Physicochem. Probl. Miner. Process. 49(2), 2013, 659−672

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received April 6, 2013; reviewed; accepted April 23, 2013

EXPERIMENTAL STUDY ON ELECTROKINETIC OF KAOLINITE PARTICLES IN AQUEOUS SUSPENSIONS

Fanfei MIN, Qing ZHAO, Lingyun LIU

Anhui University of Science and Technology, School of Materials Science and Engineering, Huainan 232001, China

Abstract. Influence of aqueous phase properties and process parameters on kaolinite particle zeta potential was quantified by electrophoresis experiments. The results indicated that pH strongly altered the zeta potential of kaolinite and it decreases at the beginning and then increases in the range of pH = 2–13. The activity of different cations changes the zeta potential and has the following tendency of $Al^{3+} > Ca^{2+} > Mg^{2+} > Na^{+}$ and the zeta potential increases due to heterocoagulation of different mineral particles in suspension. It was found that the zeta potential of kaolinite particles increases after the suspension was stirred and decreases at the beginning, and then increases with soaking time. The FTIR results showed that the zeta potential takes into account ion adsorption and the change of Si–O, Al–O and Al–OH groups on the surface of the kaolinite particles.

Keywords: *kaolinite, zeta potential, pH, immersion time, electrophoresis*

Introduction

In recent years, with the improvement of coal mining mechanization degree and geological conditions change, a lot of reject enters coal and increases ash in raw coals in China. The raw coal which includes much reject will produce a lot of slimes in water of the coal washing process. The slime contains a considerable amount of ultrafine particles such as clay particles. The removal of ultrafine particles from the slurries is usually slow and incomplete because the colloidal particles are extremely small（Zbik et al., 2008). In addition, the surfaces of these colloids usually have the same charge, which causes repulsion forces and prevents aggregation. Investigations showed that kaolinite particles, which are one of the predominant minerals in coal slime, are commonly generated in mineral processing at neutral to high pH and they are always charged negative in the process water. The kaolinite particles tend to form stable dispersions with poor dewatering characteristics (Kihc and Hosten, 2010) .

http://dx.doi.org/10.5277/ppmp130225

Dai et al. (2010) found that the zeta potential of the mixed metal layered hydroxide-kaolinite suspension system decreased with increasing pH values. Yang and Fan (2010) have shown that ferric-polysilicate can change the zeta potential of kaolin from negative to positive and polymers of ferric-polysilicate ion in polysilicate iron has a strong neutralize effect with its positive charge. Gan and Liu (2008) reported that kaolinite carried negative charges in the entire pH range tested from 3 to 12. The zeta potential increased in the negative direction with increasing pH from 4 to 8 and stabilized at about –50 mV above pH 8. The zeta potential of kaolinite in the presence of Ca^{2+} became much less negatively charged between pH 6 and 12. The zeta potential of kaolinite in the presence of Mg^{2+} closely followed that in Ca^{2+} solutions from pH 6 to 10. However, above pH 10, the zeta potential increased sharply and reached zero at pH 10.4, then moved into positive region. Hou *et al.* (2010) have studied interaction of the diffuse layers of electric double layer between negatively charged kaolinite particle and positively charged particles of goethite, gibbsite, hematite and found the interaction of the diffuse layers increases with the increase in the ratio of kaolinite to Fe/Al oxides and decreases with the rise of system pH. Electrokinetic studies, mostly in terms of electrophoretic mobility measurements (some electroacoustic or dielectric spectroscopy measurements have also been performed), have been done for kaolinite (Williams,1978; Smith and Narimatsu,1993; Hussain et al., 1996; Chassagne et al., 2009; Alkan et al., 2005; Rao et al., 2011; Duman et al., 2012) .

From the forgoing review, it can be seen that the surface electric potential characteristics of kaolinite particles in single mineral system has been studied extensively. Few studies investigated the effects of different mineral particles and process operating conditions on zeta potential of kaolinite particles in the coal slime water. The major objectives of this study are to investigate the difference of zeta potential between the single system of kaolinite and the binary systems containing kaolinite and coal or quartz, and to discuss the effects of stirring intensity, immersion time, pH, electrolyte and mineral on the change of kaolinite particles zeta potential.

Materials and methods

Minerals and chemicals

The coal-associated kaolinite sample was supplied by Huainan Mining Industry Co..Ltd., Huainan, China, which was used for zeta potential measurements. Chemical analysis and X-ray diffraction indicated that the kaolinite sample contained about 87% kaolinite and 10% quartz (see Fig. 1). The FTIR analysis of the sample (see Fig. 2) shows that 3698 cm^{-1}, 3617 cm^{-1} is –OH stretching vibration, 1200 to 1000 cm^{-1} the Si–O stretching vibration; 1000 to 900 cm^{-1} the Al-OH bending vibration; the majority of absorption peaks of 500 ~ 400 cm^{-1} the vibration of Si–O or Al–O on the surface of the sample. Particle size analysis by SALD-7101 (Shimadzu Corporation, Japan) showed that the sample particle size is less than 5 μm and the average particle size is 0.74 μm.

