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Article

Study of Wettability Alteration of Hydrophobic Carbonate Rock by Surfactant-Containing Chelating Agent Solutions

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Abstract: Chelating agents' application for well stimulation is gaining more and more interest, as they can perform under harsh conditions. However, the mutual influence of surfactants and chelating agents on the wettability alteration of hydrophobic carbonate rock under conditions of high-temperature well stimulation is relatively unexplored. This paper aims to study interfacial processes on the surface of hydrophobic rock in the presence of the EDTA-based chelating agent and surfactants of different classes. Cationic (cetyltrimethylammonium bromide, CTAB, and cetylpyridinium bromide, CPB), anionic (sodium dodecyl sulfate, SDS), and amhoteric (alkyldimethyl aminooxide, AO) surfactants were studied. Wettability alteration of model hydrophobic rock was studied under conditions specific to well stimulation. It was shown that chelating agent (CA) alone and its mixture with SDS could not lead to sufficient wettability alteration. CTAB, CPB, and AO were able to change the wettability effectively. A synergistic effect between CA and these surfactants was observed and a possible mechanism was proposed. AO was selected as the most promising surfactant. The influence of surfactant on the CA's dissolution capacity towards carbonate rock was investigated; dissolution capacity strongly depends on wettability alteration. Finally, the effect of CA, AO, and their mixture on the wettability of aged reservoir rock was studied and the absence of negative effects was proven.

Keywords: wettability alteration; surfactant; chelating agent; EDTA; aminooxide; dissolution capacity; hydrophobic rock; carbonate

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1. Introduction

Constantly growing energy demand is one of the features of the 21st century. As hydrocarbons are still the main source of energy, new technological solutions to increase gas and oil recovery with maximal profit are highly required. Different unconventional sources, such as shales, oil sands, and hydrates are widely studied; however, about 70% of world oil reserves are located in carbonate reservoirs [1,2]. These reservoirs are still problematic for hydrocarbon recovery. Two key features of carbonate reservoirs are their heterogeneity and oil-wetness.

Carbonate rocks have two main constituents: low-permeable matrix, occupying most of the reservoir, and dissolution structures, such as fractures, caverns, and vugs. Such a variety of void space types leads to high scattering of porosity values even for the rock samples of the same reservoir [3]. The absolute and relative permeability of carbonate rocks are determined primarily by dissolution structures. For instance, the presence of a fracture changes the shape of relative permeability curves [4], narrowing the range of mobile oil saturation and decreasing the recovery factor upon water flooding. This shift in petrophysical properties leads to oil displacement primarily from fractures with early water breakthrough [5], with the rock matrix being unswept. The final result is low oil recovery values [6]. The problem is aggravated in tight carbonate rocks, i.e., having matrix permeability less than 0.1 mD [7], as oil flow constrictions become more pronounced. These constrictions are narrow pore throats [8] and the oil-wetness of pore walls. Pore size distribution is difficult to change; however, the wettability state of the carbonate rock can be controlled.

Bare carbonate rock is considered hydrophilic; however, its surface, which has been in contact with crude oil for millions of years, has changed its state towards hydrophobic or intermediate-wet. The surface alteration mechanism is very complex and includes several fluid-rock interaction types: polar interactions, surface precipitation, acid-base interactions, and ion binding [9]. The presence, content, and chemical nature of oil polar constituents, such as asphaltenes, resins, and naphthenic acids, as well as the brine salinity and ionic composition [10,11] determine the wettability state of the rock. Carbonate rock adsorbs the highest amount of asphaltenes [12,13]. The reason for such a high activity is the presence of weakly basic Ca-OH groups, which dissociate in water and react with polar groups of asphaltenes [14]. The presence of water film, which can always be found in the reservoir, enhances adsorption of polar compounds on the carbonate, as opposed to silicates [15]. First-principles and molecular dynamics calculations also demonstrate the role of asphaltene–resin and asphaltene–asphaltene clustering on the carbonate's surface [16,17]. All these phenomena lead to the hydrophobicity of carbonate rocks [18] which results in some negative consequences.

Hydrophobicity of the rock's surface leads to the oil sticking to the pore walls and corners. Heterogeneous small-radius pores, which are typical for carbonate's matrix, retain oil. Negative values of contact angle cosine lead to negative capillary pressure at the oil–water interface in pores, which makes the pore unswept by water during waterflooding [19,20]. All these factors result in the alteration of relative permeability curves, which is well described by several researchers [21,22]. Generally, oil-wetness leads to lower oil permeability at a given saturation, a higher value of residual oil saturation, and an intersection point shift to higher water saturation values. Thus, the wettability of oil-containing carbonate rock should be altered to the water-wet state. However, in gas reservoirs, a hydrophobic or gas-wetting state in the near well-bore zone is expected [23,24] to reduce liquid mobility.

Wettability alteration is usually achieved by using surface active agents (surfactants). A huge number of papers are devoted to surfactant-assisted wettability alteration. An excellent review of recent works was given by Isah et al. [25]. Cationic surfactants are known to cause the highest degree of wettability alteration. The possible mechanism includes ionic pairing between positively charged ionic headgroup and negatively charged carboxylic groups of adsorbed oil compounds with its following desorption [26]. Desorbed oil compounds are then solubilized in surfactant's micelles, and this process does not allow such compounds to adsorb again [27]. However, surfactants themselves can also adsorb on the rock surface and cause wettability alteration to both hydrophobic or hydrophilic state, depending on the type of layer which is formed on the surface [28,29]. Therefore, the process of surfactant-induced wettability alteration is very complex and requires thorough investigation for each specific case.

