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Specific ion effects: The role of anions in the aggregation of permanently charged clay mineral particles

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Abstract

Purpose Understanding how anions affect the colloidal behavior of clay mineral is greatly important in determining soil particle dispersibility. The surface of soil particles, especially for silicate clay mineral components, is often net negatively charged. However, how anions influence soil particle interactions and affect soil structure has not been fully studied. This study investigated how specific anions (SO_4^{2-}, Cl^-, and phosphate) affect the aggregation of permanently charged montmorillonite particles.

Methods The effects of anions on colloidal montmorillonite particle aggregation were investigated at different ionic strengths using dynamic light scattering. Anion adsorption on montmorillonite particles in equilibrated solutions was measured by ion chromatography.

Results Anions were adsorbed onto a permanently charged clay mineral surface, which induced strong specific effects in inhibiting montmorillonite particle aggregation. Phosphate had the greatest inhibiting effect on coagulation, followed by Cl^- and SO_4^{2-}. The critical coagulation ionic strength (CCIS) for K_2SO_4, KCl, and KH_2PO_4 was 9.915, 11.38, and 180.7 mmol/L, respectively. The activation energy between particles in the different anion solutions quantitatively characterized this specific anion effect. The difference in the various anion solutions increased with decreasing ionic strength (i.e., increasing electric field). Second, the amount of phosphate adsorbed by montmorillonite was the greatest among the three anions, followed by Cl^- and SO_4^{2-}, under the given solution conditions, consistent with the observed specific anion effects.

Conclusions Phosphate, Cl^-, and SO_4^{2-} adsorbed onto the surface of permanently charged mineral particles and increased the negative surface charge through non-classic polarization. The strength of the electric field strongly influenced this polarization. The combined roles of cations and anions regulate aggregation, whereas CCIS is determined by specific ion adsorption. Our findings emphasize the importance of specific anion adsorption and double-layer interfacial effects on the aggregation of permanently charged clay mineral colloids. Our findings have important implications for interpreting the behavior of clay minerals in the environment.

Keywords Anion · Montmorillonite · Dispersion and aggregation · Polarization · Electric field

1 Introduction

Soil solutions contain anions and cations. Anion effects on the surface of negatively charged particles are generally assumed to be especially small or negligible. With the recent discovery of specific ion effects in colloidal systems, it is necessary to determine whether anions can significantly influence negatively charged soil particle interactions. Previous experiments have found that many biophysical and chemical systems, such as DNA nuclease activity and protein surface charge, depend strongly on the supposedly irrelevant influence of anions (Gokarn et al. 2011; Kim et al. 2001). Thus, predicting whether strong anion adsorption and specific ion effects will occur near negatively charged interfaces is now possible.

Systematic studies on colloidal particle aggregation-dispersion have demonstrated that particle aggregation is

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affected by ionic valence and species. Ionic species are known to have specific ion effects (Oncsik et al. 2015; Pavlovic et al. 2016; Peula-García et al. 2010; Takeshita et al. 2019). Specific ion effects have been found in a wide range of phenomena in air–water (Boström et al. 2001a; Jungwirth and Tobias 2001, 2006; Padmanabhan et al. 2007) and solid–liquid interfaces (López-León et al. 2008), inorganic and organic systems (Nucci and Vanderkooi 2008), and biological systems (Moreira et al. 2006). These ion effects impact physical, chemical, and biological processes (Kunz et al. 2004; Ninham 2002; Tobias and Hemminger 2008). Studies on the origin of specific ion effects have mainly focused on ionic volume effects (Parsons et al. 2011), polarization, induction forces (Parsons et al. 2011), ionic hydration (Nucci and Vanderkooi 2008; Tielrooij et al. 2010; Wang et al. 2021), hydrophobic and hydrophilic forces (Katana et al. 2020; Peula-García et al. 2010), and ionic dispersion forces (Boström et al. 2001b; Ninham et al. 2011). Hydration radius and dispersion forces become important only at high electrolyte concentrations (Borukhov et al. 1997; Boström et al. 2001b; Moreira et al. 2006; Parsons et al. 2011). Therefore, with decreasing electrolyte concentration, specific ion effects should decrease. At considerably low electrolyte concentrations, specific ion effects should disappear. However, Liu et al. (2012) and Kim et al. (2001) found that specific ion effects sharply increase with decreasing electrolyte concentration. Some studies claim that quantum fluctuations of ionic outer-shell electrons are the main reason for specific ion effects. Hydration forces also depend on quantum fluctuations (Parsons et al. 2011). Additionally, coupling effects between the quantum fluctuations of the ionic outer-shell electrons and the surface electric field increase specific ion effects (Liu et al. 2013).

