

Characterization of Kaolinite ζ Potential for Interpretation of Wettability Alteration in Diluted Bitumen Emulsion Separation[†]

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Initial processing of Athabasca oil sands obtained from the water-based extraction process yields stable water-in-bitumen emulsions. When the bitumen is diluted with naphtha to reduce its viscosity and density, partial separation can be obtained with a suitable demulsifier. However, a “rag layer” forms between the clean oil and free water layers. The partially oil-wet kaolinite in clay solids can retard water-in-oil emulsion coalescence, entrap oil drops, and form aggregates, which results in a rag layer in the middle of the sample. Once formed, this rag layer prevents further coalescence and water separation. We show here that wettability of kaolinite can be characterized via ζ potential measurement and modeling. A simplified Gouy–Stern–Grahame model and an oxide site binding model can be used to correlate the ζ potential of kaolinite in brine with different additives. Sodium silicate has the greatest effect per unit addition on changing the ζ potential of kaolinite and can be used to change the wettability of clay solids. The separation of water in diluted bitumen emulsion can be enhanced by changing the wettability of clay solids using silicate and pH control.

1. Introduction

Stable water-in-oil emulsions, which persist in bitumen froth derived from surface mining of Athabasca oil sands, are problematic because of asphaltene and clay solids. Individually, asphaltene and oil-wet fine solids can stabilize water in diluted bitumen emulsions.^{1–3} When both are present, the capacity of the diluted bitumen to stabilize water emulsions is greatest.³ Adding demulsifier PR₅ can result in nearly complete oil–water separation in the absence of clay solids. However, a “rag layer” containing solids and having intermediate density forms between the clean oil and free water layers when clay solids are present.⁴ This rag layer prevents further coalescence and the complete separation of the emulsified water.⁴

Most of the clay solids in Athabasca bitumen are kaolinite and illite.⁵ Kaolinite in oil sands slurry has a heterogeneous

surface charge⁶ and will present heterogeneous wettability with the adsorption of carboxylates or sulfates/sulfonates from bitumen, which is very important to the emulsion stability. Kaolinite is finely divided crystalline aluminosilicate. The principal building elements of the clay minerals are two-dimensional arrays of silica and alumina layers. Sharing of oxygen atoms between silica and alumina layers results in two-layer mineral.⁶ Kaolinite has permanent negative charge sites on the basal planes, owing to the isomorphic substitution of the central Si and Al ions in the crystal lattice by lower positive valence ions.^{6–9} Al–OH and Si–OH groups are exposed hydroxyl-terminated planes. The amphoteric sites are conditionally charged, either positive or negative, depending upon the pH. Positive charges can develop on the alumina faces and at the edges by direct H⁺/OH[−] transfer from the aqueous phase.^{7,8}

The point of zero charge (PZC) of amphoteric (mainly edge) sites ranges from pH 5 to 9 depending upon the kaolinite used.⁶ PZC is determined by titration. It is not known which sites are responsible. The pH in the oil sands operation process is around 8.5. At this pH, the basal surface of kaolinite is negatively charged, while the edge surface of kaolinite is likely positively charged.

Surface charge 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 the bitumen/water interface.¹⁰ It was found that adsorption of Ca²⁺ on silica can

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make the silica surface positive. Adsorption of an anionic surfactant on the positive surface makes silica oil-wet and promotes coagulation with bitumen.¹¹ Similarly, the positively charged edges of the kaolinite may adsorb negatively charged carboxylate components of the oil and make that portion of clay solids partially oil-wet. The partially oil-wet clay solids can retard water-in-oil emulsion coalescence. They also entrap oil drops and form aggregates, which results in a rag layer in the middle of the sample.⁴ It was found that adding water-wet kaolinite can destabilize the emulsion.¹ If the surface charge of clay solids can be made more negative, the surface of the solids may be more hydrophilic, which may enhance the separation of clay from the rag layer. In this case, some of the adsorbed oil on the solid surface may be replaced by water, allowing the solid to settle to the bottom. The ζ potential can be used to characterize oxide surface charge,^{12,13} which is related to wettability. The ζ potential of clay solids can also directly characterize the wettability change of clay solids. Liu et al. used the ζ potential measurement to study the wettability of clay solids and the interactions between bitumen and clay.^{14,15} Wettability change may be important to the stability of water-in-bitumen emulsions. Silicate has been used to change the wettability of clay in bitumen froth treatment.¹⁶ 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.¹⁶ The ζ potential of clay is more negative with acidified sodium silicate, and adding acidified sodium silicate can effectively minimize the coagulation between bitumen and clay.¹⁶

To characterize the wettability change of kaolinite, ζ potentials of kaolinite in synthetic brine with different additives were measured. In the ζ potential study, sodium hydroxide (NaOH), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), sodium *meta*-silicate (Na_2SiO_3), sodium *ortho*-silicate (Na_4SiO_4), and sodium carbonate (Na_2CO_3) were used to change the surface charge and further change ζ potentials of kaolinite. To analyze and correlate the experimental ζ potential of kaolinite in synthetic brine, a simplified Gouy–Stern–Grahame model is used.¹⁷

2. Materials and Methods

2.1. Materials. Samples of Athabasca bitumen were provided by Syncrude Canada Ltd. Bitumen samples were diluted with naphtha (naphtha/bitumen = 0.7, w/w).

Unless otherwise stated, the aqueous phase used here is synthetic brine with pH 8.3. Table 1 shows the composition of synthetic brine, which is close to the composition of inorganic ions present in industrial process water for bitumen extraction. Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] is obtained from Sigma-Aldrich

Table 1. Syncrude Brine Composition

component	concentration (mM)
NaCl	25.0
NaHCO_3	15.0
Na_2SO_4	2.0
CaCl_2^a	0.3
MgCl_2^a	0.3

^a Absent in brine without Ca/Mg.

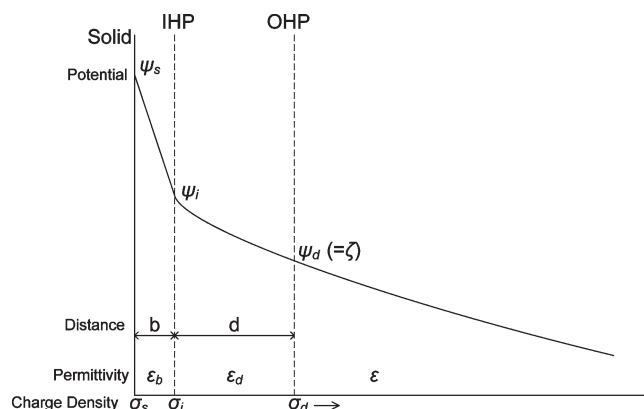


Figure 1. Gouy–Stern–Grahame model of the double layer.¹⁸

(product 228834), with a particle size of 0.1–4 μm and specific surface area of 17.44 m^2/g [measured by Brunauer–Emmett–Teller (BET) adsorption]. Alumina (Al_2O_3) is obtained from Sigma-Aldrich (product 19944-3), with a particle size of 150 mesh (104 μm), pore size of 5.8 nm, and specific surface area of 155 m^2/g . All of the salts in the synthetic brine were obtained from Fisher Scientific. Demulsifier PR₅ was from Nalco Chemical Company.⁴

2.2. Emulsion Sample Preparation and Separation. Emulsion samples (60 mL) were prepared by mixing 30 mL of brine and 30 mL of diluted bitumen in a glass tube (inner diameter of 44 mm and length of 230 mm) with a six-blade turbine⁴ at ambient temperature. The stirring speed of the turbine was 3600 rpm, and the mixing time was 10 min. Under these preparation conditions, the emulsion is stable without a demulsifier. Different additives (e.g., Na_2SiO_3) were added to the brine prior to emulsion preparation. 200 ppm demulsifier PR₅ (on the basis of the total volume of the emulsion sample) was added to the emulsion samples immediately after the preparation.

2.3. Sample Preparation and ζ Potential Measurement. All of the samples of 50 mL of 1% (w/w) kaolinite/alumina suspension were prepared in the brine with different additives. Branson Sonic Probe 450 was used for the sonication of the mixture (the probe tip was placed about $1/2''$ into the solution, with the 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 for the sedimentation of larger particles and to obtain a stable suspension. Beckman Coulter Delsa 440 was used to measure the ζ potential of kaolinite/alumina in the brine.

The standard mobility solution (conductivity, 1000 mS/cm; mobility, $-4 \mu\text{m cm V}^{-1} \text{s}^{-1}$; 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) reflects the true mobility of the solution.¹⁸ The kaolinite/alumina sample was measured at lower and upper stationary levels 3 times. The average value of ζ potentials of lower and upper stationary levels was chosen as the ζ potential value of the sample.

2.4. ζ Potential Model. In the Gouy–Stern–Grahame model, the double layer can be divided into two regions: (1) the compact

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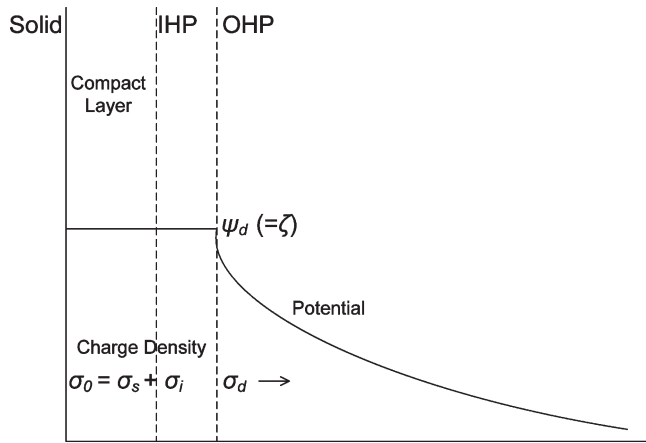


Figure 2. Simplified model of the double layer.

or Stern layer very near the solid surface, in which the charge and potential distribution are determined by the geometrical restrictions of ion and molecule size and interactions between ions and solid surface, and (2) the diffuse layer, where the potential distribution can be predicted by the Poisson–Boltzmann equation, as shown in Figure 1.¹⁹ The distance between the solid surface and inner Helmholtz plane (IHP) is b . The distance between the inner and outer Helmholtz planes is d . The solid surface has surface charge density σ_s and potential ψ_s . The IHP has potential ψ_i . The Stern layer has charge density σ_i . The outer Helmholtz plane (OHP) has surface potential ψ_d . The charge density of the diffuse layer is σ_d .

