Molecular dynamics simulation on the interaction mechanism between polymer inhibitors and calcium phosphate

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Abstract. Investigation on the microscopic interaction between polymer inhibitors and calcium phosphate contributes to the understanding of their scale inhibition mechanism. The results obtained may provide a theoretical guidance to developing new scale inhibitors. In this study, molecular dynamics simulations have been performed to simulate the interaction between hydrolyzed polymaleic anhydride (HPMA), polyaspartic acid (PASP), polyepoxysuccinic acid (PESA), polyacrylic acid (PAA) and the (001) and (110) surfaces of hydroxyapatite (HA) crystal with and without water. Results show that the simulations of polymer inhibitors and the (001) surface of HA with water is closer to the actual situation. On the same HA (001), binding energy of four polymer inhibitors with water has the order of HPMA > PASP > PESA > PAA. On the different surface of HA, the binding energy does not vary much between the same polymer and the two surfaces of HA. But, deformation energies of the same polymer with and without water vary widely. Pair correlation function of Ca (HA)-O (-C=O) implies that the Ca-O bonds formed between the calcium atoms of HA crystal and oxygen atoms of the carboxyl groups in polymers, and water molecules change the distances between polymer inhibitors and HA crystal. The system of polymer-HA is mainly contributed by the non-bond interaction. Polymer inhibitors do not interact directly with HA crystal, but indirectly through the interactions between inhibitor-H₂O and H₂O-HA. Water molecules cannot be ignored when the interaction models are constructed, i.e., solvent effect must be considered.

Keywords. Polymer inhibitor; hydroxyapatite; molecular dynamics; binding energy; pair correlation function.

1. Introduction

Scale deposition, unlike other types of deposition, is a complex crystallization process and one of the most common problems in industrial circulating cooling water systems. Main components of the scale are calcium carbonate, calcium sulphate, calcium phosphate, etc.^{1–6} Scale inhibitors are considered to have very marked effects on the growth rate of crystals deposited in a scaling environment. With the improvement of environment protection awareness, phosphorus-free polymer inhibitors such as hydrolysed polymaleic anhydride (HPMA), polyaspartic acid (PASP), polyepoxysuccinic acid (PESA), and polyacrylic acid (PAA) have already been widely used,

their configurations are seen in figure 1. These threshold inhibitors function by adsorbing onto the growing crystals and distorting the lattice, which disrupts the crystal growth process. The dispersant products are also used to prevent scale formation by modifying the crystal structure of the deposit-forming substance. This crystal distortion prevents deposition, and the highly irregular stressed crystals tend to slough off as crystal growth occurs. There are many experimental studies on the scale inhibition properties of polymer inhibitors for calcium carbonate, calcium sulphate, calcium phosphate, etc.^{7–11} These studies explain qualitatively some experimental phenomena, while quantitative studies on the inhibition mechanism are few.^{12,13} Water molecules have not been involved in the models in these studies. These computational results can not match, even may be the reverse of the experiment results.^{14,15}

In this article, with and without water, molecular dynamics simulations (MDS) of the interaction

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Figure 2. Supercells of the (001) and (110) faces of HA crystal.

2. In order to facilitate the study, torsion angles of each configuration were initially set to be 0° , $\pm 45^\circ$, $\pm 90^\circ$, $\pm 135^\circ$ and 180° which yield a total of 32 configurations. Then, all these configurations were optimized with molecular mechanics (MM) method and COMPASS force field. According to literature data,^{12,14,28} COMPASS force field was used to model the interaction between scale inhibitors and calcite crystal. This is the first *ab initio* forcefield 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 forcefield enables accurate and simultaneous prediction of structural, conformational, vibrational and thermophysical properties for a broad range of molecules in isolation and in condensed phases, and under a wide range of conditions of temperature and pressure.

According to previous studies and literature,^{12,14,15,28} interaction systems with and without water were constructed using the amorphous cell module. Taking PASP and HA (001) face with water as an example, first, the amorphous cell composed of the optimized PASP and 200 H_2O molecules was placed on HA (001) face to construct the layer model of the interaction (figure 3a). SPC/E model was used as water model during the calculation. Model construction without water (figure 3b) is analogous to the model with water. To eliminate the effect of periodic boundary condition on the system, vacuum thickness was set to 30 Å. The MM method was used to optimize the system to produce initial configuration of MD simulation. Then, MD simulations were carried out with the Discover module. As the crystal grows along with rigid sequence and orientation, in this study, the atoms in the (001) and (110) surfaces of HA crystal were frozen during simulations as done earlier, while all molecules were in free state.

