Dynamic adsorption of asphaltenes on quartz and calcite packs in the presence of brine films

Soheil Saraji, Lamia Goual *, Mohammad Piri

Department of Chemical and Petroleum Engineering, University of Wyoming, 1000 E. University Avenue, Laramie, WY 82071, United States

**HIGHLIGHTS**

- The dynamic adsorption of asphaltenes was measured on quartz and calcite packs.
- The effect of brine chemistry on adsorption was studied.
- Electrostatic and hydration forces determine the stability of thin brine films.
- Hydration forces become dominant at high ionic strength for all quartz packs.
- Hydration forces are only dominant when calcite surface is positively charged.

**ABSTRACT**

The adsorption of asphaltenes on mineral surfaces in the absence of brine has been extensively studied in the past. However, brine is often present in reservoir formations and remains in porous media after drainage by oil as a continuous film of various thicknesses. The presence of a thick brine layer on the mineral surface can act as a mechanical barrier between asphaltenes and the mineral and therefore hinders the adsorption. On the other hand, a thin brine film (less than 100 nm thickness) can rupture under favorable conditions and allow asphaltenes to directly adsorb on the mineral surface. The stability of thin brine films and hence the amount of asphaltene adsorption depends on the nature of asphaltenes, the type of minerals in the rock, and the brine chemistry. This study investigates the dynamic adsorption of asphaltene-in-toluene solutions on packs of wet quartz and calcite. Unlike quartz, calcite is very reactive in aqueous media and can dissolve or precipitate under certain conditions. To the best of our knowledge, this is the first study of asphaltene adsorption on calcite packs in the presence of brine and under flow conditions. All experiments were performed on mineral packs with comparable mesh sizes and porosities and containing an irreducible brine saturation of about 15%. A UV–vis spectrophotometer was used to monitor the outlet concentration of asphaltenes. The effect of brine chemistry (ion concentration, type, and valency) on the dynamic adsorption of asphaltenes on quartz and calcite was systematically studied. Different adsorption trends were observed with quartz and calcite and explained on the basis of the surface forces involved in the stability of thin brine films. The results of this study can help to understand the complex wettability behavior of carbonate reservoirs.

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1. Introduction

The adsorption of surface-active components of crude oils (such as asphaltenes) on rock surfaces in the absence of brine (or water) has been extensively studied in the last few decades. The majority...
of these studies investigate adsorption under static [1–3], dynamic [4,5], and flow conditions [6,7]. In dilute toluene solutions (<1000 ppm), asphaltenes tend to form nanoaggregates [8] and adsorb as a monolayer on mineral surfaces [1,5,7]. More adsorption is usually observed on calcite than quartz [3,7], and is promoted at low flow rates [6,7]. However, brine is often present in reservoir formations and remains in porous media after drainage by oil phase as a continuous film of various thicknesses [9]. Fig. 1 shows a schematic of the distribution of immiscible phases in an unconsolidated porous medium after brine drainage by oil. Kaminsky and Radke [10] found that the mechanism of asphaltene adsorption on minerals in the presence of a brine film is not due to the diffusion of water-soluble asphaltene molecules through the film. Instead, asphaltentic material directly adsorbs on the mineral surface after film rupture. A thick stable brine layer will provide a mechanical barrier between the asphaltene and the mineral surface and therefore hinders the adsorption of asphaltenes [10]. On the other hand, a thin brine film may become unstable, rupture, and consequently promote asphaltene adsorption on minerals [11].

The stability of brine films on quartz, glass, or mica surfaces has been studied in the past. Buckley et al. [11,12] performed adhesion tests where a drop of oil was pressed on a glass microscope slide, immersed in brine, and then retracted. The adhesion of crude oil on glass surface was considered as a sign of film instability (i.e., film rupture). They investigated the effect of brine pH and salinity and found that non-adhesion regions (i.e., stable films) occur at high pH and high ionic strengths, whereas the system was adhesive (i.e., unstable films) at low pH and low ionic strengths. Basu and Sharma [13,14] used an Atomic Force Microscope (AFM) to measure the total surface force between an oil coated cantilever and a glass surface in brine. They observed that brine films are more stable at higher salt concentration and higher pH and explained their findings on the basis of Derjaguin and Landau, Verwey and Overbeek (DLVO) forces. On the other hand, Hiorth et al. [15] studied the effect of brine chemistry on the wettability of carbonate cores by water imbibition. The authors could not explain the wettability behavior of calcite (chalk cores) by considering only DLVO forces in the disjoining pressure of the brine film. Van et al. [16] measured the adsorption of 250-ppm asphaltenes in toluene solution on Berea sandstone cores with an irreducible brine saturation of about 25%. They observed an increase in asphaltene adsorption (i.e., less stable brine films) when the ionic strength and ion valency increased.

