



Stability of kaolinite dispersions in the presence of sodium and aluminum ions

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ABSTRACT

The stability of colloidal kaolinite dispersions in the presence of NaCl and AlCl₃ was studied by measuring turbidity, electrophoretic mobility and adsorption. The kaolinite particles coagulated at pH 2.5–3.5 and were dispersed at pH >4.5. These results well obeyed the classic DLVO theory if the mean zeta potential of the kaolinite particles in aqueous solutions was taken into account in the computation of potential energy of electrical double layer repulsion, which suggests that the kaolinite particles might coagulate in the same way as normal colloidal particles. The kaolinite particles in aqueous aluminum salt solution only coagulated at a medium AlCl₃ concentration, and formed a stable dispersion at a high salt concentration. This is caused by Stern-layer adsorption of hydrolyzed aluminum species, probably adsorbed on the kaolinite surfaces through hydrogen bonds between the hydroxyl groups of the aluminum species and the oxygen atoms on the kaolinite surfaces.

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1. Introduction

Kaolinite particles consist of about 50 silicate layers, which are held together by hydrogen bonds and van der Waals interaction. Each layer is composed of a tetrahedral SiO₄ sheet and an octahedral sheet containing Al³⁺ ion. The kaolinite particles are plate-like and the aspect ratio (particle diameter/particle thickness) is about 5–15 (Solomon and Hawthorne, 1983). Similar to other clay minerals, they are of colloidal particle size (<2 μm) (Bergaya et al., 2006). The layers are composed of edges and faces, which are characterized by different electrokinetic properties, making the interpretation of stable aqueous dispersions complicated (Lagaly, 1989; Aurell and Wistrom, 2000; Wypych and Satyanarayana, 2004; Lagaly, 2006).

Kaolinite is applied in many areas, such as myths, art, medicine, agriculture, construction, environmental engineering, mineral processing and biological engineering. It is an important functional material for paper, paint and plastics, and is also a catalyst support in the chemical industry, as well as an adsorbent for heavy metal ions (Bhattacharyya and Gupta, 2008) and organic and biological compounds (Okada et al., 2005). In many cases, the stability of aqueous kaolinite dispersions is a decisive factor. For instance, in mineral concentration, fine kaolinite particles had to be well stabilized (dispersed) in aqueous dispersions (Johnson et al., 1999). In water treatment, fine kaolinite particles had to be coagulated (Murray, 2000). In paper industry, the exact tuning of the rheological properties of highly concentrated kaolinite slurries is needed, which depends on the stability of the aqueous kaolinite dispersions (Murray et al., 1993).

There were numerous studies on the stability of aqueous clay mineral dispersions (Swartzen-Allen and Matijevic, 1976; Chow, 1991; Penner and Lagaly, 2001; Andreola et al., 2006; Lagaly, 2006). The critical coagulation concentration (*c_k*) of NaCl for aqueous kaolinite dispersions was 7–12 mmol/L (Hsi and Clifton, 1962; Lagaly, 2006). It is accepted that the coagulation resulted from the compression of the electrical double layer around the colloidal particles (Hiemenz and Rajagopalan, 1997) or with pronounced Stern-layer adsorption of di- and trivalent cations (McCooke and West, 1978; Gan and Liu, 2008). In addition, heterocoagulation between edges and faces of montmorillonite particles at very small salt concentration was assumed to be the main coagulation mode (van Olphen, 1977; Lagaly and Ziesmer, 2003). In this work, the salt stability of aqueous kaolinite dispersions is studied.

2. Experimental

2.1. Materials

The kaolinite sample was collected at the Silicatos y Derivados plant in the state of Jalisco, Mexico. It was purified in our laboratory by using a high-intensity magnetic separator to remove iron mineral particles, and by screening to remove coarse particles. The kaolinite particles of the <18 μm fraction were dispersed in 1 mol/L NaCl solution for 12 h, followed by centrifugation at 3000 rpm to replace the exchangeable cations by sodium ions. The kaolinite particles were washed 6 times with pure water to remove the excess of Na⁺ ions. Centrifugation was performed at 7000 rpm because of the formation of stable colloidal dispersions.

The particle size distribution was determined by a Shimadzu SALD-1100 laser diffraction particle size analyzer (Japan). D₅₀ (cumulative

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particle size at 50% distribution) and D_{85} of the kaolinite sample were of 4.0 and 9.2 μm (Fig. 1).

The X-ray diffraction (XRD) pattern was obtained with a Rigaku 2200 X-ray diffraction meter (Japan) with $\text{Cu K}\alpha$ radiation. The XRD pattern indicated (Fig. 2) ordered kaolinite particles of high purity. The kaolinite contained 38.51% Al_2O_3 , 45.48% SiO_2 , 0.23% Fe and 0.04% Ti.

A Quantachrome Autosorb gas adsorption analyzer (USA) was used to determine the specific surface area of the kaolinite by N_2 adsorption. The specific surface area was of 25 m^2/g .

Sodium chloride and aluminum chloride of analytical purity were obtained from Sigma-Aldrich Corporation (USA). Sodium hydroxide and hydrochloric acid from the same company were used for adjusting the pH value of the dispersions. The water was first distilled then passed through resin beds and a 0.2 μm filter.