Considering the practical conditions, 343 K was selected and MD simulation was carried out in the NVT ensemble.^{31–33} Coupling to the heating bath to control temperature was carried out using the Berendsen method³⁴ with relaxation time of 0.1 ps. Simulation was

Figure 3. Layer models of PASP-HA (001) with (a) and without (b) water.

started by taking initial velocities from a Maxwell distribution. Solution of Newton's Laws of Motion was based on the assumptions of periodic boundary condition and time average being equal to the ensemble average. Integral summation was performed with the Verlet velocity integrator. Non-bond van der Waals and electrostatic interactions were computed with the atom-based summation method, with a cutoff radius of 9.5 Å. Based on the convergence of potential, kinetic, non-bond, and total energy, MD simulation ran for 3000 ps with the time step of 1 fs. The trajectory was recorded once in every 1000 fs. Interaction systems of PASP with the (001) face of HA crystal with (a) and without (b) water produced from MD simulation are seen in figure 4. Whether the model system has reached equilibrium was ascertained by equilibrium criteria of temperature and energy simultaneously,^{34,35} i.e., fluctuations of temperature and energy should be confined to 5–10%. Taking PESA-HA (001) as an example, fluctuations of total energy with (figure 5a) and without (figure 5b) water are less than 1%, indicating that the systems with and without water have reached an equilibrium state. In addition, fluctuation with water differs from without water, which indicates that solvent effect has an effect on the interaction between polymer inhibitors and HA.

Figure 4. Interaction systems of PASP-HA (001) with (a) and without (b) water produced from MD simulation.

3. Results and discussion

3.1 Binding energy

Seen from figure 4, supermolecule systems can be formed between polymer inhibitor and HA with and without water. The HA-scale inhibitor interaction energy (ΔE_1) is computed using the following equation:^{36–38}

$$\Delta E_1 = E_{\text{complex}} - (E_{\text{SI}} + E_{\text{SF}}),$$

where E_{complex} is the total energy of the binding HA-polymer inhibitor system from MD simulations, E_{SI}

and E_{SF} are the single point energies of the polymer inhibitor and HA surface after MD simulation, respectively. Binding energy was defined to be $-\Delta E_1$, i.e., $E_{\text{bind}} = -\Delta E_1$. A larger E_{bind} implies that the polymer inhibitor combines with HA surface more easily and tightly, as a result, the inhibitive performance will be better. A similar equation can also be applied to calculate the HA-water and inhibitor-water interaction energies (ΔE_2 and ΔE_3). Taking PASP-HA (001) as an example, PASP has clung to HA (001) with and without water (figure 4), indicating that there exist stronger attracting interactions between the inhibitors and HA (001) with and without water. Interaction energies of all HA-polymer inhibitor systems with and without water are listed in tables 1 and 2. All the energy data in tables 1 and 2 (including tables 3, 4, 5 and 6) are averages of the last 10 frames from MD simulation. RSD is relative standard deviation of ΔE_1 , ΔE_2 and ΔE_3 , respectively.

All binding energies in tables 1 and 2 are positive, showing that the combination processes of polymer inhibitors with HA crystal are exothermic. This is mainly because of the strong $\pi-\pi$ interactions between the π_4^3 delocalized bonds of $-\text{COOH}$ groups in polymer inhibitors and the π_4^6 delocalized bonds in the surface of HA crystal.¹² Thereby, polymer inhibitors occupy the growing point of HA crystal and hinder further sedimentation of the scale ions; that is, polymer inhibitors hinder the interaction between Ca^{2+} and PO_4^{3-} and inhibit the crystal growth or distort the lattice of HA. So, the scale is not easy to agglomerate and is easily carried away by the flow of water. With water or without water, comparing the E_{bind} of the same polymer inhibitor on the (001) and (110) faces of HA crystal, binding energy of the former is not significantly different from that of the latter. This indicates that the combination of the same polymer inhibitor with

Figure 5. Total energy fluctuations of PESA-HA (001) with (a) and without (b) water.

Table 1. Binding energies (in kJ/mol) between polymer inhibitors and HA without water.

