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Effect of anions on dispersion of a kaolinitic soil clay: A combined study of dynamic light scattering and test tube experiments



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ABSTRACT

Dispersion is an important issue for clay leaching in soils. In this study, effects of various anions (Cl^- , SO_4^{2-} , acetate, oxalate and citrate) on dispersion of a kaolinitic soil clay were determined at different pH values and ionic strengths by dynamic light scattering and test tube experiments. Adsorption of anions on clay samples was characterized by the zeta potential (ζ) in a pH range of 2 to 11. At a pH range between 2 and 6, the effects of different anions on decreasing ζ were obvious and followed the order oxalate > citrate > SO_4^{2-} > Cl^- > acetate, while fluctuated changes in ζ were observed at pH > 6. Based on a comparison of hydrodynamic radii (r_h) obtained from dynamic light scattering and of transmission of 50% (T_{50} values) from the test tube experiments, the ability of anions to facilitate the dispersion of the clay fraction followed the sequence of oxalate > citrate > acetate > SO_4^{2-} > Cl^- . It implies that adsorption of anions on positively charged edge sites of kaolinite resulting in a decrease in ζ is a key factor for dispersion of the clay fraction. Also, the results suggested that the dynamic light scattering can be used in combination with the test tube experiments in order to evaluate the effect of anions on dispersion at broader ranges of pH, ionic strength and clay concentration.

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1. Introduction

Clay loss is common in bare soils subjected to rainfall or sprinkler irrigation. In a dispersed state, clays can be easily transported by the surface runoff. Frenkel et al. (1992) reported that anions interact with 1:1 clay minerals, e.g., kaolinite, and facilitate dispersion. We can infer that the presence of dissolved anions might be an important factor for clay loss in tropical soils, where kaolinite is the most dominant clay mineral. In recent years, dispersion properties of the pure clay minerals under the influence of anions have received much attention (Kretzschmar et al., 1998; Obut, 2005; Xu et al., 2004). However, the effect of anions on making surface charge more negative and dispersion properties of such kaolinite-rich soil clays has been neglected.

Organic anions originate from the exudation of plant roots and microorganisms, and the decomposition of soil organic matter is ubiquitous in soils, especially in the rhizosphere (Strobel, 2001). Inorganic anions such as sulfate and chloride may enter into soils through the degradation of soil organic matter and the application of mineral

fertilizers. At acidic conditions, positively-charged edge sites of the clay minerals might favor the formation of edge-to-face structures, the so-called “card house” (van Olphen, 1977), which facilitates coagulation. Adsorption of inorganic anions (SO_4^{2-} and Cl^-) onto these positively-charged edge sites may counteract clay coagulation (Nguyen et al., 2009). Similarly, low-molecular-weight organic anions such as acetate, oxalate and citrate can also associate with positively-charged edge sites and result in a decrease of the zeta potential (ζ) of the clay particle (Xu et al., 2004). However, effects of these organic anions on dispersion properties have not been studied systematically.

Test tube experiments, introduced by Lagaly et al. (1997), have been utilized to study colloidal properties of clay minerals (Nguyen et al., 2009; Schmidt and Lagaly, 1999) but this technique requires a highly concentrated suspension of clay. In contrast, dynamic light scattering is known as a suitable technique for investigating clay coagulation at lower clay concentrations (Kretzschmar et al., 1998; Mori et al., 2001). Few comparable investigations on the dispersion of clay particles using both of these methods, however, have been reported. In the present work, a combination of dynamic light scattering and test tube experiments has been employed to investigate the dispersion state of the clay fraction under the influences of anions (Cl^- , SO_4^{2-} , acetate, oxalate and citrate) as a function of both pH and ionic strength. ζ was also investigated to provide more information on the adsorption of anions on clay minerals.

