

Adsorption of cationic and anionic surfactants on natural and synthetic carbonate materials

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ABSTRACT

Adsorption of cationic and anionic surfactants on carbonate materials is investigated in this study. Cetylpyridinium chloride (CPC) and sodium dodecyl sulfate (SDS) are chosen as typical cationic and anionic surfactants, respectively. It is found that the cationic CPC exhibits negligible adsorption on synthetic calcite in deionized water compared with the adsorption of the anionic SDS. However, a substantial amount of adsorption of CPC is observed on natural carbonates, such as dolomite and limestone. X-ray photoelectron spectroscopy (XPS) reveals that a substantial amount of silicon and aluminum exists in natural dolomite and limestone but not in synthetic calcite. The adsorption plateau of CPC on carbonates highly depends on the silicon composition in the carbonate samples due to the strong electrostatic interaction between CPC and negative binding sites in silica and/or clay. The adsorption of CPC on natural carbonates is reduced in the presence of 1 atm CO₂ compared with the case under 1 atm air, while SDS precipitates out of the solution under 1 atm CO₂ due to its intolerance to divalent ions released from the carbonate surface as a result of CO₂ acidification.

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1. Introduction

Surfactants are commonly used in enhanced oil recovery (EOR) processes for various purposes, including reduction of oil/water interfacial tension, wettability alteration, and foam generation [1]. Examples of these processes were reported in the literature such as high-temperature, high-salinity surfactant flooding [2,3], alkaline/surfactant/polymer (ASP) flooding [4–6] and foam mobility control [7–12]. Different EOR processes require different strategies to optimize the surfactant selection, and the choice of surfactants highly depends on the conditions of oil reservoirs. Among all different surfactant-based EOR processes at various conditions, a critical requirement for surfactants is that adsorption on reservoir formation be low to ensure effective propagation of the surfactants in porous media. High adsorption on reservoir formation leads to chromatographic retardation of the surfactants when they transport through a reservoir, making the designed EOR processes inefficient and economically unfeasible.

Oil reservoirs are generally divided into two categories based on the formation rocks: sandstone and carbonate. In sandstone reservoirs, anionic surfactants are usually preferentially employed due to the relatively low adsorption compared with other types of surfactants (cationics, nonionics and zwitterionics) [13–16]. Typical sandstone contains large amount of quartz (silica, SiO₂) and small

amount of carbonate and silicate minerals [14,17], and the composition depends on the sedimentology of the reservoir formation. Electrostatic interactions play a governing role over other forces in surfactant adsorption in systems where both the surfactants and the solid surface are charged [18]. Silica bears negative charge over a large range of pH (the isoelectric point (IEP) of silica is 1.7–3.5 [19]) and the electrostatic repulsion between the formation and the anionic surfactants inhibits the adsorption [20]. However, some clay minerals (mainly kaolinite and illite) in sandstone may cause certain amount of adsorption of anionic surfactants [17,21] because of the heterogeneous surface charge in clay [22,23]. In this case, the adsorption is dependent on how the clay minerals spread over the surface of sandstone.

In carbonate reservoirs, the surface chemistry of carbonates in aqueous solutions has an important influence on surfactant adsorption. Complex dissolution behavior was found in the salt-like minerals in carbonate formations, such as calcite (CaCO₃), dolomite (CaMg(CO₃)₂) or magnesite (MgCO₃) [24–27]. The electrokinetic data of the IEPs of calcite were summarized by Wolthers et al., which ranged from 7.8 to 10.6, and were even undetermined (always positive or negative charged) in some cases within this range of pH [27]. The value of the IEP of calcite depends on the sources of materials, the equilibrium time, and the ionic strength in aqueous solutions. Given the same ionic strength (10^{−3} mol dm^{−3} NaCl) in the pH range of 7–11, it was found that the natural calcite (Polcarb, ECC International) was more negatively charged than the synthetic calcite (Socal-U1, Solvay, UK) [28]. It

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was thought that a very small amount of impurities (clay and/or silica) possibly led to significant changes of the zeta potential of calcite in aqueous solution [29].

The complication of surface charge on carbonates makes it challenging to determine whether anionic or cationic surfactants should be used to minimize electrostatic interactions between the surfactants and the formation surfaces. Tabatabai et al. [30] performed static adsorption experiments to compare the adsorption of anionic and cationic surfactants on carbonates. An anionic surfactant, sodium dodecyl sulfate (SDS), and two cationic surfactants, cetylpyridinium chloride (CPC) and dodecylpyridinium chloride (DPC), were evaluated on natural dolomite (Ward Scientific, Salasvann, Norway) and synthetic calcite (Aesar, Johnson Matthey Inc., USA) powder. Their results showed that CPC/DPC exhibited significantly less adsorption on both dolomite and calcite than that exhibited by SDS without adjusting pH in the solutions. It was also shown that divalent ions, such as Ca^{2+} and Mg^{2+} , can reduce the adsorption of CPC/DPC on carbonates. In their study, CPC showed negligible adsorption on synthetic calcite powder compared with SDS, and the presence of 0.05 M CaCl_2 or MgCl_2 turned the adsorption of CPC on calcite to be negative. The presence of divalent ions makes the surface of carbonates more positively charged, and the coulombic interactions repelled CPC from the interfacial region. However, negative adsorption was not observed in the case of DPC on either dolomite or calcite.

Other researchers, however, did not show the advantage of low adsorption on carbonates using cationic surfactants instead of anionic surfactants. For example, on an ordinary garden grade limestone, the adsorption plateaus of the cationic surfactants decyltrimethylammonium bromide (C_{12}TAB) and tetradecyltrimethylammonium bromide (C_{14}TAB) were 5.70×10^{-7} mol/g and 8.25×10^{-7} mol/g, respectively; while the adsorption plateaus of the anionic surfactants monosodium monodecylphenylether monosulfonate (MAMS) and disodium didecylphenylether disulfonate (DADS) were 1.07×10^{-6} mol/g and 5.12×10^{-7} mol/g, respectively [31]. In their work, it was also shown that the molar adsorption on limestone of the cationic gemini surfactants was much larger than that of their corresponding conventional surfactants due to the increased hydrophobic interaction between the hydrophobic chains of the surfactants. Another work showed an adsorption plateau of 6.9×10^{-6} mol/m² (2.51 mg/m²) for the cationic cetyltrimethylammonium bromide (C_{16}TAB) on limestone (containing 99% calcium carbonate) in deionized water [32]. This value was a substantial amount of adsorption, which was higher than the adsorption of some ethoxylated anionic surfactants on synthetic calcite, such as alkyl aryl ethoxylated sulfonated phenol (Oil Chem 4-22, adsorption plateau 0.9 mg/m²) and alkyl aryl ethoxylated sulfonate (Oil Chem SS6566, adsorption plateau 1.3 mg/m²) [33]. A recent study showed higher adsorption of C_{16}TAB than SDS on either natural magnesite (magnesite mine Grochow, lower Silesia, Poland) or natural dolomite (old quarry Kletno, lower Silesia, Poland) in a low-salinity solution containing 10^{-4} M NaCl [34]. Based on the isotherms reported in their study, the adsorption plateaus of C_{16}TAB were 6.9 and 5.8 mg/m² on magnesite (pH = 8.5) and dolomite (pH = 10.4), respectively; while the adsorption plateaus of SDS were 1.1 and 2.2 mg/m² on magnesite and dolomite, respectively. Chemical analysis showed that the magnesite and dolomite used in their work contained 88% and 98% of carbonates, respectively.