Chelating agents (CA) are a novel class of reagents, which has recently been investigated as promising EOR and well-stimulation reagents. These chemicals also alter wettability of carbonate minerals at moderate or high temperatures [30,31]. The positive effect of CAs on oil recovery was demonstrated at the core scale several times [32,33]. Calcium or magnesium ions leaching from the surface are believed to be the reason for wettability alteration by CAs [34]. Therefore, the surface of the carbonate becomes more negatively charged, which leads to the spontaneous desorption of negatively charged oil constituents. The presence of surfactants, such as erucamidopropylbetaine [35,36] or ethoxylated quaternary ammonium Gemini surfactant [37,38], enhanced wettability alteration by CAs.

Application of CAs as well-stimulation fluids is based on their ability to dissolve carbonate minerals, which are usually insoluble in water by surface complexation [39]. CAs were proposed for the stimulation of high-temperature wells [40], which are problematic for the use of conventional HCl-containing fluids. Low corrosivity, low reaction rate, and a good compatibility with crude oil ensured the applicability of CAs.

It should be noted that dynamic wettability alteration, i.e., desorption of oil components from pore walls during treatment, and eventual water-wetness play a crucial role in well stimulation effectiveness [41]. The effect of hydrochloric acid on carbonate rock wettability is widely known [42]; however, the wettability alteration of hydrophobic carbonate rock by surfactant-containing solutions of CAs has not been studied thoroughly.

As most studies are focused on CAs' application for the EOR, duration of experiments is on the order of several days or even months, whereas a residence time of acid during the normal well stimulation is about 3–6 h [43]. In addition, core samples are usually aged in dead crude oil, which is unique for every field, therefore a unique wettability state occurs in every study. Ambient conditions, which are the best choice for routine experiments, do not represent well conditions properly. All these circumstances hinder comparison of results obtained by different researchers and their application for the development of CAs-based well stimulation fluids.

This paper aims to explore the wettability alteration of hydrophobic carbonate rock by surfactant-containing CA-based fluids. Model carbonate rock was chosen to draw the main tendencies and eliminate the influence of reservoir rock and oil properties. Samples were treated with surfactant-containing solutions under ambient and harsh reservoir conditions. We studied cationic, amphoteric, and anionic surfactants in the absence and presence of the CA, as well as the CA alone. Surfactant concentration was chosen after interfacial tension (IFT) measurements. Wettability alteration before and after the rock treatment was assessed by the means of contact angle measurement and Washburn capillary rise. The influence of surfactant type, treatment conditions, and the presence of the CA on the wettability alteration were revealed. We selected the most promising surfactant and assessed its influence on the dissolution capacity of the CA towards hydrophobic carbonate rock. Finally, dolomitic reservoir rock, aged in crude oil, was treated with the CA-surfactant composition to check if there are any negative effects in the presence of natural oil compounds.

2. Materials and Methods

2.1. Materials

Disodium EDTA (99.2%), NaOH (99%), citric acid (99%), stearic acid (70%), and sodium dodecyl sulfate (SDS, 99.5%) were purchased at Rushim, Moscow, Russia. Decane, toluene, heptane ("pure" grade) and normal octane ("reference" grade) were purchased at Komponent-Reaktiv, Moscow, Russia.

Cetyltrimethylammonium bromide (CTAB, 70%) was purchased from Shanghai Wandefa Trade Co., Shangai, China. Cetylpyridinium bromide (CPB) was supplied by Chemstore, Moscow, Russia. Alkyldimethylamine oxide (AO) with a chain length of 12–18 (30%) was supplied by NIIPAV, Vologodonsk, Russia. All the surfactants were used without further purification. Molecular structures of surfactants are shown in Figure 1.

Iceland spar samples were purchased from Sisterstone, China. 10 × 10 × 10 cm rock samples were cut into slices with 1 cm thickness, and slices were polished and dipped into 4% HCl until gas bubbling stopped. Marble powder with particles size of 0.2–0.5 mm was purchased from Rushim. The powder was treated with 4% HCl the same way as the Iceland spar. XRD showed that both rock samples consisted of 99%+ calcite.

A rock sample from one of the Russian oilfields consisted of dolomite (96.8%), quartz (1.3%), and calcite (1.9%). The rock sample was disintegrated with a grinding mill and sieved, and a fraction of 0.125–0.500 mm was separated and aged in crude oil [44]. The properties of the crude oil are shown in Table 1.

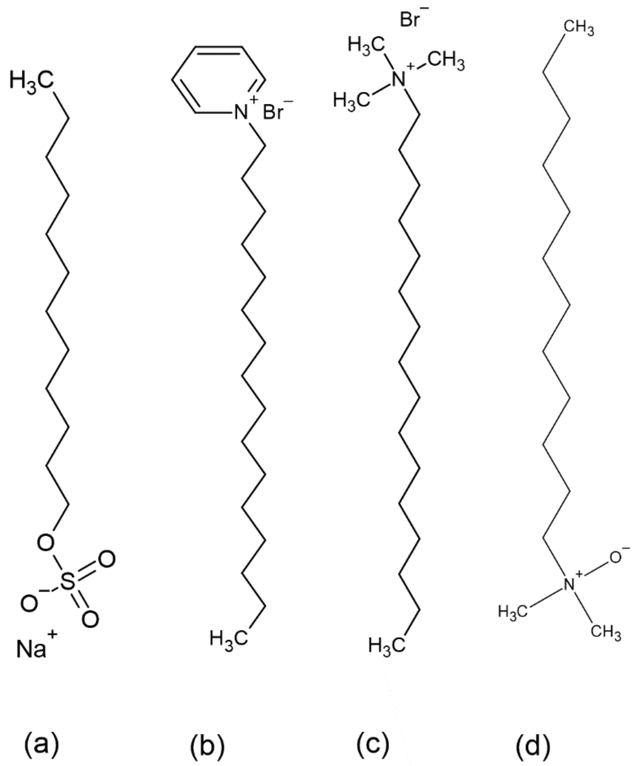


Figure 1. Surfactants used in the study: (**a**)—sodium dodecyl sulfate (SDS), (**b**)—cetylpiridinium bromide (CPB), (**c**)—cetyltrimethylammonium bromide (CTAB), (**d**)—alkyldimethylamine oxide (AO).