The equations for the Gouy–Stern–Grahame model are as follows:^{18,19}

$$\sigma_s + \sigma_i + \sigma_d = 0 \quad (1)$$

$$\psi_s - \psi_i = \frac{b\sigma_s}{\epsilon_b} \quad (2)$$

$$\psi_i - \psi_d = \frac{-d\sigma_d}{\epsilon_d} \quad (3)$$

$$\sigma_d = -\text{sign}(\sigma_d) \{2\epsilon RT \sum_i c_i^0 [\exp(-z_i e \psi_d / kT) - 1]\}^{1/2} \quad (4)$$

where b and d are the thicknesses of the compact and diffuse layers, respectively, σ_s , σ_i , and σ_d are charge densities of the solid surface, Stern layer, and diffuse layer, respectively, ψ_s , ψ_i , and ψ_d are the potentials of the solid surface, IHP, and OHP, respectively, ϵ_b and ϵ_d are the permittivities in the compact and diffuse layers, respectively, z_i is the valency of ion species i , ϵ is the permittivity of the bulk solution, and c_i^0 is the concentration of ion species i in the bulk.

The Gouy–Stern–Grahame model can be simplified if we make the following assumptions: (1) The shear surface coincides with the OHP; thus, ζ potential = ψ_d . (2) The charge of the solid surface and Stern layer are combined into the net surface charge. $\sigma_0 = \sigma_s + \sigma_i$.

Figure 2 shows the simplified model of the double layer.

Equations 1 and 4 can be rewritten as

$$\sigma_0 + \sigma_d = 0, \quad \sigma_0 = -\sigma_d \quad (5)$$

$$\sigma_0 = -\text{sign}(\sigma_0) \{2\epsilon RT \sum_i c_i^0 [\exp(-z_i e \zeta / kT) - 1]\}^{1/2} \quad (6)$$

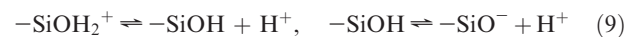
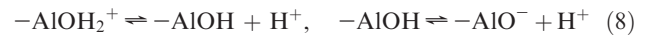
Near the charged surface, the ion concentration is different from the bulk solution because of the electrostatic attrac-

tion or repulsion. From the Boltzmann equation, ion activity near the kaolinite surface a_s is different from the bulk ion activity a_b

$$a_s(M^{z_i}) = a_b(M^{z_i}) \exp\left(-\frac{z_i e \zeta}{kT}\right) \quad (7)$$

where a_s and a_b are the activities at the surface and in the bulk, respectively, M is the ion species (cation or anion), and z_i is the valency of ion species i .

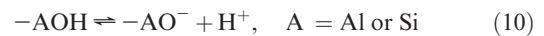
A simplified Gouy–Stern–Grahame model established the relationship between the ζ potential and surface charge. To study the effects of pH and adsorption of counterions, the site-binding model of the oxide/water interface is widely used.^{20–25} The surface charge of kaolinite can be explained by proton donor–acceptor reactions occurring simultaneously on alumina or silica sites of kaolinite,²⁵ as expressed in eqs 8 and 9.



To apply the site-binding model, the following assumptions are made: (1) The surface of kaolinite has amphoteric silica and alumina sites, which are pH-dependent. H^+ and OH^- will react with such surface sites. Permanent negatively charged sites $-\text{B}^-$ are inert sites, which are independent of pH. (2) The indifferent ions, such as Na^+ and Cl^- , will not specifically adsorb in the compact layer. (3) The specifically adsorbed ions, such as Ca^{2+} , Mg^{2+} , and HSiO_3^- , will adsorb in the compact layer.

For counterion adsorption, we consider kaolinite surface containing amphoteric groups $-\text{AOH}$ (A can be Al or Si) and permanent negatively charged sites $-\text{B}^-$. Here, silica and alumina sites are considered to have the same electrostatic interactions with counterions. Amphoteric groups $-\text{AOH}$ ($-\text{AlOH}$ and $-\text{SiOH}$) are pH-dependent and can form either positively charged sites $-\text{AOH}_2^+$ or negatively charged sites $-\text{AO}^-$. Positively charged sites $-\text{AOH}_2^+$ can adsorb anions. Negatively charged sites $-\text{AO}^-$ can adsorb cations.

Equations 10 and 11 show the dissociation equilibrium of amphoteric groups $-\text{AOH}$ and the equilibrium equation.



$$K = \frac{[\text{AO}^-]a_s(\text{H}^+)}{[\text{AOH}]} = \frac{[\text{AO}^-]a_b(\text{H}^+) \exp\left(-\frac{e\zeta}{kT}\right)}{[\text{AOH}]} \quad (11)$$

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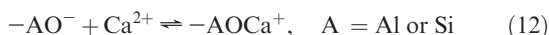
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Table 2. Equilibrium of Surface Reactions

reaction	K
$-\text{AlOH}_2^+ \rightleftharpoons -\text{AlOH} + \text{H}^+$	$K_{\text{Al}^+} = ([\text{AlOH}][a_b(\text{H}^+)])/([\text{AlOH}_2^+])e^{-(e\zeta)/(kT)}$
$-\text{AlOH} \rightleftharpoons -\text{AlO}^- + \text{H}^+$	$K_{\text{Al}^-} = ([\text{AlO}^-][a_b(\text{H}^+)])/([\text{AlOH}])e^{-(e\zeta)/(kT)}$
$-\text{SiOH}_2^+ \rightleftharpoons -\text{SiOH} + \text{H}^+$	$K_{\text{Si}^+} = ([\text{SiOH}][a_b(\text{H}^+)])/([\text{SiOH}_2^+])e^{-(e\zeta)/(kT)}$
$-\text{SiOH} \rightleftharpoons -\text{SiO}^- + \text{H}^+$	$K_{\text{Si}^-} = ([\text{SiO}^-][a_b(\text{H}^+)])/([\text{SiOH}])e^{-(e\zeta)/(kT)}$
$-\text{AO}^- + \text{Ca}^{2+} \rightleftharpoons -\text{AOCa}^+, \text{A} = \text{Al/Si}$	$K_{\text{Ca}} = ([\text{AOCa}^+])/([\text{AO}^-][a_b(\text{Ca}^{2+})])e^{-(2e\zeta)/(kT)}$
$-\text{AO}^- + \text{Mg}^{2+} \rightleftharpoons -\text{AOMg}^+, \text{A} = \text{Al/Si}$	$K_{\text{Mg}} = ([\text{AOMg}^+])/([\text{AO}^-][a_b(\text{Mg}^{2+})])e^{-(2e\zeta)/(kT)}$
$-\text{AOH}_2^+ + \text{HSiO}_3^- \rightleftharpoons -\text{AOH}_2\text{HSiO}_3, \text{A} = \text{Al/Si}$	$K_{\text{HSiO}_3} = ([\text{AOH}_2\text{HSiO}_3])/([\text{AOH}_2^+][a_b(\text{HSiO}_3^-)]e^{(e\zeta)/(kT)})$
$-\text{AOH}_2^+ + \text{H}_3\text{SiO}_4^- \rightleftharpoons -\text{AOH}_2\text{H}_3\text{SiO}_4, \text{A} = \text{Al/Si}$	$K_{\text{H}_3\text{SiO}_4} = ([\text{AOH}_2\text{H}_3\text{SiO}_4])/([\text{AOH}_2^+][a_b(\text{H}_3\text{SiO}_4^-)]e^{(e\zeta)/(kT)})$
$-\text{AOH}_2^+ + \text{HCO}_3^- \rightleftharpoons -\text{AOH}_2\text{HCO}_3, \text{A} = \text{Al/Si}$	$K_{\text{HCO}_3} = ([\text{AOH}_2\text{HCO}_3])/([\text{AOH}_2^+][a_b(\text{HCO}_3^-)]e^{(e\zeta)/(kT)})$
$-\text{AOH}_2^+ + \text{SO}_4^{2-} \rightleftharpoons -\text{AOH}_2\text{SO}_4^-, \text{A} = \text{Al/Si}$	$K_{\text{SO}_4} = ([\text{AOH}_2\text{SO}_4^-])/([\text{AOH}_2^+][a_b(\text{SO}_4^{2-})])e^{(2e\zeta)/(kT)}$
$-\text{AOH}_2^+ + \text{L}^{3-} \rightleftharpoons -\text{AOH}_2\text{L}^{3-}, \text{A} = \text{Al/Si}, \text{L} = \text{citrate}$	$K_{\text{L}} = ([\text{AOH}_2\text{L}^{3-}])/([\text{AOH}_2^+][a_b(\text{L}^{3-})])e^{(3e\zeta)/(kT)}$

where K is the surface reaction or surface adsorption equilibrium constant and a_s and a_b are the activities at the surface and in the bulk, respectively.

