Effect of total organic carbon content and structure on the electrokinetic behavior of organoclay suspensions

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Abstract
This experimental investigation measured the zeta potential of the clay mineral, montmorillonite, which was modified with six different quaternary ammonium cations. The organic cations were chosen to quantify the effect of cation functional groups, including chain length and cation size, on the resulting zeta potential; each of the six cations were exchanged onto the clay surface at three levels of total organic carbon. The zeta potential of the unmodified and the organically modified clays was measured as a function of pH, and in all cases, became less negative as the total organic carbon was increased and as the length of the attached carbon chain was increased, indicating that the organic cations were more strongly bound within the particle’s shear plane as total organic carbon content was increased. Measured zeta potential was also less negative for all clays tested (including unmodified montmorillonite) as pH was decreased. When compared on the basis of total organic carbon content, increasing the length of one carbon chain in the quaternary positions was a more effective method of neutralizing surface charge than was increasing the overall size of the cation (i.e., increasing the chain length in all quaternary positions).

Keywords: Montmorillonite, Organobentonite, Quaternary ammonium cation, Zeta potential

1. Introduction
Bentonite is a naturally occurring mixed mineral soil that is composed primarily of montmorillonite, a commonly occurring aluminosilicate clay mineral. Due to isomorphous substitution, montmorillonite exhibits a permanent structural surface charge which attracts weakly bonded interlayer cations to neutralize that charge [1]. Typically, interlayer cations are inorganic (e.g. Na+, Ca2+); however, organic–clay complexes, known as organoclays, can be made by exchanging the clay’s naturally occurring inorganic cations with a variety of organic cations. Quaternary alkyammonium cations, with a nitrogen head group and four positions for functional groups, have been extensively studied as exchange cations in montmorillonite. The organic phase sorbs on the mineral surface through electrostatic attraction to the nitrogen head group, and, as the sorbed organic content is increased, can change the clay from a hydrophilic surface to a hydrophobic surface. The cation exchange results in an organic–enriched phase on the mineral surface that is highly sorbent for nonpolar organic compounds, with potential applications as wastewater and groundwater sorbents [2].

In addition to changing the mechanical and hydraulic properties of the clay soil [3], exchanging organic cations onto the clay surface also has significant impacts on the electrokinetic behavior of the mineral. When a charged particle is immersed in water and is subjected to an electric field, it will move relative to the bulk solution. The particle, along with sorbed ions and a sorbed fluid phase, will translate through the bulk fluid; the zeta potential (ζ) represents the electric potential measured at the interface between this slipping plane and the bulk fluid. The measured zeta potential yields insight into the surface charge of the clay mineral and its electrokinetic interactions with the fluid phase.

Previous work has quantified either the electrophoretic mobility or the zeta potential of montmorillonite in NaCl solutions, with measured values of ζ ranging from –60 mV to –30 mV [4–7]. The reported differences may be attributed to variation in parameters such as the degree of isomorphic substitution of the montmorillonite or concentration of the background solutions. Additionally, when the bulk solution background electrolyte was changed to a different inorganic cation, the measured zeta potential was altered in part according to the affinity of the clay for the inorganic cation [6–15].

Similarly, the addition of an organic cation to the charged clay surface will also influence the resulting zeta potential. A variety of organics can be used to create organic rich clays, including surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple surfactants such as sodium dodecyl sulfate and dodecyltrimethylammonium bromide [8,16], humic acid and fulvic acid [17–19], and many types of polymers [8,20–22]. Zeta potential measurements of these organic rich clays showed that anionic surfactants, such as dodecyl sulfate anion, decrease the zeta potential, while cationic surfactants, such as dodecyltrimethylammonium cation, increase the zeta potential, and charge neutral organic compounds, including some humic and fulvic acids, have little or no effect on the measured zeta potential. Polymers are more complex than simple
organic ions because they often consist of more than one functional group, and the resulting zeta potential can be increased, decreased, or not affected.

Previous studies on adsorption of organic compounds and surfactants onto solid surfaces demonstrated that there were multiple driving forces for adsorption, including electrostatic or coulombic interaction, covalent bonding, hydrogen bonding (in systems containing hydroxyl, phenolic, carboxylic and amine groups on the surfactants), hydrophobic lateral interactions (transferring the hydrocarbon chains from the aqueous environment into the hydrophobic interior of the aggregates, when hemi-micelles formed), hydrophobic interaction between the hydrocarbon chains and hydrophobic sites on the solid like talc or graphite, solvation (due to dissolution or solvation of the adsorbate species or any species displaced from the interface due to adsorption), and desolvation (when a hydrated head group of the surfactant transfers from the bulk to the mineral–solution interfacial region, water from the secondary solvation shell around the surfactants head groups may be partially removed) [23–25].

