Urea Simulation as a Biofunctional Material

MIRELA NICOLOV, ZOLTAN SZABADAI, CRISTINA TRANDAFIRESCU*, DAN DRAGOS
Faculty of Pharmacy, Victor Babes University of Medicine and Pharmacy, 2nd Eftimie Murgu Sq., 300041, Timisoara, Romania

Considering the growing interest of urea in different fields the researchers studied the simulation of growth, equilibrium, Wigner Seitz and Brillouin Zone of urea crystals. By using these methods is presented for the first time the form of this crystal related to the attachament energy and to the surface energies.

Keywords: urea crystals; growth form; equilibrium form

Urea is widely distributed in nature and its analysis is of considerable interest in clinical, pharmaceuticals and agricultural chemistry. Urea has not only clinical applications. There is a great demand of instrumentations to estimate urea in the field of food science and environmental monitoring. Urea is used as an important indicator of protein feeding efficiency for the principal component of non-protein nitrogen cow milk [1]. Urea plays a strategic role in marine nitrogen cycle, including sources of excretion by inter-vertebrates, fish, bacterial decompositions of nitrogenous material and terrestrial drainage. Urea estimations is important during environmental monitoring. Annual world production of urea is almost 100 million metric tons and majority is used as fertilizer. Urea can be the responsible for reduction of soil pH.

A lot of papers have been written on the relation between crystal structure and crystal morphology. Almost all of these are based on the work of Hartman and Perdok [2]. The theory of Periodic Bond Chain explains crystal morphology from the crystal structure. Intermolecular energies were taken into account and in this way prediction of the kinetic growth form was possible [3]. Hartman and Bennema introduced the proportionality of the growth rate of the F face with its attachment energy [4]. Rijpkema et al. introduced a theory based on the idea that F faces can be calculated in two dimensional Ising model where connected nets are related to critical roughening temperatures [5].

In the present paper is calculated the morphology of urea with a highly idealized structure. We present in the present paper a simulation of growth and equilibrium form of urea crystals. Wigner Seitz and Brillouin Zone analysis of urea crystals was done. The theoretical growth forms of urea are presented in this paper. Moreover, the theoretical equilibrium forms based on the specific surface energies will also be computed. In the present paper, by using these methods, is presented for the first time, Wigner Seitz and Brillouin Zone form of this crystal related to the attachment energy and to the surface energies in the crystal.

Experimental part
Material and methods
Urea crystal structure (CH,N,O) was studied by Caron and Donohue [6,7] and Swaminathan et al. [8]. The molecules in the structure of urea lay in a special position of the Space group P-42/m where the molecular point symmetry is fully utilized (mm2). The crystal structure of urea was determined by Prior, Sanger, and Gut et al. [9,10]. Urea crystal was grown from aqueous solution with a trace amount of bromide. The crystals had F forms as: {110} and {001} [11]. Parameters for the unit cell of urea, Space Group which is : P-42/m, were traited different from different authors : Guth et al., 1980[11] considered : a = 5.572 Å, b = 5.572 Å, and c = 4.686 Å for T= 60K and a = 5.578 Å, b = 5.578 Å, and c = 4.695 Å for T= 123K, Swaminathan et al., 1984 [8] considered: a = 5.578 Å, b = 5.578 Å, and c = 4.686 Å for T= 123K and Mullen and Hellner, 1978 [11] considered: a = 5.576 Å, b = 5.576 Å, and c = 4.676 Å. We used in our simulations the structure for urea crystals from Swaminathan et al., 1984 [8].

Calculations should be carried out with this structure obtained from Rietveld refinements. The crystal structure of urea shows several chemically remarkable features: the molecule adopts a flat conformation in the crystal with the symmetry mm2. In contrast the isolated molecule is non planar, the NH group is twisted slightly out of the molecular plane is determined by microwave spectroscopy and by initio calculations [12]. Now is accepted that C molecular structure is the most stable followed by C conformation. C structure found in the urea crystal is a saddle point separating these two stable conformers. A very interesting aspects of urea crystal is that hydrogen bonds pattern where O atom accepts four hydrogen bonds which is extremely rare. Birkedal et al reported a high precision study of charge density for urea using synchrotron data [12].

