

Formation and modulation mechanisms of interfacial property in Middle Eastern carbonate reservoirs

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GRAPHICAL ABSTRACT



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ABSTRACT

Recognizing and modulating reservoir interfacial property are essential prerequisites for optimizing surfactant flooding efficacy and sustaining petroleum production. Through systematic examination of mineral composition, rock wettability, and elemental redistribution, this study investigates interfacial property evolution during crude oil saturation process. Through comprehensive analysis of wettability alterations, elemental redistribution, and electron binding energy shifts, the modulation effects of surfactants on rock interfacial property are further elucidated. Subsequently, through the displacement efficiency measurement and core flooding experiment, the enhanced oil recovery capability of relevant surfactants was verified. The experimental results indicate that negatively charged polar molecules in crude oil undergo chemisorption on carbonate rock surfaces, while only physical adsorption occurs on sandstone. Both adsorption mechanisms result in the transition of rock surfaces from water-wetting to oil-wetting. Surfactants modulate interfacial property from oil-wetting to water-wetting by removing crude oil from rock surfaces. For carbonate rock, cationic surfactant efficiently removes negatively charged polar molecules from crude oil adsorbed on the rock surface, exhibiting the strongest interfacial modulation capability, while anionic surfactant demonstrates superior interfacial modulation capability for sandstone. Cationic surfactant achieves 88 % displacement efficiency and enhances oil recovery by 8.33 % in core flooding experiment, which aligns consistently with the principles of interfacial property modulation. This study contributes to reconstructing the formation process of interfacial property in carbonate rocks and elucidating the

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modulation mechanisms of surfactant, thereby laying a crucial foundation for ensuring crude oil production for carbonate formations reservoir.

1. Introduction

Surfactant flooding constitutes a critical enhanced oil recovery (EOR) technique for late-stage, high water-cut reservoirs [1–6]. Surfactants exhibit amphiphilic properties and interfacial adsorption capabilities, enabling EOR through three primary mechanisms: substantial reduction of oil-water interfacial tension [7–14], crude oil emulsification [15–27], and mitigation of oil adsorption on rock surfaces [28–37]. Elucidating interactions between surfactants and reservoir rocks and precisely modulating interfacial properties are pivotal for optimizing recovery efficiency.

Recent years have witnessed extensive research on surfactant-mediated interfacial modifications in oil reservoirs. Lu et al. [38] engineered a novel Guerbet alkoxy carboxylate surfactant system and conducted core flooding experiments. Results revealed its efficacy in shifting wettability from strongly oil-wetting to water-wetting states in carbonate cores, underscoring wettability alteration as a dominant mechanism for enhanced oil recovery (EOR) in carbonate reservoirs. Trivedi et al. [39] systematically investigated the impact of ionic surfactants with varying hydrophobic chain lengths on carbonate interfacial properties. Heterogeneous core flooding tests demonstrated that interfacial wettability modification constitutes the primary EOR driver in oil-wetting carbonates, with longer-chain surfactants exhibiting superior wettability-altering capabilities. Shi et al. [40] attributed low recovery in carbonate reservoirs to inherent oil-wetting and heterogeneity. Homogeneous and heterogeneous core imbibition tests confirmed that sufficient surfactant retention time enhances interfacial property optimization, enabling significant crude oil mobilization. Zhang et al. [41] synthesized an amino acid-derived eco-friendly surfactant and evaluated its interfacial effects on both carbonate and sandstone substrates. Contact angle measurements indicated a transition from oil-wetting to neutral-wet (leaning water-wetting) states across lithologies. Subsequent dynamic core flooding experiments further validated that lithology-specific wettability modulation markedly improves EOR efficiency. However, although carbonate rock represents one of the primary targets for crude oil production [42–44], current research on surfactant effect on carbonate interfacial properties predominantly focuses on macroscopic contact angle alteration, with insufficient investigation into interaction mechanism. Present understanding of microscopic interaction between surfactant and carbonate interface remains limited, while the modulation influence of surfactant structural types (cationic, anionic, nonionic) on interfacial property remains essentially unexplored. Therefore, elucidating the microscopic interactions between crude oil and carbonate rock, along with analyzing the microscopic modulation mechanisms of surfactant on carbonate interface, becomes imperative to achieve a comprehensive understanding and effective modulation of carbonate interfacial property.

To clarify the interaction mechanism between surfactant and carbonate rock surface, as well as the modulation effect and mechanism of surfactant on carbonate rock interfacial property, this study investigates the formation mechanism of carbonate rock interfacial wettability by examining microscopic interaction between crude oil and rock surface. Further analysis examines microscopic interactions of surfactants at carbonate rock interface and evaluates the modulation effect and mechanism of different surfactants on reservoir interfacial wettability, obtaining macroscopic and microscopic distinctions in surfactant interactions with carbonate versus sandstone interfaces. This study contributes to establishing fundamental understanding of surfactant interaction with carbonate rock interface, laying a crucial foundation for comprehending the influence patterns of surfactant on reservoir rock interfacial property.

