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Article

The kinetics and mechanisms of using cationic surfactants to reduce the dissolution of clay minerals

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Abstract

The dissolution kinetics occurring on clay minerals are influenced by various factors, including pH, temperature and mineral lattice structure. However, the influence of the surfactant is rarely studied. In the present work, cationic surfactants were investigated in terms of the dissolution of clay minerals in acidic environments. Kaolinite was selected as the representative clay mineral. The cationic surfactant inhibited the dissolution of clay minerals because it limited the attack of H^+ on the kaolinite surface and then inhibited the dissolution of kaolinite by modifying the hydrophilicity of the kaolinite surface towards hydrophobicity. The inhibition ability of the surfactant might be related to its molecular structure and the type of acid used in dissolution experiments.

Keywords: Cationic surfactants; dissolution kinetics; kaolinite; modification; surface control

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The study of the dissolution kinetics of clay minerals is a multidisciplinary field with wide-ranging implications for geology, environmental science and engineering. It provides fundamental insights into the interactions between minerals and their environments under various conditions, helping to address both practical and theoretical challenges in geochemical modelling, palaeoclimate reconstruction, carbon sequestration, soil and sediment formation, nutrient cycling, geothermal energy extraction and petroleum geology, among others.

The kinetics and mechanisms of clay mineral dissolution under various conditions have been studied and discussed for decades (Nagy & Lasaga, 1992; Ganor *et al.*, 1995; Belver *et al.*, 2002; Köhler *et al.*, 2003; Golubev *et al.*, 2006; Yang & Steefel, 2008; Rozalen *et al.*, 2009; Khawmee *et al.*, 2013; Bibi *et al.*, 2014). In 2015, Jordi Cama and Jiwchar Ganor provided a comprehensive overview of clay mineral dissolution kinetics (Cama & Ganor, 2015), reviewing the kinetics of clay dissolution grounded in the kinetic theory developed to describe and quantify mineral dissolution, especially of silicate minerals. These authors explored various clay dissolution rate laws and interpretations of dissolution mechanisms proposed over the past four decades, thereby enhancing our understanding of the kinetic theory of mineral dissolution. The dissolution rates and dissolution mechanisms of clay minerals are related to the dissolution behaviour of mineral surfaces in various environments. The clay minerals discussed in by Cama & Ganor (2015) fall into two categories: 1:1 clay minerals, such as kaolinite, and 2:1 clay minerals, which include dioctahedral smectites (montmorillonite, beidellite and nontronite), trioctahedral smectites (hectorite and saponite), dioctahedral micas (illite and muscovite), trioctahedral micas (biotite and phlogopite), vermiculite and chlorite (Bergaya *et al.*, 2011). The authors addressed how such environmental variables as pH, temperature, catalysts/inhibitors, solution saturation state and ionic strength influence the dissolution kinetics of clay minerals.

The adsorption of surfactants onto the surface of clay minerals has been studied widely (Kalam *et al.*, 2021); however, studies that focus on the consequences for dissolution of such adsorption are less common. There is a lack of studies investigating the effects of surfactants, especially cationic surfactants, on the dissolution of clay minerals under acidic conditions.

In this study, the effects of a cationic surfactant on the dissolution of clay minerals are discussed. Kaolinite was chosen as an example to study the kinetics of clay mineral dissolution with cationic surfactants under acidic conditions. Kaolinite is a 1:1 clay mineral with a small specific surface area, and its negative surface charge is also small under neutral conditions. If cationic surfactants can adsorb onto the surface of kaolinite and inhibit its dissolution, then, under the same conditions, clays with a more negative surface charge should theoretically adsorb more cationic surfactants and be inhibited from dissolving. Hydrochloric acid, nitric acid and acetic acid were used for the dissolution of kaolinite over a 12 h period. The molecular formula of kaolinite is $Al_2Si_2O_5(OH)_4$. Compared with other clay minerals, the composition of kaolinite

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is more favourable for determining a dissolution rate. Wieland & Stumm (1992) studied the determination of the dissolution rate of clays through the release of Al^{3+} and the acid dissolution kinetics of kaolinite. The dissolution reaction mechanisms of silicoaluminate can be divided into proton promotion (in acidic environments), water promotion (in near-neutral environments) and hydroxyl promotion (in alkaline environments) according to the acidity of the environment in which such dissolution occurs. As this paper studies the dissolution kinetics of clay minerals under acidic conditions, in terms of the implementation of the element detection method, the release of Al^{3+} is selected to determine the dissolution of clay minerals.

Four cationic surfactants with various structures are selected to compare their inhibitory effects, and the surfactant with the strongest inhibitory effect is selected to study the dissolution kinetics of the modified minerals. The concentration of aluminium in the acidic solution is measured at various timepoints to investigate the dissolution kinetics of kaolinite under variously acidic conditions. The ability of cationic surfactants to inhibit kaolinite dissolution is determined and the mechanisms of this inhibition are discussed. By studying the effects of cationic surfactants on the dissolution of clay minerals under acidic conditions, a new way of controlling the dissolution of clay minerals through surface regulation is provided.

Experimental

Materials

The kaolinite samples used in this paper were purchased from Chengdu Kelong Chemicals Co., Ltd (Chengdu, China). Their purity was greater than 99.5%.

Four cationic surfactants were used in this research: cetane trimethyl ammonium bromide (CTAB), *n*-tetrabutylammonium bromide (TBAB), benzyl trimethyl ammonium bromide (BTAC) and glycidyl trimethyl ammonium chloride (GTA). All of them were of analytically pure grade. The surfactants were purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China).

Method of measuring the dissolved Al^{3+}

The general equation of kaolinite dissolution under acidic conditions can be expressed as in Equation 1:

$$Al_2Si_2O_5(OH)_4 + H^+ \rightarrow Al^{3+} + H_2SiO_4 + H_2O \qquad (1)$$

The Al^{3+} content in the solution was determined using ultraviolet (UV) spectrophotometry (UV5000 UV spectrophotometer, Aoyi Instruments Shanghai Co., Ltd, Shanghai, China). A 1 mL pipette was used to accurately transfer a quantitative amount of leaching solution into a 10 mL colorimetric tube. Then, the acid solution was added to acidizing water (0.8 mL dilute nitric acid solution into 200 mL of water) and shaken well. Following this, 0.40 mL mixed reagent, 0.40 mL catechol purple solution and 2.00 mL hexamethylenetetramine buffer solution were added to the colorimetric tube with a pipette, and each reagent was shaken well. After the reagent was left for colour development for 15 min, the absorbance of the reagent was measured with 1 cm colorimetric dishes at a wavelength of 580 nm within 60 min.

The content of Al^{3+} in the solution was calculated using a standard curve. A standard solution of Al^{3+} (1000 μg L^{-1}) was used to configure the gradient solution, and the standard curve of Al^{3+} concentration between 0 and 500 μg L^{-1} was drawn. The standard curve of Al^{3+} concentration is shown in Fig. 1. The absorbance is linearly correlated with the concentration, with the linear equation fitting result being $y = 0.0018x + 0.0188$, $R^2 = 0.9996$ (Fig. 1).