Higher order electrostatic models electrostatic moments can be calculated by the distributed multipole analysis (DMA) method. Model of potential using DMA electrostatic models and empirical repulsion-dispersion models have been applied to study the interaction of a wide range of organic molecules in the gas and crystalline phase [13]. Engkvist et al. used such models for crystallization of urea [13]. They used a variety of surface calculations using ORIENT program package to study the morphology of crystalline urea CO(NH2)2. Vapour growth of urea crystals has a well defined prismatic habit bounded by (110), sides with {001} ends and {111} polar cap facets [13]. Engkvist et al in his work used a new nanocrystallite computational model which incorporates into ORIENT program package a variety of interaction energies and structures of surfaces and adsorbed molecules, clusters or pairs of surfaces. This method was used by Engkvist et al to predict morphology of urea crystals [13]. The calculations were carried out on the Space group P-42/m where the molecular point symmetry is mm2. The crystal structure of urea was determined by Prior, Sanger, and Gut et al. [9,10]. Urea crystal was grown from aqueous solution with a trace amount of bromide. The crystals had F forms as: {110} and {001} [11]. Parameters for the unit cell of urea, Space Group which is : P-42/m, were traited different from different authors : Guth et al., 1980[11] considered : a = 5.572 Å, b = 5.572 Å, and c = 4.686 Å for T= 60K and a = 5.578 Å, b = 5.578 Å, and c = 4.695 Å for T= 123K, Swaminathan et al., 1984 [8] considered: a = 5.578 Å, b = 5.578 Å, and c = 4.686 Å for T= 123K and Mullen and Hellner, 1978 [11] considered: a = 5.576 Å, b = 5.576 Å, and c = 4.676 Å. We used in our simulations the structure for urea crystals from Swaminathan et al., 1984 [8].

Calculations should be carried out with this structure obtained from Rietveld refinements. The crystal structure of urea shows several chemically remarkable features: the molecule adopts a flat conformation in the crystal with the symmetry mm2. In contrast the isolated molecule is non planar, the NH group is twisted slightly out of the molecular plane is determined by microwave spectroscopy and by initio calculations [12]. Now is accepted that C molecular structure is the most stable followed by C conformation. C structure found in the urea crystal is a saddle point separating these two stable conformers. A very interesting aspects of urea crystal is that hydrogen bonds pattern where O atom accepts four hydrogen bonds which is extremely rare. Birkedal et al reported a high precision study of charge density for urea using synchrotron data [12].

Higher order electrostatic models electrostatic moments can be calculated by the distributed multipole analysis (DMA) method. Model of potential using DMA electrostatic models and empirical repulsion-dispersion models have been applied to study the interaction of a wide range of organic molecules in the gas and crystalline phase [13]. Engkvist et al. used such models for crystallization of urea [13]. They used a variety of surface calculations using ORIENT program package to study the morphology of crystalline urea CO(NH2)2. Vapour growth of urea crystals has a well defined prismatic habit bounded by (110), sides with {001} ends and {111} polar cap facets [13]. Engkvist et al in his work used a new nanocrystallite computational model which incorporates into ORIENT program package a variety of interaction energies and structures of surfaces and adsorbed molecules, clusters or pairs of surfaces. This method was used by Engkvist et al to predict morphology of urea crystals [13]. Based on these results we obtained in the present paper the growth and equilibrium form of
urea crystals, to continue the results of Engkvist. In this paper from 2000 the researcher concluded that polar facets of urea crystals cannot be predicted by attachments energy model. It seems probably that large relaxation of {111} surface related to all others including {-1-1-1} inhibits the growth of these surfaces sufficiently to produce the polar caps but cannot be quantified yet [13]. We used these values in our paper.

