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Defect-driven water migration in MgCl₂ tetra- and hexahydrates

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Abstract

This molecular dynamics simulations study elucidates how water diffusion in $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$ ($n=4$ and 6) is facilitated by defects and dopants. Both the impact of a single vacancy (one water molecule was removed) and an interstitial (one water molecule was added) on long range water motion has been investigated. Spontaneous vacancy-interstitial pair defect formation was not observed, which is in line with the predicted high energy costs for defect formation: 150 and 200 kJ/mol for the tetrahydrate and hexahydrate, respectively. The vacancy defects did not show long range mobility, which we relate to the strong bonding of water in the coordination shell of the Mg-ion that prevents water molecules from shifting to neighbouring magnesium ions. On the contrary, the addition of an extra water molecule, facilitates long range motion, which was found as a sequence of hopping events. The interstitial motion is anisotropic in both tetrahydrate and hexahydrate crystals, as interstitials preferentially reside at locations of unfavourable Cl-Cl interactions. Strikingly, $\text{Mg} \leftrightarrow \text{Ca}$ substitutional defects neither increase the mobility of vacancies nor facilitates interstitial motion in the MgCl_2 lattice. While Ca dopants slightly facilitate vacancy formation, it also stabilizes interstitial water molecules by incorporating these molecules in its coordination shell. As a consequence, the interstitial becomes trapped and loses its mobility. Therefore, Ca dopants will not increase the hydration/dehydration kinetics of MgCl_2 hydrates and cannot be used to boost the power output of MgCl_2 -based heat storage devices.

1. Introduction

To implement systems for harvesting thermal energy from solar irradiation and industrial processes, long term storage media are needed. Therefore, there is a renewed interest in exploring hydrates for heat storage. Interesting candidates for inexpensive, non-toxic materials of this kind are salt hydrates; i.e. CaCl_2 , MgSO_4 , MgCl_2 , Na_2S , etc^{1,2,3}. The transitions underpinning heat storage in these materials are (de)hydration reactions, illustrated below by the example of MgCl_2 .

The storage or release of heat ΔG happens during dehydration or hydration, respectively.

Several hydrates phases of MgCl_2 have been reported ($n=0, 1, 2, 4, 6, 8, 12$) that are stable at different combinations of temperature and water vapour pressure^{4,5,6}. At room temperature and at significant water vapour pressure, the most stable phase is the hexahydrate ($n=6$).

Charging the material happens via dehydrating it to either the tetra-, di- or monohydrate ($n=4, 2$ and 1) at elevated temperatures. Note that complete dehydration should be avoided as it is accompanied by HCl outgassing⁷. The maximal heat storage/release is hence reached when a hexahydrate is transferred into a monohydrate, or vice versa, leading to a heat of $\Delta G = 2.79$ GJ per cubic meter of the storage material⁸.

To make stable performing systems of $\text{MgCl}_2 \cdot n\text{H}_2\text{O}$, challenges related to stability and kinetics arise. Mechanical stability has to be ensured over many loading/unloading cycles, as the transitions involve large volume changes, melting might happen and the risk of deliquescence exists. The other challenge is connected to the kinetics of the transitions, which

limits the rate of loading/unloading. These transitions involve water exchange with the environment and water diffusion inside the crystal lattice. Fundamental understanding of water diffusion will therefore significantly facilitate technological solutions of heat storage by salt hydrates.

So far, little work has been done on long range water motion inside crystal lattices of salt hydrates in general, but also for MgCl_2 in particular. Despite the fact that many experimental studies on the water mobility in hydrates have been reported, all of them focus on local motions (rotations, vibrations, etc.) with techniques like NMR^{9,10,11} or IR/Raman techniques¹². The potential of Molecular Dynamics (MD) simulations have hardly been used for mechanistic studies of water hopping in salt hydrates. Only quite recently attempts have been reported to use MD to simulate dehydration of MgCl_2 and MgSO_4 nano-particles^{13,14}. Despite the fact that the aforementioned studies report values for the water diffusion coefficient, the mechanisms of water diffusion through the crystal were not studied. Furthermore, the reported values are much higher than one would expect for crystalline materials in general and hydrates in particular: i.e. approximately $10^{-10} \text{ m}^2/\text{s}$ at 300 K for water in a magnesium chloride nanoparticle¹⁴. It might well be that the predicted fast diffusive motion is stress facilitated as the calculations were done on dehydrating nanoparticles.

