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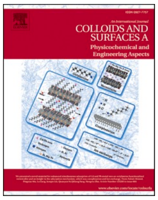


A mechanistic comparison of formate, acetate, and glycine as wettability modifiers for carbonate and shale formations

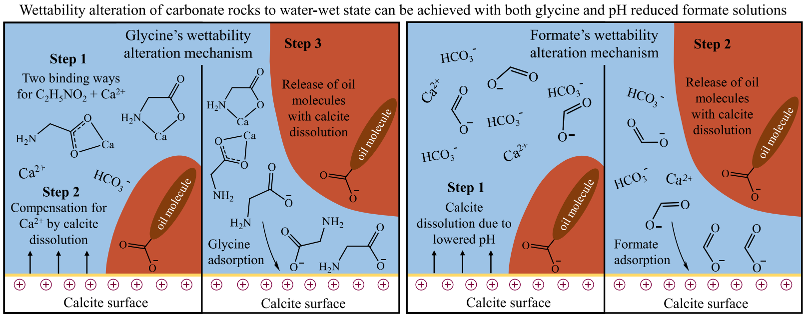
Ilgar Baghishov, Gayan A. Abeykoon, Mingyuan Wang, Oluwafemi Precious Oyenowo,
Francisco J. Argüelles-Vivas *, Ryosuke Okuno

Hildebrand Department of Petroleum and Geosystems Engineering, The University of Texas at Austin, 200 E. Dean Keeton Street, Stop C0300, Austin, TX 78712, USA

HIGHLIGHTS

- Formate, glycine and acetate were tested as wettability modifiers for oil recovery.
- The importance of amino group in glycine was investigated.
- The chelate effect makes glycine an effective wettability modifier.
- Calcite dissolution can trigger the wettability alteration by glycine and formate.

GRAPHICAL ABSTRACT



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ABSTRACT

Previous studies indicated the efficacy of the simplest amino acid, glycine, as a wettability modifier that enhances the imbibition of water in carbonate reservoirs. The objective of this research was to compare the performance of formate, acetate, and glycine as wettability modifiers for carbonate and shale formations. Formate and acetate were studied for the first time as novel wettability modifiers. Note that the aminomethyl and amino groups are the only structural differences between formate and glycine, and acetate and glycine, respectively. The experiments consisted of contact-angle measurements on oil-aged calcite and shale plates, and imbibition displacements (spontaneous and forced). The comparison among these additives was made with/without adding hydrogen chloride (HCl) for adjusting the pH of the solutions. Amott indexes of glycine and formate + HCl solutions were noticeably higher than the rest of the cases in the imbibition experiments. We found that formate can be very effective in altering the wettability of carbonate rocks to water-wet state when the pH of the solution is reduced. This indicates the synergy of pH adjustment and the attraction of formate to the rock surface, which resulted in an improvement of the oil recovery. Glycine showed a superior behavior as a wettability modifier in comparison to formate and acetate for all the experimental conditions of this study. This indicated that the amino group, in the presence of the carboxyl group, plays a key role in altering the rock wettability. We demonstrated that the ability of glycine to alter wettability comes from two factors: one is the chelate effect caused by the amino group as an electron donor in the presence of the carboxyl group. The chelate effect makes glycine

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Abbreviations: pI, Isoelectric point; pzc, Point of zero charge; pH, Measure of acidity; pK_a, Negative base-10 log of the acid dissociation constant; RB, Reservoir Brine; Oil1, Crude oil used with carbonates and calcite chips; Oil2, Crude oil used with Eagle Ford shale.

* Corresponding author.

E-mail address: fjarvi@utexas.edu (F.J. Argüelles-Vivas).

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entropically more favorable for binding to calcium cation in the brine, which triggers calcite dissolution, and/or attaching directly to the calcite surface. The other factor is the calcite dissolution induced by pH reduction, followed by the attraction of glycine to the rock surface.

Nomenclature

Symbols

L	Core length, m
k°_{rw}	Endpoint water relative permeability
N_{vc}	Capillary number
N_{RL}	Rapoport and Leas number
v	Interstitial velocity, m/s
u	Superficial velocity, m/s
$V_{o,SI}$	Oil volume produced by spontaneous imbibition, cm^3
$V_{o,FI}$	Oil volume produced by forced imbibition, cm^3
I_w	Amott index to water

Greek

θ	Oil/water contact angle, degrees
μ_o	Oil viscosity, Pa s
μ_w	Water viscosity, Pa s
σ	Water/oil interfacial tension, N/m

1. Introduction

Waterflooding in carbonate oil reservoirs is generally inefficient because the large contrast in permeability between the matrix and fracture results in channeling flow. Also, carbonate rocks tend to be oil wet, and therefore, spontaneous imbibition of water into the matrix from the fracture is not effective in oil recovery. A shift in wettability to a more water-wet state is expected to improve oil recovery in oil-wet carbonate reservoirs [1].

Interactions between rock minerals, brine, and oil affect the rock wettability, among other factors. Formation water (or brine) is the initial wetting phase in conventional oil reservoirs before the oil migration. After the oil migration, brine is still the wetting phase as long as the film of brine is stable [2]. When the stability of brine starts changing, the connection forms between rock surfaces and oil. This process is followed by the adsorption of surface-active components of oil, which results in the reduction of water-wetting or even switching the surface to oil-wet. It is possible to reverse the wettability from oil-wet to water-wet by improving thin brine stability or/and disconnecting adsorbed oil components from the surface of the rock [3].

A widely studied method for alteration of rock wettability is surfactant injection. Yao et al. provided a comprehensive review of wettability alteration using surfactants for carbonate reservoirs [4]. However, wettability alteration by surfactants is usually expected to occur with a reduction of interfacial tension between oleic and aqueous phases [5,6]. However, IFT should not reach an ultralow value (10^{-3} mN/m) in tight formations according to Alvarez et al. [7–9]. Kathel et al. also demonstrated that oil recovery was limited by ultralow IFT because of reduced surfactant imbibition rate [10].

Another wettability alteration method that gained popularity is low-salinity waterflooding (LSW) both for sandstone and carbonate reservoirs. Wettability alteration mechanisms in carbonate reservoirs during low salinity waterflooding were reviewed in detail by Sagbana et al. [11]. During the waterflooding process, low-salinity water can modify the wettability in carbonate rocks by changing their total charge and increasing the electric double layer of brine-rock and oil-brine interfaces [12]. Multivalent ions, such as CO_3^{2-}, SO_4^{2-}, Ca^{2+} and Mg^{2+}, are reported as potential determining ions, which control the charge of rock surfaces [13].

The effect of seawater on oil recovery especially in carbonate reservoirs was widely investigated by Austad's research group [14–16]. Based on spontaneous imbibition experiments using seawater, a change in rock wettability was observed in the presence of sulfate ions, which displaced naphthenic acids from carbonate rock surfaces. They also found that sulfate ions were aided by calcium and magnesium ions in the wettability alteration.

LSW has been evaluated by coreflooding experiments in the literature [17]. Results from sequentially injecting seawater and its diluted solution showed an incremental oil recovery factor of 0.18. The impact of ions was studied individually using surface potential experiments [18,19]. They demonstrated that the major ions that changed the wettability of carbonates were sulfate and calcium. Since surface potential did not entirely explain the oil improvement by LSW, Hiorth et al. [20] proposed calcite dissolution as one of the potential mechanisms for wettability alteration.

Chemicals other than surfactants have also been studied as wettability modifiers for carbonate reservoirs. Deng et al. [21] reviewed different wettability modifiers for carbonate rocks including, but not limited to, gemini surfactants, alkalis, and nanoparticles, which are low-cost and capable of reducing contact angle significantly. Wang et al. [22] evaluated an aqueous solution of 3-pentanone for enhanced oil recovery by wettability alteration. They performed a comprehensive analysis through contact angle, imbibition, and coreflooding experiments. Their results showed a marked improvement in oil recoveries with limestone cores after adding 3-pentanone to brine. Argüelles-Vivas et al. [23] presented a review of the studies related to 3-pentanone as a wettability modifier in tight formations and shales.

Amino acids have also been studied as another class of wettability modifiers. Lara Orozco et al. [24] explored the simplest amino acids and introduced glycine as an effective wettability modifier. Surfactants synthesized from amino acids were also studied as oil-recovery agents and for some other applications [25,26]. These amino acids contain the carboxylic (–COOH) and amine (–NH_2) groups within the same molecule. An important property of glycine is that its overall charge depends on the pH of the solution, as shown in Fig. 1. If the solution pH is higher than the isoelectric point (pI), which is 5.97 at room temperature, then glycine is negatively charged. Otherwise, glycine is positively charged. Glycine is effective when the solution pH is between its pI and point of zero charge (pzc) of calcite, as in Lara Orozco et al. [24] and the current paper.

The main goal of this research was to investigate the capability of carboxylate anions, specifically formate and acetate, to change the wettability of carbonate mineral surface from oil-wet to water-wet state. This was performed by comparing formate and acetate with glycine, a proven wettability modifier, through contact angle and imbibition experiments. The aminomethyl and amino groups are the only structural difference between formate and glycine, and acetate and glycine, respectively (Fig. 2). We also analyzed how these carboxylate anions could become more effective for wettability alteration under slightly lowered pH. A positive effect of a reduced pH on wettability alteration was also observed in low salinity water flooding [27,28]. The negative charge of formate and acetate ions may result in wettability alteration because of the interaction between positively charged calcite surfaces and the carboxyl group.

Inspired by the results of the comparative study, we also investigated the importance of the amino group of glycine for the rock wettability alteration and effective enhancement of water imbibition into carbonate rocks. The comparison among glycine, formate, and acetate was convenient for studying two possible mechanisms of wettability alteration by glycine. One is the chelate effect, which can occur with glycine only. The other is the synergy between calcite dissolution and the carboxyl group, which is expected to occur also with formate and acetate.

In what follows, Section 2 provides details about the materials used and experimental methods. Section 3 discusses and analyzes the experimental results. Finally, Section 4 provides the main conclusions from this research.

2. Materials and methods

The main experiments in this research consisted of contact angle measurements with calcite surfaces and Eagle Ford shale plates, and spontaneous and forced imbibition tests with Texas Cream Limestone core plugs.

