Effect of Low-Concentration of 1-Pentanol on the Wettability of Petroleum Fluid-Brine-Rock Systems

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ABSTRACT: High-concentration brines generally cause the wettability of petroleum fluid-brine-rock systems to become less water-wet (more oil-wet). The addition of alcohols to the brine, however, may produce an opposite effect. In this work, we investigate the synergic effects of a low concentration of 1pentanol and brines on the wettability of petroleum fluidbrine-rock systems. The variables examined include the mineral type (mica, quartz, calcite), brine concentration (0-3)



M), ion type (monovalent and divalent), crude oil (samples from sandstone and carbonate reservoirs), and 1-pentanol concentration (0.5 and 1 wt %). Adding 1 wt % 1-pentanol to the brine only slightly affects the wettability of a petroleum fluid on sandstone-like mineral surfaces (mica and quartz), whereas the effect is significant for carbonate-like mineral surfaces (calcite). A maximum reduction of 80° in contact angle (measured through the brine phase) is observed at 0.1 M NaCl and 0.5 wt % 1-pentanol. ζ -Potentials of both brine-petroleum fluid and brine-rock interfaces are found to be insensitive to the presence of 1-pentanol in the brine. Based on these observations, we propose that the accumulation of 1-pentanol in the thin brine film confined between the petroleum fluid and the rock surface results in a significant change of the wettability. Our finding may have various practical applications, one of which is the use of a low concentration of 1-pentanol for improving oil production.

1. INTRODUCTION

Low-salinity waterflooding is gaining increased attention as an innovative and efficient method to improve oil recovery from hydrocarbon formations. The attraction of low-salinity waterflooding originates from its simple nature: the method only involves low-salinity brines and requires no additional chemicals. Research has shown that low-salinity waterflooding when effective is superior to other conventional enhanced oil recovery methods in several aspects including higher efficiency in displacing light- to medium-gravity crude oils and low associated capital and operating costs.^{1,}

The underlying mechanisms governing low-salinity waterflooding have attracted considerable research interests, especially in the field of colloid and interface chemistry.³⁻⁸ Many studies believe that the low-salinity effect occurs as a consequence of wettability alteration, 3^{-8} and recently, interfacial elasticity has also been proposed to be important. In relation to wetting, the injection of low-salinity brines may alter the wettability of oil reservoir rocks toward a state more favorable for oil recovery. Multiple hypotheses have been proposed to explain how the wettability alteration occurs, and there is still much debate in the LSW literature due to the complex interactions between the components of brine, oil, and rock. The mechanism that has received attention is related to the stability of the thin brine film formed between the oil and rock.¹ Results from small-angle neutron scattering have shown that the thickness of this thin brine film has an order of Angstroms.¹⁰ Factors causing the increase in the thickness and thus the stability of the thin brine film are believed to be favorable for improving oil recovery.

Alcohols are amphiphilic molecules that may significantly affect the interfacial properties of aqueous systems.¹¹ In the upstream industry, alcohols are widely employed as coadditives to enhance the performance of various enhanced oil recovery techniques, in particular surfactant-polymer flooding and alkaline-polymer flooding.¹²⁻¹⁴ Early studies have established that surfactant-polymer flooding can benefit from the alcohol additives.^{12,13} When alcohol is employed together with a surfactant, a middle-phase microemulsion may appear and generate an ultralow interfacial tension that could not be achieved by the surfactant alone.¹⁴ Very low interfacial tension may lead to low residual oil saturation and thus is favorable for oil recovery in homogeneous media. However, at very low interfacial tension, the sweep may not be favorable in layered and heterogeneous media. The sweep efficiency can be improved with the addition of mobility control agents like polymers.

