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Novel Approach to Study the Impact of Asphaltene Properties on Low Salinity Flooding

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Abstract

Low salinity water flooding (LSW) has gained significant attention, because of its advantages compared with other enhanced oil recovery (EOR) methods. LSW's positive contribution to recovery factor has been demonstrated in the literature at lab and field scales. However, LSW flooding does not always increment oil recovery. It is a specific combination of properties of an asphaltenic crude oil, chemically equilibrated brine, and rock surface that may explain the success or failure of LSW. In this work, we introduce a novel experimental approach to study asphaltene-like chemical interactions with surfaces rock minerals to evaluate the effectiveness of applying LSW.

When studying the impact of asphaltene properties on incremental recovery, one aims to detach some of the immobile oil, which is semi-irreversibly stuck on rock surface. This is a difficult task, because of varying crude oil composition, as well as asphaltene interfacial and chemical properties. To overcome these issues, we split the problem into several parts. We study how mono- and poly-functional chemical compounds mimic asphaltene interactions with mineral surfaces, like silica and calcium carbonate, which are proxies for sandstones and limestones, respectively. For example, amines, quaternary ammonia or carboxylates represent asphaltene functional groups that are mainly responsible for crude oil base and acid numbers, respectively. Adsorption of polymers and oligomers containing such groups mimics the irreversible asphaltene deposition onto rock surface through formation of chemically active polymer-like structures at the oil-brine interface.

The silica surface is negatively charged in brines with pH above 2. Silica attracts positively charged ammonia salts, such as cetrimonium chloride (CTAC). However, negatively charged mono-functional carboxylates, i.e. anionic surfactants, like sodium hexanoate (NaHex), hardly adsorb onto silica, even in the presence of a bridging ion, like calcium.

In contrast to silica, calcium carbonate surface has both positive and negative charges on its surface. We found that CTAC adsorbs onto calcium carbonate in any brine tested. NaHex shows minimal adsorption onto calcium carbonate only in the presence of calcium ions suggesting a contribution of an ion-bridging mechanism.

Adsorption of all studied mono-functional surfactants is fully reversible and, consequently not representative of asphaltenes. Multifunctional compounds, i.e., polymers, demonstrate irreversible, asphaltene-like, adsorption. We studied adsorption of carbohydrates decorated with individual amines and quaternary ammonia functional groups.

The carbohydrates with amine functional groups adsorb irreversibly on calcium carbonate and silica in all tested brines with pH up to 10. Therefore, a lower base number (BN) in crude oils indicates a higher potential for LSW.

Our findings demonstrate the proof of concept that contribution of different functional groups to asphaltene adsorption/deposition can be studied using functionalized water-soluble polymers. This framework is useful for assessment of adsorption strength vs. number of active groups as well as screening of efficient detachment process of asphaltenic crude oils from rock surface.

Introduction

More than 60% of the world's oil reserves are in carbonate reservoirs (Bai and Xu, 2014), which justifies the strong interest in testing low salinity water (LSW) injection in such environments. Up to date, there are different theories explaining the underlying mechanisms of LSW, with no general agreement in among the many researchers who study different aspects of LSW (Liu and Wang, 2020). This is expected, because the complexity of the process that requires a deep knowledge of surface chemistry and physics. Taking a step-back to understand the mechanisms of oil deposition onto a mineral surface might help in answering part of the question.

The practice of controlling salinity and composition of injected water has been receiving wide attention from academia and industry, because of its economical and logistical advantages. Significant effort has been invested into the understanding of the underlying

mechanisms of LSW and demonstrating its potential. The positive impact of deploying this technique has been demonstrated in sandstones (Tang *et al.*, 1997; Morrow *et al.*, 2011; Brady *et al.*, 2015), limestone (Yousef *et al.*, 2011), and dolomite (Strand *et al.*, 2016), (Shariatpanahi *et al.*, 2016).