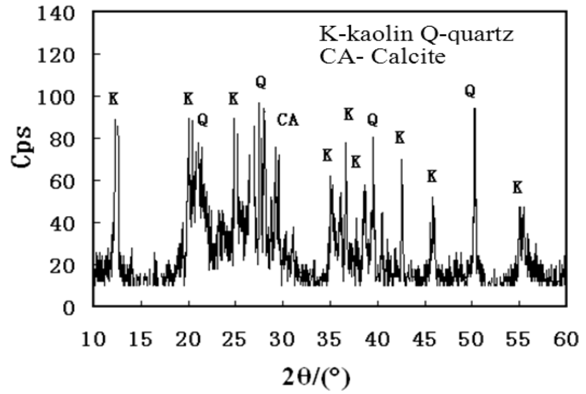

Fig. 1. XRD trace of kaolinite

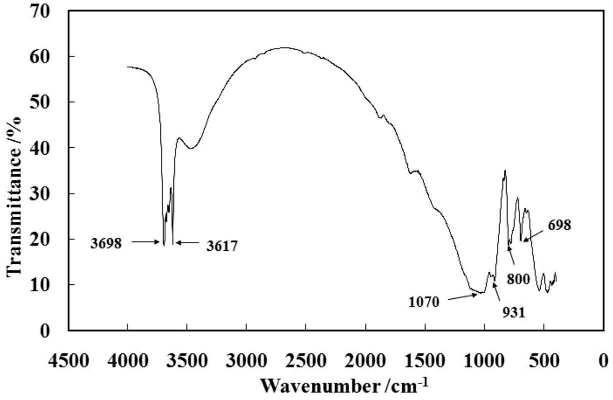

Fig.2. The FTIR spectra of kaolinite

The bituminous coal sample was provided by Huainan Mining Industry Co. Ltd., Huainan, China. The bituminous coal sample was crushed to less than 75 μm. The results of bituminous coal sample proximate analysis in air dry basis are moisture 2.15%, ash 8.33%, volatile matter 29.30%, fixed carbon 60.22%. The bituminous coal sample was mixed with kaolinite sample for zeta potential measurements.

The quartz sample was purchased from sub-Sheng Chemical Co. Ltd., Wuxi, China. The diameter of the quartz particles is less than 110.00 μm with a median diameter (d_{50}) of 49.98 μm. The quartz sample was mixed with kaolinite sample for zeta potential measurements.

The chemicals used in this study were certified A.C.S. grade reagents and purchased from Shanghai Reagent Company, Shanghai, China. NaCl (>99%), $CaCl_2$ (>99%), $MgCl_2$ (>98%), and $AlCl_3$ (>98%) were used as sources of Na^+, Ca^{2+}, Mg^{2+} and Al^{3+}. NaOH (99.0%) and HCl (36.5–38%, solution) were used as pH regulators. All solutions used in this study were prepared using distilled water made by a glass still.

Experimental methods

Preparation of stock suspensions for zeta potential measurement

Stock suspension of kaolinite was prepared by dispersing 20 g of the kaolinite sample in 1 dm^3 of deionized water. For the binary colloid suspensions, kaolinite/coal or kaolinite/quartz were placed in the same container according to their different quantitative ratio. The suspension was mildly stirred with a agitator (JJ-1, made in China) at 300 rev/min for 10 min at 25 ºC. The pH of the suspension was controlled at 7.0 adjusted with HCl or NaOH. Next, the suspensions were equilibrated for another 30 min before zeta potential determination.

Determination of zeta potential

The zeta potential of the kaolinite and other samples were measured at 25±0.5 ºC with a JS94G + micro-electrophoresis apparatus made in China. The zeta potential for each sample was determined by taking the average of 6 runs. The standard deviation for the 6 runs was within ±3 mV. The colloid suspension was agitated and transferred to the electrophoresis vessel after wetting the electrode to avoid any disturbance due to air bubble. The values of zeta potential were calculated using the computer with the specific software.

Other measurements

The different types of functional groups on kaolinite samples were identified by the Fourier Transform Infrared (FTIR) Spectroscopy in the range of 4000–400 cm^{-1}. BRUKER Vector33 was employed to study the infrared spectroscopy of the sample. The samples were first dried at 50 ºC and mixed with KBr and then pressed into pellets which contained approximately 0.5 wt. % samples.

In X-ray diffraction analysis (XRD) a Rigaku's D/Max-3B XRD X-ray spectrometer diffractometer was used. All the analyses were done using Cu Kα radiation with Cu/Ni electrodes and goniometer speed of 2°/min, sampling interval: 0.02°. X-Ray Diffraction (XRD) allows identification and quantification of unknown phases in a mixture by using search/match software.

Results and discussion

The effect of agitation on zeta potential of kaolinite particle surface

Zeta potentials of kaolinite at different agitating speeds were presented in Fig. 3a. The infrared spectroscopy results of kaolinite samples agitated at different speeds were shown in Fig. 3b.