Previous studies have mainly focused on the application of alcohols in surfactant-polymer flooding and alkaline-polymer flooding. To the best of our knowledge, the synergic effects of

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alcohols and brines have not been investigated. These gaps in the literature have motivated our research. The objectives of this study are to systematically investigate the impacts of alcohols on the wettability of petroleum fluid-brine-rock systems as well as the potential benefits of using alcohols as additional additives to enhance the performance of low-salinity waterflooding. Given the nature of the system being studied, we selected an intermediate-chain-length alcohol, 1-pentanol, in our investigation. Compared with short-chain-length alcohols, longer linear alcohols are more likely to produce pronounced effects on surface wettability due to their tendency to accumulate at the fluid-fluid and fluid-solid interfaces. The solubility of very long alcohols in water, however, is typically low. Thus, an intermediate-chain-length alcohol like 1pentanol appears to be a good choice. Another reason 1pentanol is selected is because it has been reported to yield a higher tertiary oil recovery than other alcohols in alcoholassisted alkaline flooding.¹⁴ We investigate the effect of the ion species, brine concentration, and mineral types on the wettability of a petroleum fluid-brine-rock system at two different 1-pentanol concentrations. The results show that 1pentanol at low concentrations may be effective in wettability alteration in carbonate rocks when used together with highsalinity seawater.

2. MATERIALS AND METHODS

2.1. Materials. Two petroleum fluids provided by Chevron Corporation are used in this work; they are referred as oil 1 and oil 2. Oil 1 is from a sandstone reservoir and oil 2 is from a carbonate reservoir. Their properties have been provided in our previous work and are also summarized in Table 1.15

Table 1. Basic Properties of Oil 1 and Oil 2

	oil 1	oil 2
density (g/mL)	0.93	0.86
asphaltene content (wt %)	3.3	2.1
resin content (wt %)	36.8	15.9
TAN (mg of KOH/g of oil)	0.21	0.18
TBN (mg of equiv KOH/g of oil)	5.60	1.14
viscosity at 25 °C (cP)	561	20

Muscovite mica, quartz, and calcite substrate slides are employed to represent the surface of sandstones and carbonates. Mica and quartz are the most abundant components of sandstones and calcite is the primary component of carbonates.¹⁵ Mica and quartz slides are from Tedpella; calcite slides are from Chevron Corporation. Prior to testing, we cleaned the surface of mica and quartz slides using the protocol developed in our previous work and polished the surface of calcite slides using silicon carbide film disks with sizes in the order of 30, 15, 5, and 1 μ m.^{15,19} Both sodium chloride (NaCl) and magnesium chloride (MgCl₂) aqueous solutions are used to evaluate the effect of monovalent and divalent ions on wettability. All chemicals used in this work (i.e., NaCl, MgCl₂, 1-pentanol) are of analytical grade and obtained commercially.

2.2. Contact Angle Measurement Procedure. We employ the procedure developed in our previous work to measure the contact angle.^{15,19} Approximately 500 mL of degassed brine solution is loaded into a square-shaped beaker. The desired amount of 1-pentanol is then added to the brine solution and it is stirred to achieve complete mixing. The substrate slide, supported by a customized stainless-steel holder, is submerged in the brine solution for 1 h. The aging time has been shown to be adequate for the substrates to reach equilibrium with the brine.^{15,19} We use the inverted pendant drop method, which has been widely used to measure the contact angle of petroleum fluids and brine solutions.^{15–19} Once placed, the droplets are allowed to

evolve for 3 days before the measurement is conducted. We have shown that the 3 day aging is sufficient for the contact angle to become stable.^{15,19} The droplet images are captured by a 12X ThorLabs camera and are then analyzed by the "DropSnake" Image J program to obtain the contact angle. A constant 100 μ L droplet volume is used to eliminate the influence of droplet size on the contact angle.^{15,19} Four droplets are placed on the slides under each condition and we report the results by their average and standard deviation.

2.3. ζ -Potential Measurement Procedure. We employ a ζ -Potential Analyzer & Particle Sizer (Brookhaven Instruments) to measure the ζ -potential of rock—brine and petroleum fluid—brine interface.^{15,19} The samples used for the ζ -potential of the petroleum fluid—brine interface are prepared by mixing the brine and the petroleum fluid at a 10:1 v/v ratio followed by sonication for 30 s. To prepare the samples used for the ζ -potential of the rock—brine interface, we add 0.1 g of rock powders to 5 mL of brine solution and sonicate the mixture for 30 s. The mixtures are then allowed to settle for 2 h before the ζ -potential measurement is conducted. Although longer equilibration times have been used in several previous works,²⁰ we find that the ζ -potentials of the systems examined in the present work stabilize after 2 h.¹⁹

In a typical ζ -potential measurement, we load 1.5 mL of sample into the cuvette. The instrument is set to automatically select the appropriate magnitude and frequency of the applied electrical field based on the conductance of the sample. Ten runs of 30 cycles are performed for each sample and the results are reported by average and standard deviation. We replicate each test two times to ensure statistical significance.

