Wettability Alteration of Clay in Solid-Stabilized Emulsions

Tianmin Jiang,†,§ George J. Hirasaki,*† Clarence A. Miller, † and Samson Ng‡
† Rice University, Houston, Texas, United States
‡ Syncrude Canada Ltd., Edmonton Research Center, Edmonton, Alberta, Canada

ABSTRACT: Processing of bitumen froth obtained from surface mining process of Athabasca oil sands yields stable water-in-diluted bitumen emulsions. Even with a demulsifier, a “rag layer” forms between the oil and free water layers when clay solids are present. Experiments reveal that wettability of clay solids has a significant effect on emulsion stability. Kaolinite in toluene–brine mixture was chosen as model system to study clay wettability alteration related to emulsion separation in bitumen froth treatment. Sodium naphthenate was added to simulate the presence of naphthenic acid in diluted bitumen. The fraction of the kaolinite that settled to the bottom of the aqueous phase was measured, and was referred to as “water-wet fraction”, to characterize the wettability of kaolinite. Without any additives, 96% of the kaolinite was water-wet. Addition of only 100 ppm sodium naphthenate reduced the water-wet fraction to only 18%. Wettability of kaolinite was altered by pH control, silicate, and surfactant under different mechanisms. Addition of 366 ppm silicate at pH 10 resulted in 80% of kaolinite being water-wet. To prevent emulsion formation at high pH, cationic and amphoteric surfactants were evaluated as an alternative to alkali. Over 90% of kaolinite became water-wet when adding alkyl quaternary ammonium bromide, betaine, or amine oxide with optimal dosages.

1. INTRODUCTION

Bitumen water-in-oil emulsions, which persist in bitumen froth derived from surface mining of Athabasca oil sands, are stabilized by asphaltene and clay solids.1–3 In the absence of clay solids, the emulsion is stable due to asphaltene even when the bitumen froth is diluted with naphtha to reduce its viscosity and density. However, the emulsion stabilized by asphaltene reaches nearly complete oil–water separation with a suitable demulsifier PRx, at room temperature.4 When clay solids are present, a “rag layer” containing partially oil-wet clay solids forms between the clean oil and free water layers, which prevents complete emulsion separation.5 Studies showed that oil-wet clay solids appear to adsorb on the oil–water interface and prevent bridging between approaching water droplets and therefore hinder coalescence.5 Oil-wet solids that remain suspended in the continuous oil phase also enhance emulsion stability by preventing close contact between droplets.5 In addition to the stable emulsion problem, the residual clay solids in bitumen upgrading are entrained with volatile overheads and cause fouling in reactor systems and catalyst deactivation in catalytic hydrotreating, which can lead to excessive pressure build-up and premature shutdown of units.6–12 Oil-wet clay is one of the key factors in bitumen emulsion stability and the alteration of clay solids from oil-wet to more water-wet is of great importance to bitumen froth treatment. In general, process water in bitumen froth treatment contains 100 ppm naphthenic acid and oil sand contains up to 500 ppm.13 The naphthenic acid in oil sand makes clay solids oil-wet.4,5

Kaolinite and illite are two major clay solids in Athabasca bitumen.6 However, kaolinite and illite have different wettability properties. Infrared and X-ray absorption spectroscopy results indicated that illite has a preference for water; whereas kaolinite preferentially adsorbs oil.14 Therefore kaolinite is the major component of oil-wet solids in bitumen. Kaolinite in oil sands slurry has heterogeneous surface charge,15 which is important to kaolinite wettability from the interaction between kaolinite and bitumen. Takamura et al. found that the carboxyl groups in bitumen can dissociate and form negatively charged sites on bitumen/water interface.16 Experiments also showed that the adsorption of an anionic carboxylate on a positive surface of solids makes it oil-wet and promotes its coagulation with bitumen.17 The pH in bitumen froth treatment is around 8.5. At this pH, the basal surface of kaolinite is negatively charged, while the edge surface of kaolinite is positively charged. The positively charged edges of kaolinite will adsorb negatively charged carboxylate (e.g., naphthenate) and become partially oil-wet when contacting with crude oil. The combination of naphthenates and clays is believed to stabilize the emulsion.18 The partially oil-wet kaolinite adsorbs at oil–water interfaces and retards water-in-oil emulsion coalescence. Masliyah et al. found that the treated oil-wet kaolinite can stabilize water-in-oil emulsions.19 Considerable efforts have been devoted to investigating the wettability of clays including kaolinite. Silicate has been used to change the wettability of clay in bitumen froth treatment.20 Sodium n-silicate and pH control can make clay solids more water-wet and eliminate the rag layer to reach nearly complete emulsion separation.21,22 Adding acidified silicates during the bitumen extraction process resulted in a higher degree of bitumen liberation from sand grains, a faster bitumen flotation rate, and a better bitumen froth quality than adding caustic.20 It was also found that adding water-wet kaolinite can destabilize the emulsion.1