Equation 12 shows the surface adsorption equilibrium of Ca^{2+} on negatively charged groups $-\text{AO}^-$. Equation 13 shows the equilibrium equation.

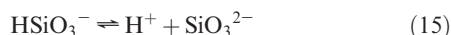
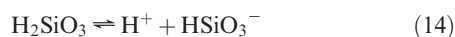


$$K_{\text{Ca}} = \frac{[\text{AOCa}^+]}{[\text{AO}^-]a_s(\text{Ca}^{2+})} = \frac{[\text{AOCa}^+]}{[\text{AO}^-]a_b(\text{Ca}^{2+})\exp\left(-\frac{2e\zeta}{kT}\right)} \quad (13)$$

Both $-\text{AlO}^-$ and $-\text{SiO}^-$ sites can adsorb divalent cations. In the surface adsorption of divalent cations, these two sites are not distinguishable. In eq 13, $-\text{AlO}^-$ and $-\text{SiO}^-$ sites having the same equilibrium constant are assumed. For positively charged sites, $-\text{AlOH}_2^+$ and $-\text{SiOH}_2^+$ sites having the same equilibrium constant for adsorption of anions are also assumed. Table 2 shows equilibrium of different surface reactions.

Here, the adsorption of the HSiO_3^- ion is considered instead of the SiO_3^{2-} ion, because the concentration of the HSiO_3^- ion is much higher than the SiO_3^{2-} ion in the brine. For the similar reason, the H_3SiO_4^- and $\text{C}_6\text{H}_5\text{O}_7^{3-}$ ions have the highest concentration and are considered in the adsorption.

For a weak electrolyte, such as the SiO_3^{2-} ion, an ion dissociation equilibrium needs to be considered.



$$\frac{a_{\text{H}^+}a_{\text{HSiO}_3^-}}{a_{\text{H}_2\text{SiO}_3}} = K_{\text{a1}}, \quad \frac{a_{\text{H}^+}a_{\text{SiO}_3^{2-}}}{a_{\text{HSiO}_3^-}} = K_{\text{a2}} \quad (16)$$

If more than one cation or anion adsorb on the surface, all of the possible reactions need to be considered. Table 3 shows equilibrium constants of different species in the bulk solution.^{26,27}

The ionic strength of synthetic brine is 0.0478 M. For non-ionic solute (e.g., H_2SiO_3), the concentration is low enough to consider the activity coefficient as 1.0. However, for ions, the activity coefficients need to be calculated using an extended Debye–Hückel equation²⁸

$$\log(\gamma_i) = -\frac{0.509z_i^2\sqrt{I}}{1 + 0.328a_i\sqrt{I}}, \quad I = \frac{1}{2} \sum_i c_i z_i^2 \quad (17)$$

where γ_i is the activity coefficient of ion species i , z_i is the charge number of ion species i , a_i is the effective diameter of the

Table 3. Equilibrium Constants of Reactions in Bulk Solution^{26,27}

reaction	K
$\text{Ca}^{2+} + \text{C}_6\text{H}_5\text{O}_7^{3-} \rightleftharpoons \text{CaC}_6\text{H}_5\text{O}_7^-$	7.9×10^4
$\text{Mg}^{2+} + \text{C}_6\text{H}_5\text{O}_7^{3-} \rightleftharpoons \text{MgC}_6\text{H}_5\text{O}_7^-$	2.2×10^3
$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	5.0×10^{-9}
$\text{MgCO}_3 \rightleftharpoons \text{Mg}^{2+} + \text{CO}_3^{2-}$	6.8×10^{-6}
$\text{CaSiO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{SiO}_3^{2-}$	8.3×10^{-12}
$\text{MgSiO}_3 \rightleftharpoons \text{Mg}^{2+} + \text{SiO}_3^{2-}$	4.0×10^{-12}
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	4.3×10^{-7}
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	4.0×10^{-11}
$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}^+ + \text{H}_3\text{SiO}_4^-$	2.2×10^{-10}
$\text{H}_3\text{SiO}_4^- \rightleftharpoons \text{H}^+ + \text{H}_2\text{SiO}_4^{2-}$	2.0×10^{-12}
$\text{H}_2\text{SiO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{HSiO}_4^{3-}$	1.0×10^{-12}
$\text{HSiO}_4^{3-} \rightleftharpoons \text{H}^+ + \text{SiO}_4^{4-}$	1.0×10^{-12}
$\text{H}_2\text{SiO}_3 \rightleftharpoons \text{H}^+ + \text{HSiO}_3^-$	2.0×10^{-10}
$\text{HSiO}_3^- \rightleftharpoons \text{H}^+ + \text{SiO}_3^{2-}$	1.0×10^{-12}
$\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \rightleftharpoons \text{H}^+ + \text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$	7.1×10^{-4}
$\text{H}_2\text{C}_6\text{H}_5\text{O}_7^- \rightleftharpoons \text{H}^+ + \text{HC}_6\text{H}_5\text{O}_7^{2-}$	1.7×10^{-5}
$\text{HC}_6\text{H}_5\text{O}_7^{2-} \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{O}_7^{3-}$	4.1×10^{-7}

Table 4. Effective Diameter of the Hydrated Ions²⁸

ion	a (nm)	ion	a (nm)
H^+	0.9	SiO_4^{4-}	0.4
OH^-	0.35	SO_4^{2-}	0.4
HCO_3^-	0.4	H_2L^-	0.35
CO_3^{2-}	0.45	HL^{2-}	0.45
HSiO_3^{-a}	0.4	L^{3-}	0.5
SiO_3^{2-a}	0.4	Ca^{2+}	0.6
H_3SiO_4^-	0.4	Mg^{2+}	0.8
$\text{H}_2\text{SiO}_4^{2-}$	0.4	CaL^{-b}	0.35
HSiO_4^{3-}	0.4	MgL^{-b}	0.35

^a Data obtained by the estimation using carbonate and sulfate ions as the reference. ^b Data obtained by the estimation using H_2L^- ion as the reference. L represents citrate.

Table 5. Calculated Activity Coefficients of Ions in Synthetic Brine ($I = 0.0478$ M)

ions	γ	ion	γ
H^+	0.935	SiO_4^{4-}	0.250
OH^-	0.915	SO_4^{2-}	0.707
HCO_3^-	0.917	H_2L^-	0.915
CO_3^{2-}	0.714	HL^{2-}	0.714
HSiO_3^-	0.917	L^{3-}	0.478
SiO_3^{2-}	0.707	Ca^{2+}	0.732
H_3SiO_4^-	0.917	Mg^{2+}	0.753
$\text{H}_2\text{SiO}_4^{2-}$	0.707	CaL^-	0.915
HSiO_4^{3-}	0.459	MgL^-	0.915

hydrated ion species i , I is the ionic strength of the aqueous solution, and c_i is the concentration of ion species i .

Table 4 shows the effective diameter of the ions in the synthetic brine.²⁸ Table 5 shows the calculated activity coefficient of ions at the ionic strength of synthetic brine.

3. Results and Discussion

3.1. Effects of Additives on Kaolinite ζ Potential in Synthetic Brine. As discussed in the Introduction, kaolinite

(26) Lide, D. R. *Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boca Raton, FL, 1990–1991.

(27) Sillén, L. G.; Martell, A. E. *Stability Constants of Metal–Ion Complexes*; The Chemical Society: London, U.K., 1971; Special Publication 17.

(28) Kielland, J. Individual activity coefficient of ions in aqueous solutions. *J. Am. Chem. Soc.* **1937**, *59*, 1675–1678.

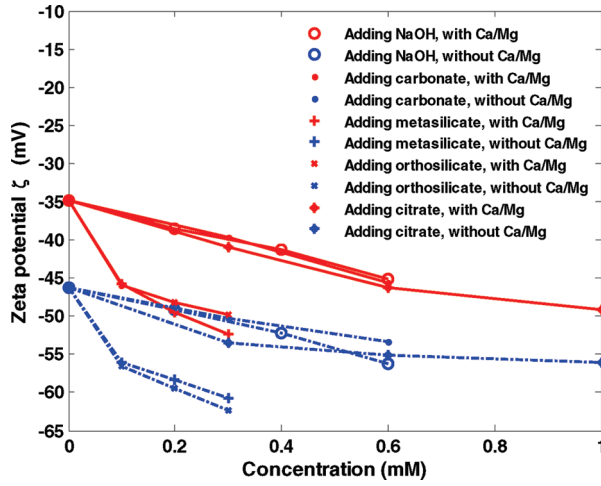


Figure 3. ζ potentials of kaolinite in synthetic brine with different additives.

wettability can affect the emulsion stability. Kaolinite ζ potentials in synthetic brine with different additives were measured, as shown in Figure 3, to characterize the wettability change of kaolinite.

For all of the samples, ζ potentials are more negative without Ca/Mg ions than with Ca/Mg ions. The reason may be the adsorptions of Ca/Mg ions on the negatively charged surface sites of kaolinite. When Ca/Mg ions adsorb on the surface of kaolinite, the negatively charged sites will become positively charged. Thus, the net surface charge of kaolinite will become less negative.

In the figure, ζ potential becomes more negative when adding sodium hydroxide, sodium silicate, sodium citrate, or sodium carbonate.

Figure 4 shows the ζ potential change (mV/mM) as a function of the additive concentration. The central difference method is used for calculation.

$$\frac{\Delta\zeta}{\Delta c} \left(\frac{c_1 + c_2}{2} \right) = \frac{\zeta(c_2) - \zeta(c_1)}{c_2 - c_1} \quad (18)$$

Here, ζ is ζ potential, and c is the concentration of the additive.