The effects of anions on negatively charged mineral surfaces have not been extensively studied. However, many biological and chemical systems depend strongly on anions, such as cleavage of DNA by enzymes (Kim et al. 2001; Weissenborn and Pugh 1995, 1996) and determination of protein surface charge (Gokarn et al. 2011). Surface tension also depends on both cations and anions in solutions (Weissenborn and Pugh 1995, 1996). Studies have shown that anions are ubiquitous. However, their effects on several macroscopic phenomena have not received much attention, particularly in net negatively charged surface systems (Gao et al. 2019; Tian et al. 2014). In general, if only static electricity is considered, anions will be repelled by negatively charged surfaces via electrostatic repulsion. However, anions can adsorb to charged surfaces through complex interactions, resulting in a greater negative surface charge and thereby increasing the repulsive force between colloid particles, favoring the dispersed state of clay minerals in suspension (Hou et al. 2010; Ling et al. 2021). Anions can adsorb onto clay mineral surfaces through various mechanisms, including electrostatic attractive forces (Schwierz et al. 2013), specific adsorption (Al-Sagheer and Hey 2004; Nguyen et al. 2013), and cation and water bridging in the presence of hydrated surface cations (Murphy and Zachara 1995; Yang and Zhao 2011).

For the permanently charged mineral montmorillonite, hydrogen and chemical bonds on the basal surfaces can be completely disregarded due to the tetrahedral sheets because the molecular structure is symmetric and the surface atoms of the clay mineral (except for atoms at the edges of clay mineral plates) are saturated with chemical bonds (Haldar and Tišljar 2014; Newton et al. 2016). Additionally, because of the symmetrical structure of Si–O tetrahedra in montmorillonite and the asymmetry of water molecules, it is easier to form hydrogen bonds between two water molecules than between the oxygen atom of a Si–O tetrahedron and the hydrogen atom of a water molecule. Therefore, it is difficult to form chemical and hydrogen bonds on the montmorillonite basal surface. For montmorillonite colloids containing particles from 1–1000 nm, numerous negative charges on the surface can form a strong negative electric field near the surface. For example, Li et al. (2011) found that the field strength near the surface is as high as 10^8–10^9 V/m for colloidal montmorillonite particles. This strong electric field makes it difficult for anions to approach the montmorillonite surface via intermolecular attraction. Anions have a much larger radius than cations, resulting in much stronger quantum fluctuation effects in their electron clouds. Once anions cross the electrical double layer and reach the particle surface using thermal motion, the anions can be adsorbed on the surface owing to the strong dispersion forces between the anions and the montmorillonite surface. Therefore, if anions with high kinetic energy cross the electrostatic repulsion barrier near the interface and reach the montmorillonite particle surface, they may adsorb onto the montmorillonite surface. This adsorption would change the electrostatic interactions between montmorillonite particles, thereby altering montmorillonite particle aggregation.

Previous studies have reported that specific anion effects in the aggregation of particles with variable and permanent surface charges are influenced by the interaction energies between anions and cations and the proton affinities of the anions (Tian et al. 2014). To further investigate the effects of anion adsorption on permanently charged clay mineral particle interactions, montmorillonite was selected as the research object and K_2SO_4, KCl, and KH_2PO_4 were used as electrolytes. Dynamic light scattering (DLS) and ion chromatography were used to investigate the aggregation kinetics of montmorillonite particles and to quantify anion adsorption onto the clay mineral. The findings of this study will provide insights into how fertilizer anions affect soil structure.

2 Materials and methods

2.1 Materials

The montmorillonite powder used in this study was purchased from Wu Hua Tian Bao Mineral Resources Co. Ltd. (Chifeng, China). Colloidal K^+-montmorillonite was separated by sedimentation and decantation (Xiong et al. 1985). The pH of the treated suspension was adjusted to 7.5 ± 0.1 using 0.5 mol/L KOH. After 15 min of intensive sonication (SCIENTZ-IID; Ningbo Scientz Biotechnology Co., Ltd, Ningbo, China; 350 W output, equipped with a 10-mm-diameter titanium probe) at a frequency of 20 kHz, the suspension was diluted to 5 L with ultrapure water and was stirred. The suspension was left undisturbed for approximately 30 days (25 °C). Afterward, the upper 10-cm colloidal suspension layer (particle size < 200 nm) was collected (Xiong et al. 1985). DLS determined the effective hydrodynamic diameters of the collected colloids as 97.4 ~ 458 nm, with an average of 211 nm. Simultaneously, the particle concentration in the sample suspension was estimated to be approximately 2.48 g/L. The K^+ concentration in the bulk suspension was measured using a flame photometer (6400A; Huayun, Cangzhou, Hebei, China). The K^+ level was less than 0.01 mmol/L and was therefore ignored. The cation exchange capacity and specific surface area (S) were determined to be 84.8 $\mathrm{cmol}_{(+)}$/kg and 716 m^2/g, respectively, using the method of Li et al. (2011). The surface charge density (σ) was estimated to be 0.114 C/m^2.