Several methods can be used to characterize the wettability of clay for water–crude oil system. Contact angle measurement is usually used to quantify the wettability.23 However, the clay size is too small to measure contact angle directly. Gu et al. studied the distribution of kaolinite between oil-in-water emulsion layer and aqueous layer in toluene-diluted bitumen/water mixture and
found that it was consistent with the contact angle measurements. Experimental results showed that kaolinite in aqueous phase had contact angle around 20°, which was water-wet; whereas kaolinite in emulsion had contact angle around 120°, which was oil-wet. This confirms that the kaolinite distribution in oil—water mixture can be used to characterize the wettability. Zeta potential was used to characterize oxide surface charge, which is related to wettability.19–21 Liu et al. used zeta potential measurement to study the wettability of clay solids and the interactions between bitumen and clay.26 Zeta potential of clay is more negative with acidified sodium silicate and adding acidified sodium silicate effectively changes the wettability of clay and minimizes the coagulation between bitumen and clay.20

The objective of our work is to investigate the clay wettability alteration related to emulsion separation in bitumen froth treatment and find the mechanisms of wettability change. In our study, kaolinite in toluene—brine mixture was chosen as the model system. Sodium naphthenate was added to simulate the presence of naphthenic acid in diluted bitumen. Kaolinite distribution in toluene—brine mixture was used to characterize the wettability. To alter the wettability of kaolinite, the interaction between kaolinite and naphthenate should be reduced. There are two possible ways to reduce the interaction: changing kaolinite surface charge; or using surfactants to inhibit the adsorption of naphthenate on kaolinite surface. Surface properties of kaolinite can be changed by pH control and m-silicate,26 which reduce the adsorption of anionic naphthenate on positively charged surface of kaolinite and thereby change the wettability of kaolinite to be more water-wet. Cationic surfactants can form ion pairs with carboxylates, which reduces the interaction between anionic carboxylates and positively charged surface of solids.29–31 This also makes solids more water-wet. Surfactants used here are cationic surfactant octyltrimethylammonium bromide (C₈TAB) and several betaines and amine oxides. C₈TAB is used here as a model cationic surfactant. The other two types of surfactants exhibit equilibrium between zwitterionic and cationic forms, which depends on pH.

In our study, effects of naphthenate, pH, m-silicate, and surfactant on wettability of kaolinite have been studied. Zeta potential measurements were used to interpret the results of kaolinite wettability test and possible mechanisms of wettability alteration.

2. MATERIALS AND METHODS

2.1. Materials. The aqueous phase used in the experiment was synthetic brine with pH 8.3, which contained 0.025 M NaCl, 0.015 M NaHCO₃, 0.002 M Na₂SO₄, 3.0 × 10⁻³ M CaCl₂, and 3.0 × 10⁻⁴ M MgCl₂. The composition of synthetic brine is close to that of inorganic ions present in industrial process water for bitumen extraction. All the salts in the synthetic brine were obtained from Fisher Scientific. Kaolinite (Al₂Si₂O₅(OH)₄) was obtained from Sigma-Aldrich (product 228834), with particle size 0.1 μm and specific surface area 17.44 m²/g. Toluene used as oil phase was from Fisher Scientific.