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2. Materials and methods

2.1. Soil and clay

The soil used in this study was selected from a soil series collected from a hilly area of northern Hanoi, Vietnam. It was taken from the surface horizon (0–25 cm depth) of a Ferralic Acrisols on the down slope of a hill (105°48'48" E; 21°16'17" N). The sample was air-dried and passed through a 2-mm sieve. The pH was determined using 0.2 M KCl (w/v = 1:2.5). Cation-exchange-capacity (CEC) was determined as the sum of Ca, Mg, K, Na and Al extractable in 0.1 M BaCl₂ (w/v = 1:20). Particle-size distribution was determined by the pipette method. Organic-C was quantified by an Elementar Vario EL elemental analyzer (Hanau, Germany). The sandy clay loam soil (sand: 56%, silt: 15%, clay: 29%) was acidic (pH 3.9) with a cation-exchange-capacity (CEC) of 109 mmol_c kg⁻¹. The organic-C content was 3.0%, which is typical for a Ferralic Acrisols in Northern Vietnam. XRD analysis of the clay fraction by a PHILIPS X-ray diffractometer PW2404 with oriented samples on glass slides has shown that the clay mineralogy of the soil was dominated by kaolinite, but the <2 μm fraction also contains minor amounts of chlorite and vermiculite.

Fine soil was dispersed by shaking overnight in de-ionized water. The clay fraction (<2 μm) was separated by sedimentation and decantation. The suspension was flocculated with NaCl, centrifuged, washed until salt-free, and freeze-dried. The obtained clay sample was used for dynamic light scattering and test tube experiments.

2.2. Dynamic light scattering

Time-resolved dynamic light scattering, where the hydrodynamic radius of particles in suspension is quantified, has been applied to monodisperse model colloids such as latex microspheres (Holthoff et al., 1996) and clay colloids (Mori et al., 2001). However, very few dynamic light scattering studies have been published to date on clay mineral suspensions. In this study, the procedure introduced by Kretzschmar et al. (1998) was used to examine the effect of anions on clay coagulation.

Solutions for the evaluation of anion effects were prepared from pure analyzed sodium salts from Merck KgaA including NaCl, Na₂SO₄, CH₃COONa, Na₂C₂O₄ and C₆H₅Na₃O₇ at concentrations of 0.01 and 0.05 mol_c L⁻¹. Acid solutions with concentrations of 0.01 and 0.05 mol_c L⁻¹ including HCl, H₂SO₄, CH₃COOH, H₂C₂O₄ and C₆H₈O₇ were correspondingly used to adjust the pH to 3.5. Effects of pH and ionic strength on coagulation of the clay fraction were studied by conducting pH-dependent experiments in 0.01 and 0.05 mol_c L⁻¹ NaCl electrolyte solutions, and pH values were adjusted by appropriate additions of HCl or NaOH to targeted values.

Each 25 mg of the clay fraction was added to 100 mL of the prepared aqueous solutions. The suspensions were treated for 30 s with an ultrasonic tip to maximize particle dispersion. A subsample (3 mL) was then quickly transferred with a pipette into a cylindrical glass cuvette, and the average hydrodynamic particle radius (r_h) was monitored every 6 min for 2 h. Dynamic light scattering experiments were conducted using a Brookhaven-ZetaPALS Analyzer at a 90° scattering angle.

2.3. Test tube experiments

Coagulation of the clay fraction in the presence of anions as a function of pH was determined in test tubes following the procedure of Lagaly et al. (1997). Solutions of NaCl, Na₂SO₄, CH₃COONa, Na₂C₂O₄ and C₆H₅Na₃O₇ with concentrations of 0.01 and 0.05 mol_c L⁻¹ were prepared from pure analyzed salts from Merck KgaA, and adjusted to pH values between 2 and 9 by corresponding additions of 0.01 and 0.05 mol_c L⁻¹ HCl, H₂SO₄, CH₃COOH, H₂C₂O₄ and C₆H₈O₇, respectively. For determination of clay coagulation as a function of anion

concentration, solutions were prepared using concentrations determined in preliminary experiments: 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045 and 0.05 mol_c L⁻¹ for Cl⁻, SO₄²⁻ and acetate, and 0.001, 0.002, 0.003, 0.004 and 0.005 mol_c L⁻¹ for oxalate and citrate. Lower concentrations of oxalate and citrate were used because these anions can accelerate dispersion of the clay fraction more strongly in comparison with acetate, SO₄²⁻ and Cl⁻. Required amounts of NaNO₃ solution were added to maintain ionic strength at 0.05 mol_c L⁻¹.

