Desalination 291 (2012) 8–14

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Molecular dynamics simulation for interaction of PESA and acrylic copolymers with calcite crystal surfaces

Wen-Yan Shi [a,c,*], Cheng Ding [b], Jin-Long Yan [b], Xiang-Yun Han [b], Zhi-Min Lv [a,*], Wu Lei [c], Ming-Zhu Xia [c], Feng-Yun Wang [c]

[a] School of Chemical and Biological Engineering, Yancheng Institute of Technology, 9 Yingbin Avenue, Yancheng 224051, China
[b] School of Environmental Science and Engineering, Yancheng Institute of Technology, 9 Yingbin Avenue, Yancheng 224051, China
[c] The Institute of Chemistry &Technology, Nanjing University of Science & Technology, Nanjing 210094, China

ARTICLE INFO

Article history:
Received 22 June 2011
Received in revised form 19 January 2012
Accepted 20 January 2012
Available online 11 February 2012

Keywords:
Polyepoxysuccinic acid
Acrylic copolymer
Molecular dynamics simulation
Scale inhibition mechanism
Pair correlation function

ABSTRACT

The interactions between four scale inhibitors, namely, polyepoxysuccinic acid (PESA), acrylic acid–maleic acid copolymer[P(AA-*co*-MA)], acrylic acid–hydroxypropyl acrylate copolymer[P(AA-*co*-HPA)], acrylic acid–methyl acrylate copolymers[P(AA-*co*-MAE)] and (104), ($1\bar{1}0$)surfaces of calcite crystal are simulated using a molecular dynamics (MD) method. The results show that the order of corrected binding energy of the four polymers is as follows: PESA > [P(AA-*co*-MA)] > [P(AA-*co*-HPA)] > [P(AA-*co*-MAE)]; however, the interaction of polymers with the ($1\bar{1}0$) surface is significantly stronger (2.5 to 2.8 times) than that with the (104) surface. The binding energy is mainly provided by the ionic bond and the Coulomb interaction, which is verified by analysis of pair correlation functions. The structures of the polymers are deformed during their combining processes with the surfaces. However, the deformation energies are far less than their non-bonding energies respectively. With increasing processing temperature, both the binding energy and the corrected binding energy decrease. The simulation results agree with the static anti-scaling experimental results, which indicate the simulation is correct and reasonable. The simulation results provide theoretical knowledge to assess the performance of scale inhibitors and to synthesize new, highly effective water treatment agents.

1. Introduction

The use of circulating water treatments increases the concentration of minerals and can cause scaling and corrosion of pipes and other fittings. The most common and effective way to prevent the corrosion of pipes in the device and the deposition of inorganic scales is to add corrosion and scale inhibitors to the circulating water system. The growth of scales could be prevented or slowed with the use of scale inhibitors and the amount of scale inhibitors required is very low in many cases. Thus far, scale inhibitors widely used in circulating water system are mainly acrylic acid polymers, maleic acid polymers, and phosphonates. These agents have important properties including distinct solubility threshold effect, low dosage effect, the cooperative effect with other reagents, and high temperature endurance. The scale inhibitors discussed in the paper are acrylic copolymers and polyepoxysuccinic acid (PESA). PESA is an environment-friendly scale inhibitor synthesized in recent years and has successfully realized industrial production.

Physical methods such as crystallization dynamics methods are widely used to study the action mechanism of scale inhibitors [1], but they are mainly used to study the effect of scale inhibitors on the formation of inorganic scale, not to reveal the quantitative structure–activity relationships (QSAR) of scale inhibitors. In contrast to many experimental studies, few theoretical studies about the QSAR of scale inhibitors have been done at the molecular level [2–8]. Experimental and experience extrapolation methods are the leading methods for performance evaluation of new scale inhibitors, which commonly waste time, manpower and material resources. Closer investigation is needed to understand the scale inhibition process at the molecular level. The results obtained reveal the QSAR of scale inhibitors and will help develop new, effective agents. Our team [1–7] has done systematic investigation about the inhibition mechanism of scale inhibitors against calcium carbonate scale and found some useful conclusions.