2.1. Materials

Table 1 presents the properties of the dead crude oil sample used in the contact-angle experiments with calcite pieces and limestone cores. This oil is referred to as Oil1, and its reservoir temperature is 347 K. Table 2 shows the oil used in the contact-angle experiment on Eagle Ford shale. This oil is referred to as Oil2 and its reservoir temperature is 337 K. Reservoir brine (RB) was the same in all experiments as shown in Table 3, and its salinity is 68,722 mg/L. X-ray powder diffraction indicated that the Eagle Ford shale sample consisted of 75 % calcite, 14 % quartz, 4 % dolomite, 2 % kaolinite, 1 % K-spar, 1 % pyrite, and others. The Texas Cream Limestone cores consisted of 98 % calcite, 1 % pyrite, and other minerals in negligible amounts [23].

Glycine, acetate, and formate samples (Sigma-Aldrich) had a purity greater than 99 %. Glycine has a pI of 5.97 at room temperature [29]. Fig. 2 illustrates the molecular structure of glycine, acetate, and formate. The aqueous stability of all three chemicals was confirmed with RB at reservoir and room temperatures.

2.2. Contact angle experiments

Contact angle experiments were performed on calcite surfaces and Eagle Ford shale plates. Contact angle experiments with calcite focused on determining an optimal concentration of glycine, formate, and acetate while experiments on shale plates were performed to verify the efficacy of the solutions with another carbonate-rich rock. After cutting the plates in the appropriate sizes, they were polished with a diamond grinder to result in a smooth surface. Then, these calcite and shale plates were first aged for one day in RB, and then, they were placed in heavy crude oil for at least three weeks at 347 K until reaching oil-wet state.

The pH values of the chemical solutions were measured before and after the experiment. To test the impact of solution pH, contact angle experiments with calcite surfaces were performed not only with different concentrations of formate and acetate, but also with HCl added to reach the pH level of glycine.

The chemical solutions were made in glass chambers and placed in an oven at 363 K to degas them for at least one day. RB was made first by adding salts and adjusting the total mass of the solution to 1 kg with deionized water. Then, an appropriate amount of either glycine, formate, or acetate was added to reach the desired concentration. For solutions with HCl, HCl was added to solutions of formate and acetate at room temperature while stirring slowly. The final pH level was adjusted to correspond to the glycine solution at the same concentration. After aqueous solutions were prepared and degassed, they were placed in an oven at the desired reservoir temperature (347 K for calcite and 337 for Eagle Ford shale). Table 4 summarizes the aqueous solutions tested.

After being aged in heavy oil for at least 3 weeks, the calcite or shale pieces were retrieved, and the excess oil was removed from the surfaces carefully. To start the experiment, the rock pieces were immersed in the chambers containing the corresponding solutions and then oil droplets were placed on the bottom of the rock pieces. The chambers were put in the oven at reservoir temperature and images of the oil droplets were taken every day until equilibration. The second and the third oil droplets were placed on days 7 and 12, respectively. Then, images of the new oil droplets were taken until angles equilibrated. The equilibrium contact angles of the new oil droplets were smaller than the equilibrium contact angle of the first oil droplet indicating the change in wettability of the calcite surface. The setup for contact angle experiments is shown in Fig. 3. Contact angles were measured from photos with the on-screen protractor software.

A similar procedure was followed for another set of experiments with Eagle Ford shale plates. Five cases (5 wt% glycine, 5 wt% acetate, 5 wt% acetate + HCl, 5 wt% formate, and 5 wt% formate + HCl) were used to test the impact of HCl (pH adjustment) on the wettability alteration mechanism of formate and acetate. Only two oil droplets were placed on the bottom of shale plates (at days 0 and 3). There was no need for the third oil droplet because the contact angle change was already observed with the second oil droplet placed on day 3.

2.3. Spontaneous imbibition

Spontaneous imbibition tests were carried out with glycine, formate, and acetate. The impact of the solution pH was also tested for formate and acetate. The Amott cell used was approximately 15 cm in height and 5 cm in diameter as shown in Fig. 4. The Amott cell's neck was graduated, and the graduation was calibrated to the actual volume before starting the experiments.

The Texas Cream limestone core plugs used were 38 mm in diameter and 92 mm in length. Cores were evacuated with a vacuum pump for 30 min and then, brine was injected at a constant pressure of 689 kPa (100 psig) to saturate cores fully with brine. This was carried out under room temperature. Then, the porosity and permeability of the core plugs were measured with RB. The experimental setup consisted of two accumulators (RB and Oil1), one vacuum pump, one pump, one manual hydraulic pump to maintain the overburden, one Hassler-type core holder, one differential pressure gauge, and one oven.

Then, Oil1 was injected into the core at a constant rate of 60 cm^3/hour. This was performed under room temperature and without any backpressure; that is, the effluent side was open to the atmospheric pressure. After the oil breakthrough, the rate was increased to 100 cm^3/h to minimize the capillary end effect with a capillary number of approximately 2×10^{-5}. The oil injection continued until no brine was produced at the effluent, from which the residual water saturation, S_{wr}, was determined. Tables 5 and 6 summarize the rock properties for each core used in spontaneous and forced imbibition experiments. The

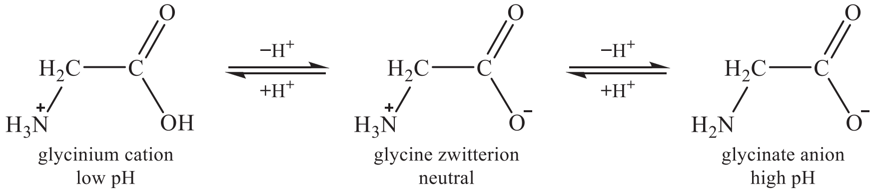


Fig. 1. Molecular structure of different forms of glycine.

measured rock properties were similar to those reported in the literature [30].

The four cores given in Table 5 were used for imbibition experiments with the following solutions: Reservoir Brine (RB), 5 wt% glycine in RB, 5 wt% acetate in RB, and 5 wt% formate in RB. To test the impact of the solution pH, the six cores given in Table 6 were used with the following solutions: RB, RB + HCl, 2.5 wt% glycine, 5 wt% formate + HCl, and 5 wt% acetate + HCl. The acetate + HCl was repeated for two experiments because the first attempt resulted in an unexpectedly small amount of oil recovery.

After being saturated with Oil1, the four cores given in Table 5 and the six cores given in Table 6 were placed in a glass chamber filled with Oil1 for 30 days. However, the former set of cores was aged at room temperature for 10 days and at 347 K for the rest of 30 days. The latter set of cores was aged at 347 K for the entire 30 days. The difference in the aging temperature affected the initial oil wetness for the two sets, as will be shown in Section 3.2. Therefore, the RB case was used as a control experiment for the two sets of cores given in Tables 5 and 6.

The solutions were placed in an oven at 363 K for one day for degassing and then, they were placed in the oven at 347 K (the experimental temperature). Oil-saturated cores were then introduced into the Amott cell. Immediately after that, an aqueous solution was poured carefully so that the bubble formation was avoided. Note that this Amott test was initiated with all materials heated at 347 K to avoid the thermal expansion/shrinkage of the oil. Atmospheric pressure was maintained inside of the cell throughout the experiment. Finally, oil recovery was monitored every day.

2.4. *Forced imbibition*

The Amott cell was cooled down after the spontaneous imbibition experiment and then, oil and brine (or other solution) were recovered from the cells using a glass pipette and their volumes were measured. The core was retrieved from the Amott cell and placed immediately in a core holder for forced imbibition.

Fig. 5 shows the experimental set-up for forced imbibition. The experiment was performed at 347 K. There was no backpressure; that is, the effluent side was open to the atmospheric pressure during the experiment. The corresponding solution for each case was injected at a constant flow rate of 100 cm^3/hr. The flow rate was increased to 300 cm^3/hr after no more oil was produced, to minimize the capillary end effect. Produced fluids were collected in vials to calculate oil recovery.

Results were used to estimate the Amott index to water I_w as follows [31]:

$$I_w = \frac{V_{o,SI}}{V_{o,SI} + V_{o,FI}}, \tag{1}$$

where $V_{o,SI}$ and $V_{o,FI}$ are the oil volumes recovered by the spontaneous imbibition and forced imbibition experiments, respectively.

The rate for the forced imbibition experiment was chosen similarly to the core saturation procedure. The rate was set to give a capillary number of 2×10^{-5}. The equation for capillary number N_{vc} used in this research is as follows:

$$N_{vc} = \frac{v\mu_w}{k_{rw}^{\circ}\sigma\cos\theta} \quad , \tag{2}$$

where v is interstitial velocity, μ_w is water viscosity, k_{rw}° is endpoint water relative permeability, σ is water/oil interfacial tension, and θ is oil/water contact angle. It was assumed that $k_{rw}^{\circ}\sigma\cos\theta = 1 mN/m$, as given commonly in the literature for water-wet media [32].

The increased injection rate for minimizing the capillary end effect was based on a Rapoport and Leas number (N_{RL}) of 2.5 cp-cm^2/min or greater. This value was recommended by Lake et al. [30]. N_{RL} in [cp •

Table 1
Properties of crude oil "Oil1" used in the contact angle experiments with calcite and in the imbibition experiments.

Molecular weight, g/mol		210
Density, kg/m^3		878 (at 293 K)
		849.6 (at 347 K)
Viscosity, cP		2.6 (at 347 K)
SARA, wt%	Saturates	71.6
	Aromatics	24.8
	Resins	3.0
	Asphaltenes (pentane insoluble)	< 0.1

Table 2
Properties of crude oil "Oil2" used in the contact angle experiments with shale plates.

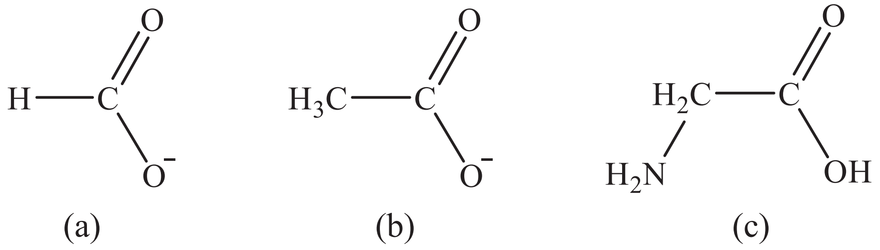
Molecular weight, g/mol		239
Density, kg/m^3		821.3 (at 295 K)
Viscosity, cP		1.09 (at 338 K)
SARA, wt%	Saturates	86.1
	Aromatics	9.8
	Resins	< 4.3
	Asphaltenes (pentane insoluble)	< 0.1

Table 3
Composition of reservoir brine (RB) used in this research.