Understanding the development of mixed-wettability of reservoir rock at the micro-scale is an important step toward optimizing the recovery of crude oil at macro-scale (Benner *et al.*, 1941; Morrow, 1990; Buckley, 1999; Jadhunandan and Morrow, 1995). Once oil invades a reservoir rock, which initially is water-wet and characterized by low contact angles, it starts to drain out the interstitial water bodies (Kovscek *et al.*, 1993; Salathiel, 1973; Patzek, 2001). High capillary pressure is required to allow oil deposition onto rock surface (Kovscek *et al.*, 1993; Patzek, 2020). At high capillary pressures, the oil/water interface presses against the rough rock surface, whose asperities are filled with water. The roughness peaks can then dewet, and allow asphaltene at the interface to deposit onto the elevated parts of the rock surface, making it oil-wet such that now the surface is characterized by high contact angles. At the same time the pore surface develops mixed-wet state, i.e. some part of the pore are oil wet and some part of the pore are water-wet. It is the mixed-wet state of the pores that is essential to LSW. The fundamental understanding of the underlying mechanisms of how reservoir rock surface changes wettability from water-wet to mixed-wet is an essential step in optimizing the enhanced oil recovery (EOR) processes.

Adsorption of polar components is suggested as the main contributor of changing wettability of parts of the rock surface from water- to oil-wet (Anderson, 1986; Buckley *et al.*, 1998; Mwangi *et al.*, 2018), thus impacting oil recovery (Bourrel and Passade-Boupat, 2017). Asphaltene is the part of oil containing these polar components, and – hence – their adsorption onto rock surface governs the process of irreversible adsorption (deposition) and wettability alteration (Buckley *et al.*, 1997). How asphaltene adsorbs in the presence of thin water films has been investigated by several groups, e.g., (Hu *et al.*, 2019; Daughney, 2000; Gonzalez and Taylor, 2016). Gonzalez and Taylor (2016) investigated how asphaltene adsorb onto quartz powder by varying thickness of the pre-adsorbed water. In our earlier study (Hu *et al.*, 2019), we concluded that a 500 nm water film would be sufficient to mask the rock surface and block all asphaltene components from reaching the surface.

Several groups have investigated the LSW, e.g., (Awolayo *et al.*, 2018; Gandomkar and Rahimpour, 2017). Drummond and Israelachvili (2002) generated a “wettability map” to correlate changes in wettability, represented by dynamic contact angle, with adsorption under different conditions of pH and salinity. A number of hypotheses attempt to explain the mechanism(s) of LSW in sandstones: multicomponent ion exchange (MIE) (Lager *et al.*, 2008), electric double layer expansion (DLE) (Ligthelm *et al.*, 2009; Nasralla and Nasr-El-Din, 2014; Xie *et al.*, 2014, 2019; Tian and Wang, 2017a), fines migration (Tang and Morrow, 1999; Yu *et al.*, 2019), pH increase similar to alkaline flooding followed by saponification (McGuire *et al.*, 2005), and wettability modifiers (Morrow *et al.*, 1998; RezaeiDoust *et al.*, 2009). Suggested mechanisms for calcium carbonate include MIE (Srisuriyachai and Meekangwal, 2017), wettability alteration (Austad *et al.*, 2011; Rashid *et al.*, 2015), DLE (Mahani *et al.*, 2016, 2017), and rock dissolution (Buckley and Morrow, 2010; Hiorth *et al.*, 2010; Zahid *et al.*, 2012; Al-Shalabi and Sepehrnoori, 2016; Lashkarbolooki *et al.*, 2016). Other efforts include attempts to understand electrokinetics of LSW (Tian and Wang, 2017b; Takeya *et al.*, 2019). However, literature still indicates that more work is needed in investigating and understanding mechanisms, especially on calcium carbonate (Derkani *et al.*, 2018; Al-Shalabi and Sepehrnoori, 2016; Katende and Sagala, 2019).

Asphaltenes, which can be difficult to handle, are giant molecular conglomerates that are formed of several stacked benzene rings with chains that contain polar and non-polar groups (Sjöblom *et al.*, 2015; Mullins *et al.*, 2012; Mullins, 2011). Our goal is to mimic asphaltene depositing onto a water-covered solid surface by selecting a number of representative functional groups, whose adsorption can illuminate asphaltene adsorption behavior. In summary, the main focus of this paper is to develop an understanding of how asphaltene adsorb irreversibly on rock surface and change the rock wettability.

