

The effects of electrolyte concentration, ion species and pH on the zeta potential and electrokinetic charge density of montmorillonite

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ABSTRACT: In this study, the influence of pH, electrolyte concentration and type of ionic species (such as LiCl, NaCl, KCl, RbCl, CsCl, CaCl₂, AlCl₃) on the electrokinetic properties (zeta potential and electrokinetic charge density) of montmorillonite has been quantified. The zeta potential of montmorillonite particles did not change significantly with change in pH. The valencies of the ions have proven to have a great influence on the electrokinetic behaviour of the suspension. There is a gradual decrease in the zeta potential (from –24 mV to –12 mV) with increase in monovalent electrolyte concentration (from 10^{–4} M to 10^{–1} M). At any monovalent electrolyte concentration, the magnitude of the zeta potential increased with the electrolytes in the order Li⁺ > Na⁺ > K⁺ > Rb⁺ > Cs⁺. The zeta potential of the montmorillonite minerals in CaCl₂ solutions illustrated the same behaviour as the monovalent cations. Less negative values were obtained for the CaCl₂ electrolyte (~–10 mV) due to the greater valence of the ions. A sign reversal was observed at an AlCl₃ concentration of 5 × 10^{–4} M, and, at greater concentrations, zeta potential values had a positive sign (~20 mV).

The electrokinetic charge density of montmorillonite showed similar trends of variation in mono- and divalent electrolyte solutions. Up to concentrations of ~10^{–3} M, it remained practically constant at ~0.5 × 10^{–3} C m^{–2}, while for greater electrolyte concentrations the negative charge produced more negative values (–16 × 10^{–3} C m^{–2}). The electrokinetic charge density of montmorillonite particles was constant at low AlCl₃ concentrations, but at certain concentrations it increased rapidly and changed sign to positive.

KEYWORDS: electrical double layer, electrokinetic charge density, monmorillonite, zeta potential.

The physicochemical properties of suspended particles and sediments in natural environments are dominated by the properties of clay minerals. Due to their surface chemical properties, i.e. large specific surface area (SSA) (Grim, 1968), cation exchange capacity (CEC) (Busenberg & Clemency, 1973), and adsorptive affinity for organic and inorganic compounds (Cohen Stuart & Mulder,

1985; Sequaris *et al.*, 1999; Sjöberg *et al.*, 1999; Billingham *et al.*, 1997), clay minerals have attracted much interest and have been studied intensively and used widely 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 mineral. These potentials are the primary factor in the dispersion and flocculation of clays (Swartzen-Allen & Matijevic, 1976). The electrical and adsorptive properties of the clay-

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water interface are of primary importance in soil chemistry (Tan, 1998) and environmental chemistry (Ma & Pierre, 1999), as well as in catalysis (Kadkhodayan & Pinnavaia, 1993), composites (Xavier & Sharma, 1986), and several industrial processes (Penner & Lagaly, 2000). The interaction of the clay surface with ions has a great influence, for example, on 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 (Avena & De Pauli, 1998).

Montmorillonite has a large CEC, good adsorption properties, a large SSA, and it swells in the presence of water. These properties play a key role in soil structure and in paint, pharmaceutical and other technological systems. Some authors have attempted to use the electrokinetic properties of montmorillonite as models for the application of double layer theories to soil systems (Miller & Low, 1990). Electro-osmosis and streaming potential (Srivastava & Avasthi, 1973; Cohen Stuart & Mulder, 1985) and particularly electrophoresis (Swartzen-Allen & Matijevic, 1975; Rossi *et al.*, 2002) are among the most frequently used techniques. Similar studies have been carried out with other clay minerals such as perlite (Doğan *et al.*, 1997), clinoptilolite (Ersoy & Çelik, 2002), kaolinite (Vane & Zang, 1997), sepiolite (Alkan *et al.*, 2005) and imogolite (Tsuchida *et al.*, 2005).

Study of the electrochemical properties of the clay-water interface is important in understanding many properties of clay-rich porous media and the 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 govern the flotation, coagulation and dispersion properties in suspension systems and provide information about the clay particles, their interactions with the surrounding medium, and the electrical properties of particles (Somasundaran & Fuerstenau, 1966).

