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Molecular dynamics study of polyether polyamino methylene phosphonates as an inhibitor of anhydrite crystal

Wenyan Shi [a,b], Mingzhu Xia [a,*], Wu Lei [a], Fengyun Wang [a]

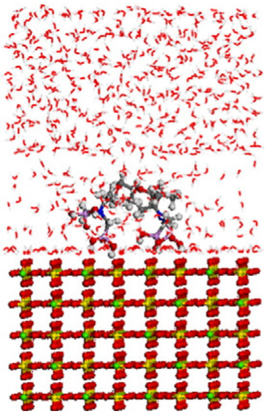
[a] *The Institute of Chemistry & Technology, Nanjing University of Science & Technology, Nanjing 210094, China*
[b] *School of Chemical and Biological Engineering, Yancheng Institute of Technology, 9 Yingbin Avenue, Yancheng 224051, China*

HIGHLIGHTS

- MD simulation of the interaction of PAPEMP with anhydrite in presence of water
- The interactions with (010) and (020) surfaces of anhydrite show small differences.
- Phosphonate carboxyl oxygen atom and calcium ion form electrovalence bond.
- The number of functional groups and stereo-hindrance effect influence binding energy.

GRAPHICAL ABSTRACT

The MD simulation result of PAPEMP (n = 3) interacting with the (010) surface of anhydrite crystal indicates that PAPEMP molecule has clung to the surface of anhydrite crystal in presence of water after molecular dynamics, which indicates they have attracted each other no matter how the initial configurations of PAPEMP molecules had been laid. For the same mass of PAPEMP(n = 1–7), PAPEMP exhibits different abilities to inhibit the growth of anhydrite in the order of PAPEMP (n = 3) > PAPEMP (n = 2) > PAPEMP (n = 1) > PAPEMP (n = 4) > PAPEMP (n = 6) > PAPEMP (n = 5) > PAPEMP (n = 7).



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ABSTRACT

Molecular dynamics (MD) simulations were employed to investigate the interactions between polyether polyamino methylene phosphonate (PAPEMP) with different degrees of polymerization (n = 1–7) and (010), (020) crystal surfaces of anhydrite. An aqueous environment was added through the introduction of water in the simulation cell. The results showed that PAPEMP molecules attach to the surfaces rather than remain in the bulk water and the interactions of the same PAPEMP molecule with the two surfaces show small differences; under the same mass of PAPEMP (n = 1–7), the order of the binding energy E_m of PAPEMP is as follows: PAPEMP (n = 3) > PAPEMP (n = 2) > PAPEMP (n = 1) > PAPEMP (n = 4) > PAPEMP (n = 6) > PAPEMP (n = 5) > PAPEMP (n = 7). The number of the functional groups and the stereo-hindrance effect are two main factors influencing the interactions between PAPEMP and anhydrite. When n ≤ 3, the former is the main factor; while n > 3, the latter is the main factor. The binding energies are mainly provided by the ionic bond and the non-bonding interaction. The structures of the polymers are deformed during the combining processes. Simulation results provide theoretical guidance to judge the performance of scale inhibitors, and synthesize new highly effective scale inhibitor.

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[*] Corresponding author. Tel.: +86 25 84315190.
E-mail address: dxf7569@sina.com (M. Xia).

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1. Introduction

Polyether polyamino methylene phosphonate (PAPEMP) is very capable of controlling calcium carbonate, calcium sulfate and calcium phosphate scales at extremely high supersaturations and temperature. So PAPEMP is widely used as scale inhibitor in a variety of fields including industrial equipment cleaning, industrial water treatment, petrochemical industry and oil field application [1,2]. In practice, the scale inhibitor is a mixture of various compositions, having different degrees of polymerization, so the antiscaling by PAPEMP is the average effect of various compositions. The structural formula of PAPEMP is shown in Fig. 1.

Up to now, the research and performance evaluation of new scale inhibitors still mainly rely on experimental and experience extrapolation methods, which will be prone to bring on the waste of time, manpower and material resources. However, the experimental results could not provide us enough microscopic details about how the scale inhibitors interact with the inorganic scale crystal, and the interaction mechanism is still not clear.

In contrast to many experimental studies, few theoretical researches about the quantitative structure–activity relationships (QSAR) of scale inhibitors have been done at the molecular level [3–10]. Quantum chemical calculation method has been used to study the mechanism of scale inhibition as the dominant technique, however, the information obtained was nothing more than static characteristics of the molecule, such as molecular geometry, electronic structure, the energy and components of frontier molecular orbitals, while the interactions between scale inhibitor molecules and scale crystal have not been explored, which are critical to understand the scale inhibition phenomena. Moreover, quantum chemical calculation method is computationally expensive and is usually only applied to small systems containing less than one hundred atoms, or small molecules. It is not practical to model a large system, such as a system containing many hundreds of solvent molecules or polymers.