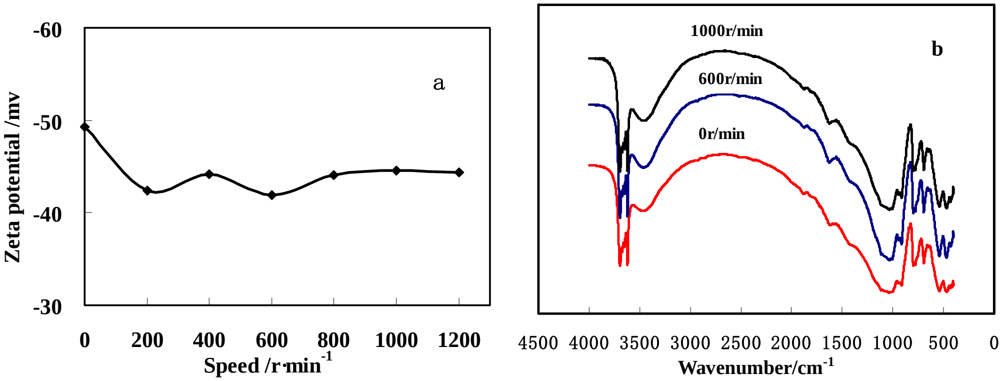

Fig. 3. Zeta potential (a) and FTIR spectra (b) of kaolinite at different agitating speeds

It can be seen from Fig. 3a that as the agitating speed increases the absolute value of zeta potential of kaolinite particles surface first decreases, then slightly increases and when agitating speed reaches 800 rpm, the zeta potentials get stability around –44 mV. At low agitating speed, some metal cations, such as Ca^{2+}, Mg^{2+} and other cations dissolute from kaolinite samples (see Table 1), and these cations will be adsorbed on the negatively charged surface of kaolinite particles, the multivalent metal cations would theoretically reduce the thickness of the electric double layers of kaolinite (edges) and the reduced electric double layer thickness means that the zeta potential of the particles would be lower and lead to lower electrostatic repulsion. As the agitating speed increases, the kaolinite particles turns into fine particles, which leads to producing a number of new breaking bonds of Al–O and Si–O negatively charged on the particle surface, so the absolute value of the zeta potential of kaolinite particles surface increases. As can be seen from Fig. 3b that the intensity of –OH stretching vibration in 3698 cm^{-1}, 3617 cm^{-1} and Al–OH bending vibration in 1000 to 900 cm^{-1} increases with the agitating speed increases. The results indicate that there are a certain number of Si–OH and Al–OH generated on fine kaolinite particles surface which is caused by Al–O and Si–O bond adsorption of H^+ (Yang et al., 2001).

Table 1. Ion composition of kaolinite suspensions

Ions	Ca^{2+}	Mg^{2+}	Na^{+}+K^{+}	Cl^{-}	SO_4^{2-}	CO_3^{2-}	HCO_3^{-}
Concentration, mg/dm^3	12.02	1.21	55.00	62.03	7.20	0.00	61.02

The effect of pH value on zeta potential of kaolinite particle surface

pH is an important factor influencing the zeta potential value of kaolinite. The effect of pH value on the zeta potential of kaolinite is shown in Fig. 5a. It can be seen that the absolute value of zeta potential gradually increases and reaches its maximum at pH 8 and then tends to decrease with the pH value increasing. It agrees with the result gotten of Gans and Liu (2008). The isoelectric point is a pH value at which the total amount of positive charge on the surface of solid is equal to the total amount of negative charge on it. The amount of net surface charge of solid or zeta potential value is zero at the isoelectric point. The isoelectric point is a characteristic property of solid particles. Therefore, it is important to know the isoelectric point of clay and surface charge of the clay particles for the adsorption or flotation processes (Duman et al., 2012). Figure 5a shows that kaolinite has no isoelectric point in range of 2–13 pH value, which indicates that the isoelectric point of kaolinite is lower than pH 2. The result is agreement with the result gotten by Duman et al. (2012) and Yang et al. (2001), which is lower than the literature value (Hu and Liu, 2003; Alkan et al., 2005). The low isoelectric point of kaolinite may be because the sample is coal-associated kaolinite containing quartz and other minerals. Besides, the number of solid particles facilitate the surface charge generation by producing the ionic species at the solid/liquid interface, kaolinite concentration in the suspension and this also can affect the zeta potential value of the suspension (Tunc and Duman, 2008).

The absolute values of kaolinite zeta potential in colloid suspensions are the largest when the pH value reaches about 8. The pH value of coal slurry is usually about 8, so the negativity of slime kaolinite particles surface is the largest, which causes repulsion forces and prevents aggregation.

Kaolinite is a 1:1 layer mineral, in which one layer consists of an alumina octahedral sheet (termed as O-face) and another consists of silica tetrahedral sheet (termed as T-face), as shown in Fig. 4. The two layers share a common plane of oxygen atoms, and the repeating layers are bound together by hydrogen bonds between hydroxyl groups of O-face and the highly electronegative oxygen of the T-face (Ma and Eggleton, 1999). It is an acceptable fact that the isomorphic substitution in the tetrahedral sheet results in permanent negative charges at the T-face (which is pH-independent), and the protonation/deprotonation of the silanol and aluminol groups at the edges leads to the results that surface charges vary with the medium (which is pH-dependent). The O-faces behave the same characteristics of surface charges as the edges, as reported elsewhere (Tombacz and Szekeres, 2006).