These puzzling results indicate that the source of carbonate materials can have an important impact on ionic surfactant adsorption, and cationic surfactants may not have low adsorption if the material is not pure carbonate. For example, higher adsorption of octadecyltrimethylammonium bromide (ODTMA) (cationic) is observed compared with that of SDS (anionic) on various clay minerals such as montmorillonite and illite [35]. If abundant silica

and/or clay exist in carbonate formation, a substantial amount of adsorption of cationic surfactants may be expected. To understand the mechanism of surfactant adsorption on carbonates and guide the selection of surfactants for EOR processes in carbonate reservoirs, we investigate the adsorption of cationic and anionic surfactants with various carbonate materials, including natural and synthetic carbonate. Possible impurities in natural carbonate, such as silica and clay, are also investigated in this study. The surface charge and the surface chemistry are characterized in various materials to identify the binding sites for cationic and anionic surfactants.

2. Materials and methods

2.1. Materials

Hexadecylpyridinium chloride monohydrate [$\text{C}_{21}\text{H}_{38}\text{ClN} \cdot \text{H}_2\text{O}$] (CPC) and sodium dodecyl sulfate [$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$] (SDS) are supplied by Sigma-Aldrich. CPC is a cationic surfactant and SDS is an anionic surfactant.

Four natural carbonate materials, including dolomite and limestone, are used in this work. The particle size in terms of the diameter, surface area, ζ -potential and source of these materials are listed in Table 1. The particle size is obtained from either sieve sizing in the laboratory (for dolomite and limestone) or the material safety data sheet provided by the manufacturer (for calcite, silica and kaolin). To distinguish different sources of the carbonate samples, the dolomite samples supplied by Vital Earth/Carl Pool and Sciencelab.com, Inc are referred as dolomite (Carl Pool) and dolomite (Sciencelab.com), respectively. The limestone samples supplied by Franklin Minerals and Carthage Crushed Limestone are referred as limestone (Franklin) and limestone (Carthage), respectively.

Chemical-grade synthetic calcium carbonate (99.5% metals basis) powder supplied by Alfa Aesar is used as a standard calcite sample. According to the manufacture, this calcite sample has a uniform size of 5 μm . Fine round silica flour (MIN-U-SIL10, U.S. Silica Company) is used as a representative silica [SiO_2] material. In order to remove Fe_2O_3 and other metal oxides in the original sample, the silica flour is washed with 1 mol/L HCl, 0.01 mol/L NaHCO_3 solution and deionized water sequentially and is dried in a convection oven at 80 °C overnight prior to use. Kaolin [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] powder (Sigma-Aldrich) is used as a typical clay material in this study.

The BET (Brunauer–Emmett–Teller) surface areas of the samples are measured using a Quantachrome Autosorb-3b BET Surface Analyzer. This instrument utilizes multipoint BET to fit experimentally measured data (11 data points for each sample) using nitrogen as the adsorbate gas. The correlation coefficients for the fit to all samples are larger than 0.999. The results are shown in Table 1.

2.2. Static adsorption experiments

CPC and SDS are dissolved in deionized water at various concentrations to serve as initial surfactant solutions, respectively. The adsorbent material is mixed with surfactant solution in 50-mL centrifuge tubes at various weight/volume ratios to obtain different data points on the adsorption isotherm. For the experiments in the presence of 1 atm CO_2 , CO_2 is loaded to the system by repeatedly applying CO_2 above the surface of the solution in the centrifuge tube at a gauge pressure of 3.4 kPa for one minute to remove residual air in the gas phase and shaking the tube for five seconds after the cap of the centrifuge tube is closed. The chemical equilibrium with 1 atm CO_2 is approached by repeatedly performing this CO_2 -displacement and tube-shaking procedure until a sta-

Table 1

Characterization of adsorbent materials used in this study.

Material	Diameter	BET surface area (m ² /g)	ζ-potential (mV)	HCl-insoluble impurity (wt%)	Source
Dolomite	≤74 μm (200+ mesh)	0.97	8.0 ± 3.5 (pH = 10.0)	>2.4	Vital Earth/Carl Pool, Gladewater, TX, USA
Dolomite	≤74 μm (200+ mesh)	0.89	19.5 ± 6.6 (pH = 10.1)	>0.7	Sciencelab.com, Inc. (Catalog# SLD4477), USA
Limestone	420–840 μm (20/40 mesh)	0.29	NA ^a	>1.7	Franklin Minerals, Nolanville, TX, USA
Limestone	≤420 μm (40+ mesh)	1.23	29.6 ± 2.7 (pH = 10.0)	>2.8	Carthage Crushed Limestone, Carthage, MO, USA
Calcite	5 μm	1.65	4.2 ± 7.2 (pH = 9.8)	0	Alfa Aesar (Catalog# 11403), USA
Silica	≤10 μm	1.16	−47.3 ± 2.5 (pH = 6.0)	NA ^a	U.S. Silica Company, Pacific, MO, USA
Kaolin	0.1–4 μm	26.61	−38.0 ± 7.6 (pH = 4.8)	NA ^a	Sigma–Aldrich (Catalog# K7375), USA

^a Not measured.**Table 2**Equilibrium constants for carbonate equilibrium and the dissolution of CaCO₃ [41].

