First principle study towards the influence of Cd^{2+} on the morphology of sodium chloride

Ajeet Singh, Anik Sen, Bishwajit Ganguly *

Analytical Science Discipline, Central Salt & Marine Chemicals Research Institute, (CSIR), Bhavnagar, Gujarat 364002, India

ABSTRACT

The influence of Cd^{2+} on the morphology of sodium chloride has been investigated with Density functional methods. The preferential interactions of Cd^{2+} ion with the {1 1 1} surface of NaCl support the observed octahedron morphology of NaCl. The calculations were performed both in the gas phase and aqueous phase using continuum model (COSMO). We have examined the interaction of Cd^{2+} with various surface sites of sodium chloride such as, flat face, steps and kinks. The stabilization of {1 1 1} NaCl surface by mixed Cd^{2+} ion and explicit water molecules in the ratio of (1:3) is in agreement with the SXRD results (Surf. Sci. 599 (2005) 196 [17]). The Cd^{2+} ion prefers to interact with {1 0 0} surface of NaCl by surrounding with water molecules, whereas, the mixed layer formation on {1 1 1} is not specific in nature. The interaction of $CdCl_2$ with the surface of sodium chloride is ineffective to induce this phenomenon.

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1. Introduction

Surface chemistry and surface phenomena is always under debate, even more rigorous, if we talk about crystal habit. The nucleation, growth and morphology of crystals can be significantly altered by the presence of low concentrations of impurities. These impurities may be reaction by-products or impurities present in the reactants or they may be additives purposely added to alter the crystallization process. The effects of impurities and additives on crystallization are summarized in some recent reviews [1,2]. Additives can reduce crystal growth rate and alter morphology by binding to crystal faces and interfering with propagation steps [3,4]. The control of crystal morphology by use of additives is a subject of great interest which has been studied experimentally and theoretically employing molecular modeling techniques [5–7]. Rome de 1'Isle showed that octahedrons instead of normal cubes are formed, if rock salt is grown in the presence of urine [8]. Many authors have since reported the cube–octahedron shape transition under various experimental conditions. In this regard, earlier work reported that octahedron crystals can also be obtained from pure water solution [9–11]. A schematic diagram for the change in the shape of an alkali halide crystal from cubic to octahedron was shown in Scheme 1. The morphological changes appears in the crystals is due to the interaction of additives on a specific face which reduces the growth of that face, as a result, other fast growing surfaces disappear and eventually, the slow growing surface controls the morphology. Mathieu et al. have measured the adsorption isotherms of Cd^{2+} ions onto {1 0 0} and {1 1 1} faces of NaCl crystal in saturated solutions of sodium chloride [12]. This study concluded that the impurity adsorbs on the high energy kink sites instantaneously compared to steps and flat sites and hence the growth of surfaces would predominantly be governed by such kink sites [2]. Growth kinetics can be measured by adsorption isotherm of impurity onto the crystal faces under study or else by estimating the surface fee energies of the faces with incorporation of new solute units into the crystal lattice [13].

A significant effort in investigating the role of impurities on the occurrence of NaCl {1 1 1} faces during growth from aqueous solutions has been made by Kern [14], Boistelle [15] and Bienfait et al. [11]. Cd^{2+} shows the strongest effect, because even small concentration results in the appearance of {1 1 1} faces, which are not present in clean solutions. Boistelle and Simon proposed that the NaCl covered by an epitaxial layer consists of $CdCl_2 \cdot 2NaCl \cdot 3H_2O$ instead of $CdCl_2$, responsible for the morphological change of salt [16]. Recent study performed to understand the proposed model for the epitaxial layer interaction with NaCl concluded that the observed adsorption isotherm is negligibly small and may not be responsible for the change in the habit of NaCl. Further, it was concluded that the Cd^{2+} ion is in direct contact with the crystal surface and the polar {1 1 1} NaCl is stabilized by a
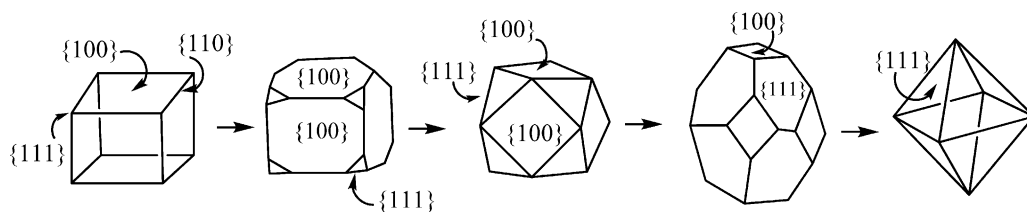
Scheme 1. A schematic diagram from cubic to octahedron for alkali halide crystals.

mixed monolayer of Cd^{2+} and water in a ratio of 1:3 based on SXRD results [17].

Cabrera and Vermilyea hypothesized that strongly adsorbing immobile impurities on terraces of crystal surfaces and steps drastically impede the movement relative to that expected without impurities present causing the morphological change in crystals [18]. The Cd^{2+} ions were also expected to retard the specific planes of sodium chloride and render the morphological change of this alkali halide [19]. Therefore, the models proposed for the adsorption of Cd^{2+} ions on sodium chloride planes with or without water molecules warranted a theoretical study.