Cations	ppm	Anions	ppm
Na^+	25,170	Cl^-	41,756
K^+	210	SO_4^{2-}	108
Ca^{2+}	1292		
Mg^{2+}	187		

Table 4
Summary of solutions tested in contact angle experiments with calcite.

Solution name	Solution	Concentrations in RB (wt%)
RB	Reservoir Brine	–
RB + HCl	pH adjusted Reservoir Brine	–
Glycine	Glycine	0.5, 1, 2.5, 5
Formate	Sodium Formate	0.5, 1, 2.5, 5
Acetate	Sodium Acetate	0.5, 1, 2.5, 5
Formate + HCl	pH adjusted Sodium Formate	0.5, 1, 2.5, 5
Acetate + HCl	pH adjusted Sodium Acetate	0.5, 1, 2.5, 5



(a) (b) (c)

Fig. 2. Molecular structure of chemicals used in this research: (a) formate anion, (b) acetate anion, and (c) glycine.

Fig. 3. Contact angle setup used in the research.

cm^2/min] is given as follows [33]:

$$N_{RL} = Lu\mu_o, \tag{3}$$

where L is core length, u is superficial velocity, and μ_o is water viscosity.

3. Results and discussion

This section discusses the experimental results from contact angle and imbibition experiments. The contact angle experiments consisted of two sets: calcite and Eagle Ford shale pieces. The imbibition experiments consisted of spontaneous and forced imbibition.

3.1. *Contact angle experiment*

The overall charge of glycine depends on the pH of the solution (Fig. 1). An overall negative charge occurs if the pH is greater than the pI of glycine, i.e., 5.97. Calcite's pzc is reported to be 8.8 [34]. Therefore, glycine is expected to alter the wettability if the solution pH is between 5.97 and 8.8, as explained and confirmed by Lara Orozco et al. [24]. Table 7 summarizes the solution pH measured before and after the contact angle experiments for all the cases. This table shows that the pH values for all glycine cases were within the pH window for wettability alteration. The acetate and formate solutions were basic, unlike the glycine solutions.

Photos of oil droplets from contact angle experiments with calcite surfaces in RB and different concentrations of glycine, acetate, and formate (with and without HCl) are shown in Figs. 6 through 9. Meanwhile, Figs. 10 through 13 present the graphs of measured contact angle values for the same experiments. The y-axis represents equilibrium contact angles and the x-axis is the day when this oil droplet was placed under the rock piece. For example, the contact angle reported on day 7 is the equilibrium contact angle for the oil droplet placed on day 7 (not necessarily a contact angle measured at day 7, equilibrium can be reached on anytime form day 8–10). A significant reduction in contact angle was observed over time for most glycine cases. For example, it reached nearly 40° at the glycine concentrations of 2.5 and 5 wt% (Fig. 7). However, the RB and acetate cases without HCl did not significantly reduce the contact angle. The formate cases without HCl resulted in a slightly water-wet state with contact angles of approximately 80° (Fig. 9).

Table 7 indicates that the initial solution pH of glycine was smaller than that of formate and acetate. With the lowered pH, calcite dissolution reaction might have occurred for the glycine cases, as also shown by Lara Orozco et al. [24]. Calcite dissolution may cause absorbed polar components to be released from the rock surface [35]. Then, wettability alteration is possible if negatively charged ions are attracted by the

Fig. 4. Amott cell used in the research. An oil aged core was placed in the Amott cell and then the solution to be tested was poured slowly into the Amott cell. All components were at reservoir temperature (347 K) while setting up the experiment to avoid fluid expansion. The produced oil was accumulated at the top and its volume was measured from the grating available on the Amott cell.

Table 5
Petrophysical properties of the first set of Texas Cream limestone cores.

Core number	Porosity, %	Absolute permeability (with brine), mD	Residual water saturation, %
1	30.1	14.47	29.5
2	30.3	17.11	29.2
3	28.3	11.12	27.0
4	29.2	16.08	30.4

Table 6
Petrophysical properties of the second set of Texas Cream limestone cores.

Core number	Porosity, %	Absolute permeability (with brine), mD	Residual water saturation, %
1	27.1	12.4	28.1
2	27.7	14.4	29.2
3	28.0	14.0	29.2
4	28.9	15.7	28.9
5	27.9	13.5	28.7
6	31.1	18.7	31.1

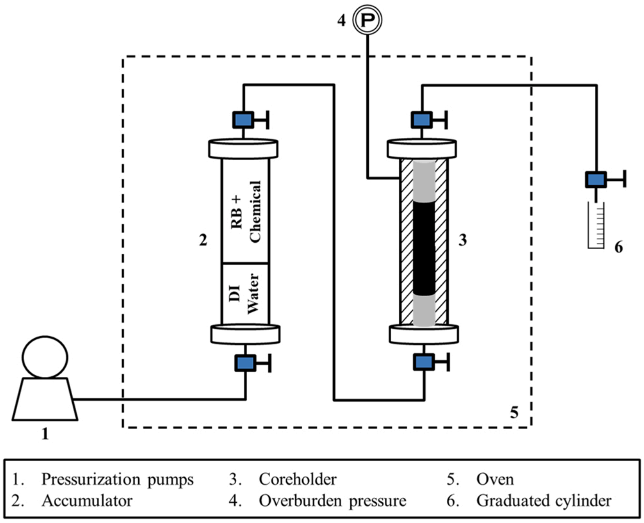


Fig. 5. Diagram of the experimental set-up used for forced imbibition.

Table 7
pH measurements before and after the contact angle experiments with calcite (at room temperature).

	0 wt%	0.5 wt%	1 wt%	2.5 wt%	5 wt%	Solution
Before	6.82					RB
After	7.78					
Before	6.08					RB + HCl
After	7.89					
Before		6.68	6.42	6.24	6.10	Glycine
After		7.94	7.73	7.53	7.62	
Before		8.15	8.31	8.44	8.64	Acetate
After		8.04	7.89	7.87	7.85	
Before		8.07	7.96	8.12	8.11	Formate
After		8.26	8.22	8.05	7.96	
Before		6.67	6.40	6.23	6.10	Acetate + HCl
After		7.66	7.50	7.28	7.11	
Before		6.71	6.39	6.23	6.10	Formate + HCl
After		7.80	7.83	7.87	8.07	

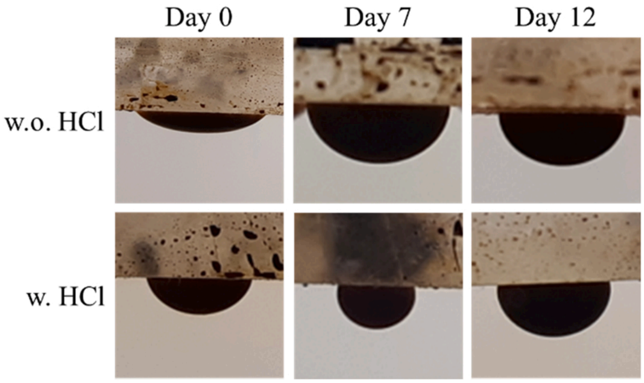


Fig. 6. Photos of oil droplets from RB contact angle experiments with calcite.

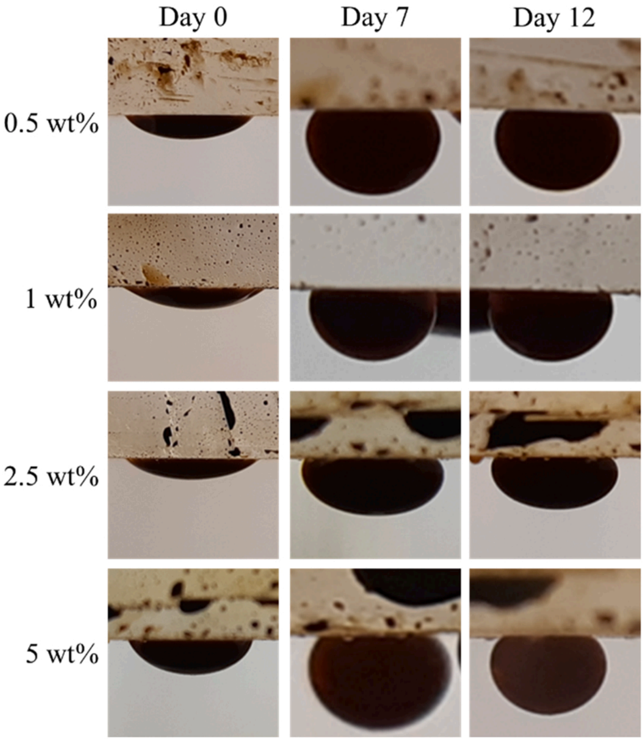


Fig. 7. Photos of oil droplets from glycine contact angle experiments with calcite.

positively charged calcite surface, as is the case with glycine at pH between its pI and the surface pzc.

We further hypothesized that wettability alteration to water-wet state could be enhanced when formate or acetate anions were present in the solution, after calcite dissolution occurred. This is because formate and acetate anions could be attached to a positively charged calcite surface once calcite dissolution resulted in a release of oil molecules from the calcite surface. Table 7 shows that the cases of acetate and formate with HCl had pH values close to the pH of glycine solution at the same concentration. Reducing the solution pH for the formate and acetate cases enhanced the wettability alteration as shown in Figs. 10 through 13. In particular, a significant improvement was observed with formate; the contact angle was reduced to 50 – 60° with the formate cases with HCl. Even though the lowered pH improved the RB case as well, the contact angle was still around 80°. This observation confirms that it is essential to have negatively charged ions (e.g., glycine with pH value above its pI and carboxylate anions) along with calcite dissolution for a greater wettability alteration.

