

## Effects of Inorganic Salts Addition on Na-montmorillonite Clay at High Temperature and High Pressure: Insights from Molecular Dynamics Simulation

Moussa Camara<sup>1</sup>, Hualin Liao<sup>1</sup>, Jiafang Xu<sup>1\*</sup>, Tingji Ding<sup>1</sup>, Rogers Swai<sup>1</sup> and Jun Zhang<sup>2</sup>

<sup>1</sup>Shandong Provincial Key Laboratory of Oilfield Chemistry, Key Laboratory of Unconventional Oil & Gas Development, School of Petroleum Engineering, China University of Petroleum, Qingdao, China

<sup>2</sup>School of Material Science and Engineering, China University of Petroleum, Qingdao, China

### Abstract

In the present work, we performed a molecular dynamics (MD) simulation of Na-montmorillonite (Na-Mt) in non-ambient environment under the crystalline swelling to evaluate the effect of temperature and inorganic salts addition on the interlayer structure and the swelling behavior of Na-Mt. The activities of inorganic salts ( $\text{NH}_4\text{Cl}$ ,  $\text{AlCl}_3$ ,  $\text{MgCl}_2$  and  $\text{FeCl}_3$ ) on the hydration process of Na-Mt at high temperatures (200, 300, 400, 500, and 600 K) and high pressure (HTHP) of  $P=6$  GPa in an isobaric isothermal ensemble (NPT) were investigated. The results showed that addition of inorganic salts into Na-Mt enhanced mobility of the interlayer species, and shrunk the hydration shell of the interlayer ions with a rise in temperature. The salts inhibited swelling by reducing the mobility of the interlayer species and the basal spacing. The type of cations present between the layers, their hydration energies affected the structure and properties of Na-Mt. Chlorine played an important role in the inhibition process of inorganic salts by exerting strong attractive forces on interlayer  $\text{H}_2\text{O}$  molecules. Compared with the other salts, the most stable state of Na-Mt at HTHP is achieved with  $\text{NH}_4\text{Cl}$ . These results could help a better understanding of the inhibition effect of inorganic salts on Na-Mt and predict the hydration process of Na-Mt at HTHP for further improvement of its structure.

### Highlights

- Cl anion hydration energy change is more evident with salt type than temperature
- Inorganic salt and temperature increase shrink the hydration shell of interlayer ions
- $\text{NH}_4\text{Cl}$  addition provides a good inhibition at high temperature and high pressure
- Increasing temperature and hydration degree promote the cation exchange process

**Keywords:** Na-Mt; Inorganic salts; Molecular dynamics; Radial distribution function; Self-diffusion coefficient

### Introduction

Clay minerals are fine grained, poorly crystalline, porous and ubiquitous materials found in large quantities in the earth's geologic deposits, terrestrial weathering environments and marine sediments. Swelling clay mineral play important roles in many engineering applications including environmental remediation, clay mineralogy, repository design for nuclear waste disposal, sedimentary geology, abnormal subsurface pressure, borehole stability in drilling operation and as additives for numerous industrial processes and commercial products [1]. Inorganic salts are extensively used to lower water retention in clay by mechanism of ion adsorption on clay surface and osmotic pressure, minimizing the hydration of argillaceous formations in the well [2]. The swelling properties of clay minerals are influenced by several factors such as thermodynamic variables (temperature, external pressure, water chemical potential, and osmotic pressure) [3,4] and structural variables (layer charge, charge location and interlayer cations) [4,5]. Montmorillonite (Mt) belongs to the smectites class of clay family that comprises tetrahedral and octahedral sheets in a 2:1 ratio. They consist of two tetrahedral sheets separated by an octahedral sheet. Isomorphic substitution of  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in octahedral site and  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in tetrahedral results the negative charges in Mt which are balanced by the inorganic cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  [6]. In water solution, these counter ions are exchangeable with other cations by the ions exchange (CEC) process. In contact with water and polar solvent, Na-Mt has a high ability to swell and exhibits two different regimes which are crystalline and osmotic swellings [7-9]. These

characteristics are well known from experimental and simulation studies under ambient temperature and pressure [10,11], but less are known at HTHP [12]. To understand the swelling behavior and the effect of inorganic salts addition on Na-Mt, there is need to analyze the mechanism of water adsorption and the impact of the salts on its surface to gain knowledge of the structural and thermodynamic factors [13,14]. Stefani et al. [15] used X-ray diffraction and scanning electron microscopy with energy dispersive X-ray spectroscopy to study the stability of Mt structure saturated with lanthanum at high pressure (up to 12GPa) and room temperature and high pressure and high temperature. Huang et al. [16] employing real-time diffraction and X-rays from the Cornell High Energy Synchrotron Source (CHESS) showed that montmorillonite hydrate with three water layers was stable at most T-P conditions found in sedimentary environments. Camara et al. [17] by molecular dynamics simulation showed the great impact of inorganic salt ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ) addition on hydrated Na-

**\*Corresponding author:** Jiafang Xu, Shandong Provincial Key Laboratory of Oilfield Chemistry, Key Laboratory of Unconventional Oil & Gas Development, School of Petroleum Engineering, China University of Petroleum, Qingdao, China, Tel: 18678986873; E-mail: [xjiafang@upc.edu.cn](mailto:xjiafang@upc.edu.cn)

Received May 17, 2019; Accepted June 04, 2019; Published June 11, 2019

**Citation:** Camara M, Liao H, Xu J, Ding T, Swai R, et al. (2019) Effects of Inorganic Salts Addition on Na-montmorillonite Clay at High Temperature and High Pressure: Insights from Molecular Dynamics Simulation. J Material Sci Eng 8: 525.

**Copyright:** © 2019 Camara M, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Mt at HTHP. Colten [18] studied the hydration state of Na-saturated montmorillonite at elevated temperatures and water pressures using HTHP device to demonstrate that montmorillonite with two layer of water was stable at temperature between 50 and 200°C and pressure up to 456 bars. Tuck et al. [19] in their experimental study used the quasi-elastic neutron scattering to measure the diffusion of water molecules in a two layered Ca-Mt at three different temperatures. Jiafang Xu et al. [20] have investigated the swelling behavior of hetero-ionic Na/Cs-Mt, Na/Mg-Mt and compared them with those of the homo-ionic Na-, Cs-, Mg-Mt through a molecular dynamics simulation. Morodome and Kawamura [21] have used the X-ray diffraction at temperature up to 150°C to investigate the swelling behavior of Na-, Ca- Mt. de Carvalho and Skipper [12] have performed a Monte Carlo simulation in the grand canonical ensemble to investigate the stability of K-Mt hydrates under 353 K and 625 bar. Zheng and Zaoui [22] have employed molecular dynamics simulation to study the effect of temperature on the diffusion of water and monovalent counter ions in hydrated montmorillonite under temperature range between 260 and 400 K. Several studies have contributed to our understanding of Clay-H<sub>2</sub>O-shale inhibitor system, but few comparative studies of salts effect on Na-Mt swelling inhibition have been investigated at microscopic level. The purpose of this study is to examine the swelling characteristics of Na-Mt at HTHP in the regime of crystalline swelling with inorganic salts and to predict the essential feature of inorganic salts as swelling inhibitors. The effect of temperature and pressure on the mobility of interlayer species, the interaction between water-oxygen and interlayer ions, the effect of inorganic salts on the stability of Na-Mt and the changes that occurred on its structure at increasing temperature and constant pressure are studied.

## Methodology

### System set up

The clay mineral used in this study was taken from the model derived by skipper and co-workers [7]. The unit cell formula is:

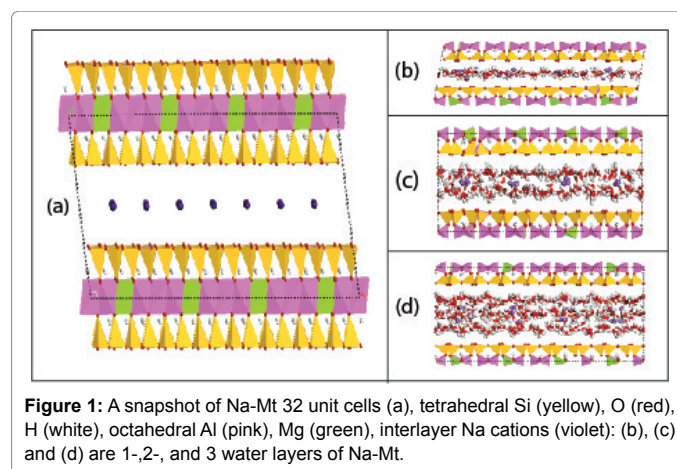
$$Na_{0.75}[Si_{7.75}Al_{0.25}](Al_{3.25}Mg_{0.75})O_{20}(OH)_4 \quad (1)$$

Na-Mt model was constructed, and the atomic coordinates were derived from the space group of monoclinic C2/m with  $a=5.23$  Å,  $b=9.06$  Å,  $c=9.60$  Å (with no water in interlayer spaces),  $c$  value changed with water molecule content between the layers,  $\alpha=90^\circ$ ,  $\beta=99.00^\circ$ ,  $\gamma=90^\circ$ , and the symmetrical L2PC structure. The clay mineral layers were considered as rigid molecules and mirror image.

The atomic charge assigned to each atom sites in the clay were given by Smith [23]. Based on the primitive unit cell, the supercell of the model ( $8a \times 4b \times 1c$ ) was built (Figure 1). The measure of the three-dimensional, periodic boundary conditions applied to the system was  $41.84 \times 36.24$  Å<sup>2</sup>, which consists of 1280 atoms in the clay mineral layers equivalent to 32 unit cells and 24 atoms of sodium. Based on this formula, our clay sheets with 32 unit cells have 16 isomorphic substitutions of Al by Mg ion in the octahedral sheets, 8 isomorphic substitutions of Si by Al ion in the tetrahedral sheets, and 24 compensating Na cations in the interlayer region.