Suspensions, prepared by mixing each 20 mg of the clay fraction and 10 mL of the prepared solutions, were transferred to test tubes and dispersed in an ultrasonic bath (Sonorex, RK 106) for 15 s. After 2 h of sedimentation at room temperature, 2 mL of each suspension was sampled from the surface of the suspension and the transmission (T) was determined using a UV-VIS photometer (Varian, Cary-50 Scan) at a wavelength of 600 nm. A transmission of 50% (T₅₀ value) was used to compare the effectiveness of different anions on dispersion.

2.4. Examination of the electrophoretic mobility

It is well-known that the ζ is an important parameter for characterizing clay dispersion. In this study, ζ was determined for the clay suspension in the presence of anions as a function of pH and ionic strength. Aqueous solutions containing different anions were prepared as described in Section 2.3 at concentrations of 0.01 and 0.05 mol_c L⁻¹ and the pH of the solutions was adjusted to values between 2 and 11 by the addition of corresponding acids. Each 1.4 mL of suspension obtained by adding 5 mg of the clay fraction into 20 mL prepared solution was used to determine ζ using a Brookhaven-ZetaPALS Analyzer (Brookhaven, Holtsville, New York, USA).

3. Results

3.1. Evaluation of dynamic light scattering

Coagulation of the clay fraction in the presence of different anions at pH 3.5 is shown in Fig. 1a, b. At the electrolyte background (EB) of 0.01 mol_c L⁻¹, r_h was maintained around 200 nm in the presence of oxalate, which confirms a dispersed state of the clay fraction. The presence of Cl⁻, SO₄²⁻, acetate and citrate, however, facilitated coagulation and r_h values increased within 2 h from 212 to 633, 207 to 609, 204 to 538 and 215 to 378 nm, respectively. At the EB of 0.05 mol_c L⁻¹, organic anions showed a relatively similar effect that dispersion was favored, and the r_h values were maintained at 200 and 230 nm. On the other hand, coagulation of the clay fraction was still observed in the presence of Cl⁻ or SO₄²⁻ where the r_h values increased from 225 to 502 nm and 222 to 447 nm, respectively. Preliminary determinations of the dynamic light scattering conducted at pH < 3 and pH > 4 did not show different effects in r_h values among anions. At pH < 3, increases in r_h with time were found in all suspensions, while almost no change in r_h values was observed at pH > 4 (data not shown).

3.2. Coagulation of the clay fraction in the test tube experiments

Fig. 2 shows the influence of different anions on the coagulation of clay as a function of pH. At the EB of 0.01 mol_c L⁻¹, oxalate and citrate were found to be most effective on dispersion, and the transmission values of the suspension were maintained at approximately 1% over the entire pH range of 2 to 9. Other anions including acetate, SO₄²⁻ and Cl⁻ produced a lower effect on clay dispersion. T values of ~80% indicating coagulation of the clay fraction were found at pH < 3.5. The dependence of clay coagulation on pH based on T₅₀ values was in the order (pH): acetate (3.7) < SO₄²⁻ (3.9) < Cl⁻ (4.2). At the EB of 0.05 mol_c L⁻¹, oxalate was the only anion which facilitated dispersion with a T value of ca. 1%. In the presence of citrate, acetate, SO₄²⁻ and Cl⁻, the T values of ~80% can be observed between pH 2.5 and