In the present work, we have explored the interaction of Cd^{2+} with specific surfaces of NaCl in absence and presence of water molecules employing density functional theory calculations. An approach similar to surface docking developed to predict the influence of additives on the crystal morphology has been employed here [20–26]. The basis of this approach is to analyze the effect of additives on the individual crystal faces, which are cleaved from a crystal. If the additive has a preferred interaction on special face, the growth of this face will be slower, as a result, the other fast growing surfaces will disappear and eventually, the slow growing surface will control the morphology. In this way, the additive influences the morphology of crystals. The surface docking studies can, in principle, be undertaken both with the slab and cluster models [27]. In the cluster models, the crystals are mimicked with finite size representation whereas the slab models mimic the infinite surface of solids and are generally considered to be a better approach. Hence, we have employed the slab models for sodium chloride planes to study the interaction with cadmium ions using surface docking approach. A conventional array of these alkali halide ions has been employed in slab (constructed using periodic boundary conditions) using respective crystal data. The stable {1 0 0} surface of sodium chloride was modeled with alternating arrangement of Na^+ and Cl^- ions. However, modeling the electrostatically polar {1 1 1} surfaces of these alkali halide crystal structure was considered a mystery in surface science, because it is difficult to investigate both experimentally and theoretically [28,29]. Since the bulk structure consists of alternating cationic and anionic sheets stacked along the {1 1 1} directions, the {1 1 1} polar surfaces must have a very high divergent electrostatic energy, which makes them theoretically highly unstable [30]. It has been shown in the earlier studies that the adsorption of negatively charged site of additives would be preferred with the positive ions on top of the surface of alkali halides. Recently, it was determined that the rock salt {1 1 1} surface is Na^+ terminated in presence of aqueous solution and formamide [30]. However, the interaction with positive ions of additive would be preferred with the negative ions of rock salt on top of the surface, i.e. {1 1 1} surface of is Cl^- terminated [17]. Hence for this study, {1 1 1} NaCl surface was modeled with the Cl^- ions on top of the surface.

2. Computational procedure

Study of interactions of Cd^{2+} with 3D slabs of NaCl has been performed employing the density functional program DMol[3] in

Material Studio (version 4.1) of Accelrys Inc., the electronic wave functions are expanded in atom-centered basis functions defined on a dense numerical grid [31–34]. We used DND and DNP double numerical basis sets which are comparable to 6-31G* and 6-31G** basis sets, respectively. The interaction of Cd^{2+} on surfaces of NaCl was optimized with local spin density approximation with Perdew–Wang correlational (LDA/PWC) [35]. The LDA is one of the earliest approximations in DFT. It includes correction for electron correlation effects. However, it is known that the LDA overestimates the binding energies. Generalized gradient approximations (GGA's) go beyond LDA descriptions by including density gradients, and improve the energies significantly [35–44]. The functional Vosko, Wilk, and Nusair–Becke and Perdew–Wang (VWN-BP) [37,38] was used to calculate the interaction energies of Cd^{2+} with NaCl surfaces [33]. Flat face (F), double step (S) and kink (K) were generated for {1 0 0} and {1 1 1} planes of sodium chloride (Scheme 2). All the three possible situations with these planes were considered in the study to determine the highly preferred sites of interaction of additive in each case. To generate the surfaces, the 3D models depend not only on number of layers in the slab, but also on the vacuum gap between the successive slabs. In each case, F, S and K, the slabs generated with periodic boundary conditions was electrically neutral. We have investigated this dependence by optimizing the numbers of layers in the slab as well as the vacuum gap thickness. We have optimized the supercell lattice by varying the number of layers in each case and keeping the sufficiently large vacuum thickness 20 Å fixed. Further, the vacuum thickness was varied from 8 to 20 Å in 2 Å steps with the previously optimized layers and considered the values when the total energy as a function of the vacuum thickness separations was minimum. Our optimized supercell lattice for NaCl was found to be consistent with Ermoshkin et al. results in that six layered slabs are large enough to reproduce surface states and bulk states of alkali halide crystals [45]. The k-points were generated by Monkhorst-Pack schemes [46]. This scheme produces a uniform grid of k-points along the three axes in reciprocal space. The k-points used in this study were $2 \times 2 \times 1$ with separation from origin 0.30744, 0.0355 and 0.03955/Å respectively. The tolerances of energy, gradient, and displacement convergence were 2×10^{-5} Ha, 4×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively (1 Ha = 627.5095 kcal/mol). The SCF convergence criteria for all calculations were 1.0×10^{-5}. The electrical neutrality was maintained for the slabs, however, the bare cadmium ion was placed with charges on it and no counter-ion was used in these cases. The conductor-like screening model (COSMO) has been employed for implicit solvent calculations [47–52]. The LDA/PWC/DND optimized gas phase geometries of Cd^{2+} on the surface of slab models of
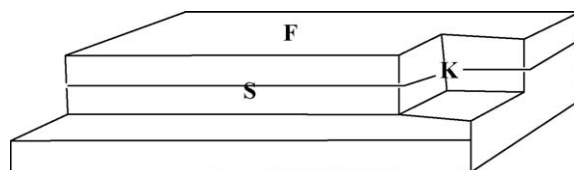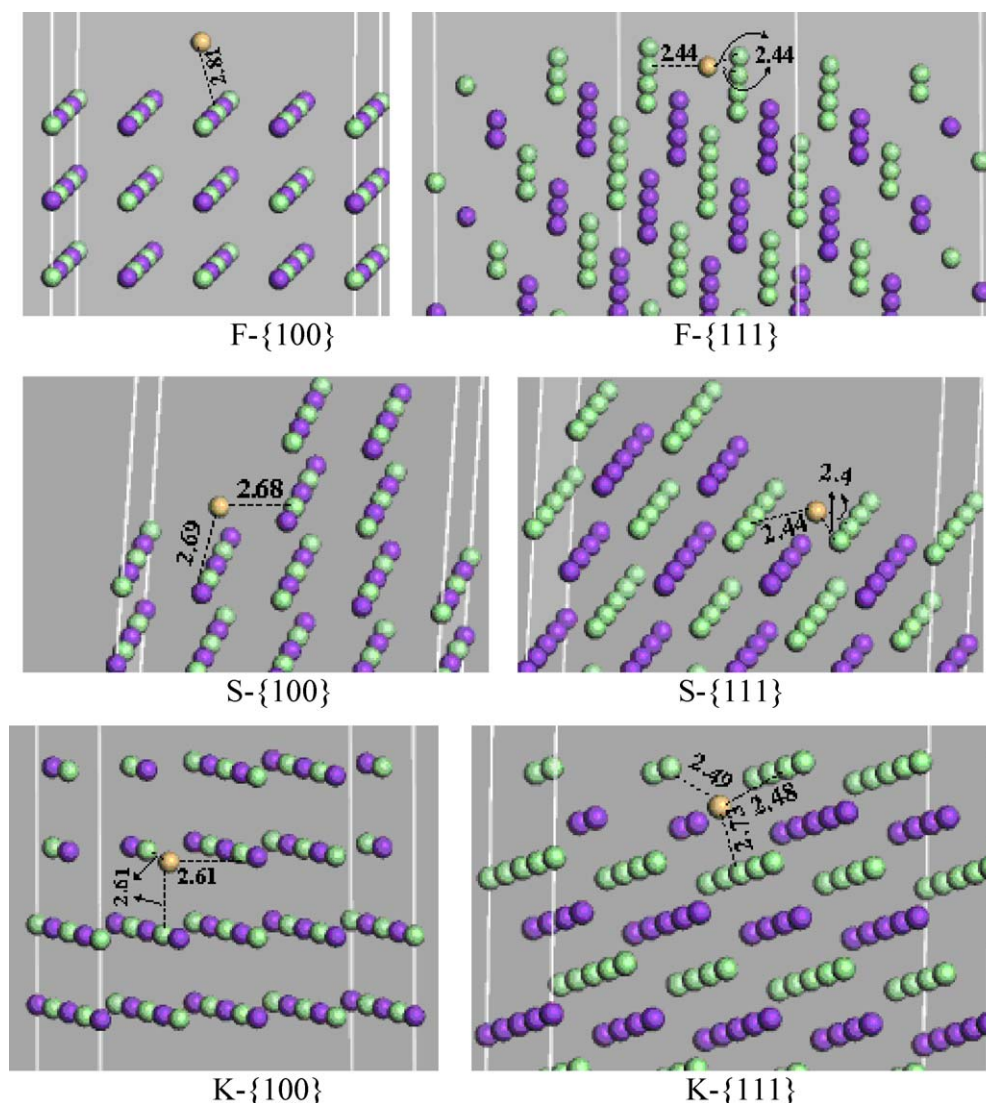