### Molecular dynamic simulation

Molecular dynamics simulation was performed under the module "Forcite" of Materials Studio 7.0 software to investigate the effect of inorganics salts on the hydration process of Na-Mt at HTHP. The interaction between the atoms was described by Universal Force Field (UFF) which is a wider applicable force field, and its parameters spread



**Figure 1:** A snapshot of Na-Mt 32 unit cells (a), tetrahedral Si (yellow), O (red), H (white), octahedral Al (pink), Mg (green), interlayer Na cations (violet): (b), (c) and (d) are 1-, 2-, and 3 water layers of Na-Mt.

all over the entire element of the periodic table [24]. Metal-Oxygen interactions were based on a Lennard-Jones potential combined with electrostatics. For the water behavior SPC/E model of Berendsen et al. [25] was used. The simulation was carried out at  $P=6$  GPa and temperature changing from 200 to 600 K in the isobaric isothermal ensemble (NPT), in which the temperature and pressure were constant via a Nose-Berendsen thermobroastat, while the volume of the system was allowed to vary [26,27]. We chose to output the atomic positions every 1.0 fs during production runs, the total simulation time were set to 2000 ps, the number of steps was 2,000,000, and the frame output was obtained every 5000 steps. The short range van der Waals forces were applied with a 15.5 Å cut-off distance. To calculate the long range electrostatics, the Ewald summation method was used. The total potential energy was given by the summation of all interaction sites of the system [23]:

$$U = \sum_i \sum_j \left( \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \right) \quad (2)$$

Where  $q_i$  and  $q_j$  are the charges on atoms  $i$  and  $j$ ,  $r_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $\epsilon_{ij}$  and  $\sigma_{ij}$  are Leonard-Jones parameters deduced from Lorentz-Berthelot rule. All the interaction terms of Leonard-Jones are from combination of these relationships [23]:

$$\sigma_{ij} = 1/2(\sigma_i + \sigma_j) \quad (3)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (4)$$

The potential parameters used for oxygen and hydrogen were those used in water [28]. The method of velocity initialization used for the dynamics calculation was Random. The water contents considered in these simulations were 4, 8 and 12 water molecules per unit cell (128, 256 and 384 H<sub>2</sub>O molecules), corresponding to one-, two- and three water layers, respectively, and the initial basal spacing were 12.5 Å, 15.5 Å and 18.5 Å for one-, two- and three- water layers systems [29]. From the output data obtained, radial distribution functions (RDF), basal spacing, total energy and diffusion coefficient profiles were calculated.

### Analysis of simulation results

The basal spacing ( $c$ ) was calculated from the NPT simulations

$$c = \langle V \rangle / (2 \times S) \quad (5)$$

where  $\langle V \rangle$  denotes the statistically averaged volume of the simulated system, and  $S$  is the basal surface area.

The RDF of water molecules around the interlayer cations was calculated as [30]:

$$g(r) = 1 / (4\pi\rho r^2) dN / dr \quad (6)$$

where  $\rho$  is the number density of water molecules,  $dN$  is the average number of particle of water molecules lying at the region of  $r + dr$  from a cation.  $N$  is the coordination number  $n(r)$  of water molecules around the cation.

The self-diffusion coefficient  $D$  of the interlayer species was calculated with a two-dimension Einstein relation.

$$D = 1 / 4d / dt < r(t)^2 > \quad (7)$$

Where  $< r(t)^2 >$  is the mean square displacement of the particle defined by  $r(t) = R(t) - R(0)$ , with  $R(t)$  is the particle position at time  $t$ , and  $R(0)$  is the initial particle position.

## Results and Discussion

### Interaction between interlayer ions and water molecules

The effect of temperature increase on the interaction between interlayer ions and  $H_2O$  molecules was investigated by analyzing the RDF between ions and  $H_2O$  molecules' oxygen ( $O_w$ ) and hydrogen ( $H_w$ ), and their coordination numbers. The results showed that the rise in temperature reduced the attractive forces exerted by interlayer ions on  $H_2O$  molecules after inorganic salts addition (Figure 2). The RDF peaks of Na-Ow,  $NH_4$ -Ow, Mg-Ow, Al-Ow, Fe-Ow and Cl-Ow in one, two and three hydration layers of Na-Mt with inorganic salts decreased with the rise in temperature from 200 to 600 K (Figures 3-5 and S1-S3).

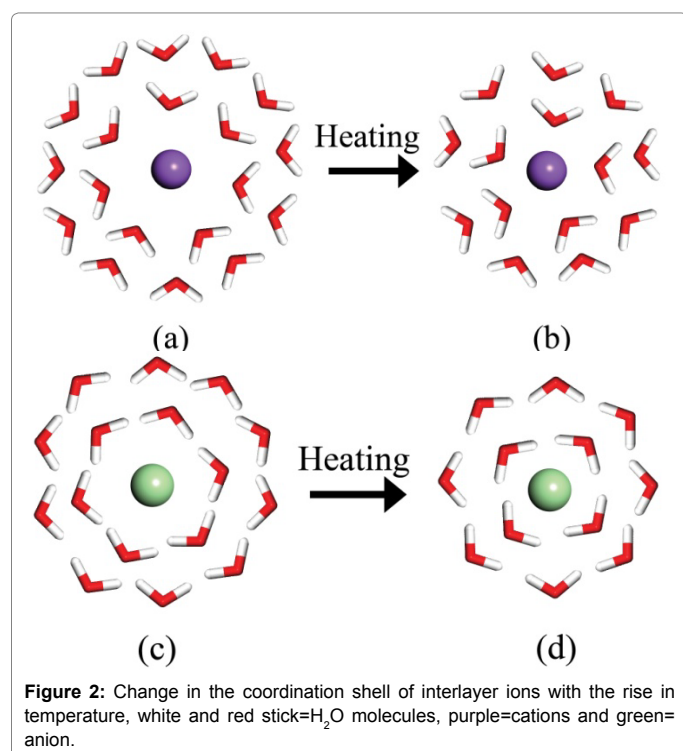
This decrease can be explained by the reduction of the amount of  $H_2O$  molecules around the interlayer ions due to the weakening of the electrostatic attractive forces between them and  $H_2O$  molecules (Figure 2a and b), and between the negative charged layers and interlayer species when the temperature and the hydration degree increased

[17]. The decrease of their hydration shell in this process facilitated the motion of both  $H_2O$  molecules and interlayer ions because of the weakening of the attractive forces and the hydrogen bonds formed between  $H_2O$  molecules in the interlayer space. The interlayer ions are surrounded by  $H_2O$  molecules and exerted strong electrostatic attraction forces on them in one hydration layer than in two and three hydration layers as indicated by the intensity of the RDF peaks obtained in one hydration layer compared with those of two and three hydration layers. The position of the RDF peaks of Na-Ow,  $NH_4$ -Ow, Mg-Ow, Al-Ow and Fe-Ow were almost the same for the three hydration states after  $FeCl_3$ ,  $MgCl_2$ ,  $NH_4Cl$ , and  $AlCl_3$  addition (Figures 3, 4 and S1, S2) and the average distance obtained were 2.23, 1.92, 2.25, 2.53 and 2.87 Å, respectively. Those of Cl-Ow were 2.64, 2.68, 2.72, 2.78 Å for  $NH_4Cl$ ,  $AlCl_3$ ,  $MgCl_2$  and  $FeCl_3$ , respectively. These results show that temperature change and inorganic salts addition do not have significant effects on the hydration energy of the interlayer cations, and also that the type of inorganic cations has a significant effect on the hydration energy of Cl anions.