2. Materials and methods

2.1. materials

Although some simplifications in composition and differences in surface morphology exist, calcite is selected as the simulant for carbonate rock since it constitutes one of the primary components of actual carbonate rock [42] and demonstrates high consistency with actual carbonate rock in terms of surface properties and chemical composition. Similarly, quartz is selected as the simulant for sandstone. Calcite: Purchased from Anluo Lun Biotechnology Co., Ltd. Quartz sand: Purchased from Beijing Mairuida Technology Co., Ltd.

Crude oil for rock saturation/aging treatments and core flooding experiments: provided by Research Institute of Petroleum Exploration and Development (RIPED). Decane: Analytical grade, purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. Benzyl dodecyl dimethyl ammonium chloride (BDDAC): Analytical grade, purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., coded as CIS-B11. Sodium dodecyl benzene sulfonate (SDBS): Analytical grade, purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., coded as LAS-1. Octylphenyl polyoxyethylene ether: Analytical grade, purchased from Shanghai Macklin Biochemical Co., Ltd., coded as TX-100.

2.2. Rock-crude oil saturation and aging

Crude oil (6 wt%) was mixed with clean sandstone and carbonate samples in 100 mL reagent bottles. The mixtures were homogenized at 500 rpm for 24 h and aged in a constant-temperature chamber for 7, 14, and 30 days to simulate interfacial evolution in Middle Eastern carbonate reservoir rock.

2.3. Surfactant modulation

Surfactant solutions (0.3 wt%) were equilibrated with aged carbonate/sandstone samples in volumetric flasks at 30°C (200 rpm, 24 h). Post-equilibration rocks were rinsed thrice with deionized water to remove surfactants/inorganic salts and dried at 70°C for 3 h.

2.4. Wettability characterization

Wettability was characterized using an SCA20 contact angle analyzer. Contact angles were calculated by curve-fitting droplet profiles in captured images: water-oil contact angles (θ_{WO}) in deionized water and oil-water contact angles (θ_{OW}) in decane.

2.5. Elemental composition profiling

(1) X-ray fluorescence (XRF): Quantified elements from Na to U using a PANalytical Zetium spectrometer (Netherlands).

(2) Elemental analysis (EA): Measured C, N, H, O, and S contents with a Vario EL analyzer (Elementar, Germany; precision: $\leq 0.1\%$ for C/H/N/O, $\leq 0.05\%$ for S).

(3) Energy-dispersive X-ray spectroscopy (EDS): Performed using a Hitachi SEM accessory. Cleaned rock, aged rock, and surfactant-treated rock were mounted on SEM stubs and scanned eight times.

2.6. Interfacial electronic state analysis

X-ray photoelectron spectroscopy (XPS) was conducted at 1000–1500 eV to measure electronic binding energy of characteristic atoms (e.g., Ca), ensuring valence electron ionization and inner-shell

Table 1
Properties of cores used in experiments.

Property	1st test	2nd test
length (cm)	10.60	10.60
diameter (cm)	0.38	0.38
Area (cm ²)	0.11	0.11
Bulk volume (cc)	117.80	117.80
Pore volume (cc)	22.17	22.17
Porosity (%)	18.82	18.82
Water Permeability (mD)	0.71 (0.2 mL/min)	0.70 (0.2 mL/min)

Table 2
Properties of water used in experiments.

Types of ions	ion concentration	Mineralization degree
Na ⁺	2617	60186
Ca ²⁺	438	17521
Mg ²⁺	77	1848
Cl ⁻	3631	128905
HCO ₃ ⁻	3	191
SO ₄ ²⁻	4	392
total	6770	209138

electron excitation.

2.7. Displacement efficiency evaluation

A mixture of 0.5 g oil sand and 5 mL surfactant solution was combined in a test tube and oscillated at 200 rpm for 24 h in a constant-temperature water bath shaker. After 24 h of shaking, the oil removal process reached equilibrium, with the residual oil content of the oil sand

remaining essentially constant. The experimental temperature was maintained at 30°C, and the surfactant concentration was set at 0.3 wt%.

Following surfactant treatment, the oil sand was washed three times with deionized water to remove adhered surfactants or inorganic salts. Solid oil sand samples were then collected via centrifugation. Subsequently, the samples were dried at 70°C for 3 h to eliminate residual moisture. The oil removal efficiency was determined using thermogravimetric analysis. The displacement efficiency E_D was calculated using Eq. (1):

$$ED = \frac{m_e}{m_0} * 100\% = \frac{x_e - x_0}{(1 - x_0) * x_e} * 100\% \quad (1)$$

In Eq. (1), m_0 and m_e represent the initial oil mass and the oil mass after washing, respectively; x_0 and x_e denote the thermogravimetric mass percentages (%) of the oil-bearing rock before and after surfactant treatment, respectively.