Octyltrimethylammonium bromide (C₈TAB, MW 252.24) was from Lancaster Synthesis. Betaine samples were from Rhodia-McIntyre Group Ltd. Amine oxide samples were from Stepan Chemical Company. Sodium naphthenate was from Acros Organics. Tables 1 and 2 show the betaine and amine oxide samples used in the wettability test.

2.2. Wettability Test. Unless otherwise stated, 100 ppm (based on the total volume of the sample) sodium naphthenate and other additives were added to the synthetic brine prior to sample preparation. The equivalent naphthenate concentration is 2.25 × 10⁻⁷ M based on Hyamine titration, which means that this part of naphthenate can form ion pairs with Hyamine. The actual concentration of naphthenate is likely larger because some molecules in naphthenate, e.g., those with low molecular weight, do not form such ion pairs with Hyamine. All samples of brine—toluene (1:1, v/v) mixture containing 1.0 wt % kaolinite were prepared by mixing 25.0 mL of synthetic brine, 25.0 mL of toluene, and 0.50 g of kaolinite in a flat-bottom glass bottle with a six-blade turbine. Stirring speed of the turbine was 2000 rpm.
and the mixing time was 5 min. After preparation, all the samples were sealed and left at ambient temperature for 24 h to allow separation. Kaolinite in aqueous phase was considered water-wet and collected by centrifugation at 5000 rpm for 30 min. After centrifugation, water was removed and the open centrifugation tube was put in the oven at 50 °C overnight for drying. Water-wet fraction was calculated based on the amount of kaolinite obtained by centrifugation and the original weight of kaolinite in toluene—brine mixture. The accuracy of weight measurement is 0.01 g. Therefore the error of water-wet fraction measurement is about 2%. Water-wet fraction is 100% when all the kaolinite is water-wet. The value is zero when all the kaolinite is oil-wet. Thereby water-wet fraction was used to characterize the wettability of kaolinite.

2.3. Sample Preparation and Zeta Potential Measurement. All the samples of 50.0 mL 1.0% (w/w) kaolinite suspension were prepared in the brine with different additives. Branson Sonic Probe 450 was used for the sonication of the mixture (probe tip was placed about 1/2 in. into the solution, rate at setting 4, for 1 min). The mixture was left overnight. Before measurement the mixture was shaken and settled for 30 min to allow the sedimentation of larger particles and get a stable suspension. Beckman Coulter Delsa 440 was used to measure zeta potential of kaolinite/alumina in the brine.

Standard mobility solution (conductivity 1000 mS/cm, mobility \(-4 \mu m \cdot cm/V\cdot s\), Beckman Coulter, PN 8301351) was measured at different position levels for calibration. The measured value at upper and lower stationary levels (84% and 16% of the depth) reflect the true mobility of the solution.\(^{32}\) Kaolinite sample was measured at lower and upper stationary levels for three times respectively. The average value of zeta potentials of lower and upper stationary levels was chosen as the zeta potential value of the sample.

3. RESULTS AND DISCUSSION

3.1. Effect of Naphthenate. Figure 1 shows the separation results 24 h after preparation of the samples containing 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with and without naphthenate. The first bottle is the sample without sodium naphthenate. This sample has almost complete separation of toluene, brine, and kaolinite. Nearly all the kaolinite settles to the bottom of the aqueous phase. This suggests that kaolinite is naturally water-wet. The second bottle is the sample with 100 ppm sodium naphthenate. The upper layer of the sample is oil-in-water emulsion stabilized by partially oil-wet kaolinite. Water is the continuous phase, which was verified by contacting small samples of emulsion with water and toluene. The lower layer is the aqueous phase with kaolinite at the bottom. The third and fourth bottles are the samples with 100 ppm sodium naphthenate adding \(6.0 \times 10^{-4} M\) NaOH (24 ppm) or \(3.0 \times 10^{-4} M\ Na_2SiO_3\) (37 ppm), respectively. These two samples have separation results similar to the second sample. Comparing the first sample and other samples, adding naphthenate changes the wettability of kaolinite to more oil-wet. In the last three samples, some of the kaolinite becomes partially oil-wet and stays in the upper oil-in-water emulsion layer.

