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Electrokinetic Properties of Acid-Activated Montmorillonite Dispersions

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In this study, the influence of pH, electrolyte concentration, and type of ionic species on the electrokinetic properties (zeta potential and electrokinetic charge density) of the acid-activated montmorillonite mineral have been investigated using the microelectrophoresis method. The electrokinetic properties of acid-activated montmorillonite dispersions have been determined in aqueous solutions of mono-, di-, and trivalent salts and divalent heavy metal salts. Zeta potential experiments have been performed to determine the point of zero charge (pzc) and potential determining ions (pdi). The zeta potential values of the acid-activated montmorillonite particles were negative and did not vary significantly within the pH range studied. Acid-activated montmorillonite dispersions do not have point of zero charge (pzc). The valence of the electrolytes has a great influence on the electrokinetic behavior of the suspension. A gradual decrease in the zeta potential (from $-25\,mV$ to $-5\,mV$) occurs with the monovalent electrolytes when concentration increased. Divalent and heavy metal electrolytes have less negative z-potentials due to the higher valence of ions. A sign reversal of z-potential has been observed at $AlCl_3$, $FeCl_3$, and $CrCl_3$ electrolytes (potential determining ions) and zeta potential values have had a positive sign at high electrolyte concentrations.

The electrokinetic charge density of acid-activated montmorillonite has shown similar trends for variation in mono- and divalent electrolyte solutions. Up to concentrations of ca. $10^{-3}\,M$, it has remained practically constant at approximately $0.5 \times 10^{-3}\ C\,m^{-2}$ For higher concentrations of monovalent electrolytes more negative values ($-16 \times 10^{-3}\ C\,m^{-2}$) were observed. It has less negative values in divalent electrolyte concentrations according to monovalent electrolytes ($-5 \times 10^{-3}\ C\,m^{-2}$). For low concentrations of trivalent electrolytes, the electrokinetic charge density of montmorillonite particles is constant, but at certain concentrations it rapidly increased and changed its sign to positive.

Keywords acid-activated monmorillonite; electrical double layer; electrokinetic charge density; electrolyte concentration; zeta potential

INTRODUCTION

Physicochemical properties of suspended particles and sediments in natural enviroment are dominated by properties of clay minerals. Due to their surface chemical properties, that is, large specific surface area (1), cation exchange capacity (2), and adsorption properties for organic and inorganic compounds (3–6), clay minerals have attracted much interest and have been intensively studied and widely used in many industrial products and processes.

Clay minerals are known to exhibit a variable zeta potential according to solution pH, ionic strength, type of ionic species present, temperature, and type of clay minerals. These potentials are the primary factor in the dispersion and flocculation of clays (7). The electrical and adsorption properties of the clay-water interface are of primary importance in soil chemistry (8) and enviromental chemistry (9), as well as in catalysis (10), composites (11) and several industrial processes (12). The interaction of the clay surface with ions significantly affects soil fertility, soil aggregation, and chemical speciation in different environmental systems. Among the great variety of clays existing in nature, montmorillonites are important because they can completely delaminate in some aqueous solutions, offering a large surface area for interaction with water molecules and dissolved ions (13).

Montmorillonite has a large cation exchange capacity, good adsorption properties, a high specific surface area and swells in the presence of water. These properties have a key role in soil structure, paint, drugs, and other technological applications. Some authors have attempted to use the electrokinetic properties of montmorillonite as models for the application of double layer theories to soil systems (14). Electroosmosis and streaming potential (15,16) and particularly electrophoresis (16,17) are among the most frequently used techniques to measure zeta potential of montmorillonite particles. Similar studies have been carried out with other clay minerals such as perlite (18), clinoptilolite (19), kaolinite (20), sepiolite (21), imigolite (22), and kaolin in high ionic strength (23).

Many of the important properties of colloidal systems are determined directly or indirectly by the electrical charge (or potential) on the particles. Adsorption of ions and dipolar molecules is determined by this charge and potential distribution. The potential distribution itself determines the interaction energy between particles, and this is in many cases

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responsible for the stability of particles towards coagulation and for many aspects of the flow behavior of the colloidal suspension. It is also possible to correlate the zeta potential with the sedimentation behavior of colloidal systems and with the flotation behavior of minerals. Since much of the theoretical basis of colloid chemistry demands a knowledge of the potential distribution around the particles, it is essential to gain access to accurate knowledge of that potential. It can be determined by measuring electrophoretic mobilities.