Reaction	−log10K at 25 °C	Definition of K
CaCO ₃ (s) = Ca ²⁺ + CO ₃ ^{2−}	8.42	K _{SO} = [Ca ²⁺][CO ₃ ^{2−}]
H ₂ CO ₃ [*] = H ⁺ + HCO ₃ [−]	6.35	K ₁ = [H ⁺][HCO ₃ [−]]/[H ₂ CO ₃ [*]]
CO ₂ (g) + H ₂ O(l) = H ₂ CO ₃ [*]	1.47	K _H = [H ₂ CO ₃ [*]]/P _{CO₂}
HCO ₃ [−] = H ⁺ + CO ₃ ^{2−}	10.33	K ₂ = [H ⁺][CO ₃ ^{2−}]/[HCO ₃ [−]]
H ₂ O = H ⁺ + OH [−]	14.0	K _w = [H ⁺][OH [−]]

ble pH is achieved. Other dissolved gases in the system are expected to decrease each time this procedure is performed due to decreased partial pressure of other gases in the gas phase. The pH is found to be stabilized at 6.13 after the 8th shaking in a control experiment with limestone (Franklin) in the absence of surfactants. After 24-h shaking, the pH of the CO₂-loaded control system is 6.17, indicating that the air-tightness of the centrifuge tube is good and that the control system has reached an equilibrium at a partial pressure of CO₂ close to 1 atm (theoretically pH = 5.95 when P_{CO₂} = 1 atm at 25 °C as indicated in Table 3).

The centrifuge tubes with adsorbent-dispersed surfactant solution are subsequently placed on a reciprocal shaker (Model E6010, Eberbach Corporation) and shaken at 180 osc/min (oscillations per minute) for at least 24 h at room temperature. After that, the samples are centrifuged at 8000 rpm for 30 min and the supernatant is titrated to determine residual (equilibrium) surfactant concentration.

The concentrations of both CPC and SDS are analyzed by potentiometric titration using an automatic titrator (716 DMS Titrimo, Metrohm USA) and an ion selective electrode (Part No. XT12-0001, Analytical Sensors & Instrument, Ltd). The titrant used for measuring CPC concentration is 0.001 mol/L SDS; the titrant used for measuring SDS concentration is 0.001 mol/L 1,3-didecyl-2-methyl imidazolium chloride (TEGO[®] trant A100) supplied by Metrohm USA. The pH values of the supernatants after centrifugation are determined by a pH meter (Corning 320). The pH electrode is calibrated with standard pH calibration solutions (OMEGA Engineering Inc.) at pH of 4 and 7 for measurements in acidic conditions and at pH of 7 and 10 for measurements in alkaline

conditions. The uncertainty of the pH meter is ±0.02, according to the manufacturer.

The main source of experimental uncertainty in the static surfactant adsorption measurements arises from the sample-to-sample differences rather than the potentiometric titration measurements. Typical experimental errors in a single sample in this work are within ±2.0% (error bars not shown in Figs. 1 and 2) using the potentiometric titration technique. However, the experimental errors from sample to sample appear much larger, as shown in Figs. 1 and 2. These errors are likely from the differences in degrees of mixing in the shaking process between surfactant solutions and adsorbent materials in different samples. We performed experiments using a variety of samples to obtain sufficient data to determine adsorption plateaus with error bars showing differences among different samples in Figs. 5 and 6.

2.3. Characterization of surface chemistry with XPS and XRD

X-ray Photoelectron Spectroscopy (XPS) is performed on the adsorbent materials using a scanning XPS microprobe (PHI Quantera XPS, Physical Electronics, Inc). At depths of 3–5 nm from the surface of the sample, the chemical composition is revealed using XPS. Three parallel experiments are conducted with different sampling spots for each adsorbent to identify the surface heterogeneity of the material. The atomic composition is attained by analyzing the characteristic peaks of binding energy through high resolution scan of the elements.

The HCl-insoluble impurities in carbonate samples are obtained by dissolving the samples in HCl solution and collecting the insoluble solids with centrifugation. In order to make sure that enough acid is used in the dissolving process, the HCl concentration is twice the required concentration for dissolving the carbonate samples predicted by the stoichiometric ratio. Powder X-ray Diffraction (XRD) is conducted to examine the physico-chemical make-up of HCl-insoluble solids in natural carbonate samples using Rigaku D/Max Ultima II Powder XRD instrument. This instrument uses Cu Kα radiation with a characteristic wavelength of 1.54 Å. The results are analyzed with JADE 9.4 data processing software (MDI, Inc.) using the ICDD (International Center for Diffraction Data) PDF4+ database to identify the mineralogy.

Table 3Calculation of pH, ion concentrations and ionic strength in DI water equilibrated with CO₂ and calcite based on the information in Table 3.

P _{CO₂} in atm	pH	[CO ₃ ^{2−}] in mol/L	[HCO ₃ [−]] in mol/L	[Ca ²⁺] in mol/L	Ionic strength in mol/L
1	5.95	5.62 × 10 ^{−7}	1.35 × 10 ^{−2}	6.76 × 10 ^{−3}	2.03 × 10 ^{−2}
3.16 × 10 ^{−4}	8.28	8.13 × 10 ^{−6}	9.12 × 10 ^{−4}	4.68 × 10 ^{−4}	1.41 × 10 ^{−3}
3.16 × 10 ^{−5}	8.94	1.70 × 10 ^{−5}	4.17 × 10 ^{−4}	2.24 × 10 ^{−4}	6.95 × 10 ^{−4}