As mentioned in Section 2.2, five cases (5 wt% glycine, 5 wt% acetate, 5 wt% acetate + HCl, 5 wt% formate, and 5 wt% formate + HCl) were tested with Eagle Ford shale rock surfaces in the contact angle experiment as shown in Fig. 14. This was done to reconfirm that addition

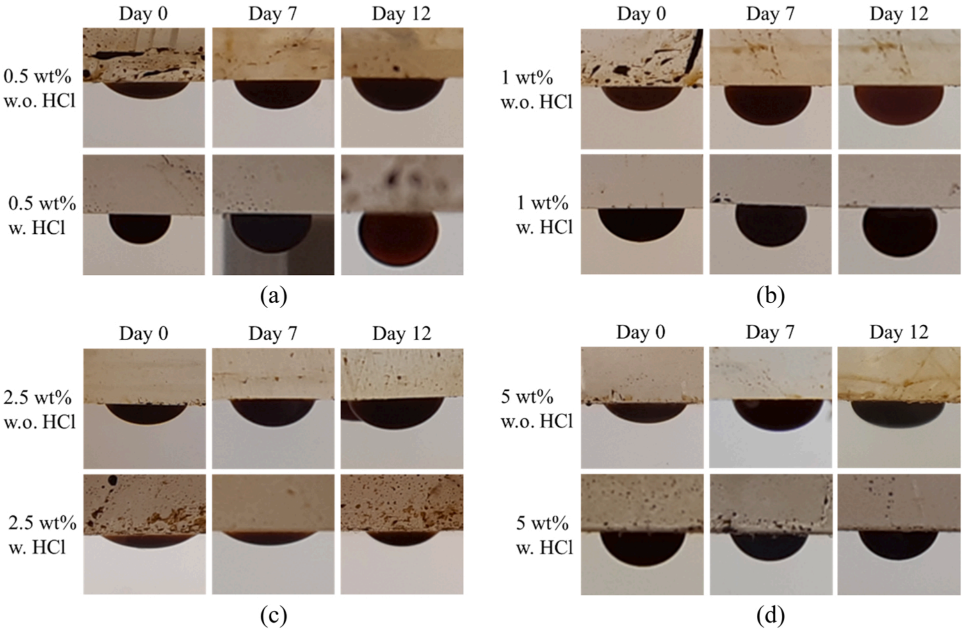


Fig. 8. Photos of oil droplets from acetate contact angle experiments with calcite: (a) 0.5 wt% acetate solution, (b) 1 wt% acetate solution, (c) 2.5 wt% acetate solution, and (d) 5 wt% acetate solution.

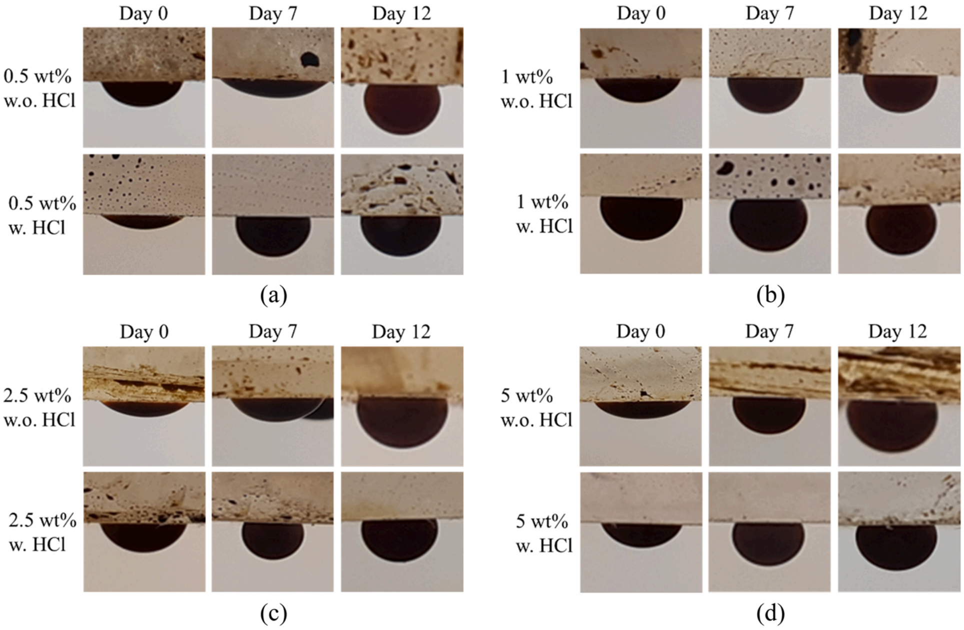


Fig. 9. Photos of oil droplets from formate contact angle experiments with calcite: (a) 0.5 wt% formate solution, (b) 1 wt% formate solution, (c) 2.5 wt% formate solution, and (d) 5 wt% formate solution.

of HCl improves the wettability alteration of formate and acetate with other calcite-bearing rocks like shales. In contrast to previous contact angle figures, x-axis in Fig. 14 represents the day when contact angle was measured. First oil droplet was placed on day 0 and then it equilibrated the next day (day 1), following this, the second droplet was placed on day 3 and then equilibrated on day 4. Essentially, contact angle measurements from day 0 and 1 correspond to the first oil droplet, and measurements from day 3 and 4 correspond to the second oil droplet. The figure shows that the final contact angles of formate and acetate reduced to approximately 60° with HCl and to about 80° without HCl. Reducing the pH of the carboxylate solution (formate and acetate) made the wettability alteration strength similar to that of glycine, which also resulted in a contact angle reduction to 60°.

3.2. Spontaneous and forced imbibition experiments

The contact angle experiment indicated wettability alteration; however, further testing of the additives at a core scale was performed to verify the observed wettability alteration. As described in Section 2.3, the first set of experiments used RB, 5 wt% glycine, 5 wt% acetate, and 5 wt% formate with no HCl for the four cores given in Table 5. The second set of experiments used RB, RB + HCl, 2.5 wt% glycine, 5 wt% formate + HCl, and 5 wt% acetate + HCl for the six cores given in Table 6. These concentrations were chosen because they performed best

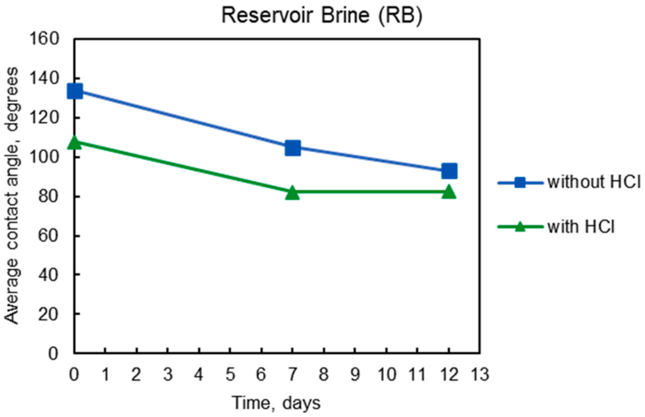


Fig. 10. Results of RB contact angle experiments with calcite.

for glycine and formate. In the case of acetate, 5 wt% was also selected since this concentration reduced the contact angle on shale plates similarly to the rest of the chemicals.

IFT values between Oil1 and four solutions were also measured (Table 8) to verify that the oil recovery improvement was because of wettability alteration, not a reduced IFT. Even though the IFT values for carboxylate solutions/oil1 are slightly lower than those for RB and glycine solutions, this small difference does not lead to a reduction of capillary pressure by an order of magnitude.

In addition to rock properties, it is important to consider the units used for oil recovery calculations as was shown by Li et al. [36] and verified by Argüelles-Vivas et al. [30]. Therefore, Figs. 15a–18a show the oil recovery in the units of Original Oil In Place (OOIP), and Figs. 15b–18b display the oil recovery in terms of the Pore Volume (PV).

Fig. 15 shows the oil recovery factors from the spontaneous imbibition experiments. The differences between the core properties require the oil recovery data to be corrected with the Leverett factor, $\sqrt{k/\varphi}$, for a fair comparison [37,38]. Each experiment was terminated when a plateau was reached. Glycine outperformed the other cases, reaching a recovery factor of 32 % in spontaneous imbibition. The oil recovery factors of acetate and formate were 20 % and 23 %, respectively, which is close to RB recovery of 22 % (Fig. 11a).

The forced imbibition experiments were carried out immediately after the spontaneous imbibition. Fig. 16 shows oil recoveries during the forced imbibition experiments with respect to the pore volumes of injection. Even though final oil recoveries were similar between the cases, early-time responses (e.g., 1 PV) showed that glycine was superior to the other chemicals. Table 9 shows Amott indexes to water, and the water saturation at the beginning of the experiments, after spontaneous imbibition, and after forced imbibition, for the first set of cores (see Table 5). The Amott index to water for glycine was significantly higher than those for RB, formate, and acetate, indicating that the glycine case became more water wet. These results are consistent with the contact angle results presented in the previous section.