The study of the electrochemical properties of the clay-water interface is important to understand a large number of properties of clay-aqueous media and colloid suspension of clays. Electrokinetic properties of fine particles in an aqueous solution play a significant role in understanding the adsorption mechanism of inorganic and organic species at the solid-solution interface. They also control the flotation, coagulation, and dispersion properties in suspension systems and give information about the clay particles, their interactions with the surrounding medium, and the electrical properties of particles (24). This can then be used to estimate the effect of the particle charge on properties aggregation behavior, flow, sedimentation, and filtration (25). The zeta potential and electrokinetic charge density of purified montmorillonite from Anatolia in monovalent electrolyte solutions was also investigated by the authors of this paper in their previous study (26).

The aim of this paper is to determine the effects of electrolyte concentration, type of ionic species, and pH on the electrokinetic properties of acid-activated montmorillonite minerals. For this purpose, the electrophoretic experimental data of a wide range of electrolyte concentration is used. Although several studies have been conducted on the zeta potentials of natural montmorillonite, there are not any reports on the variation of the zeta potential and electrokinetic charge density of the acid-activated montmorillonite mineral in terms of the types of electrolyte and different electrolyte concentrations have been published so far. Furthermore, a calculation of the electrokinetic charge density with the help of some specific equations is among the objectives of this paper.

MATERIALS AND METHODS

Materials

The acid activated montmorillonite was obtained from Aldrich (Specific surface area 220–270 m^2/g, bulk density 300–370 g/L). The chemical composition of acid-activated montmorillonite was determined by X-Ray Fluorescence Spectrometer (XRF) and given in Table 1. The zeta potential of montmorillonite particles was measured by using a Zeta- Meter 3.0+ (with Zeiss DR microscope, GT-2 type quartz cell, molybdenum cylinder anode, and platium rod cathode electrode). All chemicals used in this study were acquired from Merck.

TABLE 1
Chemical composition of acid-activated montmorillonite

Component %	Acid-activated montmorillonite
SiO_2	66.65
Al_2O_3	14.42
Fe_2O_3	3.46
MgO	1.60
Na_2O	0.21
CaO	0.23
K_2O	2.19
SO_3	0.21

Measurements of Zeta Potential

When two phases are placed in contact, there generally occurs a difference in potential between them. There are four distinct methods, electrophoresis, electroosmosis, streaming potential, and sedimentation potential, by which this potential difference can be determined. In this study, the electrophoresis method was used to determine the electrokinetic potential. In electrophoresis, the particles are moved by applying an electric field across the system. The effect of pH, electrolyte concentration, and ionic species on the zeta potential was measured. The zeta potential of acid-activated montmorillonite suspensions was calculated automatically from measured electrophoretic mobilities employing the Smoluchowski Equation (27).

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \zeta \tag{1}$$

where ζ is the zeta potential, η is the viscosity of the medium, μ is the electrophoretic mobility at the actual temperature, and ε_r and ε_0 are the dielectric constants of the medium and free space, respectively.

The pH was measured with a combine glass electrode (WTW pH meter). pH of dispersions were adjusted by HCl or NaOH solutions. Then, zeta potential of the clay particles was measured as a function of pH between 2 and 10 without addition of electrolytes. For determinations of the influence of ionic strength on the zeta potential, 0.5 g/L of dry montmorillonite was added to aqueous solutions of mono-, di- and trivalent ions of concentrations, 10^{-1}–10^{-5} M. The solutions were prepared using NaCl, KCl, LiCl, RbCl, CsCl, $NaNO_3$, $NaCH_3COO$, $CaCl_2$, $MgCl_2$, $BaCl_2$, $SrCl_2$, Na_2CO_3, Na_2SO_4, $AlCl_3$, $FeCl_3$, $CrCl_3$, and divalent metal salts such as $ZnCl_2$, $CuCl_2$, $NiCl_2$, $CoCl_2$, $MnCl_2$, $CdCl_2$, and $Pb(NO_3)_2$. Triplicate dispersions were prepared for each concentration. All solutions were prepared with distilled deionized water (<2.0 µS/cm). Prior to each measurement, the clay dispersions were shaken in a thermostatic shaker at 25°C for two hours at a constant pH. At least ten particles were timed in each experiment for both directions of the applied electric field. The value of zeta potential assigned to each dispersion was the average of the data obtained from three experiments. The applied voltage during the measurements was varied in the range 50–150 mV.