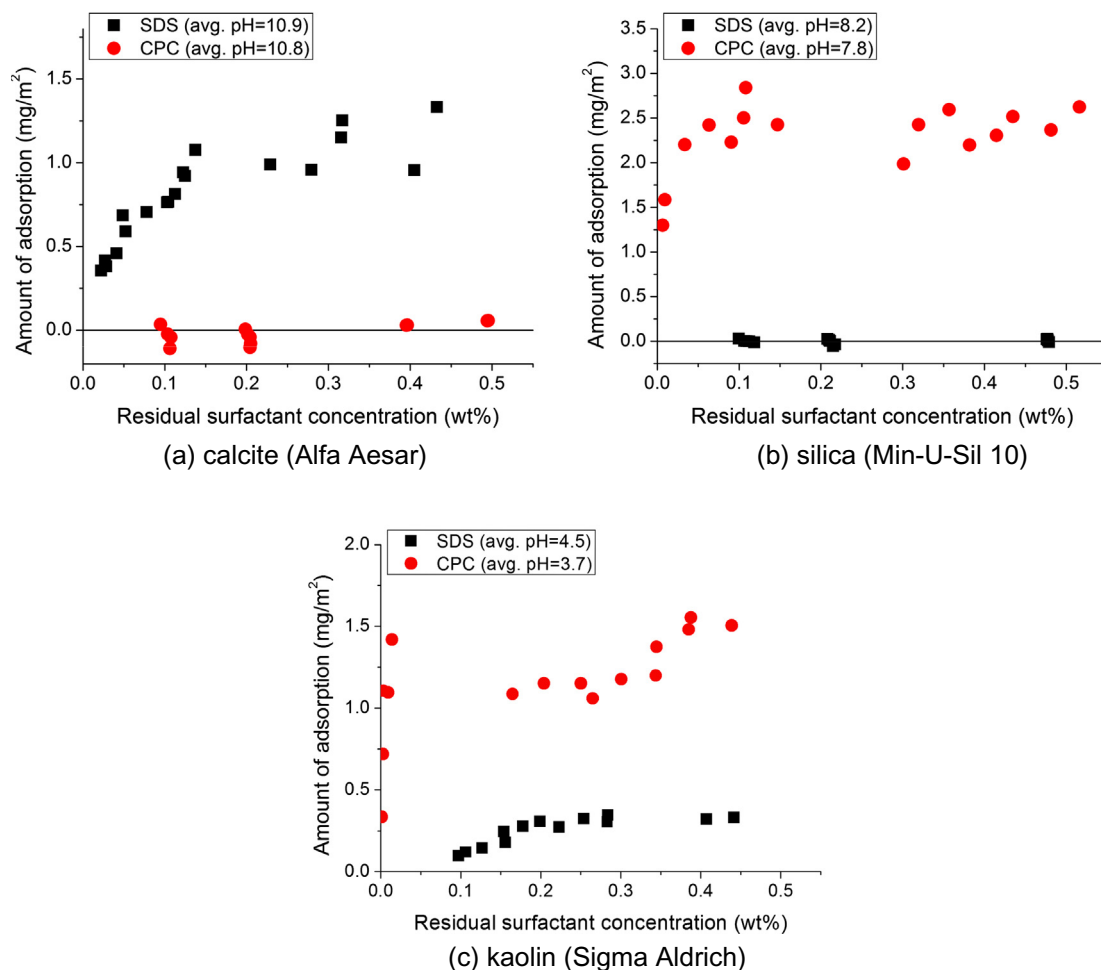


Fig. 1. Comparison of static adsorption of SDS and CPC on synthetic calcite, silica and kaolin in DI water at room temperature. The pH is not adjusted with either acid or alkaline.

2.4. ζ potential measurements

The ζ potential measurements follow the procedure of Jiang et al. [23] with a slight modification. The samples are prepared in 0.01 mol/L NaCl solution with a suspension of 1.0 wt% absorbent material. Unless otherwise specified, the pH or ionic strength of the suspension is not adjusted. The mixture is subsequently shaken overnight at 180 osc/minute to reach equilibrium. Before each measurement, the mixture is taken out from the shaker and settled for 30 min to obtain a stable suspension after sedimentation of larger particles.

The ζ potential of the suspension is measured by a zeta potential analyzer (ZetaPALS, Brookhaven Instruments Corporation). Each sample is analyzed by ZetaPALS through 10 repetitive measurements. The average ζ potential of 10 measurements is chosen as the ζ potential value of the sample.

3. Results and discussion

3.1. Results of ζ potential and static adsorption

Fig. 1 shows a comparison of static adsorption between CPC and SDS on synthetic calcite powder, silica flour and kaolin powder. The average pH indicated in Fig. 1 is not adjusted with either acid or alkali, which reflects the natural interactions between surfactant solution and mineral surface. The adsorption of CPC on synthetic

calcite is negligible compared with that of SDS as indicated in Fig. 1(a), which is consistent with the literature [30]. Some of the data points show negative adsorption of CPC on calcite surface in Fig. 1(a). This means that the concentration of CPC in the vicinity of calcite surface is lower than that in the bulk, which is presumably caused by the strong electrostatic repulsion between the cationic CPC and the positively-charged calcium ions on calcite. The ζ -potential of calcite is close to zero (4.2 ± 7.2 mV) at a pH of 9.8 (Table 1), which is consistent with the finding in the literature for synthetic calcite suspended in 0.01 mol/L NaCl solution with an isoelectric pH of 9.6 [36]. Since the surface of calcite is not strongly charged near a pH around 10, it is likely that the electrostatic attraction between CPC and negatively-charged carbonate ions at the calcite surface is weak compared with the repulsion between CPC and calcium ions.

Table 1 shows a negative zeta potential (-47.3 ± 2.5 mV) when silica flour is suspended in 0.01 mol/L NaCl solution. At a pH around 8 the silica surface is strongly negatively charged. High adsorption of positively-charged CPC and negligible adsorption of negatively-charged SDS on silica flour are observed in Fig. 1(b). The behavior is completely opposite to the case with synthetic calcite in Fig. 1(a). Therefore, if natural carbonates contain a substantial amount of silica, significant adsorption of CPC may occur.

We use kaolin as a typical clay material to compare the adsorption of CPC and SDS. An acidic condition (pH = 4.8) is observed when kaolin is suspended in 0.01 mol/L NaCl solution as shown in Table 1. The zeta potential of kaolin under this condition is