For sodium hydroxide, sodium citrate, and sodium carbonate, ζ potential change per unit additive concentration is around 15–25 mV/mM. However, for *meta*- or *ortho*-silicate, ζ potential change is much larger than other additives at low concentrations ($< 10^{-4}$ M). In addition, ζ potential change decreases very fast with the increase of the sodium silicate concentration. In comparison to other anions, silicate ions have the greatest effect per unit addition on changing the ζ potential of kaolinite.

3.2. Model Parameters Evaluation and Experimental Data Correlation. To correlate ζ potentials of kaolinite in synthetic brine, values of parameters in the model are needed. Synthetic brine is a relatively complicated system for the ζ potential model, and the effects of pH, SO_4^{2-} , HCO_3^- , Ca^{2+} , and Mg^{2+} need to be considered. Because Na^+ and Cl^- are indifferent ions, ζ potential measurements of kaolinite in a simple system (NaCl brine or deionized water) with different cations and anions are performed to obtain parameter values in the model.

3.2.1. Surface Site Density and Dissociation Constant. To study the effect of pH, ζ potentials of kaolinite in 0.05 M NaCl brine (the ionic strength is close to that of synthetic

brine) at different pH were measured. Here, HCl and NaOH were used to adjust the pH. Equations for charge density and site dissociation equilibrium of kaolinite are

$$\sigma_0 = e([\text{AlOH}_2^+] - [\text{AlO}^-] + [\text{SiOH}_2^+] - [\text{SiO}^-] - [\text{B}^-]) \quad (19)$$

$$[\text{AlOH}_2^+] = \frac{[\text{AlOH}] a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right)}{K_{\text{Al}^+}} \quad (20)$$

$$[\text{AlOH}] = \frac{[\text{AlO}^-] a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right)}{K_{\text{Al}^-}} \quad (21)$$

$$[\text{SiOH}_2^+] = \frac{[\text{SiOH}] a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right)}{K_{\text{Si}^+}} \quad (22)$$

$$[\text{SiOH}] = \frac{[\text{SiO}^-] a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right)}{K_{\text{Si}^-}} \quad (23)$$

$$[\text{AlO}^-] = \frac{N_{\text{Al}}}{1 + \frac{1}{K_{\text{Al}^-}} a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) + \frac{1}{K_{\text{Al}^+} K_{\text{Al}^-}} \left[a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) \right]^2} \quad (24)$$

$$[\text{AlOH}_2^+] = \frac{\frac{N_{\text{Al}}}{K_{\text{Al}^+} K_{\text{Al}^-}} \left[a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) \right]^2}{1 + \frac{1}{K_{\text{Al}^-}} a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) + \frac{1}{K_{\text{Al}^+} K_{\text{Al}^-}} \left[a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) \right]^2} \quad (25)$$

$$[\text{SiO}^-] = \frac{N_{\text{Si}}}{1 + \frac{1}{K_{\text{Si}^-}} a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) + \frac{1}{K_{\text{Si}^+} K_{\text{Si}^-}} \left[a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) \right]^2} \quad (26)$$

$$[\text{SiOH}_2^+] = \frac{\frac{N_{\text{Si}}}{K_{\text{Si}^+} K_{\text{Si}^-}} \left[a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) \right]^2}{1 + \frac{1}{K_{\text{Si}^-}} a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) + \frac{1}{K_{\text{Si}^+} K_{\text{Si}^-}} \left[a_b (H^+) \exp\left(-\frac{e\zeta}{kT}\right) \right]^2} \quad (27)$$

Here, K ($K_{\text{Al}1}$, $K_{\text{Al}2}$, $K_{\text{Si}1}$, and $K_{\text{Si}2}$) and N (N_{Al} , N_{Si} , and N_{B}) are equilibrium constants and surface site densities, respectively, which can be obtained by fitting with the experimental data. From eqs 19–27, the ζ potential ζ_{cal} can be calculated from the initial evaluates of K and N . Parameter estimation was performed using the Matlab optimization toolbox. The object function to be determined is $\| \zeta_{\text{cal}} - \zeta_{\text{exp}} \|$. Iteration terminates until $\| \zeta_{\text{cal}} - \zeta_{\text{exp}} \| < \text{tolerance}$.

Figure 5 shows the experimental data and fitted curve of kaolinite ζ potentials in 0.05 M NaCl brine at different pH. The ζ potential of kaolinite becomes more negative with the increase of pH. Table 6 shows the calculated parameters from data fitting. The total amphoteric sites ($N_{\text{Al}} + N_{\text{Si}}$) have a density of $2.33 \times 10^{-7} \text{ mol/m}^2$ (0.14 site/nm²). Williams et al.

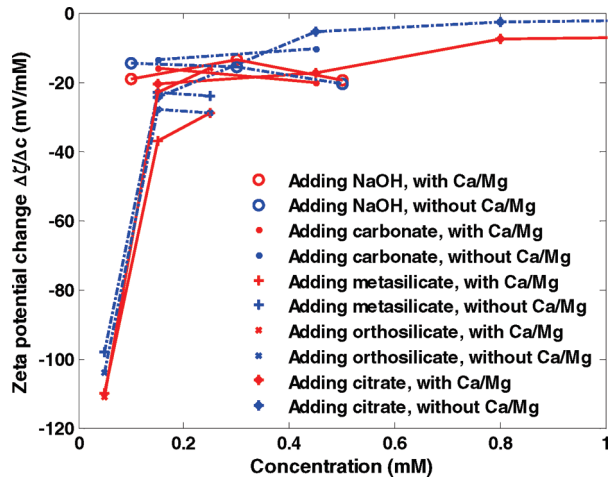
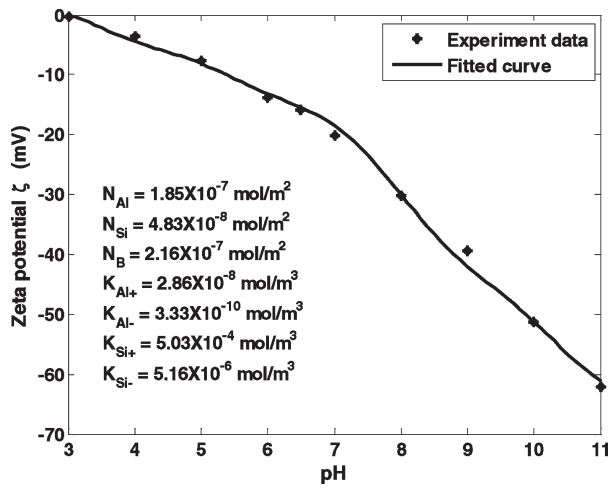
Figure 4. ζ potential change of kaolinite samples in synthetic brine.Figure 5. ζ potential of kaolinite in 0.05 M NaCl brine at different pH.

Table 6. Kaolinite Surface Site Densities and Dissociation Constants

reaction	K (mol/m ³)	N ($\times 10^{-8}$ mol/m ²)
$-AlOH_2^+ \rightleftharpoons -AlOH + H^+$	2.86×10^{-8}	18.5
$-AlOH \rightleftharpoons -AlO^- + H^+$	3.33×10^{-10}	
$-SiOH_2^+ \rightleftharpoons -SiOH + H^+$	5.03×10^{-4}	4.83
$-SiOH \rightleftharpoons -SiO^- + H^+$	5.16×10^{-6}	
inert sites		21.6

used the cation-exchange capacity titration method to obtain the amphoteric charge density.²⁹ The values are from -3 to $-25 \mu\text{C}/\text{cm}^2$ (site density from 3.1×10^{-7} to $2.6 \times 10^{-6} \text{ mol/m}^2$). The fitted site density is close to the lower bound of the literature value.

Figures 6 and 7 show the sites fraction of $-AOH$, $-AO^-$, and $-AOH_2^+$ (A can be Al or Si) in $-SiOH$ and $-AlOH$ sites as the function of bulk pH in 0.05 M NaCl. As pH increases, the fraction of positively charged sites $-AOH_2^+$ will decrease and the fraction of negatively charged sites $-AO^-$ will increase. At pH 8–9, almost all silica sites are negatively charged; for alumina sites, the fraction of positively charged sites is higher than that of negatively charged sites.

In section 2.4, amphoteric silica and alumina sites on the kaolinite surface are assumed. On the basis of the results of

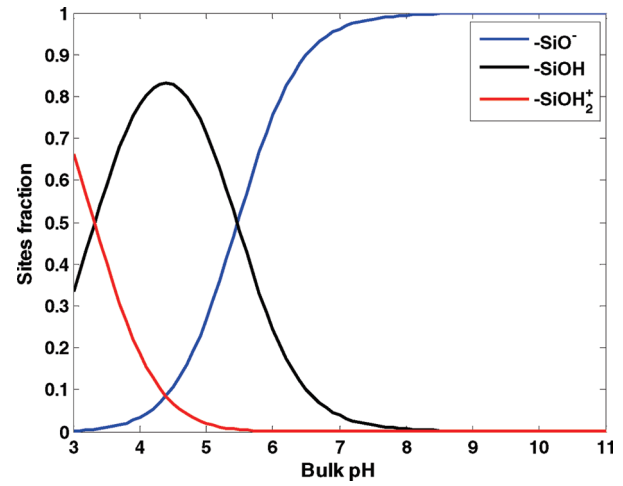


Figure 6. Silica sites fraction in kaolinite at different bulk pH in 0.05 M NaCl.