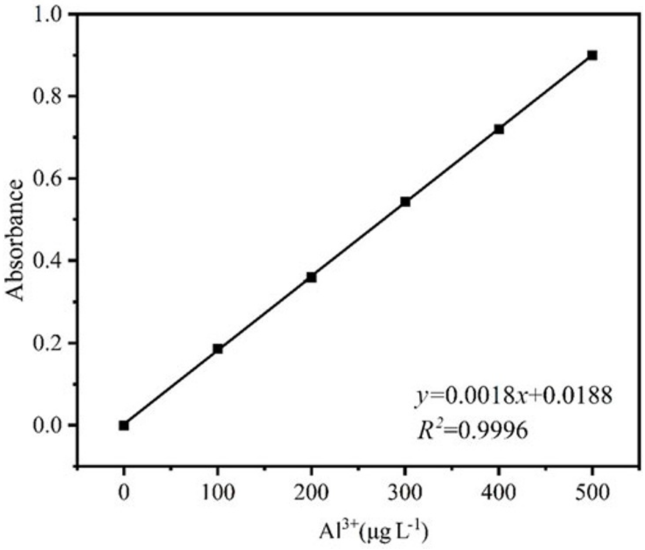

Figure 1. The standard curve of Al^{3+}.

The dissolved amount of Al^{3+} was used to indicate the inhibition rate of the surfactant inhibiting the dissolution of clay using Equation 2:

$$A = \frac{a - b}{a} \times 100\% \qquad (2)$$

where A is the inhibition rate (the rate of the difference in Al^{3+} dissolution of kaolinite (before and after modification) from the Al^{3+} dissolution of unmodified kaolinite), a is the Al^{3+} content dissolved from the primitive clay (μg L^{-1}) and b is the Al^{3+} content dissolved by the surfactant modified clay (μg L^{-1}).

Modification of kaolinite and dissolution experiments

A series of four cationic surfactant solutions with mass concentrations of 0–30 g L^{-1} were prepared in the experiment, and the inhibition of various cationic surfactants of the dissolution of kaolinite was investigated under the condition of mixing 3% KCl and 2% (volume fraction) acetic acid (pH 2.49) solution and dissolving them for 0.5 h. Four different surfactants were used to modify the kaolinite. A precision balance was used to weigh 3.00 g of kaolinite. Cationic surfactants were added to 100 mL of ultrapure water for preparing the solutions with concentrations between 0 and 30 g L^{-1}. Kaolinite were stirred for 20 h at room temperature at a stirring speed of 500 rpm (6.24 *g*) in the solution.

After stirring, washing and centrifugation were performed, the material was dried for 5 h at 60°C. Then, 0.2 g of modified kaolinite was taken and dissolved in 25 mL of acid solution (adding 3% bulking agent KCl) at room temperature for 0.5 h under shaking. The supernatant was taken and the content of Al^{3+} was measured. Equation 2 was used to calculate the dissolution inhibition rate of the clay. The surfactant with the greatest inhibitory effect was selected for computer molecular simulation and for studying the influences of other acid dissolution conditions.

Temperature

The leaching temperature (30–80°C) was varied to explore the influence of temperature on the dissolution amount and inhibition rate of Al^{3+} when the modified kaolinite was dissolved in 2% acetic acid solution mixed with 3% KCl for 0.5 h. The reaction temperature was controlled using a water bath. During the measurement of dissolution, the CTAB concentration was 25 g L^{-1} and the concentration of acetic acid was 2% (volume fraction). Under the conditions of 25 g L^{-1} CTAB concentration and 0.5 h dissolution time, the leaching temperature was varied to explore the influence of temperature on the dissolution amount and inhibition rate of Al^{3+} when CTAB–kaolinite was dissolved in a 2% (volume fraction) acetic acid (pH 2.49) solution mixed with 3% KCl.

Acid solution kinetics

Three acid solutions containing 3% KCl were prepared, namely 2% HCl, 2% HNO_3 and 2% CH_3COOH, to explore the influences of various acids on the dissolution amount and inhibition rate of Al^{3+} in kaolinite and modified kaolinite. Dry kaolinite samples of 0.2 g adsorbed by CTAB were placed in a 50 mL beaker, and 35 mL of acid solution containing 3% KCl was added. The supernatant was removed at 0.3, 0.8, 1.5, 2.5, 3.0, 4.5, 6.5 and 12 h, respectively, and centrifuged at 10 000 rpm to determine the content of Al^{3+}. CTAB–kaolinite was placed in 2% (volume fraction) acetic acid, nitric acid and hydrochloric acid with 3% KCl added and dissolved in oscillations for 12 h. The concentration of Al^{3+} in the solution at various timepoints was determined. The change in Al^{3+} concentration over time was plotted and the kinetic equation was fitted.

In theory, the dissolution of kaolinite involves a diffusion process of an ionic solid phase and a liquid phase, which accords with the kinetic characteristics of the proton-promoting mechanism dominating mineral dissolution under acidic conditions (Bibi *et al.*, 2014). Equations 3–5 were used to conduct a kinetic analysis of the dissolution data of Al^{3+} from the modified kaolinite under the action of 3% KCl acid.

$$C_t = a + bt^{1/2} \tag{3}$$

$$C_t = a + b\ln(t) \tag{4}$$

$$C_t = a[1 - \exp(-kt)] \tag{5}$$

In these equations, C_t is the dissolution amount of Al^{3+} at time t (h) (μg L^{-1}), t is the dissolution time (h), a is the initial concentration (μg L^{-1}), b is one reaction rate constant and k is a different reaction rate constant.

Equation 3 is a parabolic equation (diffusion equation). The physical significance of parabolic rate dynamics can be explained in terms of changing the diffusion transfer of the surface layer through the solid phase, and it is often used to represent a reaction controlled by the diffusion step. A parabolic equation is not suitable for the whole solution range of a closed system. Equation 4 is an empirical equation (Elovich equation), which can represent the analytical process of adsorption in chemistry. This equation is suitable to represent a reaction in which the activation energy changes greatly, as well as a complex reaction mechanism in a slow reaction process, such as solute diffusion at the solution phase or interface, surface activation and deactivation and surface reaction. Equation 5 is a first-order kinetic equation, which can represent ion exchange, adsorption and chemical reaction processes at a mineral reaction site.

Quantum chemistry analysis and molecular dynamics calculations

To study the relationship between the molecular structures of the cationic surfactants and their inhibitory effects, quantum chemistry analysis and molecular dynamics calculations were carried out, and the density functional method and molecular dynamics theoretical calculations and simulation methods were adopted. The adsorption configuration of surfactant molecules on the (001) surface of kaolinite was studied using quantum chemistry and molecular dynamics simulation, and the adsorption force between the cationic surfactant and kaolinite was explained by studying the mechanism involved in the cationic surfactant adsorbing onto the surface of kaolinite.

The software *Forcite* was used to conduct a geometry optimization simulation of the adsorption configuration calculated using *CASTEP*, and the initial adsorption configuration of surfactant was obtained. The specific simulation conditions are: a COMPASSII force field was used, Ewald mode was used for the electrostatic force, atom-based force is was for van der Waals forces and the cut-off energy was set to 10 A. Based on the obtained initial configuration, the macroscopic canonical ensemble was selected to be 298 K temperature, the time step was 1 fs and the non-bonding interaction (electrostatic forces and van der Waals forces) was calculated using the *vdw&Coulomb* mode. The total simulation time was 100 ps to simulate the adsorption kinetics.

