking in the MM force field used for classical MD simulations. MD studies performed with other unstable planes of the KCl crystal lattice like {110} and {111} showed much faster solvation than the {100} plane which is also corroborated with MSD analysis. The separation of ion pair from the crystal lattice is observed with {110} plane, where as Cl$^-$ ions separate out initially for the {111} plane. At longer time scales, solvated ions or ion pairs separate out from
different sites within these crystal lattices. These studies are relevant to the studies of reactivity of atmospheric chemistry.
References

50. Materials Studio DMOL3 Version 4.1 Accelrys Inc., San Diego, USA