3. RESULTS AND DISCUSSION

3.1. Contact Angle. 3.1.1. Oil 1–NaCl Brine–Mica System and Oil 1–NaCl Brine–Quartz System. Figures 1



Figure 1. Effect of 1-pentanol on the contact angles of the oil 1–NaCl brine–mica system. Error bars represent the standard deviation from multiple measurements.



Figure 2. Effect of 1-pentanol on the contact angle of the oil 1–NaCl brine–quartz system. Error bars represent the standard deviation from multiple measurements.

and 2 depict the variations of the contact angle with increasing NaCl concentrations at two 1-pentanol concentrations for the oil 1-NaCl brine-mica and oil 1-NaCl brine-quartz systems, respectively. The trends observed in both systems are similar. Without 1-pentanol in the brine, the contact angle first decreases and then increases with increasing NaCl concentration, a nonmonotonic trend that is in agreement with recent investigations for similar systems.^{15,19} Results from molecular dynamics simulations suggest that such a nonmonotonic trend is from the combined effect of ion adsorption to the substrate surface as well as the interactions between the substrate components and the surface-active components of the petroleum fluid.²¹ In both Figures 1 and 2, the maximum change of the contact angle caused by the addition of 1pentanol is less than 5°. Given the experimental uncertainty, we conclude that the addition of 1-pentanol up to 1 wt % has a weak effect on the contact angle for the oil 1-NaCl brinemica and oil 1-NaCl brine-quartz systems.

3.1.2. Oil $1-MgCl_2$ Brine-Mica System. Figure 3 shows the variation of the contact angle with increasing MgCl₂



Figure 3. Effect of 1-pentanol on the contact angle of the oil $1-MgCl_2$ brine-mica system. Error bars represent the standard deviation from multiple measurements.

concentration at two 1-pentanol concentrations for the oil $1-MgCl_2$ brine-mica system. Without 1-pentanol in the brine, the contact angle changes nonmonotonically with increasing $MgCl_2$ concentration, with a maximum value at 0.5 M. This trend is similar to those observed in previous works.^{15,19} Noticeable change in the contact angle due to 1-pentanol is observed only at a moderate $MgCl_2$ concentration.

3.1.3. Oil 2-NaCl Brine-Mica System and Oil 2-MgCl₂ Brine-Mica System. To explore whether the trends observed in Figure 1 are related to a specific petroleum fluid, we performed contact angle measurements with oil 2, the petroleum fluid from a carbonate reservoir. Figures 4 and 5 depict the variations of the contact angle with increasing brine concentrations at two 1-pentanol concentrations for the oil 2-NaCl brine-mica and oil 2-MgCl₂ brine-mica systems, respectively. Figure 4 shows that the contact angle remains virtually constant at low and moderate NaCl concentrations, followed by a sharp increase when the NaCl concentration exceeds 0.5 M. This trend is different from the one observed in the oil 1-NaCl brine-mica system, suggesting that the nonmonotonic trends observed in Figure 1 depend on the properties of petroleum fluids. Similar to the results observed for the oil 1-NaCl brine-mica and oil 1-NaCl brine-quartz systems, adding 1 wt % 1-pentanol to the brine produces no measurable effect on the contact angle for the oil 2-NaCl brine-mica system. Taken collectively, Figures 1, 2, and 4



Figure 4. Effect of 1-pentanol on the contact angle of the oil 2–NaCl brine–mica system. Error bars (which are small) represent the standard deviation from multiple measurements.



Figure 5. Effect of 1-pentanol on the contact angle of the oil $2-MgCl_2$ brine—mica system. Error bars (which are small) represent the standard deviation from multiple measurements.

suggest that 1-pentanol is not effective in altering the wettability of these systems.