Crystal structure properties of kaolinite

The crystal chemical formula of kaolinite is $2SiO_2{\bullet}Al_2O_3{\bullet}2H_2O$, and kaolinite minerals belong to the 1:1 phyllosilicate type. The crystal is mainly composed of silico-oxygen tetrahedra and aluminium hydroxide octahedra, in which the silico-oxygen tetrahedra share the top angle along the two-dimensional direction to form a hexagonal arrangement of a grid layer, with each silico-oxygen tetrahedron without a common apex oxygen being arranged towards one side. The unit layer of 1:1 is composed of the silico-oxygen tetrahedral layer and the alumino-oxygen octahedral layer, which share the apex oxygen of the silico-oxygen tetrahedral layer. Belonging to the Cc space group, the crystal cell parameters are $a = b = 5.226$ Å, $c = 14.590$ Å, $\alpha = \beta = 86.801°$ and $\gamma = 120.135°$, and the main cleavage plane is plane (001).

Interaction energy

CTAB molecules were geometrically optimized and adsorbed on the surface of kaolinite. The optimized adsorption complex model, adsorbent model and adsorbed surface model were used to explore the interaction energy between the surfactant functional groups and the surface atoms. The energy was calculated using Equation 6. The values of the interaction energy (ΔE) indicate the stability of the adsorption system. The more negative the ΔE is, the more stable the adsorption system is and the more likely it is that adsorption will occur. When ΔE is 0 or positive, it is more difficult for the adsorption to occur (Yin *et al.*, 2021).

$$\Delta E = E_A - (E_B + E_C) \tag{6}$$

In this equation, E_A is the energy of the optimized adsorption system model (kcal mol^{-1}), E_B is the energy of the CTAB model (kcal mol^{-1}), E_C is the energy of the kaolinite model (kcal mol^{-1}) and ΔE is the energy of interaction between CTAB and kaolinite (kcal mol^{-1}).

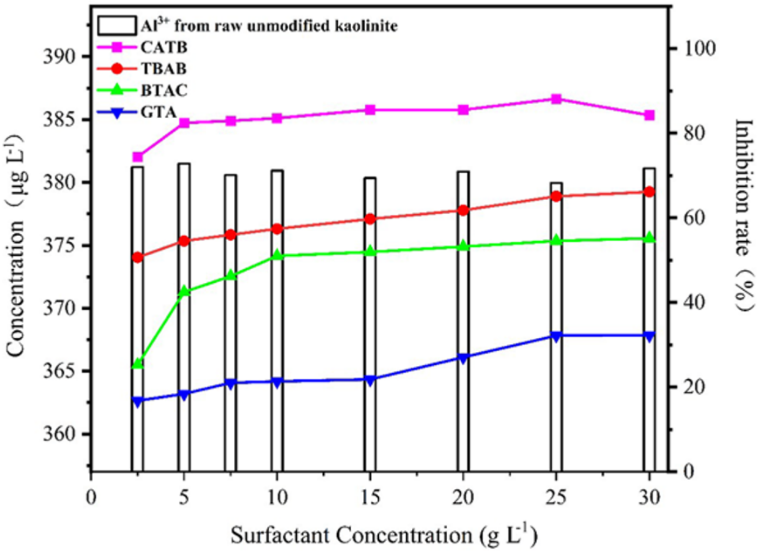

Figure 2. Effects of various cationic surfactants and their concentrations on the dissolution inhibition rate of Al^{3+} in kaolinite.

Determination methods for the modified kaolinite

X-ray diffraction analysis

X-ray diffraction (XRD) tests were performed on a DX2700-type X-ray diffractometer (Fangyuan Instrument Co., Ltd, Dandong, China). The kaolinite and CTAB–kaolinite samples were fully ground in an agate mortar to refine their particle sizes to ~200 mesh. An appropriate amount of the sample was then evenly spread in the groove of the sample holder, compacted at an appropriate pressure and scraped to make the surface flat, ensuring its close fit and smoothness. Subsequently, the sample holder was accurately placed in the testing position of the X-ray diffractometer. Regarding the setting of instrument parameters, the accelerating voltage of the X-ray tube was set to 35 kV and the tube current was set to 35 mA. The 2θ scanning range was set from 5° to 70°, the scanning rate was set at 4° min^{-1} and the step size was set to 0.05°. After the testing process was completed, the obtained XRD *in situ* data were processed and analysed.

Fourier-transform infrared spectrometry analysis

Fourier-transform infrared spectrometry (FTIR) tests were carried out using an FTIR 650S Fourier-transform infrared spectrometer (Thermo Fisher Scientific, USA). Quantities of 0.002 g of CTAB, kaolinite and CTAB–kaolinite were accurately weighed. Each sample was then ground with 200 mg of dried potassium bromide powder. After pressing the mixture into a pellet, it was placed in the sample cell of the FTIR scanner. Within the wavenumber range of 4000–400 cm^{-1}, under appropriate parameter conditions and with the resolution set to 1 cm^{-1}, the background was subtracted and then 50 reciprocal scans were conducted on the sample.

Zeta-potential analysis

Zeta-potential tests were performed using a NanoBrook zeta-potential analyser (Brookhaven Instruments, USA). First, 0.1 g of kaolinite soaked with various concentrations of CTAB was weighed and dispersed in 10 mL of deionized water. Under the condition of pH 6.8, the zeta-potential of each sample was determined, and the relationship between the concentration of CTAB and the zeta-potential of kaolinite was studied. The measurement parameters were set as cycles = 3, runs = 3, inter-cycle delay = 5 s, temperature = 20°C and liquid = water.

Results and discussion

Inhibitory effects of the cationic surfactants

Among the four cationic surfactants, the dissolution amount of Al^{3+} decreased with increasing concentration of cationic surfactants and then tended towards equilibrium. CTAB maintained a significant inhibition rate at various concentrations (Fig. 2), so CTAB was selected as the cationic surfactant to be studied subsequently.

Characterization of kaolinite and CTAB–kaolinite

The XRD traces of the samples were clear, demonstrating characteristic peaks indicating that the used kaolin had good crystallinity (Fig. 3). The CTAB–kaolinite did not generate new characteristic peaks, and the peak values of the characteristic peaks hardly changed, indicating that the crystal structure of kaolinite did not change after soaking with CTAB. In addition, by calculating the layer spacing of the samples before and after soaking, it was found that the characteristic peaks of d_{001} before and after soaking were 12.257 and 12.257, and the layer spacings were 0.721 and 0.721 nm, respectively. The °2θ characteristic peaks did not demonstrate significant shifts, and the layer spacing did not change greatly, indicating that CTAB did not enter the kaolin interlayer but only adsorbed onto the surface, mainly because kaolinite is a non-expansive mineral with a small cation-exchange capacity, and so CTAB molecules cannot easily enter its interlayer structure.