2.2. Measurements

The stability of the aqueous kaolinite dispersions was evaluated by turbidity measurements in a Beckman DU 650 spectrophotometer (USA) with a cell of 1 cm optical path at 400 nm. First, 50 ml aqueous kaolinite dispersion with 0.2% in mass were prepared at the pH value where the kaolinite dispersion was the most stable. After the salt solution was added, the dispersion was stirred for 30 min on a magnetic stirrer at 300 rpm and 5 ml of the dispersion was transferred into the cell of the spectrophotometer. The turbidity of the aqueous kaolinite dispersion as a function of time was recorded. The turbidity of clean water was defined as zero, and that of the dispersion with completely dispersed particles was defined as 100%. The lower was the turbidity; the stronger the coagulation was.

Adsorption was determined through a batch depletion method at 22 °C. First, 5 g kaolinite were dispersed in 250 ml water, a given amount of AlCl_3 was added during adjusting the pH at the given value. The dispersion was conditioned on a magnetic stirrer for 30 min at 300 rpm, then centrifuged at 5000 rpm for 30 min. The solution from the centrifugation was sampled and then analyzed for the aluminum concentration by an atomic absorption spectrophotometer. The amounts of aluminum ions adsorbed by the kaolinite particles were calculated from the concentration differences.

The turbidity and adsorption measurements were done in duplicates, and the arithmetic average values were reported.

The Colloidal Dynamics ZetaProbe Analyzer (Australia) with electroacoustic technology was used to determine the electrophoretic mobility of the kaolinite particles in aqueous solutions. The detailed

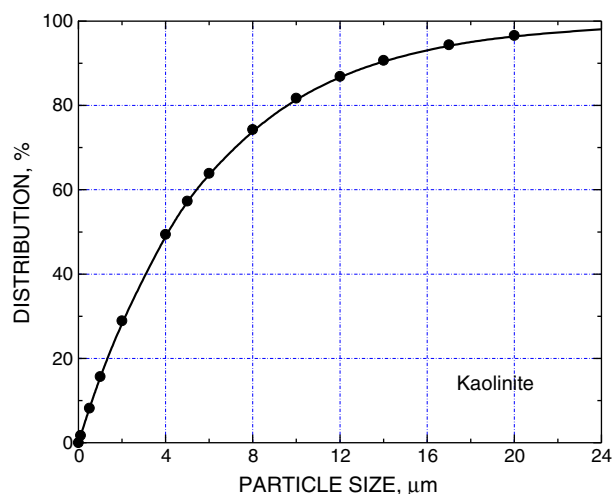


Fig. 1. Particle size distribution of the purified kaolinite.

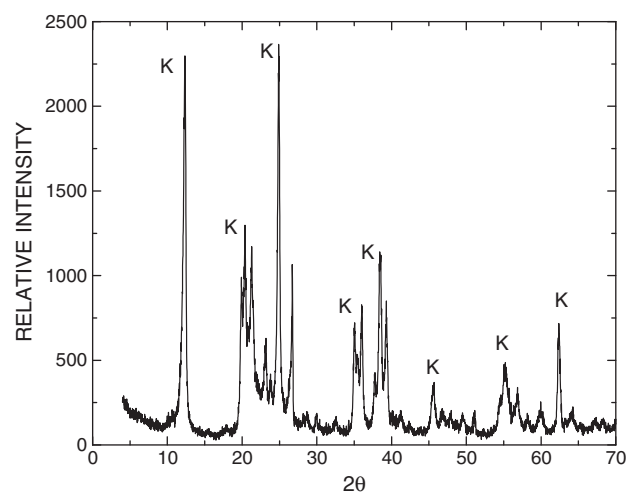


Fig. 2. XRD pattern of the purified kaolinite.

description for the instrument and the measurement can be found in our previous paper (Rao et al., 2009).

A Philips XL30 scanning electron microscopy (SEM) (Netherlands) was used to observe the form and size of the coagulated kaolinite particles. The attached energy-dispersive X-ray spectroscopy (EDX) was used to derive the mineral composition. For SEM observation, a drop of the kaolinite dispersion was carefully put on a pin-type mushroom specimen mounts, dried at room temperature before the particles were coated with 20-nm thick gold film (Watt, 1997).

3. Results and discussions

Fig. 3 showed the turbidity of the kaolinite dispersions as a function of pH at a settling time of 200 min. The turbidity was 8% at pH 2.5, suggesting coagulation of the particles. At pH 2.5–5, the turbidity sharply increased from 8% to 75% and reached plateau at pH 5–10.5, indicating a stable dispersion.

The SEM image of coagulated kaolinite particles at pH 2.5 (Fig. 4) showed aggregated particles around 20 μm in size.

According to the DLVO (Dejaguin–Landau–Verwey–Overbeek) theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948), the stability of colloidal dispersions is due to the existence of a potential energy barrier between the particles, which arises as a result

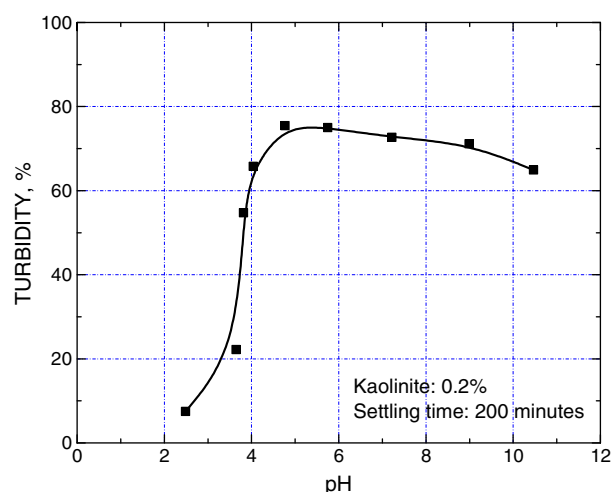


Fig. 3. Sedimentation of kaolinite particles as a function of pH in aqueous solutions.

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