The aim of this work is to determine the effect of pH, electrolyte concentration and type of ionic species present on the electrokinetic properties of montmorillonite minerals, and the calculation, from electrophoresis experimental data, of the electrokinetic charge density of montmorillonite particles

at different electrolyte concentrations. Although the zeta potentials of montmorillonites have been studied, reports on the variation of the electrokinetic charge density of montmorillonite minerals with electrolyte concentration and electrolyte type are scarce. Such calculations, using theoretical formulations, are among the objectives of this paper. The electrokinetic charge density calculations can help in understanding montmorillonite's electrical properties.

MATERIALS AND METHODS

Materials

The montmorillonite sample was obtained from West Anatolia. It was purified from bentonite before use. Particles <1.5 µm in diameter were obtained by sedimentation (Israel *et al.*, 2001).

The zeta potential of montmorillonite particles was measured using a Zeta-Meter 3.0+ with Zeiss DR microscope, GT-2 type quartz cell, molybdenum cylinder anode and platinum rod cathode electrode.

LiCl, NaCl, KCl, RbCl, CsCl, CaCl₂, AlCl₃, HCl and NaOH were acquired from Merck.

Methods

Chemical analysis of the montmorillonite was carried out using an X-ray fluorescence (XRF) spectrometer and the results are shown in Table 1. The montmorillonite was characterized using X-ray diffraction and Fourier transform infrared spectrometry.

When two phases are placed in contact, there generally occurs a difference in potential between them. There are four distinct effects by which this

TABLE 1. Chemical analysis (wt.%) of the main elements of montmorillonite.

Component	
SiO ₂	66.21
Al ₂ O ₃	13.94
Fe ₂ O ₃	0.95
MgO	1.99
Na ₂ O	0.06
CaO	2.44
K ₂ O	0.69

potential difference can be determined. These are electrophoresis, electro-osmosis, streaming potential and sedimentation potential. In this study, the electrophoresis method was used to determine the electrokinetic potential. In electrophoresis, the particles move by applying an electric field across the system.

The zeta potential of montmorillonite suspensions was calculated automatically by the instrument from measured electrophoretic mobilities using the Smoluchowski equation (Callaghan & Ottewill, 1974). The basic formula indicates a direct relationship between zeta potential and electrophoretic mobility:

$$\mu = \frac{\epsilon_r \epsilon_0}{\eta} \zeta \tag{1}$$

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

The effect of pH, electrolyte concentration and ionic species on the zeta potential was evaluated using the automated micro-electrophoresis instrument. Migration rates of particle can be changed by varying the zeta-meter's voltage gradient. All solutions were prepared with distilled deionized water (<2.0 $\mu\text{S/cm}$).

The pH was measured with a combine glass electrode (WTW pH meter). The pHs of the dispersions were adjusted by dropwise addition of HCl or NaOH solutions. Then the zeta potential of the clay particles was measured as a function of pH between 2 and 10 when no electrolytes were added.

To determine the effect of ionic strength on the zeta potential, dry montmorillonite was mixed with solutions which contained different concentrations, between 10^{-1} and 10^{-6} M, of the respective chloride salts (LiCl, NaCl, KCl, RbCl, CsCl, CaCl₂, AlCl₃) to produce dispersions containing 0.5 g dm⁻³ of montmorillonite. Three dispersions were prepared for each concentration. Prior to the measurement, the clay dispersions were shaken in a thermostatic shaker for 2 h at a constant temperature of 25°C.

Before analysing each set of dispersions, the optics of the zeta-meter were aligned and the quartz capillary was cleaned with bidistilled water and measuring solutions. At least ten particles were timed in each experiment for both directions of the applied electric field, and the value of zeta potential assigned to each dispersion was the average of the data obtained from three experiments. The standard

deviation of samples was automatically calculated and averaged by the zeta-meter for all measurements.

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 was stopped at the shear plane (so $\psi = \zeta$ was assumed), the net charge per unit area over the shear plane which was called electrokinetic charge density (σ_e) was obtained. The electrokinetic charge density of montmorillonite dispersions was calculated from zeta potential measurements using the following equations (Hunter, 1981). For symmetrical electrolytes:

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

and for asymmetrical electrolytes:

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

where σ_e is the electrokinetic charge density (C m⁻²), n^0 is 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 the Boltzmann constant (N m K⁻¹ ion⁻¹), T is the salt temperature (K), ϵ is relative permittivity (C² N⁻¹ m⁻²), n_i^0 is the concentration of ion i (ion m⁻³), and z_i is the valency of the ion i .

