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Theoretical insight into the effect of solvent polarity on the formation and morphology of 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20)/2,4,6-trinitro-toluene(TNT) cocrystal explosive

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ABSTRACT

Molecular dynamics simulations were employed to study the effect of solvents of varying polarity on the formation and morphology of 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20)/2,4,6-trinitro-toluene(TNT) cocrystal explosive. Six solvents, i.e. *n*-heptane, toluene, ethanol, acetonitrile, methanol and dimethyl sulfoxide with a wide range of polarity were used. The cocrystal morphology was predicted by Growth Morphology Model. The surface conformation and polarity were used to estimate the molecular parking of cocrystal surface. The interaction energies and binding energies were used to determine the influence of solvent properties (i.e. polarity, permittivity, molecule weight and vapor pressure) on the formation and morphology. The results indicate that the predicted morphology of CL-20/TNT cocrystal is dominated by the (0 0 2), (1 1 1), (0 2 0) and (0 2 1) in vacuum. CL-20/TNT cocrystal is easier to form in moderately polar solvents, that is, ethanol and acetonitrile. CL-20 molecules are more inclined to interact with TNT in (1 1 1) and (0 2 1) CL-20/TNT-solvent interfaces than in (0 0 2) and (0 2 0) interfaces. The predicted cocrystal morphology is in good agreement with the experimental morphology in ethonal solution. In addition, radial distribution function (RDF) analyses further proved the existence of interactions between the cocrystal faces and solvents.

1. Introduction

Cocrystallization, which is a solid-state energineering technique applied successfully in pharmaceutical industry, is proved to be a promising way to counteract the power-safety contradiction of energetic materials [1–3]. It is defined by composing two or more neutral components in a defined molar ratio through non-covalent interactions (e.g. H-bond, van der Waals forces, etc.) [4,5]. The preparation of energetic cocrystal is a complicated process, which depends on the selection of solvents, coformers, temperature and so on [6–10]. Among them, the solvent is a crucial factor determining whether the cocrystal can form and affecting its morphology.

The solvents affect the preparation of crystals in two aspects, i.e. nucleation process and crystal growth [11]. At the nucleation period, prenucleation solute molecule clusters in solution are closely associated with solvent molecules, and it might be a barrier to formation of crystal [12]. Subsequently, these prenucleation solute clusters can further influence the nucleation rate and crystal morphology. During crystal growth, the interaction between solvent and crystal facets will impact the growth rates of crystal surfaces, and then it will result in different crystal morphologies [13,14]. The polarity is usually revealed to typical C,H,N,O explosive molecules [15]. When the cocrystals are cultivated from solvents, the solvents in different polarity can promote or inhibit a molecular motif which is preserved in the crystal structure through specific chemical interactions [11,16,17]. However, few studies have been done on the formation and morphology of cocrystals which are affected by the polarity of solvents.

Currently, molecular dynamics (MD) simulation is widely used to explore the crystallization mechanism at the atomistic and molecular levels. Duan et al. and Yan et al. explored the solvent effects of 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in contact with acetone [18] and acetonitrile (ACN) [19] with MD simulation, respectively. Chen et al. studied a series of MD simulations about solvent effects on hexogen (RDX), they calculated the adsorption interactions of RDX surfaces with acetone and cyclohexanone (CYC) [20–22]. Shi et al. simulated the interaction of habit faces of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) with trifluoroacetic acid by molecular modeling techniques [23]. Liu et al. used

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the modified attachment energy (MAE) model to elucidate the cosolvent effect (H_2O/acetic acid (AcOH) and H_2O/ethyl alcohol (EtOH)) on the crystal morphology of 3,4-bis (3-nitrofurazan-4-yl) furoxan (DNTF) [24]. Parambil et al. studied the effect of solvents of different polarity on the nucleation of carbamazepine crystal polymorphs by the template-induced nucleation [25]. Liang et al. reported the solvent effects on crystal growth morphology of benzoic acid using the MAE model [26]. Gao et al. studied the temperature effect on formation and morphology of diacetone diperoxide (DADP)/1,3,5-tribromo-2,4,6-trinitrobenzene (TBTNB) cocrystal by MD method and quantum-chemical calculation [27].

However, there is hardly the theoretical study on the effect of polarity of the solvents on the formation and morphology of cocrystal. 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20)/2,4,6-trinitro-toluene(TNT) cocrystal which has high power and excellent insensitivity has been prepared by Bolton [28] and Yang [29] from several solvents. But its preparation is not easy. In this present work, MD simulations were performed to study the effect of solvents of varying polarity on the formation and morphology of CL-20/TNT cocrystal explosive. Six solvents, i.e. n-heptane (HEP), toluene (TOL), ethanol (EtOH), acetonitrile (ACN), methanol (MeOH) and dimethyl sulfoxide (DMSO) with a wide range of polarity were used. The different properties of solvents were analysed. The interactions at cocrystal/solvent interfaces were obtained by MD simulation. The structural features of cocrystal surfaces were analysed to explain solvent influences on cocrystal morphology. The MAE model was used to predict the cocrystal morphology in different solvents. Moreover, the radial distribution function (RDF) analyses further proved the existence of interactions between the cocrystal faces and solvents.