Song *et al.* (2020) emphasized the importance of understanding the role of surface-active components present in asphaltene in the reverse wettability alteration process during LSW. Orozco *et al.* (2019) indicated how amino acids can act as wettability modifiers for carbonate surface from oil- to water-wet in their case. The work by Mwangi *et al.* (2018) indicates that oil-wetness in sandstone and carbonate rocks increased in the presence of long-chain acids, while water-wetness increased in the presence of short-chain acids. Several groups have looked into the role of carboxylates (Wang *et al.*, 2016) in depositing crudes irreversibly on surface.

Acid number (AN) is an indication of the free acidic content available in the crude and tested by a standard approach (ASTM, 1989a), later revisited by Fan and Buckley (2007) to improve measurements. In the oil literature, acid number is sometimes attributed to the activity (concentration) of carboxylates, which are only one of several acidic crude components such as, e.g., naphthenic acids. The impact of carboxylic groups on rock wettability and oil recovery was evaluated by several groups (Fathi *et al.*, 2011; Norrman *et al.*, 2018). Others evaluated adsorption of several active crude components (Thomas *et al.*, 1993). On the other hand, base number (BN) is an indication of the basic components available in the crude and measured using ASTM (1989b). The literature sometimes ascribes base number to the activity of components contributing to crude alkalinity such as amines.

Both numbers are the lumped indicators of activity of crude acids or bases, with no further insights. Details of group density, monomeric vs. polymeric, or structure, short vs. long chains, are concealed in these numbers. Correlating the magnitudes of both numbers with wettability has been investigated for a long time, e.g., Dubey and Doe (1993); Farooq *et al.* (2019); Song *et al.* (2020). Some researchers have tried to vary the values of both numbers or the ratio between the numbers to be correlated with recovery (Punternvold *et al.*, 2007). It is worth noting that formulating a model-oil by only relying on matching acid or base numbers can be misleading, if the functional groups and structures are not representative of crude oil.

Our experimental approach aims to demonstrate presence or absence of irreversible adsorption of active chemical groups on silica and calcium carbonate surfaces. We use a model polymer to represent the surface-active polar crude components in the asphaltenes. For demonstration purposes, we have selected amino functional groups. We evaluate whether mono-amines and poly-amines can be model-compounds to mimic asphaltene interactions with silica and calcium carbonate surfaces at different ionic compositions. Amines are polar groups and form relatively strong bonds, see (Wu *et al.*, 2017), at pH = 8, similar to reservoir conditions. In addition, we also evaluate adsorption of mono carboxylates onto calcium carbonate surface after we studied monocarboxylates adsorption onto silica (Hu *et al.*, 2019).

This approach allows identification of the main contributing species/functional groups to asphaltene adsorption. The knowledge of these functional groups will assist in the understanding of asphaltene bonding to the rock surface and consequently promote research on debonding of the asphaltenes fully or partially to achieve incremental oil production.

Experiments and Methods

Chemicals

Surfactants: Cetyltrimethylammonium chloride (CTAC) as 25%_{wf} in water was obtained from (Sigma-Aldrich, USA). Cetyltrimethyl ammonium bromide (CTAB), high purity powder was obtained from VWR Life Science, USA. Sodium hexanoate powder was obtained from Sigma-Aldrich, USA.

Polymers: Dextran-quaternary amine with 20k Dalton (1 amine group to 4 glucoses) powder was obtained from TdB Labs, Sweden.

Brines: Deionized (DI) water was obtained from Milli-Q water purification system, which delivers ultrapure type 1 water with 18.2 MΩ·cm at 25 °C, and TOC below 5 ppb (Merck Millipore Corporation, USA). Calcium chloride dihydrate powder with purity of 99.5% was obtained from Sigma-Aldrich, USA. Sodium carbonate decahydrate powder was obtained from Sigma-Aldrich, USA. Sodium chloride powder was obtained from Fisher Scientific, USA. For zeta potential measurements, we used 5 μm calcite powder of 99.5% purity (metal base) obtained from Alfa Aesar, USA.