2.8. Core flooding experiment

The core samples, crude oil, and formation water utilized in the core flooding experiments were sourced directly from the NEB reservoir and provided by the Research Institute of Petroleum Exploration and Development (RIPED). Detailed physicochemical parameters are summarized in Table 1 and Table 2.

Core samples were mounted in a core holder and heated to 90°C. Sequential saturation with formation water and crude oil was performed, followed by initial waterflooding at a displacement rate of 0.05 mL/min. Oil recovery was calculated as the ratio of produced oil volume to initial oil in place, with flooding continuing until effluent water cut exceeded 99%.

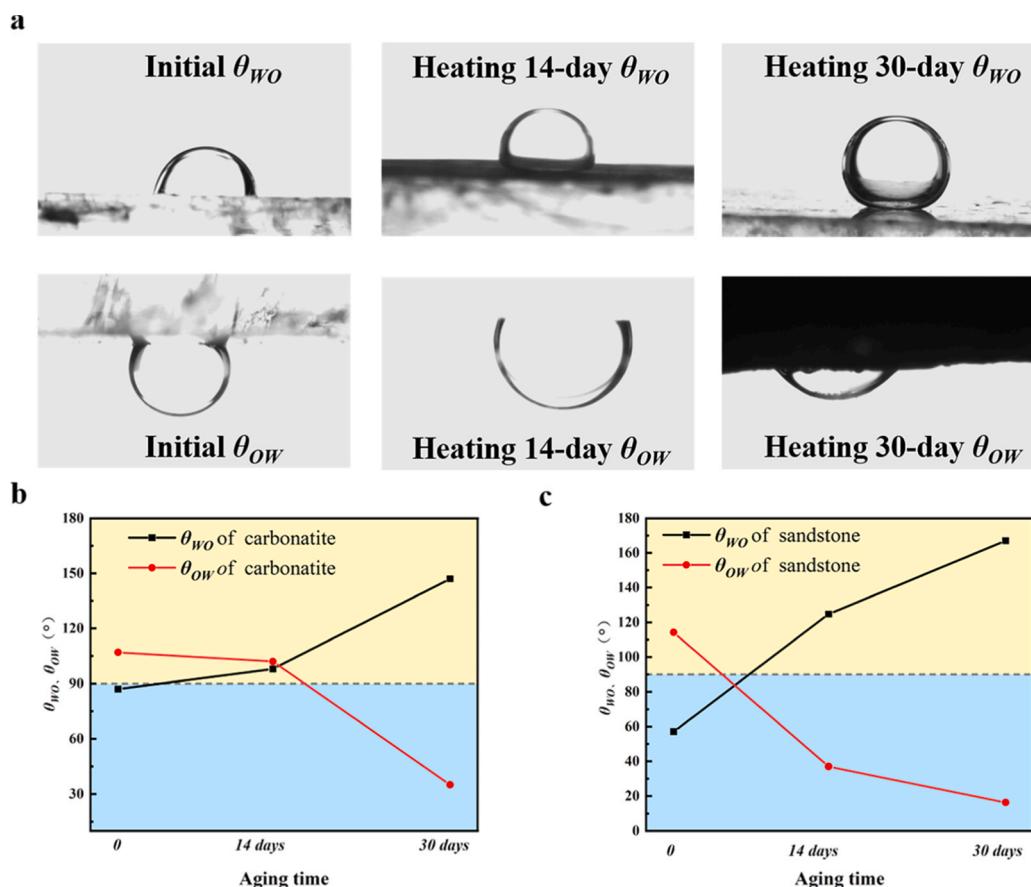


Fig. 1. (a) Images of contact angle at different heating times of carbonate rock. (b) Contact angles of carbonate rock with different aging time. (c) Contact angles of sandstone rock with different aging time.