2.2 Monitoring aggregation kinetics

A BI-200SM multi-angle laser light-scattering goniometer with a BI-9000AT autocorrelator (Brookhaven Company, New York, NY, USA) was used for DLS measurements. These experiments were performed as a function of ionic strength at a near-neutral pH, where the net charge of montmorillonite is negative. Potassium salts with various anions (K_2SO_4, KCl, and KH_2PO_4) were used as electrolytes. To determine montmorillonite particle aggregation as a function of ionic strength, solutions were prepared using ionic strength determined in the preliminary experiments: 4.5, 6, 7.5, 9, 10.5, and 12 mmol/L for K_2SO_4; 5, 7.5, 9, 10, 12, and 13 mmol/L for KCl; and 7.5, 9, 12, 300, 600, 900, 1200, 1500, and 1650 mmol/L for KH_2PO_4. Lower ionic strength K_2SO_4 and KCl were used because the preliminary experiments showed that the coagulation abilities of K_2SO_4 and KCl were stronger than those of KH_2PO_4. All solutions were passed through a 0.2-µm syringe filter. All measurements were performed at 25 °C.

In the aggregation experiment, 200 µL montmorillonite suspension was added to the scattering bottle. Appropriate amounts of the electrolyte solution (K_2SO_4, KCl, or KH_2PO_4) and ultrapure water were added to the bottle to obtain the required ionic strength and a total volume of 10 mL. The montmorillonite concentration was maintained at 0.0496 g/L. The average hydrodynamic particle diameter was monitored every 30 s for 30 min for each ionic strength. All light-scattering measurements were conducted with the detector positioned at an angle of 90° from the incident laser beam.

The total average aggregation (TAA) rate $\widetilde{v}_T(t, c_0)$ at electrolyte concentration c_0 is given by

$$\widetilde{v}_T(t, c_0) = \frac{1}{t}\int_0^t v(t, c_0)dt \tag{1}$$

where $\widetilde{v}_T(t, c_0)$ (nm/min) represents the growth rate from $t = 0$ to an arbitrary time t ($t > 0$) and $v(t, c_0)$ (nm/min) is the growth rate of the effective diameter for the aggregates in the DLS measurements (Jia et al. 2013).

2.3 Measuring anion adsorption

An appropriate concentration of electrolyte solution was added to the montmorillonite suspension. The Cl^-, SO_4^{2-}, and phosphate concentrations in the supernatant were determined using a DX-120 ion chromatograph (Dionex, Sunnyvale, CA, USA) after the aggregation was complete (over 24 h) according to US EPA Method 300 Revision 2.1 (Pfaff 1993). The amount of anion adsorbed on the montmorillonite surface was the difference between the added anion and the amount remaining after aggregation.

3 Results and discussion

3.1 Specific anion effects on aggregate size

Representative temporal changes in the effective hydrodynamic diameter of montmorillonite in K_2SO_4, KCl, and KH_2PO_4 at various ionic strengths are shown in Fig. 1. The growth rates of the average effective hydrodynamic diameters of the aggregates indicated the presence of specific ion effects for these three anions. For example, at an ionic strength of 7.5 mmol/L, linear aggregate growth over time occurred in the KCl and KH_2PO_4 solutions, suggesting a slow aggregation regime, whereas exponential aggregate growth over time occurred in the K_2SO_4 solution, indicating a fast aggregation regime. The average effective hydrodynamic diameter increased from 393.8 to 1875 nm and

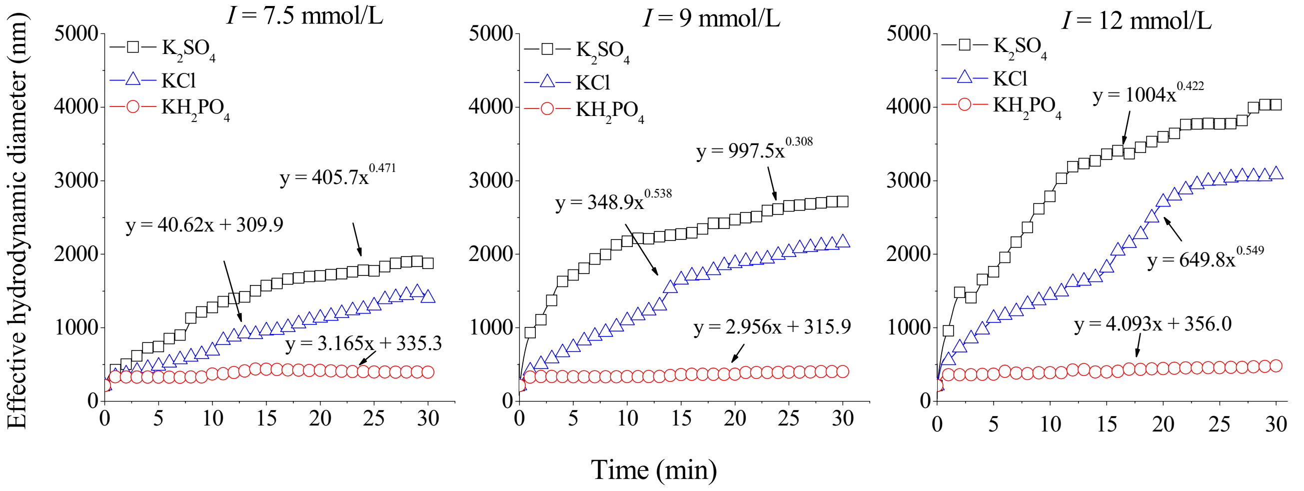


Fig. 1 Changes in the average effective hydrodynamic diameter of montmorillonite aggregates over time in K_2SO_4, KCl, and KH_2PO_4 solutions of different ionic strengths. From left to right, the ionic strengths are 7.5, 9, and 12 mmol/L, respectively