Surface	Inhibitors	E_{complex}	E_{SI}	E_{SF}	$E_{\text{SI}} + E_{\text{SF}}$	ΔE_1	E_{bind}	RSD %
(001)	HPMA	340863.1	2123.8	338867.6	340991.4	-128.3	128.3	2.79
	PASP	340467.2	1752.7	338867.6	340620.3	-153.1	153.1	2.15
	PESA	340683.6	1950.1	338867.6	340817.7	-134.1	134.1	2.16
	PAA	339452.5	643.5	338867.6	339511.1	-58.6	58.6	2.54
(110)	HPMA	342792.2	2238.1	340686.4	342924.5	-132.3	132.3	3.21
	PASP	342298.4	1887.4	340686.4	342573.8	-275.4	275.4	2.25
	PESA	342690.3	2138.6	340686.4	342825.0	-134.7	134.7	2.18
	PAA	341852.8	1358.5	340686.4	342044.9	-192.1	192.1	2.12

Table 2. Binding energies (in kJ/mol) between polymer inhibitors and HA with water.

Surface	Inhibitors	E_{complex}	E_{SI}	E_{SF}	$E_{\text{SI}} + E_{\text{SF}}$	ΔE_1	E_{bind}	RSD %
(001)	HPMA	340909.5	2218.2	338867.6	341085.8	-176.3	176.3	1.54
	PASP	340387.5	1662.6	338867.6	340530.2	-142.7	142.7	1.62
	PESA	340702.6	1960.2	338867.6	340827.8	-125.2	125.2	1.44
	PAA	339933.8	1154.5	338867.6	340022.1	-88.3	88.3	1.69
(110)	HPMA	342806.5	2268.3	340686.3	342954.6	-148.1	148.1	1.26
	PASP	342330.8	1755.6	340686.3	342441.9	-111.1	111.1	1.33
	PESA	342518.1	1968.2	340686.3	342654.5	-136.4	136.4	1.56
	PAA	341998.0	1433.4	340686.3	342119.7	-121.7	121.7	1.61

Table 3. Interaction energies (kJ/mol) calculated for H₂O-HA (001) with the effect of water.

Inhibitors	$E_{\text{W-Surface}}$	E_{W}	E_{SF}	$E_{\text{W}} + E_{\text{SF}}$	ΔE_2	RSD %
HPMA	338879.8	359.3	338867.6	339226.9	-347.1	1.39
PASP	339235.2	508.8	338867.6	339376.4	-141.2	1.35
PESA	339238.2	478.5	338867.6	339346.1	-107.9	1.42
PAA	339007.6	288.3	338867.6	339155.9	-148.3	1.29

Table 4. Interaction energies (kJ/mol) calculated for inhibitor-H₂O with the effect of water.

Inhibitors	$E_{\text{Polymer-W}}$	E_{W}	E_{SI}	$E_{\text{W}} + E_{\text{SI}}$	ΔE_3	RSD %
HPMA	2452.5	359.3	2218.2	2577.5	-125.0	1.09
PASP	1977.9	508.8	1662.6	2171.4	-193.5	1.28
PESA	2219.2	478.5	1960.2	2438.7	-219.5	1.35
PAA	1299.7	288.3	1154.5	1442.8	-143.1	1.48

ΔE_2 and ΔE_3 are interaction energies between water-HA (001), and inhibitor-water, respectively.

Table 5. Non-bond interaction and deformation energies (in kJ/mol) between inhibitors and two faces of HA crystal with water.

Surface	Inhibitors	$\Delta E_{\text{coulomb}}$	ΔE_{vdw}	$\Delta E_{\text{non-bond}}$	$E_{\text{SI-free}}$	E_{SI}	ΔE_{deform}	RSD %
(001)	HPMA	1656102.7	55908.3	1712011.0	3474.5	2218.2	-1256.3	1.59
	PASP	1877012.3	55588.9	1932601.2	1036.3	1662.6	626.3	1.77
	PESA	1732258.0	55828.2	1788086.2	19151.8	1960.2	-17191.6	0.57
	PAA	1595467.5	55689.4	1651156.9	2513.0	1154.5	-1358.5	1.55
(110)	HPMA	2437695.7	36737.7	2474433.4	3407.6	2268.3	-1139.3	1.48
	PASP	2593822.1	36491.5	2630313.6	2406.9	1755.6	-651.3	1.87
	PESA	2562411.2	36735.8	2599147.0	22748.8	1968.2	-20780.6	0.44
	PAA	2717486.9	36487.7	2753974.6	1587.0	1433.4	-153.6	1.95

Table 6. Non-bond interaction and deformation energies (in kJ/mol) between inhibitors and two faces of HA crystal without water.