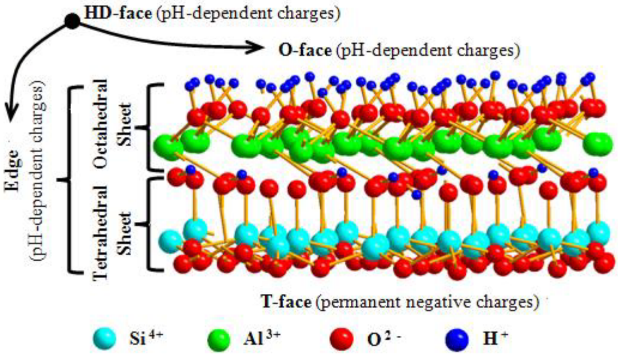

Fig. 4. Molecular structure of kaolinite layer

Kaolinite splits easily along the level parallel direction, and produces a number of negatively charged breaking bonds of Al–O and Si–O bond on the particle surface. The particle surface easily forms large number of Al–OH and Si–OH groups. As it is known, the surface charges of oxide mineral particles are originated from the protonation and deprotonation of the surfaces as follows:

$$\text{M–OH} + \text{H}^+ \rightarrow \text{M–OH}_2^+$$

$$\text{M–OH} + \text{OH}^- \rightarrow \text{M–O}^-$$

where M represents metal, such as Al and Si in this case. At low pHs, the protonation of the surfaces leads to be positively charged, while at high pHs the deprotonation results in negative charges. The value of the surface charge on oxide minerals (or zeta potential) closely correlates with pH value of the mineral suspension. It will affect the surface charge density or electric potential (Yin et al., 2006). In acidic medium, H^+ and the particle surface-OH can have neutralization reaction to compress particle surface electric double layer, so the absolute value of zeta potential with the acidic enhancement becomes smaller and smaller. In alkaline medium, due to complexation reactions, the particle surface have a large number of OH^- to make particle surface charge negatively, so the electronegativity of kaolin particles surface increases.

Figure 5b shows that when pH is neutral or acidic, the stretching vibration intensity of -OH in the range of 3700～3600 cm^{-1} is stronger, which indicates that there are a large number of –OH groups generated on kaolinite particle surface in acidic and neutral aqueous media. When the pH value is about 13, the stretching vibration intensity of –OH in the range of 3700～3600 cm^{-1} weaken, and the stretching vibration intensity of Al–O and Si–O bonds is significantly enhanced, which shows

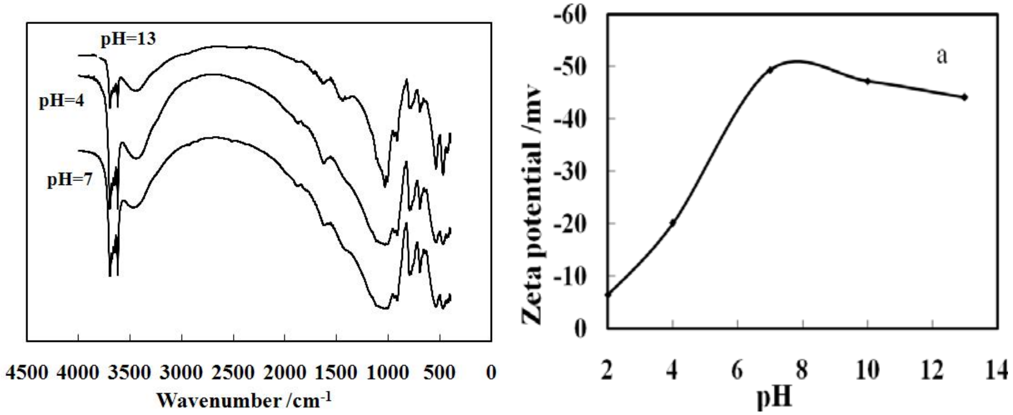

Fig. 5. Zeta potential (a) and FTIR spectra (b) of kaolinite at different pH values

that the –OH on particle surface has complexation reactions with the –OH in alkaline medium to increase the electronegativity of kaolin particles surface. However, when pH value is larger than 8, the absolute values of zeta potential trend to decrease. The DLVO theory (Hu et al., 2001) shows that the excess NaOH added to the solution to adjust the pH has increased the concentration of ions in the solution, and these ions compress particle surface electric double layer leading to reducing the potential value of the particle surface.

The effect of immersion time on zeta potential of kaolinite particle surface

Zeta potentials of kaolinite at different immersion times are presented in Fig. 6a. The infrared spectroscopy results of kaolinite samples soaked in different time are shown in Fig. 6b.