PALS Zetasizer: Zetasizer Nano ZS (Malvern Instruments Ltd, Malvern, UK) was used to measure the potential of tested brines at room temperature of 21 °C. Disposable folded capillary cells (DTS1070) were used by applying AC voltage of 40 V across the electrodes spaced by 16 mm. Smoluchowski's formula was then used to convert the measured electrophoretic mobilities to zeta potentials (Hunter, 1981). Ionic strength of the tested brines was a key factor in setting the speed of the applied electric field. Fast field mode (monomodel) was applied for brines with high ionic strength suspensions (100 mM) yielding a clear sharp response. To check for reproducibility, measurements were repeated five times for every sample showing a precision range within ± 5 mV.

Atomic Force Microscopy (AFM): Evaluation of a sensor's surface topography was performed with the Atomic Force Microscopy (AFM) apparatus using the z-sensor channel (topography channel). Tests were performed using the Bruker Dimension Icon Model (Bruker Corporation, Massachusetts, CA, USA) with a RTESPA tip (MPP-11120, k = 20–80 N/m) under air tapping mode. The scan rate was 0.996 Hz with a resolution of 512 samples per line. For testing the sensors, a sample point around the center was selected to be scanned at different ranges (1 × 1 μm²). To process, visualize and analyze the data, the free Gwyddion software was used (Nečas and Klapetek, 2012). Our analysis captured surface roughness over the scanned area in terms of the arithmetical mean (Ra) and the root mean square (Rq) elevations. Fig. 1 shows scans of a new cleaned silica and calcite sensor topography with a maximum roughness of ± 1 nm which confirms the smoothness of coatings.

Figure 1: Examples of AFM topography scans of the central area of a new silica and calcite coatings on QCM-D resonators

Quartz Crystal Microbalance with Dissipation (QCM-D)

Setup: Adsorption of the selected polymers was measured with the advanced quartz crystal microbalance with dissipation (QCM-D) Omega model with 8 cells (Biolin Scientific, Sweden). Fig. 2 shows a QCM schematic. The testing protocol ensured reproducibility by allowing the use of resonators only once.

Sensors: The silica and calcium carbonate quartz resonators were obtained from Biolin Scientific, Sweden, coated with silica (QSX 303) and calcite (QSX 999). To prepare the sensors, new silica sensors (QSX 303) were first sonicated in a cleaning solution for 5 minutes followed by purging with Grade-6 99.9999% nitrogen until fully dried. Then, sensors were placed in the chamber of pico low-pressure plasma system (Diener electronic, Germany) to be treated at the 13.56 MHz generator frequency. Power was set at 15% of the setup maximum power of 200 W. The chamber was first vacuumed down to 0.3 mbar, and then plasma was ignited while a continuous oxygen stream was injected at a rate of 5 sccm for 10 min. Finally, sonication was repeated for 5 minutes followed by plasma exposure for 10 minutes. Calcium carbonate sensors (QSX 999) underwent a different cleaning procedure due to the risk of dissolving the coatings. The cleaning included purging with Grade-6 99.9999% nitrogen followed by plasma exposure with a continuous flow of oxygen for 5 minutes.

Steps: The cleaned sensors were placed in QCM-D cell holder and transferred to the chamber to start the experiments at the flow rate of 50 $\mu\text{L}/\text{min}$ at the set temperature of 20 °C. Data were collected at resonant frequencies and dissipation of the first to the thirteenth overtone was recorded. The first part of all experiments was establishing a stable baseline with a frequency drift less than 0.1 Hz/min and a dissipation drift less than $10^{-7}/\text{min}$ for at least 5 overtones and a minimum of 2 min to ensure signal stability. Once the baseline was established, a reference brine was flowed for 20 minutes, and then the polymer solution was injected for 30 min, followed by flushing with the reference brine for 30 minutes. It should be noted that all brines were equilibrated with a concentration of (1 g/L) of 5 μm calcite powder at air partial pressure of $\text{CO}_2 \sim 350$ pp). Every experiment was reproduced at least twice. Data for the 5th overtone were processed and analyzed with MATLAB, R2016a, MathWorks. The data were filtered using the Butterworth MATLAB function with a 2nd order low-pass filter and a cutoff frequency of 0.05 Hz.