Figure 2 shows water-wet fraction of kaolinite in the four samples shown in Figure 1. The first bar is water-wet fraction (96%) in the sample without sodium naphthenate at pH 8.3. Almost all the kaolinite is water-wet in absence of naphthenate. The second bar is water-wet fraction (18%) in the sample with 100 ppm sodium naphthenate at pH 8.3. In this case, water-wet fraction is much lower with the presence of naphthenate. This indicates naphthenate in the oil changes the wettability of kaolinite from water-wet to more oil-wet and kaolinite preferentially stays in the oil. This change is due to the adsorption of anionic naphthenate on positively charged sites of kaolinite. The third bar is water-wet fraction (30%) in the sample with 100 ppm sodium naphthenate adding \(6.0 \times 10^{-4} M\) NaOH at pH 9.0. Compared with the second bar, water-wet fraction increases. The last bar is water-wet fraction (38%) in the sample with 100 ppm sodium naphthenate adding \(3.0 \times 10^{-4} M\ Na_2SiO_3\) at pH 9.0. Compared with the second and third bars, water-wet fraction in the sample adding silicate is larger than adding NaOH, which
means that silicate is more effective to change the wettability of kaolinite.

Figure 3 shows zeta potential values of kaolinite in synthetic brine with different amounts of naphthenate at pH 8.3. Kaolinite is partially positively charged, but the net surface charge is negative. Therefore zeta potential of kaolinite is negative at pH 8.3. The results show that the addition of naphthenate makes zeta potential of kaolinite more negative, which means the net surface charge of kaolinite becomes more negative. This indicates the adsorption of anionic naphthenate on positively charged sites of kaolinite. Zeta potential results in Figure 3 are consistent with the wettability results Figures 1 and 2 that the net surface charge and wettability change of kaolinite are due to the interaction between naphthenate and kaolinite.

Previous zeta potential results in the absence of naphthenate showed that increase of pH or silicate ion concentration converts some of the positively charged sites of kaolinite to neutral or negatively charged sites. The decrease of positively charged sites of kaolinite reduces the adsorption of naphthenate on kaolinite surface and makes kaolinite more water-wet. This interpretation is consistent with the observation that the kaolinite in samples 3 and 4 is more water-wet than that in sample 2 (Figure 1). At the same pH, adding silicate makes the surface charge more negative than adding sodium hydroxide, owing to adsorption of multivalent silicate ions. Therefore the adsorption of naphthenate on kaolinite surface with the addition of silicate is less effective than that with sodium hydroxide, which makes kaolinite more water-wet. This is consistent with the wettability results of kaolinite in samples 3 and 4 (Figure 1).

3.2. Effect of Naphthenate Concentration, NaOH, and Na2SiO3. Figure 4 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with 100 ppm naphthenate adding NaOH or Na2SiO3 at different pH. The red and blue bars are water-wet fractions of kaolinite adding 100 ppm/500 ppm naphthenate as well as hydroxide or silicate at different pH. The dashed line shows as control the water-wet fractions of kaolinite without added naphthenate, NaOH or Na2SiO3.

At the same dosage of NaOH or silicate, kaolinite with 500 ppm naphthenate is less water-wet than that with 100 ppm naphthenate. The results in Figure 3 show that zeta potential of kaolinite becomes more negative with increase of naphthenate concentration, which indicates that more naphthenate adsorbs on kaolinite surface. Thus the increase of naphthenate concentration makes naphthenate adsorption effect more significant and kaolinite is more oil-wet. For all the samples, kaolinite becomes more water-wet as pH increases. At higher pH, the surface of kaolinite is more negatively charged. Hence the effect of naphthenate adsorption on kaolinite wettability is less significant at higher pH and kaolinite is more water-wet. At the same pH, adding silicate makes kaolinite more water-wet than adding NaOH. Sodium hydroxide only has caustic effect to increase pH. For silicate, besides caustic effect, the adsorption of silicate ion on kaolinite positively charged sites makes the surface of kaolinite more negatively charged and reduces the adsorption of naphthenate, which makes kaolinite become more water-wet.