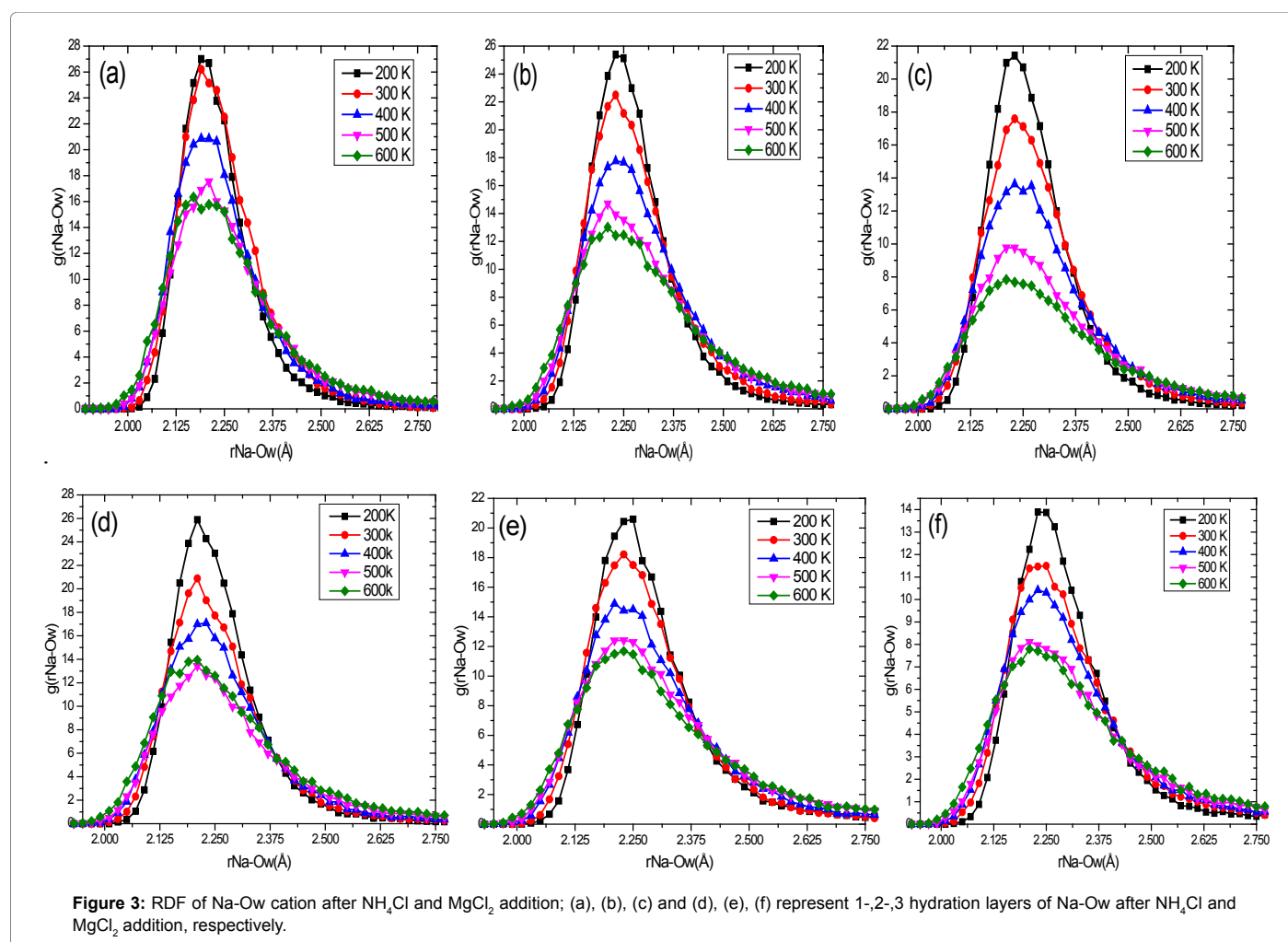
The hydration energy of Cl anions obtained after  $NH_4Cl$  addition was higher than those obtained with  $AlCl_3$ ,  $MgCl_2$  and  $FeCl_3$ , respectively.  $NH_4$  cations had the least radius and attractive forces on  $H_2O$  molecules and hence lowest hydration energy compared to Fe and Mg cations, and least binding forces on  $H_2O$  molecules compared to Fe, Mg, and Al. Al cations had the lowest hydration energy compared to the four cations despite their size and valence.  $NH_4$  cations diffused close to the clay surfaces and Cl anions diffused in the outer-sphere complexes where they shared interlayer  $H_2O$  molecules with only Na cations after  $NH_4Cl$  addition. This phenomenon was also observed for Al cations which diffused in the inner sphere complexes after  $AlCl_3$  addition. Comparing the RDF of Na-Ow and Cl-Hw after adding the salts with those of  $NH_4$ -Ow, Mg-Ow, Al-Ow, and Fe-Ow, it was observed that RDF peaks of Cl-Hw obtained for  $NH_4Cl$  addition was higher than those of  $AlCl_3$ ,  $MgCl_2$  and  $FeCl_3$ , indicating that Cl anions attracted more  $H_2O$  molecules in the hydration shell after the addition of  $NH_4Cl$  than the other three inorganic salts.

This result shows that Cl anions exert good inhibition effect on  $H_2O$  molecules by attracting them when  $NH_4Cl$  is added. Na cations attracted  $H_2O$  molecules in their surrounding in one hydration layer with  $FeCl_3$  addition than  $AlCl_3$ ,  $NH_4Cl$  and  $MgCl_2$  due to the restricted layer spaces caused by the attractive forces exerted by Fe cations on clay surfaces in two and three hydration layers for  $NH_4Cl$  than for  $FeCl_3$ ,  $MgCl_2$ , and  $AlCl_3$  addition because Na cations moved from the inner sphere complexes to the outer sphere complexes due to the exchange of Na by  $NH_4$  cations. Na cations certainly diffused in the outer sphere complexes after salts addition and remained hydrated irrespective of the type of salts, however, the presence of inorganic salts and the rise in temperature minimized the hydration degree of Na cations. In the case of the RDF of  $NH_4$ -Ow, Mg-Ow, Al-Ow, and Fe-Ow, it was observed that the RDF peaks obtained for  $NH_4$ -Ow were smaller than those of Al-Ow, Mg-Ow and Fe-Ow cations, indicating that Fe cations were more hydrated in the interlayer of Na-Mt and exerted strong attractive forces on  $H_2O$  molecules than Mg, Al and  $NH_4$  cations.

Less  $H_2O$  molecules are in the hydration shell of Al than Mg and Fe cations but attracted more  $H_2O$  molecules there than  $NH_4$  cations which diffused in the inner sphere complexes where they were attracted by the negative charged clay surfaces to form coordination cages with siloxane oxygen atoms than  $H_2O$  molecules [20]. Al cations certainly diffused close to the clay mineral surface, where they are less coordinated by  $H_2O$  molecules.







### Interaction between interlayer water molecules

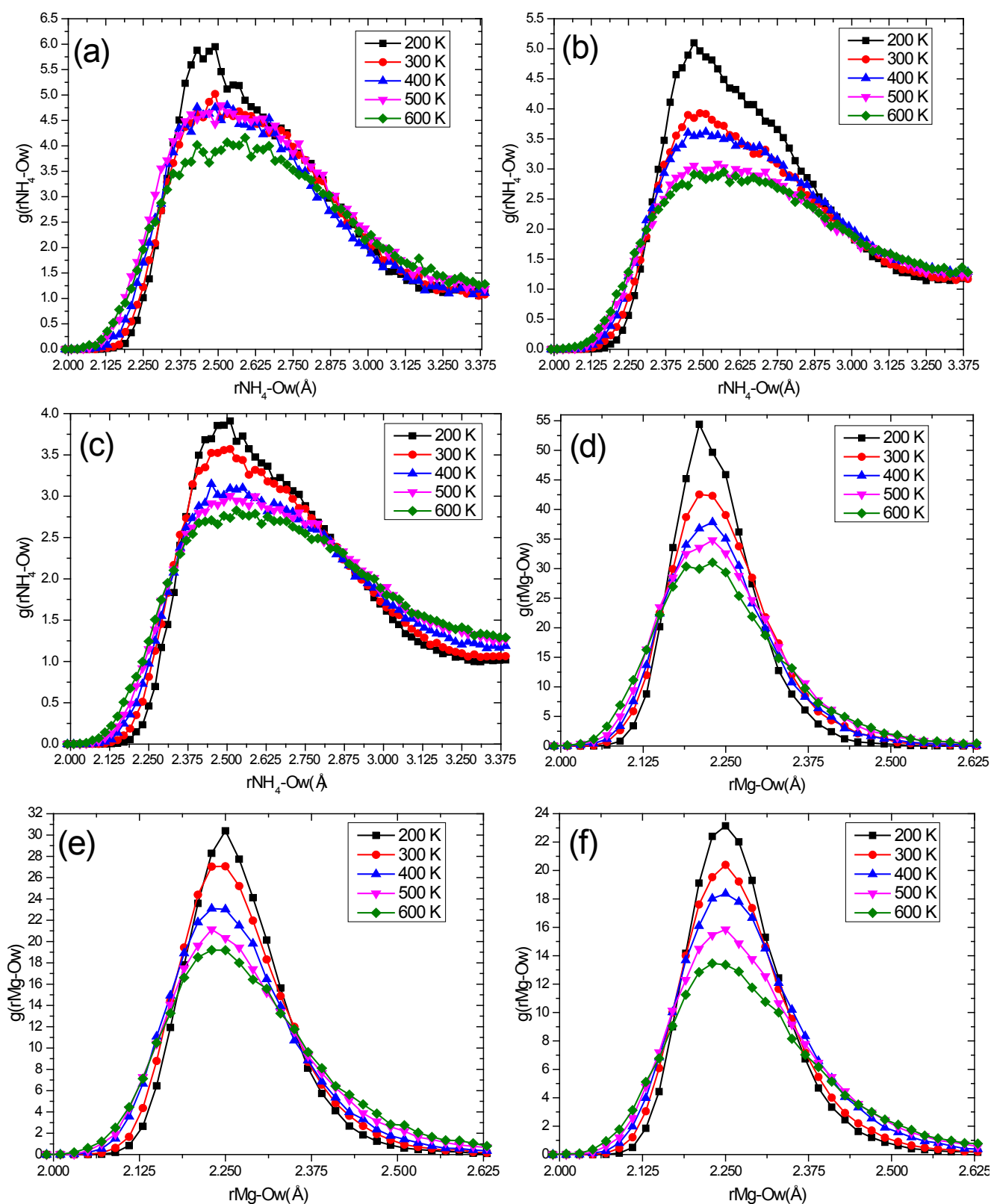
Inorganic salts addition caused a decrease in the RDF peaks of  $\text{H}_2\text{O}$  oxygen with the rise in temperature and hydration degree (Figures 5-8 and S4-S6).  $\text{H}_2\text{O}$  molecules are well organized in one hydration layer than in two and three hydration layers, due to the restricted geometric of clay layers. As the temperature and the amount of  $\text{H}_2\text{O}$  molecules increase, the swelling pressure increases reducing the confinement effect of clay layers, leading to the increase in the mobility and distance between them. The structure of  $\text{H}_2\text{O}$  molecules was mainly affected by the formation of hydrogen bonds between them and clay surfaces [31]. However, with the rise in temperature and hydration degree, the hydrogen bonds between  $\text{H}_2\text{O}$  molecules, the electrostatic attractive forces exerted by inorganic cations, and the negative charged clay surfaces on  $\text{H}_2\text{O}$  molecules became weak, leading to the reduction of the electrostatic interaction between interlayer species, and interlayer species - clay surfaces. The distance between  $\text{H}_2\text{O}$  molecules are almost the same in each layer after inorganic salts addition, and the average distances are 3.11, 3.07, 2.99 and 3.13 Å for  $\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2$ ,  $\text{AlCl}_3$  and  $\text{FeCl}_3$ , respectively. This result indicates that  $\text{H}_2\text{O}$  molecules remained close to each other despite the rise in their mobility as the temperature increases. The highest RDF peak of Ow-Ow obtained in the case of  $\text{NH}_4\text{Cl}$  addition, implying that  $\text{H}_2\text{O}$  molecules are more clustered in the interlayer of Na-Mt than in the case of any other salts due to the presence of Cl anions which exerted strong attractive forces on them.

