Influence of Mg^{2+}, SO_4^{2-} and Na^+ ions of sea water in crude oil recovery: DFT and ab initio molecular dynamics simulations

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ABSTRACT

A detailed understanding of surface interaction between crude oil molecule and calcite can pave a way to explain several fundamental challenges of wettability alteration of calcite surface and hence provide a guidance for further enhancement of crude oil recovery. In the enhanced crude oil recovery stage, additives, Mg^{2+} and SO_4^{2-} ions of sea water alter the relative wettability characteristics (from oil-wet to less oil-wet) of calcite surface that enhances the crude oil recovery. In this paper, we consider naphthenic acid is a model compound of crude oil molecule, perform Density Functional Theory (DFT) and ab initio molecular dynamics simulations and checking its relative binding energy (i.e. the binding energy difference between water and oil molecule) is an indication of relative wettability alteration of calcite surface. Ab initio molecular dynamics simulations suggest that Mg^{2+} ion replaces Ca^{2+} of calcite and then SO_4^{2-} ion replaces CO_3^{2-} of calcite. The relative binding energy of oil molecule is larger on modified calcite.$MgSO_4$ surface than on pure calcite surface, providing an indication of less oil wet calcite surface. Ab initio molecular results also show that few Na^+ ions of sea water reach to the calcite surface as a precipitate and form Na naphthenates that make oil molecule more sticker (more oil-wet) to the rock surface. Combined study of DFT and ab initio molecular dynamics simulations can help to understand the surface interaction between oil molecule and calcite surface in aqueous sea water environment that has global impact on crude oil recovery from calcite oil reservoirs.

1. Introduction

Magnesium, calcium, sodium, sulphate ions play an important role in a wide range of biological and inorganic systems, where these cations and anions are being used to stabilize biological structures, such as cell membranes, proteins, DNA and RNA [1–5]. Mostly these cations and anions are available in the environment from ocean waters and mineral salts. The interaction of these anions and cations with water, acids and mineral surfaces provide accurate description of mineral interface properties such as mineral adsorption, desorption, dissolution, and precipitation. These investigations provide several information for geological processes on how bone growth, tooth decay and other geological process happen over long period of time. Hence, our better understanding of surface interaction among water, complex acid molecules and mineral surfaces is beneficial for biomedicine, as they are being used for ion exchange, contaminant migration, biomineralization, flocculation, and dispersion of nanoparticles [6–18].

In addition, magnesium, calcium, sodium, sulphate ions have significant impact on recovery of crude oil from calcite oil reservoirs. The crude oil molecule consists of a long chain of hydrocarbons at one end

and −COOH at the other [19–22]. Hence, detailed understanding of interaction between acid molecule and calcite surface plays an important role in oil industry. To enhance oil recovery, several methods are being applied such as injecting natural gases, bio-minerals, tap water, sea water, high pH solutions of surfactant, low salinity water, microbial and thermal methods. These are some of the examples for possible ways of enhancing crude oil recovery [23,22,19,21,20,24–31].

Recent experimental studies have shown that low salinity water or removing some of Na^+ and Cl^- ions from sea water enhances oil recovery [19], however there is a lack of theoretical descriptions in the literature in terms of their influence on the binding of oil molecule to the mineral surface. In Ref. [22], Zhang et al. found that oil recovery can be enhanced up to 60% by considering Ca^{2+}, Mg^{2+} and SO_4^{2-} ions in the sea water due to relative wettability alteration of rock surfaces [22,21]. The relative wettability is related to the binding energy (i.e., the binding energy difference between water and oil molecules) [21]. For example, if the relative binding energy on modified calcite surface due to additives of sea water is larger than on pure calcite surface, oil recovery is enhanced. Hence, the binding energy calculation is helpful for exploring the possibility of enhancing crude oil recovery. Prior
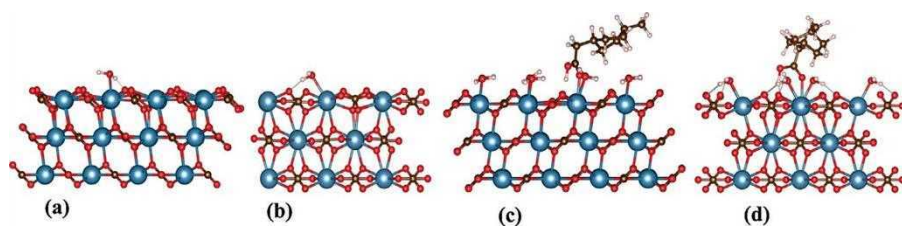
Fig. 1. Optimized relaxed structure of water ((a) in *yz* plane and (b) in *xz* plane) and naphthenic acid ((c) in (*yz*) plane and (d) in (*xz*) plane) with $(H_2O)_7$ on calcite surface. The distance between O of water and Ca of calcite is 2.36 Å and distance between O of carbonate and H of water is 1.72 Å. Also, the distance between O of naphthenic acid and Ca of calcite is 2.35 Å. The distance between O of carbonate and carboxyl H of naphthenic acid is 1.42 Å.

