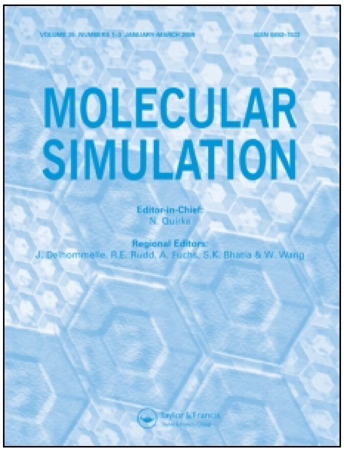

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DFT study of urea interaction with potassium chloride surfaces

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DFT study of urea interaction with potassium chloride surfaces

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In this work, interaction of urea on the important surfaces of potassium chloride has been investigated using density functional theory (DFT) approach. We have performed the DFT calculations using slab models for the interactions of urea with {100}, {110} and {111} surfaces of KCl. Furthermore, the influence of solvent effect was computed with the COSMO continuum model. While sodium chloride crystals are known to change their habit in presence of urea impurity, the higher homologue KCl has not been extensively studied. In one of our earlier articles, we have shown that the preferential interaction of urea with the specific surface of sodium chloride can lead to change the habit from cubes to octahedrons [A. Singh, S. Chakraborty and B. Ganguly, *Computational study of urea and its homologue glycinamide: conformations*, *rotational barriers*, *and relative interactions with sodium chloride*, Langmuir 23 (2007), pp. 5406–5411]. The similar surface docking approach for the interaction of urea with the KCl surfaces suggests that urea would not influence the morphology of KCl. The computed interaction energies were found to be comparable for all the important surfaces of KCl with urea. We have performed experimental studies to examine our computational analysis. The experimental results suggest that the growing KCl crystals in urea solution are cubic in nature. The combined computational and experimental studies corroborate the model of effective interaction of additives with the certain face of crystals and responsible for the change in the morphology [R. Speidel, *Neues Jahrbuch fur Mineralogie*, Part 4, 81m (1961); N. Cabrera, D.A. Vermilyea. *Growth and Perfection of Crystals*; John Wiley & Sons Inc. 393. (1958); C.W. Bunn, *Adsorption oriented overgrowth and the mixed crystal formation*, Proc. R. Soc. A 141 (1933), pp. 567–593].

Keywords: density functional theory calculations; habit modification; KCl; COSMO model; urea

1. Introduction

The study and engineering of crystal faces have attracted immense interest among artists and the crystal grower community since at least the Bronze Age [1]. Although significant efforts have been made over the last few decades to predict precisely the growth morphology of crystals, it remains a challenging task to this date. Crystal growth morphology has diverse applications ranging from drug design [2] to explosives [3] and inverse gas chromatography data [4]. Therefore, knowledge of crystal growth habits and their morphological properties is important in understanding and exploiting many of their physico-chemical properties. In this regard, the influence of additives on crystal habit has received considerable attention. It has been found that the nucleation, growth and morphology of crystals can be significantly altered by the presence of low concentrations of impurities such as reaction byproducts, impurities present in the reactants and additives that are purposely added to alter the crystallisation process [5,6]. Additives can reduce crystal growth rate and alter morphology by binding to crystal faces and interfering with propagation steps [7,8]. Rome de 1'Isle [9] showed that octahedrons are formed instead of normal cubes if rocksalt is grown in the presence of urine. Many authors have since reported the cube-octahedron shape transition for various experimental conditions. Some early work reported that octahedron can also be obtained from pure water solution [10–12]. Radenovic et al. [13,14] have experimentally studied the habit change of sodium chloride from cubic to octahedron in the presence of smaller amides. The observed results have been rationalised on the basis of charge distributions and strong interaction between the more exposed carbonyl oxygen of amides like formamide and urea with the sodium ions, which stabilise the {111} surface of sodium chloride and leads to the octahedron morphology of sodium chloride [13,14]. In earlier observations, Speidel and Cabrera [15–17] also considered that the additive strongly interacts with certain crystal faces to influence the morphology of the crystal. Bunn [17] explained the habit modification of NaCl by urea in aqueous solutions is due to adsorption of the impurity on certain crystal faces during crystal growth. There are many proposals that have been reported to explain the habit of sodium chloride; however, studies on the interactions at the molecular level are limited. We have recently performed a detailed computational analysis of urea interaction with the surfaces of sodium chloride [18]. The calculated results suggest that the interactions of additives with certain crystal faces are among the most important factors in the change

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in morphology of alkali halides. A number of studies have been performed on the habit of sodium chloride crystals in the presence of impurities; however, the higher homologue KCl has received little attention. Recently, there have been some efforts to crystallise KCl in carbon nanotubes [19]. The KCl crystals were grown in cubic form with predominantly stable {100} faces. It is mentioned in one of the reports that urea can act as an additive for KCl [20,6]. However we have not come across any detailed experimental study of the effect of urea on KCl crystals. Our effort to understand the growth of alkali halide crystals prompted us to examine the effect of impurities on KCl crystals. Therefore, we have undertaken the computational approach to study the influence of urea on the morphology of KCl crystals followed by the experimental observations. The experimental results would be useful to examine the predictive nature of these computational analyses.