Table 1. Crude oil properties.

Density, kg/m^3	Viscosity, cP	Asphaltenes, % wt.	Resins, % wt.
0.850	27	0.37	15.9

2.2. Methods

2.2.1. Rock Hydrophobization

Two hydrophobization methods for rock slices and powder, described in [45,46], were applied in this study. 0.02 M stearic acid solutions in toluene and decane were prepared by heating to 70 °C and manual stirring. Iceland spar samples were first immersed in distilled water for 5 min and then transferred to a beaker with the stearic acid solution in decane without drying. Dry marble powder was immersed in a solution of stearic acid in toluene. Treatment time was 3 and 7 days for Iceland spar slices and marble, respectively. Then, rock samples were removed from the solution, rinsed with heptane to remove excess stearic acid, and then dried at 120 °C.

Disintegrated reservoir rock sample was aged in crude oil for 7 days. After the treatment was finished, powder was rinsed with gasoline to remove excess oil and heptane to remove gasoline. Then, the aged rock was dried at 120 °C.

2.2.2. Solutions Preparation

Solutions preparation method was described in our previous study [47]. For CA–based solutions, 0.4 M disodium EDTA, 0.4 M NaOH, and 0.05 M citric acid were dissolved in bi-distilled water at 70 °C, and then the necessary amount of surfactant was added. All of the solutions were stable at room temperature, i.e., no precipitates or cloudiness were observed. pH values of solutions lay near 6.7. Plain surfactant solutions were prepared with pure surfactants and bi-distilled water.

2.2.3. IFT Measurement

IFT was measured with DataPhysics OCA 15 Pro apparatus. First, the cuvette was filled with an aqueous solution and placed on the table for the specimen. Then, a 1 mL syringe with a 0.64 mm J-shaped needle was filled with octane and inserted into a holder under the piston. The syringe was positioned in such a way that the end of the needle was immersed in the aqueous solution. 0.5–1.0 µL drops were formed automatically by moving the piston. IFT was measured with the "pendant drop" method. At least three parallel measurements were made. The temperature was 25 ± 2 °C. Stable values of dynamic IFT were used in the study. However, when concentrations of surfactant were low, stabilization required long periods. Liquid evaporation effects may have influenced the results. In such cases, the first 500 s of the measurement were approximated with Equation (1) [48].

$$\gamma = \gamma_e + (\gamma_0 - \gamma_e)e^{-\frac{t}{\tau}} \tag{1}$$

where γ is the current IFT value, γ_0 is the IFT at the zero point, γ_e is the equilibrium IFT, τ is the parameter, related to the relaxation time, and t is the time from the start of the measurement. γ_e value was used.

2.2.4. Rock Treatment

Twenty-five grams of powdered rock or single-piece samples were placed into either a bottle with a cap for experiments under ambient conditions or a high-pressure vessel, equipped with a pressure gauge and a valve, for experiments under reservoir conditions (120 °C, 2 MPa). A solution of CA, surfactant, or CA–surfactant mixture was added to the rock (powdered or single-piece) with a ratio of 10 mL solution for 1 g of rock. Then, the caps of the bottle and high-pressure vessels were closed. Nitrogen (99.99%) from a gas cylinder was used to pressurize high-pressure vessels, and they were placed into an oven. Treatment time was 3 h, and manual shaking of bottles or vessels was performed every hour. After the treatment was finished, rock slices were rinsed three times with distilled water, powder was filtered through a Blue ribbon filter paper and rinsed with distilled water three times. All samples were dried at 120 °C in an oven.

2.2.5. Contact Angle Measurement

Direct contact angle measurement was performed with DataPhysics OCA 15 Pro. Flat samples (Iceland spar or marble cube) were placed on the specimen table. A 1 mL syringe with a 1.64 mm straight needle was filled with distilled water and placed into a holder. Five µL drops were formed and contacted with the rock surface (Figure 2a) by moving the table upward. Then, the table was moved downward and the drop was transferred to the rock surface (Figure 2b) and contact angle was measured automatically. An experiment was repeated 5–7 times for the same surface in different points.

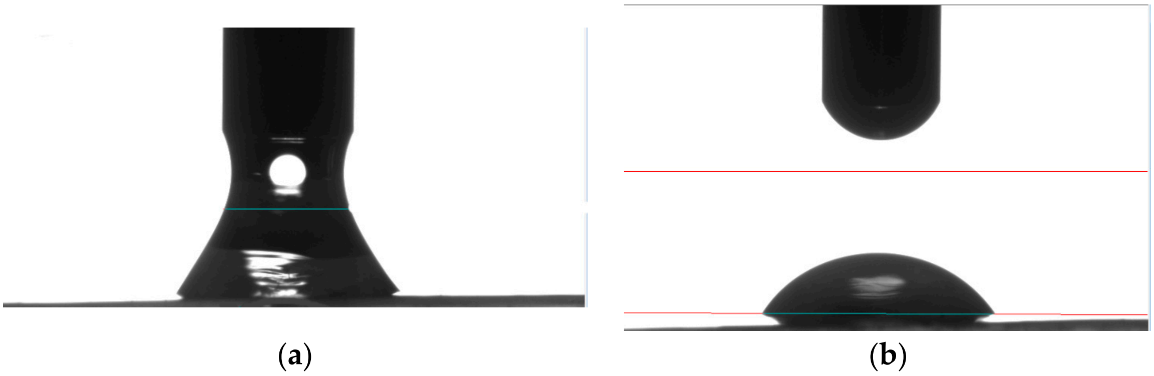

(a) (b)

Figure 2. Contact angle measurement (**a**) Drop-surface contact (**b**) Drop on the surface. Lower red line means baseline of a drop, upper red line denotes the end of field.