The stability of thin brine films (less than 100 nm) located between rock surfaces and crude oils depends on the surface forces acting on the brine-oil and rock-brine interfaces [11,13,17]. These surface forces are believed to have three components: electrostatic, dispersion, and structural forces [18]. The electrostatic forces result from excess counterion accumulation near a charged surface to satisfy local electroneutrality. When two charged surfaces (rock and oil) are brought close to each other in brine, the electrostatic interactions between their ion clouds could be attractive or repulsive. The dispersion forces (usually attractive) are a result of van der Waals London interactions between oil and mineral molecules. These first two components (dispersion and electrostatic) are well known as part of the DLVO theory. However, non-DLVO forces, such as hydration and hydrophobic forces, are believed to play an important role on the stability of thin films. Hydration forces arise from cation hydration by water molecules. At high ion concentrations, hydrated cations bind to negatively charged surfaces and can give rise to repulsive hydration forces between surfaces at very short range. Hydrophobic forces on the other hand are long-range attractive forces and exist between hydrophobic particles or surfaces in aqueous solutions. Among all these surface forces, van der Waals dispersion and hydrophobic interactions are usually not affected by the concentration and type of ions in the brine, whereas electrostatic and hydration forces are sensitive to the brine chemistry [18–20]. Therefore, any change in the brine composition that affects the stability of brine films can be explained through the competition between electrostatic and hydration forces. For instance, increasing the concentration of counterions in brine reduces the electrostatic repulsion due to double layer compression. At the same time, this causes an increase in repulsive hydration forces. However in some cases, divalent anions such as SO\textsubscript{4}\textsuperscript{2–} can enhance hydrophobic adhesion, as will be shown in this study.

Quartz and calcite are minerals frequently found in petroleum reservoir rocks. They both have crystalline structures but different surface energies. For instance, calcite is very reactive in aqueous media; it dissolves into ions and re-crystalizes dynamically [21]. On the other hand, quartz is quite stable in brine at a pH range of 1–10 [22]. The source of surface charges of calcite and quartz are also different in aqueous media. In quartz, the surface charges stem from acid-base reactions of superficial hydroxylated groups of quartz in brine. In calcite, surface charges are due to the hydrolysis of surface ions or the adsorption of species from aqueous solution on calcite [23].

Very limited studies have been performed on the adsorption of asphaltenes on minerals in the presence of brine films. To our best knowledge, there have been no studies on the dynamic adsorption of asphaltenes on calcite packs in the presence of brine films. In this work, we investigate the effect of brine chemistry (ion concentration and valency) on the dynamic adsorption of asphaltene-in-toluene solutions on pure quartz and calcite minerals. A series of flow experiments were conducted on mineral packs in the presence of irreducible brine using asphaltene-in-toluene solutions as model oil. The total amount of adsorbed asphaltenes was related to the stability of thin brine films on the surface of minerals. The adsorption behavior of asphaltenes on wet quartz and calcite surfaces was explained based on the surface forces involved.
2. Materials and methods

2.1. Materials

Materials include crude oil from Gibbs formation in Wyoming [7], n-pentane (98%, EMD Chemicals), HPLC grade Toluene (Fisher Scientific), pure quartz and calcite crystals (Wards Natural Science), certified HPLC grade de-ionized water (VWR International) with resistivity of 18.2 MΩ, Soltrol 170 (Chevron Phillips), 1-lodoctane (98%, Sigma–Aldrich), silica gel (Sigma–Aldrich), activated alumina (Sigma–Aldrich), hydrochloric acid (37 wt%, VWR International), sodium hydroxide pellet (Mallinckrodt Chemicals), sodium chloride (Columbus Chemical Industries), anhydrous calcium chloride (JT Baker), magnesium chloride (JT Baker), anhydrous sodium carbonate (EMD Chemicals), and sodium sulfate (EMD Chemicals).