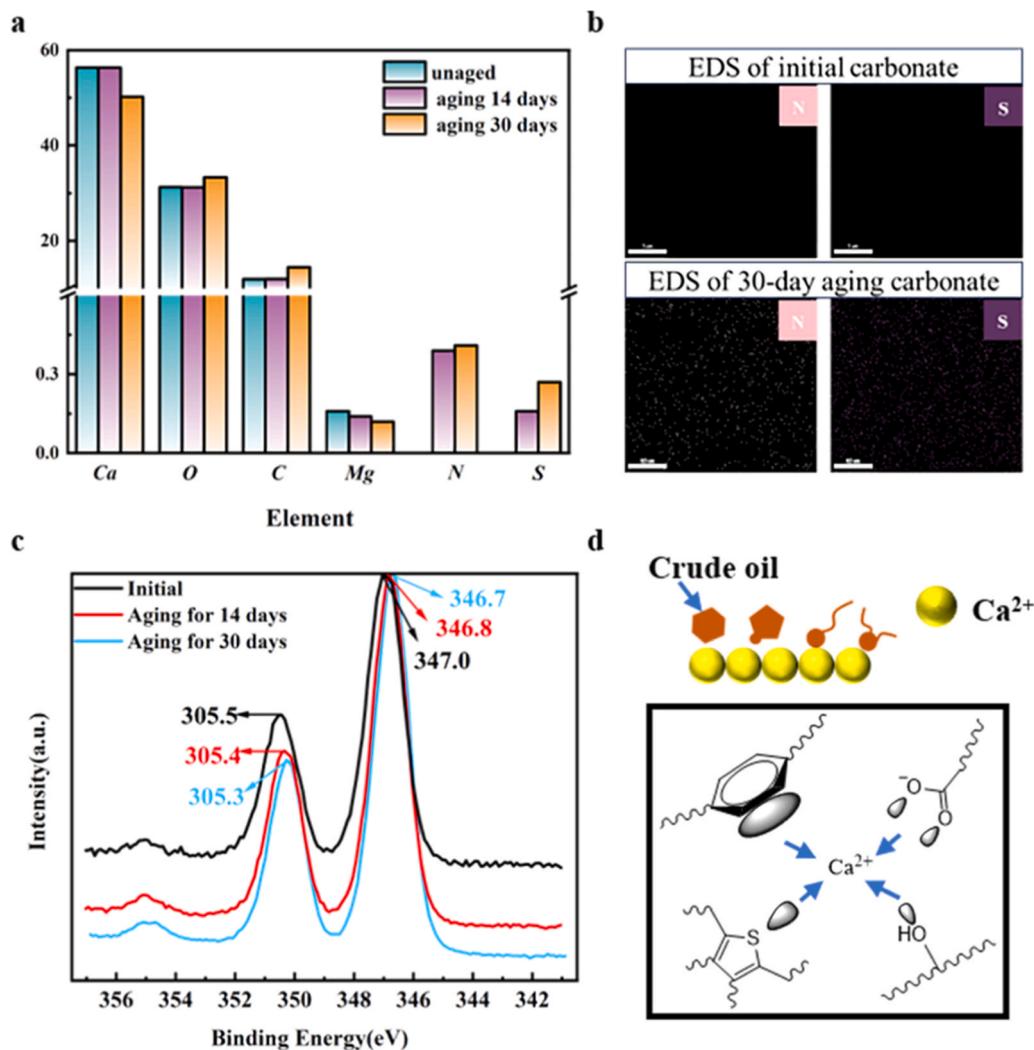


Fig. 2. (a) Elemental variation in carbonate rock at different aging periods. (b) EDS analysis of carbonate rock at different aging periods. (c) XPS analysis of carbonate rock at different aging periods. (d) Formation mechanism of carbonate rock interface property.

Subsequently, surfactant flooding (0.3 wt%) was initiated. Upon injecting 0.5 pore volumes (PV) of surfactant solution, secondary waterflooding commenced and persisted until oil-free effluent was achieved.

3. Results and discussion

3.1. Formation mechanisms of interface property

Interfacial property evolution of variably aged carbonate and sandstone rocks under conditions representative of reservoir environments were quantified through contact angle measurements. To eliminate gaseous phase artifacts inherent to laboratory settings, oil-water-rock three-phase contact angle measurements were conducted in preference to gas-liquid-rock systems, consistent with subsurface multiphase flow dynamics. Fig. 1a presents contact angle profiles of carbonate rocks, while Fig. 1b and Fig. 1c illustrate the temporal evolution of contact angles for both carbonate and sandstone samples during aging. The contact angle images of sandstone with different aging time are shown in Fig. S1.

Analysis of contact angle evolution during aging demonstrates that both carbonate and sandstone rocks undergo a wettability transition from water-wetting to oil-wetting under reservoir conditions. For carbonate samples after 14 and 30 days of aging, θ_{WO} increases from 87° to

98° and 147° while θ_{OW} decreases from 107° to 102° and 35° . Sandstone rocks exhibit similar trends with θ_{WO} increasing from 57.1° to 124.7° and 167° alongside θ_{OW} decreasing from 114.2° to 37° and 16.3° after equivalent aging periods. The directional changes in both θ_{WO} and θ_{OW} quantitatively confirm strengthening oil-wetting characteristics across both rocks.

Further explore the reasons for the formation mechanisms of carbonate rock interface property. Carbonate rock interfacial characteristic is governed by two determinants: (1) intrinsic mineral composition dominated by salts and metal oxides, and (2) organometallic adlayers formed through geological deposition of indigenous organic constituents (e.g., crude oil) onto mineral surfaces.