In a previous study, we elucidated the performance of molecular mechanics models, i.e. force fields for MgCl_2 hydrates for characterizing water mobility in perfect single crystals¹⁵. The force fields correctly reproduce the structures for the mono-, tetra-, hexa- and dodecahydrate phase of MgCl_2 . Moreover, such models also allow the molecular dynamics simulation of water mobility mechanisms – which were identified as ring-like local motions of water molecules in the coordination shell of the Mg^{2+} ions. However, even at elevated temperatures

(up to 550 K) long range diffusion of water inside crystal on time scales of 10 – 40 ns was not seen. It seemed that the magnesium-water bonding is so strong that water only can escape from the coordination shell on much longer time scales. This is in line with experiments on the hydration shell of magnesium ions in aqueous solutions – which have indeed shown that debonding happens on time scales of 2 μ s at 25°C¹⁶. This suggests that long range diffusion of water only can take place, when defects and/or stresses are present.

As water diffusion is a necessary element for (de)hydration processes, the aim of the present study is to understand the mechanisms of hydrate water migration. For this purpose, molecular dynamics simulations are directed to the question if and how defects could facilitate water diffusion through $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ crystals. In what follows, we discuss water vacancies / interstitials in the otherwise pure compound and next to substitutional ($\text{Mg} \leftrightarrow \text{Ca}$) defects.

2. Methods

2.1. Force fields

Our molecular mechanics models are based on Lennard-Jones type potentials in combination with coulombic interactions. The interaction potential u_{ij} between the atoms of type i and j , is given hence by:

$$u_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r} \quad (1)$$

Where r , ϵ_{ij} and σ_{ij} are distance between the two atoms and parameters that reflect the nature of the van-der-Walls interactions, respectively. Further, q_i , q_j and ϵ_0 are the partial charge of atom i , that of atom j and the dielectric permittivity of vacuum, respectively. Mixed parameters were created from the Lorentz-Berthelot rules as $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ and $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$, respectively. The force field of the MgCl_2 hydrate is fully adopted from our earlier study¹⁵, which is force field using the SPC (Single Point Charge) water model and optimized on the ion-oxygen distance (IOD) for the magnesium and chloride ions^{17,18}. For the Ca ion we used the IOD-optimized Lennard-Jones parameters from the aforementioned study¹⁷.

2.2. Simulation protocol

For the molecular dynamics simulations, we used the DL_POLY 1.9 Classic software¹⁹.

Periodic boundary conditions are applied to 8x6x5 and 6x8x10 supercell models of the tetra- and the hexahydrate, respectively. Starting configurations of perfect tetra- and hexahydrate MgCl_2 crystals were made by constructing super cells from crystallographic data^{20,21}. We use the N , σ , T ensemble (constant number of particles, stress and temperature) to allow variations in orientation and length of the lattice vectors Throughout all molecular dynamics simulations. To impose constant temperature, the Nose-Hoover thermostat with a relaxation time of 0.5 ps is combined to constant-pressure (imposing 100 kPa for each of the diagonal

elements of the stress tensor) using a barostat relaxation time of 10 ps. The equations of motion were integrated by the Verlet algorithm with time steps of 2 fs. The long range nature of the electrostatic forces was accounted for with the Smooth Particle Mesh Ewald method (SPME), switching from real to k-space at a cut-off distance of 14 Å.

Various kinds of defect structures were studied and compared with perfect single crystals. Before sampling data was started, each structure was allowed to relax for at least 1 ns, ensuring that temperature and box size fluctuations were below 5 K and 0.2 Å, respectively. For studying the long range mobility of water molecules runs of 14 ns (at 550 K) up to 80 ns (at 450 K) were performed.

As mentioned above, various defect structures have been studied. First of all, MgCl_2 crystals with a water vacancy were generated by removing a randomly chosen water molecule from the perfect single crystal. In case of the hexahydrate, this implies one of the magnesium ions was no longer six-fold but five-fold coordinated by water. In turn, for the tetrahydrate, we impose that one of the Mg^{2+} ions will have only three water molecules in its coordination shell. Secondly, MgCl_2 lattices with an extra water molecule (interstitial) were generated, where the extra water molecule was (initially) not bonded to magnesium ions. In order to generate stable structures, the interactions between the inserted water molecule and its direct environment had to be gradually ramped up. This was implemented by starting from a “soft-sphere”-type interstitial in which the partial charges of the extra water molecule were switched off and the Lennard-Jones-parameters were reduced by 90%. In small runs of 10 ps at 300 K, first the LJ parameters and later the charges of the molecule were step-wise increased to their actual values. Finally, the structure was equilibrated using the full interaction potentials within a 1 ns run at 300K.