As can be seen from Fig. 4, the absorption peaks of Si–O stretching vibrations appear at 979 and 977 cm^{-1}, and the absorption peaks of 815 and 823 cm^{-1} are Si–O, Si–O–Si and Si–O–Al vibrations. The absorption peaks of Si–O bending vibrations appear at 653 and 665 cm^{-1}, and the absorption peaks of 1623 and 1625 cm^{-1} are the offset vibration peaks of H_2O.

By comparing the three infrared absorption lines, two strong absorption peaks of CTAB–kaolinite can be observed at 2919 and 2850 cm^{-1}. The absorption peak at 2919 cm^{-1} is the C–H asymmetric stretching vibration of $-CH_3$, and the absorption peak at 2850 cm^{-1} is the C–H symmetric stretching vibration of $-CH_2-$. The results show that CTAB was successfully adsorbed onto the surface of kaolin (Zhao *et al.*, 2007).

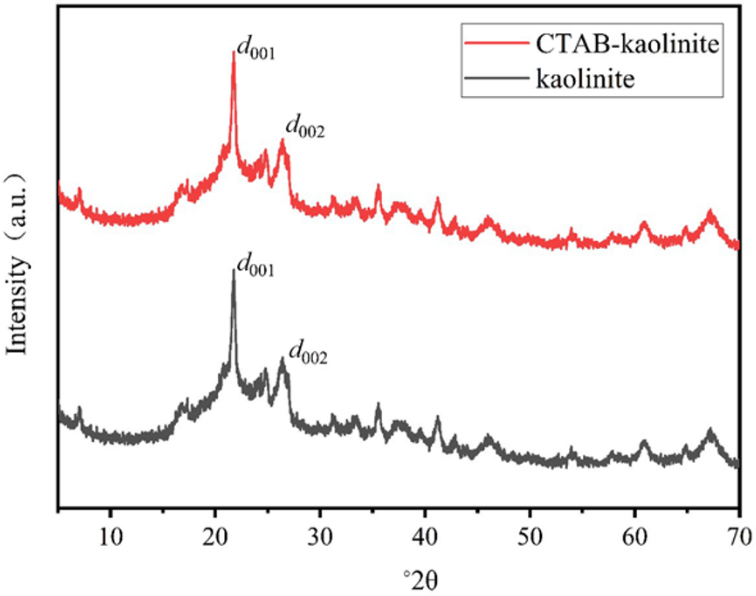

Figure 3. XRD traces of kaolinite and CTAB–kaolinite.

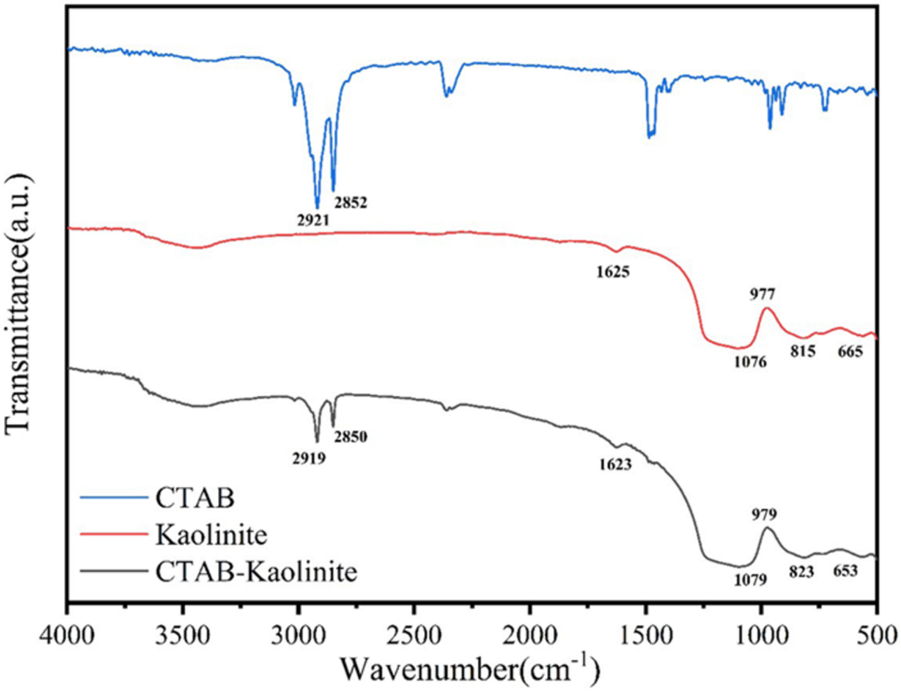

Figure 4. FTIR spectra of CTAB, kaolinite and CTAB–kaolinite.

During the interaction between CTAB and kaolinite, the electrostatic interaction energy between CTAB and kaolinite at 10 ps was –30.47 kcal mol^{-1}, van der Waals interaction energy was –54.90 kcal mol^{-1} and the total interaction energy was –85.36 kcal mol^{-1}. Over time, the absolute values of the three interaction energies showed increasing trends. At 40 ps, the electrostatic interaction energy of CTAB with kaolinite was –116.79 kcal mol^{-1}, the van der Waals interaction energy was –113.23 kcal mol^{-1} and the total interaction energy was –230.03 kcal mol^{-1}. After that time, these interaction energies remained in a relatively stable state, and the electrostatic energy and van der Waals action energy did not significantly differ (Fig. 5). At 100 ps, the electrostatic and van der Waals interaction energies accounted for 48.36% and 51.64% of the total adsorption energies, respectively, in the distribution of interaction energies between CTAB and kaolinite (Table 1).

Table 1. Interaction energy between CTAB and kaolinite at 100 ps.

	Interaction energy (kcal mol^{-1})	Percentage
Total interaction energy	−231.21	100
van der Waals interaction energy	−119.43	51.64
Electrostatic interaction energy	−111.79	48.36

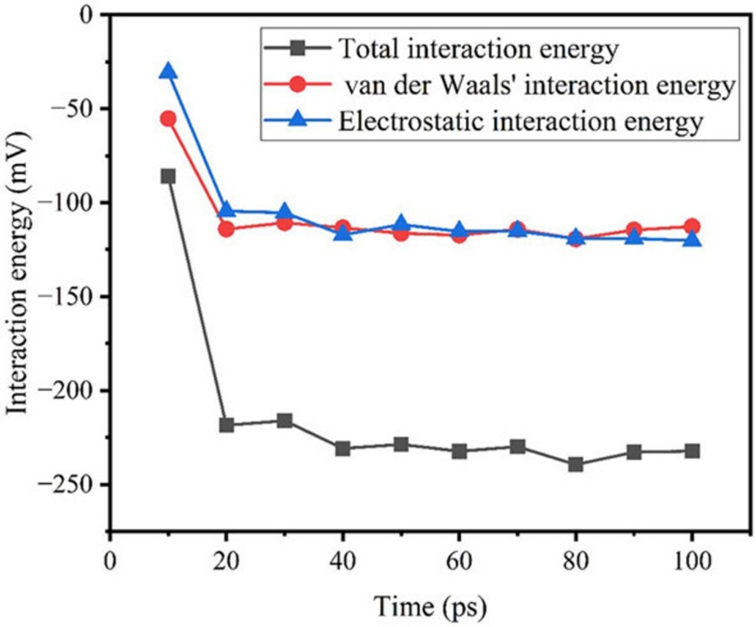

Figure 5. Change of interaction energy between CTAB and kaolinite with simulation time.