calculation suggests that the crude oil molecule binds stronger than the water molecule because the crude oil molecule consists of a long chain of hydrocarbons at one end and −COOH group at the other end that binds strongly to the calcite surface [21,32–36]. Further calculation of binding energy shows that on the calcite surface when Mg^{2+} replaces Ca^{2+} and then SO_4^{2-} replaces CO_3^{2-}, the relative binding energy of oil molecule on modified calcite surface is larger than oil molecule on pure calcite surface [21,19,22]. Hence, oil recovery is enhanced due to wettability alteration of the calcite surface.

In this paper, we consider that the naphthenic acid is a model compound of crude oil molecule [37] and perform quantum mechanical calculations based on density functional theory and ab initio quantum molecular dynamics simulations to find the influence of additives (Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}) ions of sea water on the binding energies of naphthenic acid and water on the calcite surface. We found that Mg^{2+} and SO_4^{2-} ions modify the relative wettability characteristics of calcite rock surfaces. The relative binding energy of oil molecule is larger on modified calcite surface due to Mg^{2+} and SO_4^{2-} ions than on pure calcite surface that turns the rock surface into less oil-wet (enhancement of crude oil recovery). On the other hand, ab initio quantum molecular dynamics simulation shows that few Na^+ ions can reach to the oil molecule near the calcite surface as a precipitate and form sodium naphthenate, which has smaller relative binding energy. Therefore, sodium naphthenate becomes more sticker on the calcite surface that causes the reduction of the oil recovery (more oil-wet). We suggest that smaller relative binding energy of sodium naphthenate causes to reduce the crude oil recovery, which may explain the observations found experimentally in Ref. [19].

2. Computational methods

Ab initio molecular dynamics and density functional theory (DFT) calculations are performed under periodic boundary conditions, which are implemented in the Quantum Espresso software package [41]. Ultrasoft pseudopotentials and plane wave basis set with a kinetic energy and charge density cut-off at 60 Ry and 600 Ry are used. We include exchange and correlation effects within Perdew–Burke–Ernzerhof (PBE) functional [42]. Van der Waals interactions are also included with the Semiempirical Grimme's DFT-D2 corrections term [43]. We use a 7.95 Å × 5.02 Å × 30.75 Å supercell that contains three layers (120 atoms) of orthorhombic (4 × 2) calcite slab model. During geometry optimization, all atoms except the bottom layer are fully relaxed until the forces on atoms are smaller than 0.01 eV/Å. We have tested several *k*-point samplings. Calculation at Γ-point sampling fulfills convergence criteria. The optimized lattice constant of calcite is 3.97 Å along *x*-direction and 5.02 Å along *y*-direction which are in good agreement with the experimental data [44]. Since initial configuration of a molecule is important for finding the global minimum energy configuration, we performed ab initio quantum molecular dynamics simulations to find a reasonable initial configuration for naphthenic acid and water molecules on calcite surface. To be sure that we eventually reached the overall minimum energy configuration, 21 possible initial configurations were tested and lower energies were selected to find biding energies of adsorbed molecule on calcite surface. The VESTA program was used to draw the molecular structure [45]. The binding energy is calculated as:
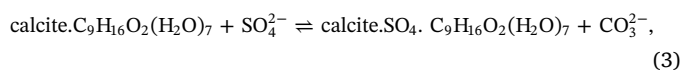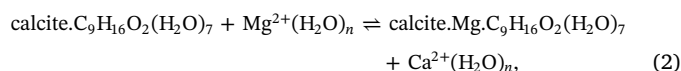
$$E_b = E_{surf} + E_{mol} - E_{surf.mol}, \tag{1}$$