### Hydration state of the interlayer ions

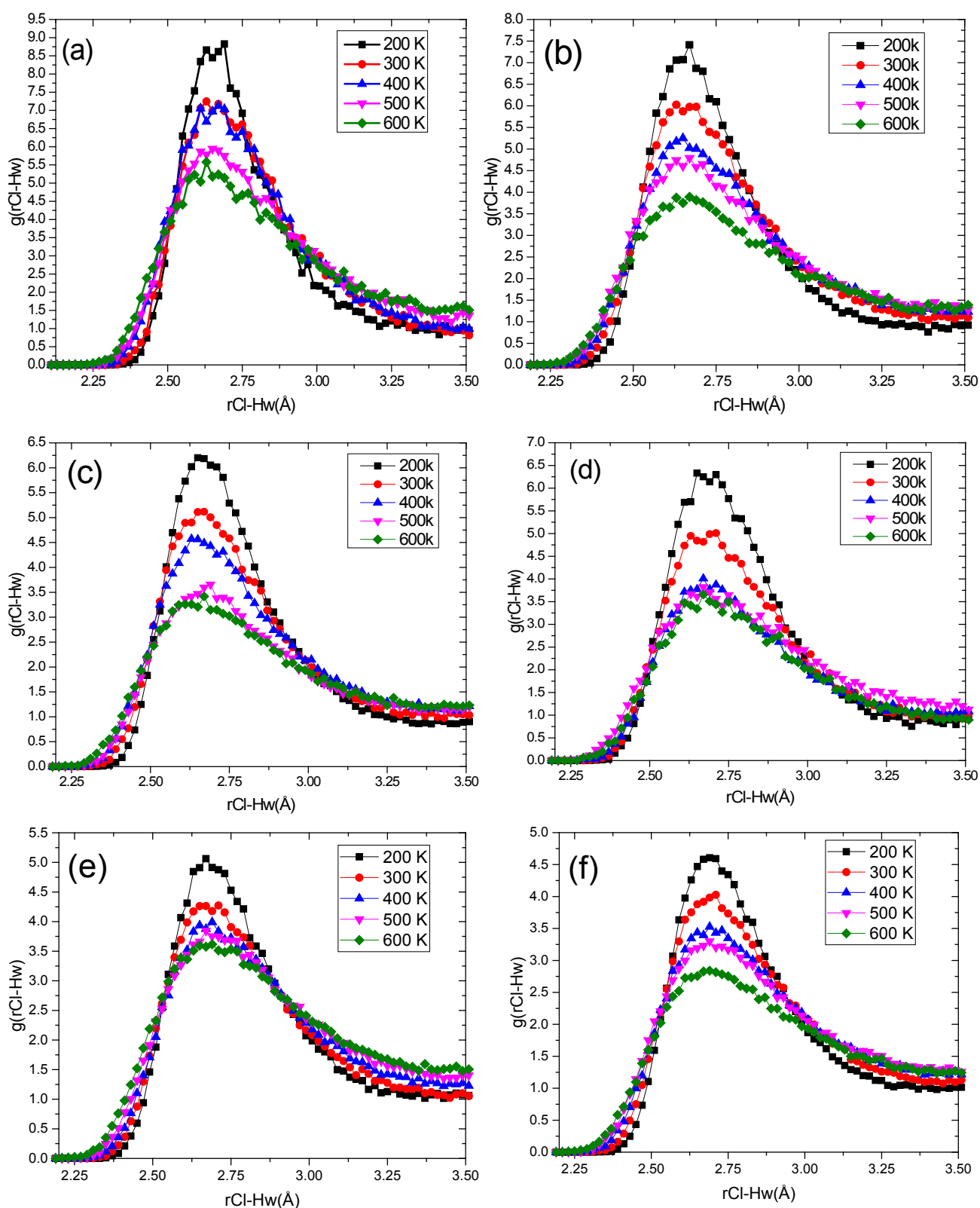
The hydration state of both inorganic cations and anions was investigated by calculating the coordination number, which gives clear ideas about the number of  $\text{H}_2\text{O}$  molecules around them as the temperature was increased (Figure 2). After adding inorganic salts into Na-Mt at increasing temperature and constant pressure, the coordination number of inorganic ions decreased from 200 to 600 K and the hydration degree (Figures 6 and 7) [17,32]. As temperature increases binding and electrostatic forces between inorganic ions and  $\text{H}_2\text{O}$  molecules and between  $\text{H}_2\text{O}$  molecules become weaker, and  $\text{H}_2\text{O}$  molecules coordinated to inorganic ions detached leading to the enhancement of their mobility between the layers [28]. The coordination number of Fe cations was higher than those of Mg, Al and  $\text{NH}_4$  cations (Figure 6), and that of Cl anions after  $\text{NH}_4\text{Cl}$  addition was also higher than those of  $\text{AlCl}_3$ ,  $\text{MgCl}_2$  and  $\text{FeCl}_3$  (Figure 7), indicating that these two ions attracted more  $\text{H}_2\text{O}$  molecules in their hydration shell than others ions. These results show that  $\text{NH}_4\text{Cl}$  had a good inhibition effect on the hydrated Na-Mt due to the low hydration state of  $\text{NH}_4$  cations and the high attractive forces exerted by Cl anions on  $\text{H}_2\text{O}$  molecules after  $\text{NH}_4\text{Cl}$  addition.

### Diffusion of interlayer species in hydrated Na-Mt

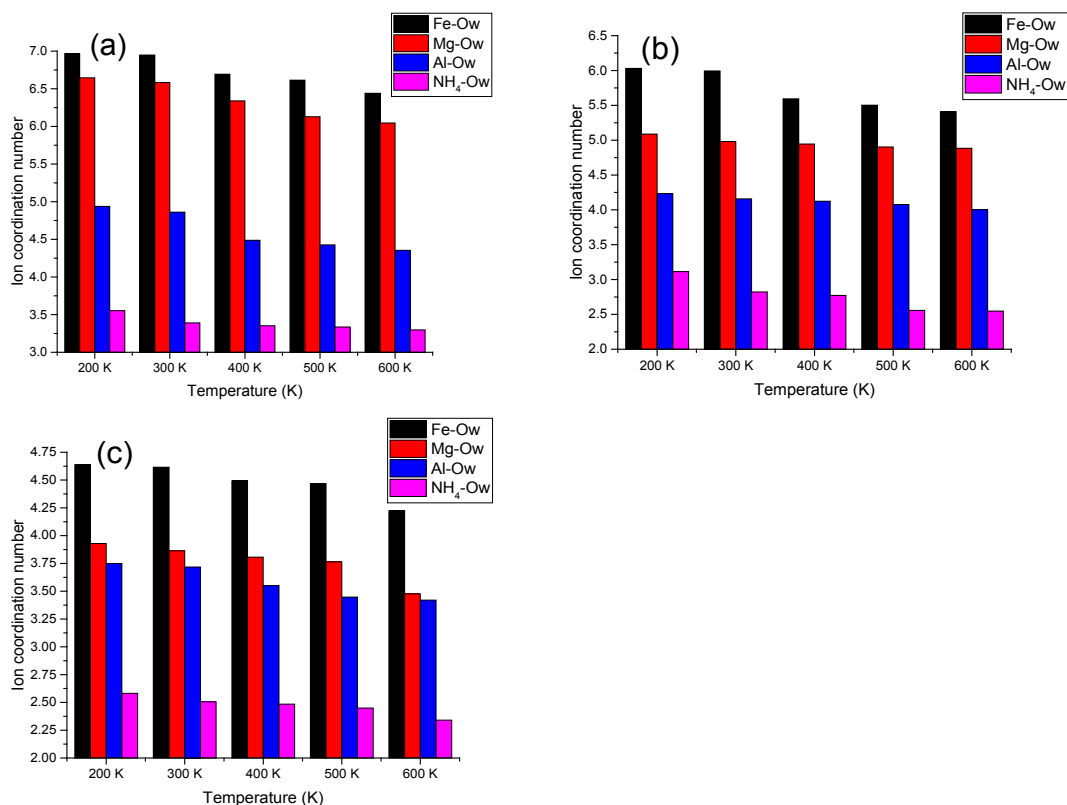
After adding salts into Na-Mt, the mobilities of Na,  $\text{NH}_4$ , Mg, Fe cations, Cl anions and  $\text{H}_2\text{O}$  molecules increased in each hydration