Fig. 17 presents the oil recoveries from spontaneous imbibition for the second set of experiments. As expected from the contact angle experiment, the wettability alteration by formate was enhanced by the reduced pH. The formate solution with HCl was comparable to 2.5 wt% glycine, which recovered more than twice greater than RB or RB + HCl. This observation reconfirmed the synergy of the solution pH effect and the negatively charged carboxyl group. However, this synergy was not observed in two duplicated experiments for the acetate case. The first

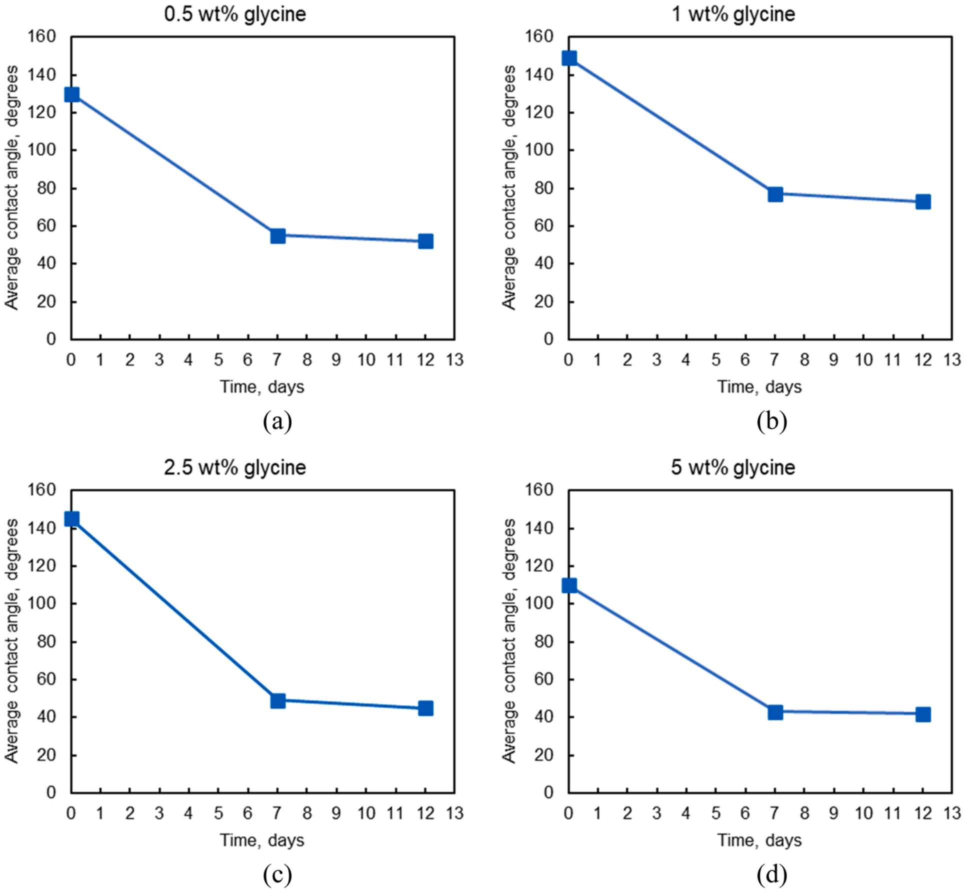


Fig. 11. Results of glycine contact angle experiment with calcite: (a) 0.5 wt% glycine solution, (b) 1 wt% glycine solution, (c) 2.5 wt% glycine solution, and (d) 5 wt % glycine solution.

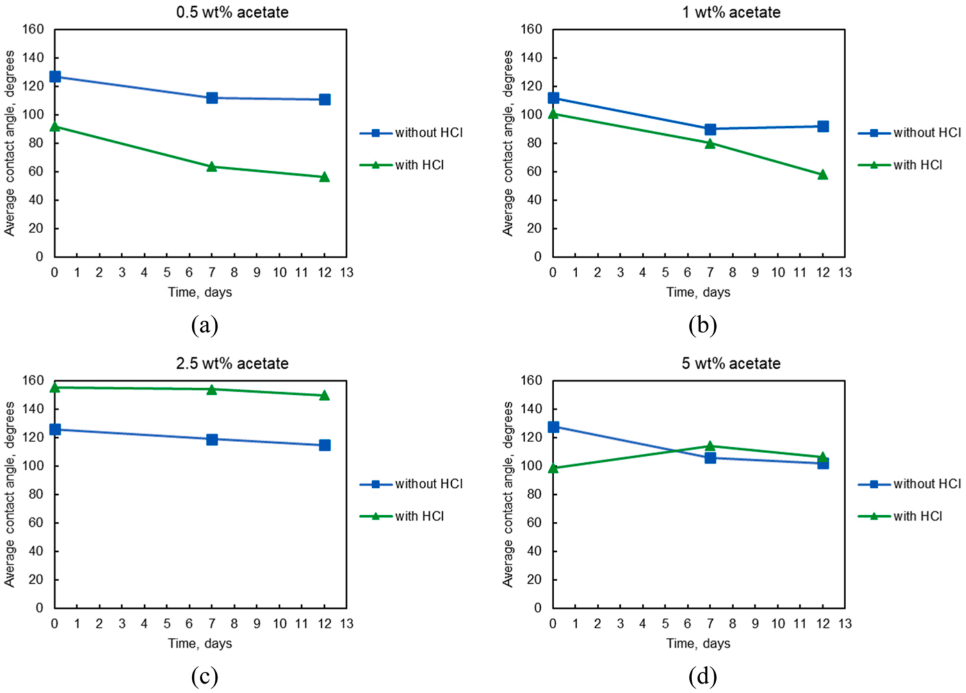


Fig. 12. Results of acetate contact angle experiment with calcite: (a) 0.5 wt% acetate solution, (b) 1 wt% acetate solution, (c) 2.5 wt% acetate solution and (d) 5 wt% acetate solution.

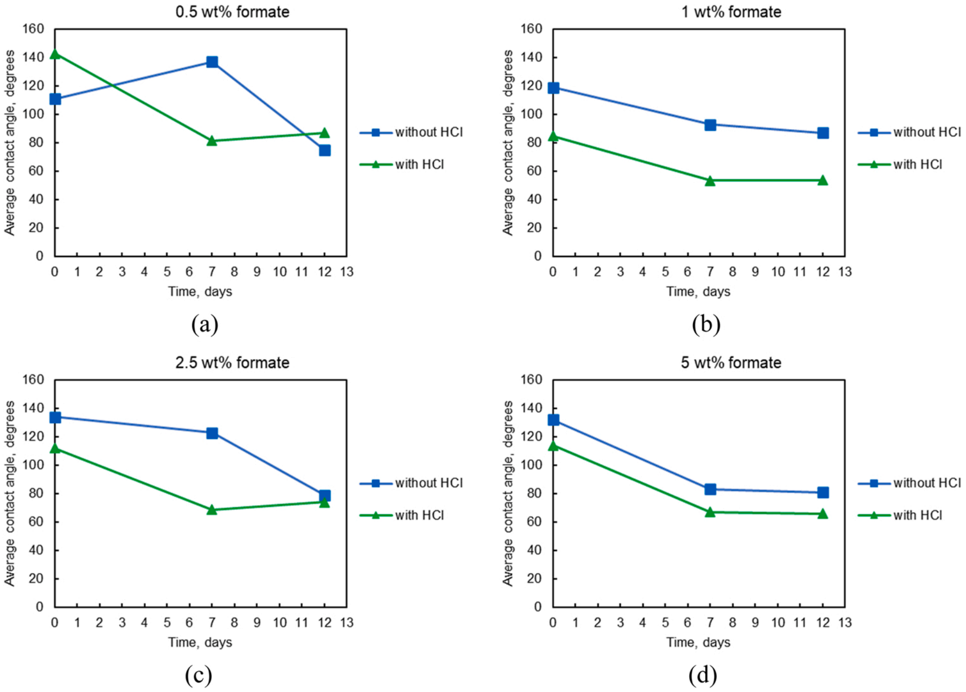


Fig. 13. Results of formate contact angle experiment with calcite: (a) 0.5 wt% formate solution, (b) 1 wt% formate solution, (c) 2.5 wt% formate solution and (d) 5 wt% formate solution.

attempt of 5 wt% acetate + HCl resulted in a similar amount of oil to RB, and the second attempt resulted in a slightly smaller amount of oil recovery. The lower oil recovery from core #6 of the second attempt can be because of the longer aging time, which resulted in a stronger oil-wet state. These two experiments do not indicate that acetate will be an effective wettability modifier for enhanced oil recovery.

Fig. 18 shows the oil recoveries from forced imbibition for the second set of experiments. Since the core used for the first attempt of 5 wt% of acetate was discarded before reaching a plateau in spontaneous imbibition, it was not possible to continue with forced imbibition. Therefore, Fig. 14 illustrates the results of only the second attempt for acetate. Table 10 shows Amott indexes to water, and the water saturation at the beginning of the experiments, after spontaneous imbibition, and after forced imbibition, for the second set of cores (see Table 6). The 2.5 wt% glycine case has the greatest value of Amott index and is slightly greater than the 5 wt% formate + HCl case. Comparison between “RB + HCl”

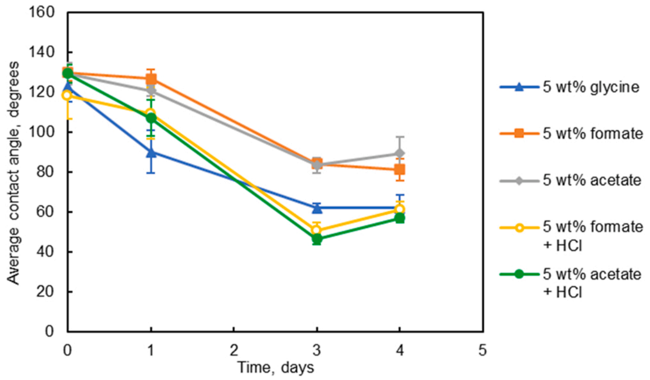
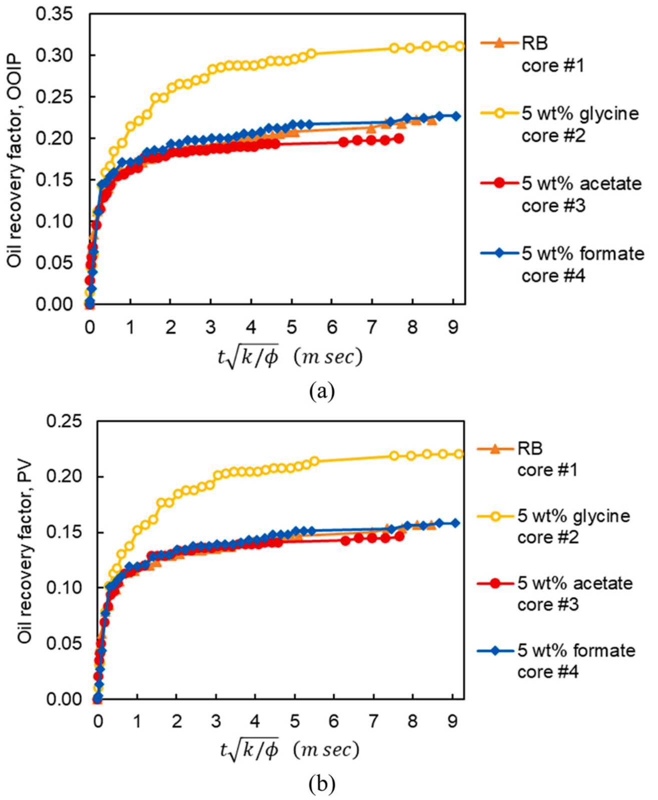


Fig. 14. Results of contact angle experiments with Eagle Ford shale plates.