Finally, Ca doped MgCl_2 structures were generated by replacing one Mg^{2+} ion by a Ca^{2+} ion.

For this, the relaxed MgCl_2 hydrate models as discussed earlier were used as starting points.

When selecting the Mg ion to be substituted by Ca, we discriminate against metal ions in immediate contact to and more remote from water interstitials/vacancies. This allows studying relaxation of combined defects at minimal bias from starting geometries.

3. Results

3.1. Formation energies of single vacancies and interstitials in a MgCl_2 crystal.

As defects are crucial for mobility in crystals, first the formation energies of water vacancies and interstitials defects are studied. All defects were created “manually” (see methods section), spontaneous formation of interstitial/vacancy pairs was never observed in our molecular dynamics runs.

Figure 1 Average potential energy for forming of a single defect in the tetrahydrate (open symbols) and the hexahydrate crystals (solid symbols). Three types of defects are shown: isolated vacancies (blue triangles), interstitials (red circles) and vacancy-interstitial pairs (black squares). The errors bars refer to the standard errors.

The potential energy change for the formation of a vacancy-interstitial pair within otherwise single-crystalline models is quite significant, approximately 200 and 150 kJ/mol, in the hexa- and tetrahydrate respectively. This explains the low concentration of spontaneously formed defects in the temperature window of 300 – 400 K, where the hexahydrate transfers to tetrahydrate. Consequently, also water diffusion (that is long-range displacement in random

directions, not ring-type motion within constant coordination shells¹⁵) is rather low. As can be seen in Figure 1, the major difficulty is the formation of the vacancy. In both hydrates around 150 kJ is needed to pull a water molecule out of the Mg^{2+} coordination shell and to bring it into an ideal vapour phase. In contrast to this, the energy to insert a water molecule from an ideal vapour phase into the crystal lattice, the formation of an interstitial is considerably lower: approximately 50 kJ/mol for the hexahydrate and even practically 0 kJ/mol for the tetrahydrate, respectively.

That interstitials are formed more easily than vacancies, is rather uncommon for anhydrous crystals. Interstitial formation demands local expansion of the crystal lattice involving a strong increase of the elastic energy, which is not needed for vacancy formation. However, little is known about the interstitial formation in hydrated crystals. As already mentioned, the strong Mg-water interaction opposes in MgCl_2 the formation of the vacancy. This might imply that hydration might occur via one-by-one insertion of water molecules, whilst dehydration must involve a more complex, concerted transformation/propagation of extended phase fronts.

Interestingly, interstitial formation is much easier in the tetrahydrate than in the hexahydrate. Possibly in the tetrahydrate unfavourable Cl-Cl contacts are shielded less effectively by water as there is less water in the lattice, making insertion of extra water in the lattice easier. As such, interstitial formation is a precursor of the hydration transition that occurs at sufficiently high water vapour pressures and low temperatures.

Figure 2 Visualizations of interstitial locations in a unit cells of a tetrahydrate (A) and hexahydrate crystal (B). The blue octahedrons and green spheres respectively represent the Mg^{2+} -ions coordinated by water and Chloride ions. The red spheres mark the positions of the oxygen-atom of the interstitial water molecule during simulation runs at 500 K. Loose chloride ions in the tetrahydrate structure (A) are actually coordinated with Mg^{2+} -ions outside the visualized region.

To understand how an interstitial is incorporated in the lattice, snapshots of unit cells of both hydrates are visualized together with all locations visited by the interstitial during a simulation run at 500 K, see Figure 2. The blue octahedra represent the complexes of a central magnesium ion with six water molecules in case of the hexahydrate or four water molecules and two chloride ions in case of the tetrahydrate, respectively. The green spheres represent the chloride ions. The red spheres mark the positions visited by the oxygen atom of the interstitial water molecule.

A typical feature of the hexahydrate is that in the *b*-direction of the lattice every magnesium-ion is separated by parallelogram-like structures of four Cl^- ions. According to Figure 2B, the center of these parallelogram-type structures seem to be the preferential sites for interstitial water molecules in the hexahydrate. On the other hand, In the tetrahydrate lattice tubes of Cl^- ions are presented that are aligned with the *c*-vector of the lattice. These tubes are stacks of parallelogram-like structures of 4 Cl^- ions. Figure 2A shows that in the tetrahydrate the

interstitial water molecule preferentially occupies the space between two subsequent Cl-parallelograms.