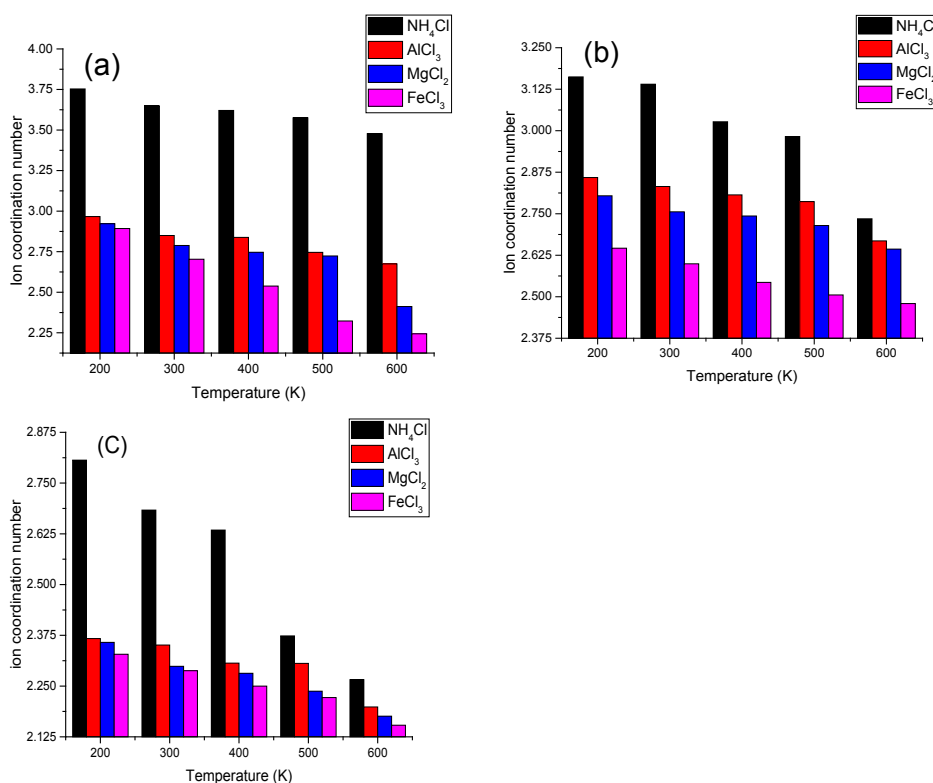
**Figure 4:** RDF curves of Mg-Ow and  $\text{NH}_4\text{-Ow}$ ; (a), (b), (c) and (d), (e), (f) represent 1-,2-,3 hydration layers of  $\text{NH}_4\text{-Ow}$  and Mg-Ow after  $\text{MgCl}_2$  and  $\text{NH}_4\text{Cl}$  addition, respectively.



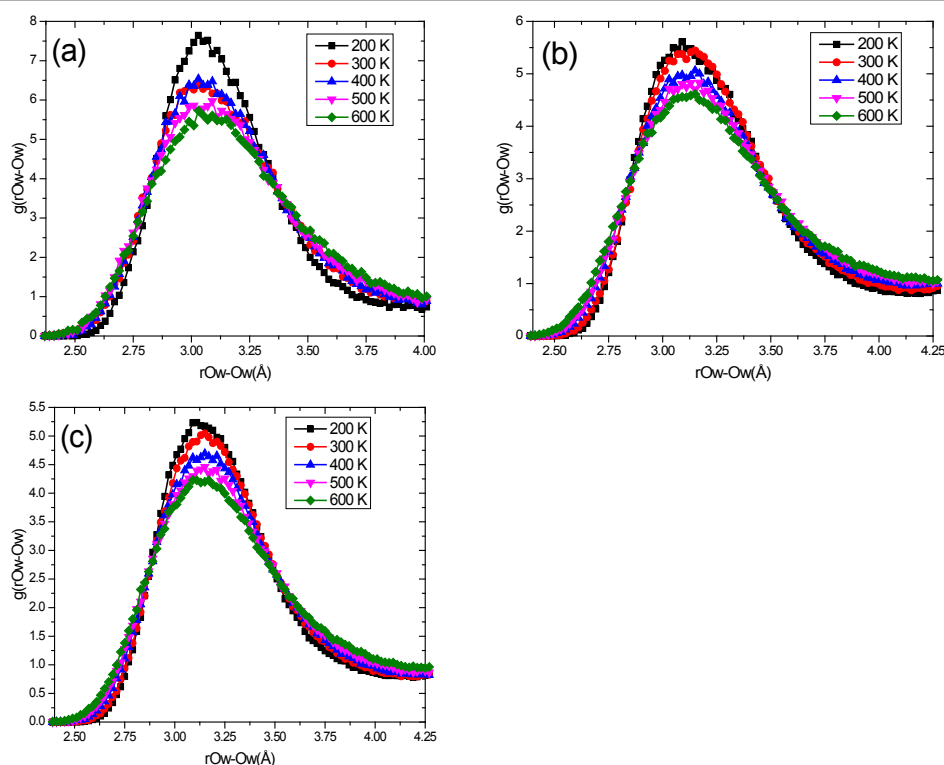
**Figure 5:** RDF of Cl-Hw cation after  $\text{NH}_4\text{Cl}$  and  $\text{AlCl}_3$  addition; (a), (b), (c) and (d), (e), (f) represent 1-, 2-, 3 hydration layers of Cl-Hw after  $\text{NH}_4\text{Cl}$  and  $\text{AlCl}_3$  addition, respectively.



**Figure 6:** Ion coordination number of interlayer inorganic cations after inorganic salts addition; (a), (b), (c) represent 1-, 2-, and 3 hydration layers respectively.



**Figure 7:** Ion coordination number of Cl anions after inorganic salts addition; (a), (b), (c) represent 1-, 2-, and 3 hydration layers respectively.



**Figure 8:** RDF curves of Ow-Ow after  $\text{NH}_4\text{Cl}$  addition; (a), (b), (c) represent 1-, 2-, and 3 hydration layers respectively.

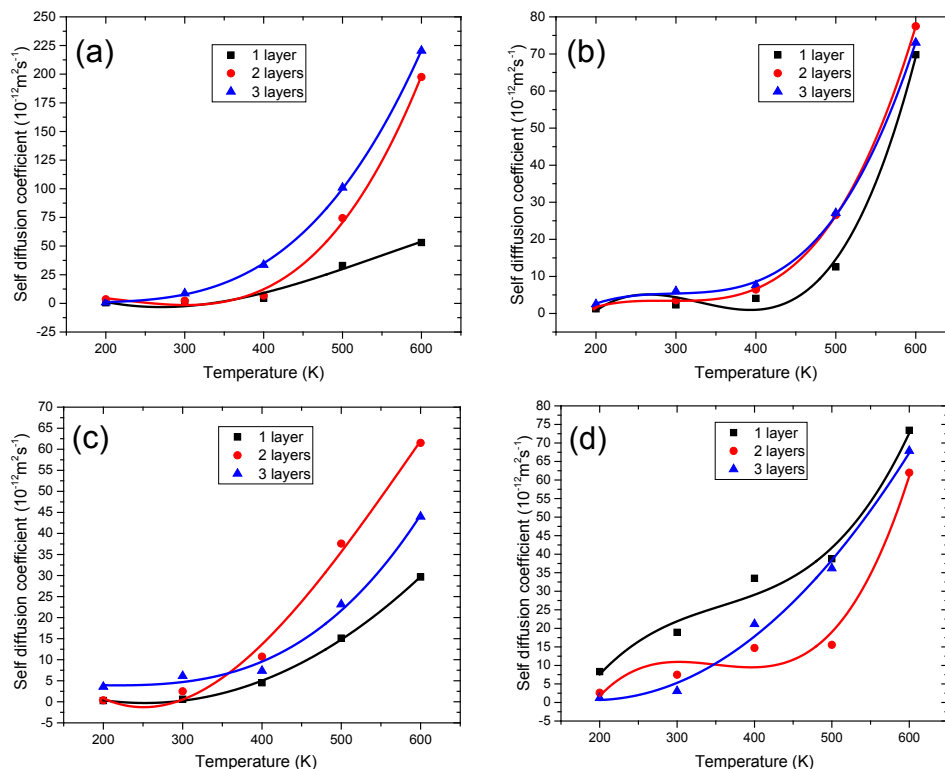
layer with the rise in temperature (Figures 9-12). This increase in their mobility was due to the decrease of the electrostatic forces between them and between the clay surfaces and interlayer species when temperature was increased. Low mobility of the interlayer species was observed in the three hydration states from 200 to 300 K due to the restricted geometry of the interlayer spaces, the attractive forces exerted by clay surface on them and the increase of the interaction between interlayer species. Na cations hardly diffused after  $\text{NH}_4\text{Cl}$  and  $\text{MgCl}_2$  (Figure 9a and 9b) addition because of the bounded  $\text{H}_2\text{O}$  molecules, the electrostatic forces exerted by Cl anions and clay surfaces on them and the large hydration shells of Mg,  $\text{NH}_4$  cations and Cl anions which obstructed their mobility in the interlayer. Figure 9b to 9d show that the mobility of Na cations was independent of the hydration degree because of the inhibition effect of  $\text{AlCl}_3$ ,  $\text{MgCl}_2$  and  $\text{FeCl}_3$  on the mobility of Na cations. It was dependent on the position of Na cations when the hydration shell of Mg, Fe and Al cations were formed, and became lower in the outer-sphere complexes where they were in contact with  $\text{H}_2\text{O}$  molecules, Cl anions and inorganic cations, and higher in the inner-sphere complexes where they interacted with clay surfaces and  $\text{H}_2\text{O}$  molecules oxygen's.