Results and discussions
Attachment and surface energies
The attachment energies including only Coulomb interactions are presented in table 2. These values are based on the charges of O, C, H and N atoms as follows: \( \text{O} (q_\text{O} = -2|\text{e}|), \text{C} (q_\text{C} = +4|\text{e}|), \text{H} (q_\text{H} = +|\text{e}|); \text{N} (q_\text{N} = -3|\text{e}|) \). We can see from table 2 that we can get from simulations two types of (001) as an F face. One has attachment energy higher than the other.

In table 2 we can see surface energy of urea crystals too and F faces as {200}, {101}, and {111} having two maybe three values for surface energy. In this situation it is possible to have different combinations of faces and we get in for this reason more types of crystals.

Theoretical growth form of urea crystals
The theoretical growth form in this paper has been obtained by assuming that the attachment energy \( E_a \) is directly proportional to the growth rate of face (hkl). In the so-called Wulf-Plot the length of the normal perpendicular to these faces (hkl) are then proportional to the corresponding attachment energy values.

The growth forms presented in figure 1 A,B,C,D,E,F used the normal charges. The theoretical growth form of urea presented here shows well developed F forms as follows: {001}, {110}, {101}, {200}, {-1-1-1} and {111}.

In figure 1 we can see as follows: in figure A there is a crystal having 6 F faces, 12 edges, 8 angles and a volume \( V = 2.8066 \text{A}^3 \) and a surface \( S = 12.169 \text{A}^2 \). We can see here a well developed F forms for 001 and 110. In figure B there is an urea crystal having 10 F faces, 24 edges, 16 angles and a volume of \( V = 6.0902 \text{A}^3 \) and a surface of \( S = 19.879 \text{A}^2 \). In figure C we can see very well developed F faces as follows: {001}, {200} and {111}. In figure C there is a crystal having 14 F faces, 36 edges, 24 angles and a volume of \( V = 11.692 \text{A}^3 \) and a surface of \( S = 30.393 \text{A}^2 \). Figures A, B and C are closer to real growth form of crystals that are shown later in this paper. From simulations we obtained crystal from figure D too which has 20 F faces, 44 edges, 44 angles and a volume of \( V = 8.1886 \text{A}^3 \) and a surface of \( S = 22.656 \text{A}^2 \). In this crystal is missing 001 as an F face and appear faces like {101}, {200}, {111} and {-1-1-1}. In figure E we obtained from simulation a crystal with the next characteristics: 16 F faces, 32 edges, 18 angles, a volume of \( V = 19.396 \text{A}^3 \) and a surface of \( S = 41.710 \text{A}^2 \). In this figure we have F faces {101}, {111} and {-1-1-1}. In figure F which seems to be closer to C is missing {001} as an F face. We obtain in figure F a urea crystal having 12 F faces, 28 edges, 18 angles , a volume \( V = 4.2416 \text{A}^3 \) and a surface of \( S = 16.048 \text{A}^2 \). We can see in figure F (101) and (110) as F faces. We can see a growth form of crystal which similar to A and is closer to B, image obtained by Boek et al. [3]. We can see a growth form of urea crystal according to Donnay -Harker presented by Boek et al. [3].

Equilibrium form of urea crystals
In figure 2, the equilibrium forms of the urea crystals are presented. These forms are obtained in idealized conditions, considering the urea crystals as purely ionic.
compounds. The equilibrium forms shown here were constructed by using the surface energies presented in figure 3. We can see here as F forms: {001}, {110}, {111}, {-111}, {200} and {101}.