To calculate the κ values, the following equation (Hunter, 1981) was used:

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

RESULTS AND DISCUSSION

Zeta potential

To assess the optimum shaking time, the zeta potentials of the montmorillonite dispersions were measured at different time intervals. A curve of zeta potential vs. shaking time is presented in Fig. 1. The optimum shaking time was determined to be 2 h in bidistilled water.

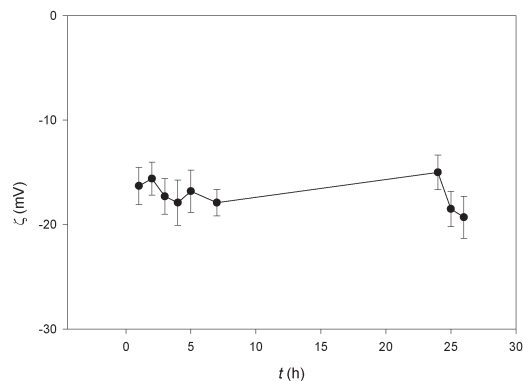


FIG. 1. Zeta potential of montmorillonite as a function of shaking time, at 25°C.

To determine the effect of the montmorillonite concentration on the zeta potential, seven different montmorillonite dispersions were prepared at concentrations between 0.05 and 1 g dm⁻³ in bidistilled water and their zeta potentials were measured. The variation of the zeta potential of the dispersions vs. montmorillonite concentrations, shown in Fig. 2, indicates that there is no significant effect of the montmorillonite concentration. Thus, for all dispersions, a montmorillonite concentration of 0.5 g dm⁻³ was used.

The zeta potential of montmorillonite particles was plotted as a function of pH of the dispersions (Fig. 3). This study is of great importance in the analysis of the electrokinetic properties of clays due to its effect on the charge distribution of the particle surface. It can be observed in Fig. 3 that the zeta potential is negative for the whole pH interval and it is essentially independent of pH, in good agreement with results published by other authors. It was

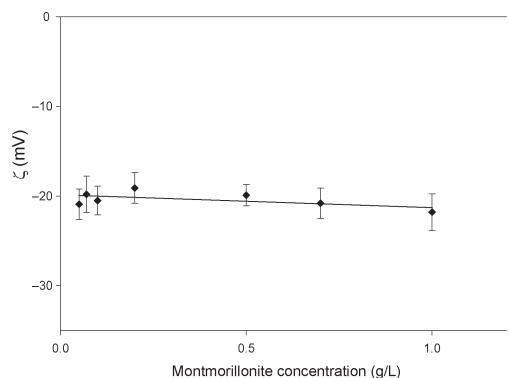


FIG. 2. Zeta potential of montmorillonite as a function of its concentration, at 25°C.

suggested that edges play a negligible role in determining the electrokinetics (dominated by the constant negative charge of faces) of smectites (Heath & Tadros, 1983; Sondi *et al.*, 1997; Benna *et al.*, 1999). The face charge density is independent of solution pH. Conversely, the edge surface charge, which is thought to arise from broken and hydrolysed Al–O and Si–O bonds, is pH dependent (Grim, 1968). In this figure, two different types of charge on the montmorillonite particle surface are apparent. The increase in zeta potential at high pH is mainly due to the interaction between OH⁻ ions and the positive edges of the clay particle which are rendered neutral or negative by the adsorption of the hydroxyl ions. 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 (Vane & Zang, 1997). This behaviour is not observed in another well characterized clay, kaolinite, which shows a positive zeta potential at pH 3–4 (Williams & Williams, 1978). This difference was to be expected since only ~1% of the surface area of montmorillonite can be ascribed to edges, this fraction being greater in kaolin-group clays (van Olphen, 1977).