In the same range of temperature, the decrease of the mobility of inorganic cations, Cl anions and  $\text{H}_2\text{O}$  molecules was also observed, and was due to the increase of their hydration shells, which were the result of their strong electrostatic attractive forces exerted on  $\text{H}_2\text{O}$  molecules because of the strong electrostatic forces exerted by clay surfaces and between interlayer species. Mg, Fe cations and Cl anions diffused in the outer sphere complexes and exerted strong attractive forces on  $\text{H}_2\text{O}$  molecules leading to the formation of large hydration shells which obstructed their mobility [20]. Whereas  $\text{NH}_4$  and Al cations diffused in

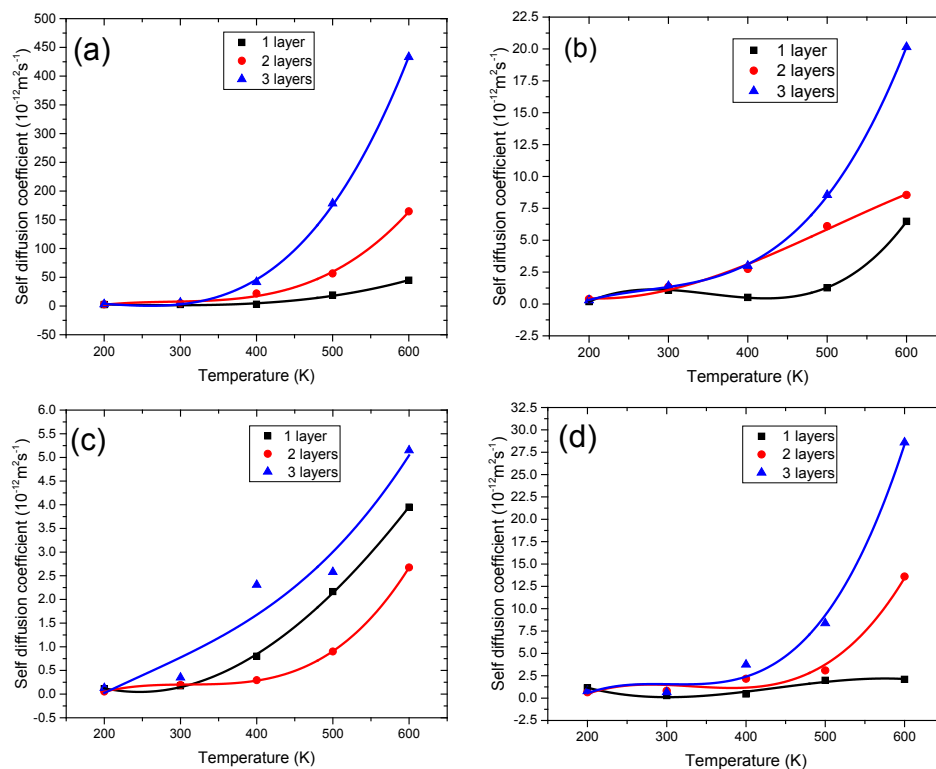
the inner-sphere complexes where they were attracted by both negative charged clay surface and  $\text{H}_2\text{O}$  molecules, delaying their movement in the interlayer spaces.

With increasing temperature from 300 to 600 K, the mobility of interlayer species increased in each hydration layer as a result of the weakening of the hydrogen bonds formed between  $\text{H}_2\text{O}$  molecules, the electrostatic forces between interlayer species and between clay surfaces and interlayer species, leading to the reduction of the size of the interlayer ion's hydration shell, enhancing the relative mobility of  $\text{H}_2\text{O}$  molecules around the interlayer ions, and thus, enabling their free mobility. A comparative analysis of the four salts shows that the highest mobility of Na cations is observed in the case of  $\text{NH}_4\text{Cl}$  addition indicating that Na cations become less hydrated after  $\text{NH}_4\text{Cl}$  and  $\text{MgCl}_2$  addition than  $\text{FeCl}_3$  and  $\text{AlCl}_3$  addition (Figure 9). But in all cases, their diffusion coefficient was generally weak at low temperature in each layer and increased with the rise in temperature. On comparing the mobility of inorganic cations, and  $\text{H}_2\text{O}$  molecules (Figures 10 and 11) it was observed that the mobility of  $\text{H}_2\text{O}$  molecules for  $\text{NH}_4\text{Cl}$  addition was higher than those for  $\text{FeCl}_3$ ,  $\text{MgCl}_2$  and  $\text{AlCl}_3$ , and that of  $\text{NH}_4$  was higher than those of Mg, Fe and Al cations. These results show that the attractive forces exerted by clay surfaces on  $\text{NH}_4$  cations and those exerted by  $\text{NH}_4$  on interlayers species were not strong enough than those of Mg, Fe and Al cations when temperature was increased. Figure 10c shows that the mobility of Al cations in two hydration layer is lower than that in one and three hydration layers after adding  $\text{AlCl}_3$ , this decrease of the mobility in two hydration layers was due to the presence of  $\text{H}_2\text{O}$  molecules and Cl anions, which interacted with them in the outer sphere complexes than in the inner sphere complexes where they were in contact with clay surface and  $\text{H}_2\text{O}$  molecules. The mobility of Cl anions obtained for  $\text{NH}_4\text{Cl}$  addition was higher than

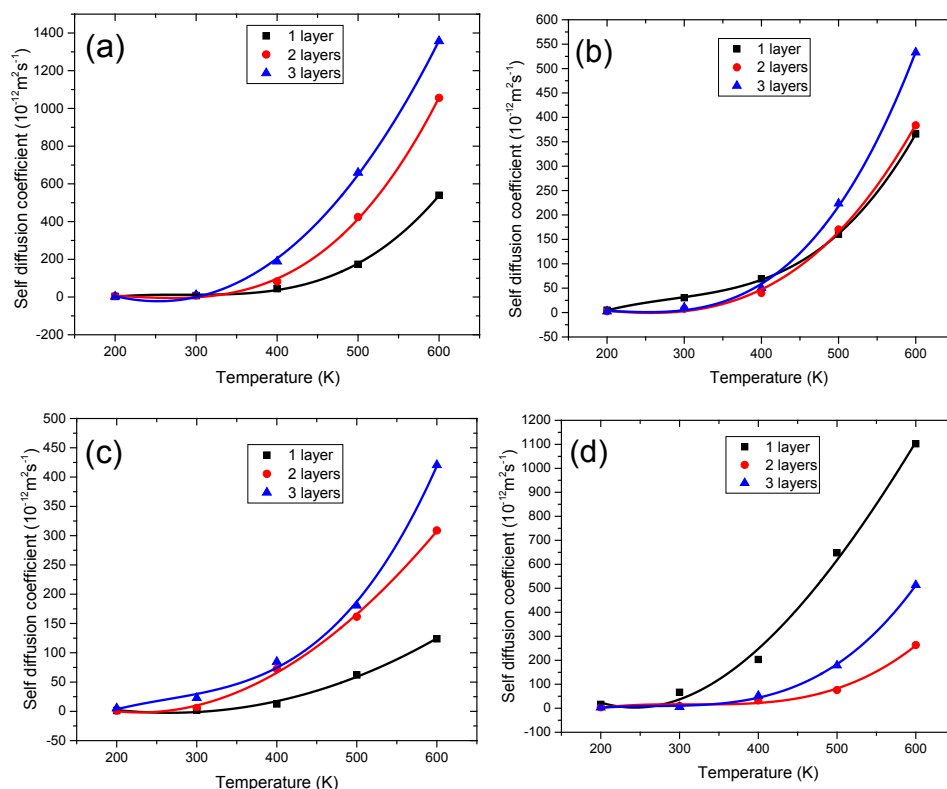




**Figure 9:** Diffusion coefficient of the interlayer Na cations after inorganic salts addition;  $\text{NH}_4\text{Cl}$  addition (a),  $\text{MgCl}_2$  addition (b),  $\text{AlCl}_3$  addition (c), and  $\text{FeCl}_3$  addition (d).



**Figure 10:** Diffusion coefficient of inorganic cations after salts addition;  $\text{NH}_4^+$  (a),  $\text{Mg}^{2+}$  (b),  $\text{Al}^{3+}$  (c), and  $\text{Fe}^{3+}$  (d) cations.



**Figure 11:** Diffusion coefficient of H<sub>2</sub>O molecules after salts addition; NH<sub>4</sub>Cl (a), MgCl<sub>2</sub> (b), AlCl<sub>3</sub> (c), and FeCl<sub>3</sub> (d).

those obtained for MgCl<sub>2</sub>, AlCl<sub>3</sub> and FeCl<sub>3</sub> (Figure 12). This effect was due to NH<sub>4</sub><sup>+</sup> cations tendency to remain close to the clay sheets, which enhanced the attraction of H<sub>2</sub>O molecules by Na cations and Cl anions in the outer sphere complexes. The increase in temperature exerted energy to break free these H<sub>2</sub>O molecules from the attractive forces of Cl anions, which in turn increased Cl anions and H<sub>2</sub>O molecules mobility compared to the other salts addition. The impact of NH<sub>4</sub>Cl addition on the diffusion of H<sub>2</sub>O molecules was observed from 200 to 300 K (Figure 11a), because at these temperatures their diffusion coefficient was almost the same despite the hydration states of Na-Mt. The same effect was observed for K cations when KCl was added into Na-Mt at HTHP [17]. These observations sum up to a conclusion that NH<sub>4</sub><sup>+</sup> and K cations have almost the same behaviors in the interlayer space despite the difference in their physical and chemical properties. The attractive forces exerted by Fe cations on H<sub>2</sub>O molecules were not strong enough during the rise in temperature, because of the release of more water molecules in their hydration shell compared to Mg and Al cations.

This phenomenon was observed by the increase in the diffusion coefficient of H<sub>2</sub>O molecules in the case of FeCl<sub>3</sub> than those of MgCl<sub>2</sub> and AlCl<sub>3</sub> addition (Figure 11). The reduction of the mobility of H<sub>2</sub>O molecules in three and two hydration layers compared to that of one hydration layer was due to the inhibition effect of FeCl<sub>3</sub> on H<sub>2</sub>O molecules.