Figure 5 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with 100 ppm naphthenate adding NaOH/Na2SiO3 at different pH. The dashed line again shows water-wet fraction of kaolinite without naphthenate, NaOH, or Na2SiO3 added. Below pH 10.0, water-wet fraction of kaolinite increases rapidly as pH increases. At pH 10.0, water-wet fractions of kaolinite adding NaOH or Na2SiO3 are 70% and 84%, respectively. Above pH 10.0, water-wet fraction increases slowly as pH increases and reaches a plateau. Zeta potential results show that the positively charged sites of kaolinite decrease fast as pH increases up to 10.0 and reaches a plateau close to zero when pH is above 10.0. The surface charge change trend of kaolinite is consistent with the wettability change. At high pH, the water-wet fraction plateau of kaolinite with the addition of silicate is closer to the case without naphthenate (96%) than that with the addition of NaOH. Experimental results suggest that higher pH makes kaolinite more water-wet. However, water/crude oil system at high pH will emulsify spontaneously, which should be avoided in the emulsion separation process. Hence, pH 10.0 is upper limit for employing wettability change using NaOH or Na2SiO3 in separation process.

3.3. Effect of C8TAB. Figure 6 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with 100 ppm/200 ppm naphthenate adding different amounts of C8TAB at pH 8.3. The dashed lines show water-wet fractions of kaolinite with or without naphthenate as control, without C8TAB added. The blue and red dotted lines show 1:1 stoichiometry of C8TAB with 100 ppm/200 ppm naphthenate (2.25 × 10⁻⁵/4.50 × 10⁻⁵ M). This 1:1 ratio is based on the assumption that C8TAB will interact with those naphthenate
molecules that form ion pairs during titration with Hyamine. For both cases adding 100 ppm/200 ppm naphthenate, as concentration of naphthenate increases, water-wet fraction of kaolinite increases to a maximum and then decreases. The optimal concentration of C8TAB (when water-wet fraction of kaolinite reaches a maximum) is close to the 1:1 stoichiometry value (equal molar concentration of C8TAB and naphthenate) with 100 ppm/200 ppm naphthenate. If the amount of naphthenate doubles, the optimal concentration of C8TAB also doubles. The results indicate that C8TAB will form 1:1 stoichiometric ion pairs with naphthenate. The formation of ion pairs reduces or eliminates the interaction between kaolinite and naphthenate. Therefore at the optimal concentration of C8TAB, kaolinite is most water-wet and the wettability is close to that of the sample without naphthenate. However, the wettability alteration is very sensitive to the dosage of C8TAB. Kaolinite remains oil-wet when C8TAB is underdosed or overdosed.

Figure 7 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) adding different amounts of C8TAB at pH 8.3, without naphthenate added. In the figure, water-wet fraction of kaolinite decreases as C8TAB concentration increases. This reveals that adding C8TAB alone makes kaolinite more oil-wet. Cationic surfactant C8TAB interacts with negatively charged groups, for instance, negatively charged sites on kaolinite surface, or with naphthenate. In the absence of naphthenate, C8TAB will interact with negatively charged sites of kaolinite and make these surfaces more oil-wet. If the system contains naphthenate, C8TAB will interact preferentially with naphthenate and form ion pairs. If naphthenate and C8TAB are added in stoichiometric amounts, the adsorbed naphthenate and C8TAB are minimized. If C8TAB is overdosed, the excess C8TAB will adsorb on the negative surfaces of kaolinite and make them more oil-wet. Hence as C8TAB concentration increases, water-wet fraction of kaolinite increases to a maximum and then decreases.

3.4. Effect of Betaine. Figure 8 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with 100 ppm naphthenate and 1000 ppm betaine (based on activity of betaine and total volume of the mixture) at pH 8.3. The betaines used were those listed in Table 1. The red and black dashed lines show water-wet fraction of kaolinite with/without naphthenate as control, without betaine added. The results show that all the samples become more water-wet and the
sample with caprylamidopropyl betaine (betaine 5 in Table 1) has largest water-wet fraction of kaolinite (90%). Accordingly this betaine was chosen in the following wettability test to study the effect of betaine dosage.