Surface	Inhibitors	$\Delta E_{\text{coulomb}}$	ΔE_{vdw}	$\Delta E_{\text{non-bond}}$	$E_{\text{SI-free}}$	E_{SI}	ΔE_{deform}	RSD/ %
(001)	HPMA	1647205.7	55638.2	1702843.9	4470.0	2123.8	-2346.2	2.96
	PASP	1526326.9	55491.7	1581818.6	2043.3	1752.7	-290.6	2.35
	PESA	1489984.6	55688.3	1545672.9	19355.8	1950.1	-17405.7	0.71
	PAA	1190496.5	55436.5	1245933.0	1252.4	643.5	-608.9	2.84
(110)	HPMA	1945199.8	36555.4	1981755.2	9600.0	2238.1	-7361.9	2.45
	PASP	2307755.6	36369.9	2344125.5	1424.3	1887.4	463.1	2.89
	PESA	2372356.5	36692.3	2409048.8	16818.9	2138.6	-14680.3	0.89
	PAA	1631875.4	36437.1	1668312.5	2650.8	1358.5	-1292.3	2.98

HA (001) is not much different from HA (110) combination. Comparing binding energies of different polymer inhibitors with HA (001) with water, the sequence of the binding energies is HPMA > PASP > PESA > PAA, which is in accordance with the results of the related references.^{11,39-42} However, the sequences with HA (110) with water, with HA (001) without water and with HA (110) without water differ from that of the references. This indicates that the interaction models between polymer inhibitors and HA (001) with water are more in line with the actual situation. Besides, on HA (001), water molecules increase binding energies of HPMA and PAA, but decrease those of PASP and PESA through the comparison of tables 1 and 2. This shows that water molecules have a different impact on each interaction between polymer inhibitor and HA, with and without water, i.e., solvent effect cannot be ignored.

3.2 Influence of water

From figure 4a, we find that water molecules have also clung to the surface of HA. In order to investigate the influence of water, considering the interaction between polymer inhibitors and HA (001) with water as an example, HA-water and inhibitor-water interaction energies were calculated and are listed in tables 3 and 4.

All ΔE_2 and ΔE_3 are negative in tables 3 and 4, showing that interaction systems of water and scale crystal surface, and water molecules and inhibitor can be stabilized. Comparing ΔE_1 , ΔE_2 and ΔE_3 , their differences in magnitude are not significant. This indicates that the interactions between inhibitor-HA, water-HA and water-inhibitor are relatively close. These may show that polymer inhibitor interacts with HA surface indirectly through the water molecules, i.e., the water

molecules play an important role in investigating the action mechanism of scale inhibitor in solution by MD simulation and cannot be ignored. This result is different from that of Zhang⁴³ in vacuum, where H₂O is absent.

3.3 Deformation of polymer inhibitor

Seen from figures 3 and 4, polymer inhibitor has deformed before and after MD simulation of the interaction system between polymer inhibitor and HA, with and without water. Deformation degree of the polymer inhibitor can be evaluated by deformation energy ΔE_{deform} .^{14,15,44}

$$\Delta E_{\text{deform}} = E_{\text{SI}} - E_{\text{SI-free}},$$

where E_{SI} and $E_{\text{SI-free}}$ are the single point energies of polymer inhibitor in adsorbed and free states, respectively. Absolute value of deformation energy denotes deformation degree. Comparing figures 3 and 4, PASP deforms when it interacts with HA crystal with and without water, but its deformations are totally different. In order to explore the interaction mechanism of polymer inhibitor to HA crystal, their non-bond energies and deformation energies of four polymer inhibitors, with and without water, are calculated in tables 5 and 6. Calculation formula of non-bond energy ($\Delta E_{\text{non-bond}}$) is as follows:

$$\Delta E_{\text{non-bond}} = \Delta E_{\text{coulomb}} + \Delta E_{\text{vdw}},$$

where $\Delta E_{\text{coulomb}}$ and ΔE_{vdw} are the Coulomb interaction energy and van der Waals (vdW) interaction energy, respectively. ΔE_{deform} of PESA in tables 5 and 6 is significantly larger than those of three other polymer inhibitors in magnitudes with and without water, which indicates that deformation of PESA is the most dramatic. Adsorption of polymer inhibitors can cause the

distortion of HA crystal which may lead to the fracture of crystal surfaces and hinder the growth of HA crystal, as was found in experiments.¹² We can also see that the binding energies are much smaller than the values of non-bond energies and the deformation energies in magnitude. Thus, polymer inhibitor can overcome its intense deformation and closely combine with the face of HA.