Data Interpretation: *Sauerbrey* (1959) developed a relationship between the change of mass of a resonating crystal and the oscillation frequency

$$\hat{\Gamma} = -C \frac{(f - f^*)}{n} = -C \frac{\Delta f}{n} \quad (1)$$

Here $\hat{\Gamma}$ is the mass per unit area, f^* is the natural frequency of the crystal (5 MHz), f is the actual measured frequency, and n is the overtone number (1, 3, 5 etc.). $C = 17.7 \text{ ng}/[\text{cm}^2 \cdot \text{Hz}]$ is the resonator constant for a 5 MHz AT-cut quartz crystal.

Total change of frequency consists of two parts: the deposited mass and change in the bulk density, ρ , and the viscosity, η , of the investigated fluid. The change in physical properties can be accounted for as in *Kanazawa and Gordon* (1985)

$$\frac{\Delta f}{n^{1/2}} = -f_0^{3/2} \left(\frac{\eta \rho}{\pi \rho_Q \mu_Q} \right)^{1/2} \quad (2)$$

where ρ_Q is the quartz density and μ_Q is the shear modulus of quartz. This term is called the “density-viscosity” effect.

In our experiments, the frequency shifts are measured relative to a baseline brine, which makes the combined change

$$\Delta f_n = -n \frac{1}{C} \hat{\Gamma} - \left(\frac{n f_0^3 \eta_L \rho_L}{\pi \rho_Q \mu_Q} \right)^{1/2} \quad (3)$$

The first term on the right of Eq. 3 is Eq. 1. The second term is the “density-viscosity” effect from Eq. 2.

Figure 2: Schematic of a Quartz Crystal Microbalance with Dissipation (QCM-D)

Results and Discussion

Surface Charge of Silica and Calcium Carbonate

Surface charge or charge accumulated in the β -plane can be inferred from zeta-potential measurements. According to *Grahame* (1947, Eq. 41), in case of silica, negative zeta potential means accumulation of positive charge in the diffuse layer, preferential adsorption of positively charged ions in the β -plane, and a negatively charged surface.

Since silica surface is negatively charged, cations, like sodium or calcium adsorb in the β -plane, but never fully compensate the surface charge (*Iler*, 1979). Hence, zeta potential of silica in brines containing sodium or calcium is always negative down to pH 1-2. Therefore, zeta potential reversal for silica happens only at extreme conditions. Our working conditions, which are shown in Table. 1, are far from any of such extremes, and we can safely assume negative charge at silica surface. Previously we confirmed these conclusions by studying and modeling the chemistry of silica surface (*Hu et al.*, 2019, Appendix).

In comparison, the $\langle 104 \rangle$ calcite surface is essentially neutral from the crystallography point of view, because it has the same number of positive and negative charges/sites. Calcium carbonate surface is highly reactive with the possibility of having both positive and negative charges on its surface which makes its chemistry different than that of most other minerals. This implies that calcium carbonate surface charge is always neutral or close to neutral and all charges accumulate in the β -plane due to preferential adsorption, as illustrated in Fig 3.

Figure 3: For calcium carbonate, charge accumulating in the β -plane is neutralized in the d -plane

For calcium carbonate, we measured zeta potential using the phase analysis light scattering method (PALS), which is relatively simple to operate, but can suffer from laser light scattering problems. Zeta potentials of calcium carbonate powder were measured for three different brines containing 100 mM of Na_2CO_3 , CaCl_2 , or NaCl , which presents the ionic strengths of 100 mM and 300 mM, respectively, with and without the presence of calcium ions (*Hassan et al.*, 2019). These brines were pre-equilibrated with calcite (in addition to ambient CO_2) until reaching the equilibrium pH which was calculated using the PHREEQC software, see Table. 1.