In the current research, the mechanism by which polyepoxysuccinic acid (PESA), acrylic acid–maleic acid copolymer[P(AA-*co*-MA)], acrylic acid–hydroxypropyl acrylate copolymer[P(AA-*co*-HPA)], and acrylic acid–methyl acrylate copolymer[P(AA-*co*-MAE)] affect calcite ($CaCO_3$) crystal growth is investigated using a molecular dynamics simulation method. The nature of the interaction between scale inhibitor and calcite, and the effect of temperature on the interaction will be studied, based on the status that few studies have been done before, to provide a theoretical basis for research and the development of new, effective agents.

* Corresponding author. Tel.: +86 515 88297361; fax: +86 515 88298191.
E-mail addresses: waterswy@126.com (W.-Y. Shi), y_clzm@126.com (Z.-M. Lv).

0011-9164/$ – see front matter
doi:10.1016/j.desal.2012.01.019

2. Experimental

2.1. Materials

PESA, [P(AA-*co*-MA)], [P(AA-*co*-HPA)] and [P(AA-*co*-MAE)] were all provided by Changzhou Wujin Water Quality Stabilizer Factory (Jiangsu, China) and were all industrial products. Anhydrous calcium chloride anhydrous and sodium bicarbonate were purchased in analytical purity.

2.2. Static anti-scaling method

The static anti-scaling method was used to determine the scale inhibition efficiency over a range of concentrations for PESA and the acrylic copolymers. Briefly this was as follows:

A simulated water sample containing 250 mg/L calcium ion and bicarbonate was obtained with anhydrous calcium chloride and sodium bicarbonate, and the scale inhibitor to be assessed was added to the simulated aqueous solution. The solution was heated at 80 °C until the concentration of Ca^{2+} and HCO_3^- increased to higher than 300 mg/L, and then was let stand for 10 h at 80 °C. After this stage was completed, the solution was cooled and then filtered. Finally, the concentration of calcium ion in the filtrate was measured with EDTA solution of known concentration. All tests were done in triplicate and the average of the three scale inhibition rates was taken.

2.3. Molecular dynamics simulation method

According to the literature [9], inorganic scale crystallization results from three processes that interact mutually, namely, supersaturation, nucleation, and crystal growth. Scale inhibitors influence each of these processes [10]. The action mechanism of inhibitors is still unclear up to now because of the complexity of the processes and many assumptions have been put forward, such as chelation, threshold effect, crystal lattice aberrance, dispersion effects, regeneration and self disengagement film hypotheses, electric double layer effect, space-matching effect of functional groups, etc. In summary, three further mechanisms for scale inhibition are conceivable with calcite as an example: (1) scale inhibitors prevent or affect calcite nucleation; (2) scale inhibitors stabilize the calcite crystals or precursors that have formed as colloids; (3) the additives prevent or affect the growth of calcite crystals. Currently, treating the first two mechanisms with simulation methods at atomistic level is not possible, so the third mechanism is simulated in detail in the paper.

2.3.1. Simulation force field

COMPASS force field [11], available from molecular modeling program Materials Studio 3.0 [12] from Accelrys Software Inc. (USA), was used to simulate the interaction of scale inhibitors with calcite crystal surfaces. This is the first *ab initio* force field that has been parameterized and validated using condensed phase properties, in addition to various *ab initio* and empirical data for molecules in isolation. Consequently, this force field enables the accurate and simultaneous prediction of structural, conformational, vibrational, and thermophysical properties for a broad range of molecules in isolation or condensed phases under a wide range of conditions of temperature and pressure. The detailed expressions used to represent the energy surface of COMPASS force field were shown in literatures [11–14].

2.3.2. Model construction

The models were built with Visualizer module, molecular dynamics (MD) and the energy minimization (EM) calculations were performed on Discover module.