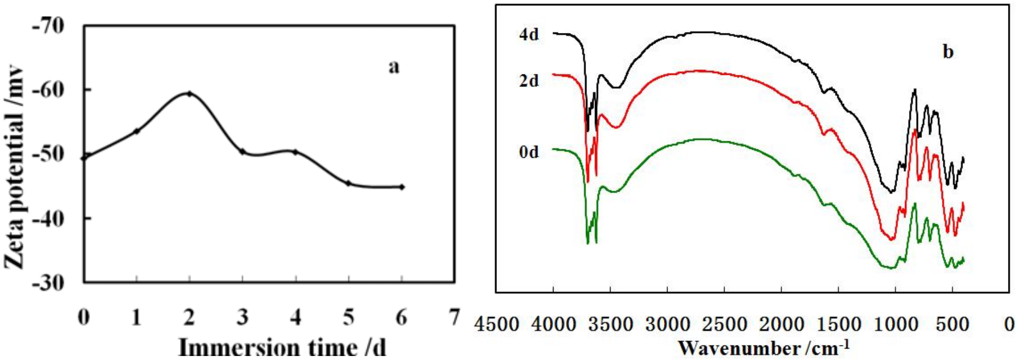

Fig. 6. Zeta potential (a) and FTIR spectra (b) of kaolinit with different immersion times

As shown in Fig. 6a, the absolute value of zeta potential increases with immersion time prolonging and the absolute value reaches the maximum 59.37 mV in the second day, and then the zeta potential absolute value gradually decreases with the extension of immersion time. Water will gradually undermine the cohesiveness between the mineral particles of kaolinite in saturated state and enter the pores between the chip-shaped particles resulting in uneven inner-stress and a lot of micropores in mudstone and induce softening and degradation (Huang and Che, 2007). Kaolinite breaks into fine particles within a certain immersion time which would produce new bonds of $–SiO^-$ and $–AlO^-$. With the further extension of the immersion time, some salts mixed internally in particles more easily dissolve into the solution along with ionization of Ca^{2+} and Mg^{2+} and other cations. The adsorption of these cations onto the the $–SiO^-$ or $–AlO^-$ groups on the surface of kaolinite will compress particle surface electric double layer to reduce the potential value of the kaolin particle surface. Duman et al. (2012) reported that the adsorption of H^+ ions in water onto the negatively charged kaolinite surface leads to increasing pH value.

Figure 6 b shows that the stretching vibration intensity of -OH group in the range of 3700–3600 cm^{-1} is stronger when the soaking time is 2 days. The stretching vibration intensity of –OH in the range of 3700–3600 cm^{-1} will weaken after the kaolinite sample soaked for 4 days.

The effect of cation on zeta potential of kaolinite particle surface

The zeta potentials of kaolinite at pH 7 as a function of Ca^{2+} concentration are shown in Fig. 7a. The zeta potentials of kaolinite at pH 7 in the presence of 86 mg/dm^3 multivalent metal cations (0.00374 mol/dm^3 Na^+, 0.00215 mol/dm^3 Ca^{2+}, 0.00358 mol/dm^3 Mg^{2+} or 0.00319 mol/dm^3 Al^{3+}) were measured and results are presented in Fig. 7b.

As can be seen from Fig. 7a, with Ca^{2+} concentration increasing, the absolute value of the surface zeta potentials of kaolinite gradually decrease. When Ca^{2+} concentration reaches 0.00215 mol/dm^3, the absolute value of zeta potential is decreased by 51.66%, and then tends to balance, the absolute value of zeta potential does not change significantly. This proofs that the adsorption of Ca^{2+} to kaolinite particle tends to be stability and saturation (Zhang et al., 2011). It can be seen from Fig. 7b that the zeta potential absolute value decreases with the increase of metal cationic valence.

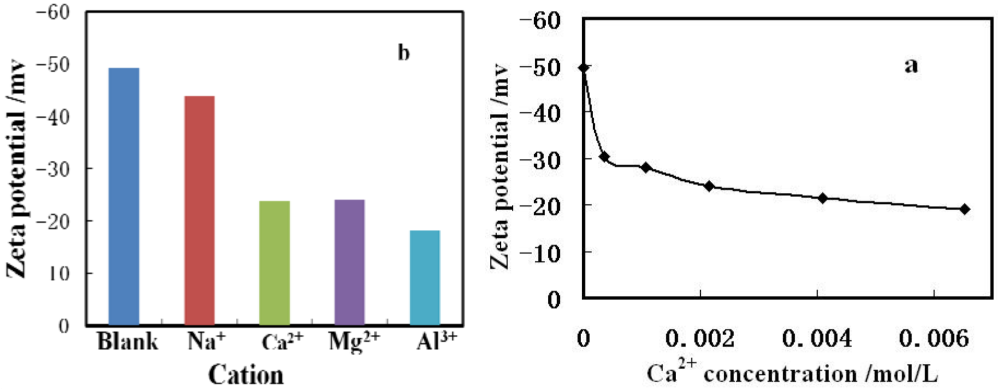

Fig.7 Zeta potential of kaolinite in the presence of Na^+,Ca^{2+}, Mg^{2+}, Al^{3+}