$\Delta E_{\text{coulomb}}$, ΔE_{vdw} and $\Delta E_{\text{non-bond}}$ in tables 5 and 6 are positive, and are higher than 0. This indicates that the Coulomb and vdW interactions between polymer inhibitor-HA manifest repulsion. Comparing $\Delta E_{\text{coulomb}}$ and ΔE_{vdw} , the former is significantly greater than the latter, that is, the Coulomb interaction is obvious between the negatively charged functional groups of the polymer inhibitor and the positively charged calcium ion of HA. Comparing tables 1, 2, 5 and 6, $\Delta E_{\text{non-bond}}$ is significantly greater than E_{bind} . This indicates that the systems of inhibitor-HA, with and without water, are mainly contributed by non-bond interactions.

In order to further explore the Coulomb interaction between inhibitor-HA, taking PASP as an example, natural bond orbital (NBO) charges¹⁴ (table 7) of the repeat unit of PASP (figure 6) are calculated by B3LYP/6-31G* method in Gaussian 03 program. From the charge distribution in table 7, negative charges on O4 and O7 atoms of the carboxyl groups are more than that on other positions. This indicates that strong adsorption can be raised by the Coulomb interaction between the negatively charged groups of inhibitors and the positively charged Ca^{2+} of HA. Table 7 can also show that NBO charge of O atom of hydroxyl group is significantly smaller than those of carbonyl groups in magnitude. This indicates that O atoms of carbonyl groups are nearer to the surface of HA crystal than O atoms of hydroxyl groups, which is consistent with figure 4.

Table 7. Natural bond orbital chargesa (in e) of PASP repeat unit.

Repeat unit	Atom	Charge
PASP	C(1)	0.111
	C(2)	-0.059
	C(3)	0.822
	O(4)	-0.594
	O(5)	-0.227
	C(6)	0.578
	O(7)	-0.520
	N(8)	-0.120

^aNatural bond orbital charges with hydrogens summed into heavy atoms

Figure 6. Repeat unit of PASP.

3.4 Pair correlation functions of the interaction system

To further investigate the interactions between the atom pairs of the model system and to reveal the essence of solvent effect on polymer inhibitor to calcium phosphate scale, pair correlation functions (PCFs) of polymer inhibitors and HA crystal supermolecular systems with and without water solution, $g(r)$, are obtained by analysing the MD simulation trajectories.

Generally, the peak of the PCF curve within 3.5 Å is caused by the hydrogen bonds and chemical bonds, and that outside 3.5 Å is from the non-bond (Coulomb and VDW) interactions.¹⁵ Taking HA (001) as an example, PCF $g(r)_{\text{Total}}$ of all the atoms of the interaction models between polymer inhibitor and HA crystal with and without water are shown in figure 7a and b. Seen from figure 7a and b, the weak peaks of $g(r)_{\text{Total}}$ of four polymer inhibitors without water appear around 3.5 Å, which are significantly higher than those with water. This indicates that at the same distance, the probability of all the atoms of the interaction model without water is less than with water, that is, water molecules can change the interaction distance between polymer inhibitors and HA crystal. This is line with the results of the binding energy in section 3.1. From the trends of $g(r)_{\text{Total}}$, the value outside 3.5 Å is significantly greater than that within 3.5 Å, indicating that the non-bond interactions between polymer inhibitor-HA is significantly stronger than the chemical bonds or the hydrogen bonds. This is consistent with section 3.3. In addition, outside 3.5 Å, the sequence of $g(r)_{\text{Total}}$ of four polymer inhibitors with water is also consistent with that of the binding energy.

Figure 7. PCFs $g(r)_{\text{Total}}$ of four polymer inhibitors with HA(001) with (a) and without (b) water.