All acids, bases, and salts used in this study were A.C.S. reagent grade.

2.2. Mineral preparation

Pure quartz and calcite minerals were received as 1–2 in. long pieces. They were crushed and ground in three steps using various grinding machines until they were in a powder-like consistency. Mineral powders with sizes between 100 and 200 mesh (74–150 μm) were separated by sieving. The separated powders were washed and rinsed with de-ionized water over 200 mesh sieve and dried at 110 °C. The color of quartz powder changed after grinding and washing from white to light brown, possibly due to metal contamination. Calcite minerals did not exhibit such a change in color because they have a much weaker structure and were not ground as hard. Therefore, we used an extra cleaning procedure to wash possible metal contamination off the quartz surface: (1) three solutions of hydrochloric acid at 1 N, 2 N, and 3 N were prepared by diluting concentrated acid (37 wt%, ~10 N); (2) 100 g of quartz powders (100–200 mesh) were mixed and soaked in 500 cc of 1 N hydrochloric acid solution; (3) the supernatant was decanted after 12 hours and this procedure was repeated with 2 N and 3 N acid solutions; (4) the quartz powder was neutralized by mixing and then soaking in 0.1 N sodium hydroxide solution for about an hour; (5) the powder was then washed thoroughly and rinsed with de-ionized water over a 200-mesh sieve; and (6) the quartz powder was dried in an oven at 110 °C.

2.3. Solution preparation

Asphaltene were separated from Gibbs crude oil by pentane precipitation. The separation procedure is described elsewhere [7]. Stock solutions of 500–ppm asphaltene in water–saturated toluene were prepared and used as model oil in this study. Brines were prepared with degassed, de-ionized water and pure salt at low (9 mM) and high salinity (900 mM) solutions. The salts used in this study were: NaCl, CaCl₂, MgCl₂, and Na₂SO₄. No attempts were made to manipulate the pH of the solutions. Soltrol 170, used as displacing fluid in drainage, was freshly purified before each experiment by passing it through an alumina–silica gel column.

2.4. Zeta potential measurements

Zeta potential measurements were carried out on quartz and calcite suspensions in brine using ZetaPALS zeta potential analyzer (Brookhaven Instruments Co.). Quartz powder was prepared by further grinding acid-washed particles (with a size range of 100–200 mesh) in agate mortar. Also a portion of the crushed calcite powder that passed through 200-mesh sieve was used for making suspensions. Samples were prepared by adding 10 g of the desired powder to 25 cc of brine and then sonicating the solution for half an hour. The suspension solutions were left to rest for about an hour before performing zeta potential measurements.

2.5. Experimental apparatus and procedure

The apparatus consists of a dual-cylinder Teledyne Isco pump model 260D to provide a continuous constant flow rate, two 2-liter stainless-steel accumulators, an aluminum sand-pack holder (2.53 cm inner diameter and 10.4 cm length) with fixed and adjustable end caps, and a double-beam UV-Vis spectrophotometer (Cary 4000, Varian, Inc.) to measure concentrations (see Fig. 2). The flow experiments were started by packing the dried mineral (74–150 μm) inside the pack holder. The weight and length of the pack were recorded and used to calculate the porosity. The pack was then vacuumed and saturated with freshly made brine stored in one of the accumulators. The brine-saturated pack was left for about 40 h so that the brine and the mineral reach chemical equilibrium. Then, purified Soltrol was injected from one accumulator into the pack to reduce the brine content of the porous medium to irreducible saturation. In order to reach uniform saturations along the pack, the flow rate was increased in small steps from 0.1 cc/min up to 5 cc/min. During this step, the density and volume of the produced brine were measured and used to calculate the irreducible brine saturation. The pH of the produced brine was also recorded for each experiment. After establishing the irreducible brine saturation inside the pack, the Soltrol was replaced with pure water–saturated toluene by injecting several pore volumes (at least 5 PV) of the liquid. Finally, the asphaltene solution was injected through the pack with a constant flow rate of 0.5 cc/min. The concentrations of the outlet asphaltene solution were monitored automatically by the spectrophotometer at a pre-defined frequency of 510 nm. The spectrophotometer was pre-calibrated as described elsewhere [7] by a standard toluene solution of known asphaltene concentration.