Calculations of Electrokinetic Charge Density

In the derivation of equations for the surface charge density, the integration process can be taken from the bulk solution up to any plane parallel to the surface. The accumulated surface charge per unit area up to that plane was obtained and this is balanced by the charge between the chosen plane and the particle surface. If the integration is stopped at the shear plane ($\psi = \zeta$), the net charge per unit area over the shear plane (electrokinetic charge density (σ_e)) is obtained. The electrokinetic charge density of montmorillonite dispersions was calculated from zeta potential measurements by using Eq. (2) for symmetrical electrolytes (25);

$$\sigma_e = \frac{4n^0 ze}{\kappa} \sin h(ze\zeta/2kT) \tag{2}$$

and Eq. (3) for unsymmetrical electrolytes;

$$\sigma_e = \left\{ 2\varepsilon kT \sum_i n_i^0 [\exp(-z_i e\zeta/kT) - 1] \right\}^{1/2} \tag{3}$$

where σ_e is the electrokinetic charge density (Cm^{-2}), n^0 is the electrolyte concentration (ion m^{-3}), z is valency of the counterions, $1/\kappa$ is the thickness of the double layer (m), ζ is zeta potential (V), e is electron charge (C), k is Boltzmann constant (Nm K^{-1} ion^{-1}), T is temperature (K), ε is relative permittivity (C^2 N^{-1} m^{-2}), n_i^0 is the concentration of ion i (ion m^{-3}), z_i is the valency of ion i.

For the calculation of the κ values the following equation was used:

$$\kappa = \left(\frac{e^2 \sum n_i^0 z_i^2}{\varepsilon kT} \right)^{1/2} \tag{4}$$

RESULTS AND DISCUSSION

Effect of Shaking Time

For the assessment of optimum shaking time, the zeta potential of the acid-activated montmorillonite dispersions were measured at different time intervals. The zeta potential of the montmorillonite dispersions was not affected significantly by shaking time. The optimum shaking time was determined to be 2 hours in bidistilled water.

Effect of Solid Concentration

The solid concentration in solution is a major parameter governing the surface charge generation. To determine the effect of the acid-activated montmorillonite concentration on the zeta potential, different montmorillonite dispersions were prepared at concentrations between 0.05–1 g/L in bidistilled water and their zeta potentials were measured. It was observed that there is no significant effect of the solid concentration on the zeta potential of montmorillonite suspensions. Thus, for all dispersions a montmorillonite concentration of 0.5 g/L was used.

Effect of pH on the Zeta Potential

The zeta potential of acid-activated montmorillonite particles was plotted as a function of the dispersion pH (Fig. 1). The zeta potential is negative for the whole pH interval and it is essentially pH independent and in good agreement with results published by other authors (13). Acid-activated montmorillonite particles do not have point of zero charge like natural montmorillonite particles. In this figure, two different types of charge on the montmorillonite particle surface are apparent because of acid-activating. The increase in zeta potential at pH > 5.5 is mainly due to the adsorption of OH$^-$ on the positive edges of the clay particles, which acquire neutral or negative charge. It has slightly lower the point of zero charge of the edges compared to natural montmorillonites (pH 6–7) due to acid activated (28). At the lowest pH values, the zeta potential indicates lower negative values owing to the H$^+$ adsorption on the negative charge on the particle surface (20). This behavior is not observed in kaolinite, which shows a positive zeta potential at pH 3–4 (29). This difference is expected since only about 1% of the surface area of montmorillonite can be ascribed to edges, this fraction being higher in the kaolinite group clays (30).

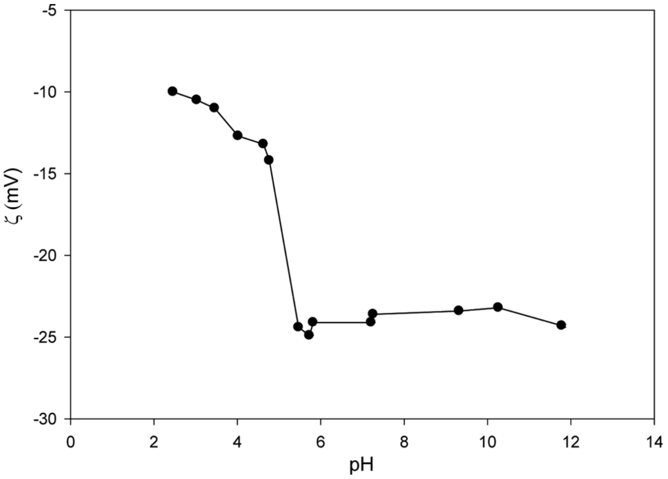


FIG. 1. Zeta potential of the montmorillonite as a function of pH, at 25°C.