Scheme 2. .

Fig. 1. Interaction of Cd²⁺ ion with flat, step and kink sites of {1 0 0} and {1 1 1} NaCl planes at LDA/PWC/DND level of theory. The distances are in angstroms (purple: sodium, green: chlorine and yellow: Cd²⁺).

alkali halides were taken from COSMO calculations. The dielectric constant (ε = 78.4 for water) was used for COSMO calculations with GGA/VWN-BP/DNP level of theory. Interaction energies were computed by subtracting the energies of the additive molecules (Cd²⁺:$E_{additive}$) and surface (alkali halides:$E_{surface}$) from the energy of the adsorption system (alkali halides with Cd²⁺:$E_{additive/surface}$) as shown in the following equation:

$$E_{int} = E_{additive/surface} - \{E_{additive} + E_{surface}\} \qquad (1)$$

The explicit solvent molecules (water) were also used in another set of calculations with the Cd²⁺ ion to model the NaCl surface coverage for {1 0 0} and {1 1 1} planes. To examine the dynamical aspects of interactions of water and Cd²⁺ with NaCl surfaces, molecular dynamics simulations were performed with the canonical NVT ensemble with the system temperature kept at around 300 K by using Massive GGM thermostats [53]. A 1 fs time step was used to ensure good control of the conserved quantities. The total simulation time of 3 ps was carried out. The orientations of water and Cd²⁺ were considered in each case from DFT calculated geometries on {1 0 0} and {1 1 1} planes. We have performed the simulations with two layers slab models {1 0 0} and {1 1 1} of NaCl with Cd²⁺ and water molecules to compromise with

the computational time at LDA/PWC/DND with the DMOL3 program of Material Studio version 4.1 [54,55].

3. Results and discussion

Initially, the interaction of Cd²⁺ ion was performed with the important surfaces of NaCl at density functional level of theory. The possible interactions of Cd²⁺ ion with the 3D slabs of flat, steps and kinks of {1 0 0} and {1 1 1} sodium chloride surfaces are shown in Fig. 1. The cadmium ion was allowed to optimize on these surfaces of NaCl at LDA/PWC/DND level. On flat surfaces of sodium chloride, Cd²⁺ ion prefers to interact with chloride ions due to electrostatic reasons, maximizing its interaction with more than one Cl⁻ ion. Cadmium ion prefers to interact with one chloride ion of {1 0 0} surface of NaCl, however, Cd²⁺ ion slips between the lattice planes of {1 1 1} plane as shown in (Fig. 1). We have observed that the relaxation of slab layers does not affect the interaction of organic additives with surfaces [56–58], however, it is important to examine the effect of relaxations of slabs with inorganic ions like Cd²⁺. Relaxing the top layer of {1 0 0} and {1 1 1} surface of NaCl with Cd²⁺ predicted the similar trend as observed with the fixed surfaces (Supporting information, Fig. S1 and Table S1). A minor variation was seen on the NaCl lattice ions (i.e. 2.875–

Table 1
Interaction energies calculated at GGA/VWN-BP/DNP for gas phase and GGA/VWN-BP/DNP for aqueous phase (COSMO) level using LDA/PWC/DND optimized geometries for Cd^{2+} ion with {1 0 0} and {1 1 1} flat, step and kink sites of NaCl surfaces in kcal/mol.