To summarize, spontaneous formation of vacancy/interstitial pairs is unlikely as energy for vacancy formation is high due to the high amount of energy stored in the Mg-water interaction. Insertion of interstitial water is more favourable than vacancy formation and the interstitials preferentially locate in between the chloride-ions in the lattice. The latter is a consequence of the Coulomb repulsion between these ions and reflects the driving force for hydration in case of MgCl_2 .

3.2. Interstitials diffuse fast, vacancies are pinned

3.2.1. Vacancies versus interstitials

As (de)hydration reactions intuitively should involve long range water transport in the crystal lattice, we explored water migration from extensive molecular dynamics simulations. As the high energy of vacancy/interstitial defect pair formation prevents the direct observation of spontaneous water migration, we created simulation models hosting a single vacancy or interstitial defect, respectively.

The long range mobility of the water vacancy was monitored by tracking the under-coordinated Mg^{2+} ion and by identifying the number of water molecules not present at their original Mg-hosts. In all simulation runs, covering more than 10 ns and temperature up to 550 K, neither water has hopped between different Mg-ions, nor the identifier of under-coordination of the Mg^{2+} ion switched to another lattice position. This is fully in line with the behaviour observed in perfect crystals. Long range mobility of the vacancy demands that water can easily detach from the Mg-ion in order to move to another Mg-host. A simple

estimate of the transition state to vacancy hopping reflects two adjacent vacancies with one interstitial in-between. This is however drastically disfavoured by the high energy needed for vacancy formation.

Crystals containing an interstitial water molecule were analysed in two ways. As in the case of the perfect crystal and the vacancy-containing crystal, the number of water molecules not present at their original Mg-hosts was monitored. Further, the trajectory of the interstitial water molecule was logged. Interestingly, in presence of an interstitial it was observed that water molecules were able to hop between neighbouring Mg-ions, contrary to what was observed in perfect crystal lattices and lattices containing vacancies. Given the fact that vacancy formation is unfavourable, it is intuitive to expect interstitial migration to occur via temporary over-coordination of an Mg^{2+} ion, followed by squeeze out of any of the 4+1 or 6+1 water molecules of the tetra- or hexahydrate, respectively. Indeed, our simulations showed that none of the water molecules hopped more than once within the 10 ns scales of our molecular dynamics runs.

To elucidate the precise mechanism of hopping, we first focus on the interstitial trajectory in more detail. For this, we defined “the” interstitial water molecule in a dynamical manner for every time step by identifying the water molecules not being a member of the coordination sphere of any Mg^{2+} ion. As a distance delimiter, a water molecule was considered to be interstitial when the minimal Mg-O distance exceeded 3 Å (typical distances in the coordination shell of an Mg^{2+} -ion are 2.2 – 2.5 Å at the simulated temperatures). Below we subsequently discuss the motion of an interstitial in a tetrahydrate and a hexahydrate crystal.

3.2.2. Interstitial diffusion in a tetrahydrate crystal

Based on the interstitial trajectory MSD (Mean Square Displacement) curves have been generated. In Figure 3 the MSD curves of the interstitial are plotted for a temperature of 500 K. Both total displacement and displacements $\langle x_k^2 \rangle$ along the main lattice vectors ($\vec{k} = \vec{a}, \vec{b}$ and $\vec{c}$) are shown.

Figure 3 MSD (Mean square displacement) curves of an interstitial water molecule in a tetrahydrate crystal at 500 K. The curves are the total displacement (black) and displacements along the lattice vectors $\vec{a}$ (red), $\vec{b}$ (blue), $\vec{c}$ (green).

The MSD values increase linear in time indicating that the interstitial water molecule undergoes a normal diffusive motion. The diffusion process in the tetrahydrate is anisotropic and the preferred direction of motion is parallel to $\vec{c}$ -vector of the lattice.