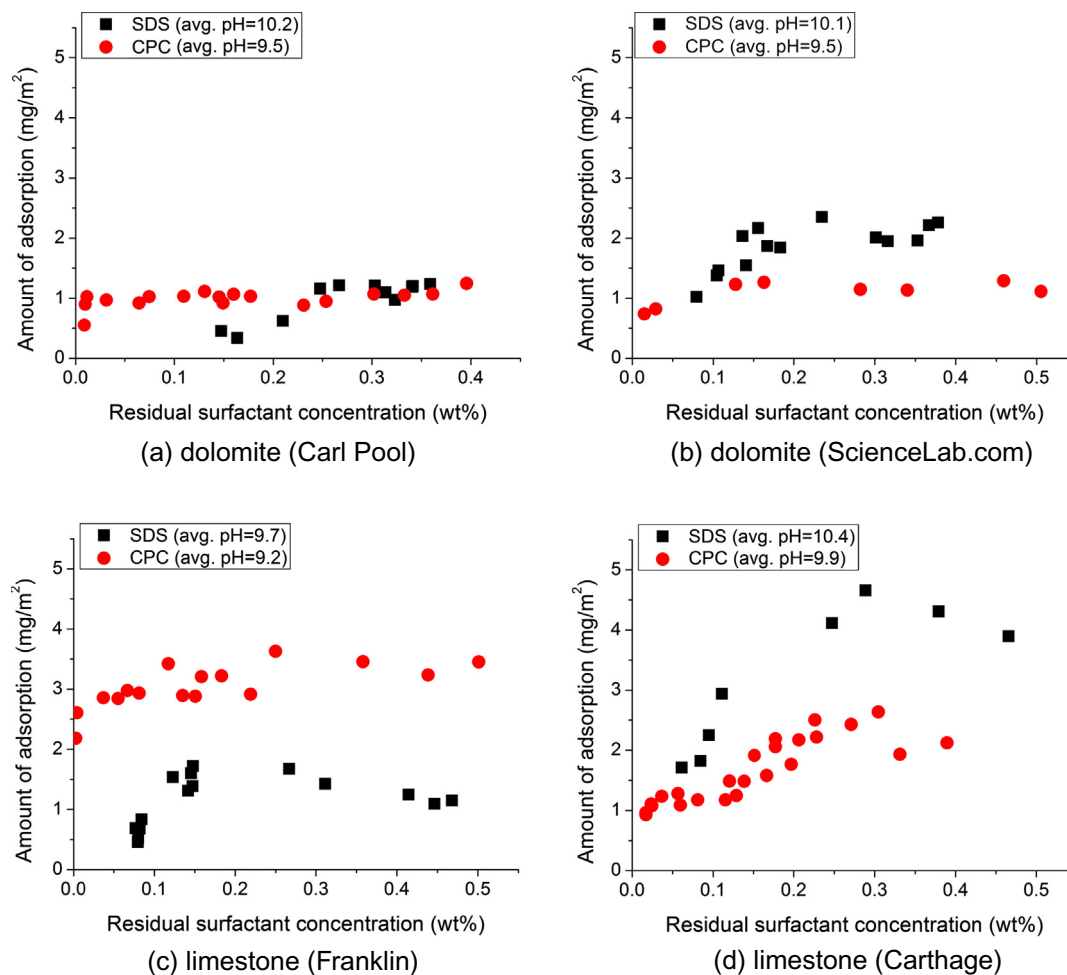


Fig. 2. Comparison of static adsorption of SDS and CPC on various natural carbonates in DI water at room temperature. The pH is not adjusted with either acid or alkaline.

-38.0 ± 7.6 mV, which indicates an overall negative surface charge. It was reported that an increase in pH led to a more negatively-charged kaolin surface [23,37]. As shown in Fig. 1(c), both the cationic CPC and the anionic SDS adsorb onto kaolin, because both positive and negative binding sites exist on this mineral surface depending on pH [23,38,39]. An increase in pH alters the charge on the edges of kaolin, which can further reduce the adsorption of SDS [38]. The basal planes of kaolin are unconditionally negatively charged, which causes a substantial adsorption of CPC as shown in Fig. 1(c). If kaolin is found to be an impurity in natural carbonate sample, the negative binding sites in kaolin may cause significant adsorption of CPC especially in alkaline conditions.

As shown in Table 1, these carbonate materials are collected from different places in the US and used without further purification. It has been noted that a very small amount of impurities in natural carbonates can possibly provide significant variations in zeta potential measurements [40]. In Table 1 we observe that the zeta potential of various natural carbonate samples suspended in 0.01 mol/L NaCl solution ranges from 8.0 to 29.6 mV, while the pH is somehow close to each other. Therefore, the effect of impurities on surfactant adsorption should not be ignored.

Fig. 2 shows the comparison of adsorption of SDS and CPC on four natural carbonates in terms of mass adsorbed per unit surface area. In Fig. 2(a), SDS and CPC show almost the same adsorption plateaus slightly above 1 mg/m² on dolomite (Carl Pool). However, the adsorption of SDS is substantially higher than that of CPC on dolomite (ScienceLab.com) (Fig. 2(b)) and limestone (Carthage) (Fig. 2(d)), and much lower than that of CPC on limestone (Frank-

lin) (Fig. 2(c)). The absolute amount of adsorption in terms of mass per unit surface area also varies a lot with different minerals. Compared with the base case of synthetic calcite in Fig. 1(a), the most probable key factor which plays an important role in SDS/CPC adsorption is the amount and distribution of impurities in natural carbonate materials.

3.2. Surface characterization by XPS and XRD

We characterize the atomic surface composition of various minerals using X-ray photoelectron spectroscopy (XPS). Fig. 3 shows the comparison of the XPS results for the elements calcium (Ca), magnesium (Mg), aluminum (Al) and silicon (Si). The elements carbon (C) and oxygen (O) are also observed in all carbonate samples, however, they are not shown in Fig. 3 since they have no apparent contribution to the cationic CPC adsorption on calcite (Fig. 1(a)) and the anionic SDS mainly interacts with Ca and Mg rather than C and O.

Ca is observed in all carbonate minerals (samples 1–5) but not in kaolin (sample 6) or silica (sample 7). Significant amount of Mg is observed in dolomite (samples 1–2) but not in calcite (sample 5). Small amount of Mg exists in limestone (samples 3–4). These observations are all consistent with the typical chemical compositions of these minerals.

What is of interest is the amount of Si and Al in natural carbonates. As shown in Fig. 3, Si is found in all four natural carbonates (samples 1–4), while Al is found in all carbonate samples except the dolomite from ScienceLab.com. Neither Si nor Al is found in

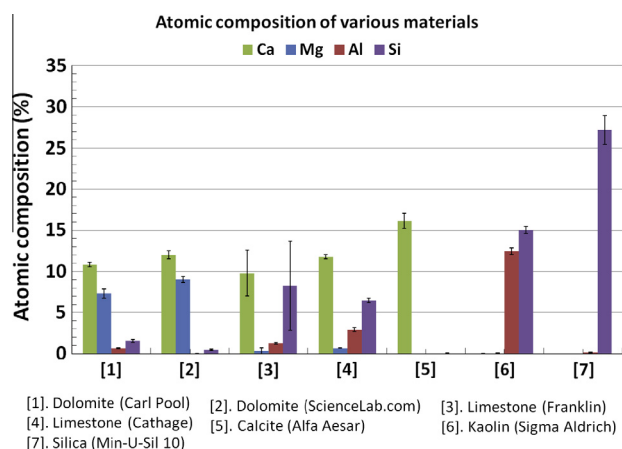


Fig. 3. Comparison of atomic composition of various materials measured by X-ray photoelectron spectroscopy (XPS).

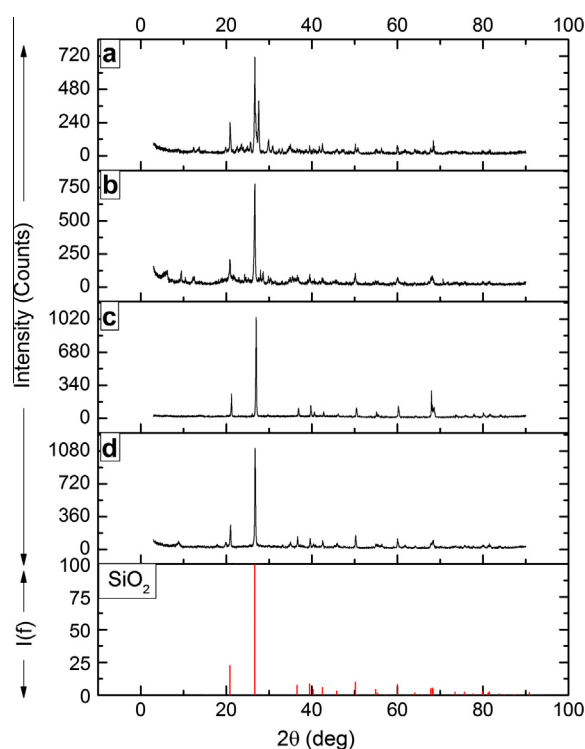


Fig. 4. Analysis of HCl-insoluble impurities with X-ray Diffraction (XRD) from top to bottom: (a) dolomite (Carl Pool); (b) dolomite (ScienceLab.com); (c) limestone (Franklin); (d) limestone (Carthage). The bottom of the stackplot (figure (d)) shows the reference pattern of SiO_2 normalized by the highest peak.