Figure 5 shows that the contact angle varies nonmonotonically with increasing $MgCl_2$ concentrations for the oil 2-mica-MgCl₂ brine system, a trend similar to that observed in the oil 1-mica-MgCl₂ brine system. These results suggest that the nonmonotonic variations of the contact angle observed for the MgCl₂ brine system are independent of the properties of these two petroleum fluids.

3.1.4. Oil 2–Calcite–NaCl Brine System and Oil 2– Calcite–MgCl₂ Brine System. Figures 6 and 7 depict the variations of the contact angle with increasing brine concentrations at 0.5 and 1 wt % 1-pentanol concentrations for the oil 2–NaCl brine–calcite and oil 2–MgCl₂ brine– calcite systems, respectively. In contrast to the results observed for mica and quartz substrates (Figures 1–5), 0.5 and 1 wt % 1-pentanol in the brine produce a pronounced effect on the



Figure 6. Effect of 1-pentanol on the contact angle of the oil 2– calcite–NaCl brine system. Error bars represent the standard deviation from multiple measurements.



Figure 7. Effect of 1-pentanol on the contact angle of the oil 2- calcite $-MgCl_2$ brine system. Error bars represent the standard deviation from multiple measurements.

wettability of calcite-related systems. Figure 6 shows that the oil 2–NaCl brine–calcite system becomes more water-wet in the entire NaCl concentration range with 1 wt % 1-pentanol in the brine. This effect is particularly pronounced at higher NaCl concentrations with a maximum reduction of $\sim 80^{\circ}$ in the contact angle observed at 0.1 M NaCl. At brine concentrations higher than 0.01 *M*, even 0.5 wt % 1-pentanol in the brine can affect the wettability significantly.

Figure 7 shows that the strongest effect of 1-pentanol is observed at 0.01 M MgCl₂. 1-Pentanol has a higher effect on wettability alteration at 1 wt % than at 0.5 wt % for MgCl₂ concentrations below 0.01 M, whereas the difference is indistinguishable at higher MgCl₂ concentrations. The observations that low concentrations of 1-pentanol reduce the contact angle for both the oil 2–NaCl brine–calcite and the oil 2–MgCl₂ brine–calcite systems are testament of the complex interactions between 1-pentanol, brine ions, and calcite components.

3.2. *ζ***-Potential.** As demonstrated by numerous theoretical and experimental investigations, the wettability of the petroleum fluid–rock–brine system is linked to the thickness

of the thin brine film confined between the rock-brine and petroleum fluid-brine interfaces, which are further regulated by the two potentials at these two interfaces, respectively.¹ In this section, we present the ζ -potential measurements at the rock-brine and petroleum fluid-brine interfaces without and with 1 wt % 1-pentanol in the brine. We note here that although the ζ -potential may provide information regarding wettability, the ζ -potentials and wettability may not be directly related, as discussed in our recent work.¹⁵

3.2.1. Rock-Brine Interface. Figure 8 displays the effect of 1-pentanol on the ζ -potential of rock-brine interfaces. Without 1-pentanol, the ζ -potentials of the quartz-brine and calcite-brine interfaces are negative at low to intermediate brine concentrations. The magnitudes of ζ -potentials are comparable to those in other studies under similar conditions.^{16,22} At the same brine concentration, the ζ potential of the quartz-brine interface is less than that of the CaCO₃-brine interface, which is probably because CaCO₃ can dissolve in the brine to release Ca^{2+} ions that can absorb to the CaCO₃-brine interface and partially neutralize the local negative charges. The ζ -potentials of all studied rock-brine interfaces become monotonically less negative with increasing salt concentration except that of the quartz-NaCl brine, in which the ζ -potential initially becomes more negative at low NaCl concentrations and then less negative as the NaCl concentration increases. These trends are consistent with those in the literature in similar systems, which are related to the increased adsorption of Na^+ or Mg^{2+} to the interface.^{16,22,23} The ζ -potential is more sensitive to the changing concentrations of divalent ions, like Mg²⁺, which may be related to the higher charges of the divalent ions and higher degree of ion adsorption to the surfaces. 16,24,25 Interestingly, adding 1 wt %of 1-pentanol to the brine has no measurable effect on the ζ potential of rock-brine interfaces at the brine concentrations examined in our work.

