Crystal Growth

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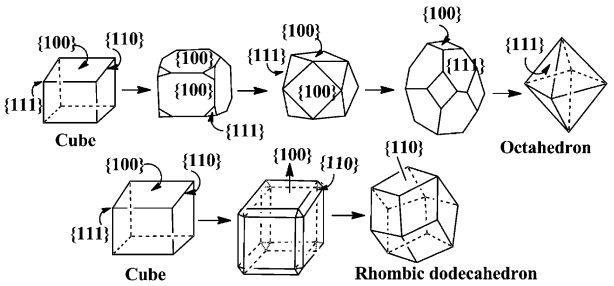
Is Dual Morphology of Rock-Salt Crystals Possible with a Single Additive? The Answer Is Yes, with Barbituric Acid**

*Anik Sen and Bishwajit Ganguly**

Sodium Chloride is one of the most important materials in our daily life. It is used as the basic raw material for the manufacture of variety of industrial chemicals, such as soda ash and caustic soda, used in the textile, dairy, dyeing, fertilizer, paper and pharmaceutical industries.[1] The caking of such an important material is a common storage problem. This occurs due to the formation of solid intercrystalline bridges that leads to agglomeration and lump formation of the salt crystals. One of the most important anti-caking agents known is ferrocyanide, ($[Fe(CN)_6]^{4-}$).[2] A trace amount of ferrocyanide (ca. 4 ppm by weight) changes the crystal habit of NaCl from cubic to dendritic and thus acts as an strong anti-caking agent. Recently, it has been shown that ferrocyanide ions actually replace sodium chloride clusters on the surface and block further growth as a result of a difference in ion charge and so prevent the caking.[3] Rome de l'Isle first showed that NaCl crystallizes with octahedron morphology instead of the simple cubic in presence of urine.[4] Since then many studies have been performed to examine the habit of NaCl using various organic and inorganic additives, such as glycine, formamide, urea, cysteine, creatinine, cadmium chloride.[5] These additives are responsible for the change in the habit of cubic NaCl to octahedron or dodecahedron crystals and such changes enhance the free-flow property of the salt crystals.[5i] We herein report for the first time, that a single additive can be used to tune the morphology of rock-salt crystals in more than one form in one pot solution.

Additives reduce crystal growth rate and alter morphology by binding to crystal faces and interfering with propagation steps.[6] The morphological changes appear in the crystals through the interaction of the additives on a specific plane which reduce the growth of that plane and as a result, other fast growing surfaces disappear and ultimately, the slow growing surface controls the morphology.[6c] Other factors, such as temperature, pressure, supersaturation, and solvation, may also play a role in controlling the morphology of alkali halides.[5] Three different crystal faces, namely, {100}, {110}, and {111} are important in the NaCl crystallization process. The growth of the {100} plane leads to the cubic form,[2b] while the growth of {111} and {110} planes lead to the octahedron and rhombic dodecahedron forms, respectively.[5,6c] The morphodogram of the modification of the alkali-halide crystal from cubic to octahedron; cubic to dodecahedron is shown in Scheme 1.[5d,i,t]



Scheme 1. Progressive change of NaCl crystal morphology from cube to octahedron (top) and to rhombic dodecahedron (bottom).

The design of an additive which is capable of inhibiting specific crystal-growth faces and thus influence the habit of crystals is a challenging problem. Such studies are not only limited to experimental trials, morphology predictions are feasible with the help of molecular modeling approaches.[7] The design strategy based on the additive recognition at inorganic surfaces has been found to be successful in controlling the morphology.[8] Further, molecular modeling studies were employed to examine the recognition of additives with different properties including lattice fit,[5e,f] multipoint adsorption,[9] conformation of the additives,[5j] pH[5m,o]. Recently, a similar study predicted that nitrilotriacetic acid (NTA) acts as a habit modifier of NaCl,[5p] which however was reported to be ineffective on NaCl crystals.[9] Furthermore, the report showed that NTA can work in much smaller quantity compared to other known organic additives.[5p] The ionic forms of NTA have been suggested to be important for such morphological changes in NaCl crystals, which has also been observed with citric acid.[5m,n] Both NTA and citric acid are flexible in nature with more than one similar binding sites, however, with these additives not all the sites bind to the NaCl surfaces.[5p,n] The design of an additive is more attractive, especially if the molecule is small and has different binding functions.[8b] The difference in binding motifs could help to recognize the different planes of NaCl crystal surfaces by considering their effective interactions.[5j,10] Such reports are not available for the habit modifications of sodium chloride crystals, where the single additive can

[*] A. Sen, Dr. B. Ganguly
Analytical Discipline & Centralized Instrument Facility
Central Salt and Marine Chemicals Research Institute
G.B. Marg, Bhavnagar, Gujarat-364002 (India)
E-mail: ganguly@csmcri.org

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influence the different planes of NaCl and can possibly induce different morphologies.