Owing to the difference between the force field of O atom of carbonyl groups and O atom of hydroxyl groups in four polymer inhibitors, their PCFs have to be studied separately. Taking Ca (HA)-O (-C=O) pair as an example, $g(r)_{\text{Ca(HA)-O(-C=O)}}$ with and without water are seen in figure 8a and b, respectively. Ca (HA) and O (-C=O) denote Ca atoms of HA crystal and O atoms of carbonyl groups in polymer inhibitors, respectively. From figure 8, the PCFs $g(r)_{\text{Ca(HA)-O(-C=O)}}$ of four polymer inhibitors without water are closer than those with water, indicating that water molecules affect the interaction distance between Ca (HA)-O (-C=O) pair. This is also consistent with the conclusion of section 3.1. In addition, the PCFs $g(r)_{\text{Ca(HA)-O(-C=O)}}$ of four polymer inhibitors, with and without water, begin to appear around 2.30 Å, which is slightly shorter than the bond length of Ca-O (2.39 Å), indicating that the Ca-O bonds are formed between the calcium atoms of HA crystal and the oxygen atoms of carbonyl groups in polymer inhibitors.⁴¹ From the trends

Figure 8. PCFs $g(r)_{\text{Ca(Crystal)-O(-C=O)}}$ of four polymer inhibitors- HA(001) with (a) and without (b) water.

of $g(r)_{\text{Ca(HA)-O(-C=O)}}$, the conclusion is also consistent with $g(r)_{\text{Total}}$. In order to see bonding, the distances (figure 9) of some of atom pairs in the model system with water are calculated. Seen from figure 9, the bonding and non-bond interactions can be formed between water molecules-HA crystal and water molecules-polymer inhibitor. This is consistent with the conclusion of section 3.2.

4. Conclusion

The MD simulations of four polymer inhibitors to HA crystal show:

- (1) Interaction models between polymer inhibitors and HA (001), (110) with and without water can be carried out with MD method, but the result between inhibitors and HA (001) with water is more in line with the actual situation.

Figure 9. Bonding and non-bond interactions in the system of PASP/H₂O/ HA(001). Distances of (1) Ca(HA)-O(carbonyl of PASP), (2) O(carbonyl of PASP)-H(H₂O), (3) O(HA)-H(H₂O) and (4) O(HA)-H(PASP) are 3.937 Å, 2.332 Å, 2.481 Å and 7.126 Å, respectively. V-shaped structure:H₂O, Line structure:PASP, ball-stick structure:HA crystal.

- (2) Four polymer inhibitors can inhibit the growth of calcium phosphate scale. Sequence of the binding energy between them and HA (001) has the order of HPMA > PASP > PESA > PAA. Binding energies between the same polymer inhibitor and the two faces of HA crystal may not vary much. On HA (001), water molecules increase the binding energies of HPMA and PAA, but decrease those of PASP and PESA.
- (3) In water solution, interactions between inhibitor-HA, water-HA and water-inhibitor are relatively close. Polymer inhibitor interacts with HA surface indirectly through water molecules. Water molecules play an important role in investigating the action mechanism of scale inhibitor in solution by MD simulation and cannot be ignored.
- (4) From analysis of the PCFs, within 3.5 Å, the bonds are formed between the calcium atoms in calcium phosphate scale and the oxygen atoms of polymer inhibitors, outside 3.5 Å, the non-bond interaction can be easily formed between them. The systems between inhibitor-HA, with and without water, are mainly contributed by the non-bond interaction. There was a significant difference between the two O atoms of carboxyl groups in polymer inhibitors.

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References

1. Zach-Maor A, Semiat R, Rahardianto A, Cohen Y and Wilson S 2008 *Desalination* **230** 239
2. Kneller JF 1988 *US* 4740314[P]
3. Ling L, Zhou Y, Huang J, Yao Q, Liu G and Zhang P 2012 *Desalination* **304** 33
4. Antony A, Low J H, Gray S, Childress A E and Le-Clech P 2011 *J. Membr. Sci.* **383** 1
5. Zhang J, Yang W and Yin X 2009 *Ind. Water Treat.* **29** 56
6. Wang J and Lu W 1998 *Rock Miner. Anal.* **17** 241
7. Zhou X, Sun Y and Wang Y 2011 *J. Environ. Sci.* **23** (Supplement) S159
8. Zhang B R, Zhang L, Li F T, Hu W and Hannam P M 2010 *Corros. Sci.* **52** 3883
9. Li X, Dong B, Wu F and Qing C 2001 *Water Purif. Technol.* **20** 16
10. Zhang Y L, Huang J L, Yang S L and Tao H C 2004 *J. Donghua Univ. Nat. Sci.* **30** 120
11. Zhang S F, Shu Y J and Tang S M 2008 *China Water Wastewater* **24** 42
12. Xia M Z, Wang F Y, Lei W and Zhang S G 2008 *Acta Chim. Sin.* **66** 476
13. Gao R, van Halseth F E D, Temminghoff E J M, van Leeuwen H P and van Valenberg H J F 2010 *Food Chem.* **122** 700