the synthetic calcite powder (sample 5). These findings may explain why there is such a large difference in SDS/CPC adsorption on different carbonates. Si and Al usually exist in the form of silica and clay on natural carbonate samples. The existence of silica and clay in natural carbonates can provide strong negative binding sites to adsorb cationic surfactants such as CPC, mainly through electrostatic interactions.

We use XRD to investigate what minerals exist in the HCl-insoluble impurities of natural carbonates which contribute to the significant differences in adsorption behavior of ionic surfactants. In Fig. 4, we include a reference pattern of SiO_2 normalized by the highest peak at the bottom of the stackplot, obtained from the ICDD PDF4+ database. The results shown in Fig. 4 indicate that

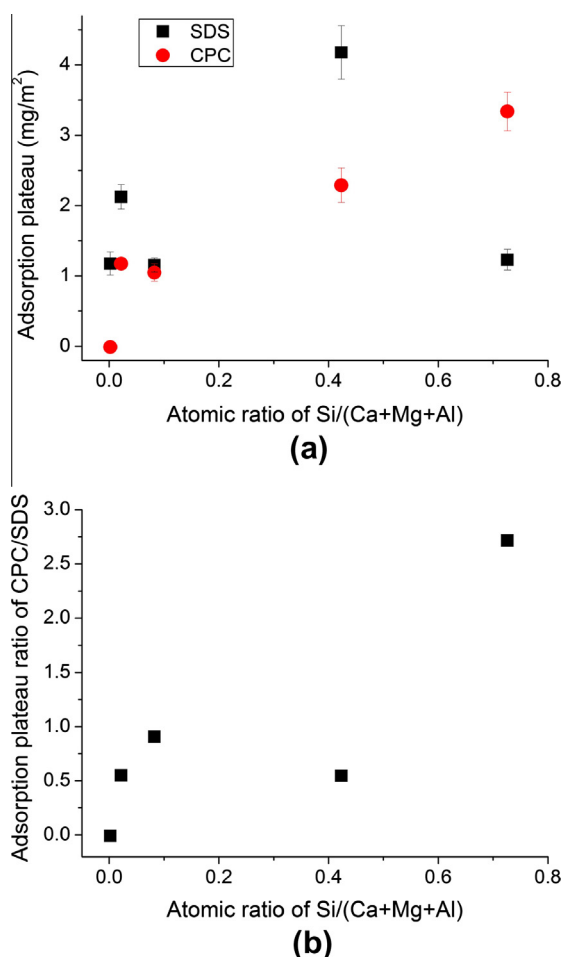


Fig. 5. Correlation between surfactant adsorption plateau and XPS results of carbonate minerals. (a) Comparison of SDS and CPC adsorption plateaus on carbonate minerals in terms of the atomic ratio of $(\text{Si})/(\text{Ca} + \text{Mg} + \text{Al})$; (b) Adsorption plateau ratios of CPC/SDS on carbonate minerals in terms of the atomic ratio of $(\text{Si})/(\text{Ca} + \text{Mg} + \text{Al})$. The pH is not adjusted with either acid or alkaline as shown in Figs. 1(a) and 2.

the majority of the HCl-insoluble impurities in all four natural carbonate samples is silica (SiO_2). Quantitative determination of the silica is not made for the HCl-insoluble samples due to the uncertainty in finding exact compositions of minor and trace components. As aluminum is also found in natural carbonate samples using XPS, it may exist as the minority component in the HCl-insoluble impurities in various forms. For example, qualitative minor component analysis in Fig. 4(d) indicates the existence of muscovite (a phyllosilicate mineral) or fuchsite (a green, chromium-rich variety of muscovite) in this sample (Carthage limestone) according to the ICDD database.

We collect the adsorption plateaus of SDS and CPC from Figs. 1 and 2 for five carbonate samples. Fig. 5(a) shows the change in adsorption plateaus of SDS and CPC with the atomic ratio of $(\text{Si})/(\text{Ca} + \text{Mg} + \text{Al})$ of the carbonate minerals. The trend indicates that the adsorption plateau of CPC increases with the atomic ratio of $(\text{Si})/(\text{Ca} + \text{Mg} + \text{Al})$, while the adsorption plateau of SDS appears not to be a monotonic function of the atomic ratio of $(\text{Si})/(\text{Ca} + \text{Mg} + \text{Al})$. This observation indicates that low adsorption of CPC occurs on natural carbonates with low Si content.

Fig. 5(b) compares the adsorption plateaus of CPC and SDS in Fig. 5(a) by plotting the plateau ratio CPC/SDS with the atomic ratio of $(\text{Si})/(\text{Ca} + \text{Mg} + \text{Al})$. Based on the five data points shown in Fig. 5(b), it is observed that the adsorption plateau ratio of CPC/