where $E_{surf.mol}$ is the total energy of adsorbed molecule on calcite surface, E_{surf} is the total energy of calcite surface alone and E_{mol} is the total energy of molecule in a vacuum. The total energies of free molecules are calculated in a large size of vacuum (20 Å × 20 Å × 20 Å) by using same the *k*-point sampling at Γ-point. The distances between the molecule and the boundaries are kept more than 8 Å to avoid any artifact interaction between molecules. For ab initio molecular dynamics simulations, we have used 57 H_2O molecules in a (7.94 Å × 10.04 Å × 21.23 Å) size supercell, which corresponds to the experimental density of water, 1 kg/L. For ab initio molecular dynamics simulations, we have used 0.96 femto-second for each ionic time step, re-scaled temperature to 350 K and used the same *k*-point sampling and energy cut-off that were used for DFT calculation.

3. Results and discussions

Relative binding energy (i.e. the binding energy difference between water and oil molecule, $\Delta E_b < 0$) is important ingredient to determine the calcite surface, which is either oil-wet or water-wet. For example, if the relative binding energy is negative then the surface of calcite is oil-wet (hydrophobic) but if its value increases towards zero then calcite surface turns towards hydrophilic (water-wet). Since the binding energy of oil molecule is always larger than the water molecule due to the presence of −COOH group, the relative binding energy is always negative. Hence, the goal is to make the relative binding energy large (hydrophilic calcite surface) for enhancement of crude oil. First, the binding energies of water and naphthenic acid on pure calcite surface are calculated. The optimized relaxed structure of water molecule is shown in Fig. 1(a) and (b) and monolayer of 7 water molecules and single naphthenic acid are shown in Fig. 1(c) and (d). By using (1), the binding energies of water molecule and naphthenic acid are 1.10 eV (consistent with Ref. [21,32]) and 1.27 eV, respectively. Hence, the relative binding energy is −0.17 eV, which is considered as the benchmark calculations for further comparison of relative binding energies alteration due to Mg^{2+}, SO_4^{2-} and Na^+. The binding mainly arises from the interaction between the O atom of H_2O and naphthenic acid, and a Ca atom of calcite. There is also weak hydrogen bond interaction between H atoms of H_2O and naphthenic acid (−COOH), and O atom of calcite.

To enhance the crude oil recovery, sea water in oil reservoirs is injected and then additives (Mg^{2+} and SO_4^{2-}) of sea water modify the calcite surface towards less oil-wet. Hence, investigating the influence of additives (Mg^{2+} and SO_4^{2-}) ions of sea water on the wettability alteration of calcite surface is useful. The optimized relaxed structures of naphthenic acids and water molecules on modified calcite surfaces are shown in Fig. 2 and their binding energies are listed in Table 1. Further, we consider the calcite surface modification due to additives of sea water by the following reaction mechanism:
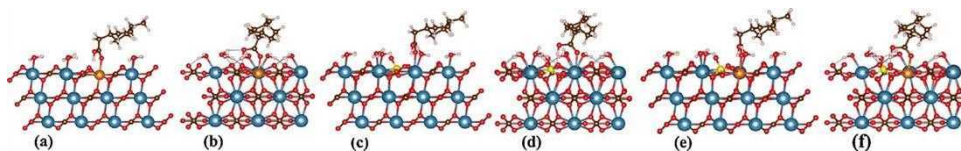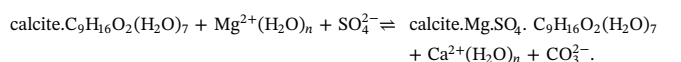
$$calcite.C_9H_{16}O_2(H_2O)_7 + Mg^{2+}(H_2O)_n \rightleftharpoons calcite.Mg.C_9H_{16}O_2(H_2O)_7$$
$$+ Ca^{2+}(H_2O)_n, \tag{2}$$

$$calcite.C_9H_{16}O_2(H_2O)_7 + SO_4^{2-} \rightleftharpoons calcite.SO_4.\,C_9H_{16}O_2(H_2O)_7 + CO_3^{2-}, \tag{3}$$