Plane	Flat		Step		Kink	
	{1 0 0}	{1 1 1}	{1 0 0}	{1 1 1}	{1 0 0}	{1 1 1}
GGA\ VWN-BP\DNP	−422.9	−479.0	−412.5	−501.8	−435.7	−551.3
GGA\ VWN-BP\DNP (COSMO)	−2.0	−83.0	−10.1	−54.2	1.9	−93.0

2.89 Å) with the Cd^{2+} sitting at the top of Cl^- ion in {1 0 0}, whereas, the cation moved in between the lattice plane while interacting with {1 1 1}. In the case of {1 0 0} and {1 1 1} step surfaces, Cd^{2+} moves away from the deleterious Na^+ ion layers to maximize the interaction with the oppositely charged chloride ion layers. Similar situation was observed with the kink surfaces of NaCl with Cd^{2+} ion, where the additive prefers to sit in between the lattice points (Fig. 1).

Generally, the interaction energies calculated for the adsorption of Cd^{2+} ion on the surfaces of NaCl suggest that the ion prefers to bind strongly with the {1 1 1} plane compared to the stable {1 0 0}

plane (Table 1). The binding energy calculated for the interaction of Cd^{2+} ion with the kink sites was more favorable than the steps and flat surfaces of NaCl. This is conceivable due to the fact that Cd^{2+} ion takes the advantage of interacting with the neighboring ions on the kink surface. Therefore, DFT calculated results also revealed that the kink site is more energetically favored than that of flat and step surfaces towards the growth of specific planes compared to steps or ledge sites [2,12]. The magnitude of interaction calculated in the case of Cd^{2+} ion is much higher than the organic additives on such surfaces [57–60]. The calculations performed in water employing the continuum model (COSMO) however, showed reasonably
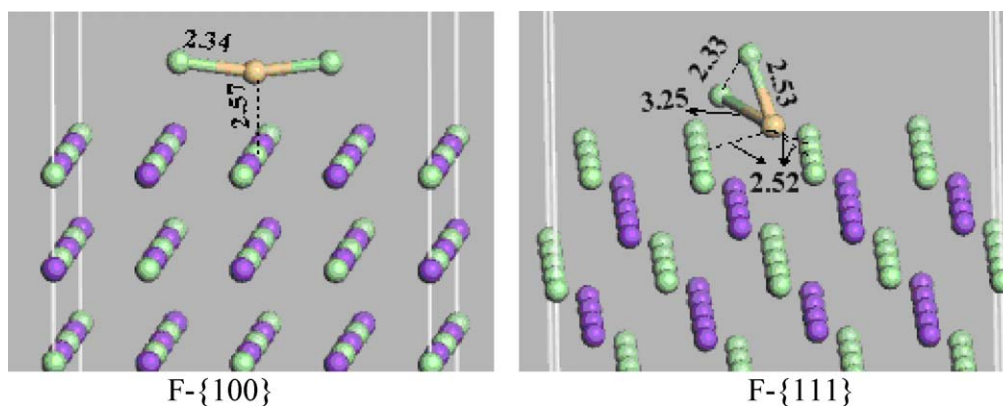

Fig. 2. Interaction of $CdCl_2$ with flat surfaces of {1 0 0} and {1 1 1} NaCl planes at LDA/PWC/DND level of theory. The distances are in angstroms (purple: sodium, green: chlorine and yellow: Cd^{2+}).
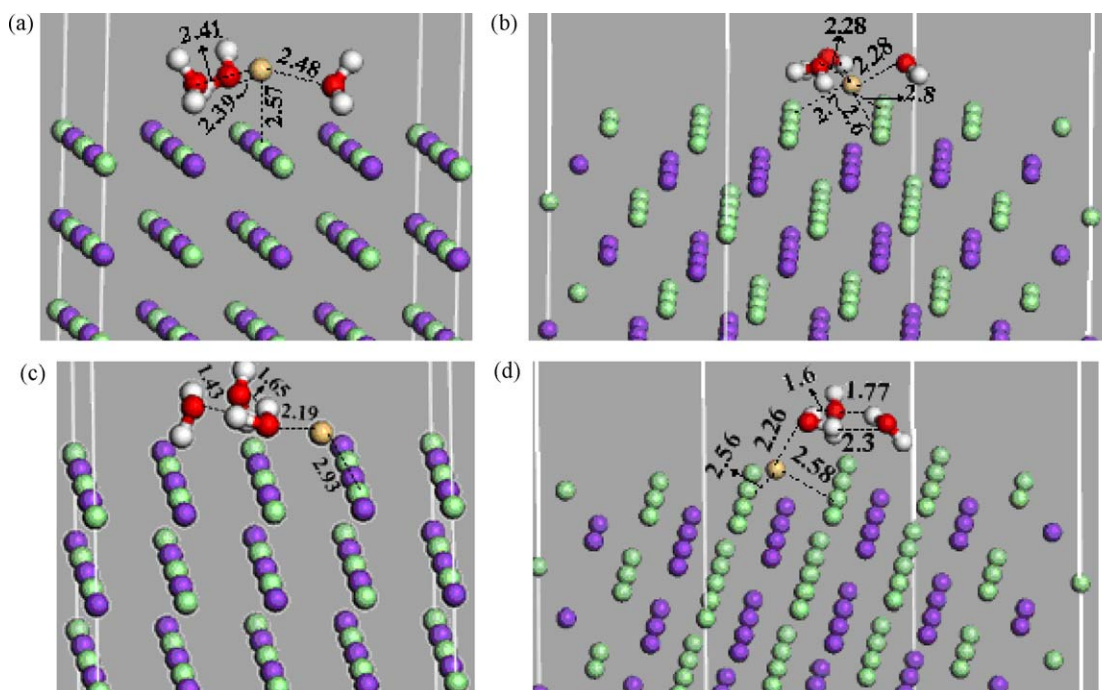

Fig. 3. Orientation of Cd^{2+} ion surrounded with water molecules on {1 0 0} and {1 1 1} flat surface of NaCl are shown in (a) and (b), respectively. (c) and (d) show the arrangement of Cd^{2+} ion outside the water cluster. The distances are in angstroms (purple: sodium, green: chlorine and yellow: Cd^{2+}, red: oxygen, white: hydrogen).