In recent years, the molecular dynamics (MD) method, often used to study the interaction of phase interfaces, has been applied to research the interactions between scale inhibitors and inorganic scale crystal. And some significant results have been obtained from those investigations, which confirmed that molecular dynamics simulation can provide insights into the design of scale inhibitor systems with superior properties, and the binding energy between the organic molecule and crystal surface given by molecular dynamics simulation can interpret the difference of inhibition efficiency among organic inhibitors and the effect of scale inhibitor on the morphology of scale crystal [10–14]. However, inorganic scale crystallization is a complex process, which involves many physical and chemical procedures, such as supersaturation, nucleation and crystal growth [15,16], and scale inhibitors can influence each of these processes. The action mechanism of the scale inhibitors is still not clear due to the complexity of the process. Many assumptions have been put forward, such as chelation, threshold effect, crystal lattice aberrance, dispersion effect, regeneration and self disengagement film hypotheses, electric double layer effect, space-matching effect of functional groups, and so on. In summary, three further mechanisms for scale inhibitors are conceivable with anhydrite as an example: (1) the scale inhibitors prevent or affect anhydrite nucleation; (2) the scale inhibitors stabilize the anhydrite crystals or precursors that have formed as colloids; and (3) the scale inhibitors prevent or affect the growth of anhydrite crystals. It is not yet possible now to treat the first two mechanisms with simulation methods at atomistic level, and few studies have been done before which were about the anti-scaling mechanism of PAPEMP against anhydrite crystal by molecular dynamics simulation method [7], so we will investigate closely the interactions between PAPEMP molecules and anhydrite ($CaSO_4$) crystal with a molecular dynamics simulation method. It would be helpful to clarify our understanding of the scale inhibition mechanism of PAPEMP on anhydrite crystal at the atomic resolution.

2. Computational method

2.1. Simulation force field

COMPASS force field [17], available from molecular modeling program Materials Studio 3.0 [18] from Accelrys Software Inc. (USA), was used to simulate the interaction of PAPEMP with anhydrite crystal surfaces. This is the first *ab initio* force field which 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 [17–20].

2.2. Model construction

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

Anhydrite crystals belong to the AMMA space group [21], orthorhombic crystal system; the lattice parameters are as follows: $a = 0.6991$ nm, $b = 0.6996$ nm, $c = 0.6238$ nm, $\alpha = \beta = \gamma = 90°$. The mode which the surface cells are created from the unit cell of the mineral at its cleavage planes was adopted to research the effect of PAPEMP dissolved in water on the growth of (010) and (020) surfaces of anhydrite crystal. The super cells of surface (010) and (020) were extended to 3D periodic super cells of 2.495 nm × 2.796 nm × 3.638 nm and 2.495 nm × 2.796 nm × 3.289 nm, respectively. And the super cells of surface (010) and (020) included 960 atoms (Ca: 160; S: 160; O: 640) and 768 atoms (Ca: 128; S: 128; O: 512), respectively. Forasmuch as it is out of the capability of the current simulation technique to take all of these factors into account simultaneously, these variables were changed step by step. In the present work, the anhydrite crystal surfaces considered were perfect planes, without defects such as vacancies, steps or kink sites. For the molecular dynamics simulation, all the spatial positions of the anhydrite crystal atoms in the simulation box were fixed because the thermal vibration of the interaction was with an adsorbed molecule and not in the physical behavior of the crystal itself.

For PAPEMP molecules with different degrees of polymerization ($n = 1–7$), the torsion angles between the monomers were set to 0°, ±30°, ±60°, ±90°, ±120°, ±150°and 180°; and for each torsion angle, ten configurations were randomly constructed. Specifically,

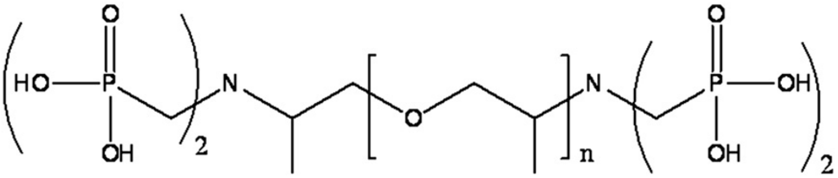

Fig. 1. Structural formula of PAPEMP.