In search of effective habit modifiers for rock-salt crystals, we have predicted, through computational studies, that barbituric acid can influence the morphology of NaCl in both octahedron and rhombic dodecahedron forms from native cubic crystals. Barbituric acid possesses binding sites similar to urea and formamide (-CONH) and also a -CH_2 group flanked with two functional groups as seen in glycine molecule. The activity of such functional units can be amplified through suitable pH conditions to interact with the important planes of NaCl surfaces. The experimental studies performed to examine the computational predictions corroborate that barbituric acid can give dual morphology of NaCl crystals through the adjustment of the pH value of the solution. Importantly, a number of additives are known to influence the habit of NaCl from cubic to octahedron, whereas, glycine is presumably the only additive that leads to the rhombic dodecahedron.[5a,i,r,s] though with a much larger amount (20–25% w/v) is required, whereas barbituric acid works with only 0.08–0.2% w/v.

Barbituric acid is widely used in pharmaceutical companies and displays little toxicity.[11] Barbituric acid was first prepared by von Baeyer at 1864,[12] and is most stable in its keto tautomeric form (**1**, Figure 1) in the gas phase as well as

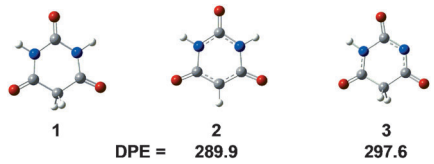

Figure 1. LDA/PWC/DND optimized geometries of barbituric acid (**1**) and the conjugate bases (**2** and **3**). The deprotonation energies (DPE) of **2** and **3** calculated at GGA/PW91/DNP level at COSMO are given in kcal mol^{-1} (gray carbon, red oxygen, blue nitrogen, white hydrogen).

in aqueous phase.[13] The UV absorption spectra of barbituric acid suggests that the deprotonation of the -CH_2 occurs at lower pH (ca. 7–11) whereas, the N–H deprotonation takes place at pH ≈ 11.[14] The deprotonation energy calculated with GGA/PW91/DNP//LDA/PWC/DND level of theory also suggests that the methylene deprotonation (to give **2**) is energetically lower than the -NH deprotonation process (to give **3**; Figure 1). The bis-protonation process is much higher in energy (see Figure S1, Supporting information) and the UV studies suggested that such ionic forms do not prevail within the range pH 0–14.[14] The optimized geometry of the keto-barbituic acid (**1**) is very similar to the crystal structure (see Figure S2, Supporting Information).[15]

From the experimental pK_a values,[14] the fractional distribution curves are plotted using the formula mentioned by Doulas et al in Ref.[16] for the pH range 0.0–14.0 (Figure 2). This plot suggests the existence of three species at different pH values (Figure 2). The detailed derivation for composition calculations is given in the Supporting Information (Scheme S1). The pH value of the keto form of barbituric acid is 2.8.

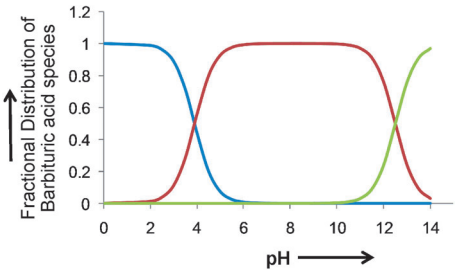

Figure 2. Fractional distributions of the three species of barbituric acid calculated from the pK_a values, are plotted as a function of pH value (blue: keto form **1**; red: conjugate form **2**; green: conjugate form **3**).