Table 2
Interaction energies calculated at GGA/VWN-BP/DNP for gas phase and GGA/VWN-BP/DNP for aqueous phase (COSMO) level using LDA/PWC/DND optimized geometries for Cd^{2+} ion with three water molecules on flat {1 0 0} and {1 1 1} surfaces of NaCl in kcal/mol.

Plane	Fig. 3(a)	Fig. 3(b)	Fig. 3(c)	Fig. 3(d)
GGA\VWN-BP\DNP	−472.1	−536.1	−464.3	−523.3
GGA\VWN-BP\DNP (COSMO)	−37.0	−93.8	−10.0	−95.2

lower binding energies compared to the gas phase data (Table 1). The preference towards the {1 1 1} plane of NaCl prevailed in the aqueous phase as well. However, the preferred interaction of Cd^{2+} ion with {1 0 0} kink site in the gas phase was found to be weaker in the aqueous phase calculations; the {1 0 0} step site is the better site for interaction (Table 1). These calculated results shows that the morphology of NaCl can be influenced from cubes to octahedron crystals with Cd^{2+} ion, which is in agreement with the experimentally observed results [17].

The interaction of cadmium ion with NaCl surfaces was examined assuming the fact that $CdCl_2$ will be dissociated due to its higher solubility in water. Nevertheless, $CdCl_2$ bonds carry covalent characters as well [61]. Therefore, it would be worth examining the interaction of $CdCl_2$ with the important surfaces of NaCl. The molecular $CdCl_2$ measured by electron diffraction studies showed that the molecule is nearly linear with an average angle of 170° [62]. The calculated $CdCl_2$ geometry was found to be linear at LDA/PWC/DND level. The LDA/PWC/DND level optimized $CdCl_2$

showed the Cd–Cl distance of 2.283 Å, which is good agreement with the experimentally observed 2.271 Å [62]. The calculated binding energies for cadmium chloride with the {1 0 0} and {1 1 1} flat surface of sodium chloride suggest that $CdCl_2$ is weakly attractive with the former plane by −9.7 kcal/mol at GGA/VWN-BP/DNP level of theory, whereas, the interaction is weaker (26.7 kcal/mol) on {1 1 1} plane of NaCl. The $CdCl_2$ deviates from linearity to attain the maximum interaction with {1 0 0} plane of NaCl, however, keeping the molecular entity intact on the surface. Interestingly, the interaction of $CdCl_2$ with the {1 1 1} plane of NaCl deviates drastically to avoid electrostatic repulsions between the chloride ions of additive and crystal plane, which, eventually leads toward the formation of Cl_2 molecule leaving Cd^{2+} ion on the surface of the crystal (Fig. 2). Relaxing the surface of NaCl with $CdCl_2$ leads to the similar distortion of additive on {1 1 1} plane and the interaction is again unfavored in this case also (Supporting information, Fig. S2 and Table S2). In absence of any report on evolution of Cl_2 gas and the change in the habit of NaCl with $CdCl_2$ indicates that the molecular cadmium chloride might not present in the solution or not suitable to bind the crystal surfaces. Comparing the interaction of $CdCl_2$ with the sodium terminated {1 1 1} surface, it appears that the chloride ions bind strongly with Na^+ ions of the surface, however, $CdCl_2$ dissociates as observed in the case of chloride terminated {1 1 1} surface (Supporting information, Fig. S3 and Table S3).

The stabilization of {1 1 1} plane of NaCl with Cd^{2+} ion seems to be important for the morphological change of sodium chloride,
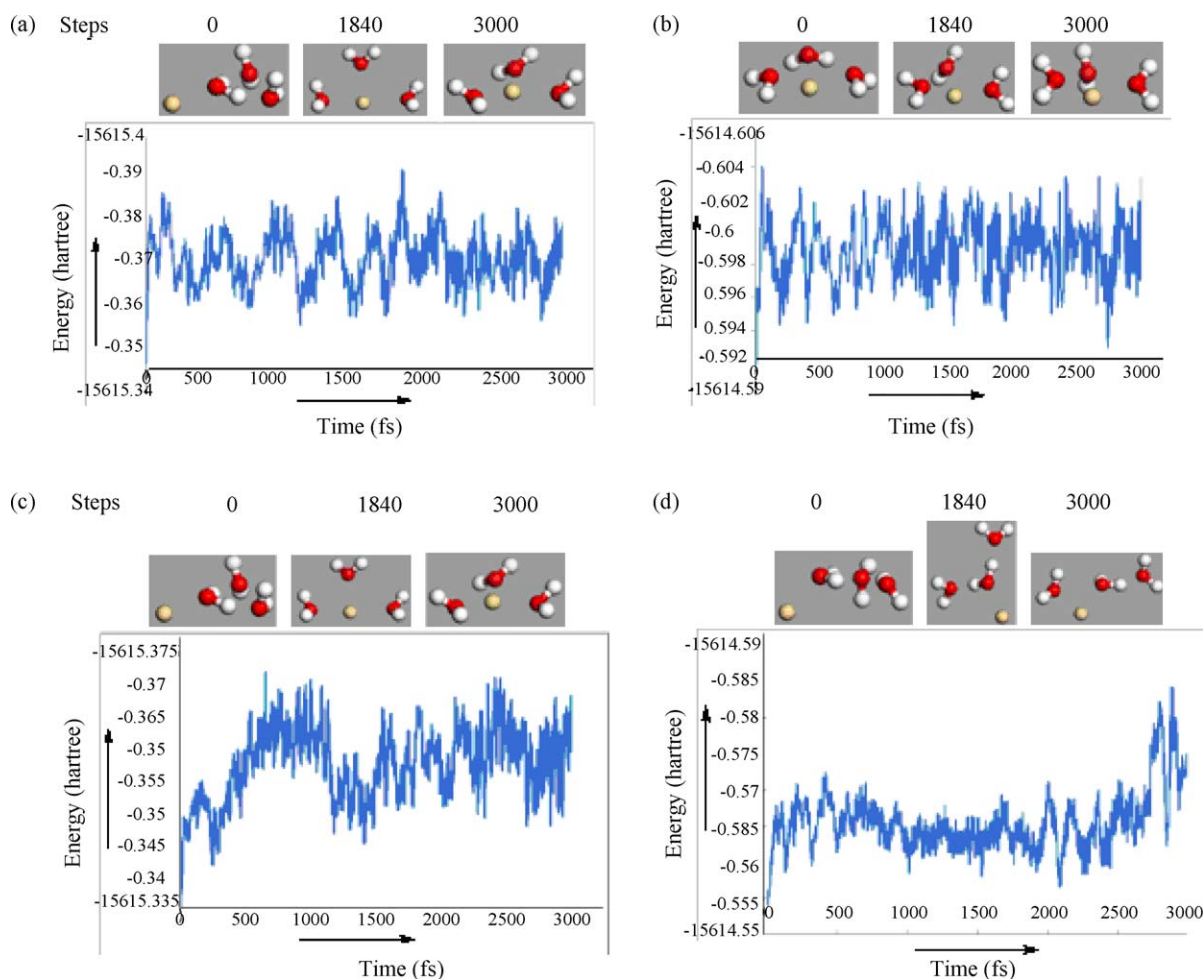