To examine the effective interaction of urea with specific surfaces of KCl, an approach similar to surface docking, developed to predict the influence of additives on the crystal morphology, has been employed [21–27]. The basis of this approach is to analyse the effect of additives on the individual crystal faces, which are cleaved from a crystal. If the additive has a preferred interaction on a 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. For simulations of surfaces of crystalline solids, slab and cluster models are nevertheless far more popular, since they are feasible from the computational point of view [28]. However, the cluster models came under scrutiny due to their finite size representation. Slab models rather mimic the infinite surface of solids and are considered to be a better approach than the cluster models. In this study, a conventional array of these alkali halide ions has been employed in slab [constructed using periodic boundary conditions (PBCs)] using respective crystal data. The stable {100} surface of potassium chloride was modelled with alternating arrangement of K^+ and Cl^- ions. However, modelling the electrostatically polar {111} surfaces of these alkali halide crystal structures was considered a mystery in surface science because it is difficult to investigate both experimentally and theoretically [29,30]. Since the bulk structure consists of alternating cationic and anionic sheets stacked along the $\langle 111 \rangle$ directions, the {111} polar surfaces must have a very high divergent electrostatic energy, which makes them theoretically highly unstable [6,29–31]. It has been shown in the earlier studies that the adsorption of a negatively charged site of additives would be preferred with the positive ions on top of the surface of alkali halides [13,14]. Recently, Radenovic et al. [31] presented a surface X-ray diffraction determination of the {111} NaCl–liquid interface structure in the presence of aqueous solution and formamide. It was determined that the rocksalt {111} surface is Na^+ terminated for both the environmental conditions. For KCl, {111} surfaces were modelled with the K^+ ions on top of the surface.

2. Computational and experimental methods

2.1 Computational procedure

The interaction study of urea with 3D-slabs of KCl has been performed employing the density functional program Dmol^3 in Material Studio® (version 4.1) of Accelrys Inc., the physical wave functions are expanded in terms of numerical basis sets [32–35]. We used DND double numerical basis set which is comparable to 6–31G* basis set. The geometry of urea and its interaction on surfaces of KCl was optimised with local-density approximation with Perdew–Wang correlational (LDA/PWC) [32–35]. The local-density approximation (LDA) is one of the earliest approximations in density functional theory (DFT). It includes correction for electron correlation effects. However, one of the most important deficiencies with the LDA exchange is the incorrect asymptotic behaviour, which overestimates the energies for the system. This has been solved by using generalised gradient approximations (GGAs) Perdew and Wang, PW91. The Larger basis set DNP compared to DND was also used to examine the influence of basis set effect. Energies were calculated for the adsorbed systems with GGA/PW91 methods. Three-dimensional (3D) slabs of KCl with [{100}, {110} and {111}] planes were generated using unit cells of these halides with PBCs as implemented in Dmol^3 [32–35]. In the 3D slab model, the slab is periodically repeated along the normal direction to the surface. The 3D slab models depend on the slab thickness and the vacuum gap separating the nearest slab images in the *z*-direction. We have investigated this dependence via optimising the number of layers in 3D slabs with vacuum thickness. We have optimised the supercell lattice by varying the number of layers in each case and keeping the sufficiently large vacuum thickness fixed at 20 Å. We have considered the numbers of layers in each case when the total energy of the system becomes minimum. Further, the vaccum thickness was varied from 8 to 20 Å in 2 Å steps with the previously optimised layers and considered the values when the total energy as a function of vaccum gap separations was minimum. For KCl, the optimised Perdew–Wang correlational (LDA/PWC) {100} slab model contains seven layers (112 ions) with a vacuum thickness of 12 Å and for {110} and {111}, the optimised slabs contain eight and seven layers with a vacuum thickness of 12 Å, respectively. Our optimised supercell lattice for KCl was found to be consistent with the results of Ermoskin et al. [36] that six layered slabs are large enough to reproduce the surface states and bulk states of alkali halide crystals. The *k*-points were generated by Monkhorst and Pack [37]. 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 = 629.5095 kcal/mol). The SCF convergence criteria for all calculations were 1.0×10^{-5}. For additive and crystal surface interactions, urea was placed at the midpoint of the KCl surface in each case and optimised at the defined level of theory. The maximum gradient for most of the optimised structures was less than 2×10^{-3} Ha/Å. Interaction energies were computed by subtracting the energies of the additive molecules (formamide:E_{additive}) and surface (alkali halides:E_{surface}) from the energy of the adsorption system (alkali halides with formamide:$E_{\text{additive/surface}}$) as shown in Equation (1).