2.2.6. Washburn Capillary Rise Method

Glass tubes with an inner diameter of 0.7 cm, a wall thickness of 0.1 cm, and a length of 20 cm, closed with 100 mesh metallic screens on one side, were used as cells for the Washburn capillary rise method. Three grams of dry powdered rock before or after treatment were placed into the cell and packed with manual shaking, as reproducibly as possible.

The cell was hung on a special apparatus for moving the cell upward and downward. Using this apparatus, the cell was immersed in the octane or water in the beaker, which stood on the zeroed analytical balance. The immersion depth was 1 cm from the liquid surface. The weight of the beaker immediately started to decrease, which meant that the liquid was imbibed spontaneously into the powder. The weight of the imbibed liquid was recorded every 5 s. The experimental setup is shown in Figure 3. Six experiments were carried out for the one rock sample (three with water, three with octane).

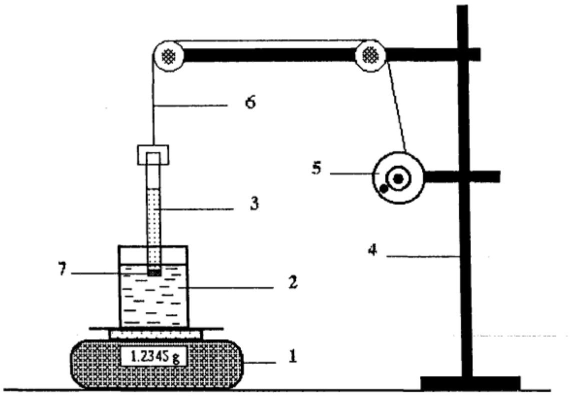


Figure 3. Experimental setup. 1—analytical balance, 2—beaker with imbibing liquid (octane or water), 3—cell, 4—tripod, 5—hoist, 6—thread, 7—100 mesh screen.

A plot of the squared weight of imbibed liquid versus time was drawn, and the slope of the linear portion (K) was calculated. Then, a ratio R, which is a ratio of adhesion tensions of n-octane and water towards rock [49], was calculated according to Equation (2).

$$R = \left(\frac{K\cdot\eta}{\rho^2}\right)_{octane}\cdot\left(\frac{\rho^2}{K\cdot\eta}\right)_{water} \tag{2}$$

η is the dynamic viscosity and ρ is the density of water and n-octane. NIST Thermophysical properties of fluid systems database was used to calculate these properties at experimental conditions (atmospheric pressure, 25 ± 2 °C). If R values are higher than unity, that means that the rock is primarily hydrophobic, and lower values mean that the rock is primarily hydrophilic.

2.2.7. Dissolution Capacity Measurement

Four cubic samples of marble with a weight of 21.0 ± 1.0 g and size of 2.0 × 2.0 × 2.0 cm were hydrophobized as described in Section 2.2.1. The initial weight (m_0) of every sample was measured with an accuracy of 0.0001 g. All samples were treated as described in Section 2.2.4 under ambient or reservoir conditions for 3 h. The volume of the liquid for the dissolution of one sample was equal to the area of the sample, multiplied by 2.5. The final weight (m_f) of the dry sample was measured. Dissolution capacity in g/g was calculated according to Equation (3). Actually, DC is the weight of marble which can be dissolved by 1 g of the CA in the solution.

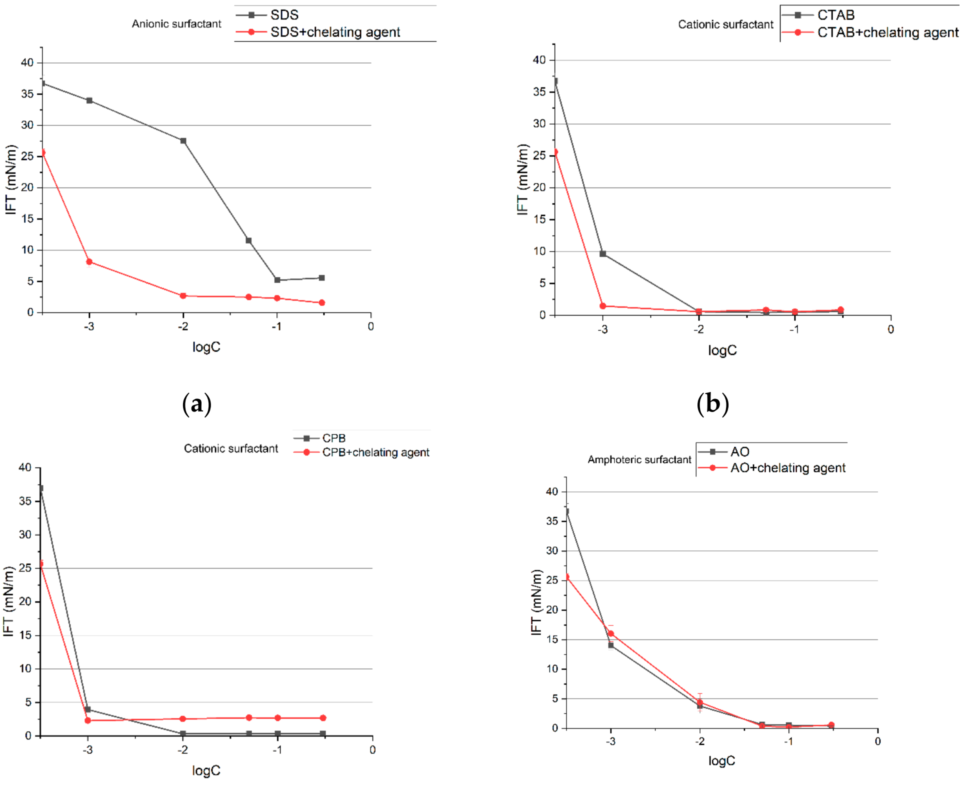
$$DC = \frac{m_0 - m_f}{V_L \times (C_{EDTA}\times M_{EDTA} + C_{citric\ acid} \times M_{citric\ acid}) + m_L \times \omega_{surfactant}} \tag{3}$$

V_L is the volume of treating solution, C_{EDTA} and $C_{citric\ acid}$ are concentrations of EDTA-Na_2 and citric acid, respectively (0.4 M and 0.05 M), and M_{EDTA} and $M_{citric\ acid}$ are molecular weights of EDTA-Na_2 and citric acid, respectively (358 and 192 g/mole). If surfactant is present, then the weight of the surfactant is added to the denominator.