from 323.8 to 1405 nm in the SO_4^{2-} and Cl^- solutions, respectively, after 30 min. However, the diameter remained relatively constant at approximately 333.0 nm after the first 2 min in the presence of phosphate, confirming an especially slight aggregation state of the montmorillonite particles. When the ionic strength was 12 mmol/L, slow aggregation occurred in the KH_2PO_4 solution, whereas fast aggregation occurred in the K_2SO_4 and KCl solutions. The effective hydrodynamic diameter increased from 815.5 to 4035 nm and from 625.5 to 3085 nm in the SO_4^{2-} and Cl^- solutions, respectively. However, we observed only a slight increase in the effective hydrodynamic diameter (from 363.6 to 479.8 nm) in the 12 mmol/L phosphate solution. The experimental results show that the montmorillonite colloidal particles in the SO_4^{2-} system have the strongest aggregation among the three systems. After 30 min, the effective hydrodynamic diameters in the Cl^- solutions were 1405, 2157, and 3085 nm for 7.5, 9, and 12 mmol/L ionic strengths, respectively. In the phosphate solutions, the colloidal suspension was relatively stable with only slight aggregation, and the effective hydrodynamic diameters after 30 min were 395.1, 404.4, and 479.8 nm for the 7.5, 9, and 12 mmol/L solutions, respectively. These results indicate that it is difficult to form montmorillonite aggregates in the presence of phosphate. In summary, phosphate had the greatest inhibiting effect on montmorillonite particle aggregation, followed by Cl^- and SO_4^{2-} at all ionic strengths, which suggests that strong specific anion effects inhibit the montmorillonite aggregation process.

3.2 Specific anion effects on the total average aggregation rate and critical coagulation ionic strength

Increased TAA rates for montmorillonite were more pronounced with increased ionic strength, indicating that montmorillonite gradually became unstable. Until the ionic strength surpassed 9.915 mmol/L for K_2SO_4, 11.38 mmol/L for KCl, or 180.7 mmol/L for KH_2PO_4, the TAA rates slowly increased with increasing ionic strength. Consequently, the TAA rates for each electrolyte solution could be described by two linear functions for low and high ionic strengths. The ionic strength corresponding to the intersection of these two straight lines is defined as the critical coagulation ionic strength (CCIS; Fig. 2).

The dramatically different CCIS values of K_2SO_4, KCl, and KH_2PO_4 originate from the effects of the anionic species, as potassium is the common cation between all three. Additionally, K^+ exhibits strong specific ion effects on anions. From Fig. 2, the CCIS value for the three electrolyte solutions was 9.915, 11.38, and 180.7 mmol/L for K_2SO_4, KCl, and KH_2PO_4, respectively. The CCIS value for KH_2PO_4 was 15.88 and 18.22 times higher than that of KCl and K_2SO_4, respectively, indicating greater anion specificity. Derjaguin-Landau-Verwey-Overbeek (DLVO) theory cannot explain the effect of ion species because only the cation valence is introduced as a variable to distinguish the ion species, and cations of the same valence and different types are not considered. The present data