Table 1: Summary of silica and calcite zeta potential with the pre-equilibrated brines

Solution ^a	pH measured	pH calculated ^b	Silica surface charge	Calcite surface charge (Measured)
Na ₂ CO ₃ , 100 mM	10	9.9	Negative	Negative (-25)
NaCl, 100 mM	8.3	8.4	Negative	Negative (-20)
CaCl ₂ , 100 mM	7.3	7.4	Negative	positive (+4)

^aAll solutions were equilibrated at atmospheric CO₂ partial pressure, around 300 ppm

^bCalculations were performed by PHREEQC

Our results for the Na₂CO₃ brine with calcium carbonate powder are comparable with the earlier findings by other researchers, if they pre-equilibrated their brines (see Table. 1, *Song et al.* (2017, Fig. 3), and *Heberling et al.* (2011, Fig. 6)). However, the calcium carbonate zeta potential readings in CaCl₂ and NaCl are shifted to more positive values, which is somewhat different from the previous report by *Song et al.* (2017, Fig. 3) of positive zeta potentials (see first points of each graph in Fig. 3 of the reference).

Selection of Mono- and Poly-Functional Groups

Impact of different crude oil components on rock wettability has been investigated for a long time, e.g., *Denekas et al.* (1959). Identifying the functional groups to be studied for adsorption depended on two factors: being present in crude oil to form the relatively strong bonds and being actively charged at reservoir pH conditions (we assumed a pH of 8). Depending on reservoir pH¹, we simulated the actively charged fractions of four functional groups (carboxylate, tertiary amine, aromatic amine and sulfates) using PHREEQC (*Charlton and Parkhurst*, 2011; *Parkhurst and Appelo*, 2013). Two key assumptions were the basis of our estimations:

1. Reservoir is always at equilibrium pH (which depends on amount of CO₂ available to the reservoir) acting as an infinite buffer. Hence, if a brine is injected (e.g., a low salinity brine with pH 6), the reservoir will equilibrate this brine back to the equilibrium pH.
2. Aliphatic groups and side chains can be neglected. The acidity constants for acid form of the selected functional groups are assumed the same as for acetic acid (CH₃COOH, pKa = 4.75) (*Serjeant and Dempsey*, 1979), protonated ammonia (NH₄⁺, pKa = 9.25) (*Haynes*, 2014), protonated pyridine (PyH⁺, pKa = 5.25) (*Binetin and Devillers*, 1994), and sulfuric acid (HSO₄⁻, pKa = 1.92) (*SIDS*, 2001)

Fig. 4 shows that amines are active in the reservoirs with pH below 9.25, aromatic amines are not actively charged for pH above 6, carboxylates are active at pH higher than 4.75, and sulfates are active in the pH range higher than 2. Hence, we excluded pyridine (and other amines whose lone pair is involved in conjugation, like amides) from further consideration, and focused on the negatively charged carboxylates, positively charged ammonium salts and negatively charged sulfates. In other words, we have selected the groups that exist at oil-brine interface and are charged at reservoir conditions. These groups are, again, carboxylates, amines, and sulfates (*Hu et al.*, 2019; *Eftekhari et al.*, 2017; *Brady and Thyne*, 2016). Dextran polymer (20 kDa) with ammonium groups was tested in this work.

Adsorption of Mono Functional Groups onto Silica and Calcium Carbonate

There are two adsorption mechanisms discussed in the literature: ion-exchange and bridging. Chemically these mechanisms can be expressed as half-reactions 4 and 5. A similar set of reactions can be written for both adsorption sites in calcium carbonate.

Recently we have studied adsorption of mono COO⁻, NH₄⁺, and HSO₄⁻ on silica and calcium carbonate (*Hu et al.*, 2019; *Hassan et al.*, 2019). Fig. 5 summarizes our findings for silica and calcium carbonate (NH₄⁺ was tested as CTAC and COO⁻ was tested as sodium-hexanoate). We conclude strong affinity of quaternary ammonium salts to silica and calcium carbonate. No irreversible adsorption was observed in either cases.