3. Results and Discussion

3.1. IFT Measurement

Surfactant concentrations were 0.001% wt., 0.01% wt., 0.05% wt., 0.1% wt., and 0.3% wt. as most often used in stimulation jobs. IFT curves are shown in Figure 4a–d.



(**a**) (**b**)

(**c**) (**d**)

Figure 4. IFT curves of surfactant solutions and surfactant-CA mixtures. (**a**)—SDS, (**b**)—CTAB, (**c**)—CPB, (**d**)—AO. Results of experiments without surfactants are shown on OY axis.

It can be seen that IFT curves of surfactants of different classes show different behavior types. IFT values of anionic sulfate SDS and cationic quaternized amine CTAB are lowered when CA is added if compared with aqueous solutions. The reason for this behavior was explained in [47]. This effect results from the salting-out nature of CA, dehydration of hydrophilic heads, enhancement of surfactant molecules' packing, and electrostatic attraction between anionic SDS and EDTA. However, the IFT of cationic surfactant CPB is increased when CA is added. It should be noted that solutions of CPB with CA have a slight yellow tincture with its deepness increasing with surfactant concentration. The yellow color may appear because of bromine formation; therefore, the possible mechanism behind IFT increase when CA is present is the oxidation of the surfactant by dissolved oxygen. N-alkyl pyridinium salts are often used as inhibitors of radical reactions [50] as they are radically oxidized easily. The CA molecule might be a catalyst for this reaction. The possible mechanism is shown in Figure A1.

The addition of CA does not influence IFT in the case of AO, which is consistent with the reference data [36]. It seems that aminoxide is stable towards salting-out, like other amphoteric surfactants [51]; therefore, the IFT of AO is not altered.

A concentration of 0.05% wt. for wettability alteration experiments is chosen, as IFT values of all solutions (except for plain SDS solution) reach a plateau at this concentration. This fact indicates that it is above critical micelle concentration (CMC). This condition is favorable for the formulation of technological fluids [52].

3.2. Wettability Alteration of Model Rock

Marble powder and Iceland spar slices were first hydrophobized with stearic acid solutions in toluene and decane, respectively. The R value of the marble powder before hydrophobization was 0.36, while the R value of the treated powder was 80, which pointed to strong hydrophobization. The contact angle of hydrophobized Iceland spar slices values lay in the range of 85–115°, whereas contact angle values of rock before treatment were 40–50°. This increase of contact angle indicated successful hydrophobization from hydrophilic to the neutral/intermediate wetting state [25]. It is assumed that ionic binding between stearate and Ca^{2+} in crystal lattice was the only mechanism, which changed rock's wettability and other ones [9] were excluded. Therefore, clear tendencies of surfactant-induced wettability alteration in the case of ionic binding can be inferred.

Results of wettability alteration by different surfactants and surfactant–CA mixtures are shown in Figures 5 and 6 (R/R_0) and Figures 7 and 8 (contact angles). The value of R/R_0 is discussed here for convenience. R is the value which corresponds to treated rock, and R_0 is the value of original hydrophobic rock; thus, R/R_0 values less than the unity point to wettability alteration towards the water-wet state, while R/R_0 values higher than 1 indicate an increase of the rock's oil-wetness during the treatment.

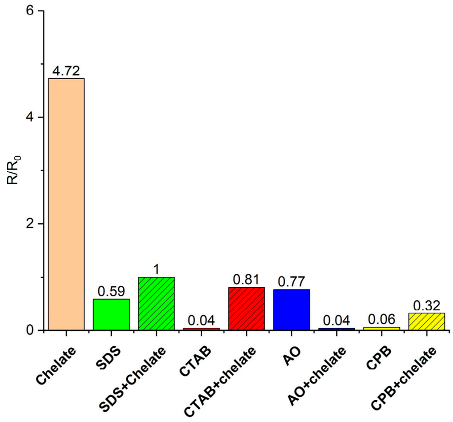


Figure 5. R/R_0 values of rock samples treated with surfactant solutions and surfactant–CA mixtures after treatment at 25 °C.

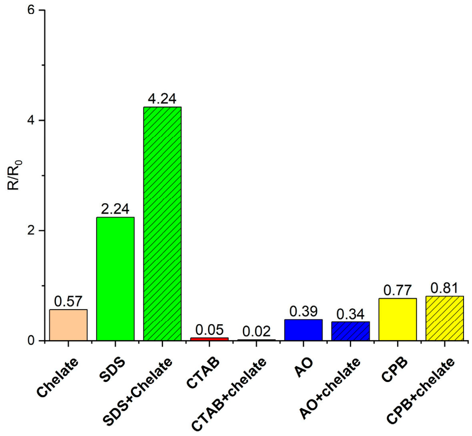


Figure 6. R/R_0 values of rock samples treated with surfactant solutions and surfactant–CA mixtures after treatment at 120 °C.