Examining the interactions of the specific forms of barbituric acid to the different surface of the NaCl crystal is performed by identifying the V_{min} of the different forms.[17] V_{min} is the most negative valued point in electron-rich regions obtained from the molecular electrostatic potential (MESP) topography calculation. The MESP is calculated using Equation (1) where Z_A is the charge on nucleus A, located at R_A and $\rho(r')$ is the electron density.[17]

$$V(r) = \sum_A \frac{z_A}{|R_A - r|} - \int \frac{\rho(r)}{|r' - r|} \quad (1)$$

V_{min} is calculated at the B3LYP/6-31G(d) level of theory[18] using LDA/PWC/DND optimized geometries with Gaussian 03 suite of programs.[19] The V_{min} for **1** and **2** lies near the two oxygen atoms, whereas, the V_{min} for **3** is located on the deprotonated nitrogen atom (see Figure S3, Supporting Information). To examine the effective interaction of barbituric acid (**1**) and its conjugate bases (**2** and **3**; Figure 1) with specific surfaces of NaCl, an approach similar to surface docking developed to predict the influence of additives on the crystal morphology has been applied.[5j–l,n–p,7,8] The slab models are developed with periodic boundary conditions using a conventional array of NaCl ions.[5j–l,n–p] The different planes of NaCl {100}, {110}, and {111} are constructed in the slab model using the crystal data.[20] It has been shown in earlier studies that the rock-salt {111} surface is Na^+ terminated in the presence of aqueous solution and organic additives.[21] In the present study, the polar {111} surfaces are modeled with Na^+ ions on the top of the surface. The interaction of additives with the NaCl surfaces has been calculated employing the density functional program DMol3 in Material Studio (version 4.1) of Accelrys Inc.[22] The geometries are optimized at LDA/PWC/DND[23] level of theory and the interaction energies are calculated with GGA/PW91/DNP level[24] using COSMO[25] continuum solvation model. The dielectric constant (ε = 78.4 for water) is used for the COSMO calculations.[25] The detailed computational procedure is provided in the Supporting Information. Interaction energies are computed with the Equation (2).

$$E_{int} = E_{additive/surface} - \{E_{additive} + E_{surface}\} \quad (2)$$

The interaction of additive **1** with the NaCl planes suggests that the {110} binds preferentially compared to

{100} and {111} planes (Figure 3). The -CONH and -$COCH_2$ units of barbituric acid **1** binds to the {100} and {110} planes of NaCl with almost equal strength (Figure 3 and see Figure S4, Supporting Information). The interaction of **1** with {111} is

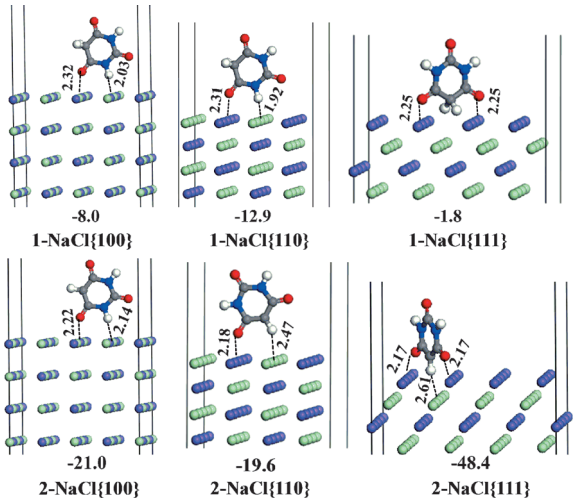

Figure 3. GGA/PW91/DNP//LDA/PWC/DND calculated geometries and interaction energies (in COSMO) of **1** and **2** with the {100}, {110}, and {111} surfaces of NaCl are given in kcal mol^{-1}. Distances are given in Å (purple sodium, green chloride, gray carbon, red oxygen, blue nitrogen, white hydrogen).

much weaker than the corresponding {100} and {110} planes (Figure 3). The keto form **1** prefers to interact individually rather than in an associative fashion with {100} and {110} planes (see Figure S5, Supporting Information). These calculated results seem to suggest that the barbituric acid **1** should influence the habit of NaCl to rhombic dodecahedron crystals. In the case of ionic form **2**, the (-COCH-) group interacts more effectively with the {110} plane, whereas the -CONH unit binds with the {100} plane (Figure 3). The computed interaction energies are found to be comparable in these cases. The ionic form **2** binds to the {111} plane of NaCl with both the carbonyl groups giving larger V_{min} values, while the methylene -CH interacts with lower chloride layer (Figure 3). The calculated results suggest that the stronger binding energy of the ionic form **2** with {111} should lead to the formation of octahedron crystals of sodium chloride. This energetic preference for the interaction of **2** towards the {111} plane also prevailed with more than one molecule (see Figure S6, Supporting Information). The conjugate base **3** also showed the preferred interaction with the {111} plane of NaCl than that of {100} and {110} planes (see Figure S7, Supporting Information).