Effect of Electrolyte Concentration on the Zeta Potential

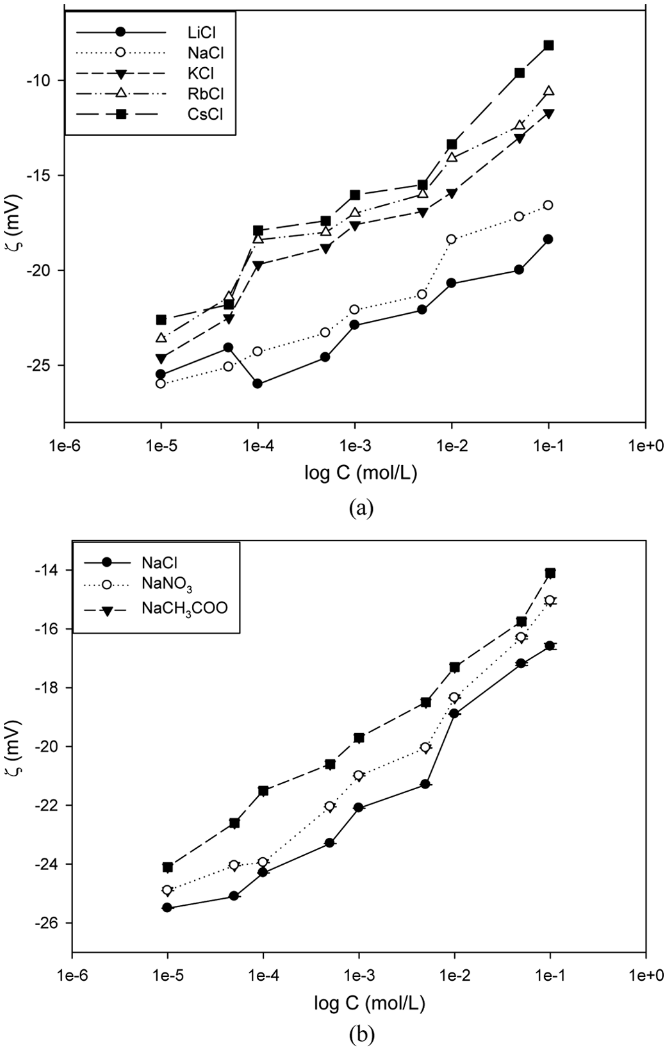
Effect of Monovalent Electrolytes

Figure 2a presents the effects of monovalent cations, i.e., LiCl, NaCl, KCl, RbCl, and CsCl, on the zeta potential of the acid-activated montmorillonite at a constant pH of 5.3 ± 0.2. Figure 2b shows the effect of monovalent anions i.e., NaCl, $NaNO_3$, $NaCH_3COO$. Within the whole concentration range, the zeta potential is negative in accordance with some previous studies (26,31). For monovalent anions, the negative zeta potential varies in the order $Cl^- > NO_3^- > CH_3COO^-$. Because of molecular or atomic radius of anions, Cl^- ions can easily enter to Stern layer and increase the negative zeta potential values.

The zeta potential of acid-activated montmorillonite particles become less negative with an increasing electrolyte concentration from 10^{-5} to 10^{-1} M due to compression of the double layer (Eq. (5) (25)). The counterions accumulate in the electrical double layer and they render the shear plane less negative. The results obtained can also be explained with the equation;

$$\frac{1}{\kappa}=\frac{3}{ZC^{1/2}} \qquad (5)$$

where $1/\kappa$ is the thickness of the diffuse layer (Å), Z denotes the valency and C represents the ion concentration (mol/L). This equation indicates that for constant valence increase of concentration decreases to the thickness of the electrical double layer and consequently reduces the zeta potential. Furthermore, the size of the hydration ion influence the thickness of the Stern layer and thus the magnitude of zeta potential. The ions with small hydrated ionic radius enter the Stern layer easily and the zeta potential decreases (became less negative) compared to other electrolytes. At any MCl concentration, the magnitude of the zeta potential increased in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ similar to natural montmorillonite. When compared to natural montmorillonite, the zeta potential values of the acid-activated montmorillonite was more negative due to exchange of H^+ ions at low electrolyte concentration. The degree of hydration of these cations affects either their dissociation from the Stern layer or the thickness of this layer. The more strongly hydrated the monovalent cations (Li^+, Na^+) are, the more weakly they are bound to the particle surface; consequently leading to more negative zeta potential values (32). The less strongly hydrated are monovalent cations (Rb^+, Cs^+), are more strongly bound to the clay surface and give rise to relatively low-potentials.