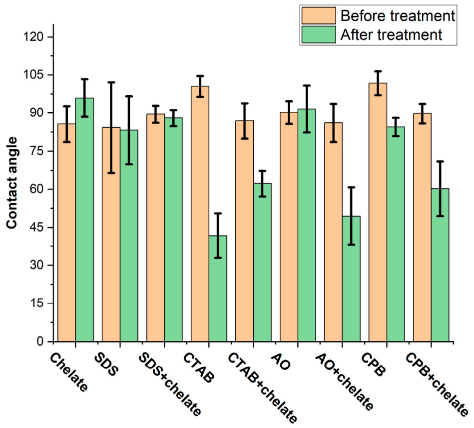


Figure 7. Contact angle values of rock samples treated with surfactant solutions and surfactant–CA mixtures after treatment at 25 °C.

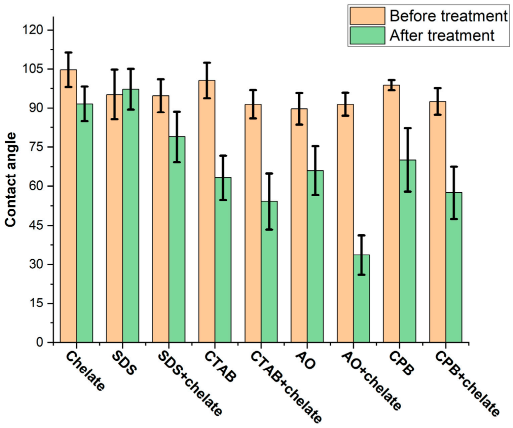


Figure 8. Contact angle values of rock samples treated with surfactant solutions and surfactant–CA mixtures after treatment at 120 °C.

Plain CA is not very efficient for wettability alteration. Contact angle values lie at the same level of intermediate and oil-wet state before and after treatment; R/R_0 value shows hydrophobization at 25 °C and mild hydrophilization at 120 °C. CA alone cannot desorb stearic acid ions because both EDTA/citric acid and stearate ions are negatively charged, which means that the surface is still covered with stearate ions after the treatment. The neutral pH value of the CA solution also does not favor the desorption of stearic acid because of its attraction to the positively charged surface, as the zero point of charge of calcite is 8–9.5 [53]. Leaching of calcium ions from the surface, which is the main mechanism of wettability alteration by CA, is also hindered by the adsorbed layer of stearic acid and short duration of the treatment. A small shift towards water-wetness at 120 °C according to capillary rise may be ascribed to diffusion enhancement and penetration of some part of the CA molecules through the adsorbed layer at high temperature, which results in leaching of a little portion of Ca^{2+} ions. Nevertheless, this effect is negligible, according to contact angle measurements.

SDS and its mixtures with CA are also inefficient for wettability alteration. Moreover, rock is found to be more oil-wet after treatment at 120 °C (R/R_0 value is higher than unity). The inefficiency of SDS and other anionic surfactants at concentrations close to 0.05% wt. was previously described [54,55]; however, no detrimental effects at high temperatures were observed. It seems that SDS washes away some excess stearic acid from the calcite surface at 25 °C and shifts it slightly towards water-wetness. The reason for strong hydrophobization at 120 °C is the adsorption of SDS at the surface. Three factors enhance SDS adsorption on the oil-wet calcite surface under studied conditions. First is the high temperature, which is known to increase the adsorption of inorganic sulfates on the calcite [56]. It is suggested that the affinity of organic sulfate towards calcite is also increased at high temperatures because of chemical similarity. The second factor is the presence of organic coverage on the surface, rendering it oil-wet initially. Such coverage also increases the adsorption of SDS [25] because of hydrophobic interactions. Finally, the highest increase of R is observed if CA is present. It is known that [57] salinity increase also leads to higher adsorption of surfactant, and CA plays the role of salt as the salting-out compound [47]. It can be concluded that SDS application at 0.05% wt. would be detrimental to the wettability state of the rock at high temperature.

All other surfactants alter the wettability towards water-wetness under investigated conditions. These findings still follow the trend of previous results [25,58,59]. As for cationic surfactants, it can be observed that CTAB is more efficient than CPB under any conditions and irrespectively of CA's presence (lower R/R_0 values and lower contact angle values). The efficiency of cationic surfactants is determined by electrostatic interaction between negatively charged carboxylic groups of adsorbate and positively charged groups of cationic surfactants with the following solubilization of desorbed compounds in micelles [60]. CTAB has a higher logP value (1.86) than CPB (1.63), according to ALOGPS 2.1 [61], which means that solubilization of hydrophobic chain of stearate in CTAB's micelles proceeds more readily. As the difference in the efficiency increases with the temperature, it can be concluded that it is the solubilization mechanism that determines the efficiency of cationic surfactants in wettability alteration. A surfactant with higher solubilization capacity is more likely to solubilize desorbed compounds in its micelles at higher temperature, as the number of micelles decreases when temperature increases [51]. If CA is present, the difference between CTAB and CPB may be caused by CPB degradation, as discussed earlier.

It is interesting to note that the presence of CA in cationic surfactants' solutions has a different impact on wettability alteration depending on the temperature. At 25 °C, plain solutions of both CTAB and CPB are more effective, whereas the situation is overturned at 120 °C, as the mixture of CTAB and CA performs better than plain CTAB and the mixture of CPB and CA becomes nearly equal to the plain CPB. It can be suggested that screening between the negatively charged CA and positively charged surfactant's head hinders the surfactant's ability to form ionic pairs with negatively charged stearic acid ions. Moreover, the reaction between CA and calcite is limited by surface kinetics at 25 °C [62]; thus, the residence time of CA on the surface is relatively long if compared to the diffusion time, which counteracts the action of surfactant. Higher temperature partially negates screening as electrostatic forces are obstructed by thermal agitation. The rate of the calcite dissolution is limited by mass transfer rate at 120 °C. Both of these factors exclude negative mutual influence. The synergistic effect between cationic surfactant and CA can be described (Figure 9). At the first stage (Figure 9a), the positively charged hydrophilic group of surfactant forms a strong ionic pair with negatively charged stearate. The ionic pair is desorbed spontaneously from the surface and moves to the bulk, where the stearate ion is solubilized in the surfactant's micelle (Figure 9b). This means that stearate cannot re-adsorb. The process described above makes some portion of the surface available for the CA reaction with carbonate. According to the surface complexation mechanism, CA leaches positively charged Ca^{2+} ions and thus increases the negative charge of the surface (Figure 9c). Excessive negative charge of the surface, in turn, causes spontaneous desorption of negatively charged stearate ions because of negative–negative repulsion (Figure 9d). The lack or absence of adsorbed long-chained stearate ions makes the surface more hydrophilic.