The strong zeta potential change in the presence of the metal ions was likely due to two reasons. The first was the compression of the electrical double layer by the multivalent metal cations. Taking Mg^{2+} as an example, the addition of 10^{-3} mol/dm^3 divalent Mg^{2+} cations would theoretically reduce the thickness of the electric double layers of kaolinite from 9.6 nm (with 10^{-3} mol/ dm^3 KCl as supporting electrolyte) to 5.6 nm (Gan and Liu, 2008; Zhang et al., 2008; Wang and Hu, 1988). If the surface potential is unchanged, the reduced electric double layer thickness means that the zeta potential of the particles would be lower. The second was the hydrolysis and adsorption of the metal-hydroxyl species on kaolinite. At above pH 8, these metal cations were hydrolyzed. The positively charged hydrolyzed species such as $CaOH^+$,

$MgOH^+$, and $AlOH^{2+}$ could adsorb on the deprotonated surface kaolinite edges. This "charge-neutralization" effect of the multivalent metal ions has been widely reported in water treatment (Duman et al., 2012; Gan and Liu, 2008). The high valence cation has more positive charge under the same concentration conditions. Its compression capacity to the particle surface electric double layer is stronger, and for the unit positive charge, Ca^{2+} and Mg^{2+} have greater impact than Al^{3+} on the electric potential of kaolin particle surface. The Ca^{2+} has better compression capacity to the particle surface electric double layer, so the absolute value of the zeta potential decreases more, which relates to their different capacity of adsorption to the surface of kaolin particles.

Change of zeta potential and interaction between kaolinite particles and other mineral particles

Figure 8 shows the comparison of the zeta potential at pH 7 between the single system of kaolinite (named K) or quartz (named Q) and the binary-system with different quantitative ratio of kaolinite to bitumen.

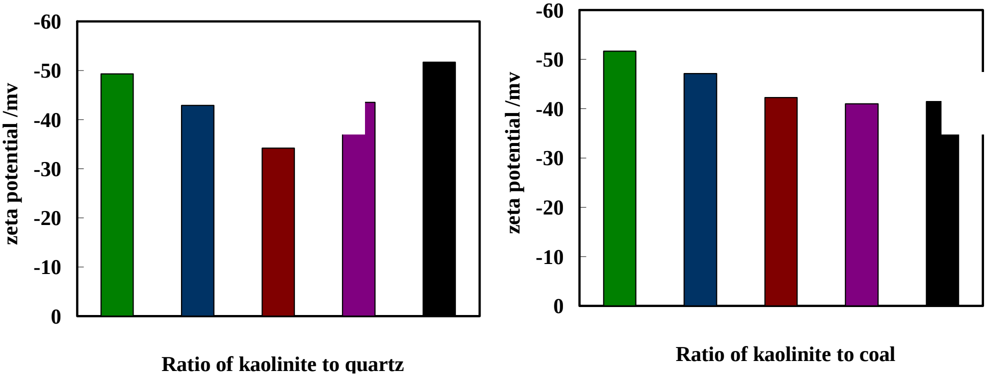

Fig. 8. Zeta potential curves in single systems of kaolinite and quartz (a) and coal and binary systems containing kaolinite and quartz or kaolinite and bitumen (b)

It can be seen that the absolute value of zeta potential in binary-system was lower than that in single kaolinite or quartz system, when the ratio of kaolinite to quartz is about 1:1. The absolute value of the surface potential of binary-system reaches the minimum, which suggested that the presence of quartz decreased the absolute value of zeta potential of the binary-system containing kaolinite and quartz. When kaolinite and quartz exist simultaneously in the same colloid suspension system, the electrostatic attraction makes the particle of kaolinite close to the particle of quartz, the interaction of the diffuse layers on oppositely charged particles decreases the value of effective charge density on kaolinite and quartz, and thus the zeta potential in the mixed charge system moves to the positive value side compared to the single kaolinite system (Hou et al., 2007; Lu and Hon, 1992; Gupta et al., 2011). In addition, the average particle size of the quartz samples used in the test is approximately 48.264 μm, the average particle size of kaolinite samples is about 0.735 μm. Since the large difference between the two samples particle size, both of them are prone to mutual coagulation, in which the kaolinite particle owning the size of less than 1μm tend to coagulate. The quartz particles which size is larger than 1μm tend to participate in mutual coagulation (Lu and Hon, 1992; Gupta et al., 2011).

In a slightly acidic solution, the kaolinite edge is positively charged through protonation of surface hydroxyl groups. On the other hand, bituminous coal particles are a mixture of hydrocarbons containing carboxylic and phenolic groups. These groups exposed to the aqueous phase are ionized at basic pH and thus carry negative charges (Gan and Liu, 2008). Thus, the kaolinite particles and bituminous coal particles can interact with negatively charged coal particles droplets through electrostatic attraction, which induced the absolute value of zeta potential decrease.

