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Molecular simulation of oligomer inhibitors for calcite scale

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ABSTRACT

Molecular simulation was performed to study the interaction between $CaCO_3$ crystal and several oligomer inhibitors, by using the equilibrium morphology method to calculate the growth morphology of $CaCO_3$ without inhibitors. The calculated morphology agreed well with SEM photographs. Then, a double-layer model was built to investigate the interaction between calcite crystal and oligomer inhibitors containing maleic anhydride (MA) and acrylic acid (AA). Interaction energy per gram of an oligomer inhibitor was introduced as a scale of inhibition efficiency of different monomers. The results indicated that, for calcite scale inhibition, acrylamide (AM) and vinyl phosphonic acid (VPA) were the most efficient monomers, while allylsulfonic acid (AS) was the poorest. Increasing proportion of AM in dimer inhibitor molecule would improve the inhibition efficiency of MA, though, for a trimer, such as MA–AA–AM, certain sequence of monomers in the inhibitor molecule was necessary besides higher proportion of AM.

1. Introduction

Polymer scale inhibitors are widely used to prevent scale formation in off-shore oil wells and in water treatment. Because they are environmentally friendly and possess high efficiency, the development and study of polymer scale inhibitors has been much promoted in recent years (Davis et al., 2003; Jordan et al., 1997; Kneller, 1988; Shakkthivel, Ramesh, Sathiyamoorthi, & Vasudevan, 2005), including carboxylic acid, sulfonic acid, phosphor-containing inhibitors and the so-called green inhibitors.

Several points are pertinent to the use of oligomer inhibitors:

i) Most researchers focus on the functions of certain kinds of inhibitors without being highly systematic.
ii) Much attention has been paid to investigating the relationship between synthesis and inhibition efficiency, but not enough between molecular structure and efficiency.
iii) A wide range of monomers have been used to synthesize polymer inhibitors, but the efficiencies of individual monomers have not been systematically compared.

In this paper, molecular simulation was applied to study the relationship between inhibitor structure and scale inhibition efficiency, in order to identify efficient monomers. Molecular simulation serves to reveal the mechanism of interaction between scale crystal and inhibitor molecule, which are critically important to predict and control scale crystal growth.

Two kinds of inhibitors, maleic anhydride (MA) and acrylic acid (AA), were studied. In order to calculate the interaction energies between calcite crystal surfaces and inhibitor molecules, the growth morphology of calcite was first simulated without inhibition. Then, interaction energies were evaluated through dynamic molecular simulation studies, from which the relationship between molecular structure and inhibition efficiency was formulated.

2. Theories

2.1. Attachment energy

Attachment energy, E_{att}, defined as the energy released upon attaching a growth slice to a growing crystal surface (Docherty, Clydesdale, Roberts, & Bennema, 1991), is computed (Berkovitch-Yellin, 1985) as:

$$E_{att} = E_{latt} - E_{slice}, \tag{1}$$

where E_{latt} is the lattice energy of the crystal, E_{slice} is the energy of a growth slice of thickness d_{hkl}. The growth rate of the crystal face is assumed to be proportional to its attachment energy; that is, faces with the lowest attachment energies are the slowest growing and, therefore, have highest morphological importance.

2.2. Crystal morphology

Attachment energy is calculated for a series of suitable slices $(h\,k\,l)$ which are determined manually or determined by

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performing a Donnay–Harker prediction (Donnay & Harker, 1937). From the energy calculation, the growth rate with respect to a center-to-face distance is assigned to each face. This information is used to deduce the morphology using a Wulff plot (Wulff, 1901).

2.3. Assumptions

The calculated attachment energy is an average on the surfaces with Miller indices $\{h\,k\,l\}$ and $\{-h\,-k\,-l\}$. This restriction is important for crystal structures that do not have a center of inversion. In addition, the growth morphology model assumes that the surface is a perfect termination of the bulk and no surface relaxation takes place, though surface relaxation has been shown to be significant in the case of inorganic systems such as Al_2O_3 and Fe_2O_3. The growth morphology model works well for many organic molecular systems.

There are no solvents effects, that is, the morphology simulation does consider factors such as the presence or absence of solvents or excipients and possible surface reconstructions, which can have a profound influence on experimentally observed morphologies.

3. Methods and calculations

All calculations were performed using Material Studio (MS) software package (Accelrys Inc., 2004). For crystal morphology simulation, Morphology module was used, both to study particle shape and to consider the effects of altering the growth rate of particular faces on crystal morphology. In particular, Morphology module can examine the effect of tailor-made additives in modifying growth.