Figure 9 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with 100 ppm naphthenate and different amounts of betaine 5 at pH 8.3. The two black dashed lines show water-wet fractions of kaolinite with or without naphthenate as control, without betaine added. The red dashed line shows 1:1 stoichiometry value based on total betaine 5 concentration with 100 ppm naphthenate (2.25 \times 10^{-5} M). Water-wet fraction of kaolinite increases from 50% to 88% when added betaine 5 increases from 100 to 200 ppm. When added betaine 5 increases to 1000 ppm, water-wet fraction increases only from 88% to 92%. If 200 ppm is chosen as optimal dosage of betaine 5, it is much larger than the 1:1 stoichiometry value with 100 ppm naphthenate.

Betaine 5 is an electrically neutral chemical compound with a positively charged cationic ammonium ion and a negatively charged functional carboxylate group, which is referred to as a specific type of zwitterion. It can accept a hydrogen ion and become positively charged. The ratio of this type of cation depends on the association equilibrium constant and pH. At pH 8.3, only a small amount of betaine becomes positively charged and interacts with naphthenate to form ion pairs. Hence the optimal dosage is much larger than the 1:1 stoichiometry value. Figure 10 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) adding different amounts of betaine 5 at pH 8.3, without naphthenate added. Similar to C8TAB, water-wet fraction of kaolinite decreases as betaine 5 concentration increases. However, the decrease is slower than for C8TAB. The decrease indicates that adding betaine 5 alone makes kaolinite more oil-wet. In the absence of naphthenate, cationic ion of betaine 5 will adsorb on the negative surfaces of kaolinite and make them more oil-wet. If the system contains naphthenate, cationic ion of betaine 5 will interact with naphthenate and form ion pairs, which makes kaolinite more water-wet. The wettability alteration mechanism of betaine 5 is similar to that of C8TAB; while the wettability alteration capability of betaine 5 is less effective than that of C8TAB.

3.5. Effect of Amine Oxide. Figure 11 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) adding different amounts of amine oxide DO at pH 8.3. All the samples become more water-wet and the sample adding 100 ppm amine oxide DO (decyl dimethyl amine oxide) has largest water-wet fraction of kaolinite (86%). Hence, amine oxide DO was used to study the effect of dosage. Figure 12 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene—brine mixture (1:1, v/v) with 100 ppm naphthenate and different amounts of amine oxide DO at pH 8.3. The two black dashed lines show water-wet fraction of kaolinite with or without naphthenate as control, without amine oxide added. The red dashed line shows 1:1 stoichiometry value of amine oxide DO with 100 ppm naphthenate. Water-wet fraction of kaolinite increases from 38% to 96% when added amine oxide DO increases from 5 to 20 ppm. Then water-wet fraction of kaolinite decreases as amine oxide DO concentration increases. Water-wet fraction of kaolinite at optimal dosage of amine oxide DO is the same as the sample without naphthenate. The optimal dosage of amine oxide DO is about 4.4 times the 1:1 stoichiometry value compared to 30 times for betaine 5 and equal amounts
for C8TAB. The wettability alteration of kaolinite is less sensitive to the dosage of amine oxide than C8TAB.

Similar to betaines, amine oxides are also zwitterionic compounds. Like betaines, amine oxides are also amphoterics and thus readily accept a proton to become cationic surfactants. However, at a given pH more amine oxide DO than betaine 5 becomes cationic. At pH 8.3, some of the amine oxide becomes positively charged and interacts with naphthenate to form ion pairs. Hereby the optimal dosage is larger than the 1:1 stoichiometry value. If amine oxide is overdosed, the excess cationic type of amine oxide will adsorb on negative surfaces of kaolinite and make them more oil-wet. Thereby as amine oxide concentration increases, water-wet fraction of kaolinite increases to maximum and then decreases, which is similar to that with C8TAB.

3.6. Comparison of C8TAB, Amine Oxide, and Betaine. Figure 13 shows water-wet fraction 24 h after preparation of 1.0 wt % kaolinite in toluene–brine mixture (1:1, v/v) with 100 ppm naphthenate adding C8TAB, amine oxide DO or betaine 5 at pH 8.3. The two black dashed lines show water-wet fractions of kaolinite with or without naphthenate as control. The blue, red, and green dashed lines show 1:1 stoichiometry values C8TAB, amine oxide DO, and betaine 5 with 100 ppm naphthenate, respectively.