The surface interaction mechanism of mixed mineral particles can be analyzed using the classical DLVO theory. The general formula of total energy (V_T) between the mineral particles can be expressed (Tombacz and Szekeres, 2006) as:

$$V_T = V_R + V_A \tag{1}$$

where V_T is the total energy, V_R and V_A are the electrostatic and van der Waals energy between the particles. The potential energy of the electrical double layer interaction between two homogeneous spheres can be expressed (Rao et al., 2011; Duman et al., 2012) by:

$$V_R = \left(\frac{\pi \varepsilon_a r_1 r_2}{r_1 + r_2}\right)\left(\psi_{01}^2 + \psi_{02}^2\right)\left(\frac{2\psi_{01}\psi_{02}}{\psi_{01}^2 + \psi_{02}^2} p + q\right) \tag{2}$$

where r_1 and r_2 are the radius of kaolinite and quartz particles, ε_a the permittivity, ψ_{01} and ψ_{02} outer Helmholtz plane (OHP) potential or zeta potential of kaolinite and quartz particles, p and q can be expressed (Rao et al., 2011 ; Duman et al., 2012) by:

$$p = \ln \frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \tag{3}$$

$$q = \ln\left[1 - \exp(-2\kappa h)\right] \tag{4}$$

where h is the shortest separation between two particles and κ the Debye reciprocal length, which is given (Tombacz and Szekeres, 2006) by:

$$\kappa^2 = 1000 e^2 N_A / \varepsilon k_B T \sum\nolimits_i z_i^2 M_i \tag{5}$$

where N_A is the Avogadro's number, Z_i and M_i are the valence of and the molar concentration of ions I, k_B the Boltzmann constant, T absolute temperature, e the elementary charge, Z the valence of determining ion;

The van der Waals interaction between two homogeneous particles is expressed (Rao et al., 2011; Duman et al., 2012) by:

$$V_A = -\frac{A_{132}}{6h}\left(\frac{r_1 r_2}{r_1 + r_2}\right) \tag{6}$$

where A_{132} is the Hamaker constant of particles 1and particles 2 in medium 3, which may be obtained (Rao *et al.*, 2011; Duman *et al.*, 2012) by:

$$A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right) \tag{7}$$

where A_{11} , $A_{22}$and A_{33} are the Hamaker constants of particles 1, particles 2 and medium 3 in vacuum, respectively.

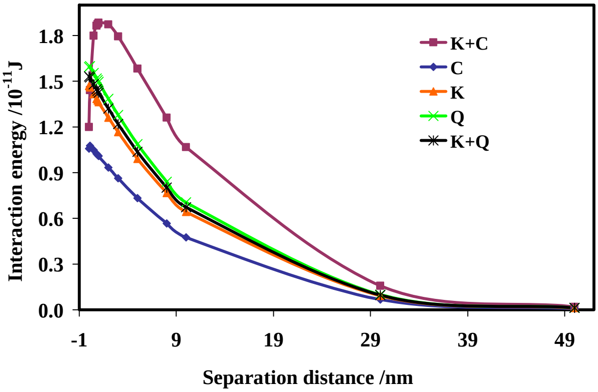

Fig. 9. Interaction energy profiles for different surface interactions of kaolinite and other mineral particles

Based on the DLVO theory, the total potential energy of interaction between particles in aqueous solutions as a function of distance between the particles was calculated. The results are presented in Fig. 9.

As can be seen, the interaction energy between the particles of different mineral is repulsive at the pH 7 due to the strong electrostatic repulsion between negatively charged particles faces. The repulsion order is as follows: (K+C) (repulsion between kaolinite and coal particles) > Q (repulsion between quartz particles) > (K + Q) (repulsion between quartz and kaolinite particles) > K(repulsion between kaolinite particles) > C(repulsion between coal particles). However, the order of the absolute value of the mineral particle surface zeta potential is $\text{zeta}_Q > \text{zeta}_K > \text{zeta}_{(K+C)} > \text{zeta}_C > \text{zeta}_{(K+Q)}$, and the result is vary with the classical DLVO theory, which may be the reason why the particles tend to occur mutual coagulation phenomen to cause the repulsion energy between the particles has been reduced.

It can be seen from Fig. 3a that as the agitating speed increases, the absolute value of zeta potential of kaolinite particles surface first decreases.

Conclusions

The absolute value of zeta potential reaches its maximum and then tends to decrease with increasing immersion time. With the pH value increasing, the absolute value of zeta potential gradually increases and reaches its maximum at pH 8. No isoelectric point was found in the experimental range of 2–13 pH value, which may be because the sample contains other heterogeneities and kaolinite suspension concentration also can affect the zeta potential value of the suspension.

The order of the ability to reduce the zeta potential of kaolin particles surface under the conditions of the different valences of cations in the same concentration is that $Al^{3+} > Ca^{2+} > Mg^{2+} > Na^{+}$.

The suspension particle surface ion adsorption and the change of surface bonds of Si–O, Al–O and Al–OH are the underlying reasons to change surface zeta potential of kaolin suspension particle.

The repulsion of different mineral particles in the mixed suspension liquid of kaolinite with quartz and coal is in dominant position, and that the existence of mutual coagulation role in the different mineral particles makes the absolute value of the zeta potential of the particle surface to reduce.

Acknowledgements

The financial supports for this work from the Natural Science Foundation of China under the grant No. 51174006, 51210105004, the Anhui Provincial Natural Science Foundation of China under the grant No.11040606M121 and Anhui Provincial Science and Technology Profect No.1106b0105063 are gratefully acknowledged.