Table 1

The binding energies (eV) of water and naphthenic acid on modified calcite.Mg, and calcite.MgSO$_4$ surfaces. The binding energy difference, $\Delta E_b < 0$, between water and naphthenic acid is the relative binding energy. On pure calcite surface, the relative binding energy is −0.17 eV, which is shown in Fig. 1. Hence, naphthenic acid on calcite.Mg surface is more oil-wet (harmful for oil recovery) but less oil-wet on calcite.MgSO$_4$ surfaces (beneficial for oil recovery).

Ion on surface	$E_b(H_2O)$	$E_b(naph)$	ΔE_b
Calcite	1.10	1.27	−0.17
Calcite–Mg	1.15	1.39	−0.24
Calcite.SO$_4$	0.98	1.25	−0.27
Calcite–MgSO$_4$	1.13	1.24	−0.11

$$\text{calcite.C}_9\text{H}_{16}\text{O}_2(\text{H}_2\text{O})_7 + \text{Mg}^{2+}(\text{H}_2\text{O})_n + \text{SO}_4^{2-} \rightleftharpoons \text{ calcite.Mg.SO}_4.\ \text{C}_9\text{H}_{16}\text{O}_2(\text{H}_2\text{O})_7$$
$$+ \text{Ca}^{2+}(\text{H}_2\text{O})_n + \text{CO}_3^{2-}.$$
(4)

where C$_9$H$_{16}$O$_2$ is the naphthenic acid and $n = 57$. The optimized relaxed structure of calcite.C$_9$H$_{16}$O$_2$(H$_2$O)$_7$, calcite.Mg.C$_9$H$_{16}$O$_2$(H$_2$O)$_7$, calcite.SO$_4$. C$_9$H$_{16}$O$_2$(H$_2$O)$_7$ and calcite.MgSO$_4$. C$_9$H$_{16}$O$_2$(H$_2$O)$_7$ are shown in Figs. 1(c), (d) and 2 (a)–(e), respectively.

First, we consider the solvation of Mg^{2+} and Ca^{2+} dications in aqueous conditions. In Fig. 3(a) and (b), we present the ab initio molecular dynamics simulation of Mg(H$_2$O)$_n^{2+}$, where the first solvation shell of Mg coordinates six water molecules [1]. The distance between Mg and O of H$_2$O ranges from 1.95 Å to 2.36 Å, which is seen in Fig. 3(c). Also, in Fig. 4(a) and (b), we present the ab initio molecular dynamics simulation of Ca(H$_2$O)$_n^{2+}$, where the first solvation shell of Ca coordinates six water molecules [38]. The distance between Ca and O of H$_2$O ranges from 2.0 Å to 2.6 Å, which is seen in Fig. 4(c).