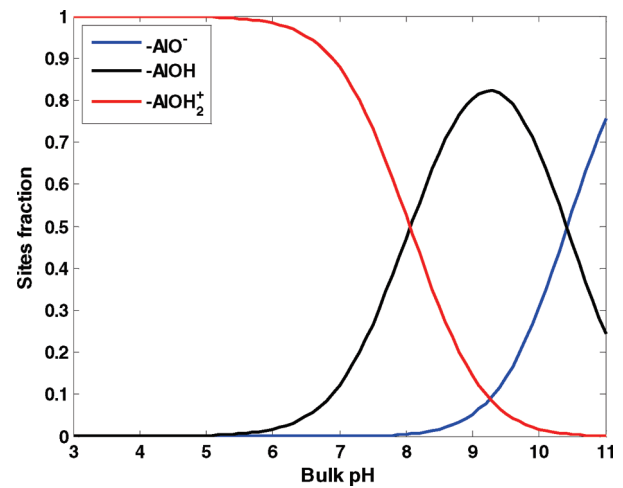


Figure 7. Alumina sites fraction in kaolinite at different bulk pH in 0.05 M NaCl.

Figures 6 and 7, above pH 8, silica sites are negatively charged and alumina sites are dependent on pH. To verify the assumption, ζ potentials of alumina in 0.05 M NaCl brine at different pH are measured.

Equations for charge density and site dissociation equilibrium of kaolinite are

$$\sigma_0 = e([AlOH_2^+] - [AlO^-]) \quad (28)$$

$$[AlOH_2^+] = \frac{[AlOH]a_b(H^+) \exp\left(-\frac{e\zeta}{kT}\right)}{K_{Al+}} \quad (29)$$

$$[AlOH] = \frac{[AlO^-]a_b(H^+) \exp\left(-\frac{e\zeta}{kT}\right)}{K_{Al-}} \quad (30)$$

Figure 8 shows the experimental data and fitted curve of alumina ζ potentials in 0.05 M NaCl brine at different pH. The ζ potential of alumina changes from positive to negative with the increase of pH. The dashed line shows a ζ potential value of 0 as the reference. Table 7 shows the calculated parameters from data fitting. Dissociation equilibrium constants and site density of alumina are 4.21×10^{-8} and

(29) Williams, D. J. A.; Williams, K. P. Electrophoresis and ζ potential of kaolinite. *J. Colloid Interface Sci.* **1977**, *65* (1), 79–87.

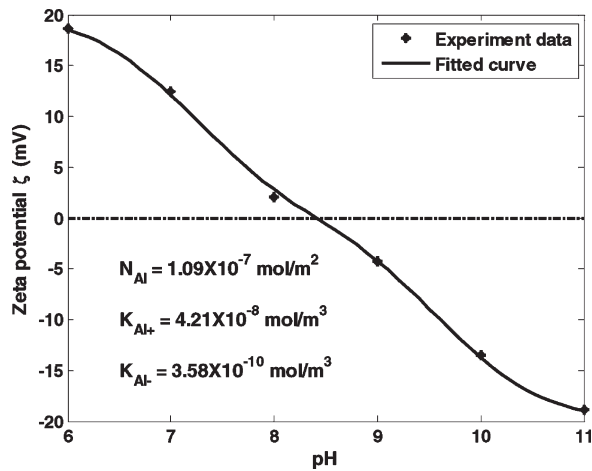


Figure 8. ζ potential of alumina in 0.05 M NaCl brine at different pH.

Table 7. Alumina Site Densities and Dissociation Constants

reaction	K (mol/m ³)	N ($\times 10^{-8}$ mol/m ²)
$-\text{AlOH}_2^+ \rightleftharpoons -\text{AlOH} + \text{H}^+$	4.21×10^{-8}	10.9
$-\text{AlOH} \rightleftharpoons -\text{AlO}^- + \text{H}^+$	3.58×10^{-10}	

3.58×10^{-10} mol/m³ and 1.09×10^{-7} mol/m², respectively. For alumina sites on kaolinite, the values are 2.86×10^{-8} and 3.33×10^{-10} mol/m³ and 1.85×10^{-7} mol/m², respectively. For amphoteric alumina sites, kaolinite has the same magnitude of dissociation equilibrium constants and site density as alumina. This indicates that kaolinite has similar amphoteric alumina sites to alumina and validates the assumption in section 2.4. Figure 9 shows the sites fraction of $-\text{AlOH}$, $-\text{AlO}^-$, and $-\text{AlOH}_2^+$ sites as a function of the bulk pH in 0.05 M NaCl. As pH increases, the fraction of positively charged sites $-\text{AlOH}_2^+$ will decrease and the fraction of negatively charged sites $-\text{AlO}^-$ will increase. This is similar to kaolinite in Figure 7.

3.2.2. Adsorption Effect of Anions SO_4^{2-} and HCO_3^- . Synthetic brine contains anions SO_4^{2-} and HCO_3^- . The ζ potentials of kaolinite in 0.05 M NaCl brine adding Na_2SO_4 at pH 6.5 were measured to study the effect of sulfate.

In 0.05 M NaCl brine at pH 6.5, positively charged sites $-\text{AOH}_2^+$ (A can be Al or Si) can adsorb the SO_4^{2-} ion and become negatively charged sites $-\text{AOH}_2\text{SO}_4^-$.



$$\begin{aligned} K_{\text{SO}_4} &= \frac{[\text{AOH}_2\text{SO}_4^-]}{[\text{AOH}_2^+]a_s(\text{SO}_4^{2-})} \\ &= \frac{[\text{AOH}_2\text{SO}_4^-]}{[\text{AOH}_2^+]a_b(\text{SO}_4^{2-})\exp\left(\frac{2e\zeta}{kT}\right)} \end{aligned} \quad (32)$$

$$\sigma_0 = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-] - [\text{AOH}_2\text{SO}_4^-]) \quad (33)$$

Here, K_{SO_4} is the adsorption equilibrium constant.

Using the similar method discussed in section 3.2.1, on the basis of eqs 6, 32, and 33, the adsorption equilibrium constant can be calculated from experimental data. For the adsorption of other ions, a similar method can be used to evaluate the adsorption equilibrium constant.

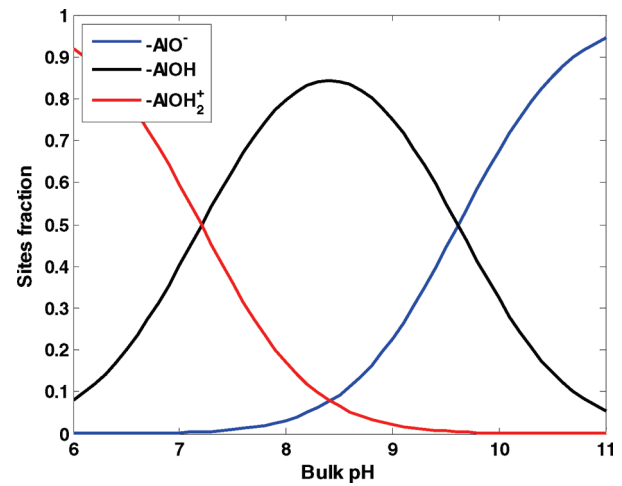


Figure 9. Alumina sites fraction at different bulk pH in 0.05 M NaCl.

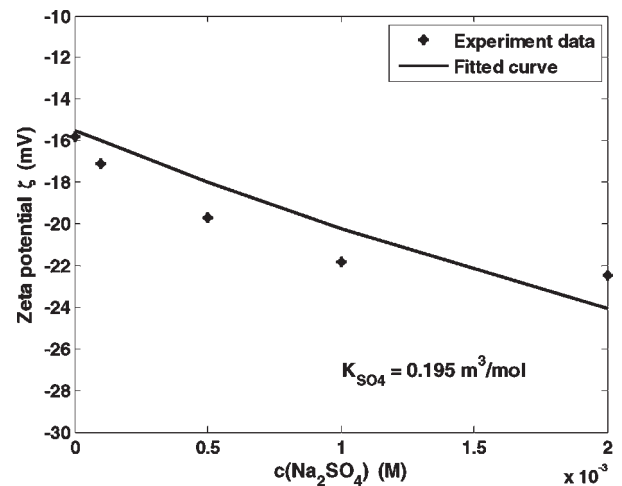
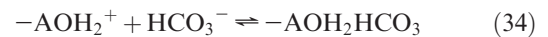


Figure 10. Kaolinite ζ potential in 0.05 M NaCl brine adding Na_2SO_4 at pH 6.5.

Figure 10 shows ζ potential of kaolinite as the function of the Na_2SO_4 concentration in 0.05 M NaCl brine at pH 6.5. The adsorption constant K_{SO_4} is 0.195 m³/mol (Table 8).

To study the effect of bicarbonate, ζ potentials of kaolinite with different NaHCO_3 in deionized water at pH 8.3 were measured. In NaHCO_3 solution, positively charged sites $-\text{AOH}_2^+$ can adsorb the HCO_3^- ion and become neutral sites $-\text{AOH}_2\text{HCO}_3$.



$$\begin{aligned} K_{\text{HCO}_3} &= \frac{[\text{AOH}_2\text{HCO}_3]}{[\text{AOH}_2^+]a_s(\text{HCO}_3^-)} \\ &= \frac{[\text{AOH}_2\text{HCO}_3]}{[\text{AOH}_2^+]a_b(\text{HCO}_3^-)\exp\left(\frac{e\zeta}{kT}\right)} \end{aligned} \quad (35)$$

$$\sigma_0 = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-]) \quad (36)$$

Here, K_{HCO_3} is the adsorption equilibrium constant.

Figure 11 shows the ζ potential of kaolinite as a function of the NaHCO_3 concentration at bulk pH 8.3. With the increased concentration of NaHCO_3 , the ζ potential becomes less negative. This is due to the increase of the ionic strength.