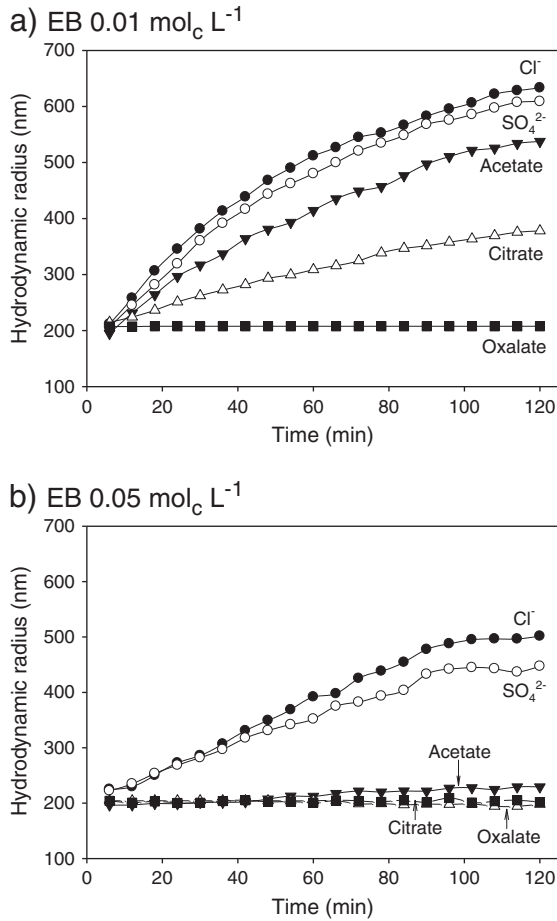


Fig. 1. Effect of different anions on hydrodynamic radius (r_h) of the clay fraction as a function of time at pH 3.5 and the electrolyte backgrounds of 0.01 mol_c L⁻¹ (a) and 0.05 mol_c L⁻¹ (b).

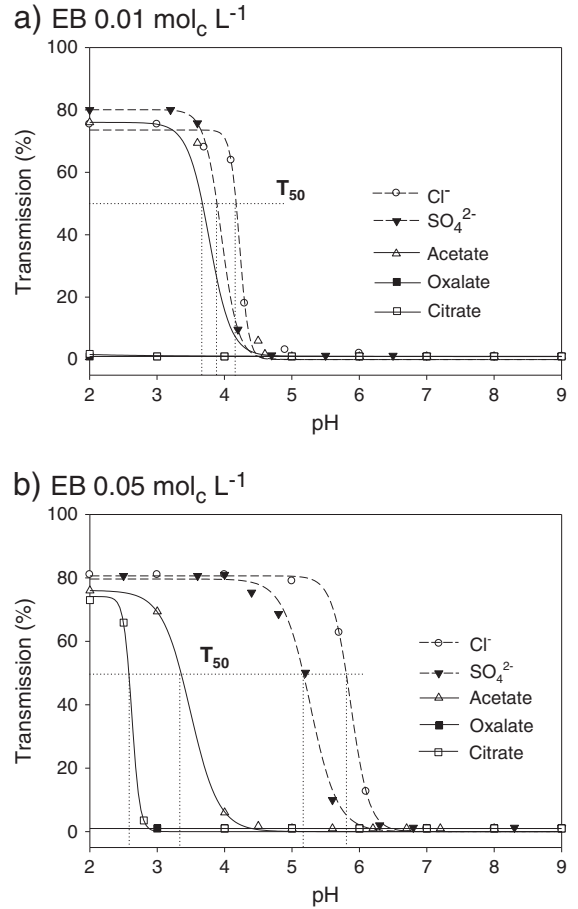


Fig. 2. Coagulation of the clay fraction in dependence on the kind of anions.

6.5, and the T₅₀ values increased in the order (pH): citrate (2.6) < acetate (3.3) < SO₄²⁻ (5.2) < Cl⁻ (5.8).

At the EB of 0.05 mol_c L⁻¹ (NaNO₃), the T value was ca. 84%, which represented coagulation of the clay fraction (Fig. 3). Replacement of NO₃⁻ by Cl⁻ as the electrolyte produced no change in the T value, while replacement by other anions including oxalate, citrate, acetate, and SO₄²⁻ resulted in decreased T values. This suggested that all these replacement anions are more effective in facilitating clay dispersion as compared to NO₃⁻ and Cl⁻. An increase in concentration of SO₄²⁻ from 0 to 0.05 mol_c L⁻¹ resulted in a decrease of T values from 84% to 73%. Complete dispersion of the clay was observed in the presence of oxalate, citrate and acetate at concentrations of 0.003, 0.005 and 0.05 mol_c L⁻¹, respectively.