3.2.2. Petroleum Fluid-Brine Interface. Measurement of the ζ -potential of the petroleum fluid-brine interface has



Figure 8. Effect of 1-pentanol on the ζ -potential of rock-brine interfaces: (a) quartz-NaCl brine, (b) quartz-MgCl₂ brine, (c) CaCO₃-NaCl brine, and (d) CaCO₃-MgCl₂ brine. Error bars represent the standard deviation from multiple measurements.



Figure 9. Effect of 1-pentanol on the ζ -potentials of oil-brine interfaces: (a) oil 1-NaCl brine, (b) oil 1-MgCl₂ brine, (c) oil 2-NaCl brine, and (d) oil 2-MgCl₂ brine systems. Error bars represent the standard deviation from multiple measurements.



Figure 10. Schematic illustration of the influence of 1-pentanol on the wettability of the petroleum fluid-brine-calcite system. Water shielding of ions and salt anions are not shown for the sake of clarity.

received lesser attention compared with rock-brine interfaces. Figure 9 depicts the effect of 1-pentanol on the ζ -potential of the petroleum fluid-brine interface. Without salts, the ζ potential of the petroleum-water interface is negative, which may be due to the adsorption of surface-active petroleum fluid components (e.g., carboxylic acids, resins, and asphaltenes) at the interface.^{26,27} The ζ -potential of the petroleum fluid-brine interface generally becomes less negative with increasing brine concentrations, a trend that is probably due to the adsorption of cations to interfaces. Figure 9 shows that the addition of 1 wt % 1-pentanol makes almost all of the petroleum fluid-brine interfaces less negatively charged at low salt concentrations expect for the oil 1-MgCl₂ brine interface. This could be interpreted as an indication of the 1-pentanol adsorption at the petroleum fluid-brine interface. The negatively charged -OH head of 1-pentanol at the interface repels some of the larger negatively charged functional groups to the petroleum fluid from the interface, which in turn reduces the overall negative interfacial charges. Moreover, the solubility of 1-pentanol in brine usually decreases with increasing salinity,²⁸ and consequently, as the brine concentration increases, more 1pentanol molecules will appear at the interface between the

two fluids. At concentrations of ~ 10^{-2} M in NaCl and 10^{-3} – 10^{-2} M for MgCl₂ brines (Figure 9), one can deduce that the interface is fully saturated with 1-pentanol molecules and the impact of 1-pentanol on interfacial charges is diminished. Therefore, at higher brine concentrations, 1-pentanol has no appreciable effect on the ζ -potential of petroleum fluid–brine interfaces. The result that 1-pentanol has nearly no appreciable impact on the interfacial charges at both rock–brine and petroleum fluid–brine interfaces provides further evidence that the wettability alteration caused by 1-pentanol may not be through the modification of interfacial charges. Such realizations lead to the mechanisms that we propose next.

3.3. Proposed Mechanism. In this section, we provide one possible mechanism for the significant impact of 1pentanol on the wettability of oil 2 on calcite for both NaCl and MgCl₂ brines as shown in Figures 6 and 7. The results in preceding sections suggest that the combination of 1-pentanol, calcite surface, and cations (Na⁺, Ca²⁺, or Mg²⁺) leads to the alteration of wettability in the petroleum fluid-brine-rock system. ζ -Potential measurements indicate that 1-pentanol has negligible effect on the electrical charge at the brinepetroleum fluid interface except at very low brine concentrations, which is caused by the adsorption of 1-pentanol to the interface. There is no appreciable effect of 1-pentanol on the electrical charge at the brine—rock interface in the entire range of brine concentrations. Our discussions are in general terms and more details can evolve from future molecular simulations and microscopic measurements.