The anions, CO$_3^{2-}$ and SO$_4^{2-}$, are not as strongly hydrated as the cations, Ca^{2+} and Mg^{2+}. In aqueous conditions, water molecules mostly interact with the cations, Ca^{2+} and Mg^{2+}. Hence, we calculate the total energy of these free anions, CO$_3^{2-}$ and SO$_4^{2-}$ in vacuum. For single Mg^{2+} ion substitution, the total ensemble average energy change is −0.43 eV, which suggests that the reaction is exothermic and Mg^{2+} ion substitution is thermodynamically preferred. For Ca^{2+} and CO$_3^{2-}$ replacement of calcite by Mg^{2+} and SO$_4^{2-}$ in proximity, the total energy change is +0.66 eV, which suggests that the reaction is endothermic. Hence, surface modification of calcite by Mg^{2+} and SO$_4^{2-}$ ions only
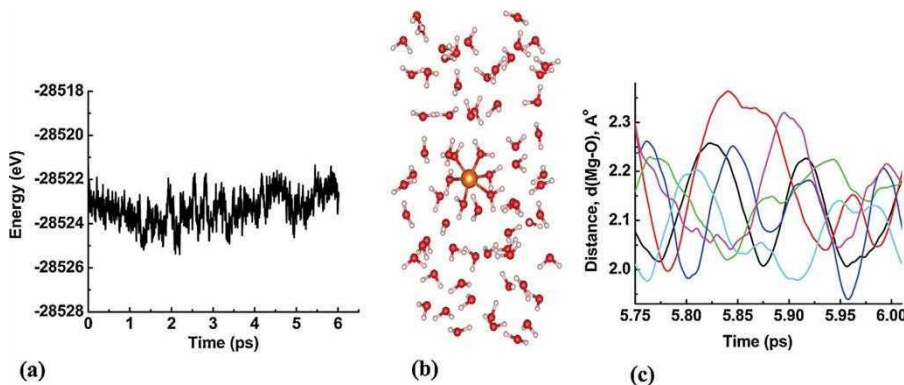
happens when the system overcome the barrier energy of +0.66 eV in the reservoir oil well conditions. The binding energies of naphthenic acid on modified calcite.Mg (Fig. 2(a) and (b)), calcite.SO$_4$ (Fig. 2(c) and (d)) and calcite.MgSO$_4$ (Fig. 2(e) and (f)) surfaces are 1.39 eV, 1.25 eV and 1.24 eV, respectively, which is also shown in Table 1. The relative binding energy (absolute value of the binding energy difference between water and naphthenic acid) on modified calcite.MgSO4 surface is smaller than of pure calcite surface (0.11 eV vs 0.17 eV), which turns the calcite surface towards less oil-wet. In other words, from Table 1, we see that the binding energy of water increases but naphthenic acid decreases on modified calcite.MgSO$_4$ surface compared to the pure calcite surface. Such interplay in the binding energies is beneficial for oil recovery. Hence, replacement of Ca^{2+} of calcite by Mg^{2+} and CO$_3^{2-}$ of calcite by SO$_4^{2-}$ of sea water enhances oil recovery. Here we conclude that the surface modification due to Mg^{2+} and SO$_4^{2-}$ ions must act together to turn into the calcite surface less oil-wet, which enhances the crude oil recovery.

Enhancement of crude oil recovery is usually determined by measuring contact angle of oil molecule on calcite surface. The contact angle for three phases (calcite surface-oil-water) system can be calculated by the Young's equation: [46–48]

$$\gamma_{os} - \gamma_{ws} = \gamma_{ow} \cos\theta,$$
(5)

where γ_{os} is the interfacial tension between oil and calcite surface, γ_{ws} is the interfacial tension between water and calcite surface, γ_{ow} is the interfacial tension between oil and water. For naphthenic acid as a model compound of oil molecule, $\gamma_{ow} = 0.0023$ eV/Å^2 is used [51,50,49]. The change in interfacial tension, $\Delta\gamma$ caused by additive Mg^{2+} and SO$_4^{2-}$ ions substitution in proximity of the calcite surface, is estimated by the changes in the binding energy per unit area for oil and water molecule on pure calcite and on modified calcite surfaces as:

$$\Delta(\cos\theta) = \frac{\Delta E_{os} - \Delta E_{ws}}{\gamma_{ow} A},$$
(6)