(a)

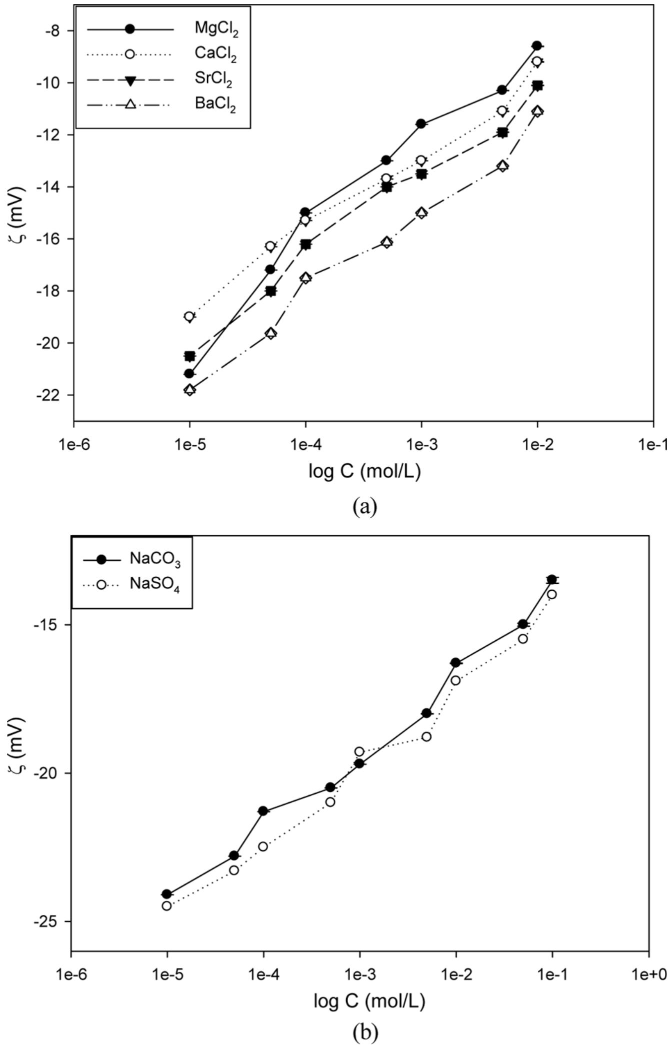
(b)

FIG. 2. Zeta potential of the montmorillonite as a function of monovalent electrolyte concentration, at 25°C; (a) cations and (b) anions.

Effect of Divalent Electrolytes

The change of the zeta potential of acid-activated montmorillonite with various divalent electrolytes, is shown in Figs. 3a and 3b shows the effect of divalent anions, i.e., CO_3^{2-} and SO_4^{2-}, and Fig. 4 displays the effect of heavy metal salts i.e., $ZnCl_2$, $CuCl_2$, $NiCl_2$, $CoCl_2$, $MnCl_2$, $CdCl_2$, $Pb(NO_3)_2$ on ζ potential. Like monovalent cations, with increasing divalent cation and anion concentration, the zeta potential of acid-activated montmorillonite particles reached less negative values due to compression of the electrical double layer.

At low divalent and heavy metal ion concentration zeta potential is negative. With increasing concentration of divalent and heavy metal ions, the zeta potential values become zero at concentrations higher than ca 5×10^{-2} M. Above this concentration, the charge of particle was zero. So the particles did not move at the applied electric field. The hydrated ion radius of divalent heavy metal and divalent alkali earth cations are very identical to both other (33). Therefore, the zeta potential data obtained in the current study have been found similar. Also, as the

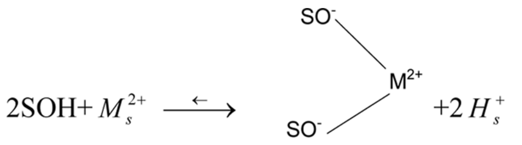


(a)

(b)

FIG. 3. Zeta potential of the montmorillonite as a function of divalent electrolyte concentration, at 25°C; (a) cations and (b) anions.

concentration of heavy metal ions increases, the dispersion pH of the montmorillonite mineral decreases from 4.5 to 2.2. This can be explained by the following reactions (1) and (2) (34).



(1)

$$SOH + M_s^{2+} + H_2O \rightleftarrows SO^- + MOH^+ + 2H_s^+ \qquad (2)$$

Effect of Trivalent Electrolytes

In the presence of trivalent electrolyte, the zeta potential of acid-activated montmorillonite is reduce gradually, as concentration increased from 1×10^{-5} to 1×10^{-1} M (Fig. 5). A sharp increase and a charge reversal occured at ca 1×10^{-4} M for $AlCl_3$, 1×10^{-4} M for $FeCl_3$ and 1×10^{-3} M for $CrCl_3$. Above these concentrations, the zeta potential became positive. Because of the specific adsorption of Al^{3+}, Fe^{3+} and Cr^{3+} counterions in the Stern layer, particulary above these concentrations (35). These ions can be called as potential determining ions. The pH range of acid-activated montmorillonite dispersions was 4.80–2.40 for $AlCl_3$, 3.50–1.60 for $FeCl_3$ and 4.80–2.50 for $CrCl_3$. In the concentration range $1 \times 10^{-5} - 1 \times 10^{-1}$ M, Al^{3+}, Fe^{3+} and Cr^{3+} ions are in the nonhydroxyl form, electrolytes containing Al^{3+} undergo solvatation, hydrolysis and polymerization reactions when they are dissolved in aqueous medium (36). They can form hydroxyl complexes