On comparing the impact of NH<sub>4</sub>Cl, MgCl<sub>2</sub>, AlCl<sub>3</sub> and FeCl<sub>3</sub> on the mobility of H<sub>2</sub>O molecules, it was observed that, MgCl<sub>2</sub> had the best inhibition effect on the diffusion of H<sub>2</sub>O molecules when temperature increased. That was confirmed by the lowest diffusion coefficient of H<sub>2</sub>O molecules, and the diffusion coefficient approximation for the

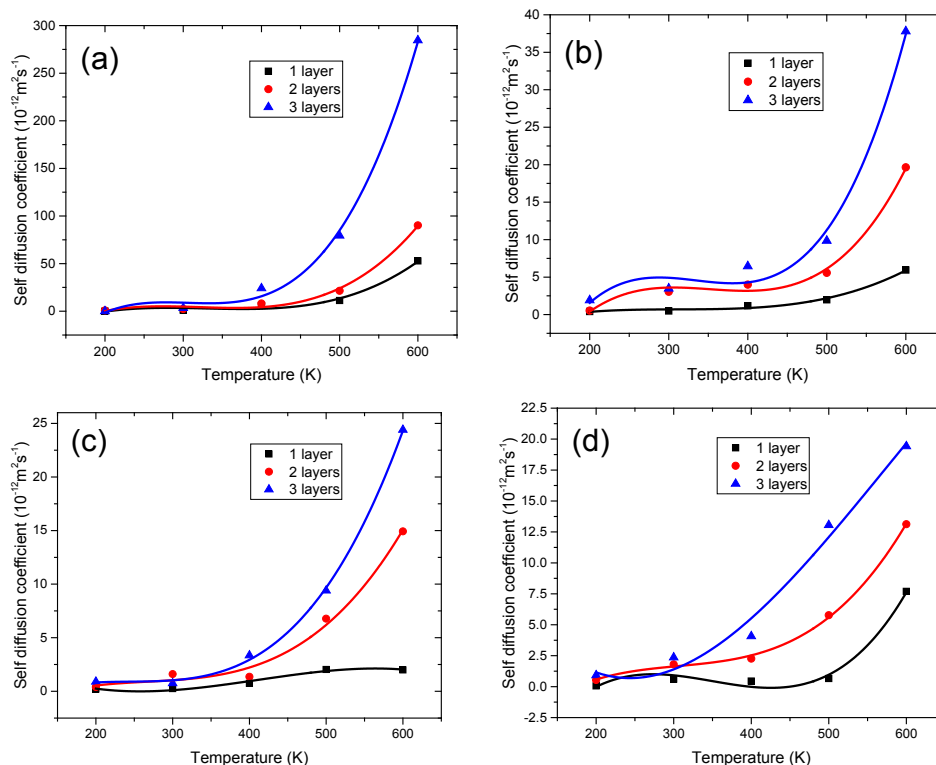
three hydration states than those of AlCl<sub>3</sub>, FeCl<sub>3</sub> and NH<sub>4</sub>Cl. Mg cations exerted stronger attractive forces on H<sub>2</sub>O molecules than Fe, Al and NH<sub>4</sub><sup>+</sup> cations [33], which was previously for Ca cations with the same valence ions [17]. The increase in temperature and hydration degree are important factors affecting the cations exchange capacity and the amount of guest particles intercalation into Na-Mt [33], because high temperature means weak electrostatic interaction and an easier ion exchange into Na-Mt would be anticipated.

### Total energy of Na-MMT after inorganic salts addition

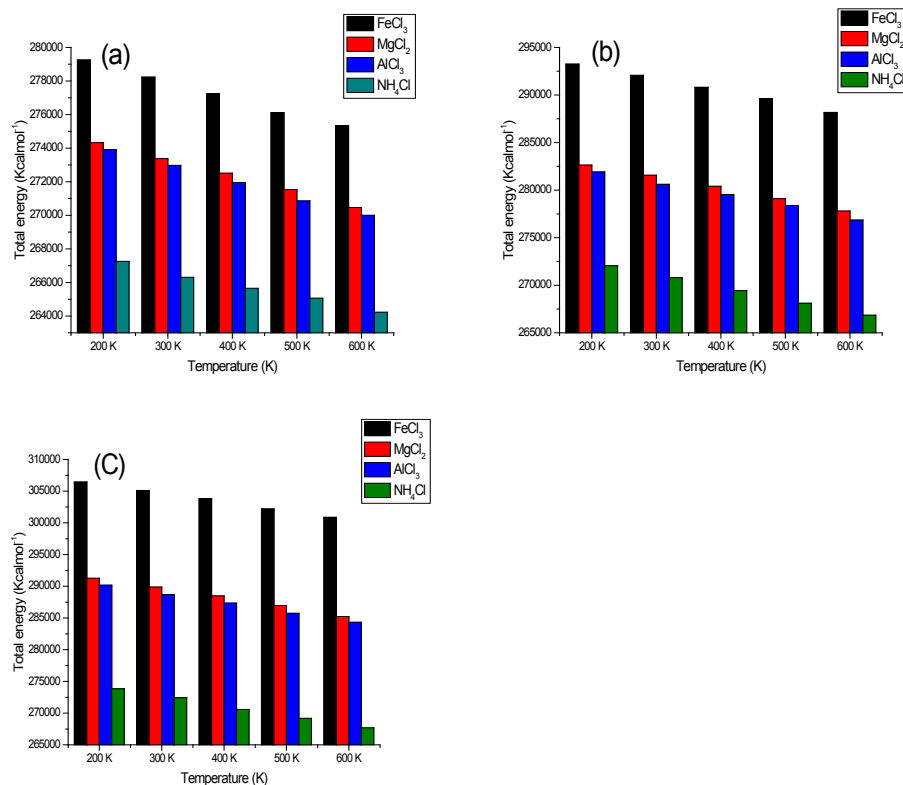
The total energy of Na-Mt increased with the rise in the hydration degree from one to three hydration layers (Figure 13). As the temperature increased, there is a rise in the activities or movement of the interlayer species between the layers and the breaking of hydrogen bonds network, reducing the electrostatic interaction between interlayer species and interlayers species - clay mineral surface. After the salts addition in each hydrated Na-Mt, the total energy of the system decreased and became stable with an increase in temperature. The most stable state of the crystal was had the lowest total energy obtained with NH<sub>4</sub>Cl addition, which was followed by AlCl<sub>3</sub>, MgCl<sub>2</sub> and FeCl<sub>3</sub> addition.

### Effect of inorganic salts on interlayer spacing

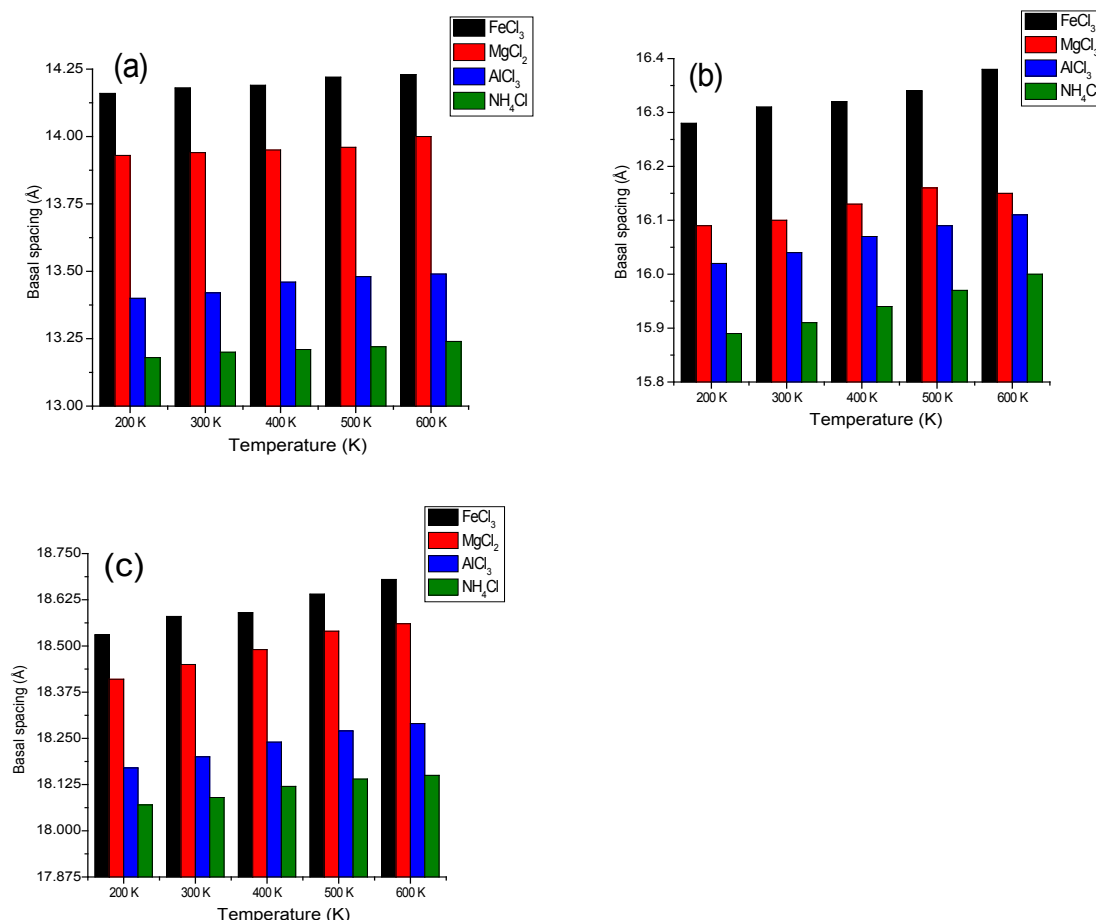
The basal spacing of Na-Mt with inorganic salts increased from one to three hydration layers at a given temperature (Figure 14). Increasing temperature increased the thermal motion of the interlayer species and the swelling pressure in the layers, leading to the increase in the basal spacing from one to three hydration layers [21]. In this work, a minimal increase in the basal spacing with the rise in temperature was observed, which means that the temperature effect is mild on the



**Figure 12:** Diffusion coefficient of Cl anions after  $\text{NH}_4\text{Cl}$  (a),  $\text{MgCl}_2$  (b),  $\text{AlCl}_3$  (c) and  $\text{FeCl}_3$  (d) addition.