The results show that as the contact time between CTAB and kaolinite surface increased, the absolute value of the interaction energy between CTAB and kaolinite surface increased, the interaction increased and the adsorption ability of CTAB and kaolinite surface increased. After 40 ps of simulation time, the interaction between CTAB and the kaolinite surface became relatively stable and no further significant changes occurred. The distribution of van der Waals forces and electrostatic forces in the interaction energy was essentially 1:1, and their contribution to the interaction energy was essentially identical. This indicates that the interaction between CTAB and the kaolinite surface was influenced by both van der Waals and electrostatic forces. It was found that the inhibition effect of CTAB on Al^{3+} dissolution was reduced to an extent with increasing temperature, which may have been related to the decrease of the orientation force (electrostatic force) between CTAB and the kaolinite surface.

Zeta-potential analysis after the interaction of kaolinite with cationic surfactants

The zeta-potential test results allow us to determine the type of charge carried by the mineral itself and the change in the surface charge of the mineral before and after the action of CTAB on the mineral. The surface electrical properties of kaolinite increased rapidly after CTAB immersion, and the negative surface charge was continuously neutralized due to the adsorption of CTAB. After the dissolution rate of kaolinite reached a certain degree, the dissolution rate increased only slowly. Finally, with increasing CTAB concentration, the surface potential of kaolinite essentially remained unchanged, indicating that the adsorption capacity of kaolinite was limited. When the adsorption saturation point was reached, the charge of kaolinite remained unchanged even with increasing CTAB concentration (Fig. 6).

In general, the zeta-potential on the surface of kaolinite changed from –25.97 to 0.41 mV. The results show that the addition of CTAB neutralized the negative charge on the surface of kaolinite, and the surface property changed from hydrophilic to hydrophobic, which made it more difficult for the hydrophilic H^+ to come into contact with the clay surface, reducing the surface reaction rate and thus inhibiting the dissolution of kaolinite.

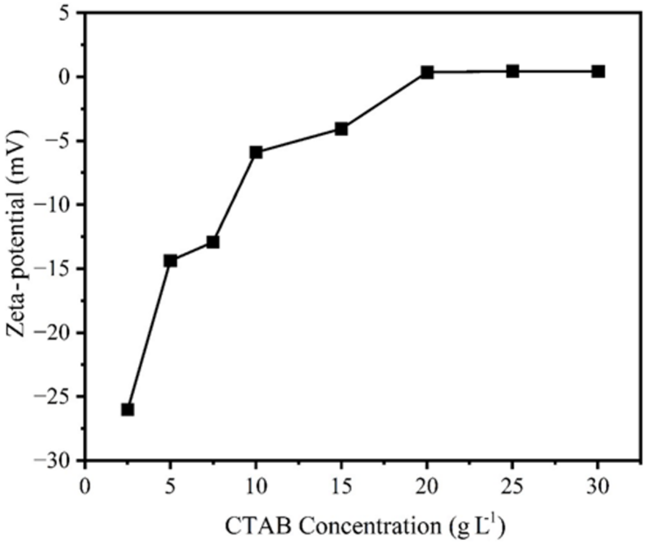

Figure 6. Effect of CTAB concentration on the zeta-potential of the kaolinite surface.

Inhibitory effect of temperature

The dissolution amount of Al^{3+} in kaolinite increased sharply with increasing dissolution temperature. The temperature had little influence on the dissolution of kaolinite after adsorption in CTAB, and the dissolution amount of Al^{3+} in CTAB–kaolinite only slightly increased with increasing dissolution temperature (Fig. 7). In addition, the adsorption stability of CTAB on the kaolinite surface was good in the temperature range of 30–80°C, and cationic

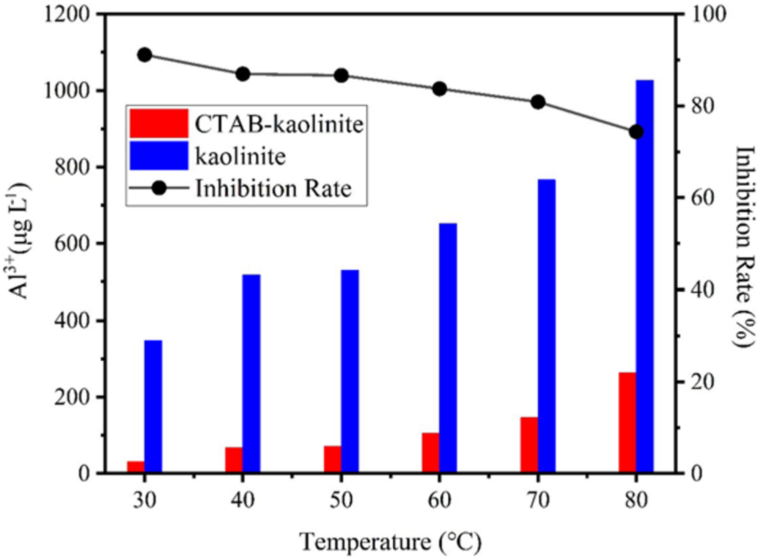

Figure 7. Influence of temperature on the dissolution amount and inhibition rate of Al^{3+} in kaolinite.

surfactant molecules do not easily desorb from the surface of kaolinite. CTAB can prevent H^+ from coming into contact with the kaolinite surface.

Moreover, it can be seen in Fig. 7 that, with increasing temperature, the inhibition rate decreased from 91% to 74%. There are two possible causes of this phenomenon: first, the forward reaction might have tended towards completion with increasing temperature; and second, CTAB adsorbed on the surface of kaolinite might have tended to have greater vibratory activity at greater temperatures. As the temperature increased, the structure formed by CTAB and kaolinite became slightly unstable. This indicates that low temperatures enabled CTAB to inhibit the dissolution of kaolinite.

Acid solubility kinetics of CTAB–kaolinite

The type of acid affected the stability of surfactant adsorption onto clay surface. Previous studies have found that changes in pH and salt solution concentration can affect the stability of surfactants adsorbed onto clay surfaces (Hue *et al.*, 2019). Under various acid dissolution conditions, cationic surfactants are variously able to inhibit kaolinite dissolution: acetic acid > nitric acid > hydrochloric acid (Fig. 8). As can be seen from the change curve of the inhibition rate over time, the inhibition rate gradually decreased with increasing time, which was related to the adsorption stability of cationic surfactants in kaolinite. With increasing time, the cationic surfactants began to desorb from the clay surface. This caused increases to the contact area between H^+ and kaolinite, thus accelerating the dissolution of kaolin and leading to a reduction of the inhibition rate.