Table 8
IFT measurements between Oil1 and four brine solutions.

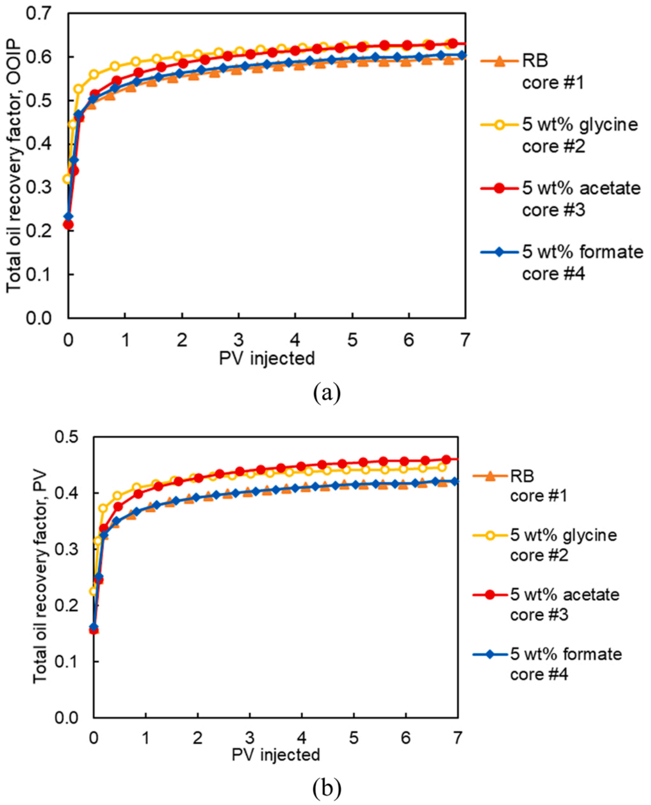
Sample	IFT (mN/m)	Standard deviation
Oil1 and RB	8.388	0.167
Oil1 and 5 wt% glycine	8.079	0.211
Oil1 and 5 wt% acetate + HCl	6.730	0.120
Oil1 and 5 wt% formate + HCl	7.137	0.115



(a)

(b)

Fig. 15. Results of the first set of spontaneous imbibition experiments with Texas Cream limestone cores: (a) oil recovery in terms of OOIP, (b) oil recovery in terms of pore volume (PV).



(a)

(b)

Fig. 16. Results of the first set of forced imbibition experiments with Texas Cream limestone cores: (a) oil recovery in terms of OOIP, (b) oil recovery in terms of PV.

Table 9
Final core saturation after the forced imbibition experiment along with the Amott index to water (first set of cores).

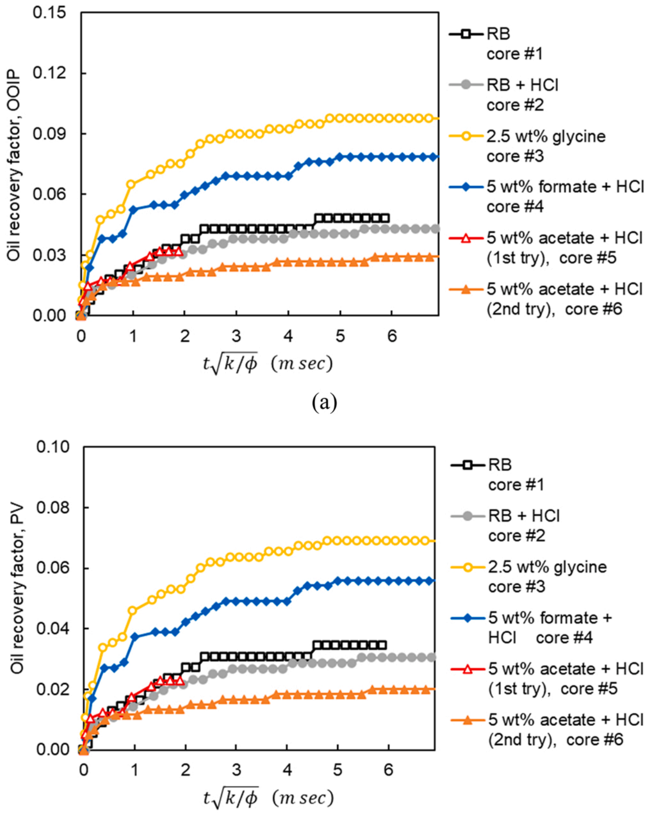
	S_{wr}, %	S_w after spontaneous imbibition, %	S_w after forced imbibition (1-S_{or}), %	Amott index to water
RB	29.5	45.3	71.6	0.377
5 wt% glycine	29.2	51.7	73.8	0.505
5 wt% formate	30.4	46.7	72.5	0.387
5 wt% acetate	27.0	42.7	73.3	0.339

and “5 % formate + HCl” demonstrates the importance of the carboxyl group in the wettability alteration (i.e., calcite dissolution alone was not effective). Furthermore, the comparison between “5 wt% formate” and “5 wt% formate + HCl” shows the importance of the addition of HCl (i.e., the presence of carboxylate anions alone was not effective). It was hypothesized that the carboxyl group interacted with the rock surfaces after calcite dissolution by the reduced solution pH as explained in Section 3.1. However, it is not entirely clear why the addition of HCl did not enhance the acetate case. Further investigation is necessary to understand the details of the binding of ions on the rock surface at different scales, for example, ab initio, molecular dynamics, and surface complexation modeling.

3.3. Discussion

Results show that glycine was more effective than formate and acetate with/without controlling the solution pH. It is reasonable to attribute this to the amino group of glycine, which is the structural difference between glycine and acetate, in the presence of the carboxyl group. That is, other than the negatively charged carboxylate side, the electron-donating amino group of glycine plays a key role in oil recovery improvement via wettability alteration.

This electron-donating group of the glycine makes it a chelating ligand, or more specifically, a bidentate ligand that can interact with



(a)

(b)

Fig. 17. Results of the second set of spontaneous imbibition experiments with Texas Cream limestone cores: (a) oil recovery in terms of OOIP, (b) oil recovery in terms of PV.

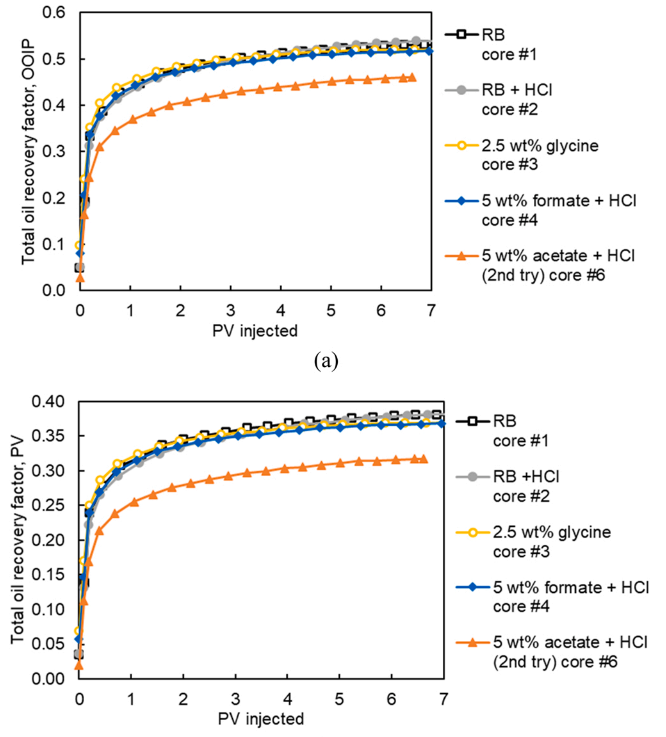
calcium cation in the solution and/or calcite surface with two functional groups in the molecule. Chelating ligands have a higher affinity for metal ions than analogous monodentate ligands, which are only capable of interacting with one functional group [39].

The chelate property of glycine that makes it possible to bind to calcite via two mechanisms was also verified by Tang et al. [40]. Fig. 19 presents two ways for calcium cation to bind to glycine [40]. We hypothesize that glycine can bind to calcium and magnesium cations in brine, and then the rock surface tends to compensate for these sequestered cations to restore equilibrium. This process will cause calcite dissolution, resulting in the wettability alteration towards a more water-wet state, since oil molecules are released from the calcite surfaces as the cations are released. This hypothesis was firstly tested by Mahmoud and Abdelgawad [41] for chelating agents such as ethylenediaminetetraacetic acid (EDTA), hydroxyethylethylenediaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA). These chelating agents were able to enhance oil recovery better than low salinity brine [41]. Moreover, Fazary et al. demonstrated the positive global stability of calcium-glycine complex and reported that a maximum complex formation was achieved in slightly acidic media (pH values from 5 to 6) as in our experiments with a pH of 6.1 [42].

Furthermore, we hypothesize that glycine is entropically more favorable to getting attached to the calcite surface than naphthenic acids from oil, which are only capable of interacting with calcite surfaces via the carboxyl group. This mechanism is illustrated in Fig. 20. This higher affinity of calcite surface towards glycine due to the chelate effect compared to carboxylate ions can be one of the reasons why glycine alters wettability more significantly than the carboxylate ions tested.

In order to test the hypothesis, we measured zeta potential of glycine and formate solutions with calcite pieces as shown in Table 11. First, measurements with NaCl brine demonstrated an increase in zeta potential when formate and glycine was added to the brine which can be attributed to the adsorption of these chemicals to the surface of calcite. The zeta potential for 5 wt% glycine in NaCl brine with calcite increased to 1.24 mV with respect to − 15.68 mV for NaCl brine with calcite. The increase in zeta potential of 5 wt% glycine was more significant than that of 4.5 wt% formate, which increased to − 3.35 mV. This observation confirms our hypothesis that glycine is more favorable to get adsorbed than formate due to the chelate effect. As expected for complex brines, zeta potential measurements with RB had large standard deviations; therefore, those experimental results are not considered in the explanation here.