The fractional distribution curve showed that the forms **1**, **2**,and **3** can be prevalent within pH 0–14 (Figure 2). The keto form **1** exists between pH 0–4, whereas, the ionic form **2** is present between pH 6–11. The ionic form **3** begins to form at pH ≈ 11 and persists to pH 14. To examine the predictions made by the DFT calculations, we have prepared the NaCl salt crystals with and without the barbituric acid and varied the pH from 2 to 13.5. The surface structure of the grown crystals is observed by scanning electron microscopy (SEM; Figure 4). The rhombic dodecahedron crystals (**a**, **a′** Figure 4) appeared at pH (2–4) and the statistical distribution of octahedron crystals grows in the pH range 4–10 (**b**, **b′**

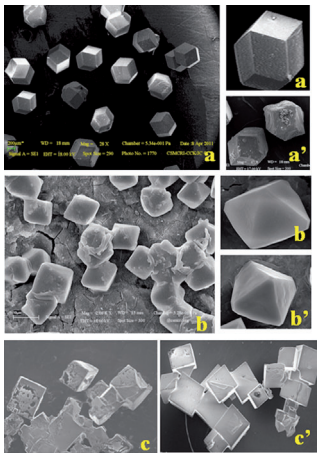

Figure 4. The SEM images for the NaCl crystals in the presence of barbituric acid at different pH values, a) pH 3.0, a′) pH 3.2, b) pH 6.0, b′) pH 10, c) pH 12.0, and c′) without the additive at pH 7.0. (The additive can also be called an impurity as it is added in a pure solution of NaCl.)

Figure 4). At much higher pH values (pH > 10) cubic crystals started to appear in the vessel (**c**, Figure 4) similar to pure NaCl crystals (**c′**, Figure 4). The higher concentration of NaOH presumably masked the effect of impurity on the salt crystals. The pilot experiments conducted with NaCl and NaOH maintaining the same concentrations used with barbituric acid, and also with even higher concentrations, formed cubic crystals (see Figure S8, Supporting information).

We have further performed powder X-ray diffraction studies with the three different crystals obtained from the NaCl solution in presence of barbituric acid. The contaminated solution (that is, the NaCl solution with the additive) at pH ≈ 12 and the pure solution of NaCl showed similar X-ray diffraction (XRD) patterns (see Figure S9, Supporting information). The intensity ratios are calculated from the XRD patterns of the contaminated solutions of NaCl at pH ≈ 3 and pH ≈ 8. Higher intensities are observed for {110} and {111} (see Figure S9, Supporting information), with integrated intensity ratio of 0.13 and 0.11, respectively. These results suggest that the influence of the additive on the NaCl surface changes with the change in the pH value. The crystalline sizes of the respective planes, calculated from powder XRD are given in the Supporting Information (see Table S1, Supporting information).

In conclusion, we have reported that barbituric acid is a new habit modifier for rock-salt crystals. We have also demonstrated for the first time that a single additive can give dual morphology of rock-salt crystals. The computational studies predicted that the barbituric acid can yield rhombic dodecahedron crystals at lower pH values and that with increasing pH value octahedron crystals are preferred, which

has been corroborated by the experimental studies. To our knowledge, barbituric acid is one of the rare additives to induce the rhombic dodecahedron morphology of NaCl crystals. The other additive reported to induce rhombic dodecahedron crystals, magnesium chloride, yielded only cubic crystals in our experimental studies (see Figure S10, Supporting Information).[5d] Barbituric acid is very effective at inducing rhombic dodecahedron NaCl crystals, it is only needed in a trace amount (0.08–0.2 % w/v) and can be useful for practical applications.[5a,i] The combined approach of computational predictions followed by the experimental corroboration appeared to be a viable manner to design new additives, a process which otherwise, is quite empirical. The modified salt crystals are useful for a broad range of applications from pharmaceuticals to food industries.

Experimental Section

The saturated NaCl solution was prepared by dissolving 32–34 g of NaCl in 100 mL of water (ca. 6.88 mol L^{-1}). Barbituric acid was added to the solution with the concentration varying from 0.06–0.6 % w/v. The solution is stirred and heated at 40–50 °C for around 2–3 min to give a clear solution. The effect of pH value on the crystallization process was studied by controlling the pH value of the saturated solution of NaCl and barbituric acid by using sodium hydroxide and HCl. The pH value is varied from 2.0 to 13.5 and is measured using an F-51 series, Navi pH meter, HORIBA. The contaminated NaCl solution (that is, the NaCl solution with the additive) was kept at room temperature for crystallization in all cases. The SEM images and the powder XRD were recorded for the grown crystals. The most effective changes occurred with 0.08–0.2 % w/v of the additive. Full details are available in the Supporting Information.

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