For temperatures ranging from 450 to 550 K the MSD curves have been constructed and diffusion coefficients were calculated from the linear part of these curves. From the linear part of the curves diffusion coefficients have been calculated by using

$$\langle |\vec{r}|^2 \rangle = 6Dt \quad (2)$$

for 3D diffusion and

$$\langle x_{\vec{k}}^2 \rangle = 2D_{\vec{k}}t \quad (3)$$

for the diffusion coefficient along the lattice vectors: $\vec{k} = \vec{a}$, $\vec{b}$ and $\vec{c}$. The diffusion coefficients are plotted in Figure 4: the data points are the calculated values and the lines represent the Arrhenius fits. The corresponding activation energies are also shown in the figure. Due to the limited statistics, diffusion constants were calculated from ns-scale simulation runs, there is quite some scatter in the data points. As in the hexahydrate the motion is rather anisotropic: the motion along the c-axis of the crystal is significantly faster than motions along the other axes of the crystal. It is noteworthy that the obtained activation energies of the diffusion coefficients $D_{\vec{c}}$ and D are similar (31 and 35 kJ), whereas activation energies for the motions along the a- and b-axis are significantly higher (56 and 52 kJ).

Figure 4 The temperature dependency of the diffusion coefficients of an interstitial water molecule in a tetrahydrate crystal. The data points represent the total diffusion coefficient (black) and diffusion coefficients along the lattice vectors $\vec{a}$ (red), $\vec{b}$ (blue), $\vec{c}$ (green). The lines represent the fits with the Arrhenius expression.

To understand this anisotropy the 80 ns long trajectory at 450 K has been analysed in terms of hops and waiting times. A threshold of 2 Å has been used to separate local vibrations from

site-to-site hops. For every single jump the hopping distances in the a-, b- and c-directions of a crystal have been calculated.

Figure 5 Probability distributions of the hop lengths in a 80 ns long trajectory of an interstitial water molecule in a tetrahydrate crystal at 450 K. Distributions for the principal lattice directions are shown: a (red), b (blue) and c (green).

Interestingly, long jumps are most probable along the c-axis of the crystal. According to Figure 2 this is the axis along which tubes of Cl-parallelograms are aligned. In this direction the most probable jumps have lengths of either 1.5 or 3.5 Å.

Figure 6 Visualization of the hop of a water molecule in the c -direction of a tetrahydrate crystal. The trajectory of the oxygen atom of an interstitial water molecule during a time interval of 2 ps is shown. To visualize time the color of the interstitial changes from red to white and later to blue. The blue octahedrons and green spheres respectively represent the Mg^{2+} -ions coordinated by water and Cl^- -ions. Loose chloride ions in the tetrahydrate structure are actually coordinated with Mg^{2+} -ions outside the visualized region. The crystal lattice itself is only shown for the moment that the interstitial has joined the coordination sphere of a Mg^{2+} , visible by the fact that this ion is coordinated by 5 water molecules.

A typical jump is along the c -axis illustrated in Figure 6; a 2ps trajectory is visualized.

Initially the interstitial water molecule resides in the neighbourhood of 4 chloride ions, see discussion of Figure 2. The interstitial water molecule intrudes into the coordination sphere of the Mg^{2+} ion that is the easiest to access by the interstitial. At the same moment another water molecule is pushed out of the coordination sphere as a 7-fold coordination is energetically unfavourable. The newly formed interstitial water moves the closest site of four chloride ions. Due to the geometry of the lattice the sites can hardly be reached via motions along the a -axis. Where water mobility in the coordination sphere was already predicted by MD calculations on perfect single crystals¹⁵, here it facilitates the long distance motion of the interstitial water molecule.

3.2.3. Interstitial diffusion in a hexahydrate crystal

In this section the diffusion of an interstitial water molecule in a hexahydrate crystal will be analysed in detail. Diffusion constants will be calculated and hopping mechanisms will be discussed in detail. First, we will discuss in detail our analysis for the case of interstitial motion at 500K. The basis of our analyses are MSD (Mean Square Displacement) curves, calculated from interstitial trajectories. The MSD curves of an interstitial in a hexahydrate crystal at 500K are shown in Figure 7. In this figure the MSD curves for the total displacement and displacements $\langle x_k^2 \rangle$ along the main lattice vectors ($\vec{k} = \vec{a}, \vec{b}$ and $\vec{c}$) are plotted.

Figure 7 MSD (Mean square displacement) curves of an interstitial water molecule in a hexahydrate crystal at 500 K. The curves are the total displacement (black) and displacements along the lattice vectors $\vec{a}$ (red), $\vec{b}$ (blue), $\vec{c}$ (green).