To reconfirm the adsorption of formate to the surface of a rock, we performed a coreflooding experiment where 0.865 PVs of 1.09 wt% formate solution in RB was injected into a Texas Cream Limestone (TCL) core, and followed by injection of 3.89 PVs of RB. Tables 12 and 13 present the core properties and experimental conditions respectively.



(a)

(b)

Fig. 18. Results of the second set of forced imbibition experiments with Texas Cream limestone cores: (a) oil recovery in terms of OOIP, (b) oil recovery in terms of PV.

Table 10
Final core saturation after the forced imbibition experiment along with the Amott index to water (second set of cores).

	S_{wr}, %	S_w after spontaneous imbibition, %	S_w after forced imbibition (1-S_{or}), %	Amott index to water
RB	28.1	31.6	66.6	0.090
RB + HCl	29.2	32.8	67.6	0.094
2.5 wt% glycine	29.2	36.0	66.5	0.184
5 wt% formate + HCl	28.9	34.6	65.3	0.158
5 wt% acetate + HCl	31.1	33.1	62.7	0.063

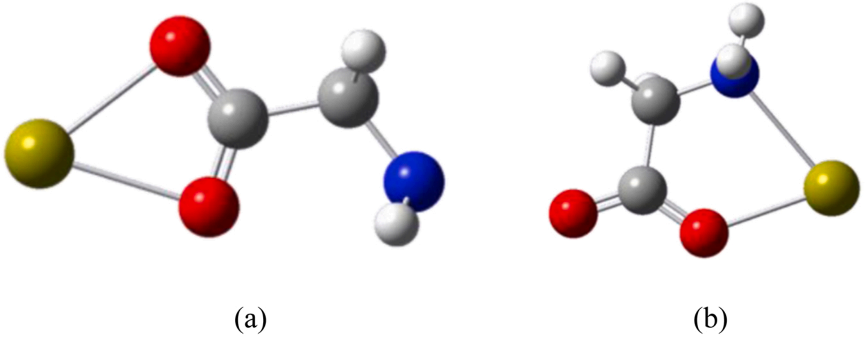


Fig. 19. Two possible mechanisms of calcium binding to Glycine: (a) Calcium binding to carboxyl group, (b) Calcium binding to carboxyl group and amino group. Calcium is shown in green, carbon in grey, nitrogen in blue, hydrogen in white, and oxygen in red. The schematics were taken from Tang et al. [35].

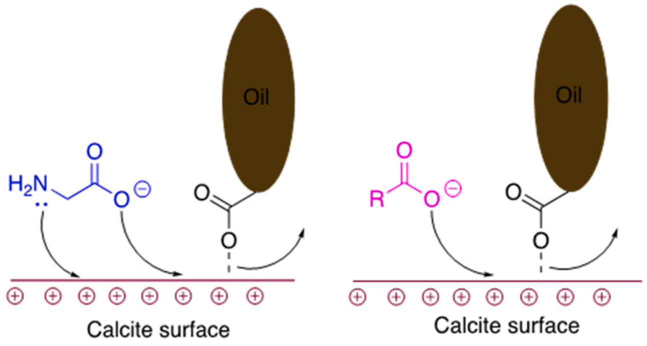


Fig. 20. Illustration of amino group's role in superiority of glycine (on the left) to adsorb on calcite surface over carboxylate anions (on the right) because of the chelate effect. Glycine is attracted to calcite surface via both amino and carboxyl group which makes it entropically more favorable than carboxylate anions, such as formate or acetate, which only interact via carboxyl group.

Table 11
Zeta potential measurements.

	Mean (mV)	Standard Deviation (mV)
NaCl brine	-15.68	2.00
NaCl brine + 5 wt% glycine	-3.35	5.05
NaCl brine + 4.5 wt% formate	1.24	6.36
RB	-3.18	7.27
RB + 5 wt% glycine	-4.40	5.26
RB + 4.5 wt% formate	2.44	4.70

Fig. 21 illustrates the concentration of formate in effluent with respect to the pore volumes injected. It was found that 0.11 mg of formate was adsorbed per gram of TCL, as shown in Table 14. In comparison to anionic surfactant 2-EH-4PO-15EO with 0.334 mg/g adsorption in TCL, formate's adsorption is lower; however, it is comparable to the adsorption of 3-pentanone with 0.10 mg/g of adsorption in TCL [23].

To recap, results in this research indicate the efficacy of formate in wettability alteration under slightly reduced pH due to a synergy between calcite dissolution and attraction of carboxyl group to calcite surface. The results also showed the importance of the amino group for the wettability alteration by glycine, which is clearly more effective than acetate with/without pH adjustment. We attribute this primarily to the presence of amino group along with the carboxyl group making glycine a chelating ligand.

Table 12
Properties of the cores used in formate adsorption experiments.

Core	Texas Cream Limestone
D (inches)	0.86
L (inches)	6.93
φ (%)	32.3
k (mD)	79.2
Pore Volume (mL)	21.43
Weight of core (g)	126.48

Table 13
Conditions for formate adsorption experiments.

Temperature, °C	23.1
Pressure, psi	atmospheric
Flow rate, cc/hr	5.41
Swi, %	100
Injection scheme	0.865 PVI of Formate in RB 3.89 PVI of RB
Concentration of formate in injection brine, wt%	1.09
Volume of chemical slug, mL	18.545 (0.865PVI)

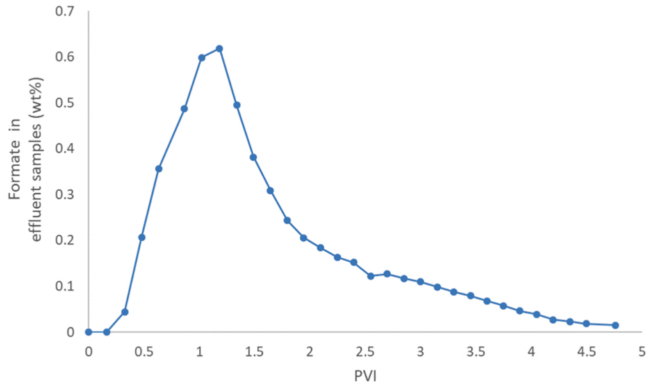


Fig. 21. Formate concentration in effluent samples collected during the injection of formate in reservoir brine slug, followed by the injection of reservoir brine into a Texas Cream Limestone (TCL) core.

Table 14
Results of formate adsorption experiments.

Texas Cream Limestone	Mass of Formate injected (g)	0.2023
	Mass of Formate produced (g)	0.1882
	Mass of Formate adsorbed (g)	0.0141
	Mass of Formate adsorbed (mg/g of TCL core)	0.1113

4. Conclusions

The main objectives of this research were to investigate, for the first time, formate and acetate anions as wettability modifiers for carbonate rocks and to clarify the importance of the amino group of glycine.

Results from contact-angle and imbibition experiments with these three chemicals were compared and analyzed. The main conclusions are as follows:

- The contact angle experiments with oil-aged calcite surfaces and with Eagle Ford shale plates showed significant superiority of glycine to acetate and slight superiority to formate. This was also reconfirmed by the subsequent Amott tests with Texas Cream limestone cores, clarifying the importance of the amino group of glycine.
- We hypothesize that the key role of the amino group to alter wettability comes from the chelate effect, which occurs with glycine, not with formate and acetate. In addition to the carboxyl group, the amino group acts as a binding functional group (electron donor group) for the chelate effect to occur. This makes the glycine a bidentate ligand and entropically more favorable to get attached to calcium cation, triggering additional calcite dissolution, and/or to get directly attached to the calcite surface with both amino and carboxyl groups. This property of glycine will result in a wettability alteration greater than that of acetate or formate, which are only capable of interacting via the carboxyl group.
- Acetate and formate became more effective in reducing the contact angle of oil droplets on the shale plates when the solution pH was lowered to the same level as glycine. RB with the reduced pH was not effective in reducing the contact angle of oil droplets on calcite surfaces. This indicates the importance of the synergy between the carboxyl group and the solution pH. In comparison to acetate, formate was better in its ability to alter the wettability.
- The imbibition tests showed the synergy of calcite dissolution and the attraction to the rock surface with glycine (via the chelate effect) and formate (via the carboxyl group). Amott indexes of glycine and formate + HCl solutions were noticeably higher than those of the other cases. It is not clear why the acetate cases were not enhanced by the addition of HCl in the imbibition tests, which suggests that further investigation is needed.
- The points mentioned above suggest using formate species at reduced pH for wettability alteration of oil-wet carbonate rocks and thus for enhanced oil recovery because of its ability to enhance the water imbibition.

CRediT authorship contribution statement

Ilgar Baghishov: Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **Gayan A. Abeykoon:** Methodology, Validation, Formal analysis, Investigation, Writing – review & editing, Visualization. **Mingyuan Wang:** Methodology, Investigation. **Oluwafemi Precious Oyenowo:** Investigation. **Francisco J. Argüelles-Vivas:** Methodology, Validation, Formal analysis, Investigation, Writing – review & editing, Visualization. **Ryosuke Okuno:** Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

Data Availability

Data will be made available on request.