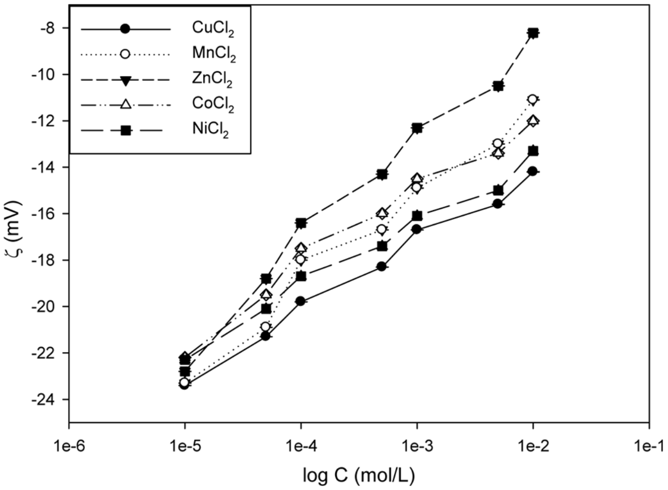


FIG. 4. Zeta potential of the montmorillonite as a function of heavy metal concentration, at 25°C.

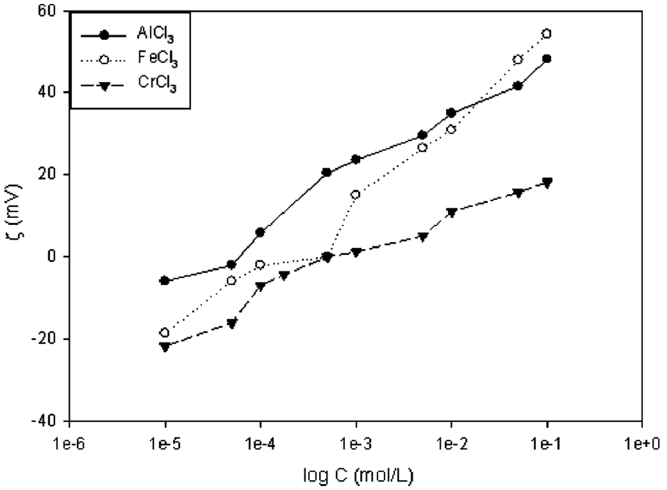


FIG. 5. Zeta potential of the montmorillonite as a function of trivalent electrolyte concentration, at 25°C.

either at concentrations lower than 5×10^{-5} M or with increasing pH.

At any trivalent electrolyte concentration, the magnitude of the zeta potential was increased with the electrolytes in the order $Al^{3+} > Fe^{3+} > Cr^{3+}$. Namely, the dispersion which include the $AlCl_3$ electrolyte has the most positive zeta potential value. The Al^{3+} ions have a small ionic radius and a small distance of the closest approach to surface in comparison with other trivalent ions. The zeta potential of the dispersion which include $AlCl_3$ electrolyte was more positive in comparison with other electrolytes. Acid-activated montmorillonite contains more H^+ ions in it's structure than natural montmorillonite that was mentioned in the previously published work by the same authors. The zeta potential of acid-activated montmorillonite was more positive in comparison with natural montmorillonite in trivalent electrolytes (26).

It can be observed from Fig. 5 that, while the trivalent electrolyte concentration was increased, the zeta potential shifted to less negative values. Although all ions tended to reduce the zeta potential, the trivalent ions were the most effective, in accordance with the Schultz and Hardy Rule (30). These ions have a small hydrated ionic radius, a small distance of closest approach and high polarizability compared to K^+ and Ca^{2+}. These properties allow trivalent ions to approach the surface of the clay more readily and become specifically adsorbed. Consequently, the electrical double layer of the particle was compressed. Therefore, the zeta potential of the montmorillonite which includes trivalent electrolyte indicates more positive values.