After fitting the dissolution data of Al^{3+} in acetic, hydrochloric and nitric acids to the diffusion equation, the Elovich equation and the first-order kinetic equation, it was found that the dissolution of CTAB–kaolinite could be well described by the diffusion equation ($R^2 > 0.917$; Fig. 9a–c) and the Elovich equation ($R^2 > 0.974$; Fig. 10a–c). The correlation coefficient after fitting the first-order kinetic equation was lower ($R^2 < 0.870$; Fig. 11a–c), indicating that, during the dissolution processes of acetic acid, hydrochloric acid and nitric acid, the diffusion equation and the Elovich equation better represented the dissolution process of Al^{3+} under the action of acid than the first-order kinetic equation (Table 2). In addition, it was found that the dissolution rate of the Al^{3+} in kaolinite in various acid solutions is as follows: hydrochloric acid > nitric acid > acetic acid. These results indicate that hydrochloric acid and nitric acid were better able to dissolve CTAB–kaolinite than acetic acid, and this was related to the ionization degree of the acids in deionized water.

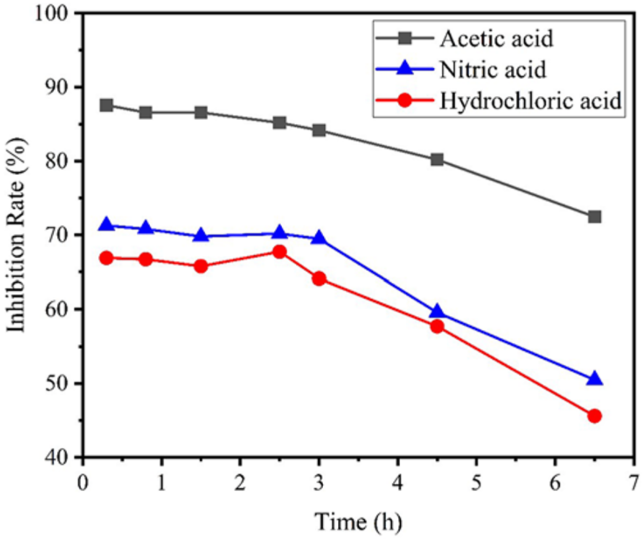

Figure 8. Inhibition rates of CTAB–kaolinite dissolved in three different acids.

Dissolution kinetics of CTAB–kaolinite

A basic concept of chemical dynamics is that reactions consist of a series of distinct physical and chemical processes that can be broken down into various steps. Berner (1978) highlighted that clay minerals are relatively insoluble, and so their reaction rates are controlled by their surfaces. For kaolinite dissolution, the dissolution reaction steps usually include at least the following:

(1) The reactants (atoms, molecules or complexes) diffuse through the solution to the surface of the clay minerals.

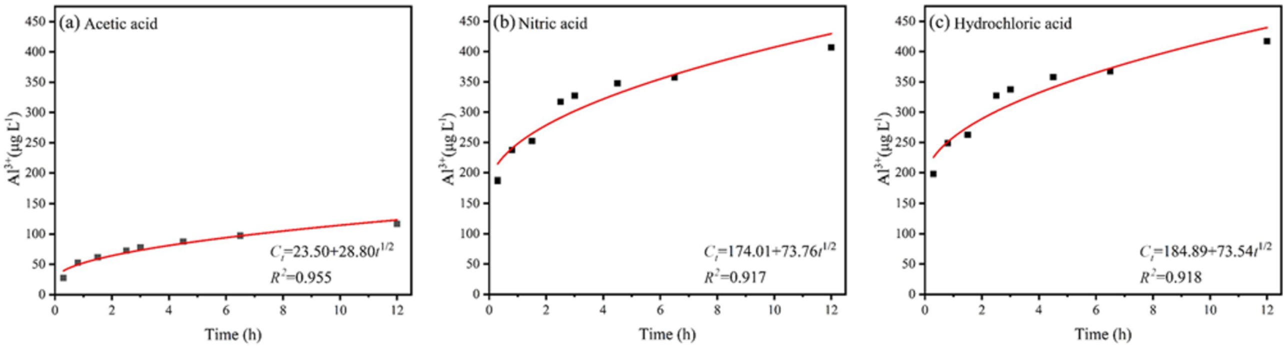

Figure 9. (a) Fitting curve for the dissolution of CATB–kaolinite in acetic acid (diffusion equation). (b) Fitting curve for the dissolution of CATB–kaolinite in nitric acid (diffusion equation). (c) Fitting curve for the dissolution of CATB–kaolinite in hydrochloric acid (diffusion equation).

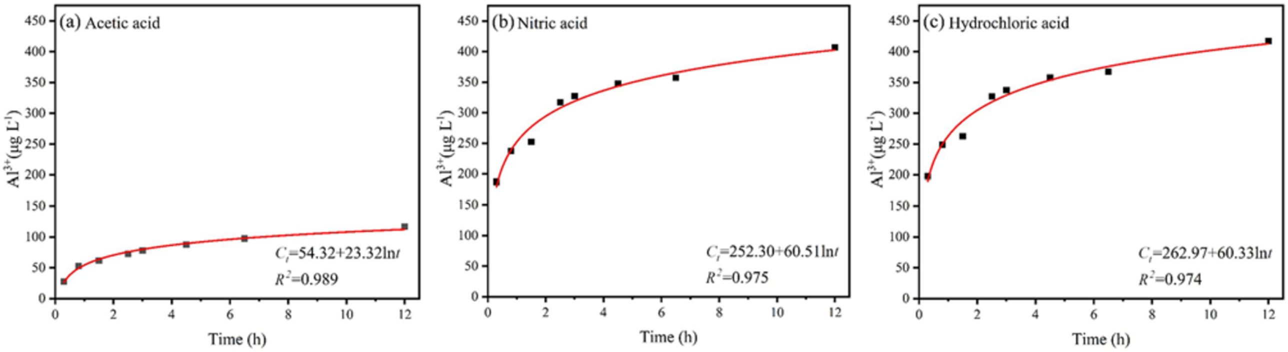

Figure 10. (a) Fitting curve for the dissolution of CATB–kaolinite in acetic acid (Elovich equation). (b) Fitting curve for the dissolution of CATB–kaolinite in nitric acid (Elovich equation). (c) Fitting curve for the dissolution of CATB–kaolinite in hydrochloric acid (Elovich equation).

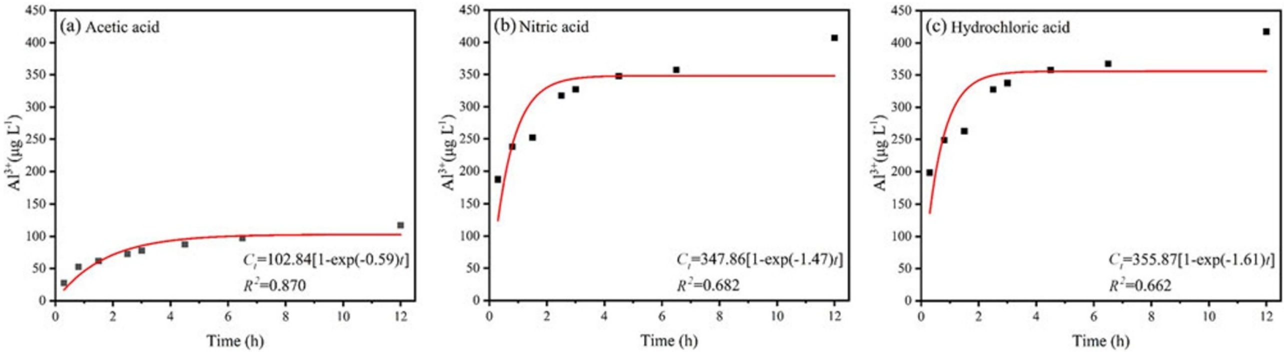

Figure 11. (a) Fitting curve for the dissolution of CATB–kaolinite in acetic acid (first-order kinetic equation). (b) Fitting curve for the dissolution of CATB–kaolinite in nitric acid (first-order kinetic equation). (c) Fitting curve for the dissolution of CATB–kaolinite in hydrochloric acid (first-order kinetic equation).