2.6. Packing quality

The packing quality of an unconsolidated porous medium can be affected by the packing procedure employed. The packing procedure affects the basic properties of the pack such as the porosity distribution and hence changes the flow pattern and fluid distribution inside the pack. Therefore, using a reliable and repeatable packing procedure is crucial to prepare comparable packs. In order to check the packing quality and repeatability of the packing procedure, a medical X-ray CT scanner was used to calculate the porosity and irreducible brine saturation distribution inside the packs. The preparation of packs with irreducible brine saturations is similar to the procedure described in Section 2.5 but instead of pure Soltrol 170, a 10% 1-lodoctane in Soltrol solution was used to increase the CT number of Soltrol so that a desired difference between the CT numbers of brine, Soltrol, and mineral were obtained for saturation analysis. First, CT numbers of asphaltene solution, 900 mM NaCl brine, tagged Soltrol (with 1-lodoctane), and minerals were measured individually. Second, a sand pack was prepared, vacuumed, and scanned entirely at consecutive 1 mm vertical planes along the porous medium. Using this information and previously measured CT numbers of brine and minerals, porosity profiles along the pack were obtained [24]. This procedure was performed for two calcite packs and one quartz pack and the results are shown in Fig. 3a. The average porosity calculated from X-ray CT scanning was 44.97% for quartz pack and 44.96% and 43.85% for two calcite packs. These values were comparable to material balance calculations (44.74%, 44.71%, and 43.50%, respectively). Fig. 3a shows that the three packs are fairly homogeneous and well packed except in the first 5 mm. This heterogeneity is located at the upper part of the holder and inevitable at the time of packing. It should be noted
that porosity variations for all of the packs are less than 2%, which confirms the repeatability of the packing procedure employed in this work. In addition to porosity determination, a saturation profile of the quartz pack was determined after drainage. The pack was saturated with the brine (900 mM NaCl), flooded with tagged soltrol as described in the previous section, and then scanned entirely with the medical X-ray CT scanner at 1 mm intervals. The irreducible brine saturation profile along the quartz pack was calculated [24] and illustrated in Fig. 3b. Except in the last 5 mm of the pack, the saturation profile is quite uniform and the average irreducible water saturation was 15.33%. This value is comparable to 15.34% obtained through material balance calculations.

3. Results and discussions

The dynamic adsorption of asphaltenes in the presence of irreducible brine was measured in quartz and calcite packs and the effect of brine salinity, ion type, and cation valency was investigated. The pack properties, brine specifications, zeta potential of the minerals, and total asphaltene adsorption amount for each test are listed in Table 1. The data in this table represent the average of three adsorption tests and the standard deviations are shown in figures as error bars. Four types of salts (NaCl, CaCl₂, MgCl₂, and Na₂SO₄) were selected in this study and brines with low ionic strength (9 mM) and high ionic strength (900 mM) were prepared from each type of salt. All the packs had comparable
3.1. Effect of irreducible brine

The dynamic adsorption of asphaltenes in dry packs was previously studied and polar interactions were found to be the dominant adsorption mechanism [7]. The adsorption results were successfully modeled using the theory of activated adsorption/desorption (i.e., Langmuir kinetic equation). In the case of wet packs, the adsorption mechanism is more complex due to the presence of brine films. However, it is reasonable to assume that the same polar interactions exist between asphaltenes and mineral surfaces whenever a brine film ruptures. Fig. 4 compares the amounts of asphaltene adsorbed on dry quartz and calcite packs [7] with the packs of this study containing 15% irreducible brine saturation (Tests 1 and 5). Although the presence of brine hinders the adsorption of asphaltenes, there is still considerable adsorption (about 105 μg/g of mineral) in the wet packs. Comparable reduction in adsorption values regardless of surface properties for quartz and calcite minerals supports the concept of mechanical barrier for asphaltene adsorption due to thick brine films.

3.2. Quartz packs

The effect of salinity and cation valency on asphaltene adsorption was investigated in quartz packs. NaCl and CaCl₂ salts were

![Graphs showing pH, zeta potential, and asphaltene adsorption](image)

Fig. 4. Comparison between adsorptions on dry packs and packs with 15% brine saturation of 9 mM NaCl (Tests 1 and 5).