Effect of Electrolyte Concentration on the Electrokinetic Charge Density

Effect of Monovalent Electrolytes

With the purpose of calculating the electrokinetic charge density of the particle in the monovalent electrolytes, Eq. (2) (for symmetrical electrolytes) was used. Figure 6 shows the variation of the monovalent electrolyte concentration with the electrokinetic charge density of the acid-activated montmorillonite particles. At all concentrations, the electrokinetic charge density was negative. Up to concentrations of ca 10^{-3} M, it remains practically constant for all monovalent cations, while for higher electrolyte concentrations the negative charge tends to shift to more negative values like natural montmorillonite.

The increase in the electrokinetic charge density (σ_e) observed with increase of the concentration of monovalent electrolytes is attributed to the decrease of the double layer thickness ($1/\kappa$) in the diffuse layer with accumulation of counter ions. Such an increase could be caused by adsorption of anions (Cl^-) on the smectite surface. This adsorption would increase the surface charge (and also σ_e). On the other hand, previous work has shown that when the concentration of NaCl was increased in the liquid medium around the particles, the net negative charge (at the Stern layer) of mica also increased due to the compression of Na^+ ions similar to acid-activated montmorillonite (34). When the monovalent ions were compared, the charge density of the particles was maximum for LiCl solution. This could be related to the large hydration radius. Li^+ ions which enter into the electrical double layer only to a small extent yielding a more negative particle charge density in LiCl solution.

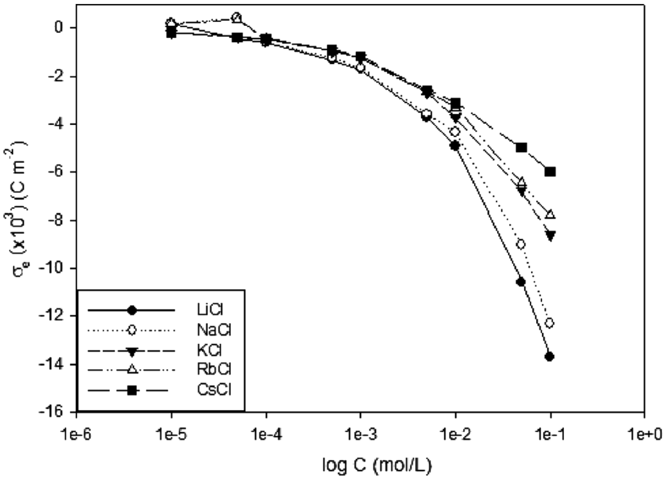


FIG. 6. Electrokinetic Charge Density of the montmorillonite as a function of monovalent electrolyte concentration, at 25°C.

Effect of Divalent Electrolytes

Equation (3) was used to calculate the electrokinetic charge density of acid-activated montmorillonite in divalent electrolytes. There was no significant variation of the charge density (0.3×10^{-3}–$5.0 \times 10^{-3}\, Cm^{-2}$) with change of salt concentration (Fig. 7). However, the charge density of particles reached to zero in high concentration of divalent electrolytes because of their charge. The increase in σ_e observed is attributed mainly to the increase in, κ when the concentration of divalent electrolyte increased. Due to the charge of divalent cations in the Stern layer, calculation of the electrokinetic charge densities of acid-activated montmorillonite had less negative values that compared to monovalent cations.

The thickness of the diffuse double layer ($1/\kappa$) is affected by the valency of the exchangeable cations according to Eq. (4). At equivalent electrolyte concentrations, monovalent cations in exchange position yield thicker diffuse double layers than divalent cations. The thickness of the double layer decreases more strongly with trivalent cations than divalent ions. This phenomenon is due to the different tendency of ions to diffuse away from the colloidal surface,

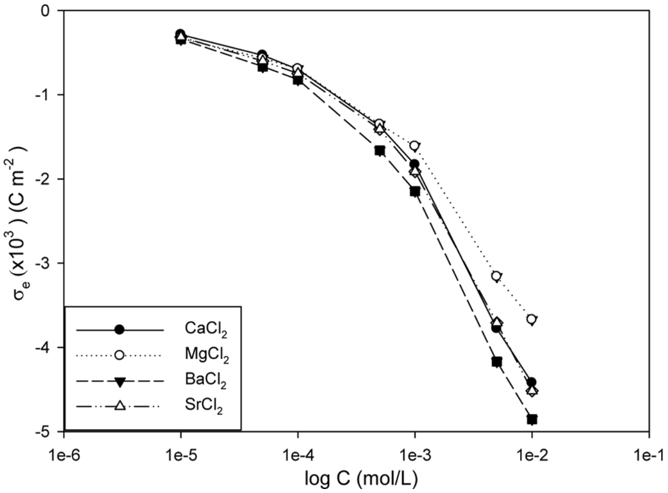


FIG. 7. Electrokinetic Charge Density of the montmorillonite as a function of divalent electrolyte concentration, at 25°C.