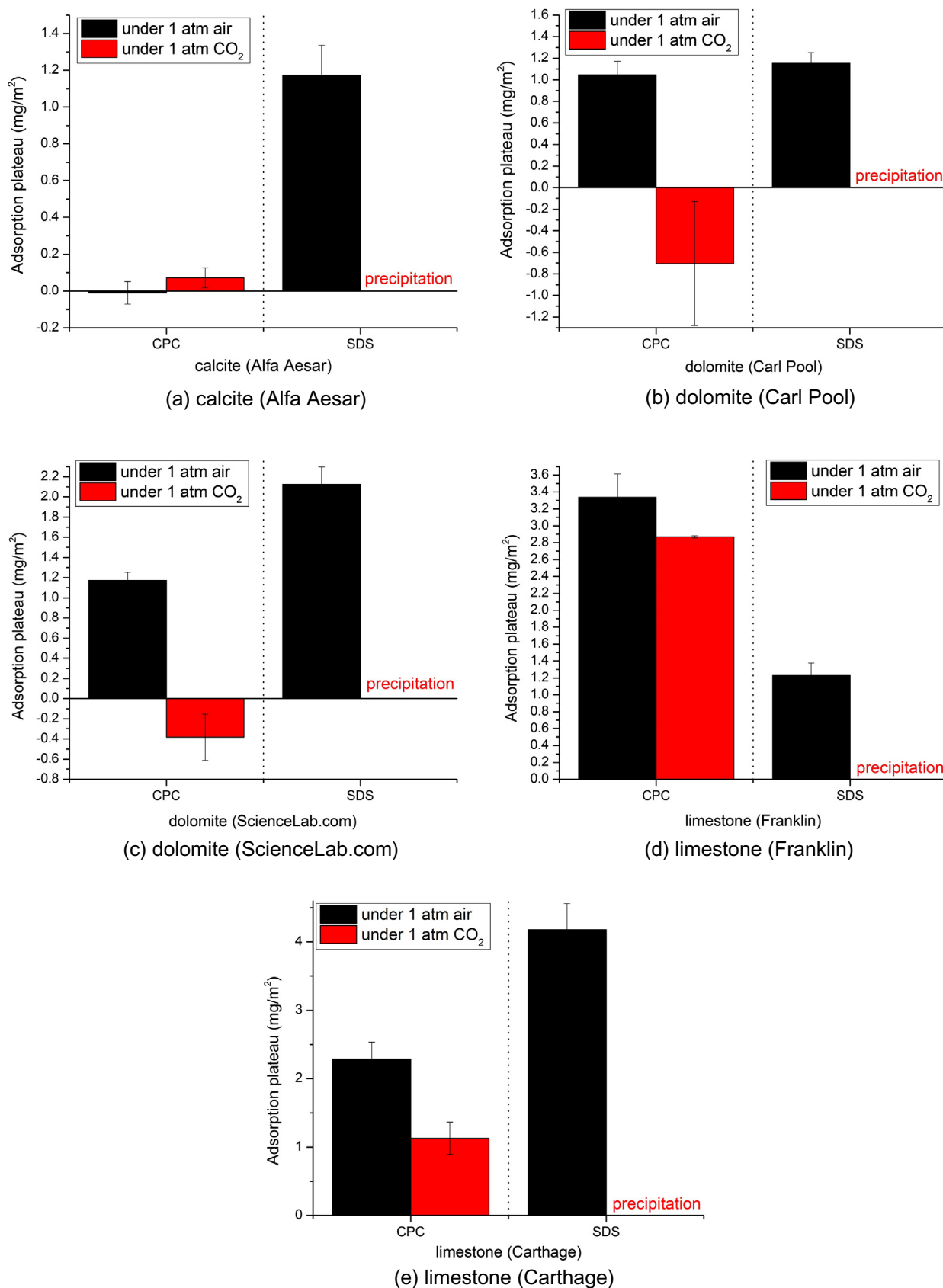


Fig. 6. Comparison of adsorption plateaus of SDS and CPC on various carbonate materials in DI water at room temperature in the absence and presence of 1 atm CO₂. In addition to the CO₂ effect, The pH is not adjusted with other acid or alkali.

SDS increases with the atomic ratio of (Si)/(Ca + Mg + Al) of the minerals at low Si regions (less than 10%). Thus, the cationic CPC

can be advantageous over the anionic SDS in terms of low adsorption if the carbonate minerals have low Si and Al. The adsorption

plateau ratio of CPC/SDS varies a lot when the atomic ratio of (Si)/(Ca + Mg + Al) becomes high (more than 40%). This indicates that complex electrostatic interactions occur when natural carbonates contain a large amount of silica and clay.

3.3. The influence of CO₂ on surfactant adsorption

It is crucial to understand the influence of CO₂ on surfactant adsorption especially in CO₂ foam EOR processes. In the following analysis, we estimate ion concentrations without surfactants in the presence of CO₂ in order to investigate how CO₂ affects the chemical equilibrium in the calcite/water system. In the absence of surfactants, the interaction of CO₂ with calcite in DI water involves the 5 reactions [41] listed in Table 2:

According to Table 2 we have the following equations when all species are in equilibrium state:

$$[\text{HCO}_3^-] = K_1[\text{H}_2\text{CO}_3^*]/[\text{H}^+] = K_1K_H P_{\text{CO}_2}/[\text{H}^+] \quad (1)$$

$$[\text{CO}_3^{2-}] = K_2[\text{HCO}_3^-]/[\text{H}^+] = K_2K_1K_H P_{\text{CO}_2}/[\text{H}^+]^2 \quad (2)$$

$$[\text{OH}^-] = K_w/[\text{H}^+] \quad (3)$$

$$[\text{Ca}^{2+}] = K_{\text{SO}}/[\text{CO}_3^{2-}] = [\text{H}^+]^2 K_{\text{SO}}/(K_2K_1K_H P_{\text{CO}_2}) \quad (4)$$

Considering the charge balance in aqueous phase, we have Eq. (5) in the system:

$$2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]. \quad (5)$$

By substituting Eqs. (1)–(4) into Eq. (5) one can get Eq. (6):

$$2[\text{H}^+]^2 K_{\text{SO}}/(K_2K_1K_H P_{\text{CO}_2}) + [\text{H}^+] = K_1K_H P_{\text{CO}_2}/[\text{H}^+] + 2K_2K_1K_H P_{\text{CO}_2}/[\text{H}^+]^2 + K_w/[\text{H}^+] \quad (6)$$

The only unknown variable in Eq. (6) is the hydrogen ion concentration $[\text{H}^+]$ or the pH ($\text{pH} = -\log_{10}[\text{H}^+]$) once the partial pressure of CO₂ (P_{CO_2}) is given. A simple way to estimate the pH is to try a series of pH values in Eq. (6) using a spreadsheet in Microsoft Excel. With an increment of 0.01, the pH which corresponds to a particular CO₂ partial pressure can be found with a precision of three significant digits. Eq. (6) can also be solved with iteration methods. After getting the pH, the concentrations of bicarbonate, carbonate, hydroxide and calcium ions in aqueous phase can be obtained through Eqs. (1)–(4). The ionic strength (I) of the solutions is calculated using Eq. (7), in which C_i is the molar concentration of ion i (mol/L) and z_i is the charge number of that ion.

$$I = \frac{1}{2} \sum_{i=1}^n z_i^2 C_i \quad (7)$$

The results for 1 atm CO₂, 1 atm air with a CO₂ partial pressure of 3.16×10^{-4} atm (typical amount of CO₂ in air) and 3.16×10^{-5} atm are shown in Table 3. The presence of 1 atm CO₂ lowers the pH of DI water to around 6.0 in equilibrium with calcite and increases the concentration of calcium ions by an order of magnitude. A decrease in carbonate ions and an increase in bicarbonate ions in the aqueous phase are also found when the partial pressure of CO₂ increases. The increase in ionic strength in the aqueous phase with the increase in CO₂ partial pressure in the gas phase indicates mineral dissolution from the calcite surface.