![Graphs showing pH, zeta potential, and asphaltene adsorption](image)

Fig. 5. Quartz packs containing 15% irreducible brines with various ion concentrations and valency: (a) pH of equilibrated brine, (b) zeta potentials of suspended quartz powder in brines, and (c) total asphaltene adsorption amount on quartz.

<table>
<thead>
<tr>
<th>Test</th>
<th>Mineral</th>
<th>Salt</th>
<th>Ionic strength (mM)</th>
<th>φ (%)</th>
<th>$S_{ir}$ (%)</th>
<th>$\Gamma$ (μg/g)</th>
<th>pH (equilibrium)</th>
<th>Zeta potential (mV)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Quartz</td>
<td>NaCl</td>
<td>9</td>
<td>44.3</td>
<td>15.6</td>
<td>105.9</td>
<td>7.70</td>
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<td>2</td>
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<td>NaCl</td>
<td>900</td>
<td>44.5</td>
<td>15.5</td>
<td>92.4</td>
<td>8.80</td>
<td>-10.14</td>
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<tr>
<td>3</td>
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<td>44.0</td>
<td>15.6</td>
<td>108.6</td>
<td>8.08</td>
<td>-30.81</td>
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<tr>
<td>4</td>
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<td>CaCl₂</td>
<td>900</td>
<td>44.0</td>
<td>15.0</td>
<td>101.0</td>
<td>7.11</td>
<td>-2.94</td>
</tr>
<tr>
<td>5</td>
<td>Calcite</td>
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<td>43.8</td>
<td>15.2</td>
<td>104.9</td>
<td>8.50</td>
<td>-13.63</td>
</tr>
<tr>
<td>6</td>
<td>Calcite</td>
<td>NaCl</td>
<td>900</td>
<td>44.0</td>
<td>15.5</td>
<td>109.4</td>
<td>9.17</td>
<td>-5.02</td>
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<tr>
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<tr>
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<td>107.7</td>
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<tr>
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<td>9.33</td>
<td>-8.41</td>
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Porosities (43–44%) and irreducible brine saturations (14–16%). Different adsorption trends were observed with quartz and calcite and explained on the basis of the surface forces involved in the stability of thin brine films (i.e., electrostatic, Van der Waals, and structural). Note that mechanisms such as acid-base interactions or ion bridging with divalent cations are inferred here through their effect on the electrostatic forces. Also, since the effects of aging or gel formation at the oil–water interface are negligible [25], interfacial rheology may not explain the effect of brine chemistry within the concentration range used in this study.
used at ionic strengths of 9 and 900 mM (Tests 1–4 in Table 1). The brine pH and the zeta potential of quartz suspensions in brine with different salts and ionic strengths are illustrated in Fig. 5a and b. The amphoteric dissociation of the surface silanol groups (SiOH) is responsible for the surface charges on quartz. In the neutral and basic range of pH, the quartz surface acquires negative charges. In the acidic range, it becomes positively charged. In this study, the brine pH for quartz packs was in the neutral range of 7–8 and no pH modifier was used to manipulate the solution pH (see Fig. 5a). The measured zeta potential of quartz surface (Fig. 5b) was indeed negative and decreased with increasing salt concentration and ion valency (Ca$^{2+}$ compared to Na$^+$. This is due to the accumulation of more cations in the vicinity of negatively charged quartz surfaces, which results in a partial neutralization of the surface charge of quartz. Fig. 5c compares the amounts of asphaltene adsorbed on quartz during Tests 1–4. The last test was repeated and the standard deviation in the adsorption amount was about 2 μg/g (see Fig. 5c). The results indicate that asphaltene adsorption is promoted at low ion concentration and high cation valency. It is reasonable to consider that the majority of asphaltene adsorption occurs directly on the quartz surface after rupturing of thin brine films [16,26].