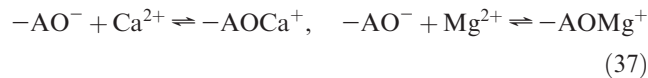
Table 8. Adsorption Equilibrium Constants of Surface Reactions

reaction	K (m ³ /mol)
$-\text{AO}^- + \text{Ca}^{2+} \rightleftharpoons -\text{AOCa}^+, \text{A} = \text{Al/Si}$	0.82
$-\text{AO}^- + \text{Mg}^{2+} \rightleftharpoons -\text{AOMg}^+, \text{A} = \text{Al/Si}$	1.71
$-\text{AOH}_2^+ + \text{HSiO}_3^- \rightleftharpoons -\text{AOH}_2\text{HSiO}_3, \text{A} = \text{Al/Si}$	13.7
$-\text{AOH}_2^+ + \text{H}_3\text{SiO}_4^- \rightleftharpoons -\text{AOH}_2\text{H}_3\text{SiO}_4, \text{A} = \text{Al/Si}$	8.7
$-\text{AOH}_2^+ + \text{HCO}_3^- \rightleftharpoons -\text{AOH}_2\text{HCO}_3, \text{A} = \text{Al/Si}$	0.018
$-\text{AOH}_2^+ + \text{SO}_4^{2-} \rightleftharpoons -\text{AOH}_2\text{SO}_4^-, \text{A} = \text{Al/Si}$	0.195
$-\text{AOH}_2^+ + \text{L}^{3-} \rightleftharpoons -\text{AOH}_2\text{L}^{3-}, \text{A} = \text{Al/Si}, \text{L} = \text{citrate}$	0.66

The dashed curve shows the fitted results assuming no HCO_3^- ion adsorption. The deviation of the experimental data and fitted result indicates the effect of HCO_3^- ion adsorption. The solid curve shows the fitted results assuming HCO_3^- ion adsorption, and the adsorption constant $K_{\text{HCO}_3^-}$ is 0.018 m³/mol (Table 8). The fitted curve assuming HCO_3^- ion adsorption is closer to the experimental data than the curve without assuming HCO_3^- ion adsorption.

From the ζ potential results, anions SO_4^{2-} or HCO_3^- can adsorb on positively charged surface sites and make kaolinite ζ potential more negative.

3.2.3. Adsorption Effect of Cations Ca^{2+} and Mg^{2+} . Synthetic brine contains cations Ca^{2+} and Mg^{2+} . The negatively charged Al/Si sites $-\text{AO}^-$ can adsorb Ca/Mg ions and become positively charged. To study the effect of Ca/Mg ions, ζ potentials of kaolinite in 0.05 M NaCl brine adding CaCl_2 or MgCl_2 at pH 6.5 were measured.



$$K_{\text{Ca}} = \frac{[\text{AOCa}^+]}{[\text{AO}^-]_a(\text{Ca}^{2+})} = \frac{[\text{AOCa}^+]}{[\text{AO}^-]_b(\text{Ca}^{2+})\exp\left(-\frac{2e\zeta}{kT}\right)} \quad (38)$$

$$K_{\text{Mg}} = \frac{[\text{AOMg}^+]}{[\text{AO}^-]_a(\text{Mg}^{2+})} = \frac{[\text{AOMg}^+]}{[\text{AO}^-]_b(\text{Mg}^{2+})\exp\left(-\frac{2e\zeta}{kT}\right)} \quad (39)$$

$$\sigma_0(\text{Ca}) = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-] + [\text{AOCa}^+]) \quad (40)$$

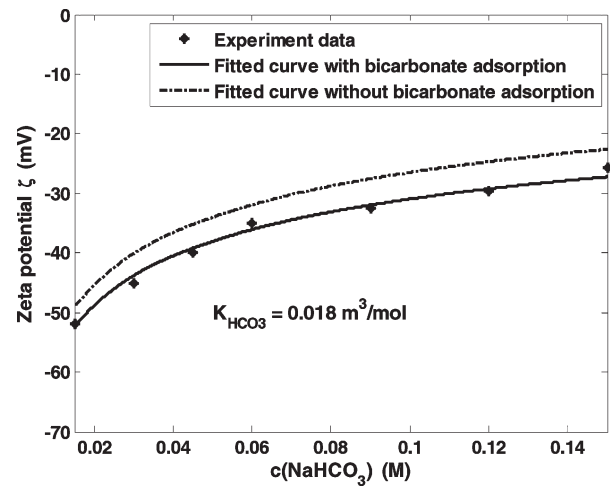
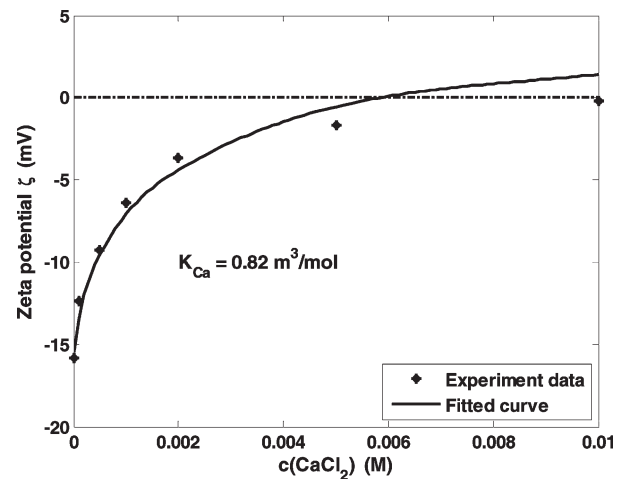
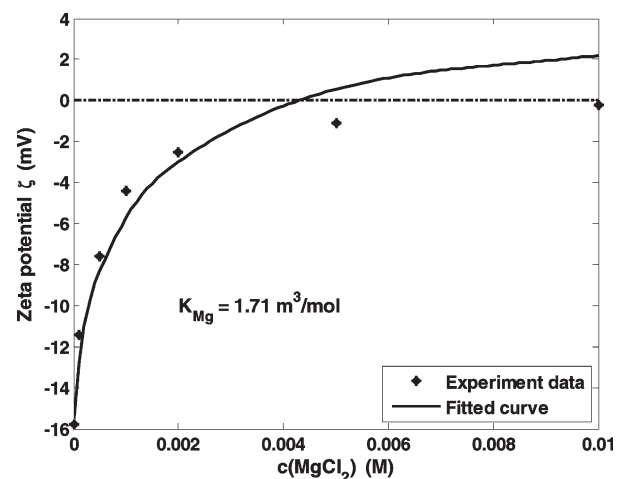
$$\sigma_0(\text{Mg}) = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-] + [\text{AOMg}^+]) \quad (41)$$

Here, K_{Ca} and K_{Mg} are surface adsorption equilibrium constants.

Using the similar method, adsorption equilibrium constants and surface sites density can be calculated from experimental data. Figures 12 and 13 show kaolinite ζ potential as a function of the $\text{CaCl}_2/\text{MgCl}_2$ concentration in 0.05 M NaCl brine at pH 6.5. The dashed line shows a ζ potential value of 0 as the reference. The equilibrium constant of the Ca^{2+} ion K_{Ca} is 0.82 m³/mol (Table 8). The equilibrium constant of the Mg^{2+} ion K_{Mg} is 1.71 m³/mol (Table 8).

From ζ potential results, cations Ca^{2+} and Mg^{2+} can adsorb on negatively charged surface sites and make kaolinite ζ potential less negative.

3.2.4. Effect of Synthetic Brine pH. On the basis of the site density and dissociation constant of kaolinite, ζ potential

**Figure 11.** Kaolinite ζ potential adding NaHCO_3 in deionized water at pH 8.3.**Figure 12.** Kaolinite ζ potential in 0.05 M NaCl brine adding CaCl_2 at pH 6.5.**Figure 13.** Kaolinite ζ potential in 0.05 M NaCl brine adding MgCl_2 at pH 6.5.

can be calculated at different pH. Figure 14 shows ζ potential of kaolinite in synthetic brine with or without Ca/Mg ions adding NaOH at different pH. In the brine with Ca/Mg, on the basis of the solubility product calculation, Ca^{2+} and

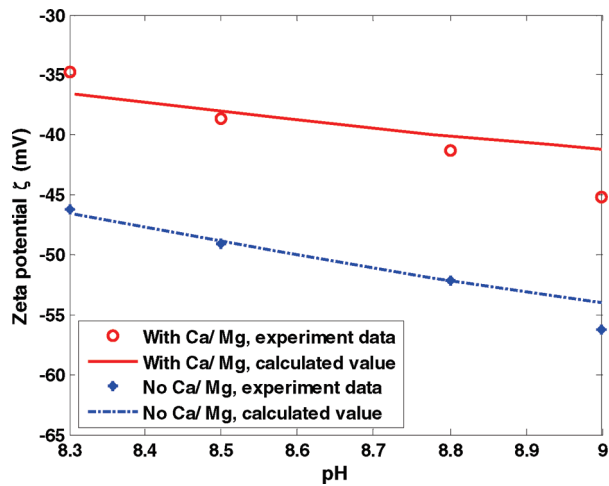


Figure 14. Kaolinite ζ potential in synthetic brine adding NaOH at different pH.

CO_3^{2-} ions may form CaCO_3 precipitation, which will reduce the concentration of Ca^{2+} . The blue dashed curve shows the calculated ζ potential of kaolinite without Ca/Mg. The red solid curve shows the calculated ζ potential of kaolinite with Ca/Mg, with the equilibrium Ca^{2+} concentration calculated from the CaCO_3 solubility product.