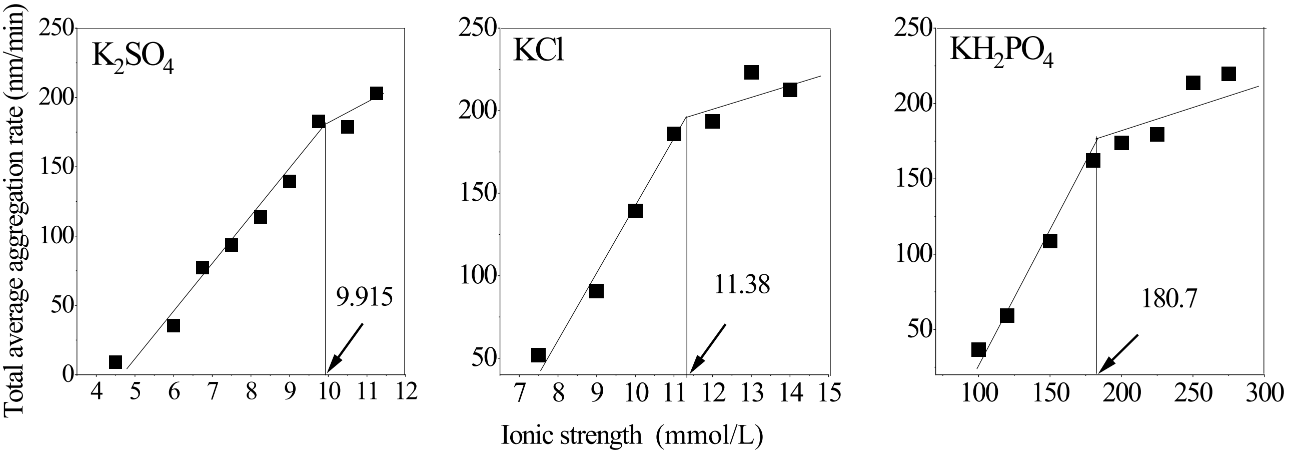


Fig. 2 Total average aggregation rates for montmorillonite particle aggregation as a function of the ionic strength in K_2SO_4, KCl, and KH_2PO_4 solutions. The turning points were critical coagulation ionic strength values (in mmol/L)

show that specific anion adsorption results in the highest CCIS values, and less hydrated anions result in a higher CCIS. Studies of other positively charged surface systems have reported the origin of specific ion effects from the anion hydration level (Katana et al. 2020). Phosphate had the greatest inhibiting effect on the coagulation capacity of potassium, followed by that of Cl^- and SO_4^{2-}.

3.3 Specific anion effects on the activation energy of aggregation between adjacent particles

It is necessary to investigate the activation energies under the effects of different anions to obtain a more in-depth understanding of specific ion effects on montmorillonite particle aggregation. According to the method developed by Tian et al. (2014), the activation energy [$\Delta E(c_0)$] and TAA rates are correlated as follows:

$$\widetilde{v}_T\left(c_0\right) = K \cdot c_0 \cdot e^{-\frac{\Delta E(c_0)}{kT}} \qquad c_0 \leq \beta(\text{CCIS}) \qquad (2)$$

$$\widetilde{v}_T\left(c_0\right) = K \cdot e^{-\frac{\Delta E(c_0)}{kT}} \qquad c_0 \geq \beta(\text{CCIS}) \qquad (3)$$

where T is the absolute temperature. Below and above the CCIS, K can be regarded as a constant. β is the conversion factor between ionic strength and ionic concentration and is 1/3, 1, and 1/6 in the K_2SO_4, KCl, and KH_2PO_4 solutions, respectively. The activation energy for aggregation at different ionic strengths was calculated using the following equations:

$$\mathrm{K} = \frac{\widetilde{v}_T(\beta\text{CCIS})}{\beta\text{CCIS}} \qquad c_0 \leq \beta(\text{CCIS}) \qquad (4)$$

$$\mathrm{K} = \widetilde{v}_T(\beta\text{CCIS}) \qquad c_0 \geq \beta(\text{CCIS}) \qquad (5)$$

The activation energies at any given K_2SO_4, KCl, and KH_2PO_4 electrolyte concentration were determined as follows:

For the K_2SO_4 solution, $\Delta E(c_0) = -kT\ln(-3.218/c_0 + 1.973)$ for $c_0 \leq (1/3)\text{CCIS}(K_2SO_4)$ and $\Delta E(c_0) = -kT \ln(0.2233/c_0 + 0.2618)$ for $c_0 \geq (1/3)\text{CCIS}\ (K_2SO_4)$.

For the KCl solution, $\Delta E(c_0) = -kT\ln(-8.972/c_0 + 1.652)$ for $c_0 \leq \text{CCIS}$ (KCl) and $\Delta E(c_0) = -kT\ln(0.04374/c_0 + 0.3983)$ for $c_0 \geq \text{CCIS}$ (KCl).

For the KH_2PO_4 solution, $\Delta E(c_0) = -kT\ln(-143.1/c_0 + 1.792)$ for $c_0 \leq (1/6)\text{CCIS}\ (KH_2PO_4)$, and $\Delta E(c_0) = -kT\ln(0.004042/c_0 + 0.2696)$ for $c_0 \geq (1/6)\text{CCIS}\ (KH_2PO_4)$.

In general, the activation energy of particles in a dispersed stable solution approaches infinity. At ionic strengths higher than the CCIS, the activation energy between the particles was approximately zero. The activation energies $\Delta E(c_0)$ of two adjacent particles at any given ionic strength less than the CCIS are plotted in Fig. 3. Our results clearly show that the $\Delta E(c_0)$ between adjacent particles in the K_2SO_4, KCl, and KH_2PO_4 solutions were significantly different at a certain ionic strength and could quantitatively characterize the specific anion effects for these three anions. For example, when the ionic strength was 9 mmol/L, the activation energies for montmorillonite particle aggregation were estimated as 0.1050 and 0.4230 kT for K_2SO_4 and KCl, respectively. The montmorillonite particles in the KH_2PO_4 solution were dispersed in a stable state. Therefore, the activation energy approached infinity, meaning that montmorillonite particle aggregation in the KH_2PO_4 system was not possible. The activation energy of the KCl system was 4.029 times higher than that of the K_2SO_4 system. Additionally, when the activation energy between particles was 1.5 kT, the ionic strengths of K_2SO_4, KCl, and KH_2PO_4 were 5.517, 6.279, and 91.21 mmol/L, respectively. Thus,