In order to explain the results in Fig. 5c, one can link asphaltene adsorption in mineral packs to the stability of thin brine films covering the mineral surface. This implies that more adsorption is the result of less stable films. Among the surface forces present in asphaltene/brine/mineral systems, van der Waals dispersion and hydrophobic forces are attractive and almost independent of brine chemistry [18–20]. Since the only variables in Tests 1–4 are the ion concentration and valency, the amount of attractive dispersion and hydrophobic forces should be the same in all the tests. Accordingly, it is the competition between the remaining forces (i.e., electrostatic and hydration forces) that determines the relative stability of thin brine films in these experiments. At low salt concentrations, the electrostatic forces between the two sides of the brine film (i.e., brine/asphaltene and brine/quartz interfaces) are repulsive because both asphaltenes [27] and quartz (Fig. 5b) are negatively charged. When the ionic strength of the brine was increased from 9 mM to 900 mM, the concentration of cations (counterions) increased 100 times, which reduced the double layer thickness (Debye length) from 3.2 to 0.32 nm and the zeta potential from −61 to −10 for NaCl and from −30 to −3 for CaCl$_2$ (see Fig. 5b). This means that the electrostatic repulsion reduced with increasing ionic strength of both salts. Therefore, one expects to have less stable brine films and hence more asphaltene adsorption at higher salt concentration. However, the magnitude of repulsive hydration forces is significant at high ionic strength (Fig. 6a and b). As a result, the thin brine films become relatively stable and less adsorption occurs on quartz for both salts. These results are well supported by previous experimental studies conducted by AFM surface force measurements [13,14] and adhesion tests [11,12].

Increasing the ionic valency of salts from 1 to 2 resulted in lower zeta potential values of quartz (Fig. 5b). This is due to the much stronger ion binding of Ca$^{2+}$ ion to quartz, as compared to Na$^+$ [18]. Therefore, the electrostatic forces are reduced at high ion valency, which results in less stable brine films and more asphaltene adsorption in CaCl$_2$ brines compared to NaCl brines. This occurred at both ionic strengths regardless of the presence or absence of hydration forces. The same trend was reported in the past [16] during the dynamic adsorption of asphaltene in Berea sandstone using 90 mM brines containing Na$^+$, Ca$^{2+}$, and Al$^{3+}$ cations. The brines with higher valency cations resulted in higher adsorption of asphaltene.

### 3.3. Calcite packs

Four salts (NaCl, CaCl$_2$, MgCl$_2$, and Na$_2$SO$_4$) with ionic strengths of 9 and 900 mM were used to study the effects of salinity, cation type, and valency on asphaltene adsorption in calcite packs (Tests 5–12 in Table 1). The pH values of the equilibrated brines with calcite mineral are shown in Fig. 7a and are in the basic range of 9–10 for all the tests. Unlike quartz, calcite crystals dissolve in brine and produce Ca$^{2+}$, CO$_3^{2−}$, and HCO$_3^{−}$. These ions undergo chemical reactions in the aqueous phase and buffer the pH of the solution toward basic values [22]. Fig. 7b illustrates the zeta potential of calcite suspensions in various brines. The calcite surface is negatively charged with NaCl and Na$_2$SO$_4$ salts and positively charged with CaCl$_2$ and MgCl$_2$ salts. Somasundaran and Agar [23] proposed that the possible mechanism of surface charging in calcite is either the hydrolysis of surface ions (Ca$^{2+}$, CO$_3^{2−}$) or the adsorption of

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**Fig. 6.** Distribution of hydrated cations in thin brine films at high ionic strength: (a) NaCl brine film on quartz, (b) CaCl$_2$ brine film on quartz, (c) NaCl brine film on calcite, and (d) CaCl$_2$ brine film on calcite.
dissolved ions. This means that H⁺ and OH⁻ are not the only ions that can change the surface charge of calcite, as it is the case for quartz. Any dissolved ions that can interact with or adsorb on calcite can change the surface charge of this mineral. These ions are called potential determining ions (PDI). There are other ions such as Mg²⁺ and SO₄²⁻ that specifically adsorb on the non-diffuse or Stern layer of the calcite double layer and modify the surface charge. Pierre et al. [21] reported that calcite surfaces acquire a positive charge in the presence of divalent cations. However, the presence of only 0.5 mM SO₄²⁻ could neutralize the surface of calcite, and higher concentrations of this ion changes the surface charge to negative. Calcite was also negatively charged in NaCl brine containing a small concentration of divalent cation (Ca²⁺). The measured zeta potential values in this study are in agreement with those found in the literature.