Table 2. Kinetic parameters of the Al^{3+} dissolution curve about CTAB–kaolinite under different acids.

		$C_t = a + bt^{1/2}$		$C_t = a + b\ln(t)$		$C_t = a[1 - \exp(-kt)]$	
Acid	Volume fraction, pH	b	R^2	b	R^2	k	R^2
Acetic acid	2%, pH = 2.49	28.80	0.955	23.32	0.989	0.59	0.870
Nitric acid	2%, pH = 0.84	73.76	0.917	60.51	0.975	1.47	0.682
Hydrochloric acid	2%, pH = 0.56	73.54	0.918	60.33	0.974	1.61	0.662

(2) Adsorption of reactants onto the surface of clay minerals occurs.
(3) Chemical reactions occur between the adsorbed reactants and clays, which may involve several intermediate steps, such as bond breaking and formation and ionic hydration, among others.
(4) The product diffuses from the clay surface into the solution.

Table 3. Kinetics parameters of Al^{3+} dissolution curve under different systems.

	$C_t = a + bt^{1/2}$		$C_t = a + b\ln(t)$		$C_t = a[1 - \exp(-kt)]$	
System	b	R^2	b	R^2	k	R^2
Acetic acid–kaolinite	46.03	0.971	41.58	0.995	0.32	0.987
Acetic acid–CTAB–kaolinite	28.80	0.955	23.32	0.989	0.59	0.870
Nitric acid–kaolinite	182.49	0.998	159.78	0.961	0.42	0.837
Nitric acid–CTAB–kaolinite	73.76	0.917	60.51	0.975	1.47	0.682
Hydrochloric acid–kaolinite	295.67	0.946	211.65	0.938	0.40	0.847
Hydrochloric acid–CTAB–kaolinite	73.54	0.918	60.33	0.974	1.61	0.662

One of the core concepts of reaction kinetics is that one of these steps is the slowest, and the rate of dissolution is determined by this slowest step. Step (1) and Step (2) describe the diffusion of reactants and products through the solution to and from the surface. When these processes are slowest, the reaction is considered diffusion-controlled. Steps (2)–(4) occur on a solid surface, and when one of them is a rate-control step, the reaction is called surface-controlled (Morse & Arvidson, 2002).

Upon comparing the equation fitting parameters of kaolinite and CTAB–kaolinite under experimental conditions, it was observed that, following the modification of kaolinite using CTAB, there was a significant decrease in R^2 value for the first-order kinetic equation of CTAB–kaolinite, whereas minimal changes to the R^2 values were noted for the diffusion equation and the Elovich equation (Table 3). The diffusion equation and the Elovich equation were more appropriate than the first-order kinetic equation for describing the dissolution of Al^{3+} in CTAB–kaolinite under the influence of various acids.

Furthermore, notable variations were observed in the parameters within each equation. When combined with the mineral characterization results before and after CTAB modification, it became evident that CTAB underwent electrostatic adsorption onto clay mineral surfaces, thereby reducing contact between the acid solution and the mineral surface, so inhibiting clay mineral dissolution without altering the crystal lattice structure. The modelling results show that the acidity constants of the surface hydroxyl groups varied greatly depending on their structural positions and the presence of isomorphic substitution at tetrahedral or octahedral sites. It is generally accepted that the rate-limiting step for the dissolution of aluminium silicate is the hydrolysis of Si–O–Si and Si–O–Al bonds (Rs & Svca, 2021). The inhibitory effect of CTAB on the dissolution of kaolinite is achieved through regulation of the dissolution kinetics of kaolinite. Both the dissolution of kaolinite and the adsorption of cationic surfactants occur on the surface of the minerals, and the surface diffusion of H^+ controls the dissolution rate, which theoretically verifies the feasibility of controlling the dissolution of these minerals by modifying their surface.

Effects of CTAB on the dissolution of clays

The inhibition abilities of the four cationic surfactants varied in the following order: CTAB $>$ TBAB $>$ BTAC $>$ GTA, and the inhibitory effect of CTAB was the greatest. The inhibition efficiency of surfactants can be attributed to the following causes: (1) greater electron density on the functional group leads to easier bond formation and adsorption, thus increasing the inhibitory effect; or (2) the increased length of hydrocarbon chains in surfactant molecules means larger molecules, which can shield the surface from attack (Migahed *et al.*, 2005). In addition, it is generally believed that the ability of cationic surfactants to modify minerals through wetting is related to the length of their carbon chain, and the greater the length of carbon chain, the greater the effect of wetting modification. Previous research has demonstrated that surfactants with shorter carbon chains are mainly adsorbed on clay surfaces in a vertical form, and surfactants with longer carbon chains are mainly adsorbed on clay surfaces in an inclined or flat form. This grants clays greater hydrophobicity, which can prevent H^+ in the solution from reaching the surface of kaolinite to a greater extent, thus inhibiting the dissolution of kaolinite (Li *et al.*, 2021).

The concentration of cationic surfactant also has an effect on the adsorption of surfactant: when the concentration is low, the adsorption of surfactant and kaolinite in the solution is also low and the modification of kaolinite is low. When the concentration is high, the dissolution of kaolinite will not be increased, even if the concentration of cationic surfactant is increased, because the adsorption capacity of kaolinite is limited. In addition, due to the increased amount of cationic surfactant adsorbed onto the kaolinite surface, the available active sites on kaolinite surface are reduced and the driving force of mass transfer is decreased. The cationic surfactants distributed on the kaolinite surface and the free cationic surfactants in the solution are prevented from engaging in further adsorption due to electrostatic repulsion. Under the combined action of these two causes, the inhibition trend reduces, and it can be considered that the dissolution of Al^{3+} has reached an equilibrium. Furthermore, previous studies have found that surfactants can aggregate on various surfaces to form micelles, semi-micelles and rod-like aggregates at high concentrations, which weaken the ability of cationic surfactants to ionize cations, thus rendering them unfavourable for adsorption modification (Kim *et al.*, 2021).

Temperature has little effect on the dissolution of kaolinite after CTAB adsorption. In the temperature range of 30–80°C, CTAB shows good adsorption stability on the surface of kaolinite and does not easily desorb. It can therefore prevent H^+ from contacting the surface of kaolinite. With increasing temperature, the inhibition rate decreased. This may be due to the forward dissolution reaction of kaolinite in acid solution being complete. However, it may be because the CTAB adsorbed on the surface of kaolinite tends to have a greater vibrational activity at higher temperatures, which results in greater instability of the structures formed by CTAB and kaolinite with increasing temperature, suggesting that lower temperatures would enable CTAB to inhibit the dissolution of kaolinite to a greater extent.