The results of CPC/SDS static adsorption on various carbonates under 1 atm CO₂ are compared with the cases under 1 atm air in Fig. 6. In the presence of 1 atm CO₂, the pH of the CPC system is reduced to between 6.1 and 6.2 at the end of the 24-h adsorption experiments in all five cases. The measured pH is close to the calculated value in the absence of surfactant (5.95 as shown in

Table 3). The presence of 1 atm CO₂ acidifies the surfactant solution, and this process is expected to make the carbonate surface more positively charged. As shown in Fig. 6(a), this effect on CPC adsorption on synthetic calcite is insignificant compared with other cases, presumably due to the weak electrostatic interaction between CPC and calcite even in the absence of CO₂. Interestingly, the presence of 1 atm CO₂ leads to negative adsorption of CPC on dolomite (Carl Pool) and dolomite (ScienceLab.com) as indicated in Fig. 6(b) and (c). To our knowledge, this is the first time that negative adsorption of CPC on natural carbonates is observed. Compared with the case of synthetic calcite, it is possible that the interaction between CO₂ and silica and clay on the surface of dolomite plays an important role in creating additional strength in electrostatic repulsion between CPC and the dolomite surface. The presence of 1 atm CO₂ also reduces the adsorption of CPC on limestone (Franklin) and on limestone (Carthage), as shown in Fig. 6(d) and (e), respectively. These findings imply the advantage of low adsorption by using CPC in CO₂ foam processes on carbonate formation. The suggested mechanisms for this adsorption reduction are shown in Fig. 7(a) and (c). At equilibrium, brine with a fugacity of CO₂ equal to one atmosphere will become saturated or even supersaturated with calcium and/or magnesium ions when in contact with calcite or dolomite surfaces. These ions may become potential determining ions (in addition to the hydronium ion and the carbonate ions) that can deposit a surface layer of calcite or dolomite onto the silica surface sites. Thus the surface charge of a surface containing silica at a pH in equilibrium with calcite or dolomite may have a surface charge closer to that of the calcite or dolomite than that of the original silica in soft brine. The surface charge of the silica sites is strongly influenced by brine conditions.

Fig. 6 also indicates that no adsorption plateau is observed for SDS adsorption on carbonates under 1 atm CO₂ in all five cases.

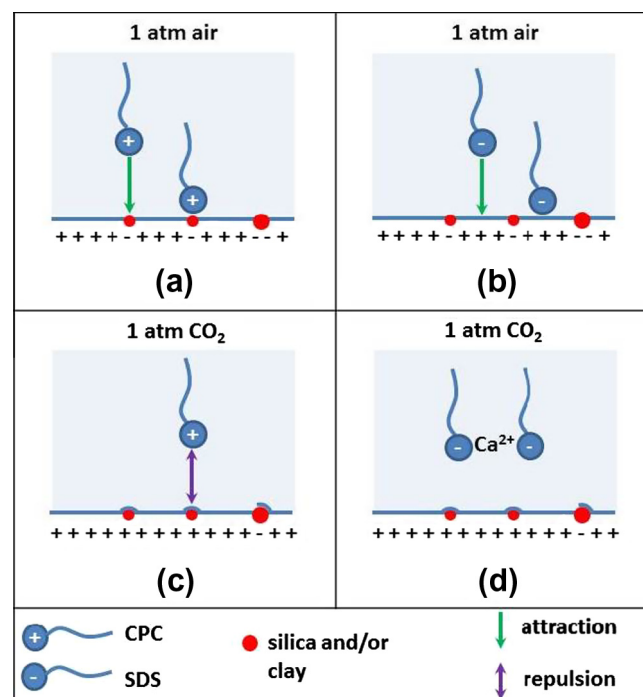


Fig. 7. Proposed mechanisms for CPC/SDS adsorption on natural carbonates in the presence/absence of CO₂. (a) CPC adsorption on natural carbonates in DI water equilibrated with 1 atm air; (b) SDS adsorption on natural carbonates in DI water equilibrated with 1 atm air; (c) CPC adsorption on natural carbonates in DI water equilibrated with 1 atm CO₂; (d) SDS adsorption on natural carbonates in DI water equilibrated with 1 atm CO₂.

The experimentally measured adsorption values increases almost linearly with equilibrium SDS concentration, which is a typical surfactant precipitation behavior. The precipitated SDS is separated from the bulk solution after centrifugation, leading to high apparent adsorption when initial SDS concentration is high. The presence of 1 atm CO₂ significantly increases divalent ion concentrations as shown in Table 3. As illustrated graphically in Fig. 7(b) and (d), the precipitation of SDS on carbonates under 1 atm CO₂ is due to strong electrostatic interactions between the multivalent counterion (dissolved Ca²⁺ and Mg²⁺ in this case) and sulfate surfactants [42,43] and subsequent formation of calcium salt of the anionic surfactant [44–46]. Therefore, SDS should not be used alone by itself for CO₂ EOR processes in carbonate reservoirs even in soft brine from practical standpoint. However, this precipitation problem can be avoided by using ethoxylated anionic surfactants such as sodium lauryl ether sulfate (3EO) (STEOL CS-330, Stepan). The ethoxy groups on sulfate surfactant add tolerance to divalent ions [1,47]. STEOL CS-330 has also exhibited lower adsorption than sulfonate surfactants without ethoxylation such as sodium (C1618) alpha olefin sulfonate and sodium (C1518) internal olefin sulfonate on natural dolomite surfaces in DI water [48]. Another way to enhance the solubility of calcium dodecyl sulfate is to add certain amount of nonionic surfactants to the system [44,49]. Nonionic surfactants are also reported to have low adsorption on natural dolomite due to weak electrostatic interactions with carbonate surfaces [48].

4. Conclusions

In summary, the adsorption of the cationic surfactant CPC and the anionic surfactant SDS on carbonates is investigated in this study. CPC shows negligible adsorption on synthetic calcite but high adsorption on some of the natural carbonates. A substantial amount of silicon and aluminum is found in natural dolomite and limestone, but not in synthetic calcite using X-ray photoelectron spectroscopy. The adsorption plateau of CPC on carbonates highly depends on the silicon composition in the carbonate samples due to the strong electrostatic interaction between CPC and negative binding sites in silica and/or clay. Compared with the adsorption of SDS, the advantage of low adsorption on carbonates using CPC is only valid when the silicon composition is low. The presence of CO₂ acidifies the surfactant solution and releases more divalent ions from the carbonate surface into the solution, causing precipitation of SDS regardless the amount of impurities in the carbonate sample. The adsorption of CPC on natural carbonates is less under 1 atm CO₂ than the one under 1 atm air.

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