This study focused on the behavior of montmorillonite that was modified with six different quaternary ammonium organic cations. For the materials studied in this investigation, the montmorillonite was hydrophilic, and the quaternary ammonium cations had alkyl functional groups with an ammonium head group; therefore, the primary driving forces for interaction at the particle surface were electrostatic interaction and hydrophobic lateral interactions. The organic cations chosen for study were selected to examine the effect of cation size (i.e., increasing the carbon chain length in all four alkyl positions), as well as the effect of cation chain length (i.e., increasing the carbon chain length in one of four alkyl positions) on the measured zeta potential. Changing the size and chain length of the organic cation altered both the packing on the clay surface as well as the hydrophobicity of the exchanged clay, which in turn altered the measured zeta potential.

2. Materials and experimental methods

2.1. Materials

Six quaternary ammonium cations were chosen for study: tetramethylammonium (TMA, denoted: 1 C1) chloride [(CH3)4NCl], tetraethylammonium (TEA, denoted: 1 C2) bromide [(CH2CH3)4NBr], tetrabutylammonium (TBA, denoted: 4 C4) bromide [(CH2CH3)4NB], decyltrimethylammonium (DTMA, denoted: 1 C10) bromide [(CH3)2NC(H2)10Br], dodecyltrimethylammonium (DDTMA, denoted: 1 C12) bromide [(CH3)2NC(H2)12Br], and hexadecyltrimethylammonium (HDTMA, denoted: 1 C16) bromide [(CH3)2NC(H2)16Br] (Fig. 1). All cations were obtained from Fisher Scientific, and were used as received. Hydrochloric acid (HCl, Fisher Scientific), sodium hydroxide (NaOH, Fisher Scientific), sodium chloride (NaCl, Fisher Scientific), and soda lime (>4% NaOH, J.T. Baker) were also used as received, and the water used in all experimentation was deion-

![Fig. 1. Structure of the quaternary ammonium cations used in the study: (a) tetramethylammonium (TMA) chloride; (b) tetraethylammonium (TEA) bromide; (c) tetrabutylammonium (TBA) bromide; (d) decyltrimethylammonium (DTMA) bromide; (e) dodecyltrimethylammonium (DDTMA) bromide; and (f) hexadecyltrimethylammonium (HDTMA) bromide. The following terminology was used to distinguish between organic cations: for increasing length of carbon chain in one quaternary position (1 Cx) (e.g., HDTMA denoted: [1 C16]), compared to increasing carbon chain length in all quaternary positions (4 Cx) (e.g., TBA denoted: [4 C4]).](image-url)
Doppler velocimetry (LDV) method to determine particle velocity

The supernatant was below 600 μS/cm, and the process was repeated until the conductivity were rinsed with deionized water to remove any salts or loosely

are separated by gravity settling. The suspension was then transfers into a nitrogen atmosphere (CO₂-free) within a glove box (Scienceware, Fisher Scientific) to prevent the dissolution of atmospheric CO₂ into the suspension. During the course of the experiments, nitrogen gas was circulated through the glove box to reduce the entry of CO₂ and soda lime was used as a CO₂ absorber within the glove box.

Table 1
Organoclay experimental matrix: Theoretical and measured organic carbon contents.

<table>
<thead>
<tr>
<th>Organoclay</th>
<th>Amount of organic cations exchanged (%CEC)</th>
<th>Theoretical organic carbon content (%)</th>
<th>Measured organic carbon content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA-bentonite</td>
<td>100</td>
<td>3.2</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>6.1</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.9</td>
<td>1.5</td>
</tr>
<tr>
<td>TBA-bentonite</td>
<td>100</td>
<td>11.4</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>7.2</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
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<td>DTMA-bentonite</td>
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<td>8.5</td>
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<td>60</td>
<td>5.9</td>
<td>6.8</td>
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<tr>
<td></td>
<td>30</td>
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<td>3.6</td>
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<td>DDTMA-bentonite</td>
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<td>7.6</td>
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<tr>
<td></td>
<td>30</td>
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</tr>
<tr>
<td>HDTMA-bentonite</td>
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<td>13.2</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>8.4</td>
<td>9.1</td>
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<tr>
<td></td>
<td>30</td>
<td>4.4</td>
<td>5.9</td>
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The zeta potential was measured for each organoclay at acidic pH values between 3.5 and 4.5, as well as over a range of pH, varying from approximately 3.5–10.5. The value of pH was adjusted using either 1 mol/L HCl or NaOH solutions. Additionally, the zeta potential of the unmodified bentonite was measured as a function of pH, ranging from pH = 2 to 11. Throughout the course of the experiments, some pH drift was observed, typically within 0.5–1.5 pH units.