Elemental analysis (XRF and EA) reveal that carbonate rock is primarily composed of Ca, C, P, and Mg (Fig. 2a), mineralogically dominated by calcite (CaCO_3) and magnesian-calcite ($\text{Ca}(\text{MgCO}_3)_2$), while sandstone comprises Si, O, Al, and Na (Fig. S2) with quartz (SiO_2) and nepheline (NaAlSiO_6) as major constituents.

Comparative analysis of organic adsorption on rock surface was conducted using specific elements of rock elements (Ca, Si) and organic signatures (C, N, S). For carbonates, N/S elemental abundance variations are prioritized to circumvent carbon interference between carbonate matrices and organic deposits.

EDS results indicate that carbonate rock before aging exhibit high abundances of Ca and O elements (Fig. S3) on surface, with minimal

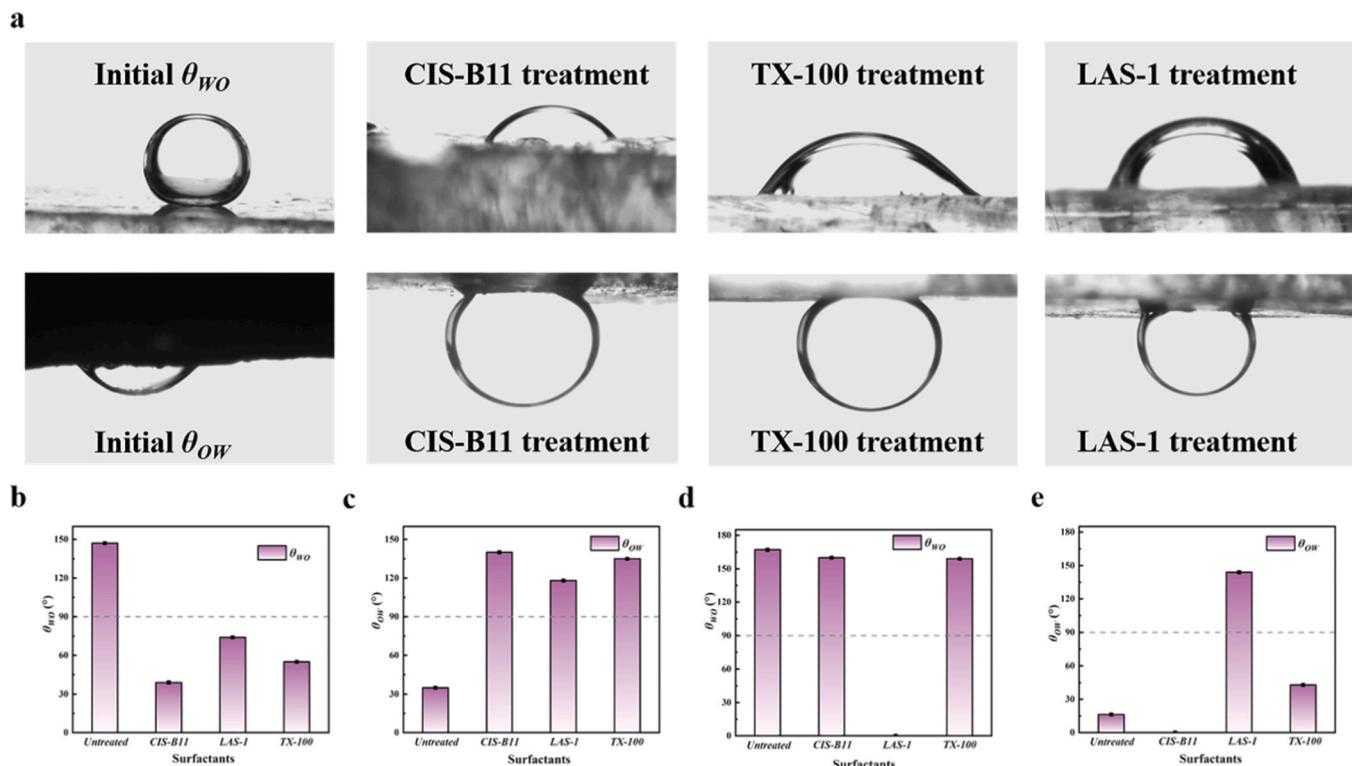


Fig. 3. (a) Images of contact angle of carbonate rocks treated with different surfactants. (b) θ_{WO} of carbonate rocks after modulation by different surfactants. (c) θ_{OW} of carbonate rocks after modulation by different surfactants. (d) θ_{WO} of sandstone rocks after modulation by different surfactants. (e) θ_{OW} of sandstone rocks after modulation by different surfactants.