Figure 4 shows the effects of monovalent electrolyte concentrations, such as LiCl, NaCl, KCl, RbCl and CsCl, on the zeta potential of the montmorillonite at a constant pH of 5.3±0.2. Over the whole concentration range, the zeta potential values indicate a negative charge on the particles. These curves are quite similar and show the same results as those found in a previous study of the electrolyte concentrations (Rossi *et al.*, 2002; Horikawa *et al.*, 1988; Delgado *et al.*, 1985). For these electrolytes, the surface should be rendered

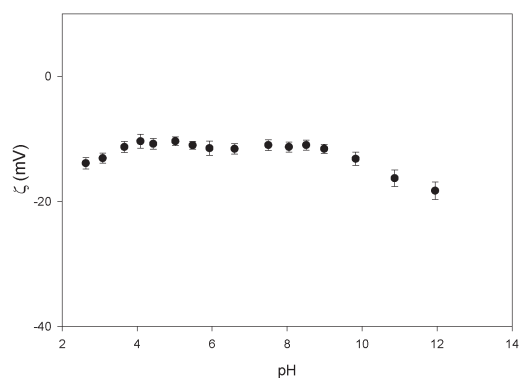


FIG. 3. Zeta potential of montmorillonite as a function of pH, at 25°C.

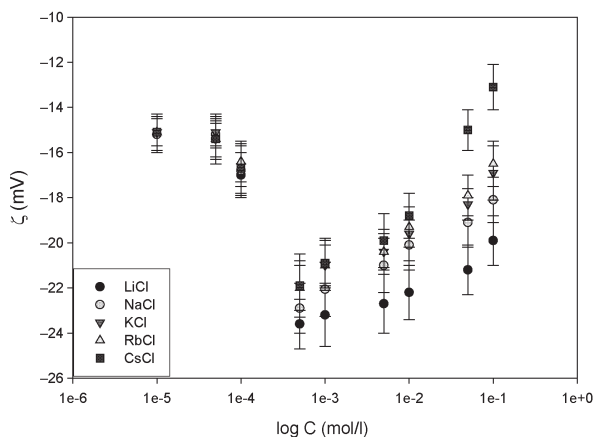
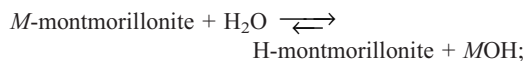


FIG. 4. Zeta potential of montmorillonite as a function of monovalent electrolyte concentration, at 25°C.

more positive with an increase in the concentration of the electrolytes. The zeta potential values of montmorillonite particles become less negative with an increase in concentration from 10^{-4} M to 10^{-1} M, due to the compression of the double layer by the presence of electrolyte (Hunter, 1981). The counterions accumulate in the electrical double layer (EDL) and they render the particle surface less negative. Yet, up to 10^{-4} M, the zeta potential became more negative and reached the zeta potential values which would occur for no electrolyte. Hydrolysis causes the replacement of M^+ by H^+ for concentrations of MCl ($M = Li^+, Na^+, K^+, Rb^+, Cs^+$) of $<10^{-4}$ M. Subsequently, Al^{3+} or Mg^{2+} is released from octahedral sites and the charge of the particle is altered.

This ion-exchange mechanism occurs in two steps: (1) a rapid exchange between hydrogen ions in solution and the exchangeable cation of the clay, according to the schematic equation:



and (2) a slow penetration of the adsorbed H^+ ions into the lattice. This attack by protons gives rise to a decomposition of the clay and a release of Al^{3+} and Mg^{2+} as exchangeable ions. On the other hand, the decomposition process just described occurs at a considerably slower rate at the higher electrolyte concentration. Therefore, it will have little effect on the zeta potential under conditions of high ionic strength (Delgado *et al.*, 1985; Gan & Low, 1993).

Note that, at any MCl concentration, the magnitude of the zeta potential increased with the electrolytes in the order $Li^+ > Na^+ > K^+ > Rb^+ >$

Cs^+ . Equilibrium constants for cation exchange, hydration free energies, hydration ion size and enthalpies of exchange and values of ψ_δ produced by various exchangeable cations show that the strength with which M^+ ions are held to the surface of the montmorillonite is in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (Gan & Low, 1993). Namely, the degree of hydration of these cations affects either their dissociation from the Stern layer or the thickness of this layer. It was concluded that the more strongly hydrated monovalent cations (Li^+ , Na^+) bind more weakly to the clay surface and therefore give rise to greater potentials (Horikawa *et al.*, 1988). In contrast, the less hydrated monovalent cations (Rb^+ , Cs^+) bind more strongly to the clay surface and give rise to relatively small potentials.

Furthermore, the size of the hydrated ion in the Stern layer should influence the thickness of the layer and thus the magnitude of the zeta potential. The Cs^+ ions have small hydrated ionic radii and a small distance of closest approach to the surface relative to other monovalent ions. Thus, Cs^+ ions could enter the Stern layer easily and the zeta potential of the dispersion which includes the $CsCl$ electrolyte was decreased (became less negative) in comparison to other electrolytes.