Morphology prediction sequence generates and outputs a list of possible growth planes that satisfy the Donnay–Harker rules (Donnay & Harker, 1937) for the current symmetry. Three different methods for predicting crystal morphology can then be applied to these possible growth planes: (1) the Bravais–Friedel–Donnay–Harker (BFDH) method is a geometrical calculation that uses crystal lattice parameters and symmetry properties to generate a list of possible growth faces and their relative growth rates, from which crystal morphology can be deduced; (2) the growth morphology method predicts the relative growth rates of possible growth faces, from which the growth morphology can be deduced, to predict more accurately the shape of a crystal than the BFDH method because it takes into account the energy of the system; (3) the equilibrium morphology method determines the equilibrium morphology of a crystal by the minimum surface free energy for a given volume and temperature (Gibbs, 1928), thus predicts the equilibrium morphology based on the relative surface energies of the possible faces. If the surface free energies are known for all relevant crystal faces, the morphology of a crystal in equilibrium with its surroundings can be visualized using a Wulff plot (Wulff, 1901). In this paper, the equilibrium morphology was used to calculate the calcite crystal morphology.

For crystal and inhibitor molecular structure optimization, and interaction energy calculation, Discover, a module of Material Studio, was used to provide a broad range of simulation methods to study molecular systems and a variety of materials types. Discover module incorporates a range of well-validated force fields for dynamic simulations, minimization, and conformational searches.

CASTEP (Cambridge Sequential Total Energy Package), a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science, was also applied to calculate the atom charge of calcium carbonate. CASTEP employs the density functional theory and uses the plane-wave pseudopotential method to perform first-principles quantum mechanics calculations that explore the properties of crystals and surfaces in materials such as semiconductors, ceramics, metals, minerals, and zeolites.

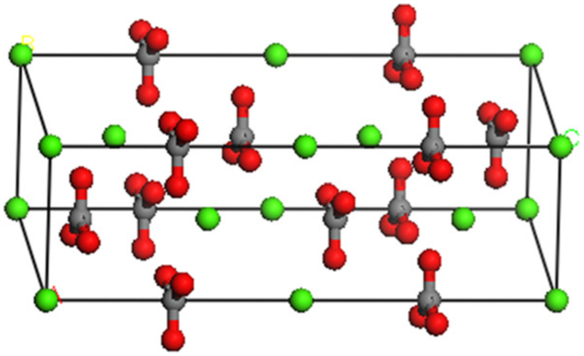

Fig. 1. Crystal structure of calcite $CaCO_3$ (green Ca, grey C, red O). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

According to the prediction theory of crystal growth, if we only adjust the attachment energy of certain crystal faces, the morphology of the crystal could be changed or even tailored. One of the most applicable ways to alter the attachment energy is to use additives to change the environment of crystal growth. This work mainly focused on interaction between additives and crystal faces.

3.1. Optimization of the crystal structure of $CaCO_3$

The experimental geometry parameters of $CaCO_3$ crystal, as shown in Fig. 1, are, $a = b = 4.99$ Å, $c = 17.06$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.

When considering ionic materials, such as calcite, the Coulomb interaction is by far the dominant term as compared to other non-bond interactions. Therefore the accuracy of the Coulomb interaction will determine the reliability of final results. For this reason, Ewald summation method was applied for all Coulomb interaction calculations. Moreover, atomic charges also play key roles in Coulomb interaction calculations, and there are several charge assignment methods in Material Studio, including charge within force field (e.g. COMPASS charge, the charge defined in COMPASS force field), QEq charge (Rappe & Goddard, 1991) and charge from quantum calculations (e.g. CASTEP calculation, here we call it CASTEP charge). Atomic charges in calcite crystal calculated by different methods are shown in Table 1. For van der Waals interaction, several methods are available, such as atom based cutoffs, group based cutoffs, and Ewald summation method. In Discover COMPASS and CVFF could be applied to calcite crystal. In this study all the factors including atomic charges in calcite crystal, summation methods for van der Waals interactions and force fields, have been taken into consideration, in order to optimize calcite crystal structure on the basis of up to 13 possible combinations of calculation methods.

Energy minimization in Discover module was used to optimize the crystal structure, in which Newtonian mechanical method was applied, and the convergence criterion was set at 1000 kcal/mol. Calculations were carried out on different combinations of force fields (COMPASS and CVFF), atomic charges (CASTEP charge, QEq charge and COMPASS charge) and cutoff methods (atom based,

Table 1
Atomic charges in calcite crystal calculated by different methods.

Calculation method	Atomic charges in calcite crystal
CASTEP method	Ca +1.42, C +0.740, O −0.720
QEq method	Ca +1.24, C +0.668, O −0.636
COMPASS charge	Ca +2.00, C +0.395, O −0.798