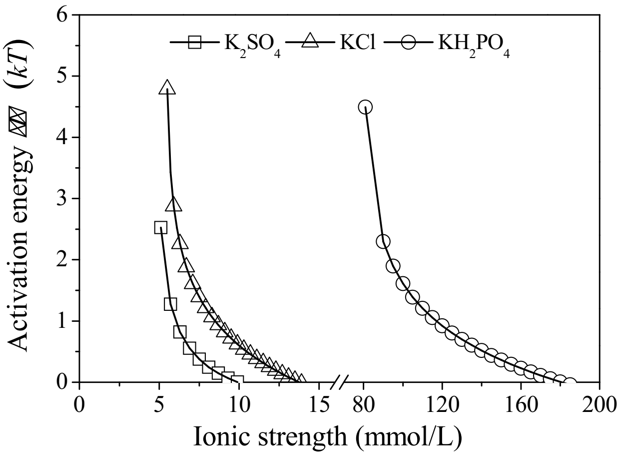


Fig. 3 Activation energies (ΔE) for montmorillonite particle aggregation in K_2SO_4, KCl, and KH_2PO_4 solutions. ΔE is expressed in kT

the ionic strength of KH_2PO_4 necessary to achieve the activation energy was 14.53 and 16.53 times higher than that of KCl and K_2SO_4, respectively. Specifically, phosphate required the greatest activation energy for montmorillonite particle aggregation, followed by Cl^- and SO_4^{2-}.

These results agree with the effects of specific ions on the TAA and CCIS values. Among the three anions, phosphate had the lowest TAA and the highest CCIS value at a certain ionic strength, which can be attributed to phosphate having the highest activation energy for aggregation. Accordingly, the anion type considerably influences montmorillonite particle aggregation. Further, the aggregation of permanently negatively charged montmorillonite particles is affected by electrolyte cations and anions.

Based on the electrostatic interaction theory, anions in solution cannot approach the particle surface via only electric forces due to the abundant negative surface charges on montmorillonite. However, the experimental results in this study show that the anions affected particle aggregation and surface interaction activation energy. Therefore, the dispersion force can provide a rational interpretation of the experimental results. Through thermal motion, anions cross the electrical double layer and reach the particle surface. Once anions reach the surface, they are adsorbed by short-range dispersion forces. Generally, the larger and softer the electronic shell of the anion, the easier it is to alter its electron clouds, resulting in a larger dispersion effect under the same conditions. For example, phosphate is more likely to adsorb onto the montmorillonite particle surface than Cl^- and SO_4^{2-} because of its stronger dispersion force. However, in the case of K_2SO_4, the large number of K^+ ions in the solution compress the double electrical layer, leading to lower activation energy than that of KCl, even though the dispersion force of SO_4^{2-} is higher than that of Cl^-. This seems to explain the results in the present study. The different affinities of the anions on the surface may cause substantial variations in activation energy and aggregation.

However, as shown in Fig. 4, the difference in the activation energies between the KCl and K_2SO_4 systems or the KH_2PO_4 and K_2SO_4 systems sharply increased with decreasing ionic strength. Generally, decreased ionic strength leads to increased electric field strength near the particle surface. The increased activation energy differences indicate that the strength of specific anion effects for the three anions increases with decreasing ionic strength. Ionic dispersion forces cannot explain these results; however, these forces likely play an important role at high electrolyte concentrations (or ionic strengths) (Borukhov et al. 1997; Moreira et al. 2006; Ruiz-Agudo et al. 2011). Liu et al. (2014) demonstrated that ions adsorbed to clay mineral surfaces in a strong electric field with dilute electrolyte solutions can be strongly polarized, and the observed polarization effects were almost 10,000 times stronger than those predicted by classic theories. This polarization effect is referred to as non-classic polarization. Considering that montmorillonite particles possess a charge density of 0.1586 C/m^2 and generate an electric field of approximately 2.2×10^8 V/m on their surfaces (Li et al. 2011), anions are inevitably attracted by the strong electric field, causing non-classic ionic polarization after they approach the surface. Non-classic polarization increases with decreasing ionic strength because decreasing ionic strength increases the electric field strength near the surface. As the difference in the activation energies increases with decreasing ionic strength, the electric field increases. Therefore, decreased ionic strength leads to an evident increase in the specific ion effects for these three anions.