Figure 5 presents the change of the zeta potential of montmorillonite with monovalent, divalent and trivalent electrolytes, KCl , $CaCl_2$, $AlCl_3$. Like monovalent ions, with increasing di- and trivalent ion concentrations, the magnitude of the zeta potential shifts to less negative values. The addition of divalent electrolyte ($CaCl_2$) reduced the zeta potential of montmorillonite particles to more

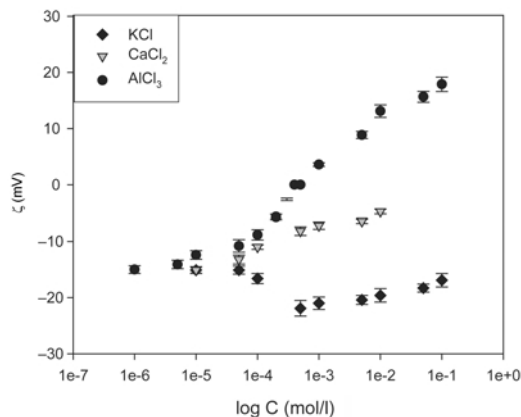


FIG. 5. Zeta potential of montmorillonite as a function of multivalent electrolyte concentration, at 25°C.

positive values in comparison to monovalent electrolyte (KCl) at constant pH (5.3 ± 0.2). In the presence of AlCl_3 as an electrolyte, the zeta potential of montmorillonite reduced steadily, as concentration changed from 1×10^{-6} to 1×10^{-1} M; a sharp increase and a charge reversal occurred at 5×10^{-4} M. This value is important for montmorillonite with regard to its stability properties. At concentrations $> 5 \times 10^{-4}$ M AlCl_3 , the zeta potential values changed sign and became positive. This can be explained on the basis of the specific adsorption of Al^{3+} counterions in the Stern layer, particularly at an AlCl_3 concentration $> 5 \times 10^{-4}$ M (Swartz-Allen & Matijevic, 1975; Pashley & Quirk, 1984).

Since, in the pH range 4.84–2.36 for AlCl_3 in the concentration range 1×10^{-6} – 1×10^{-1} M, Al^{3+} ions are in the non-hydroxyl form, electrolytes containing Al^{3+} undergo solvation, hydrolysis and polymerization reactions when they are dissolved in aqueous media (Pierre & Ma, 1999). They can form hydroxyl complexes such as $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, and $\text{Al}(\text{OH})_3$ at concentrations $< 5 \times 10^{-4}$ M or with increasing pH.

The effect of the valence of the cation can be seen from this figure. It can be observed that, while the valence of the cation was increased, the zeta potential shifted to less negative values. Although all ions tend to reduce the zeta potential, the Al^{3+} ions were the most effective, in accordance with the Schultz and Hardy rule (Van Olphen, 1977). The Al^{3+} ions have small hydrated ionic radii, a small distance of closest approach and large polarizability compared to K^+ and Ca^{2+} . These properties allow

Al^{3+} 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 AlCl_3 electrolyte indicates more positive values.

The considerable effect of these cations was to be expected, but the particular characteristics of the clay surface must be taken into account. It is well known that hydrolysed ions are very efficient at inverting the sign of the particle charge for most hydrophobic colloidal systems, but unhydrolysed ions do not cause this effect, no matter how large their charge may be. Therefore, when explaining the effect of these cations on the clay zeta potential, the 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 (van Olphen, 1977).

The thickness of the diffuse double layer ($1/\kappa$) is also affected by the valency of the exchangeable cations according to equation 4. Generally, it has been reported that at equivalent electrolyte concentrations, monovalent cations in exchange positions yield thicker diffuse double layers than divalent cations. The thickness of the double layer will decrease more strongly with trivalent cations than with divalent ions. This phenomenon is due to the tendency of ions to diffuse away from the colloidal surface in the following decreasing order, e.g. Na and K ions are frequently reported to be responsible for relatively thicker double layers than Ca, whereas double layers formed by Al ions are comparatively the thinnest (van Olphen, 1977).

Electrokinetic charge density

With the purpose of calculating the electrokinetic charge density of the particle, equation 2 (for symmetrical electrolytes) and equation 3 (for asymmetrical electrolytes) were used.