where A is the surface area. Since, additive ions Mg^{2+} and SO$_4^{2-}$ present parts per million in sea water, we consider that only 5% and 10% of additive ions participate in the wettability alteration of calcite surface. In Fig. 5, the contact angle change on modified calcite surface due to additives Mg^{2+} and SO$_4^{2-}$ ions of sea water from the reference value of the contact angle, $\theta = 90°$ (mixed oil-water-wet) is shown. In Fig. 5, it can be seen that the change in contact angle due to Mg^{2+} and SO$_4^{2-}$ ion substitution in proximity decreases, which indicates that the calcite
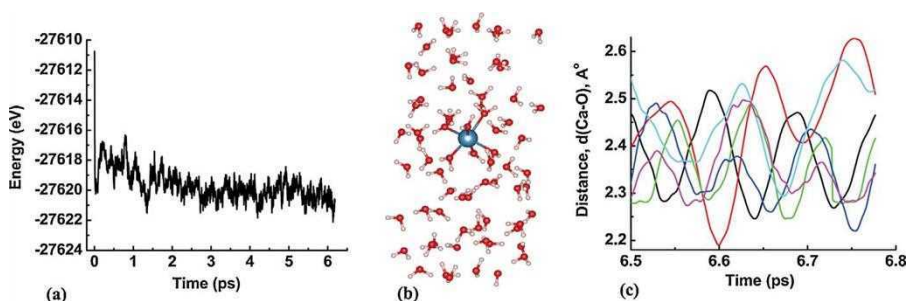

Fig. 3. (a) Ab initio molecular dynamics simulations of [Mg(H$_2$O)$_n$]$^{2+}$ with $n = 57$. (b) First solvation shell of magnesium coordinates six water molecules. (c) Variations of distances from Mg to O of first solvation shell of six water molecules in each ionic steps after 5.7 ps. It can be seen that the distances of the first solvation shell of H$_2$O vary from 1.95 Å to 2.36 Å, which is in agreement to the Ref. [1].

Fig. 4. (a) Ab initio molecular dynamics simulations of $[Ca(H_2O)_n]^{2+}$ with $n = 57$. (b) First solvation shell of calcium coordinates six water molecules. (c) Variations of distances from Ca to O of first solvation shell of six water molecules in each ionic steps after 6.5 ps. It can be seen that the distances between Ca and O of the first solvation shell of H_2O vary from 2.2 Å to 2.6 Å, which is in agreement to the Ref. [38].
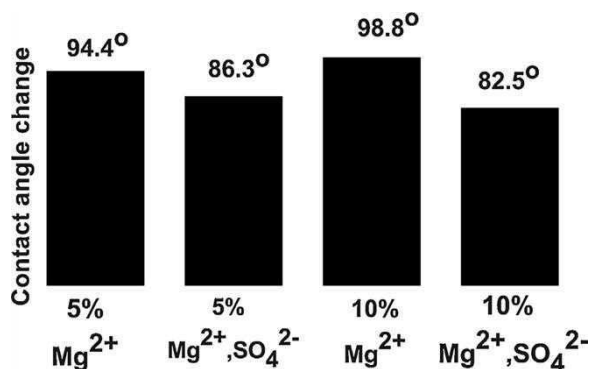

Fig. 5. Relative contact angle change due to ion-substitution on calcite surface by additive ions of sea water from reference value of contact angle, ($\theta = 90°$, mixed oil-wet). Ion substitution by Mg^{2+} alone (Fig. 4(a)) makes calcite surface more oil-wet, whereas ion substitution by Mg^{2+} and SO_4^{2-} in proximity (Fig. 4(c)) makes calcite surface less oil-wet.

surface modification due to Mg^{2+} and SO_4^{2-} turns the calcite surface towards hydrophilic characteristics (less oil-wet), which is helpful for oil recovery. Wettability alteration of calcite surface in proximity due to additive ions Mg^{2+} and SO_4^{2-} of sea water has significant effects on the global energy economy and biological systems, where calcite is synthesized for several different purposes.