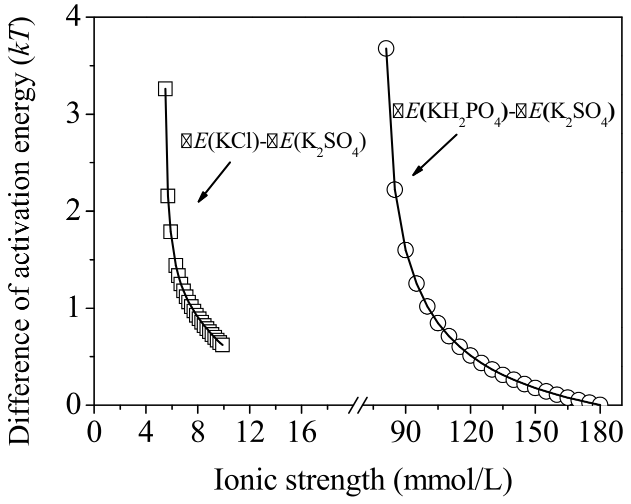


Fig. 4 Correlation between activation energy differences [$\Delta E_{(i)}$—$\Delta E_{(j)}$] for electrolyte solutions i and j and ionic strength

Accordingly, the role of specific anions in montmorillonite aggregation can be described as follows. First, anions enter the electric double layer through thermal motion. Then, an instantaneous dipole is induced by the strong electric field, which causes directional anion polarization. Stronger electric fields lead to stronger specific anion effects. Non-classic polarization effects should be responsible for the experimentally observed specific ion effects, thereby providing a rational explanation for the Hofmeister series of montmorillonite particle aggregation in various potassium anion solutions and pronounced specific ion effects at low ionic strengths.

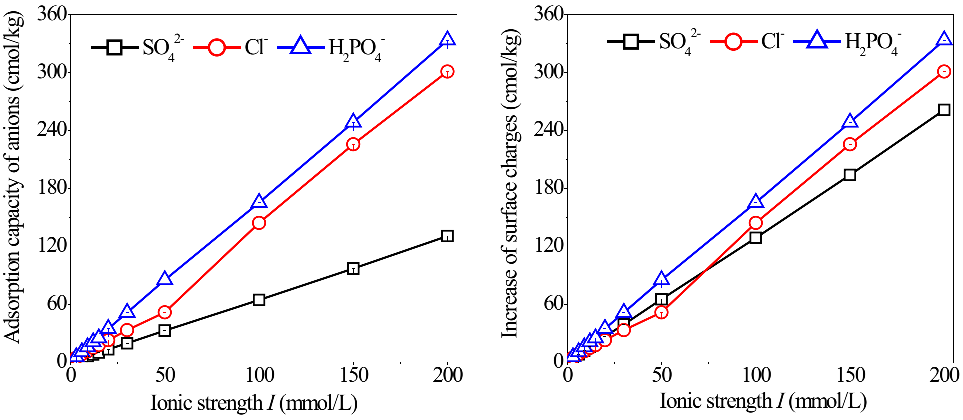
3.4 Specific anion effects of the adsorption of anions to permanently charged montmorillonite

Anions adsorbed by strong non-classic polarization effects increase the negative surface charge, thereby increasing the repulsive force between two adjacent montmorillonite particles and finally increasing the activation energy. To verify the specific anion effects of anion adsorption on the montmorillonite particle surfaces, we measured the number of anions adsorbed on the montmorillonite particle surfaces. Phosphate had the greatest number of anions adsorbed on the surface, followed by Cl^- and SO_4^{2-}. For instance, when the ionic strength was 9 mmol/L, the adsorption capacities for phosphate, Cl^-, and SO_4^{2-} were 15.57, 11.17, and 5.940 cmol/kg, respectively. However, when the ionic strength was 100 mmol/L, the adsorption capacities for phosphate, Cl^-, and SO_4^{2-} were 165.1, 144.2, and 64.35 cmol/kg, respectively. The amount of adsorbed phosphate was 1.145 and 2.566 times higher than that of Cl^- and SO_4^{2-}, respectively.

Due to the difference in the anion valences, the surface negative charge induced by SO_4^{2-} adsorption was twice that of phosphate and Cl^-. In the range of ionic strengths shown in Fig. 5, the increased number of negative charges from SO_4^{2-} adsorption was slightly higher than that for Cl^- adsorption at ionic strengths lower than 50 mmol/L. However, the larger negative charge corresponding to a smaller CCIS for SO_4^{2-} than that for Cl^- is because the electric field was somewhat obscured in the SO_4^{2-} solution due to the presence of twice as many K^+ ions at the same electrolyte concentration. As a result, there were more cations to compress the electric double layer, which decreased electrostatic repulsion.