Figure 6 shows the variation of the monovalent electrolyte concentration with the electrokinetic charge density of the montmorillonite particles. The effects of all monovalent cations on the charge density are similar. At all concentrations, the electrokinetic charge density is negative. Up to concentrations of $\sim 10^{-3}$ M of LiCl, NaCl, KCl, RbCl and CsCl, it remains practically constant, while for greater electrolyte concentrations the

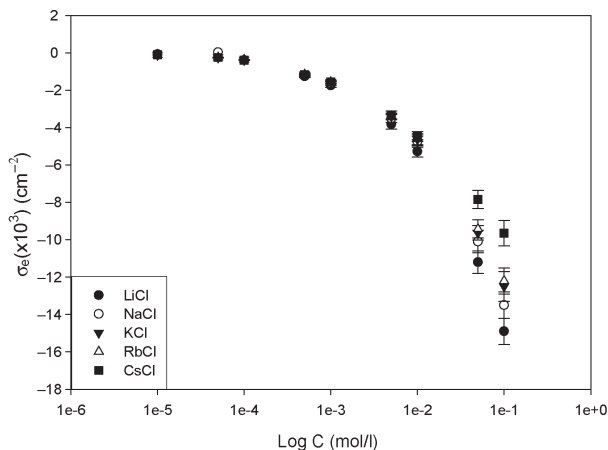


FIG. 6. Electrokinetic charge density of montmorillonite as a function of the monovalent electrolyte concentration, at 25°C.

negative charge tends to shift to more negative values.

The increase in σ_e when the concentration of the monovalent (1:1) electrolyte is increased significantly (Fig. 6) is probably a consequence of an increase in the double layer thickness ($1/\kappa$). Such an increase could be caused by adsorption of anions (Cl^-) on the surface. This adsorption would help to increase the surface charge (and σ_e). On the other hand, it was found 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 was increased, as a consequence of the packing restriction mentioned above for Na^+ ions (Pashley & Quirk, 1984).

When the monovalent ions were compared, the charge density of the particles had the greatest

value in LiCl solution. This could be related to the hydration radius of ions. Li^+ ions could enter into the electrical double layer only to a small extent owing to the large radius of this (hydrated) ion. Therefore the charge density of the particles in LiCl solution was more negative.

The situation is different in the case of CaCl_2 . There is no significant variation in the charge density (0.3×10^{-3} – $2.0 \times 10^{-3} \text{ C m}^{-2}$) when the salt concentration changes as observed for monovalent cations (Fig. 7). The increase in σ_e observed in Fig. 7 is, hence, mainly the consequence of the increase in κ when the concentration of CaCl_2 is increased.

The main change in σ_e occurred with AlCl_3 . Considering the effect of the highly charged cation, Fig. 8 shows an initial trend to remain constant at

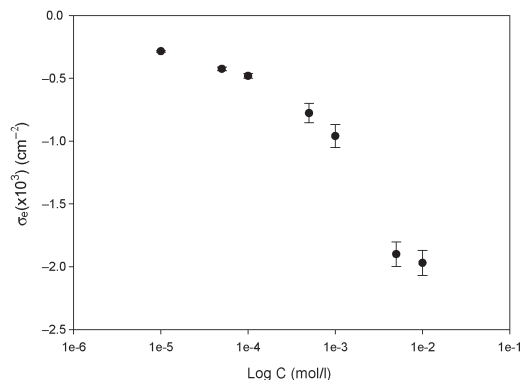


FIG. 7. Electrokinetic charge density of montmorillonite as a function of CaCl_2 concentration, at 25°C.

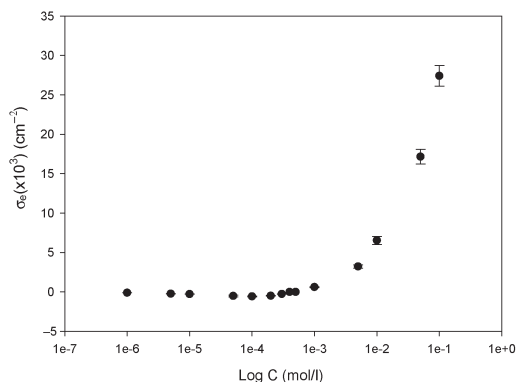


FIG. 8. Electrokinetic charge density of montmorillonite as a function of AlCl_3 concentration, at 25°C.

low concentrations for montmorillonite. Because of the cation's high charge, the electrokinetic charge density is approximately zero at low concentrations. But at concentrations $>5 \times 10^{-4}$ M of AlCl_3 solution, the value of σ_e became less negative and changed sign to positive. The adsorption of the counterions Al^{3+} can be considered to be responsible for these results (Delgado *et al.*, 1985).