Fig. 7c provides the amounts of asphaltenes adsorbed in calcite packs containing brine with different salt concentration and valency (Tests 5–12). Some tests were repeated to assess their reproducibility. The standard deviations, shown as error bars in Fig. 7c, indicate very reproducible data. It is important to note that the monolayer adsorption of asphaltenes on mineral grains is able to alter their wettability toward intermediate–oil wet. Let us consider one gram of the calcite grains used in this study with an average grain diameter of 100 μm and assume 1/3 of their surface area is available for adsorption (based on the results of Fig. 4). Knowing that asphaltenes are in the nanoaggregate state at the concentrations used in this study, with a typical size of 2 nm and density of 1000 kg/m³, adsorption of only 1 μg of asphaltenes can change the wettability of 7% of the grains in one gram of calcite and consequently develop various local contact angles inside the pack. Therefore, the small variations in asphaltene adsorption shown in Fig. 7c will have considerable effect on the wettability pattern of porous media and hence fluid distribution and flow behavior inside these media.

At low salt concentration of 9 mM, the amount of asphaltenes adsorbed on calcite is about 105 μg/g with NaCl brine and is comparable to the amount adsorbed on quartz. However, the adsorbed amounts are higher with CaCl₂ and MgCl₂ brines. This is possibly attributed to the presence of electrostatic forces between the negatively charged asphaltene/brine interface [27] and positively charged calcite/brine interface (Fig. 7b). Asphaltene adsorption on calcite is even higher in the presence of SO₄²⁻ ion (113 μg/g). Since the zeta potential of calcite is about the same in Na₂SO₄ and NaCl brines (Fig. 7b), the same repulsive electrostatic forces were expected in both cases. However, the presence of SO₄²⁻ ion increases hydrophobic attraction across the brine film and hence destabilizes the film. In addition, this ion can react with dissolved Ca²⁺ ions to precipitate anhydrate (CaSO₄) or gypsum (CaSO₄·2H₂O) [22]. The precipitated material would deposit on calcite surface and increase its surface area. Thus, the increase in asphaltene adsorption for Na₂SO₄ brine was possibly due to a combined effect of increase in hydrophobic attraction and increase in the surface area available for adsorption. The poor repeatability of these tests compared to other tests might be an indicator of random deposition of mineral in these packs.

At high CaCl₂ and MgCl₂ concentration in brine (900 mM), the magnitude of attractive electrostatic forces across the thin film reduces due to double layer compression. In addition, repulsive hydration forces increase under these conditions. As a result, the amount of adsorbed asphaltenes reduces on calcite (Fig. 7c). Note that the nature of repulsive hydration forces is different in calcite and quartz. As shown in Fig. 6a and b, the hydrated cations accumulated near the negative Silanol groups of quartz are responsible for the repulsive hydration forces. However for calcite, the hydration forces are due to the hydrated positive ions that are attached to the surface (Fig. 6d). These ions can be the original surface ion on the calcite (Ca²⁺) or other potential determining ions adsorbed from the solution (e.g., Mg²⁺). At high NaCl (and Na₂SO₄) concentrations, CO₃²⁻ (and SO₄²⁻) anions are dominant on calcite surface and result in a negatively charged surface (Fig. 6c). These ions are not as strongly hydrated as cations and therefore generate negligible hydration repulsion forces. This is why the effect of hydration repulsion is not present in the case of NaCl and Na₂SO₄ brines and the amount of adsorbed asphaltenes slightly increases on calcite at high ionic strength (Fig. 7c).

4. Conclusions

The dynamic adsorption of asphaltenes was measured on quartz packs and for the first time on calcite packs in the presence of 15% irreducible brine saturation. The effect of brine chemistry (ion concentration and valency) on the adsorption amount was investigated in a systematic manner. In quartz, the adsorbed amounts decreased at higher salt concentrations mainly due to larger repulsive hydration forces, which stabilized the thin brine films. The same behavior
was observed in calcite with CaCl₂ and MgCl₂ brines. However, hydration forces may not be dominant in NaCl brines and as a result more adsorption was recorded on calcite at high ionic strengths. The large adsorbed amounts measured with Na₂SO₄ brines are possibly due to an increase in hydrophobic attractive forces in the presence of divalent anion and/or the precipitation of anhydrate or gypsum on calcite, which increases the surface area available for adsorption. The results of this study can help understand the complex wettability behavior of carbonate reservoirs. However, it is important to note that there are other surface-active components in maltenes (such as naphthenic acids) that can play a role in the wettability alteration of rocks. Therefore, further studies are necessary to understand the combined effect of asphaltenes and naphthenic acids on the wettability alteration of minerals.

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