3.3. Effects of pH, ionic strength and anions on zeta potential

As shown in Fig. 4, a decrease of ζ with an increase of the pH of the clay suspension was a general trend. Even at pH 2, a negative ζ of the clay fraction was observed. Major decreases in ζ occurred between pH 2 and 6, whereas no obvious changes in ζ were observed at pH > 6. At the EB of 0.01 mol_c L⁻¹, with an increase of the pH value from 2 to 6, ζ values were decreased from -3 to -35, -6 to -39, -7 to -40, -21 to -49 and -39 to -49 mV for the suspensions containing acetate, Cl⁻, SO₄²⁻, citrate and oxalate, respectively. At the EB of 0.05 mol_c L⁻¹, a similar trend was obtained. When pH changed from 2 to 6, ζ of the suspensions containing acetate, Cl⁻, SO₄²⁻, citrate and oxalate decreased from +1 to -36, -0.5 to -35, -19 to -37, -25 to -56 and -33 to -46 mV, respectively. At

pH 4, which is close to the actual pH value of the studied soil, the effect of anions on ζ at both EB of 0.01 and 0.05 mol_c L⁻¹ decreases in the order: oxalate > citrate > SO₄²⁻ > Cl⁻ > acetate.

4. Discussion

Clay colloidal properties can be affected by the presence of anions which serve as negatively charged electrolytes. Anions can adsorb to the clay surface by a variety of mechanisms including electrostatic attractive forces, specific adsorption via ligand exchange with protonated surface hydroxyl groups, cation bridging and water bridging in

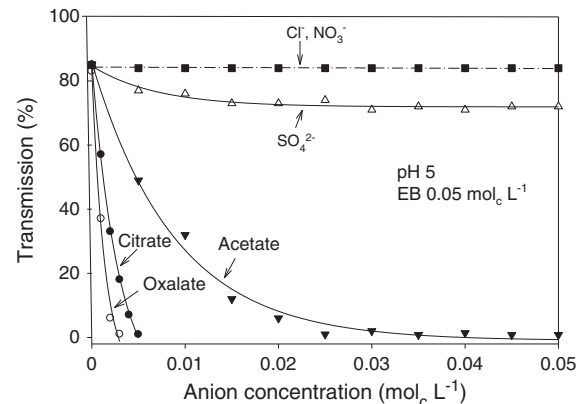


Fig. 3. Coagulation of the clay fraction in dependence on anion concentration.

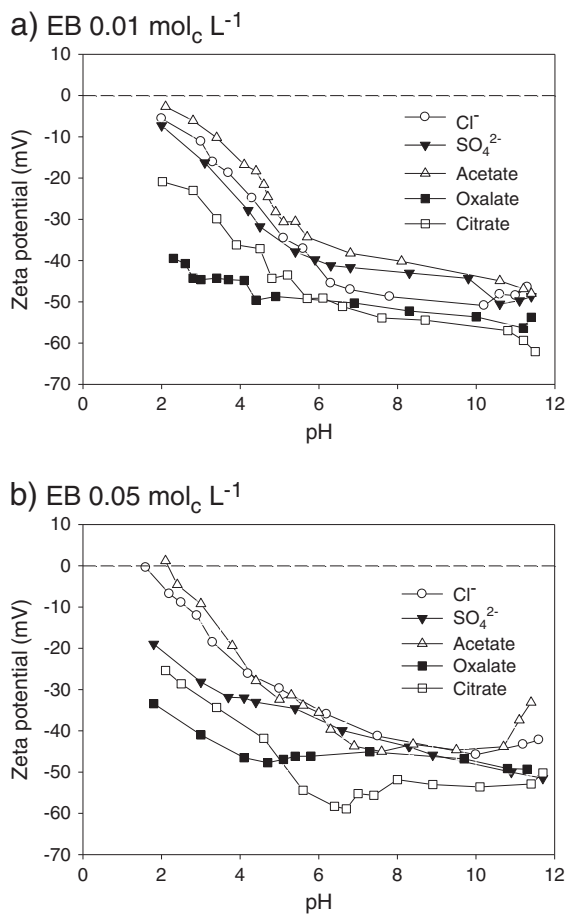


Fig. 4. Zeta potential of the clay fraction at the electrolyte backgrounds of $0.01 \text{ mol}_c \text{ L}^{-1}$ (a) and $0.05 \text{ mol}_c \text{ L}^{-1}$ (b) as a function of pH.