CONCLUSIONS

The zeta potential of montmorillonite was independent of pH. It is suggested that edges play a negligible role in determining the electrokinetics of smectites.

The zeta potential of montmorillonite in the presence of monovalent electrolytes such as LiCl, NaCl, KCl, RbCl and CsCl shifted to less negative values (from -24 mV to -12 mV) with increasing concentration from 10^{-4} M to 10^{-1} M, due to the compression of the double layer caused by the presence of the electrolyte. Yet, up to concentrations of 10^{-4} M, the zeta potential became less negative and reached the zeta potential values that would have occurred without electrolyte. The zeta potential of montmorillonite became more positive with increasing di- and tri-valent cation concentration. It reached zero at 5×10^{-4} M AlCl_3 concentration and above this concentration became positive (~ 20 mV).

The electrokinetic charge density of montmorillonite increased (became more negative) with an increase in concentration of monovalent and divalent electrolytes. Monovalent cations exert a greater influence on the σ_e of montmorillonite than divalent cations. The electrokinetic charge density increased for monovalent electrolytes in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. The electrokinetic charge density of montmorillonite remained constant and approximately zero at low concentrations of AlCl_3 electrolyte. At concentrations $>5 \times 10^{-4}$ M AlCl_3 , it became positive.

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REFERENCES

- Alkan M., Demirbaş Ö. & Doğan M. (2005) Electrokinetic properties of sepiolite suspensions in different electrolyte media. *Journal of Colloid and Interface Science*, **281**, 240–248.
- Avena M.J. & De Pauli P. (1998) Proton adsorption and electrokinetics of an Argentinean montmorillonite. *Journal of Colloid and Interface Science*, **202**, 195–204.
- Benna M., Kbir-Arighuib, N., Magnin, A. & Bergaya F. (1999) Effect of pH on rheological properties of purified sodium bentonite suspensions. *Journal of Colloid and Interface Science*, **218**, 442–455.
- Billingham J., Bren C. & Yarwood J. (1997) Adsorption of polyamine, polyacrylic acid and polyethylene glycol on montmorillonite. An in situ study using ATR-FTIR. *Vibrational Spectroscopy*, **14**, 19–34.
- Busenberg E. & Clemency C.V. (1973) Determination of the cation exchange capacity of clays and soils using an ammonia electrode. *Clays and Clay Minerals*, **21**, 213–217.
- Callaghan I.C. & Ottewill R.H. (1974) Interparticle forces in montmorillonite gels. *Faraday Discussions of the Chemical Society*, **57**, 110–118.
- Cohen Stuart M.A. & Mulder J.W. (1985) Adsorbed polymers in aqueous media: the relation between zeta potential, layer thickness and ionic strength. *Colloids and Surfaces*, **15**, 49–55.
- Delgado A., Gonzalez-Caballero F. & Bruque J.M. (1985) On the zeta potential and surface charge density of montmorillonite in aqueous electrolyte solutions. *Journal of Colloid and Interface Science*, **113**, 203–211.
- Doğan M., Alkan M. & Çakır Ü. (1997) Electrokinetic properties of perlite. *Journal of Colloid and Interface Science*, **192**, 114–118.
- Ersoy B. & Çelik M.S. (2002) Electrokinetic properties of clinoptilolite with mono- and multivalent electrolytes. *Microporous Mesoporous Materials*, **55**, 305–312.
- Gan H. & Low P.F. (1993) Spectroscopic study of ionic adjustments in the electric double layer of montmorillonite. *Journal of Colloid and Interface Science*, **161**, 1–5.
- Grim R.E. (1968) *Clay Mineralogy*. McGraw-Hill Inc., USA.
- Heath D. & Tadros Th.F. (1983) Influence of pH, electrolyte, and poly(vinyl alcohol) addition on the rheological characteristics of aqueous dispersions of sodium montmorillonite. *Journal of Colloid and Interface Science*, **93**, 307–315.
- Horikawa Y., Murray R.S. & Quirk J.P. (1988) The effect of electrolyte concentration on the zeta potentials of homoionic montmorillonite and illite. *Colloids and Surfaces*, **32**, 181–195.
- Hunter R.J. (1981) *Zeta Potential in Colloid Science*. Academic Press, London.
- Israel L., Güler Ç., Yılmaz H. & Güler S. (2001) The adsorption of polyvinylpyrrolidone on kaolinite saturated with sodium chloride. *Journal of Colloid and Interface Science*, **238**, 80–84.