The proposed mechanisms are based on the assumptions that 1-pentanol mainly dissolves in the aqueous phase. To confirm the validity of this assumption, we mixed deionized (DI) water containing 0.5, 1, and 1.5 wt % 1-pentanol with an equal volume of crude oil and found that the equilibrium concentrations of 1-pentanol in the aqueous phase are 0.49, 0.95, and 1.4 wt %, respectively, as determined by UV–vis spectroscopy. These results indicate that the partitioning of 1-pentanol in the oil phase is small.

The change in the thickness of the thin brine film between the petroleum fluid-brine and brine-rock interfaces, as illustrated in Figure 10, can shed light on the measured contact angles in Figures 6 and 7. In a recent review, Myint and Firoozabadi relate the thickness of the thin brine film to wettability.¹ As we illustrate in Figure 10, the thickness of the thin brine film is related to the 1-pentanol effect observed in Figures 6 and 7. Calcite dissociates in brine and generates Ca²⁺ ions,^{29,30} which form bridges with the negatively charged rock surface and the charged acidic groups at the petroleum fluidbrine interface.³¹⁻³³ The interactions between 1-pentanol and Ca²⁺ and the accumulation of 1-pentanol in the thin film lead to a thicker brine film and consequently a stronger waterwetting state, confirming the presence of 1-pentanol in the aqueous phase. The reason for the stronger effect of 1-pentanol at higher salt concentrations is its lower solubility in the bulk and the consequent transfer of 1-pentanol to the thin brine film. The process is very similar to the effect of salts on the enhanced adsorption of ionic and nonionic surfactants in hydrate anti-agglomeration as discussed by Jiménez-Ángeles and Firoozabadi.³⁴ Both Figures 6 and 7 show that the effect of 0.5 wt % 1-pentanol on the contact angle reaches its maximum at the brine concentration of $\sim 10^{-2}$ M. This is around the same brine concentration at which the impact of 1-pentanol on the ζ -potentials of oil 2–NaCl brine and oil 2–MgCl₂ brine interfaces diminishes (Figure 9c,d) and the thin brine film becomes fully saturated with 1-pentanol molecules. These observations further validate the proposed mechanism.

4. CONCLUSIONS

We demonstrate for the first time that a small amount of a medium-chain alcohol, 1-pentanol, in brine may significantly enhance the water-wetting of petroleum fluid-brine-calcite systems. At 1 wt % 1-pentanol in brine, there is no appreciable effect on the contact angle (measured from the aqueous phase) of the two petroleum fluids on mica and quartz substrates. In contrast to mica and quartz, adding 1 wt % 1-pentanol to the brine significantly lowers the contact angle of a petroleum fluid on calcite. The effect becomes pronounced even with 0.5 wt % 1-pentanol at high brine concentrations. We attribute the effects to the reaction of water and calcite and the production of Ca²⁺ ions. The pronounced effect at high salt concentrations in 0.5 wt % 1-pentanol may be due to the lower solubility of 1pentanol in bulk brine and the increase in the concentration of alcohol in the thin water film between the petroleum fluid and the rock. The ζ -potential measurements suggest that 1 wt % 1pentanol in brine does not appreciably alter the charges at the rock-brine and petroleum fluid-brine interfaces. The charges

at the thin film of water interfaces are likely to be different from the ζ -potential measurements of petroleum fluid—brine and rock—brine interfaces. In this work, we suggest the effectiveness of 1-pentanol to be due to bridge formation through the negative –OH of 1-pentanol and cations such as Na⁺, Ca²⁺, and Mg²⁺ in the thin film. The main conclusion from this work is that 1-pentanol at 0.5 wt % concentration may have a significant effect toward water-wetting in carbonate rocks in relation to improved oil recovery.

Based on the findings in this work, we suggest the following future studies to be conducted to gain a more comprehensive understanding of the synergic effects of alcohols and brines. First, a comprehensive parametric investigation with different alcohols and brines is beneficial to elucidate the complex interactions between alcohols and components of rock, oil, and brine. Furthermore, comparisons between experimental results and simulations including DLVO and surface complexation calculations would quantitatively validate the mechanisms proposed in this work. Finally, it is suggested to further evaluate the potential of using alcohols in low-salinity waterflooding by coreflooding tests.

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Notes

The authors declare no competing financial interest.

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