the presence of hydrated cations on the surface (Murphy and Zachara, 1995). Generally, adsorption of anions results in a more negative surface charge and enhances the repulsive force between clay particles and favors dispersion state of clay in suspension (Chorom and Rengasamy, 1995). In the dynamic light scattering experiments, coagulation of the clay fraction in the presence of almost all anions (except oxalate) was observed. This might be due to the effect of high ionic strength where Na^+ can serve as positive charges that favor coagulation of the clay. However, anions can act to mitigate the effect of Na^+ on coagulation. Results from the test tube experiments (as shown in Fig. 3) revealed that an increase of anion concentration can prohibit coagulation. In both dynamic light scattering and test tube experiments, oxalate was found to be the most effective anion in counteracting coagulation, whereas Cl^- shows the weakest effect. The anion effect in accelerating dispersion is in the order: oxalate > citrate > acetate > SO_4^{2-} > Cl^- .

For organic anions, acetate was less effective on ζ in comparison with oxalate and citrate because it associates with positively charged edges of clays as a monodentate complex. Consistent with Xu et al. (2004), we found that the presence of oxalate led to a lower ζ as compared to citrate. This phenomenon is explained by the fact that the large citrate anions may lead to a thicker electrical double layer, i.e., higher ζ values. Here, the role of the valence effect is in determining the distance between the slip plane and clay surface, which is the decisive factor in ζ (Xu et al., 2004). However, the exact mechanism is still subject to speculation. For inorganic anions, the dispersion of the clay fraction is facilitated by SO_4^{2-} more than by Cl^- (Fig. 3). This might be due to the lower affinity of Cl^- for the positively charged sites. Obviously, SO_4^{2-} can neutralize positive charges

more effectively, which consequently counteracts coagulation (Fig. 4). The strength of multivalent anions on dispersion was also confirmed by Penner and Lagaly (2001) where the addition of SO_4^{2-} and PO_4^{3-} severely increased the critical coagulation concentration of clay suspensions. These multivalent anions are known to form inner-sphere complexes on surfaces, which decreases the surface charge of the clay fraction and, as a consequence, facilitates dispersion (Xu et al., 2004).

Both dynamic light scattering and test tube experiments provided helpful evidence for distinguishing the effect of anions on dispersion properties. The increase of the hydrodynamic radii of clay fractions as a result of coagulation can be identified by dynamic light scattering, while the settling of the clay fraction due to the coagulation is clearly observed in the test tube experiments. The pH, ionic strength and clay concentration are the most important factors that influence the effectiveness of each method. For a concentrated clay suspension in the test tube experiments, the different effects (based on T_{50}) among anions at the EB of $0.05 \text{ mol}_c \text{ L}^{-1}$ were obvious and coagulation occurred over a wider pH range (2.5–6.5) (Fig. 2b). However, at the lower EB ($0.01 \text{ mol}_c \text{ L}^{-1}$), the coagulation curves were closer together, which did not provide convincing evidence for distinguishing anion effects (Fig. 2a). In contrast, the dynamic light scattering study for a system with low clay concentrations provided a better data set of the anion effect at the low EB. The effects of anions on coagulation can be clearly seen (Fig. 1a). This suggests that a combination of dynamic light scattering and test tube experiments can be a new approach that provides better evidence in measuring anion effects on dispersion properties of clays at a broader range of pH, ionic strengths and clay concentrations.

5. Conclusions

The physicochemical mechanisms of clay dispersion which is the major prerequisite for clay transport were reevaluated in this study for a slope soil in Northern Vietnam. The pH, and, to a lesser extent, the presence of certain anions, affect clay dispersion primarily by changing the negative surface charge of the clay fraction. The effect of anions in counteracting coagulation decreases in the order: oxalate > citrate > acetate > SO_4^{2-} > Cl^- . This implies that the facilitation of clay transport resulting from organic anions should be taken into account in management of kaolinite-rich soils. The data obtained in this work suggest that a system including dynamic light scattering and test tube experiments might provide better evidence for specifying the effect of various anions on dispersion properties of clays.

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