During the first 1 ns the MSD value increases linear in time indicating that the interstitial water molecule undergoes a normal diffusive motion. Clearly, the diffusion process is anisotropic and the preferred direction of motion is parallel to $\vec{b}$ -vector of the lattice. Above

the 1 ns the MSD curves deviate from linearity due to fluctuations. As a single trajectory of 18 ns has been analysed, this can be attributed to poor statistics at large diffusion times.

For a more quantitative analysis, MSD curves have been constructed for temperatures ranging from 450 – 550 K. The resulting diffusion coefficients are shown in Figure 8 (left). The data points are the calculated values and the lines represent the Arrhenius fits. The diffusion coefficients have been normalized on the values at 450K calculated from the Arrhenius fits, Figure 8 (right).

Figure 8 Left: The temperature dependency of the diffusion coefficients of an interstitial water molecule in a hexahydrate crystal. The data points represent the total diffusion coefficient (black) and diffusion coefficients along the lattice vectors $\vec{a}$ (red), $\vec{b}$ (blue), $\vec{c}$ (green). The lines represent the fits with the Arrhenius expression. Right: the diffusion coefficients normalized on their value at 450K.

Before discussing the Arrhenius fits, first the origin of the anisotropy in the motion will be discussed. As in the case of the MSD curves, the diffusion coefficients nicely demonstrate the

anisotropy in the Brownian motion of the interstitial water molecule. The diffusivity along the b-axis, $D_{\bar{b}}$, is much higher than the diffusivities in the other lattice directions. Especially the motion along the c-axis seems to be slow: at 450 K $D_{\bar{a}}:D_{\bar{b}}:D_{\bar{c}} \approx 2:4:1$.

To understand this anisotropy the 63 ns long trajectory at 450 K has been analysed as an alternating sequence of hops and waiting times. To distinguish a hop from a local vibration a threshold of 4 Å has been used. For every single jump the hopping distances in the a-, b- and c-directions of a crystal have been calculated.

Figure 9 Probability distributions of the hop lengths in a 63 ns long trajectory of an interstitial water molecule in a hexahydrate crystal at 450 K. Distributions for the principal lattice directions are shown: a (red), b (blue) and c (green).

The probability distributions of the hopping distances along the lattice directions are shown in Figure 9. This figure reveals two important features. First, there is a preference for long jump along the *b*-axis. Secondly, the preferred jump distance along the *b*-axis is rather large (approximately 7-8 Å) and close to the unit cell length in the *b*-direction is 7.23 Å^{20,21}. To understand these large jumps of the interstitial water molecule, a 2 ps trajectory of such a hop has been visualized in Figure 10. Initially the interstitial water molecule resides between 4 chloride ions, see discussion of Figure 2. At a certain moment the interstitial manages to intrude into the coordination sphere of the Mg²⁺ that is located below the original interstitial location along the *b*-axis. At the same moment the water molecule on the opposite side of the ion is pushed out of the coordination sphere as a 7-fold coordination is energetically unfavourable. The newly formed interstitial water moves to the parallelogram-like structure of four chloride ions just below its original host ion (along the *b*-axis). That there is a strong preference for hops in the *b*-direction follows from the structure of the unit cell. In the *b*-direction the preferential sites for interstitial water molecules are more easily accessible.

Figure 10 Visualization of the hop of a water molecule in the *b*-direction of a hexahydrate crystal. The trajectory of the oxygen atom of an interstitial water molecule during a time interval of 2 ps is shown. To visualize time the color of the interstitial changes from red to white and later to blue. The blue octahedrons and green spheres respectively represent the Mg²⁺-ions coordinated by water and Cl⁻ions. The crystal lattice itself is only shown for the moment that the interstitial has joined the coordination sphere of a Mg²⁺, visible by the fact that this ion is coordinated by 7 water molecules.

Finally, the Arrhenius analysis deserves attention. The fitted values for all diffusion curves resulted in values for the activation energy E_a between 41 and 43 kJ/mol. The similarity in values suggest that there is a single energy barrier determining the rate of the diffusion process. To illustrate this the diffusion coefficients have been normalized on their value at 450 K, see Figure 8 (right). Based on the hopping mechanism discussed, illustrated in Figure 10, we suggest that this activation energy is connected with the energy barrier for increasing the coordination of the Mg-ion from 6 to 7.