Approximately 1.5 mL of the suspension supernatant was extracted to a cuvette for each zeta potential measurement. The suspension was stirred before extraction in order to uniformly distribute particles. Zeta potential measurements were taken in duplicate every 1–7 days, until the measured differences of last 10 readings were within 5 mV. Measurements were continued until the readings stabilized, typically between 30 and 76 days. Equipment operation was verified daily by measuring the zeta potential of a reference material of known zeta potential (ZR-3, Brookhaven Instruments).

Fig. 2. Theoretical total organic carbon content versus experimentally determined values.
3. Results and discussion

The zeta potential of unmodified montmorillonite (with naturally occurring inorganic cations) was measured over a pH range from 2 to 10.5 (Fig. 3). The measured zeta potential was approximately –28 mV at pH = 2, becoming more negative as the pH value was increased to pH = 4.5, and then remaining relatively stable at a value of approximately –46 mV up to pH = 10.5. At extreme values of pH, the montmorillonite structure will undergo dissolution, which is generally agreed to occur at the particle edges and progress through the breaking of the bridge oxygen bond (Si-O-Al), releasing aluminum and then silicon atoms into solution [26-28].

At low values of pH, the predominant aqueous form of released aluminum is Al\(^{3+}\), which along with H\(^+\), exhibits a high affinity for the clay surface. Aluminum displaces the naturally occurring sodium, resides in the bound layer and effectively neutralizes more negative surface charge than sodium, which in turn, results in a less negative zeta potential. At values of pH in basic conditions, dissolution of the mineral will also occur; however, the predominant aqueous species of aluminum at elevated values of pH is Al\((\text{OH})_4\)\(^-\), which is repelled from the negatively charged particle surface due to electrostatic repulsion. The predominant cation at these high values of pH will again be Na\(^+\), which is weakly bound and results in less positive charge being retained within the shear plane, and a negative zeta potential over pH values in the basic range. Zeta potential of the unmodified montmorillonite in the variable pH solutions was also measured as a function of time (up to 70 days); however, the measured values did not deviate significantly from the initially measured values (<10 mV, data not shown).

The exchange of the organic quaternary ammonium cations for the clay's naturally occurring inorganic cations had significant influence on the measured zeta potential ([Figs. 4 and 5]). The effects of two variables were measured: first, the effect of the length of the carbon chain in one of the quaternary positions (methyl groups in the three remaining positions) and second, the effect of cation size (increasing the length of all four carbon chains). Increasing the length of the carbon chain in one of the quaternary positions allowed comparison of TMA (4 C\(_1\)), DTMA (1 C\(_{10}\)), DDTMA (1 C\(_{12}\)), and HTMA (1 C\(_{16}\)) (Fig. 4), while increasing the length of the chain in all four quaternary positions allowed comparison of TMA (4 C\(_1\)), TEA (4 C\(_3\)), and TBA (4 C\(_6\)) (Fig. 5).

Increasing the length of one of the carbon chains in the quaternary group resulted in two pronounced effects on the zeta potential of the clay (Fig. 4a and b). First, at each exchange level (30% CEC, 60% CEC, and 100% CEC), increasing the number of carbons (1 C\(_{16}\)) in one chain increased the zeta potential of the clay (that is, made it less negative). Over the range of tested organic content, measured values for TMA (1 C\(_1\)) were between –30 and –35 mV, while the measured values at the same exchanged percentage for HDTMA (4 C\(_{10}\)) ranged from 0 to –17 mV ([Fig. 4a]). Increasing the tail length on the carbon chain increased the hydrophobicity of the clay, which increased the hydrophobic lateral interaction between cations. This result was significant because it bonded more positive charge within the shear plane, resulting in a less negative zeta potential. The effect was most pronounced as C\(_b\) was increased because longer chains led to stronger lateral interaction [25], binding more cation within the shear plane. For example, even at 100% cation exchange capacity for DDTMA clay (1 C\(_{12}\)), a negative zeta was measured (–8 mV), indicating that not all DDTMA cations were held within the shear plane, even when 100% of the CEC was exchanged with the organic cation; however, for HDTMA (1 C\(_{16}\)) clay exchanged at 100% of its CEC, the measured zeta potential was essentially equal to zero, indicating that lateral interaction between the cation chains was strong enough to retain most of the HDTMA cations (100% CEC) within the shear plane. Note also that the measured zeta potential increased as the percentage of exchanged organic cation was increased from 30% of
the cation exchange capacity to 100% of the CEC (Fig. 4a). It is believed that the addition of the organic cation to the particle surface resulted in a hydrophobic surface phase that tended to force inorganic cations out of the sorbed layer, and into the diffuse double layer, even at low total organic carbon contents. Subsequently, much of the negative surface charge was not compensated within the bound layer, resulting in a net negative zeta potential. The effect diminished as the organic content was increased, because more positive charge was bound within the shear plane in the form of organic cations.