From the figure, an increase of pH can make kaolinite ζ potential more negative. Adding NaOH, the ζ potential change of kaolinite is around 15–20 mV/mM. Increasing pH can enhance the dissociation of surface sites and make the net surface charge more negative, thereby kaolinite ζ potential will become more negative.

3.2.5. Effect of Carbonate. Carbonate has two effects on the ζ potential of kaolinite. Adding carbonate can increase pH and the concentration of the HCO_3^- ion, which can make the ζ potential of kaolinite more negative. Here, only the adsorption of the HCO_3^- ion is considered instead of the CO_3^{2-} ion, because the concentration of the HCO_3^- ion is much higher than the CO_3^{2-} ion in the brine. Carbonate can also precipitate the Ca^{2+} ion, which can also make the ζ potential of kaolinite more negative.

Figure 15 shows the ζ potential of kaolinite in synthetic brine with or without Ca/Mg adding Na_2CO_3 . Adding 6.0×10^{-4} M Na_2CO_3 , pH of the brine increases from 8.3 to 8.9. The blue dashed curve shows the calculated ζ potential of kaolinite without Ca/Mg. The red solid curve shows the calculated ζ potential of kaolinite with Ca/Mg, with the equilibrium Ca^{2+} concentration calculated from the CaCO_3 solubility product. In the brine without Ca/Mg, the ζ potential change of kaolinite is around 15 mV/mM. In the brine with Ca/Mg, the ζ potential change of kaolinite is around 20 mV/mM. The precipitation of the Ca^{2+} ion can make kaolinite ζ potential more negative. Thus, the ζ potential change per unit addition in synthetic brine with Ca/Mg (20 mV/mM) is greater than that in the brine without Ca/Mg (15 mV/mM).

3.2.6. Effects of Silicates. Silicate has two effects on the ζ potential of kaolinite. Adding silicate can increase the pH of the brine, which can make ζ potential of kaolinite more negative. Silicate can also adsorb on the positively charged sites $-\text{AOH}_2^+$, which can also make the ζ potential of kaolinite more negative.

In synthetic brine, positively charged sites $-\text{AOH}_2^+$ can adsorb the HSiO_3^- or H_3SiO_4^- ion and become neutral sites. Equations 42–47 give the surface reaction and equilibrium

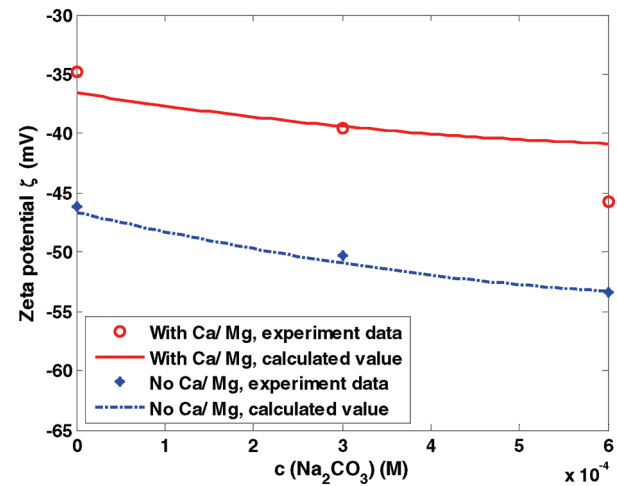
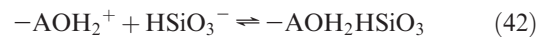


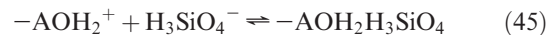
Figure 15. Kaolinite ζ potential in synthetic brine adding Na_2CO_3 at pH 8.3–8.9.

equation. Here, only the adsorption of the HSiO_3^- or H_3SiO_4^- ion is considered, because the concentration of the monovalent ion is much higher than other silicate ions with higher valency.



$$K_{\text{HSiO}_3} = \frac{[\text{AOH}_2\text{HSiO}_3]}{[\text{AOH}_2^+]a_s(\text{HSiO}_3^-)} = \frac{[\text{AOH}_2\text{HSiO}_3]}{[\text{AOH}_2^+]a_b(\text{HSiO}_3^-)\exp\left(\frac{e\zeta}{kT}\right)} \quad (43)$$

$$\sigma_0 = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-]) \quad (44)$$



$$K_{\text{H}_3\text{SiO}_4} = \frac{[\text{AOH}_2\text{H}_3\text{SiO}_4]}{[\text{AOH}_2^+]a_s(\text{H}_3\text{SiO}_4^-)} = \frac{[\text{AOH}_2\text{H}_3\text{SiO}_4]}{[\text{AOH}_2^+]a_b(\text{H}_3\text{SiO}_4^-)\exp\left(\frac{e\zeta}{kT}\right)} \quad (46)$$

$$\sigma_0 = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-]) \quad (47)$$

Figures 16 and 17 show the ζ potential of kaolinite in synthetic brine adding Na_2SiO_3 or Na_4SiO_4 . The blue dashed curve shows the fitted ζ potential of kaolinite without Ca/Mg. The red solid curve shows the fitted ζ potential of kaolinite with Ca/Mg. At a low concentration of silicate (0.05 mM), the ζ potential change per unit additive concentration is around 100–110 mV/mM, which is about 5 times that adding sodium hydroxide (20 mV/mM). With the increase of the silicate concentration, the ζ potential change per unit additive concentration decreases to around 30 mV/mM. *meta*- and *ortho*-silicates have similar effects on the ζ potential change of kaolinite. However, adding *meta*-silicate has a smaller effect on the pH change than adding *ortho*-silicate. Adding 3.0×10^{-4} M Na_2SiO_3 , pH of the brine increases from 8.3 to 9.0. Adding 3.0×10^{-4} M Na_4SiO_4 , pH of the brine increases from 8.3 to 9.2. Equilibrium constants K_{HSiO_3} and $K_{\text{H}_3\text{SiO}_4}$ are 13.7 and $8.7 \text{ m}^3/\text{mol}$ (Table 8), respectively.

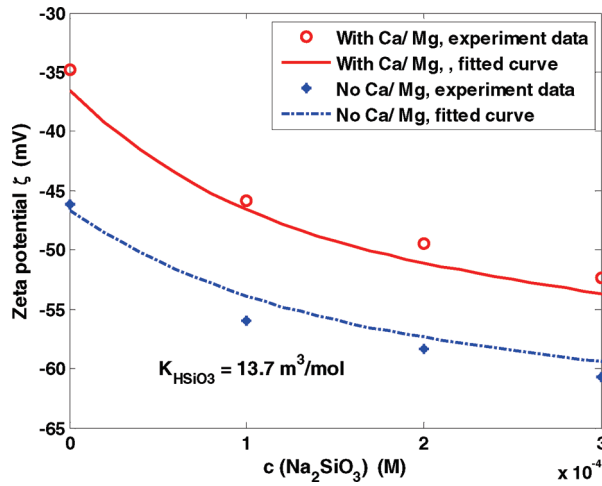


Figure 16. Kaolinite ζ potential in synthetic brine adding Na_2SiO_3 at pH 8.3–9.0.

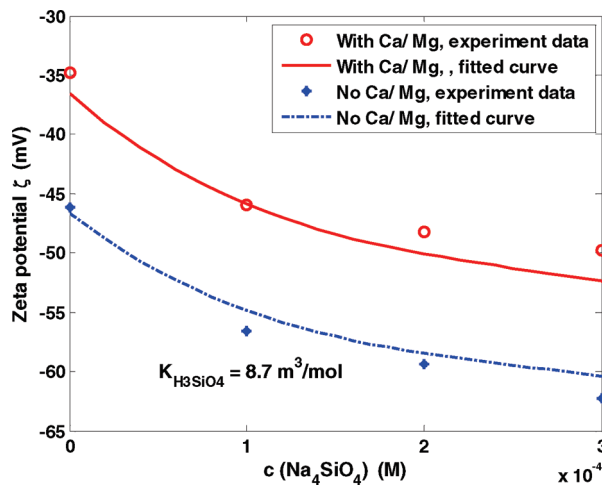


Figure 17. Kaolinite ζ potential in synthetic brine adding Na_4SiO_4 at pH 8.3–9.2.

3.2.7. *Effects of Citrate.* Citrate can chelate the Ca/Mg ion (Table 3), which can make the ζ potential of kaolinite more negative. Citrate can also adsorb on the positively charged sites $-\text{AOH}_2^+$, which can also make the ζ potential of kaolinite more negative.

In synthetic brine, positively charged sites $-\text{AOH}_2^+$ can adsorb the citrate ion $\text{C}_6\text{H}_5\text{O}_7^{3-}$ (L^{3-}) and become negatively charged sites $-\text{AOH}_2\text{L}^{2-}$. Here, only the adsorption of the L^{3-} ion is considered instead of other ions (HL^{2-} and H_2L^-) because in the brine the concentration of the L^{3-} ion is much higher than the other ions.



$$\begin{aligned} K_L &= \frac{[\text{AOH}_2\text{L}^{2-}]}{[\text{AOH}_2^+][\text{L}^{3-}]} \\ &= \frac{[\text{AOH}_2\text{L}^{2-}]}{[\text{AOH}_2^+]a_b(\text{L}^{3-})\exp\left(\frac{3e\zeta}{kT}\right)} \end{aligned} \quad (49)$$

$$\sigma_0 = e([\text{AOH}_2^+] - [\text{AO}^-] - [\text{B}^-] - 2[\text{AOH}_2\text{L}^{2-}]) \quad (50)$$

Figure 18 shows the ζ potential of kaolinite in synthetic brine adding citrate. The blue dashed curve shows the fitted

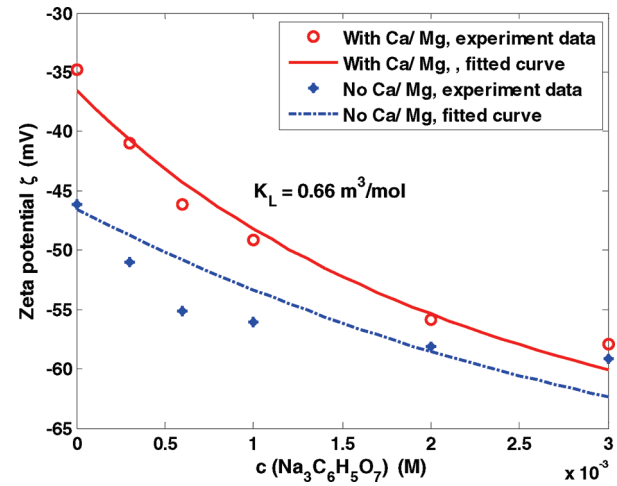


Figure 18. Kaolinite ζ potential in synthetic brine adding $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ at pH 8.3.