presence of N and S elements (Fig. 2b). Following aging treatments for 14 and 30 days, distinct N and S distributions emerge on carbonate rock surfaces, with N concentrations measuring 0.39 % and 0.41 % and S concentrations reaching 0.16 % and 0.27 % respectively, demonstrating significant organic deposition. For sandstone, comparative analysis of organic deposition was conducted using O, Si, N, and C elemental abundance variations. EDS experimental results show that pre-aging sandstone surfaces contain only 6.8 % C with negligible N, whereas following aging treatments for 14 and 30 days, C content rapidly increases to 28.70 % and 30.82 %, respectively, accompanied by pronounced N distribution (Fig. S4). This confirms organic deposition on post-aging sandstone surfaces. Following crude oil aging, carbonate and sandstone rock surfaces exhibit clear organic deposition.

To elucidate the interaction between crude oil and rock along with the mechanism of wettability alteration, XPS analysis (Fig. 2c) was conducted targeting characteristic elements specific to different lithologies (Ca in carbonate rock and Si in sandstone).

XPS analysis reveals a progressive decrease in Ca 2p binding energy in carbonate rock with aging, confirming chemisorption through coordination of negatively charged polar molecules in crude oil (hydroxyl, carboxyl, thiophenic, and aryl moieties) with Ca^{2+} ions, partially displacing carbonate counterions. Conversely, Si binding energy in sandstone remains virtually unchanged, confirming predominantly physical adsorption without significant chemical interaction (Fig. S5). These results reveal distinct adsorption mechanisms specific to different rocks. Crude oil undergoes chemisorption on carbonate rock surfaces (Fig. 2d), whereas sandstone rock exhibits physisorption on its surface. (Fig. S6).

3.2. Interfacial property modulation and mechanism

Organic adsorption on rock surfaces converts water-wetting interface to oil-wetting states, impeding oil displacement and reducing oil recovery. Surfactant modulation transforms the carbonate rock surface from oil-wetting to more water-wetting, serving as a critical enhancer

for oil recovery.

The ability of three surfactants to modulate interface property were evaluated: cationic CIS-B11, anionic LAS-1, and nonionic TX-100. Contact angle variations ($\Delta\theta_{WO}$ for water-wetting modulation capability; $\Delta\theta_{OW}$ for oleophobic modulation capability) quantitatively reflect the ability of surfactant to modulate interface property, with greater angular shifts indicating stronger modulation capability.

Contact angle data demonstrate that anionic, cationic, and nonionic surfactants collectively convert oil-wetting carbonate surface to water-wetting states (Fig. 3a), with cationic CIS-B11 exhibiting the strongest modulation efficacy (Fig. 3b, Fig. 3c): $\Delta\theta_{WO} = 108^\circ$ and $\Delta\theta_{OW} = 105^\circ$, followed by anionic LAS-1 ($\Delta\theta_{WO} = 73^\circ$, $\Delta\theta_{OW} = 83^\circ$) and nonionic TX-100 ($\Delta\theta_{WO} = 92^\circ$, $\Delta\theta_{OW} = 100^\circ$). In contrast, cationic CIS-B11 and nonionic TX-100 exhibited low modulation capability in sandstone interface (Fig. 3d, Fig. 3e). Anionic LAS-1 induced a pronounced oil-wetting to water-wetting transition on sandstone surface ($\Delta\theta_{WO} = 167^\circ$, $\Delta\theta_{OW} = 127.7^\circ$), establishing anionic LAS-1 as most effective modulation surfactant for sandstone (Fig. S7).

Interfacial adsorption of crude oil constitutes the fundamental mechanism responsible for oil-wetting characteristic on carbonate surface. To investigate modulation mechanisms of different surfactants on carbonate rock surface, variations in characteristic elements were characterized (Fig. 4a). Elemental composition analysis indicates that carbonate rock treated with surfactant exhibits significantly reduced surface nitrogen (N) and sulfur (S) content compared to untreated rock, confirming effective crude oil removal. Cationic CIS-B11 achieves the most significant element removal ($\Delta N = 84\%$, $\Delta S = 79\%$), which aligns with the change of interfacial property ($\Delta\theta_{WO} = 108^\circ$, $\Delta\theta_{OW} = 105\%$); For sandstone rocks (Fig. S8), the residual carbon (C) content remains high after treatment with CIS-B11 (15.55 %) and TX-100 (6.55 %), whereas anionic LAS-1 achieves near-complete organic stripping (C=3.41 %).