Plain AO solution is less active than plain CTAB in wettability alteration at both temperatures. AO is an amphoteric surfactant, which means that both negative and positive charges are present in its hydrophilic head. Therefore, electrostatic attraction between carboxylic groups of stearic acid and the headgroup of the surfactant is less than for cationic surfactants. However, the logP value of AO is high (4.03) and the interplay between the high affinity to hydrophobic chains of surfactant and the "lack" of positive charges determines the intermediate performance of AO, which is between CTAB and CPB.

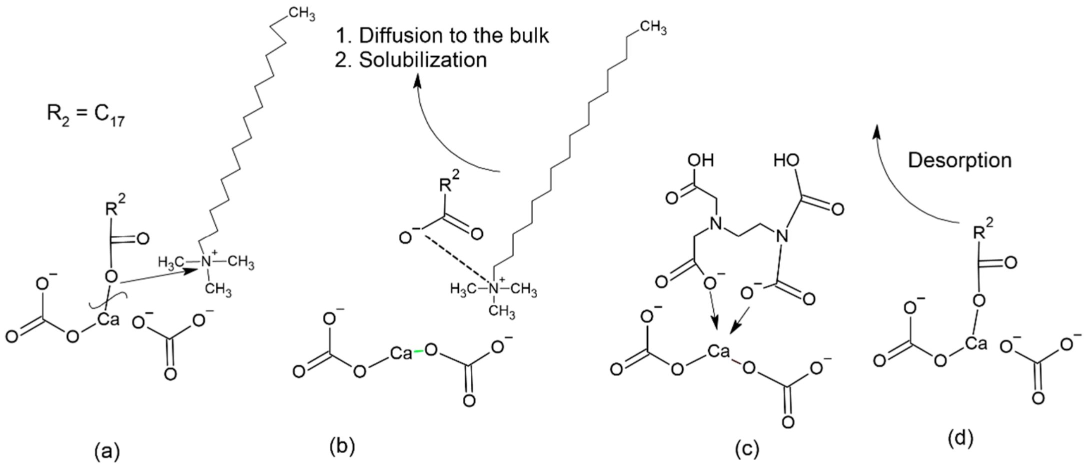


Figure 9. Mechanism of synergistic effect between CTAB and CA: (**a**) formation of ionic pair, (**b**) diffusion of ionic pair to the bulk volume with the following solubilization, (**c**) calcium ions leaching by the EDTA, (**d**) spontaneous desorption of stearate ions.

The effectiveness of the mixture of AO and CA is higher than the effectiveness of plain AO at both temperatures. This phenomenon is the opposite of the one observed in the case of cationic surfactants. It may be suggested that the presence of both charges decreases the electrostatic screening between CA and surfactant. Therefore, synergism exists under any studied condition. The possible mechanism of the synergism is the same as for cationic surfactants.

AO was selected for the following experiments because of this synergism. Another reason to select AO was the absence of halogen-containing compounds, which can negatively affect oil refining.

3.3. Effect of the Wettability Alteration on the Dissolution Capacity of CA

It was observed [41] that the efficiency of well stimulation depends on the accessibility of the rock's surface to the species which dissolve it. Accessibility of dissolving species can be estimated with the dissolution capacity (DC) of the well stimulation fluid towards the carbonate rock. DC is the weight of the carbonate rock which is dissolved by 1 g of dry CA [63]. A higher DC value means that a higher portion of the surface is accessible to the CA.

We investigated the DC of plain CA and surfactant–CA mixture towards the marble, aged in stearic acid according to Section 2.2.7. Control experiments with CA and non-hydrophobized (original) marble were performed. The results of the study are shown in Table 2.

Table 2. DC of CA with and without surfactant towards marble.

Sample	**DC, g/g**	
	25 °C	**120 °C**
Hydrophilic sample, CA	0.057 ± 0.003	0.084 ± 0.002
Hydrophobic sample, CA	0.029 ± 0.002	0.018 ± 0.005
Hydrophobic sample, CA-surfactant mixture	0.050 ± 0.011	0.086 ± 0.002

Hydrophobicity of the carbonate surface decreases the DC of plain CA, which indicates the inaccessibility of the surface to dissolving species. Moreover, the formation of caverns on hydrophobic samples treated with plain CA at 120 °C is observed (Figure 10). It seems that dissolution occurs only on the surface patches where the stearic acid layer is absent or loose.

Figure 10. Caverns formed by plain CA (upper row) and flat marble cubes after CA–surfactant treatment (lower row) at 120 °C.

However, the DC of the surfactant–CA mixture towards the hydrophobic sample is equal to the results obtained for CA towards hydrophilic samples. This indicated that wettability alteration enhanced dissolution of the carbonate rock. Other evidence includes the contact angle values of control samples (hydrophilic and hydrophobic) and samples after the treatment, which are shown in Table 3.

Table 3. Contact angle values before and after treatment.