In addition, acid properties also affect the stability of surfactant adsorption on a clay surface. A previous study found that changes in pH and salt solution concentration can affect the stability of surfactants adsorbed on clay surfaces (Hue *et al.*, 2019). As can be seen from the change curves of the inhibition rate over time (Figs 9–11), the inhibition rate gradually decreased with increasing time, related to the adsorption stability of cationic surfactants in kaolinite. With increasing time, the cationic surfactants began to desorb from the clay surface. This increased the contact area between H^+ and kaolinite, thus accelerating the dissolution of kaolinite. The inhibition rate was reduced.

As mentioned earlier, under the action of acetic acid, nitric acid and hydrochloric acid, the diffusion equation and the Elovich equation ($R^2 > 0.900$) better described the dissolution process of Al^{3+} in CTAB–kaolinite under the action of acid than the first-order kinetic equation. Under the action of these three acids, the dissolution rate results of Al^{3+} in CTAB–kaolinite were as follows: hydrochloric acid > nitric acid > acetic acid. Hydrochloric acid and nitric acid dissolved Al^{3+} to a greater extent than acetic acid. As such, the dissolution achieved with acetic acid was relatively mild, and this fitted the diffusion equation and the Elovich equation, as did the dissolution of nitric acid and hydrochloric acid. The kinetic dissolution mechanisms of the three acids are consistent, and so the difference among acids is due to their level of acidity, leading to changes in the surface diffusion dissolution rate of H^+ and slowing down the dissolution rate of kaolinite minerals.

Conclusion

In this study, cationic surfactants were used to modify clay minerals in order to inhibit the dissolution of a clay under acidic conditions. The characterization, adsorption simulation and kinetic equation of a modified clay (CTAB–kaolinite) were studied, and the following conclusions can be drawn.

Cationic surfactants adsorb onto the mineral surface through electrostatic interaction between the head group and the charged positions. The adsorption efficiency of cationic surfactants is influenced by their molecular structure. As the concentration of surfactant in the solution increases, the amount adsorbed onto the mineral surface also increases. This leads to a transition of the mineral's surface from hydrophilic to hydrophobic, resulting in a stable cationic surfactant-modified mineral structure that inhibits kaolinite dissolution in the solution. Furthermore, temperature exerts an influence on surfactant adsorption. Dissolution kinetics studies using acetic acid, nitric acid and hydrochloric acid reveal that modified kaolinite behaves more consistently with the diffusion equation and the Elovich equation than the first-order kinetic equation when exposed to these acids. In conclusion, selecting long-chain cationic surfactants (e.g. CTAB), weak acids and low temperatures, among other conditions, is beneficial for inhibiting mineral modification and dissolution by surfactants.

Competing interests. The authors declare none.

References

Belver C., Bañares Muñoz M.A. & Vicente M.A. (2002) Chemical activation of a kaoliniteite under acid and alkaline conditions. *Chemistry of Materials*, **14**, 2033–2043.

Bergaya F., Jaber M. & Lambert J.F. (2011) Clays and clay minerals. Pp. 1–44 in: *Rubber–Clay Nanocomposites: Science, Technology, and Applications* (M. Galimberti, editor). Wiley, Hoboken, NJ, USA.

Berner R.A. (1978) Rate control of mineral dissolution under Earth surface conditions. *American Journal of Science*, **278**, 1235–1252.

Bibi I., Singh B. & Silvester E. (2014) Dissolution kinetics of soil clays in sulfuric acid solutions: ionic strength and temperature effects. *Applied Geochemistry*, **51**, 170–183.

Cama J. & Ganor J. (2015) Dissolution kinetics of clay minerals. Pp. 101–153 in: *Developments in Clay Science*, vol. 6 (C. Tournassat, C.I. Steefel, I.C. Bourg & F. Bergaya, editors). Elsevier, Amsterdam, The Netherlands.

Ganor J., Mogollón J.L & Lasaga A.C. (1995) The effect of pH on kaoliniteite dissolution rates and on activation energy. *Geochimica et Cosmochimica Acta*, **59**, 1037–1052.

Golubev S.V., Bauer A. & Pokrovsky O.S. (2006) Effect of pH and organic ligands on the kinetics of smectite dissolution at 25°C. *Geochimica et Cosmochimica Acta*, **70**, 4436–4451.

Hue K.-A.A., El-Midany A.A. & El-Shall H.E. (2019) Adsorption/desorption stability of TCMA-modified clay in simulated digestion environment. *International Journal of Environmental Research*, **13**, 879–885.

Kalam S., Abu-Khamsin S.A., Kamal M.S. & Patil S. (2021) Surfactant adsorption isotherms: a review. *ACS Omega*, **6**, 32342–32348.

Khawmee K., Suddhiprakarn A., Kheoruenromne I., Bibi I. & Singh B. (2013) Dissolution behaviour of soil kaoliniteites in acidic solutions. *Clay Minerals*, **48**, 447–461.

Köhler S.J., Dufaud F. & Oelkers E.H. (2003) An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C. *Geochimica et Cosmochimica Acta*, **67**, 3583–3594.

Li F.R., Zhang H.D. & Li C.Y. (2021) Research progress on mechanism and application of surfactant modified clay. *Zhejiang Chemical Industry*, **52**, 32–35 + 42.

Migahed M.A., Abd-El-Raouf M., Al-Sabagh A.M. & Abd-El-Bary H.M. (2005) Effectiveness of some non ionic surfactants as corrosion inhibitors for carbon steel pipelines in oil fields. *Electrochimica Acta*, **50**, 4683–4689.

Morse J.W. & Arvidson R.S. (2002). The dissolution kinetics of major sedimentary carbonate minerals. *Earth-Science Reviews*, *58*(1), 51-84. https://doi.org/10.1016/S0012-8252(01)00083-6

Nagy K.L. & Lasaga A.C. (1992) Dissolution and precipitation kinetics of gibbsite at 80°C and pH 3: the dependence on solution saturation state. *Geochimica et Cosmochimica Acta*, **56**, 3093–3111.

Rozalen M., Huertas F.J. & Brady P.V. (2009) Experimental study of the effect of pH and temperature on the kinetics of montmorillonite dissolution. *Geochimica et Cosmochimica Acta*, **73**, 3752–3766.

Rs A. & Svca B. (2021) Atomic scale mechanism of clay minerals dissolution revealed by *ab initio* simulations. *Geochimica et Cosmochimica Acta*, **293**, 438–460.

Wieland E. & Stumm W. (1992) Dissolution kinetics of kaoliniteite in acidic aqueous solutions at 25°C. *Geochimica et Cosmochimica Acta*, **56**, 3339–3355.

Yang L. & Steefel C.I. (2008) Kaoliniteite dissolution and precipitation kinetics at 22°C and pH 4. *Geochimica et Cosmochimica Acta*, **72**, 99–116.

Yin Y.M., Zhao L.L. & Gao T. (2021) Molecular adsorption and dissolution of magnesium olivine surface based on molecular dynamics. *Journal of Southeast University (Natural Science Edition)*, **51**, 121–128.

Zhao S.G., Zhong H. & Liu G. (2007) Effect of quaternary ammonium salts on flotation behavior of aluminosilicate minerals. *Journal of Central South University of Technology*, **14**, 500–503.