In figure 2 we have different types of equilibrium forms of urea crystals as follows in figure A we have an urea crystal having 22 F faces, 60 edges, 40 angles, a volume of V=28.825 A³, a surface of S= 53.073 A². We can see here a well developed F forms as follows {001}, {110}, {200}, {111} and {-111}. In figure B we have an urea crystal having 26 F faces, 72 edges, 48 angles, a volume of V=21.163 A³ and a surface of S= 42.395 A². In figure B we can see quite similar F faces developed. In figure C from figure 2 we can see an equilibrium form for urea crystal having 26 F faces, 72 edges, 48 angles, a volume of V=20.195 A³ and a surface of S= 40.795 A². In figure E we can see the equilibrium form of crystals of Boek et al.[3], which is closer as form with A, B and C, having similar F faces. In table 4 we obtain as an equilibrium form for urea crystal the form from figure D which has 16 F faces, 40 edges, 26 angles a volume of V=23.396 A³ and a surface of S= 45.056 A².

Wigner-Seitz and Brillouin Zone Analysis of urea crystals

In table 3 we present the results of Wigner-Seitz and Brillouin Zone Analysis of urea crystals. And in figure 3 we can observe the urea crystals obtained from these simulations. We observe from table 5 that for Wigner Seitz forms of crystals we obtained from simulation as possible F faces as follows {001}, {010}, {100}, {0-11}, {-110},{1-11},and {1-21}. We obtained from Brillouin the next F faces {001}, {010}, {100}, {011}, {110}, {-101}, {111}.

In figure 3 we obtained Wigner-Seitz and Brillouin Zone form of urea crystals. We can see here in figure A a crystal having 8 F faces, 12 edges, 12 corners, a volume of V=72.529 A³ and surface S= 103.22A². In figure B we can see well developed f forms as {100}, {101} and {001}. We steel get another form of Wigner Seitz analysis of urea crystals in figure B with the next characteristics 14 F faces, 36edges, 24 corners, a volume of V=72.529 A³ and a surface of S= 92.749 A². In figure C we can see the next F faces {001}, {100}, {-101}, and {-110}. In figure D we have an urea crystal obtain in a Brillouin Zone Analysis having the next characteristics 6F faces, 12 edges and 8 corners with a volume of V= 6.9388 A³ and a surface of S= 21.88

<table>
<thead>
<tr>
<th>Table 3</th>
<th>WIGNER - SEITZ AND BRILLOUIN ZONE ANALYSIS OF UREA CRYSTALS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ikl</td>
<td>E(kcal/mol)Wigner-Seitz</td>
</tr>
<tr>
<td>001</td>
<td>234.2</td>
</tr>
<tr>
<td>010</td>
<td>181.85</td>
</tr>
<tr>
<td>100</td>
<td>278.25</td>
</tr>
<tr>
<td>-110</td>
<td>228.96</td>
</tr>
<tr>
<td>1-11</td>
<td>228.96</td>
</tr>
<tr>
<td>1-21</td>
<td>278.25</td>
</tr>
<tr>
<td>011</td>
<td>139.5</td>
</tr>
<tr>
<td>110</td>
<td>127.1</td>
</tr>
<tr>
<td>-101</td>
<td>139.5</td>
</tr>
<tr>
<td>011</td>
<td>139.5</td>
</tr>
</tbody>
</table>

V=72.529 A³ and surface S= 103.22A². In figure A we can see well developed f forms as {001}, {010} and {001}. We steel get another form of Wigner Seitz analysis of urea crystals in figure B with the next characteristics 14 F faces, 36edges, 24 corners, a volume of V=72.529 A³ and a surface of S= 92.749 A². In figure B we can see the next F faces {001}, {100}, {010}, and {-110}. In figure C we have an urea crystal obtain in a Brillouin Zone Analysis having the next characteristics 6F faces, 12 edges and 8 corners with a volume of V= 6.9388 A³ and a surface of S= 21.88
We can conclude that Wigner Seitz form represent better then Brillouin Zone, the urea crystals obtained from water, respectively from methanol and the obtained results are in good agreement with those from literature.

References

Manuscript received: 3.12.2014