As previously mentioned, electrostatic attraction and chemical absorption of anions on the montmorillonite surface were not possible. However, the above result shows that a high number of anions adsorbed on the interlayer surface, and the substantial differences in the montmorillonite aggregation process caused by various anions suggests the presence of specific anion-inhibiting effects in this process. The differences in the electron clouds of the anions result in different polarization effects, which might be one reason for the specific anion effects. Wang et al. (2021) emphasized that ionic hydrability and polarizability largely affect iron oxide aggregation. Cl^- and SO_4^{2-} produce different degrees of electrostatic adsorption on the surface because Cl^- has lower hydrability and polarizability than those of SO_4^{2-}. In addition to variably charged iron oxide aggregation, specific anion effects caused by polarization and hydration were observed during permanently charged montmorillonite aggregation (Fig. 6). Additionally, some studies claim that the distance between the weak ionic hydration capacity of monovalent anions and the negatively charged particle surface is lower than that for strong ionic hydration anions (Flores et al. 2012; Ling et al. 2021). Therefore, compared with phosphate, Cl^- is farther from the particle surface. The closer distance and stronger specific adsorption increased the negative surface charge, resulting in a higher adsorption capacity and higher CCIS value for phosphate than those for SO_4^{2-} and Cl^-. Although simultaneously introduced cations neutralize the negative surface charge to some degree, they cannot hinder the increased negative surface charge caused by specific adsorption of strongly polarized anions. However, as K_2SO_4 is a 2:1 electrolyte, the proportion of K^+

Fig. 5 Correlation between adsorption capacity or increased surface charges and ionic strength in K_2SO_4, KCl, and KH_2PO_4 solutions. The left figure shows changes in ion adsorption, and the right figure shows the increased surface negative charges



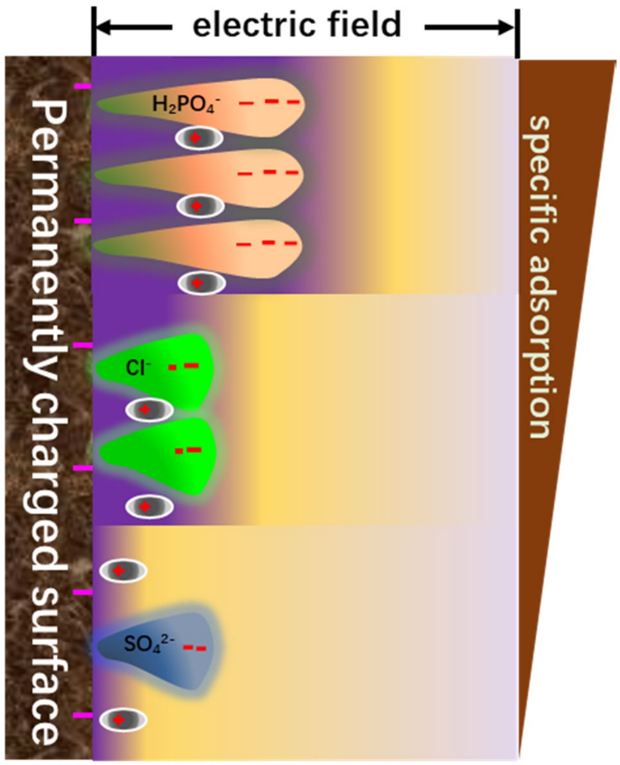


Fig. 6 Schematic diagram of strong anion adsorption to a permanently charged surface caused by polarization in the electric field

in the solution is higher than that in KCl at the same ionic strength. Considering the combined cation and anion effects, Cl^- more strongly inhibits montmorillonite aggregation than SO_4^{2-}. After anions cross the electric double layer through thermal motion, a strong electric field induces the anion electronic cloud, which causes directional ionic polarization, producing so-called non-classic polarization (Gao et al. 2019). Phosphate has the strongest non-classic polarization and the largest adsorption capacity, therefore playing the strongest role in hindering montmorillonite aggregation, followed by SO_4^{2-} and Cl^- (Fig. 6). The differences in the activation energies increased with decreasing ionic strength, indicating that a stronger electric field induces stronger ionic polarization. It is necessary to further consider the combined effects of the ionic strength of a solution, anion hydrability and polarizability, and other solution environment factors on colloidal particle behavior.

4 Conclusions

In this study, the total average aggregation rate, critical ionic coagulation strength, and activation energy were combined to quantify the aggregation kinetics of montmorillonite. As a result, strong specific anion-inhibiting effects were observed during permanently charged montmorillonite particle aggregation. Phosphate had the greatest inhibiting effect on montmorillonite aggregation, followed by Cl^- and SO_4^{2-}. Correspondingly, the critical coagulation ionic strength and activation energy for the phosphate system were much higher than those for the Cl^- and SO_4^{2-} systems.

The combined action of cations and anions regulate aggregation, while CCIS is determined by specific ion adsorption. Phosphate has much stronger non-classic polarization than Cl^- and SO_4^{2-}. Further, phosphate has the largest adsorption capacity onto the permanently charged mineral particle surface, thus inducing the largest increase in the negative surface charge. The electric field considerably impacted the specific anion effects. The stronger the electric field (lower ionic strength), the stronger the specific anion effects, as the activation energy differences for the anions sharply increased with decreasing ionic strength. Our study provides a rational explanation for the Hofmeister series for various anions during montmorillonite particle aggregation in solutions and more pronounced specific ion effects at low ionic strengths.

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Declarations

Competing interests The authors declare no competing interests.

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