14. Zeng J P, Wang F H, Zhou C and Gong X D 2012 *Chin. J. Chem. Phys.* **25** 219
15. Zeng J P, Zhang J Y and Gong X D 2011 *Comput. Theor. Chem.* **963** 110
16. Salimi M N, Bridson R H, Grover L M and Leeke G A 2012 *Powder Technol.* **218** 109
17. Pietak A M, Reid J W, Stott M J and Sayer M 2007 *Biomaterials* **28** 4023
18. Nathanael A J, Hong S I, Mangalaraj D and Chen P C 2011 *Chem. Eng. J.* **173** 846
19. Sun H 1998 *J. Phys. Chem.* **B102** 7338
20. Sun H, Ren P and Fried J R 1998 *Comput. Theor. Polym. Sci.* **8** 229
21. Martin M G 2006 *Fluid Phase Equilib.* **248** 50
22. Materials Studio 4.4, 2009 Discover/Accelrys Software Inc., San Diego, California
23. Peroos S, Du Z and de Leeuw N H 2006 *Biomaterials* **27** 2150
24. Iijima M and Moradian-Oldak J 2005 *Biomaterials* **26** 159
25. Lu X, Wang Y, Wang J, Qu S, Weng J, Xin R and Leng Y 2006 *J. Cryst. Growth.* **297** 396
26. Pradip Rai B, Rao T K, Krishnamurthy S, Vetrivel R, Mielczarski J and Cases J M 2002 *J. Colloid and Interface Sci.* **256** 106
27. Bhowmik R, Katti K S and Katti D 2007 *Polymer* **48** 664
28. Zhang H, Lu X, Leng Y, Fang L, Qu S, Feng B and Weng J 2009 *Acta Biomater.* **5** 1169
29. Zhou B S 2009 *Industrial water treatment technology* (Beijing: Chemical Industry Press)
30. Yan R X 2003 *Water treatment agent application manual* (Beijing: Chemical Industry Press)
31. Heermann D W, Translated by Qin K C 1996 *Computer simulation methods in the theoretical physics* (Beijing: Peking University Press)
32. Fraternali F 1990 *Biopolymers* **30** 1083
33. Xu L, Kumar P, Buldyrev S V, Chen S H, Poole P H, Sciortino F and Stanley H E 2005 *PNAS* **102** 16558
34. Berendsen H J C, Postma J P M and Van W F 1984 *J. Chem. Phys.* **81** 3684
35. Zeng J P, Wang A M, Gong X D, Chen J, Chen S and Xue F 2012 *Chin. J. Chem.* **30** 115
36. Huang Y C, Hu Y J, Xiao J J, Yin K L and Xiao H M 2005 *Acta Phys. Chim. Sin.* **21** 425
37. Boys S F and Bernardi F 2002 *Mol. Phys.* **100** 65
38. Wang L J, Liu G S, Song X F and Yu J G 2009 *Acta Phys. Chim. Sin.* **25** 963
39. Gao L, Guo N, Mu Q, Wang Z, Zhuo R and Wang H 2003 *Petrochem. Technol.* **32** 792
40. Zhang J, Zhang L, Ding Q, Chen C and Zhang F 2005 *Liaoning Chem. Ind.* **34** 20
41. Fu C, Zhou Y, Xue M, Xie H and Wu W 2011 *CIESC J* **62** 525
42. Brown JM, McDowell J F and Chang K T 2009 *US* 5062962[P]
43. Zhang S G, Shi W Y, Lei W and Xia M Z 2005 *Acta Phys. Chim. Sin.* **21** 1198
44. Zeng J P, Zhang S G, Gong X D and Wang F Y 2010 *Chin. J. Chem.* **28** 337