In sea water, concentrations of Na^+ and Cl^- ions are larger than other ions. Recent experimental study in Ref. [19] suggests that the crude oil recovery is enhanced when some of Na^+ and Cl^- ions were removed from sea water. From theoretical perspective, one can check whether or not Na^+ ions are energetically favourable to bind with the naphthenic acid on the calcite surface considering the following reaction:
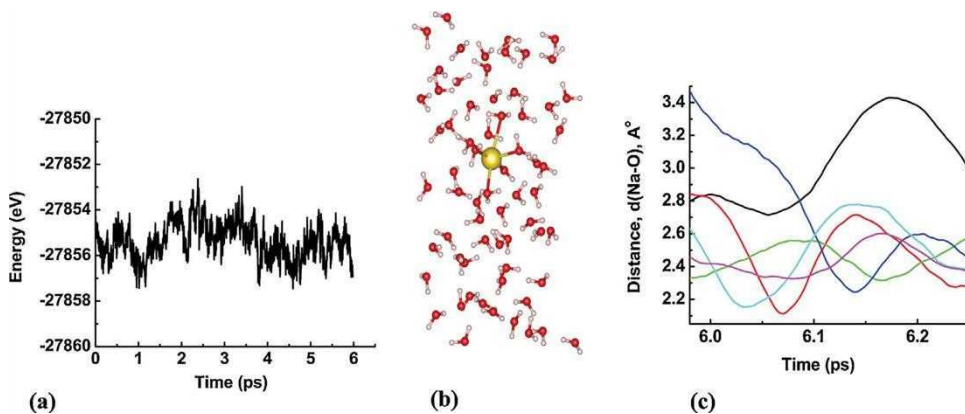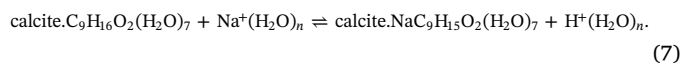
$$calcite.C_9H_{16}O_2(H_2O)_7 + Na^+(H_2O)_n \rightleftharpoons calcite.NaC_9H_{15}O_2(H_2O)_7 + H^+(H_2O)_n.$$
(7)

In Fig. 6(a) and (b), we consider the solvation of Na^+ in aqueous conditions. We present the ab initio molecular dynamics simulation of $Na(H_2O)_n^+$, where the first solvation shell of Na coordinates six water molecules [39]. The distance between Na and O of H_2O ranges from 2.1 Å to 3.4 Å, which is seen in Fig. 6(c). In Fig. 7(a) and (b), we present the ab initio quantum molecular dynamics simulation of $H(H_2O)_n^+$, where H^+ forms H_3O^+ [40]. Once finding the optimized lattice structure of Na naphthenate on calcite surface (Fig. 8(b)), one can estimate the dynamic reactions of (7) in that whether or not, Na^+ ions are energetically favourable to form Na naphthenate and kick the carboxyl hydrogen of naphthenic acid away from the calcite surface. In fact, total ensemble average energy difference for Na^+ ions to form Na naphthenate on pure calcite surface is $+1.0$ eV, which suggests that the reaction (7) is endothermic and Na^+ ions are not energetically preferred to form Na naphthenate on the calcite surface. Since the concentrations of Na^+ ions in sea water are the largest, Na^+ ions precipitate on the surface of calcite and form Na naphthenate, which is observed experimentally in Ref. [19]. The binding energy of Na naphthenate is 1.95 eV, which is larger than the naphthenic acid on calcite surface (1.94 vs 1.27 eV). Hence, the relative binding energy of Na naphthenate is -0.84 eV, which smaller than naphthenic acid (-0.84 eV vs -0.17 eV) and makes oil molecule in the form of Na naphthenate more stickier than original oil molecule (naphthenic acid). This is a possible explanation of the experimental evidence in Ref. [19] that depleting NaCl from sea water enhances the crude oil recovery.

For future work, it may be beneficial to study the surface modification of calcite due to additive ions of sea water in oil wells by considering ion substitutions in the second and third layer of calcite. For example, one can ask a question whether $MgSO_4$ localize on the top or bottom of $\{10\overline{1}4\}$ on the calcite. This will change the geometry and availability of sulfate oxygen in oil wells, and will play a role in other applications.