References

ALKAN M., DEMIRBAS Ö., DOĞAN M., 2005. *Electrokinetic properties of kaolinite in mono-and multivalent electrolyte solutions*. Micropor. and Mesopor. Mat. 83, 51–59.

CHASSAGNE C., MIETTA F., WINTERWERP J.C., 2009. *Electrokinetic study of kaolinite suspensions*. J. Colloid Interf. Sci. 336, 352–359.

DAI X.N., WANG X.F., 2002. *Effect of pH on the zeta potential of MMH-kaolinite suspentions*. J. Dezhou College. 18,42–45.

DUMAN O., TUNC S., CETINKAYA A., 2012. *Electrokinetic and rheological properties of kaolinite inpoly(diallyldimethylammonium chloride), poly(sodium 4-styrene sulfonate) and poly(vinyl alcohol) solutions.* Colloids and Surfaces A: Physicochem. Eng. Aspects. 394, 23-32.

GAN W. B., LIU Q., 2008. *Coagulation of bitumen with kaolinite in aqueous solutions containing Ca2+,Mg2+ and Fe3+: Effect of citric acid*. J. Colloid Interf. Sci.. 324, 85–91.

GUPTA V., HAMPTON M. A., STOKES J. R., 2011. *Particle interactions in kaolinite suspensions and corresponding aggregate structures*. J. Colloid Interf. Sci. 358, 95–103.

HOU T., XU R. K., ZHAO A. Z.,2007. I*nteraction between electric double layers of kaolinite and Fe/Al oxides in suspensions*. Colloids and Surfaces A: Physicochem. Eng. Aspects. 297(2007), 91–94.

HU H. M., CHEN X. Z., WANG Y., 2001. *The application of dynamic potential in determining the coal dressing wastewater*. Enviro. Protect. Sci. 104, 14–15.

HU Y., LIU X., 2003. *Chemical composition and surface property of kaolins*. Miner. Eng. 8, 1279–1284.

HUANG H.W., CHE P., 2007. *Research on micro-mechanism of softening and argillitization of mudstone*. J. Tongji Univ. 35, 866–870.

HUSSAIN S. A., DEMIRCI S., ÖZBAYOĞLU G., 1996. *Zeta potential measurements on three clays from Turkey and effects of clays on coal flotation*. J. Colloid Interf. Sci. 184, 535–541.

KIHC M.G., HOSTEN C., 2010. *A comparative study of electrocoagulation and coagulation of aqueous suspensions of kaolinite powders*. J. Hazard. Mater. 176, 735–740.

LU S. C., HON D., 1992. *Interface separation principle and application*. Beijing: Metallurgical Industry Press.

MA C., EGGLETON R. A., 1999. *Surface layer types of kaolinite: a high resolution transmission electron microscope study*. Clays Clay Miner. 47, 181–191.

RAO F., RAMIREZ-ACOSTA F. J., SANCHEZ-LEIJA R. J., SONG S.X., LOPEZ-VALDIVIESO A., 2011. *Stability of kaolinite dispersions in the presence of sodium and aluminum ions*. Appl. Clay Sci. 51, 38–42.

SMITH R.W., NARIMATSU Y., 1993. *Electrokinetic behavior of kaolinite in surfactant solutions as measured by both the microelectrophoresis and streaming potential methods*. Miner. Eng., 7, 753–763.

TOMBACZ E., SZEKERES M., 2006. *Surface charge heterogeneity of kaolinite in aqueous suspension in comparison with montmorillonite.* Appl Clay Sci. 34, 105–124.

TUNC S., DUMAN O., 2008. *The effect of different molecular weight of poly(ethylene glycol) on the electrokinetic and rheological properties of Na–bentonite suspensions*. Colloids Surf. A. 317,93–99.

WANG, D. Z., HU Y. H.,1988. *Flotation solution chemistry*. Changsha: Hunan Science and Technology Press.

WILLIAMS D. J. A., WILLIAMS K. P., 1978. *Electrophoresis and zetapotential of kaolinite*. J. Colloid Interf. Sci. 65, 9–87.

YANG H.L., FAN M.Q., 2010. *Relationship between iron consumption, silicon consumption and flocculation characteristics of PFS*. J. Enviro. Eng. 4, 2789–2792.

YANG S. J., SHEN Z. Y., YING Y. Y., 2001. *Distribution of electric charge on crystalline grain surface of kaolinite and its industrial significance.* Non-Metal. Miner. 24, 196–198.

YIN H. R., WU L. H., FU F. C., 2006. *Research and application of nano-kaolin*. Mater. Rev. 20, 196–199.

ZBIK M.S., SMART R.S.C., MORRIS G.E., 2008. *Kaolinite flocculation structure*. J. Colloid Interface Sci. 328, 73–80.

ZHANG M. Q., LIU J. T., WANG Y. T., 2008. *Effects of water hardness on the dispersion of fine coal and kaolinite in coal slurry*. J. China Coal Soci. 9, 1058–1062.

ZHANG Z. J., LIU J.T., FENG L., 2011. *A prediction model based on langmuir theory for equilibrium adsorption amount*. J. Northeastern Univ. 32, 749–756.