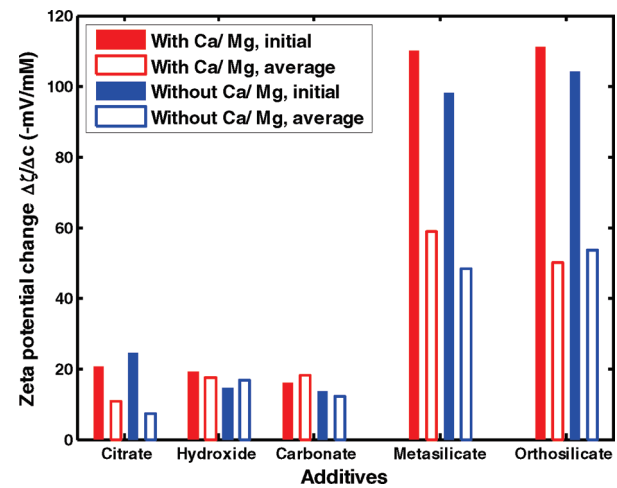


Figure 19. ζ potential change with different additives in synthetic brine.

ζ potential of kaolinite without Ca/Mg. The red solid curve shows the fitted ζ potential of kaolinite with Ca/Mg. Adding citrate will not affect the pH of the brine. Therefore, the pH of synthetic brine stays 8.3 with different amounts of citrate.

With the increase of the citrate concentration, the ζ potential of kaolinite becomes more negative. At a low citrate concentration (3×10^{-4} M), the ζ potential change of kaolinite is around 20 mV/mM. However, with the increase of the citrate concentration, the decreasing tendency of ζ potential becomes saturated. The ζ potential change of kaolinite tends to 0. The equilibrium constant K_L is $0.66 \text{ m}^3/\text{mol}$ (Table 8).

Figure 19 shows the bar diagram of the ζ potential change per unit additives of different anions based on Figure 4 in section 3.1. The initial value is calculated at lower additive concentrations. The average value is the average ζ potential change with different additive concentrations. On the basis of ζ potential results, an increase of pH can make kaolinite ζ potential more negative. Divalent cations (Ca^{2+} and Mg^{2+}) can make kaolinite ζ potential less negative, while some anions (HCO_3^- , CO_3^{2-} , HSiO_3^- , H_3SiO_4^- , and $\text{C}_6\text{H}_5\text{O}_7^-$) can make kaolinite ζ potential more negative. Silicate ions have the largest effect on the kaolinite ζ potential change compared to other anions.

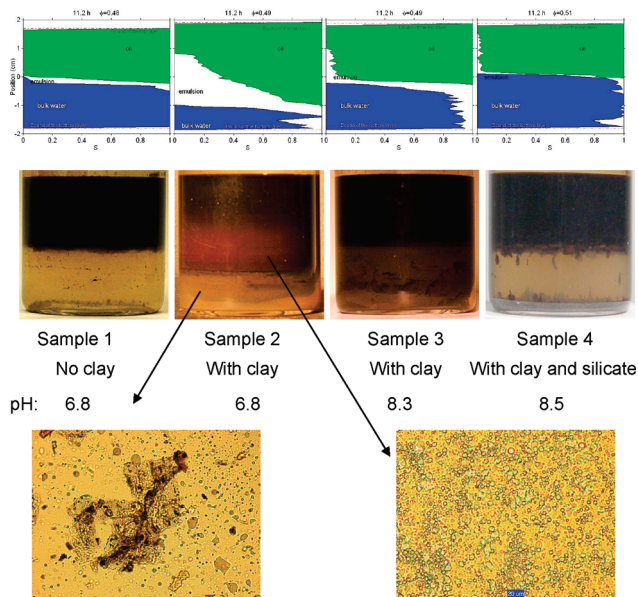


Figure 20. Water (11.2 h) in diluted bitumen emulsions adding 200 ppm PR_5 . The scale bar in micrograph is 20 μm .

3.3. Emulsion Separation. Figure 20 shows 11.2 h photographs and water fraction profiles measured with the 1D T_1 weighted profile method⁴ of brine in diluted bitumen emulsion samples with 200 ppm demulsifier PR_5 at different pH, prepared as described in section 2.2. Sample 1 is the emulsion sample without clay solids using 1.0 wt % NaCl brine at pH 6.8 (sample 4 in previous work⁴). Sample 2 is the emulsion sample with clay solids using 1.0 wt % NaCl brine at pH 6.8 (sample 2 in previous work⁴). Sample 3 is the emulsion sample with clay solids using diluted bitumen and synthetic brine at pH 8.3. Sample 4 is the emulsion sample with clay solids using synthetic brine adding 1×10^{-4} M Na_2SiO_3 at pH 8.5.

In the profile figures, the dashed lines represent the boundaries of the sample. The total height is a little less than 4 cm. The x axis S is the emulsified or free water saturation of the sample, and the y axis position is the position measured from the middle of the sample. Φ is the water volume fraction in the total sample measured by nuclear magnetic resonance (NMR). In the profile figures, the green part is the clean oil fraction, the blue part is the bulk water fraction, and the white part is the emulsified water fraction. The upper part has oil and emulsified water, corresponding to the W/O emulsion. If the water fraction is 0, it is separated clean oil. The lower part has bulk water and emulsified water, corresponding to the rag layer. If the water fraction is 1, it is separated free water. On the basis of the water fraction profiles and pictures of the samples, it is easy to find that the top is clean oil, the middle consists of an emulsion layer and a rag layer, and the bottom is mostly separated free water.

In the absence of clay solids, the separation of the emulsion is almost complete after adding PR_5 (sample 1). If the emulsion contains clay solids (sample 2), the addition of PR_5 results in coalescence of water drops but the clay solids remain as rigid “skins” dispersed in water. The photomicrographs show that the bottom of the oil-continuous phase is water-in-oil emulsion and the top of the water-continuous phase contains clay solids skins. Instead of settling to the

bottom, the clays present a partially oil-wet property and entrap oil to form skins with intermediate density, which stays in the middle between the oil and water layers. An increase of pH from 6.8 (sample 2) to 8.3 (sample 3) can obtain better separation, but a rag layer still forms in the middle. Adding *meta*-silicate at pH 8.5 (sample 4) can obtain almost complete separation, except for a thin rag layer in the middle.

In comparison of samples 1 and 2, clay solids can make emulsion more stable and prevent the complete separation of oil and water. In comparison of samples 2 and 3, increasing pH can enhance emulsion separation. In comparison of samples 3 and 4, adding silicate can obtain better separation and reduce the rag layer. The separation result of sample 4 is better than sample 2 but worse than sample 1. This indicates that increasing pH and adding silicate can change the properties of clay solids, which will reduce the stabilization effects of clay solids on the emulsion.

4. Conclusions

Emulsion separation experiments show that clay wettability is important to emulsion stability. Emulsion separation is incomplete, and a rag layer consisting of skins of solids, oil, and emulsion forms near the interface between oil and water layers when partially oil-wet clay solids are present. Increasing pH and adding silicate can make clay solids more water-wet and the volume of the rag layer smaller.

Kaolinite in clay solids has a heterogeneous surface charge, which affects its wettability. The ζ potential measurement is used to characterize the wettability change of kaolinite. Calcium and magnesium ions in the aqueous solution can make the ζ potential of kaolinite in brine less negative. Adding NaOH, *meta*-silicate, *ortho*-silicate, citrate, or carbonate can make the ζ potential of kaolinite in brine more negative. In comparison to other anions, silicate ions have the greatest effect per unit addition on changing the ζ potential of kaolinite.

A simplified Gouy–Stern–Grahame model and an oxide site-binding model can be used to correlate the ζ potential of kaolinite in brine with different additives. Different additives have various surface reactions with kaolinite, which can change the ζ potential of kaolinite in brine. Adding NaOH can increase the pH, and the hydroxyl ion can react with the surface group of kaolinite, which will make ζ potential more negative. Sulfate and bicarbonate ions can adsorb on the surface of kaolinite and make ζ potential more negative. Calcium and magnesium ions can adsorb on the surface of kaolinite and make ζ potential less negative. Silicate can adsorb on the surface of kaolinite, in addition to raising the pH. The citrate ion can both adsorb on the surface of kaolinite and chelate with Ca/Mg ions and has little effect on pH of synthetic brine. The carbonate ion can increase pH and the bicarbonate ion concentration and precipitate Ca ions, which can make ζ potential more negative. Silicate and pH control can change the surface charge of kaolinite and the adsorption of surfactants on solid surfaces, thereby manipulating solid surface wettability, enhancing emulsion separation, and minimizing or eliminating the rag layer formation.

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