$$E_{\text{int}} = E_{\text{additive/surface}} - \{E_{(\text{additive})} + E_{(\text{surface})}\}. \quad (1)$$

The conductor-like screening model (COSMO) for real solvents has been employed for solvent calculations [38,39]. The improvement of Dmol^3 version (4.1) over version 4.0 is that the continuum solvation model calculations can be performed with the slab models. Therefore, the COSMO calculations have been performed with the periodic slab models used for the gas phase calculations. This is a significant advantage over the previous version of Dmol^3, where the COSMO calculations were used to mimic the periodic surfaces with cluster models [18]. Further, we have demonstrated in our earlier study that the DFT models used in this case are accurate enough to predict the binding energies of additives with alkali halide surface [18]. The test case was performed with water molecule, whose experimental binding energies on NaCl {100} surfaces are known. Our DFT calculations have reproduced the water adsorption energies reasonably well with GGA model [40,41].

2.2 Experimental procedure

2.2.1 Batch crystallisation

We have performed experiments for crystallisation of KCl in the presence of urea as a possible habit modifier in aqueous solution. To examine the influence of urea on the morphology of KCl crystals, three different concentrations of KCl were used, namely 4.2, 5.2 M (under saturated solution) and 5.6 M (saturated solution). Urea concentration was varied from 5 to 30% [with respect to solute (w/w)] as additive in different batch crystallisations with a regular increment of 5 wt.%. We varied the concentration of analyte, i.e. KCl, dissolved in 5 ml of distilled water taken in a 10 ml capacity beakers, and to this varying wt% urea was added under ambient conditions in the laboratory (room temperature 25°C). For comparison, we repeated similar experiments with NaCl instead of KCl. Urea, KCl and NaCl, used in this study were obtained from Merck, which was 99.99% pure and were used without further purification. The morphologies obtained after crystallisation were examined by SEM and optical microscope and observed morphologies are discussed below.

2.2.2 Instrumentation

The surface structure of the grown crystals was observed by scanning electron microscopy (SEM). The samples for the SEM studies were prepared on cleaned and mirror-polished brass stubs by spreading 100 μl of the dispersion and evaporating the solvent in air. A LEO SEM model 1430 VP was used for the purpose.

2.2.3 Optical microscopy

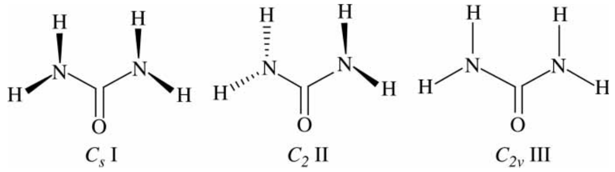
Optical microscopic images were taken by a Olympus (SZH10) research stereo microscope. The statistical distribution of the crystals was observed in the crystallisation bath (10 ml volumetric glass beaker). Individual crystals were examined by putting them on glass slides.

3. Results and discussion

3.1 Urea conformers

It has generally been assumed that urea is a planar symmetrical molecule and the crystal structure reinforced this assumption [42]. However, theoretical calculations reported on urea showed that urea is nonplanar [43–51]. We have examined the conformations of urea in the gas and in the aqueous phase at different DFT levels of theory (Scheme 1) [52–54]. The C_2 II conformer of urea is the most stable conformer and a true minimum (no imaginary frequencies) in agreement with previous reports (Scheme 1) [42–45].

For the interaction study with the surface of KCl, the most stable conformer C_2 II was considered in this study. The interactions of urea II with the 3D slabs of potassium chloride are shown in Figure 1. The optimisations of these



Scheme 1. C_s I, C_2 II and C_{2v} III urea conformers.