Figure 14 shows zeta potential values of kaolinite in synthetic brine with 100 ppm naphthenate adding C8TAB, amine oxide DO, and betaine 5 at pH 8.3. The first bar is zeta potential of kaolinite with naphthenate only with no other surfactant added as control. The second—fourth bars are zeta potential values of kaolinite with naphthenate and C8TAB, amine oxide DO, or betaine 5 at optimal dosage. The dashed line shows zeta potential of kaolinite without naphthenate or other surfactant as reference. Zeta potential difference between first bar and the reference indicates the adsorption of naphthenate. At the optimal dosages of added surfactants, zeta potential values of the second—fourth bars are close to the reference value, which indicates the least interaction between the surfactants and kaolinite. In this case, kaolinite should be most water-wet, which is consistent with wettability test results in Figure 13.

Among the three surfactants, the optimal dosages are as follows: C8TAB < amine oxide DO < betaine 5. The sensitivity of overdosage has the opposite direction: C8TAB > amine oxide DO > betaine 5. Lower optimal dosage is better for wettability change. Based on this criterion, C8TAB is the best. If naphthenate concentration is unknown, lower sensitivity of overdosage is better. Otherwise kaolinite will become oil-wet again if it is overdosed. Based on optimal dosage and overdosage sensitivity criteria, amine oxide DO is better than the other two because it has intermediate optimal dosage and overdosage sensitivity.

4. CONCLUSIONS

Kaolinite wettability alteration and possible mechanisms have been studied by wettability testing and zeta potential measurement. Kaolinite with sodium naphthenate in toluene—brine mixture is chosen as the model system for the wettability test. Kaolinite is naturally water-wet in toluene—brine mixtures. But when 100 ppm sodium naphthenate is added, most of the kaolinite becomes oil-wet due to the adsorption of naphthenate on kaolinite surface. It has been found that the higher the naphthenate concentration, the lower the water-wet fraction.

Wettability of kaolinite in the presence of naphthenate was altered to more water-wet conditions by pH control, and the addition of silicate and surfactant. In all three cases the surface charge of kaolinite became less negative, as indicated by zeta potential results, but the detailed mechanisms are different. Sodium hydroxide and silicate increase pH, which makes the kaolinite surface more negative and reduces the adsorption of naphthenate. Multivalent silicate ions can also adsorb on positive kaolinite sites, converting them to negative sites. Adding 366 ppm silicate at pH 10 gets 80% of kaolinite water-wet.

To prevent emulsion formation, which occurs when pH exceeds 10.0, cationic or amphoteric surfactants were evaluated as alternatives to alkali. Cationic groups of those surfactants interact with anionic naphthenate to form ion pairs, which minimizes the interaction between naphthenate and kaolinite and makes kaolinite more water-wet. Surfactants C8TAB, amine oxide DO (decyl dimethyl amine oxide), and betaine 5 (caprylamidopropyl betaine) with appropriate dosages (5, 20, and 200 ppm, respectively) make 90% of kaolinite water-wet in the presence of 100 ppm naphthenate. Much less C8TAB or amine oxide DO is required compared to betaine. Wettability of kaolinite is sensitive to the dosage of C8TAB and amine oxide. The adsorption of excess cationic groups on kaolinite surface makes kaolinite more oil-wet. Wettability of kaolinite does not change much if betaine 5 is
overdosed (200–1000 ppm) because only a small fraction of surfactant molecules are present in the cationic form.

**AUTHOR INFORMATION**

**Corresponding Author**

*Tel.: +1 713 348 5416. Fax: +1 713 348 5478. E-mail: ghj@rice.edu.*

**Present Addresses**

*Present address: Schlumberger Technology Corporation, 1325 S. Dairy Ashford St., Houston, Texas 77077, United States.*

**ACKNOWLEDGMENT**

We acknowledge the financial support of Syncrude Canada Ltd., Edmonton Research Centre, and Rice University Consortium on Processes in Porous Media.

**REFERENCES**