- Kadkhodayan A. & Pinnavaia T.J. (1993) Clay inter-salation compounds for selective triphase catalysis: Reaction of alkyl bromides with NaCl. *Journal of Molecular Catalysis*, **21**, 109–117.
- Ma K.S. & Pierre A.C. (1999) Clay sediment-structure formation in aqueous kaolinite suspensions. *Clays and Clay Minerals*, **47**, 522–526.
- Miller S.E. & Low P.F. (1990) Characterization of the electric double layer of montmorillonite. *Langmuir*, **6**, 572–578.
- Pashley R.M. & Quirk J.P. (1984) The effect of cation valency on DLVO and hydration forces between macroscopic sheets of muscovite mica in relation to clay swelling. *Colloids and Surfaces*, **9**, 1–17.
- Penner D. & Lagaly G. (2000) Influence of organic and inorganic salts on the coagulation of montmorillonite dispersions. *Clays and Clay Minerals*, **48**, 246–255.
- Pierre A.C. & Ma K. (1999) DLVO theory and clay aggregate architectures formed with AlCl₃. *Journal of the European Ceramic Society*, **19**, 1615–1622.
- Rossi S., Luckham P.F. & Tadros Th.F. (2002) Influence of non-ionic polymers on the rheological behaviour of Na⁺-montmorillonite clay suspensions – I. Nonylphenol-polypropylene oxide-polyethylene oxide copolymers. *Colloids and Surfaces*, **201**, 85–100.
- Sequaris J.M., Baßmann F., Hild A., Narres H.D. & Schuwuger M.S. (1999) Characterization of polyvinylpyrrolidone adsorption at inorganic soil components by a microelectrophoretic method. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **159**, 503–512.
- Sjöberg M., Bergstöm L., Larsson A. & Sjöström E. (1999) The effect of polymer and surfactant adsorption on the colloidal stability and rheology of kaolin dispersions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **159**, 197–208.
- Somasundaran P. & Fuerstenau D.W. (1966) Mechanisms of alkyl sulfonate adsorption at the alumina-water interface. *Journal of Physics and Chemistry*, **70**, 90–96.
- Sondi L., Milat O. & Pravdic V. (1997) Electrokinetic potential of clay surfaces modified by polymers. *Journal of Colloid and Interface Science*, **189**, 66–73.
- Srivastava R.C. & Avasthi P.K. (1973) Electro-osmotic effects in a bentonite-water system. *Journal of Hydrology*, **20**, 37–47.
- Swartzen-Allen S.L. & Matijevic E. (1975) Colloid and surface properties of clay suspensions: II. Electrophoresis and cation adsorption of montmorillonite. *Journal of Colloid and Interface Science*, **50**, 143–153.
- Swartzen-Allen S.L. & Matijevic E. (1976) Colloid and surface properties of clay suspensions. III. Stability of montmorillonite and kaolinite. *Journal of Colloid and Interface Science*, **56**, 159–167.
- Tan K.H. (1998) *Principles of Soil Chemistry*. Marcel Dekker, New York.
- Tsuchida H., Ooi S., Nakaishi K. & Adachi Y. (2005) Effects of pH and ionic strength on electrokinetic properties of imogolite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **265**, 131–134.
- Van Olphen H. (1977) *An Introduction to Clay Colloid Chemistry*. Wiley, New York, chapter 7.
- Vane L.M. & Zang G.M. (1997) Effect of aqueous phase properties on clay particle zeta potential and electro-osmotic permeability: Implications for electrokinetic soil remediation processes. *Journal of Hazardous Materials*, **55**, 1–22.
- Williams D.J.A. & Williams K.P. (1978) Electrophoresis and zeta potential of kaolinite. *Journal of Colloid and Interface Science*, **65**, 79–87.
- Xavier S.F. & Sharma Y.N. (1986) Structure-property relations in polypropylene mica composites. *Polymer Composites*, **7**, 42–49.