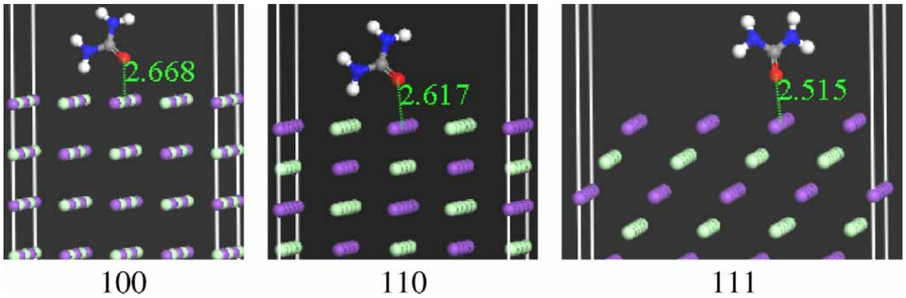


Figure 1. LDA/PWC/DND calculated geometries of urea with the fixed {100}, {110} and {111} KCl surface in slab models (purple: potassium; green: chlorine; red: oxygen; blue: nitrogen and white hydrogen).

additives on the surface of KCl have been performed at LDA/PWC/DND level of theory. Two different sets of calculations have been performed to examine the relaxation effects of KCl surfaces on the interaction energies of urea. First, the slab was kept fixed, while optimising the urea on the top of the {100}, {110} and {111} surfaces of potassium chloride. In another set of calculations, two layers of KCl surfaces were relaxed while optimising the geometry of urea on the surfaces. In this case, the rest of the bottom layers were kept fixed in the bulk position.

The interaction energies calculated for urea with potassium chloride surfaces are shown in Table 1. The computed results suggest that the interactions of C_2 II urea conformer are slightly preferred for {110} surface of KCl 2–4 kcal/mol compared to {100} and {111} planes. The binding energies calculated for the urea conformer II with fixed and relaxed surfaces of potassium chloride are not largely different; importantly, the relative trends are the same in both cases. The calculated trend at larger basis set DNP is similar to that obtained for DND (Table 1).

The mode and orientations of interaction of the urea molecule with these surfaces are shown in Figure 1. The urea moiety prefers to interact with both the potassium and chloride ions in {100} and {110} surface. The carbonyl oxygen of urea interacts with the potassium ion whereas the hydrogen of amine functionality interacts with the chloride ion. In the case of {111} surface of KCl, the carbonyl oxygen interacts with the potassium ion. Generally, the relaxed layered calculations also showed the similar mode of interactions for urea, except the additive was found tilted with {111} plane of KCl. (Figure S1, Supporting Information, available online). To examine the influence of urea conformations on the interaction energy with KCl surfaces, C_{2v} (planar) conformation of urea was also considered. The computed interaction energies for the planar conformer of urea with KCl surfaces were found to very similar to the most stable C_2 conformer of urea (Table 1 and Table S1). The {111} plane is slightly preferred over {100} plane. A similar observation was made also with the interaction of urea conformations with NaCl surfaces [18].

The DFT calculated results suggest that the interaction of urea is marginally preferred with the {110} surface of KCl and such preferential interaction can retard the growth of this face and can lead to the formation of rhomo-dodecahedrons. However, the interaction of urea with {111} plane is comparable to {110}. Therefore, a clear prediction does seem to be possible from the computed results for the formation of rhomo-dodecahedrons and or octahedrons. Nevertheless, the unstable {110} and {111} surface was found to be slightly energetically preferred over {100} of KCl with urea molecule. It is to be noted that the calculations were performed in the gas phase. It has been reported that medium can play a profound role on crystal habit [55–59]. Therefore, the interaction of solvent on the interaction of urea with surfaces of KCl should also be examined.

It is to be noted that urea interacts with the alkali halide surfaces in aqueous solution; hence the surrounding medium effect seems to be important. To examine the effect of solvent, we have performed calculations with the continuum solvation model (COSMO). The dielectrics

Table 1. Interaction energies were calculated at GGA/PW91/DND and GGA/PW91/DNP levels using LDA/PWC/DND optimised geometries for urea with {100}, {110} and (111) surfaces of KCl slab models in kcal/mol.

Plane	{100}	{110}	{111}
GGA/PW91/DND (fixed surface)	− 15.8	− 19.7	− 17.8
(Two-layered relaxed surface)	− 15.2	− 20.3	− 19.9
GGA/PW91/DNP	− 15.9	− 19.6	− 17.2

Table 2. Interaction energies were calculated at GGA/PW91/DND levels using LDA/PWC/DND optimised geometries for urea with {100}, {110} and (111) surfaces of KCl slab models in COSMO. Energies are in kcal/mol.