Calcite crystal belongs to the $R3(-)c$ space group [12,15], hexagonal crystal system; the lattice parameters are as follows: $a=b=$ 0.4988 nm, $c=1.7061$ nm, $\alpha=\beta=90°$, $\gamma=120°$. According to previous studies [16,17], the surface cells were created from the unit cell of the mineral at its cleavage planes, namely $(1\bar{1}0)$ and (104). The super cells of surfaces $(1\bar{1}0)$ and (104) were extended to 3D periodic super cells of 2.994 nm × 3.412 nm × 1.230 nm and 3.238 nm × 2.994 nm × 1.067 nm, respectively. Both super cells include 960 atoms (Ca: 192; C: 192; O: 576).

To make the simulation results comparable and the constructed model similar to industrial polymers, the degree of polymerization of all polymers was set to 20 and the monomer molar ratio of the acrylic copolymers [P(AA-*co*-MA)], [P(AA-*co*-HPA)], and [P(AA-*co*-MAE)] was 3:2, 3:1 and 4:1 respectively. The chemical formulas for PESA, [P(AA-*co*-MA)], [P(AA-*co*-HPA)], and [P(AA-*co*-MAE)] were $C_{80}H_{82}O_{101}$, $C_{68}H_{82}O_{56}$, $C_{75}H_{112}O_{45}$, and $C_{64}H_{90}O_{40}$. All structural formulas for PESA and the acrylic copolymers are shown in Fig. 1.

The alkyl chains of the polymers are flexible, free to bend and rotate. Therefore, polymers have a variety of configurations, which were continuously converted mutually. Aside from the lowest energy configuration, there were considerable higher energy configurations; however, taking over all of the possible configurations was unrealistic. With this in mind, the deviation was reduced by increasing the number of configurations, making the simulation results closer to the actual. The torsion angles between the monomers were set to 0°, ±45°, ±90°, ±135°and 180°; for each torsion angle, ten configurations were randomly constructed as a set of samples, then eight sets of samples were constructed, specifically, eighty configurations in total for each polymer. All the molecular dynamics simulations of these eighty configurations were carried out at 353 K in the NVT ensemble [18]. Dynamic simulation time was 100 ps and the time step was set to 1 fs; every 5000 steps generated one outcome and 20 frames were generated in total. The configuration of the twentieth frame was optimized to determine the minimum energy using a molecular mechanic method (MM), the smart minimizer, which combines the steepest descent algorithm, the conjugate gradient algorithm, and the Newton algorithm. The ten lowest energy conformations of the eighty configurations reform a set of samples. Considering the length of the article, only the structures and energy parameters of the lowest energy conformation of the four polymer molecules are given in Fig. 2.

The ten configurations of each polymer molecule were imposed onto the different possible binding sites of the $(1\bar{1}0)$ and (104) surfaces of calcite as starting state (each simulation box contained one polymer molecule), and the thickness of vacuum slab along the Z-axis (c) direction was 2.5 nm. During the simulation, the crystal would grow along

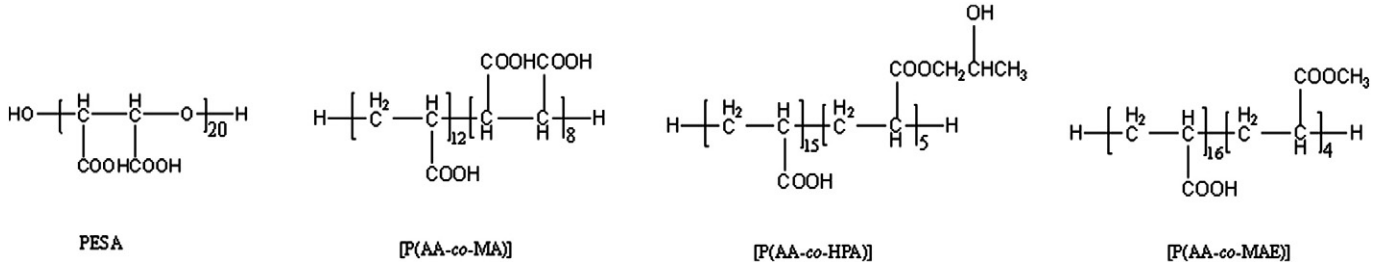

Fig. 1. Structural formulas for PESA and the acrylic acid copolymers.