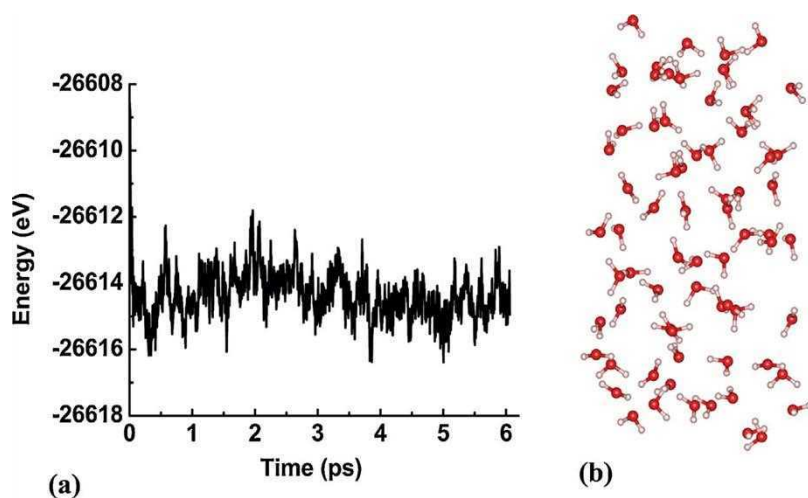**Fig. 6.** (a) Ab initio molecular dynamics simulations of $[Na(H_2O)_n]^+$ with $n = 57$. (b) First solvation shell of sodium coordinates six water molecules. (c) Variations of distances from Na to O of first solvation shell of six water molecules in each ionic steps after 6.0 ps. It can be seen that the distances between Na and O of the first solvation shell of H_2O varies from 2.1 Å to 3.4 Å, which is in agreement to the Ref. [39].

Fig. 7. (a) Ab initio dynamics simulations of $[H(H_2O)_n]^+$ with $n = 57$. (b) Snapshot image of $[H(H_2O)_n]^+$ where H^+ forms H_3O^+ which is in agreement with Ref. [40].
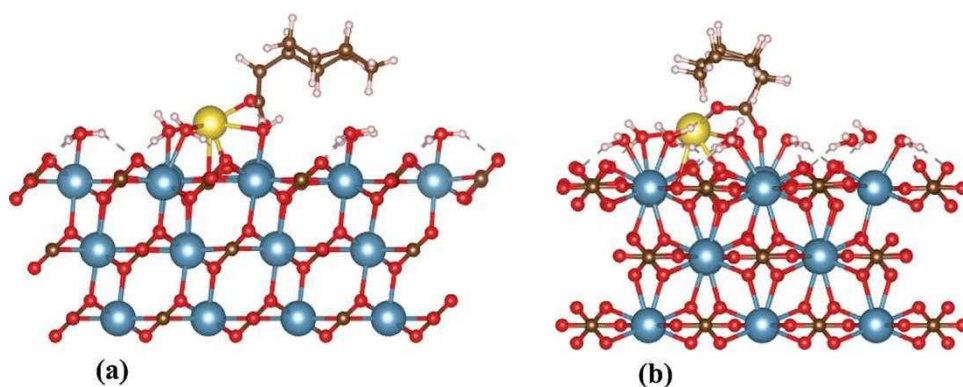

Fig. 8. The optimized relaxed structure of Na naphthenate and water molecules on pure calcite surface.

4. Conclusions

By using density functional theory and ab initio quantum molecular dynamics simulations of crude oil molecule in calcite oil reservoirs, we have shown that Na^+ ions precipitate to the calcite surface and form Na naphthenates that makes oil molecule more stickier than original oil molecule (relative binding energy -0.84 eV (Na naphthenate) vs -0.17 eV (naphthenic acid)). This provides an explanation of the experimental observations in Ref. [19] in that oil recovery rate is enhanced but not significantly (less than 8%) by removing some of Na^+ ions from sea water. Our findings also show that the wettability alteration of calcite surface by Mg^{2+} and SO_4^{2-} ions of sea water in proximity is important ingredient for making calcite surface less oil-wet. In fact, the relative binding energy of naphthenic acid on modified calcite.$MgSO_4$ surface is larger than on pure calcite surface (-0.11 eV vs -0.17 eV), that also provides an explanation of enhancing crude oil recovery due to having Mg^{2+} and SO_4^{2-} ions in sea water (see Ref. [19]). Our density functional theory and ab initio quantum molecular dynamics simulations study of oil molecule on calcite surface can assist in better to understand the binding of oil molecule to the calcite surface in aqueous sea water environment that has global impact on crude oil recovery from calcite oil reservoirs and many biological systems, where calcite is synthesized for specific purpose.

Acknowledgements

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