3.3. The impact of a calcium ion as a substitutional defect

3.3.1. Vacancies

In both hydrates studied, we found that the formation of vacancy/interstitial pair defects critically depends on the incorporation of the vacancies. In terms of energy, the formation of interstitials calls for about 50 kJ/mol in the hexahydrate, and appears even free of costs in the tetrahydrate, respectively, whereas vacancy formation is related to 200 and 150 kJ/mol, respectively. To facilitate the spontaneous formation of water vacancies, it is intuitive to consider MgCl_2 doping by a larger metal ion species such as calcium. At first sight, the additional demand in the metal ion lattice space could be compensated by shifting water molecules away from the Ca dopant and thus providing water interstitials that would then migrate into the (elsewise) pure MgCl_2 domain.

We hence incorporated a single $\text{Mg} \leftrightarrow \text{Ca}$ substitutional defect in the beforehand discussed models of tetra- and the hexahydrates and repeated our analyses of water vacancies, however now removing either a water molecule directly from the coordination shell of the Ca dopant or from the coordination shell of a magnesium ion far away (2 nm) from the dopant. To illustrate the doping effect, 20 ns molecular dynamics simulations were performed at a

temperature of 500 K and 1atm pressure. The energies for vacancy formation nearby (in the hydration shell) and far away from the Ca^{2+} ion, see Table 1. Indeed, we find the energy of vacancy formation reduced by 60 and 24 kJ/mol in the hexa- and the tetrahydrate, respectively.

Table 1 The defect formation energies in MgCl_2 hydrates doped with a single Ca^{2+} ion at 500 K. Values for defects near (in the hydration shell) and far away from the Ca-dopant are listed. The typical standard error of the calculated energy is about 11 kJ/mol.

		Far away from Ca^{2+} ion (kJ/mol)	Near Ca^{2+} ion (kJ/mol)
Vacancy	Tetrahydrate	156	132
	Hexahydrate	165	105
Interstitial	Tetrahydrate	4	-48
	Hexahydrate	5	2

Figure 11 MgCl_2 tetrahydrate (A) and hexahydrate (B) hosting a $\text{Mg} \leftrightarrow \text{Ca}$ substitutional defect along with a water vacancy. The water molecule was initially removed from the coordination shell of Ca ion (brown). In case of the tetrahydrate (A) the octahedral Ca coordination is re-established by association of a water molecule from the coordination shell of an adjacent Mg ion. This transfer is illustrated by a color ramp using blue for the initial and red for the final position of the oxygen atom of water. The metal ions are shown in combination with their coordination environment (2 Cl and 4 water) and the dashed lines are used as a help to the eye for illustrating the arrangement of Cl (green) ions. In case of the MgCl_2 hexahydrate (B) neighboring Cl-ions associate with the Ca ion to establish a 7-fold

coordination: 5 water molecules and 2 Cl ions. This association process is illustrated by a color ramp from white to green.

A closer look at the underlying mechanisms showed that the combined $\text{Mg} \leftrightarrow \text{Ca}$ /water vacancy defect quickly relaxes by increasing the overall coordination of the Ca dopant. While at the start of the simulation runs the Ca coordination shell was reduced to only 5 (3 water and 2 Cl), in the tetrahydrate the coordination of the Ca ion is re-established to 6 by abstraction of a water molecule from the coordination shell of a neighbouring Mg ion (Figure 11). In the hexahydrate the Ca coordination evolves in a different manner. In total, the coordination of the calcium dopant increases from 5 to 7, see Figure 11B, as Ca associates with two neighbouring Cl-ions. The difference between the tetrahydrate and hexahydrate can be understood as follows. In the tetrahydrate all Cl ions are by default associated with a magnesium ion. This interaction is so strong that the Ca ion can only fill its coordination sphere by stealing water from magnesium. In the hexahydrate, Cl ions are not directly associated with the metal ions, however upon water vacancy formation in the coordination sphere of the Ca ion, Ca-Cl interactions become more available. This explanation seems to be confirmed by crystallographic data of the structure of Tachyhydrite²²: $\text{CaMg}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$. In Tachyhydrite the Mg-ion is 6 fold coordinated by water, all water is in the coordination shell of magnesium, and the Ca-ion is 6 fold coordinated by chloride, all Cl ions are in the coordination shell of calcium.

Figure 12 A MgCl_2 tetrahydrate (A) and hexahydrate (B) hosting a $\text{Mg} \leftrightarrow \text{Ca}$ substitutional. For comparison the coordination spheres of the Ca dopant (brown) and one Mg ion (blue) are visualized with bonds between the species in the coordination shell. The green and red spheres represent the Cl ions and oxygen atoms, respectively.