For all clays tested, increasing the total organic carbon content resulted in a less negative zeta potential, indicating that more organic cation was bound within the shear plane as the percentage exchanged was increased (Fig. 4b). In the case of HDTMA, there was an approximately linear increase in zeta potential as the exchanged cation percentage was increased; however, as carbon chain length was reduced to 10 or 12 carbons, the function was nonlinear, and the measured zeta potential values were negative (−10 to −15 mV) at 100% CEC, indicating that some of the cations were not bound within the shear plane, but within the diffuse double layer.

The effect of increasing the size of the organic cation by increasing the chain length of all four chains in the quaternary ammonium positions was also studied (Fig. 5). As the number of carbons on each branch of the quaternary ammonium cation increased from 1 to 2 to 4 (TMA to TEA to TBA), the measured zeta potential became less negative, indicating that more of the organic cation was retained within the shear plane as the size of the cation was increased (Fig. 5a). The effect was most pronounced in the transition from TMA to TEA at high organic carbon contents. Increasing the total number of carbons in the organic cation decreased the solubility of the cation, which increased the attraction of the cation to the particle surface, resulting in more positive charge being bound within the shear plane. However, even at organic loadings as high as 100% CEC, only a portion of the positive charge was bound within the shear plane, resulting in measured zeta potential values that were still less than zero, but which, notably, increased as the total organic carbon sorbed to the clay was increased (Fig. 5b).

Comparing the measured zeta potential values for the organoclays as a function of increasing size (four carbon chains with 4 C ≥ 4) to the values measured as a function of increasing length of only one carbon chain (1 C ≥ 10), demonstrated that the longer carbon chain was a more effective method to bind cations within the shear plane (Fig. 6). Even when the total organic carbon content was similar (e.g., TBA versus DDTMA), the measured zeta potential was measurably less negative for DDTMA, indicating that the structure of the organic cation was of primary consideration, as opposed to the total mass of organic present on the clay surface, in determination of the zeta potential. The increased size of the TBA cation limited its ability to pack tightly on the clay surface, rendering a lower packing density, and subsequently, decreased exchange when compared to the cations in which only one tail length was increased (e.g. DTMA, DDTMA, and HDTMA). The resulting surface potential for TBA was consequently more negative than that of DDTMA, which was reflected in the more negative measured zeta potential.

The influence of the organic cations on the zeta potential was measured over a range of pH values, varying between approximately 3.5–10.5 (data shown for 100% CEC clays for clarity, trends were similar at other exchanged percentages) (Fig. 7). For all organo-
Fig. 7. (a) Comparison of zeta potential as a function of pH for increasing chain length of organoclays (cation with one chain increased). (b) Comparison of zeta potential as a function of pH for increasing cation size organoclays.

The zeta potential of Wyoming montmorillonite clay, and six organically modified clay samples was measured as a function of pH, cation chain length, and cation size. This study demonstrated that compared to the clay’s naturally occurring inorganic cations, exchanged quaternary ammonium cations were more likely bound within a particle’s shear plane, resulting in a less negative zeta potential for organoclays when compared to unmodified bentonite. Zeta potential became less negative as the length of carbon chain was increased (1 C₉), as the total organic carbon content was increased, and as the pH was decreased. Increasing the length of one carbon tail (1 C₉) was more effective at binding organic cations within the shear plane than increasing the size of the cation (4 C₄); when compared on the basis of total organic carbon content. Increasing the pH of the bulk solution resulted in a decrease in zeta potential for all clays measured.

4. Conclusions

The zeta potential of Wyoming montmorillonite clay, and six organically modified clay samples was measured as a function of pH, cation chain length, and cation size. This study demonstrated that compared to the clay’s naturally occurring inorganic cations, exchanged quaternary ammonium cations were more likely bound within a particle’s shear plane, resulting in a less negative zeta potential for organoclays when compared to unmodified bentonite. Zeta potential became less negative as the length of carbon chain was increased (1 C₉), as the total organic carbon content was increased, and as the pH was decreased. Increasing the length of one carbon tail (1 C₉) was more effective at binding organic cations within the shear plane than increasing the size of the cation (4 C₄); when compared on the basis of total organic carbon content. Increasing the pH of the bulk solution resulted in a decrease in zeta potential for all clays measured.

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References