To elucidate the modulation mechanism of surfactant at carbonate rock interface, X ray photoelectron spectroscopy (XPS) targeting

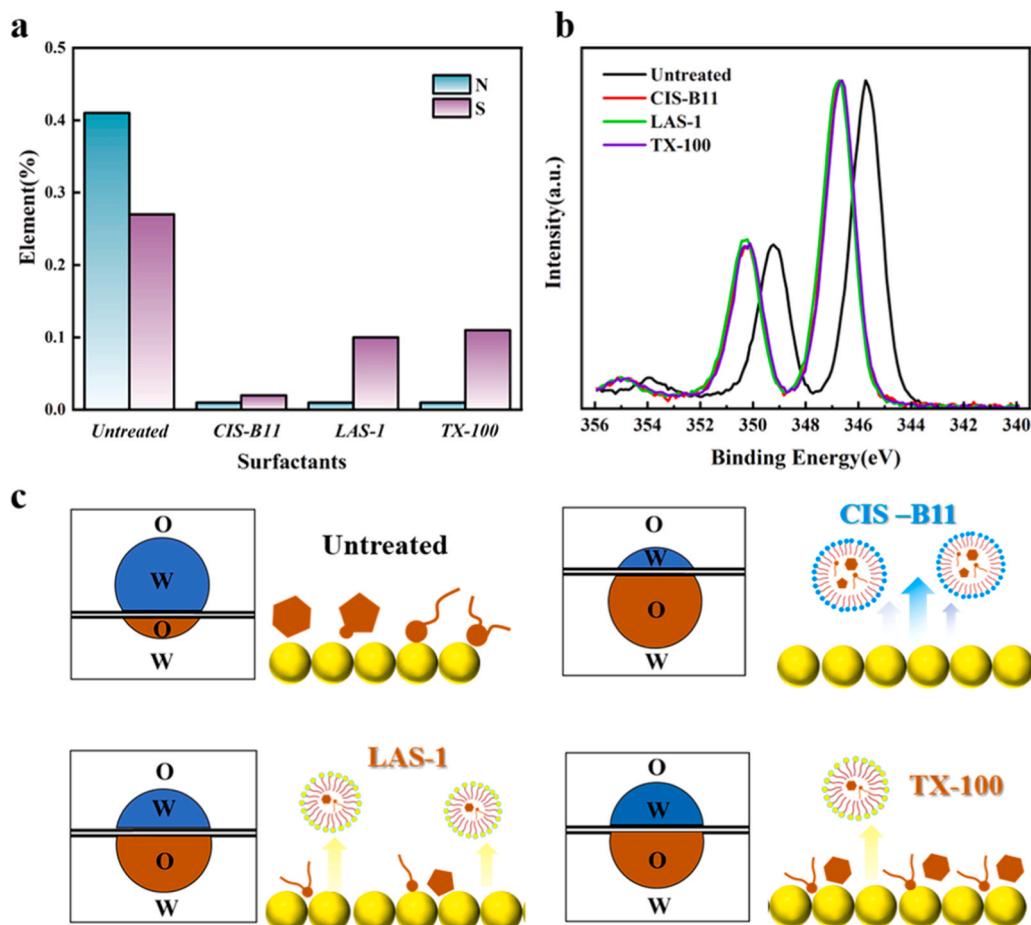


Fig. 4. (a) Variations of N and S elements on carbonate rock surface before and after surfactant modulation. (b) Electronic binding energy variations of characteristic Ca atom in carbonate rock before and after surfactant modulation. (c) Interfacial modulation mechanism of different surfactants in carbonate rock.

characteristic calcium (Ca) atoms was performed (Fig. 4b). Carbonate rock treated with surfactants exhibits distinct leftward shifts in Ca 2p binding energy compared to untreated rock, accompanied by increased electropositivity of Ca. The leftward shift in electron binding energy indicated the disruption of interactions between calcium (Ca) atoms and negatively charged polar molecules in crude oil, confirming the removal of crude oil from the carbonate rock surface. The removal of crude oil enhanced the electropositive character of the carbonate surface and led to a transition in interfacial wettability toward a more water-wetting state.

Integrated analysis of elemental variation and calcium (Ca) electron binding energy shift reveal that surfactant treatment effectively removed crude oil, eliminating organic groups originally coordinated with calcium (Ca) and consequently enhancing its electropositivity. Elemental and XPS data collectively confirm the removal of organic deposits by surfactant results in a fundamental alteration of interfacial property (Fig. 4c). The difference in interfacial property modulation capability may be attributed to variations in interaction forces between surfactants and crude oil. Compared to anionic and nonionic surfactants, cationic surfactant exhibits stronger binding capacity with negatively