Acknowledgments

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References

[1] G.J. Hirasaki, D.L. Zhang, Surface chemistry of oil recovery from fractured, oil-wet, carbonate formations, SPE J. 9 (2004) 151–162, https://doi.org/10.2118/88365-PA.
[2] J.S. Buckley, K. Takamura, N.R. Morrow, Influence of electrical surface charges on the wetting properties of crude oils, SPE Reserv. Eng. 4 (1989) 332–340, https://doi.org/10.2118/16964-PA.
[3] G.J. Hirasaki, Wettability: fundamentals and surface forces, SPE Form. Eval. 6 (1991) 217–226, https://doi.org/10.2118/17367-PA.
[4] Y. Yao, M. Wei, W. Kang, A review of wettability alteration using surfactants in carbonate reservoirs, Adv. Colloid Interface Sci. 294 (2021), 102477, https://doi.org/10.1016/j.cis.2021.102477.
[5] A. Seethepalli, B. Adibhatla, K.K. Mohanty, Wettability Alteration During Surfactant Flooding of Carbonate Reservoirs, Paper presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, April 2004. ⟨https://doi.org/10.2118/89423-MS⟩.
[6] D.L. Zhang, S. Liu, M. Puerto, C.A. Miller, G.J. Hirasaki, Wettability alteration and spontaneous imbibition in oil-wet carbonate formations, J. Pet. Sci. Eng. 52 (2006) 213–226, https://doi.org/10.1016/j.petrol.2006.03.009.
[7] J.O. Alvarez, D.S. Schechter, Wettability alteration and spontaneous imbibition in unconventional liquid reservoirs by surfactant additives, SPE Reserv. Eval. Eng. 20 (2017) 107–117, https://doi.org/10.2118/177057-PA.
[8] J.O. Alvarez, F.D. Tovar, D.S. Schechter, Improving oil recovery in the wolfcamp reservoir by soaking/flowback production schedule with surfactant additives, SPE Reserv. Eval. Eng. 21 (2018) 1083–1096, https://doi.org/10.2118/187483-PA.
[9] J.O. Alvarez, I.W.R. Saputra, D.S. Schechter, The impact of surfactant imbibition and adsorption for improving oil recovery in the wolfcamp and eagle ford reservoirs, SPE J. 23 (2018) 2103–2117, https://doi.org/10.2118/187176-PA.
[10] P. Kathel, K.K. Mohanty, Wettability alteration in a tight oil reservoir, Energy Fuels 27 (2013) 6460–6468, https://doi.org/10.1021/ef4012752.
[11] P.I. Sagbana, K. Sarkodie, W.A. Nkrumah, A critical review of carbonate reservoir wettability modification during low salinity waterflooding, Petroleum (2022), https://doi.org/10.1016/j.petlm.2022.01.006.
[12] D. Al Mahrouqi, J. Vinogradov, M.D. Jackson, Zeta potential of artificial and natural calcite in aqueous solution, Adv. Colloid Interface Sci. 240 (2017) 60–76, https://doi.org/10.1016/j.cis.2016.12.006.
[13] H. Mahani, A.L. Keya, S. Berg, R. Nasralla, Electrokinetics of carbonate/brine interface in low-salinity waterflooding: effect of brine salinity, composition, rock type, and pH on f-potential and a surface-complexation model, SPE J. 22 (2017) 53–68, https://doi.org/10.2118/181745-PA.
[14] E.J. Hognesen, S. Strand, T. Austad, Waterflooding of Preferential Oil-Wet Carbonates: Oil Recovery Related to Reservoir Temperature and Brine Composition. Presented at the SPE Europec/EAGE Annual Conference, 2005, Madrid, Spain, 13–16 June. SPE-94166-MS. ⟨https://doi.org/10.2118/94166-MS⟩.
[15] S. Strand, E.J. Høgnesen, T. Austad, Wettability alteration of carbonates—effects of potential determining ions (Ca2+ and SO42−) and temperature, Colloids Surf. A: Physicochem. Eng. Asp. 275 (2006) 1–10, https://doi.org/10.1016/j.colsurfa.2005.10.061.
[16] P. Zhang, M.T. Tweheyo, T. Austad, Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: impact of the potential determining ions Ca2+, Mg2+, and SO42−, Colloids Surf. A: Physicochem. Eng. Asp. 301 (2007) 199–208, https://doi.org/10.1016/j.colsurfa.2006.12.058.
[17] A.A. Yousef, S.H. Al-Saleh, A. Al-Kaabi, M.S. Al-Jawfi, Laboratory investigation of the impact of injection-water salinity and ionic content on oil recovery from carbonate reservoirs, SPE Reserv. Eval. Eng. 14 (2011) 578–593, https://doi.org/10.2118/137634-PA.
[18] M.B. Alotaibi, A.A. Yousef, The role of individual and combined ions in waterflooding carbonate reservoirs: electrokinetic study, SPE Reserv. Eval. Eng. 20 (2017) 77–86, https://doi.org/10.2118/177983-PA.
[19] S.C. Ayirala, M.E. Saleh, S.M. Enezi, A.A. Al-Yousef, Effect of salinity and water ions on electrokinetic interactions in carbonate reservoirs cores at elevated temperatures, SPE Reserv. Eval. Eng. 21 (2018) 733–746, https://doi.org/10.2118/189444-PA.
[20] A. Hiorth, L.M. Cathles, M.V. Madland, The impact of pore water chemistry on carbonate surface charge and oil wettability, Transp. Porous Media 85 (2010) 1–21, https://doi.org/10.1007/s11242-010-9543-6.
[21] X. Deng, M.S. Kamal, S. Patil, S.M.S. Hussain, X. Zhou, A review on wettability alteration in carbonate rocks: wettability modifiers, Energy Fuels 34 (2020) 31–54, https://doi.org/10.1021/acs.energyfuels.9b03409.
[22] M. Wang, G.A. Abeykoon, F.J. Arguelles-Vivas, R. Okuno, Ketone solvent as a wettability modifier for improved oil recovery from oil-wet porous media, Fuel 258 (2019), 116195, https://doi.org/10.1016/j.fuel.2019.116195.
[23] F.J. Argüelles-Vivas, G.A. Abeykoon, R. Okuno, Wettability modifiers for enhanced oil recovery from tight and shale reservoirs, in: R.G. Moghanloo (Ed.), Unconventional Shale Gas Development, Elsevier Inc., Cambridge, 2022, pp. 345–392.
[24] R.A. Lara Orozco, G.A. Abeykoon, M. Wang, F.J. Argüelles-Vivas, R. Okuno, L. W. Lake, S.C. Ayirala, A.M. AlSofi, Amino acid as a novel wettability modifier for enhanced waterflooding in carbonate reservoirs, SPE Reserv. Eval. Eng. 23 (2020) 741–757, https://doi.org/10.2118/195907-PA.

[25] D.B. Tripathy, A. Mishra, J. Clark, T. Farmer, Synthesis, chemistry, physicochemical properties and industrial applications of amino acid surfactants: a review, Comptes Rendus Chim. 21 (2018) 112–130, https://doi.org/10.1016/j.crci.2017.11.005.

[26] M. Madani, G. Zargar, M.A. Takassi, A. Daryasafar, D.A. Wood, Z. Zhang, Fundamental investigation of an environmentally-friendly surfactant agent for chemical enhanced oil recovery, Fuel 238 (2019) 186–197, https://doi.org/10.1016/j.fuel.2018.10.105.

[27] A. Sari, Y. Chen, Q. Xie, A. Saeedi, Low salinity water flooding in high acidic oil reservoirs: Impact of pH on wettability of carbonate reservoirs, J. Mol. Liq. 281 (2019) 444–450, https://doi.org/10.1016/j.molliq.2019.02.081.

[28] Q. Xie, A. Sari, W. Pu, Y. Chen, P.V. Brady, N.A. Maskari, A. Saeedi, pH effect on wettability of oil/brine/carbonate system: Implications for low salinity water flooding, J. Pet. Sci. Eng. 168 (2018) 419–425, https://doi.org/10.1016/j.petrol.2018.05.015.

[29] K. Karty. Organic Chemistry: Principles and Mechanisms, second ed., W.W. Norton & Company, New York, 2018.

[30] F.J. Argüelles-Vivas, M. Wang, G.A. Abeykoon, R. Okuno, Oil recovery from fractured porous media with/without initial water saturation by using 3-pentanone and its aqueous solution, Fuel 276 (2020), 118031, https://doi.org/10.1016/j.fuel.2020.118031.

[31] E. Amott, Observations relating to the wettability of porous rock, Trans. AIME 219 (1959) 156–162, https://doi.org/10.2118/1167-G.

[32] L.W. Lake, R. Johns, W.R. Rossen, G.A. Pope. Fundamentals of Enhanced Oil Recovery, second ed., Society of Petroleum Engineers, Richardson, 2014.

[33] L.A. Rapoport, W.J. Leas, Properties of linear waterfloods, J. Pet. Technol. 5 (1953) 139–148, https://doi.org/10.2118/213-G.

[34] F. Heberling, T.P. Trainor, J. Lützenkirchen, P. Eng, M.A. Denecke, D. Bosbach, Structure and reactivity of the calcite–water interface, J. Colloid Interface Sci. 354 (2011) 843–857, https://doi.org/10.1016/j.jcis.2010.10.047.

[35] S. Chen, K. Kristiansen, D. Seo, N.A. Cadirov, H.A. Dobbs, Y. Kaufman, A. M. Schrader, R.C. Andresen Eguiluz, M.B. Alotaibi, S.C. Ayirala, J.R. Boles, A. A. Yousef, J.N. Israelachviliet, Time-dependent physicochemical changes of carbonate surfaces from smartwater (diluted seawater) flooding processes for improved oil recovery, Langmuir 35 (2018) 41–50, https://doi.org/10.1021/acs.langmuir.8b02711.

[36] K. Li, K. Chow, R.N. Horne, Influence of initial water saturation on recovery by spontaneous imbibition in gas/water/rock systems and the calculation of relative permeability, SPE Reserv. Eval. Eng. 9 (2006) 295–301, https://doi.org/10.2118/99329-PA.

[37] M.C. Leverett, Capillary behavior in porous solids, Trans. Soc. Pet. Eng. 142 (1941) 152–169, https://doi.org/10.2118/941152-G.

[38] G. Mason, N.R. Morrow, Developments in spontaneous imbibition and possibilities for future work, J. Pet. Sci. Eng. 110 (2013) 268–293, https://doi.org/10.1016/j.petrol.2013.08.018.

[39] The Chelate Effect (and Macrocycle Effect). 〈https://chem.libretexts.org/@go/page/200888〉 (Accessed 13 December 2021).

[40] N. Tang, L.H. Skibsted, Calcium binding to amino acids and small glycine peptides in aqueous solution: toward peptide design for better calcium bioavailability, J. Agric. Food Chem. 64 (2016) 4376–4389, https://doi.org/10.1021/acs.jafc.6b01534.

[41] M.A. Mahmoud, K.Z. Abdelgawad, Chelating-agent enhanced oil recovery for sandstone and carbonate reservoirs, SPE J. 20 (2015) 483–495, https://doi.org/10.2118/172183-PA.

[42] A.E. Fazary, A.M. Ramadan, Stability constants and complex formation equilibria between iron, calcium, and zinc metal ions with vitamin B9 and glycine, Complex Met. 1 (2014) 139–148, https://doi.org/10.1080/2164232X.2014.941115.