Fig. 4. LDA/PWC/DND trajectories for the interaction of Cd^{2+} ion with water molecules on the {1 0 0} and {1 1 1} surfaces of NaCl with MD simulations. (a) and (b) represent the simulations performed with in capsulated Cd^{2+} ion with water molecules on {1 0 0} and {1 1 1} planes of NaCl, respectively, whereas, (c) and (d) show the trajectories for Cd^{2+} ion with outside water cluster. Snapshots of water cluster with Cd^{2+} at different time are given.

however, such interactions take place in aqueous solution. The model proposed for the slower growth of {1 1 1} surface of NaCl with Cd^{2+} ion and water has been examined with DFT study. The surface X-ray diffraction (SXRD) studies suggested the coverage of {1 1 1} NaCl surface by mixed monolayer of Cd^{2+} and water molecules in 1:3 ratio [16]. The mixed layer modeling on the surface of NaCl was performed with three water molecules and a Cd^{2+} ion. The possible arrangements of such mixed monolayers on these surfaces, where the Cd^{2+} was surrounded with 3 water molecules and in another situation the inorganic ion was placed outside the water cluster. The optimized geometries of these model monolayers are shown in Fig. 3.

The Cd^{2+} ion surrounded with 3 water molecules on {1 0 0} and {1 1 1} surface of NaCl are shown in Fig. 3(a) and (b), respectively, whereas, the Cd^{2+} ion outside the water cluster on such surfaces are given in Fig. 3(c) and (d), respectively. The optimized mixed monolayer formation of Cd^{2+} ion with water molecules show that the Cd^{2+} is sandwiched between the Cl^- of {1 1 1} surface and the water layer. Such interactions reveal that the formation of water layer is weakly interacting with the chloride surface of {1 1 1} plane (Fig. 3). However, the interaction of water layer seems to be stronger in {1 0 0} surface, where, the Cd^{2+} ion and water layer reside closely to the surface ions. The calculated interaction energies for the mixed monolayer formation on surfaces of NaCl suggest that the {1 1 1} is preferred in either arrangement of ions and water molecules (Table 2). However, the arrangement of Cd^{2+} ion surrounded with 3 water molecules is energetically more favored where, the ion is outside the water cluster. The single point calculations performed in the aqueous phase with COSMO model also showed the similar preference for the arrangement of monolayers on NaCl surfaces, nevertheless, the magnitude of interactions are much weaker compared to the gas phase calculations (Table 2). The aqueous phase data further reveals that the mixed monolayer formation in Fig. 3(a) should be preferred with {1 0 0} plane, whereas, such monolayer formations are comparable for Fig. 3(b) and (d), respectively.

To examine the dynamical profiles of monolayer formation of Cd^{2+} ion with water molecules on NaCl surfaces, molecular dynamics study was performed. The NVT ensemble calculated trajectories for Cd^{2+} and 3 water on {1 0 0} and {1 1 1} planes showed that the metal ion is surrounded by three water cluster and the variation in the energy is occurred in a periodic manner. Water molecules seem to orient around the cadmium ion with time irrespective of the guess geometries taken as incapsulated metal ions or not. The snapshots taken in both cases with time in each case are shown in the trajectory plots (Fig. 4). These results reveal that the incapsulated geometry of cadmium ion with water molecules would be preferred than the case where the Cd^{2+} ion is outside the water cluster. Besides interacting with water molecules, Cd^{2+} ion moved on the {1 0 0} surface of NaCl with an average distance of 2.65 Å with time, whereas, on the {1 1 1} surface with an average distance of 2.70 Å, which is not very different from the optimized (LDA/PWC/DND) DFT results.

4. Conclusions

In the present work, we have performed DFT methods to examine the influence of cadmium chloride towards the morphology of sodium chloride. The slab model calculations show that the adsorption of cadmium ion on the flat, step and kink surfaces of NaCl can induce the morphological change as observed in experimental studies. The molecular cadmium chloride is not an active modifier for sodium chloride. Mixed monolayer formations on {1 0 0} and {1 1 1} surface suggest that such coverage can as well induce the change suggested by SXRD studies. The in capsulated Cd^{2+} ion with water molecules seem to be energetically

preferred on {1 0 0} surface of NaCl, whereas, such specificity of arrangement was not seen for {1 1 1} plane. The molecular dynamics study supports the in capsulation of Cd^{2+} with water molecules as predicted from DFT calculations. The calculated results infer that the change in the morphology of NaCl seems to be responsible by the adsorption of Cd^{2+} ion and the water layers weakly interact with the modified {1 1 1} surface of this alkali halide and hence the stabilization of this plane due to such water layers is less important.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2009.09.007.