The observed disfavouring of Ca under-coordination (at least in its immediate coordination shell) calls for a closer look at $\text{Mg} \leftrightarrow \text{Ca}$ substitutional defects in general. We hence reconsidered our models in absence of water vacancies or interstitials and explored the nature of Ca incorporation as stand-alone defects, see Figure 12. In the absence of water vacancy or interstitial, the Ca coordination within the tetrahydrate lattice is similar to the coordination of the Mg ions. However, in case of the hexahydrate the Ca dopant associates with a neighbouring chloride. In other terms, the total coordination number of the Ca ions in the tetrahydrate is 6 (4 water and 2 Cl), whereas we find 7 (6 water and 1 Cl) in the hexahydrate. This trend, i.e. the re-establishing of these coordination numbers, seems to be the driving force for the beforehand discussed relaxation upon vacancy incorporation.

3.3.2. Interstitials

As discussed before, only interstitial water molecules show long range mobility within pure $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ compounds. Having seen the tendency of a Ca dopant ion to absorb water and Cl ions, one might argue that $\text{Mg} \leftrightarrow \text{Ca}$ substitutional defects will kill long

range water mobility instead of facilitating it. Therefore, we have added either a water molecule close to or far away (> 3 nm) from the coordination shell of the Ca dopant. At the start of the simulation runs the Ca ion is 6 fold coordinated just as all the Mg ions. To illustrate the doping effect, 20 ns molecular dynamics simulations we performed at a temperature of 500 K and 1atm pressure. The energies for adding interstitials are shown in Table 1. Indeed, we find that the energy of interstitial formation reduced by 3 and 52 kJ/mol in the hexa- and the tetrahydrate, respectively .

Figure 13 *MgCl₂ tetrahydrate (A) and hexahydrate (B) hosting a Mg ↔ Ca substitutional defect along with a water interstitial. For comparison the coordination spheres of the Ca dopant (brown) and one Mg ion (blue) are visualized with bonds between the species in the coordination shell. The green and red spheres represent the Cl ions and oxygen atoms, respectively. In both hydrates the interstitial water molecule is absorbed into the coordination shell of the Ca ion.*

The interaction between Mg ↔ Ca substitutional defect and the interstitial water molecule is shown in Figure 12. Both in the tetrahydrate (A) and hexahydrate (B) the interstitial water molecule is quickly absorbed into the coordination shell of the Ca dopant. During the course of the simulations (20 ns) the interstitials stayed pinned, demonstrating that the interstitials are strongly bound by the Ca ion. The interaction of Ca with neighbouring Cl ions is similar as in systems with a vacancy. In the tetrahydrate the Ca dopant is already associated with chloride

and does not attract new ones. In the hexahydrate the Ca ion associates with a neighbouring Cl ion.

4. Conclusions

While previous molecular dynamics simulations could not identify long range water migration in MgCl_2 tetrahydrate and hexahydrate crystals¹⁵, in the present work the influence of defects on water diffusion is demonstrated.

Indeed, the lack of spontaneous water vacancy-interstitial pair defect formation is in line with the predicted high energy costs of 150 and 200 kJ/mol for the tetrahydrate and hexahydrate, respectively. The major contribution to this is the abstraction of a water molecule from the Mg-coordination shell, which is also reflected by the slow exchange of water between the hydration shell of Mg-ions and the surrounding solution¹⁶. On the other hand, water insertion is related to comparably low energy costs, as the interstitial water molecules seems to stabilize unfavourable Cl-Cl interactions in the crystals.

While water vacancies are pinned in both the tetra- and hexahydrate models, we find water interstitials to account for long range water migration. The corresponding diffusion constants are in line with the experiment, though we caution that idealized models of perfect single crystals do not reflect the polycrystalline nature of the real material. Apart from grain boundaries, boosting water migration could also be obtained from dopant defects. Along this line, we studied the role of $\text{Mg} \leftrightarrow \text{Ca}$ substitutional defects which resulted in an ambivalent picture. While vacancy formation is somewhat facilitated by Ca dopants, such substituting of Mg ions was also found to provoke interstitial association. This pinning of the mobile species of water defects entirely disqualifies Ca doping as a means of promoting the hydration/dehydration kinetics of MgCl_2 hydrates.

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