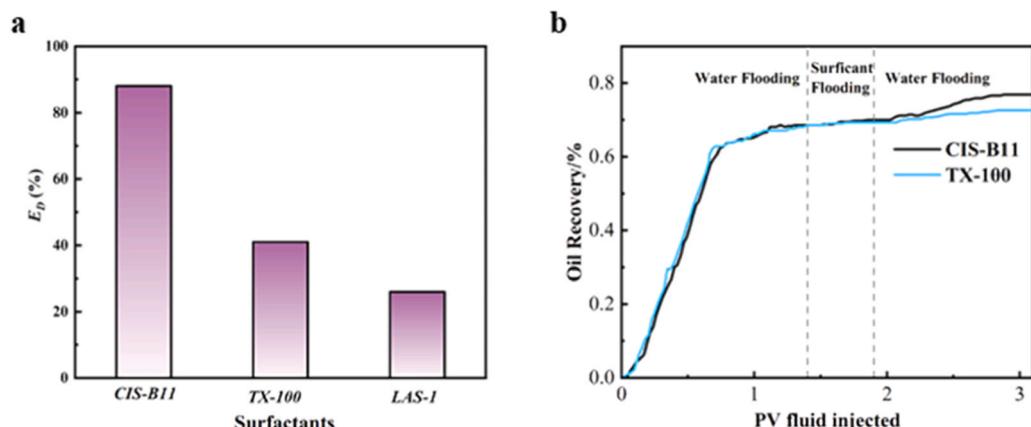


Fig. 5. (a) Displacement efficiency of different surfactants on carbonate rocks. (b) Effect of different surfactants on oil recovery in flooding experiments.

charged polar molecules in crude oil and more effectively remove crude oil from carbonate rock surface, resulting in superior interfacial property modulation capability.

For sandstone, crude oil is physically adsorbed onto the rock surface. Surfactant treatment facilitates the desorption of deposited crude oil from the solid surface, thereby enhancing interfacial hydrophilicity (Fig. S9). Anionic surfactant demonstrates superior capability in interfacial property modulation.

3.3. Displacement efficiency and core flooding evaluation

To verify the consistency between modulation effect of surfactant on carbonate rock interface and enhanced oil recovery, the displacement efficiency of rock treated by different surfactants was measured (Fig. 5a). Cationic CIS-B11 shows significantly higher displace efficiency (88 %) in carbonate rock compared to the anionic LAS-1 (26 %) and nonionic Tx-100 (41 %). This efficiency hierarchy directly corresponded to interfacial modulation capability, confirming that superior modulation capacity yields higher displacement efficiency. Sandstone exhibits same trend (Fig. S10).

To validate the practicality of the cationic surfactant CIS-B11 with optimal modulation efficiency under actual carbonate reservoir conditions (90°C, 200,000 mg/L salinity), the stability of CIS-B11 was systematically evaluated. The results (Fig. S11) demonstrate that the cationic surfactant CIS-B11 maintained phase stability and optical clarity without any precipitation or turbidity after 60 days under simulated reservoir conditions.

Fig. 5b presents the core flooding curves for CIS-B11 and TX-100. Initial waterflooding achieves 68.57 % oil recovery. Subsequent injection of 0.5 PV CIS-B11 increases oil recovery to 76.9 %, representing 8.33 % improvement. In contrast, 0.5 PV TX-100 injection yields only 72.6 % under identical conditions, corresponding to 4.03 % improvement.

While both surfactants exhibit comparable performance during surfactant flooding stage, CIS-B11 shows superior enhanced oil recovery effect during secondary waterflooding. This aligns with prior interfacial property analyses: CIS-B11 exhibits stronger carbonate interfacial modulation capability, driving the rock surface closer to the ideal water-wetting state, thereby achieving higher oil recovery.

4. Conclusion

The alteration of interfacial property during carbonate reservoir formation was simulated through crude oil saturated aging of calcite blocks. This process involved crude oil adsorption on rock surface, which transformed the surface from water-wetting to oil wet, with chemisorption occurring between crude oil and calcium in carbonate rock versus physisorption in sandstone. Surfactant achieves crude oil removal from carbonate rock surface by disrupting coordination between crude oil and calcium, and accomplish interfacial modulation from oil-wetting to water-wetting state. Cationic CIS-B11 demonstrates the strongest interfacial modulation performance for carbonate rock. The consistency between interfacial modulation capability and enhanced oil recovery was verified through oil removal experiments and core flooding tests. Cationic surfactant CIS-B11, which exhibited the most pronounced interfacial modulation effect on carbonate rock, demonstrates the highest displacement efficiency (88 %) and enhanced oil recovery rate (8.33 %). This study provides new insights into the formation of interfacial property in carbonate rock and the modulation mechanism of surfactant, thereby unlocking the production potential of carbonate reservoir.

CRedit authorship contribution statement

Cheng Ma: Writing – review & editing, Supervision. **Jianbin Huang:** Writing – review & editing, Supervision, Funding acquisition.

Xingyue Chen: Methodology. **Xinmin Song:** Methodology. **Jiaxian Qiu:** Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation. **Fang Wang:** Resources, Methodology, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2025.138826](https://doi.org/10.1016/j.colsurfa.2025.138826).

Data availability

Data will be made available on request.

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