References

[1] D.L. Klug, in: A.S. Myerson (Ed.), Handbook of Industrial Crystallization, Butterworth, Montvale, MA, 1993, p. 65.
[2] J.W. Mullin, Crystallization, 3rd ed., Butterworth, London, 1993, p. 238.
[3] R.H. Doremus, B.W. Roberts, D. Turnbull, Growth and Perfection of Crystals, Wiley, New York, 1958, p. 393.
[4] van der, J.P. Eeerden, H. Muller-Krumbhaar, Formation of macrosteps due to time dependent impurity adsorption, Electrochim. Acta. 31 (1986) 1007–1012.
[5] B.D. Chen, J. Garside, R.J. Davey, S.J. Maginn, M. Matsuoka, Growth of mChloronitrobenzene crystals in the presence of tailor-made additives: assignment of the polar axes from morphological calculations, J. Phys. Chem. 98 (1994) 3215–3221.
[6] P. Meenan, R.J. Roberts, J.N. Sherwood, Understanding and controlling the crystal morphology of some ionic crystals, Powder Technol. 65 (1991) 219–225.
[7] R.M. Geertman, A.E.D.M. van der Heijden, On the morphology of caprolactam, J. Cryst. Growth 125 (1992) 363–372.
[8] J.B.L. Rome de 1'Isle, Crystallographie, Paris (1783) 379.
[9] R. Kern, Étude du faciès de quelques cristaux ioniques á structure simple, Bull. Soc. Fr. Miner. Cristallogr. 76 (1953) 325–391.
[10] A. Johnsen, Wachstum and Auflosing der Kristallen, Engelmann, Leipzig, 1910.
[11] M. Beinfait, R. Boistelle, R. Kern, in: R. Kern (Ed.), Adsorption et Croissance Cristalline, 152, Centre National de la Recherche Scientifique, Paris, 1965 p. 515.
[12] M. Mathieu, B. Simon, R. Boistelle, Compt. Rend. (Paris) C274 (1972) 473.
[13] R.J. Davey, The effect of impurity adsorption on the kinetics of crystal growth from solution, J. Cryst. Growth 34 (1976) 109–119.
[14] R. Kern, Étude du faciès de quelques cristaux ioniques á structure simple, Bull. Soc. Fr. Mineral Cristallogr. 76 (1953) 391.
[15] R. Boistelle, Thesis, University of Nancy, 1966.
[16] R. Boistelle, B. Simon, Épitaxies de $CdCl_2$, 2NaCl, $3H_2O$ sur les faces (1 0 0), (1 1 0) et (1 1 1) des cristaux de chlorure de sodium, J. Cryst. Growth 26 (1974) 140–146.
[17] N. Radenović, W. van Enckevort, D. Kaminski, M. Heijna, E. Vlieg, Structure of the {1 1 1} NaCl crystal surface grown from solution in the presence of $CdCl_2$, Surf. Sci. 599 (2005) 196–206.
[18] N. Cabrera, D.A. Vermilyea, Growth and Perfection of Crystals, John Wiley & Sons Inc., 1958,, p. 393.
[19] B.S. Choi, T.A. Ring, Stabilizing NaCl particles with Cd^{2+} in a saturated solution during ex situ PSD measurement, J. Cryst. Growth 269 (2004) 575–579.
[20] P.C. Coveney, W. Humphries, Molecular modelling of the mechanism of action of phosphonate retarders on hydrating cements, J. Chem. Soc., Faraday Trans. 92 (1996) 831–841.
[21] P.C. Coveney, R. Davey, J.L.W. Griffin, Y. He, J.D. Hamlin, S. Stackhouse, A. Whiting, A new design strategy for molecular recognition in heterogeneous systems: a universal crystal-face growth inhibitor for barium sulfate, J. Am. Chem. Soc. 122 (2000) 11557–11558.
[22] A. Wierzbicki, H.S. Cheung, Molecular modeling of inhibition of crystals of calcium pyrophosphate dihydrate by phosphocitrate, J. Mol. Struct. (THEOCHEM) 454 (1998) 287–297.
[23] P.V. Coveney, R.J. Davey, J.L.W. Griffin, A. Whiting, Molecular design and testing of organophosphonates for inhibition of crystallisation of ettringite and cement hydration, Chem. Commun. (1998) 1467–1468.
[24] A. Wierzbicki, C.S. Sikes, J.D. Sallis, J.D. Madura, E.D. Stevens, K.L. Martin, Scanning electron microscopy and molecular modeling of inhibition of calcium oxalate

monohydrate crystal growth by citrate and phosphocitrate, Calcif. Tissue Int. 56 (1995) 297–304.

[25] A. Wierzbicki, C.S. Sikes, J.D. Madura, B. Drake, Atomic force microscopy and molecular modeling of protein and peptide binding to calcite, Calcif. Tissue Int. 54 (1994) 133–141.

[26] J.J. Lu, J. Ulrich, The influence of supersaturation on crystal morphology: experimental and theoretical study, Cryst. Res. Technol. 38 (2003) 63–86.

[27] P. Deak, Choosing Models for Solids, Phys. Stat. Sol. (b) 217 (2000) 9–21.

[28] P.W. Tasker, The surface energies, surface tensions and surface structure of the alkali halide crystals, Philos. Mag. A 39 (1979) 119–136.