2. Computational details

2.1. Theory

The attachment energy (E_{att}) is defined as the energy released when a growth slice is attached to the growth crystal surface [30]. It can be calculated using the following formula:

$$E_{att} = E_{latt} - E_{slice} \quad (1)$$

where E_{latt} is the lattice energy of the crystal, E_{slice} is the energy of the growth slice of the thickness d_{hkl}.

The attachment energy model can be used to predict the crystal morphologies in vacuum [19,23,31–33]. However, the crystals are usually grown from solution, solvents can interact with the crystal surfaces and the solvation surface layer will be formed by adsorbed solvent molecules at the crystal-liquid interface, therefore, the growth of crystal face is inhibited [34]. In general, the stronger the adsorption interactions are, the easier adsorption of solvent molecules is. The growth of the crystal face can only be achieved when the adsorbed solvent molecules are removed, and the energy will be consumed during the desolvation process. Finally, the attachment energy of different crystal surfaces will be changed.

The MAE model has been used to study the solvent effect on single crystal of the energetic materials [18–22]. In this work, the MAE model was employed to investigate the solvent effect on the energetic cocrystallization. The modified attachment energy ($E_{m,att}$) can be evaluated using the following equation:

$$E_{m,att} = E_{att} - E_s \quad (2)$$

where E_{att} is the vacuum attachment energy; E_s is the energy correction term of E_{att}, it is expressed:

$$E_s = E_a \frac{A_{acc}}{A_{model}} \quad (3)$$

where A_{acc} is the solvent accessible area of the cocrystal surface in unit cell; A_{model} is the surface area of the simulated model along the ($h\ k\ l$) plane; E_a is the interaction energy between cocrystal surface and solvent surface, and it is calculated using the relationship:

$$E_a = E_{tot} - E_{surf} - E_{sol} \quad (4)$$

where E_{tot} is the total energy of CL-20/TNT-solvent interfacial models; E_{surf} (E_{sol}) is the energy of cocrystal surface (solvent layer) without solvent layer (cocrystal surface) in the solvent interfacial models.

The crystal growth in solvent is influenced by the kinetic thermodynamics factors. The growth rate (R) of each crystal surface is proportional to $E_{m,att}$, see Eq. (5) [31,35], and hence the crystal face with the lowest attachment energy is predicted the lowest growing surface. It will have the greatest morphological importance.

$$R \propto |E_{m,att}| \quad (5)$$

2.2. Models

The initial unit cell of CL-20/TNT cocrystal was derived from Ref. [28], then the structure was relaxed until the total energy of the structure was minimized. The morphology of CL-20/TNT cocrystal in vacuum was predicted by Growth Morphology Model. The CL-20/TNT cocrystal was cleaved along the important stable faces with two depths of unit cell, and the cocrystal surfaces of (0 0 2), (1 1 1), (0 2 0) and (0 2 1) were extended to the superstructures.

The EtOH molecules were chosen as an example to construct a solvent layer. A solvent layer with 200 random EtOH molecules was constructed by the Amorphous Cell tool, its size was consistent with the corresponding extended cocrystal surface. It was optimized with the lattice lengths fixed in a and b, and then the MD simulation was performed. Finally, CL-20/TNT-solvent interfacial model was built to investigate the solvent effect on the formation and morphology of cocrystal. The solvent layer was placed along the c axis on the cocrystal surface. A gas of 3 Å vacuum was set between the solvent layer and the cocrystal surface. 60 Å thickness vacuum was built above the solvent layer to remove the effect of additional free boundaries.

2.3. Computation

The CL-20/TNT-solvent interfacial models of different solvents were built. The original interfacial model was optimized with 50,000 iteration steps, and then MD simulations with NVT ensemble were performed at 298 K for 300.0 ps (300,000 fs) with 1 fs time step. The temperature was controlled by the Andersen thermostat [36]. For the non-bonding energies, the electrostatic interaction was computed by employing the Ewald summation with accuracy of 1.0×10^{-5} kcal/mol, the van der Waals interaction was calculated to use the Atom-based summation with a cutoff distance of 12.5 Å. The whole system reached an equilibrium state when the fluctuations of temperature and energy were less than 10%, and then the most stable structure in the last 1000 frames was selected for energy calculations. The Connolly Surface Model was used to compute the solvent accessible area. Above of the whole calculations were carried out with MS 7.0 [37].

3. Results and discussion

3.1. Cell parameters and densities

In order to perform accurate MD simulations, Forcefield types need to be confirmed. In this paper, three different types of forcefields, i.e. condensed-phase optimized molecular potentials