**Figure 13:** Total energy changes with respect to temperature for different Na-Mt layered after adding inorganic salts; (a), (b), (c) represent 1-, 2-, and 3 hydration layers respectively.



**Figure 14:** Basal spacing changes with respect to temperature for different layered Na-Mt after adding inorganic salts; (a), (b), (c) represent 1-, 2-, and 3 hydration layers respectively.

interlayer spacing [17,29] after adding the salts at HTHP. The type of interlayer cations affected the structure of the interlayer spacing, the intercalation process of guest particles, the surface area, the adsorption as well as the swelling and stability of Na-Mt.

The basal spacing and swelling pressure obtained with NH<sub>4</sub>Cl addition were the smallest. A similar swelling pressure effect of a monovalent cation on the swelling pressure was also observed for KCl addition into Na-Mt at HTHP [17]. From this remark, NH<sub>4</sub>Cl can be used as a good swelling inhibitor compared to AlCl<sub>3</sub>, MgCl<sub>2</sub> and FeCl<sub>3</sub>.

## Conclusion

We have performed MD simulation of Na-Mt with inorganic salts addition to investigate the structural and dynamics properties of H<sub>2</sub>O molecules and ions into Na-Mt in the NPT ensemble under the influence of HTHP. The results obtained show that temperature greatly influences the coordination sphere of the interlayer ions. Increasing temperature reduces the attractive forces between the layers, shrinks the hydration shell of the interlayer ions by releasing more H<sub>2</sub>O molecules around them, leading to the rise in the mobility of ions and those of H<sub>2</sub>O molecules. Under each temperature H<sub>2</sub>O molecules diffuse more than ions at each hydration state and the diffusion increases with the increase of the hydration degree, which impact the intercalation of guest particles into Na-Mt. Cl anions play an important role in the stabilization of hydrated Na-Mt by attracting more H<sub>2</sub>O molecules in

their coordination spheres, which is an important factor for minimizing the ingress of H<sub>2</sub>O molecules into the clay sheets. The type of inorganic cations in the interlayer influences the hydration energy of Cl anions. Furthermore, we find that all the salts studied exhibit good inhibition effect on Na-Mt. Compared with AlCl<sub>3</sub>, MgCl<sub>2</sub> and FeCl<sub>3</sub>, NH<sub>4</sub>Cl had the least swelling performance on Na-Mt because of the lowest hydration energy and attraction of NH<sub>4</sub> cations to the clay surfaces, and the strong attractive forces of its Cl anions on H<sub>2</sub>O molecules.

## Acknowledgement

This work was supported by the National Natural Science Foundation of China (51874343, U1762212, 51874332), Natural Science Foundation of ShanDong Province (ZR2017MEE027), and PCSIRT (IRT\_14R58).

## References

- Steiger RP (1982) Fundamentals and Use of Potassium/Polymer Drilling Fluids To Minimize Drilling and Completion Problems Associated With Hydratable Clays. J Petroleum Techn 34: 1661-1670.
- Balaban RdC, Vidal ELF, Borges MR (2015) Design of experiments to evaluate clay swelling inhibition by different combinations of organic compounds and inorganic salts for application in water base drilling fluids. Applied Clay Science: Pp: 105-106.
- Anderson RL, Ratcliffe I, Greenwell HC, Williams PA, Cliffe S, et al. (2010) Clay swelling - A challenge in the oilfield. Earth-Science Reviews 98: 201-216.
- Mooney RW, Keenan AG, Wood LA (1952) Adsorption of Water Vapor by Montmorillonite. II. Effect of Exchangeable Ions and Lattice Swelling as Measured by X-Ray Diffraction. J Am Chemical Society 74: 1371-1374.

5. Meleshyn A, Bunnenberg C (2005) Swelling of Na/Mg-montmorillonites and hydration of interlayer cations: A Monte Carlo study. *J Chemical Physics* 123: 1-7.
6. Wilson MJ (2007) *Handbook of Clay Science*. Geoderma 139: 420-421.
7. Boek ES, Coveney JP, Skipper NT (1995) Monte Carlo Molecular Modeling Studies of Hydrated Li-, Na-, and K-Smectites: Understanding the Role of Potassium as a Clay Swelling Inhibitor. *J Am Chemical Society* 117: 12608-12617.
8. Cygan RT, Liang JJ, Kalinichev AG (2004) Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *J Physical Chemistry B* 108: 1255-1266.
9. Zheng AZ, Shahrour I (2011) A theoretical study of swelling and shrinking of hydrated Wyoming montmorillonite. *Applied Clay Science* 51: 177-181.
10. Chávez-Páez M, Workum KV, Pablo Ld, Pablo Jd (2001) Monte Carlo simulations of Wyoming sodium montmorillonite hydrates. *J Chemical Physics* 114: 1405-1413.
11. Yamada H, Nakazawa H, Hashizume H, Shimomura S, Watanabe T (1994) Hydration behavior of Na-smectite crystals synthesized at high pressure and high temperature *Clays and Clay Minerals* 42: 77-80.
12. de Carvalho RJFL, Skipper NT (2001) Atomistic computer simulation of the clay-fluid interface in colloidal laponite. *J Chemical Physics* 114: 3727-3733.
13. Segad M, Jönsson B, Cabane B (2012) Tactoid formation in montmorillonite. *Journal of Physical Chemistry C* 116: 25425-25433.
14. Zhang F, Zhang ZZ, Low PF, Roth CB (1993) The Effect of Temperature on the Swelling of Montmorillonite. *Clay Minerals* 28: 25-31.
15. Stefani VF, Conceição RV, Carniel LC, Balzaretti NM (2014) Stability of lanthanum-saturated montmorillonite under high pressure and high temperature conditions. *Applied Clay Science* 102: 51-59.
16. Huang WL, Bassett WA, Chungwu T (1994) Dehydration and hydration of montmorillonite at elevated temperatures and pressures monitored using synchrotron radiation. *American Mineralogist* 79: 683-691.
17. Camara M, Xu J, Wanga X, Zhang J, Chen Z, Li X (2017) Molecular dynamics simulation of hydrated Na-montmorillonite with inorganic salts addition at high temperature and high pressure. *Applied Clay Science* 146: 206-215.
18. Colten VANN (1986) Hydration states of smectite in NaCl brines at elevated pressures and temperatures. *Clays and Clay Minerals* 34: 385-389.
19. Tuck JJ, Hall P, Michael H (1984) Quasi-elastic neutron-scattering studies of the dynamics of intercalated molecules in charge-deficient layer silicates. Part. 1.—Temperature dependence of the scattering from water in Ca<sup>2+</sup>-exchanged montmorillonite. *J the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 80: 309-324.
20. Xu J, Camara M, Liu J, Peng L, Zhang R, Ding T (2017) Molecular dynamics study of the swelling patterns of Na/Cs-, Na/Mg-montmorillonites and hydration of interlayer cations. *Molecular Simulation*: 1-15.
21. Morodome S, Kawamura K (2009) Swelling behavior of Na- and Ca-montmorillonite up to 150°C BY by in situ x-ray diffraction experiments *Clays and Clay Minerals* 57: 150-160.
22. Zheng Y, Zaoui A (2013) Temperature effects on the diffusion of water and monovalent counterions in the hydrated montmorillonite. *Physica A: Statistical Mechanics and its Applications* 392: 5994-6001.
23. Smith DE (1998) Molecular Computer Simulations of the Swelling Properties and Interlayer Structure of Cesium Montmorillonite. *Langmuir* 14: 5959-5967.
24. Zhang X, Yi H, Zhao Y, Min F, Song S (2016) Study on the differences of Na- and Ca-montmorillonites in crystalline swelling regime through molecular dynamics simulation *Advanced Powder Technology* 27: 779-785.
25. Berendsen HJC, Grigera JR, Straatsma TP (1987) The Missing Term in Effective Pair Potentials. *Journal of Chemical Physics* 91: 6269-6271.
26. Cramer CJ (2004) *Essentials of Computational Chemistry: Theories and Models* (2<sup>nd</sup> edn). John Wiley & Sons Ltd, West Sussex, England.
27. Frenkel D, Smit B (2001) *Understanding Molecular Simulation from Algorithms to Applications* (Computational Science Series, Vol 1). Academic Press (2<sup>nd</sup> edn), Florida, USA.
28. Salles F, Beurroies I, Bildstein O, Jullien M, Raynal J, et al. (2008) A calorimetric study of mesoscopic swelling and hydration sequence in solid Na-montmorillonite. *Applied Clay Science* 39: 186-201.
29. Kotkoskie TS, Al-Ubaidi B, Wildeman TR, Sloan ED (1992) Inhibition of Gas Hydrates in Water-Based Drilling Muds. *Society of Petroleum Engineers* 7: 130-136.
30. Yan W, Augustine J, Francklyn C (1996) A tRNA identity switch mediated by the binding interaction between a tRNA anticodon and the accessory domain of a class II aminoacyl-tRNA synthetase *Biochemistry* 35: 6559-6568.
31. Zavitsas AA (2005) Aqueous solutions of calcium ions: Hydration numbers and the effect of temperature. *J Physical Chemistry B* 109: 20636-20640.
32. Tang CY, Huang Z, Allen HC (2011) Interfacial water structure and effects of Mg<sup>2+</sup> and Ca<sup>2+</sup> binding to the COOH headgroup of a palmitic acid monolayer studied by sum frequency spectroscopy *J Physical Chemistry B* 115: 34-40.
33. Wu L, Liao L, Lv G (2015) Influence of interlayer cations on organic intercalation of montmorillonite. *J Colloid and Interface Science* 454: 1-7.