[29] P.W. Tasker, The stability of ionic crystal surfaces, J. Phys. C: Solid State Phys. 12 (1979) 4977–4984.

[30] N. Radenović, D. Kaminski, W. van Enckevort, S. Graswinckel, I. Shah, M. in't Veld, R. Algra, E. Vlieg, Stability of the polar {1 1 1} NaCl crystal face, J. Chem. Phys. 124 (2006) 164706–164711.

[31] B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, J. Chem. Phys. 92 (1990) 508–517.

[32] B. Delley, Fast calculation of electrostatics in crystals and large molecules, J. Phys. Chem. 100 (1996) 6107–6110.

[33] B. Delley, From molecules to solids with the Dmol3 approach, J. Chem. Phys. 113 (2000) 7756–7764.

[34] Materials Studio DMOL3 Version 4.1, Accelrys Inc., San Diego, USA.

[35] J.P. Perdew, Y. Wang, Accurate and simple density functional for the electronic exchange energy: generalized gradient approximation, Phys. Rev. B 33 (1986) 8800–8802.

[36] J.P. Perdew, Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy, Phys. Rev. B 45 (1992) 13244–13249.

[37] S.J. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, Can. J. Phys. 58 (1980) 1200–6045.

[38] A.D. Becke, A multicenter numerical integration scheme for polyatomic molecules, J. Chem. Phys. 88 (1988) 2547–2554.

[39] Z. Wu, R.E. Cohen, D. Singh, Comparing the weighted density approximation with the LDA and GGA for ground-state properties of ferroelectric perovskites, J. Phys. Rev. B 70 (2004) 104112–104119.

[40] P. Ziesche, S. Kurth, J.P. Perdew, Density functionals from LDA to GGA, Comput. Mater. Sci. 11 (1998) 122–127.

[41] W. Kohn, A.D. Becke, R.G. Parr, Density functional theory of electronic structure, J. Phys. Chem. 100 (1996) 12974–12980.

[42] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.

[43] J.P. Perdew, K. Burke, Y. Wang, Generalized gradient approximation for the exchange-correlation hole of a many-electron system, Phys. Rev. B 54 (1996) 16533–16539.

[44] A.D. Becke, Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing, J. Chem. Phys. 104 (1996) 1040–1046.

[45] A.N. Ermoshkin, E.A. Kotomin, A.L. Shluger, The semiempirical approach to electronic structure of ionic crystal surface, J. Phys. C: Solid State Phys. 15 (1982) 847–861.

[46] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188–5192.

[47] A. Klamt, COSMO and COSMO-RS, in: P. v.R. Schleyer, L. Allinger (Eds.), Encyclopedia of Computational Chemistry, vol. 2, Wiley, New York, 1998, p. 604.

[48] A. Klamt, Conductor-like screening model for real solvents: a new approach to the quantitative calculation of solvation phenomena, J. Phys. Chem. 99 (1995) 2224–2235.

[49] A. Klamt, V. Jonas, T. Bürger, J.C.W. Lohrenz, Refinement and parametrization of COSMO-RS, J. Phys. Chem. A 102 (1998) 5074–5084.

[50] A. Klamt, F. Eckert, COSMO-RS: a novel and efficient method for the a priori prediction of thermophysical data of liquids, Fluid Phase Equilib. 172 (2000) 43–72.

[51] A. Klamt, F. Eckert, M. Horning, COSMO-RS: a noval view to physiological solvation and partition questions, J. Computer-Aided Mol. Des. 15 (2001) 355–365.

[52] A. Klamt, Comment on "A critical assessment on two predictive models of binary vapor–liquid equilibrium" by M. Neiman, H. Cheng, V. Parekh, B. Peterson, K. Klier, Phys. Chem. Chem. Phys. 6 (2004) 3474, Phys. Chem. Chem. Phys. 6 (2004) 5081.

[53] X. Chen, L. Zhang, Z. Wang, J. Li, W. Wang, Y. Bu, Relay stations for electron hole migration in peptides: possibility for formation of three-electron bonds along peptide chains, J. Phys. Chem. B 112 (2008) 14302–14311.

[54] Y. Pei, W. An, K. Ito, P.v.R. Schleyer, X.C. Zeng, Planar pentacoordinate carbon in CAl_5^+: a global minimum, J. Am. Chem. Soc. 130 (2008) 10394–10400.

[55] S.B. Legoas, V. Rodrigues, D. Ugarte, D.S. Galvão, Contaminants in suspended gold chains: an ab initio molecular dynamics study, Phys. Rev. Lett. 93 (2004) 216103.

[56] K. Jug, B. Ahlswede, MSINDO study of the adsorption of water molecules at defective NaCl (1 0 0) surfaces, Surf. Sci. 439 (1999) 86–94.

[57] A. Singh, M.K. Kesharwani, B. Ganguly, The influence of formamide on the habit of LiF, NaCl and KI: a DFT and aqueous solvent model study, Cryst. Growth Des. 9 (2009) 77–81.

[58] A. Singh, S. Chakraborty, B. Ganguly, Computational study of urea and it's homologue glycinamide: conformations, rotational barriers, and relative interactions with sodium chloride, Langmuir 23 (2007) 5406–5411.

[59] A. Singh, T. Selvamani, I. Mukhopadhyay, B. Ganguly, Morphology of potassium chloride in aqueous and in formamide solution—an experimental and computational investigation, Can. J. Chem. 87 (2009) 514–522.

[60] A. Singh, B. Ganguly, DFT study of urea interaction with potassium chloride surfaces, Mol. Simul. 34 (2008) 973–797.

[61] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed., Butterworth-Heinemann, Oxford, UK, 1997, p. 1211.

[62] S. Gundersen, A. Haaland, K.-G. Martinsen, S. Samdal, On the molecular structure of $CdCl_2$, J. Mol. Struct. 318 (1994) 251–255.