The adsorption results on calcium carbonate can be interpreted through Reactions 6 through 9, but detailed fundamental description of adsorption mechanisms is outside the scope of this work. For adsorption on calcium carbonate we used the equilibrated brines at 100 mM Na₂CO₃ and 100 mM NaCl to induce an excess of negative charge in the β-plane of calcium carbonate, see Table 1 and *Song et al.* (2017, Fig. 3). We also used an equilibrated brine with CaCl₂ to induce an excess positive charge in the β-plane. Mono-amine groups (presented as CTAC) showed adsorption on both negatively and positively charged calcium carbonate surface, regardless of the ionic strength and composition, see Fig. 6. However, no mono-carboxylate adsorption was detected with QCM (also in Fig. 6).

¹ see (*Hu et al.*, 2019) for details on R-COOCa⁺

Figure 4: An estimation of pH-dependent percentage of charged form of $R-COOH$ ($pK_a = 4.75$), $R-NR_3^+$ ($pK_a = 9.25$), $R-C_6H_5N^+$ ($pK_a = 5.25$), and $R-OSO_3^-$ ($pK_a = -0.09$). These calculations are based on the acidity constants of acetic acid, protonated ammonia, protonated pyridine, and sodium dodecyl sulfate, respectively.

Figure 5: Summary of the QCM-D experiments with mono-functional groups on silica showing adsorption of amines in all tested brines. For mono-carboxylates, adsorption was within the detection limits of QCM if any

Figure 6: Summary of the QCM-D experiments with mono-functional groups on calcite showing adsorption of amines in all tested brines. For mono-carboxylates, adsorption was within the detection limits of QCM if any

Adsorption of Amino Dextran Polymers onto Silica

The above results showed that none of the tested mono functional groups adsorb irreversibly to silica or calcium carbonate. However, to mimic crude oil behavior, the irreversible adsorption has to be achieved. For this purpose we propose using polymers with the same functional groups.

Fig. 7 summarizes adsorption of a poly dextran functionalized with amino and quaternary ammonium groups on silica and calcium carbonate. This polymer adsorbs to both negatively silica and variable charge calcium carbonate surfaces regardless of pH and ionic composition. Moreover, the adsorption is irreversible.

Figure 7: QCM-D experimental summary for poly-amines (20 kDa) on silica and calcite showing irreversible adsorption with all tested brines.

Conclusions

The results of this work demonstrate that a “right” combination of specific factors is necessary for the success of LSW. These factors are related to crude oil, reservoir rock and brine, and they must weaken the specific crude-brine-rock interactions.

Adsorption of mono-functional groups is mainly reversible on silica and calcium carbonate. Limited adsorption occurs in the case of mono-amine with all tested brines, while a negligible reversible adsorption of mono-carboxylate happens only in the presence of calcium ions. Hence, mono-functional groups are not the best candidates to model asphaltene adsorption behavior.

With regard to polymers, this work demonstrates that dextran polymers decorated with functional groups are good proxies to study adsorption of asphaltenes, because these polymers adsorb irreversibly. The positively charged poly-amine functional groups adsorb instantaneously and irreversibly on the surface of silica and calcium carbonate in all tested brines with pH up to 10. This result represents alternative point of view as most of the efforts have been dedicated to carboxylates.

Our findings are also important for the design of a chemically efficient detachment of asphaltenic oil from rock surface. As we see from the mono functional group adsorption, bridging mechanism with carboxylates has negligible contribution to adsorption, while ion-exchange mechanism with ammonia derivatives results in adsorption and irreversible adsorption with polymers. Therefore, oils with high acid number (AN) and low base number (BN) contain more carboxylic functional groups than amines, and the weak bridging mechanism might be the main contributor to the oil attachment. In this case, waterflood design should aim to disrupt ion bridging. No complete desorption or drastic wettability change is required. Weakening of the asphaltene interactions may lower the water advancing contact angle just enough to induce spontaneous imbibition and thus increase efficiency of two-phase displacement (Patzek, 2001). In summary, our results imply that crudes with more active amine groups (high BN) require more energy to produce an incremental oil recovery compared with crudes containing more carboxylate groups (high AN).

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