Na^+ and K^+ ions form relatively thicker double layers than Ca^{2+}, whereas the double layers formed by Al^{3+} ions are comparatively the thinnest (30).

Effect of Trivalent Electrolytes

Equation (3) was used to calculate the electrokinetic charge density of acid-activated montmorillonite in trivalent electrolytes, $AlCl_3$, $FeCl_3$, $CrCl_3$. A significant change occured in the electrokinetic charge density with the addition of the these electrolytes (Fig. 8). Initially the electrokinetic charge remained constant and approximately zero at low electrolyte concentrations up to 10^{-4} M. For higher concnetrations, σ_e became positive and increased to $80 \times 10^{-3}\,\mathrm{Cm}^{-2}$. This behavior is attributed to adsorption of Al^{3+}, Fe^{3+} and Cr^{3+} in the Stern layer (32). The negative surface charge reversed to positive at high trivalent electrolyte concentration.

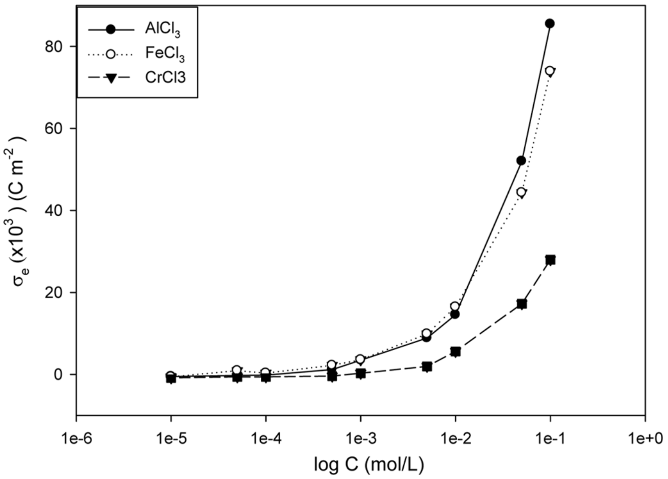


FIG. 8. Electrokinetic Charge Density of the montmorillonite as a function of trivalent electrolyte concentration, at 25°C.

Hydrolyzed ions are very efficient for inverting the sign of the particle charge for most hydrophobic colloidal systems, but unhydrolyzed ions do not cause this effect, irrespective of the magnitude of their charge. Therefore, when explaning the effect of these cations on the electrokinetic charge density, the ion exchange selectivity of the montmorillonite must be considered; the stronger the interaction between a given cation and the clay, the larger will be its effect on the particle charge. The considerable reduction caused by Al^{3+} may be indicative of its adsorption on the surface.

CONCLUSIONS

The zeta potential of acid-activated montmorillonite dispersions was negative at all montmorillonite concentrations and there is no significant effect of the acid-activated montmorillonite concentration on the zeta potential of montmorillonite dispersions.

The dispersions exhibit negative zeta potential value at all the studied pH values. Acid-activated montmorillonite dispersions have no isoelectrical point in the studied pH ranges alike natural montmorillonite dispersions.

The zeta potential of acid-activated montmorillonite in the presence of monovalent electrolytes, i.e., LiCl, NaCl, KCl, RbCl, and CsCl shifted to less negative values (from -25 mV to -5 mV) with increasing concentration from 10^{-5} to 10^{-1} M, due to the compression of the double layer. Monovalent cations like Li^+, Na^+, K^+, Rb^+, and Cs^+ and anions like Cl^-, NO_3^-, and CH_3COO^- are identical electrolytes for acid-activated montmorillonite dispersions. The zeta potential of montmorillonite become more positive with increasing divalent cation and heavy metal concentration. At low concentrations of divalent and heavy metal ions, zeta potential values are negative but with increasing concentration, it becomes zero at concentration higher than 5×10^{-2} M. For trivalent ions, the zeta potential values become positive at high electrolyte concentrations because of adsorption of Al^{3+}, Fe^{3+} and Cr^{3+} counterions in the Stern layer.

The electrokinetic charge density (σ_e) increased with increasing concentration of monovalent electrolytes due to a decrease of the double layer thickness ($1/\kappa$) in the diffuse layer with accumulation of counter ions. No significant variation of the charge density was observed for divalent cations with change of the salt concentration. Trivalent cations exert a greater influence on the σ_e than monovalent and divalent cations. The electrokinetic charge density of acid-activated montmorillonite in suspensions with trivalent cations remained constant and approximately zero at low concentration and become positive at high concentrations. The ionic valency of the solution electrolyte controls the particle charge.

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