Plane	{100}	{110}	{111}
GGA/PW91/DND	− 10.5	− 11.9	− 11.5

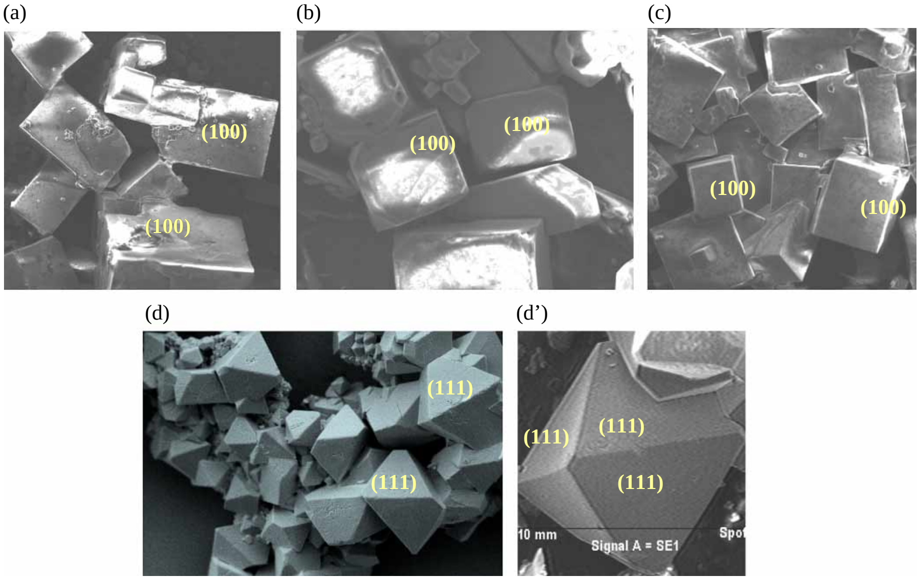


Figure 2. SEM Images of KCl grown crystals obtained from (a) 4.2 M, (b) 5.5 M, (c) 5.8 M and NaCl crystals from (d) 4.2 and 5.5 M solution in 25 wt % urea–water solution.

(€ = 78.4 for water) has been used in these cases. The optimised gas phase slabs for KCl {100}, {110} and {111} with urea were computed with COSMO model. The calculated interaction energies are shown in Table 2. Interaction energies were found to be lower in water compared to the gas phase results. Importantly, the interaction energies for urea with all three surfaces were found to be comparable. Based on these calculated results one could predict that the additional stabilisation cannot be achieved for the unstable surfaces like {111} and {110} with urea additive and hence, in the aqueous solution, the stable {100} surface should grow preferentially.

To verify the computational analysis, experiments were performed for the growth of KCl crystals in the presence of urea impurity. The experiments were carried out at different saturation levels of KCl and ratios of urea impurity as mentioned in the experimental section. It is to be noted that the organic additives were required in high concentration for habit modification of alkalihalide as by earlier report [60]. Initially we have taken lower concentration [5, 10, 15 and 20 wt.% (w/w)] of additive to examine the effect of additive on the morphology of KCl. We have observed that there is no change in morphology of KCl at these concentrations, (supporting information) and hence we used an even higher concentration of urea [25 wt.% (w/w)]. Even at this concentration of impurity, the growing KCl crystals were found to be cubes (Figure 2 and Table 3). On the other hand, the growing crystals of NaCl were found to be octahedrons at 25 wt.% of urea (Figure 2 and Table 3). The experimental results corroborate the computational predictions that the growing KCl crystals in urea solution should predominantly be cubes with {100} face.

Table 3. Experimentally observed morphologies of KCl and NaCl with 25 wt.% urea.

Sr. no.	Conc. of the halides	Urea (wt.%)	Remarks
a	4.2 M KCl	25	Cubic
b	5.5 M KCl	25	Cubic
c	5.8 M KCl	25	Cubic
d	4.2 M NaCl	25	Octahedron
e	5.5 M NaCl	25	Octahedron

4. Conclusion

In the present study, we have examined the effect of urea on the morphology of KCl crystals. The computed results predicted that the interaction of urea is not significantly preferred to any important surfaces of KCl. Importantly, the interaction energies were found to be comparable in the solvent medium. The relaxed surfaces do not alter the interaction energies for urea with the KCl surfaces. {100} and {110} planes interact with both the carbonyl and amine functionality of urea molecule. Experimental results reveal that the KCl crystals are cubic in the presence of urea impurity, however, the NaCl crystals are octahedrons under such conditions. The computational analyses support the model of effective interaction of additives with the certain face of crystals would be one of the factors responsible for the change in the morphology.

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