Sample	**Contact Angle, °**	
	25 °C	**120 °C**
Control sample, hydrophilic	57.11 ± 7.19	
Control sample, hydrophobic	82.17 ± 5.80	
Hydrophobic sample, treated with plain CA	77.52 ± 4.10	98.34 ± 4.73
Hydrophobic sample, treated with CA-surfactant mixture	35.48 ± 5.05	27.83 ± 4.14

A clear correlation between wettability alteration and DC is observed. It seems that the surfactant desorbs stearic acid from the surface, which is then dissolved by CA. Higher values of DC mean that a lower amount of CA is needed to dissolve the same amount of rock and stimulate a well.

3.4. *Wettability Alteration of Reservoir Rock*

So far, we have focused on the study of the model rock treated with stearic acid. However, oil–rock interactions include several mechanisms. Experiments with reservoir rock, aged in crude oil, were carried out to prove that mixture of CA and selected surfactant performed well under real conditions. Aged rock was treated with CA, surfactant, and CA–surfactant mixture at 25 °C and 120 °C according to Section 2.2.4 and then wettability of treated rock was assessed with Section 2.2.6. Results are shown in Table 4.

The main difference between experiments with model and reservoir rock is the ability of plain CA to alter wettability towards a water-wet state. We can conclude that CA can rupture other bonds which bind oil components to the rock surface, such as surface precipitation, polar interactions, or acid–base interaction. The most probable mechanism is the breaking of acid–base interactions, as deprotonated carboxylic groups in CA are strong conjugated bases which can interact easily with protonated acids [9], which are present in adsorbed oil high-molecular components.

Table 4. Wettability alteration of reservoir rock.

R Value	Temperature of the Treatment, °C	
	25 °C	120 °C
Before ageing	0.73	
After ageing	1.62	
CA	0.47	0.39
CA-surfactant mixture	0.89	0.51
Surfactant	2.45	1.13

AO surfactant alone has little influence on the rock's wettability, which stays hydrophobic after the treatment. This result is close to the results of the model experiment. Synergism between CA and surfactant is absent for this pair of rock and crude oil. Nevertheless, values of *R* for the surfactant–CA mixture lie in the hydrophilic range at both temperatures, and they are very close to each other at 120 °C. This fact means that the surfactant does not influence CA performance negatively, which is a sign of optimal selection of surfactant type and concentration.

4. Conclusions

We carried out an experimental investigation of how CA, surfactants, and their mixtures alter carbonate rock wettability. CA consisted of EDTA (0.4 M) and citric acid (0.05) at pH 6.7. This composition is applicable for well stimulation in hot carbonate reservoirs.

Four surfactants of three different classes (anionic, cationic, and amphoteric) were studied. Surfactant concentration of 0.05% wt. for the rock treatment was selected on the base of IFT screening. This concentration is higher than the CMC of the surfactants' mixtures with CA for all surfactants under study.

Next, we examined how CA, surfactants, and CA–surfactant mixtures affect the wettability of stearic-acid-treated model carbonate rock. Treatments were performed at 25 °C and 120 °C for 3 h, mimicking well stimulation conditions involving CA.

It is observed that CA alone cannot alter the wettability of model rock, which means that it cannot break stearate–calcite ionic bonds under conditions of medium pH and short contact time. SDS and its mixtures with CA are ineffective too. Moreover, SDS is detrimental to the rock wettability at 120 °C as it increases oil-wetness. Three factors—high temperature, the presence of organic coverage, and salting-out EDTA ions—suggest this outcome.

Cationic (CTAB and CPB) and amphoteric (AO) surfactants are more effective at wettability alteration. Mixtures of cationic surfactants and CA underperform plain surfactants at 25 °C because of partial electrostatic screening and surface-reaction-limited dissolution. However, the situation changes at 120 °C, and a synergistic effect between CA and surfactant is observed. The AO and CA mixture performs better than pure AO at both temperatures. We suggested possible mechanisms involving ionic pair formation, diffusion of the ionic pair to the bulk volume, solubilization of stearate ions in the surfactant's micelles, CA-induced Ca^{2+} leaching on the freed patches of the surface, and spontaneous desorption of stearate due to increased negative charge. AO was selected as the most promising CA additive.

Shifting the rock's wettability state towards oil-wetness significantly reduces plain CA's dissolution ability. Yet, adding 0.05% wt. AO restores this capacity. Contact angle investigation shows that this phenomenon is related to the rock's wettability alteration towards the water-wet state. The final experiment with oil-aged rock demonstrates that a mixture of CA and AO surfactant is able to alter the rock's wettability, rendering this surfactant–CA mixture suitable for practical field use.

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Appendix A

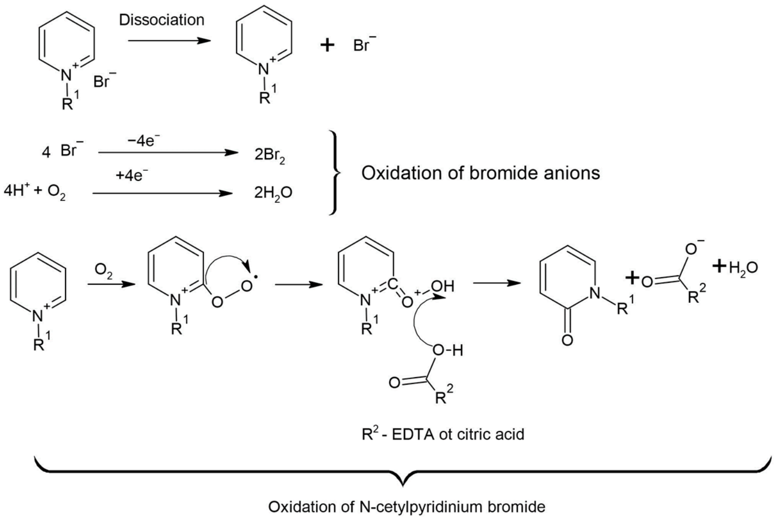

Figure A1. Possible mechanism of CPB oxidation.

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