



# Electrokinetic and rheological properties of highly concentrated kaolin dispersions: Influence of particle volume fraction and dispersant concentration

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## ABSTRACT

An industrial kaolin was selected and characterised. Different dispersions were prepared with solids volume fractions between  $\phi=0.20$  and  $\phi=0.47$  in the presence of sodium silicate (between  $X_s=0.075$  mg dispersant/m<sup>2</sup> and  $X_s=0.225$  mg dispersant/m<sup>2</sup>), to determine the electrokinetic and rheological properties. The Fe, Ca, Mg, Na, and Si concentrations, pH, and electrical conductivity of the solutions increased after dispersant addition,  $X_s$ , and/or the solids volume fraction,  $\phi$ , was raised. Electrophoretic mobility, negative for all studied dispersions, became more negative after dispersant addition and less negative with increasing solids fraction. The dispersions with  $X_s \leq 0.075$  mg dispersant/m<sup>2</sup> displayed plastic behaviour (in the shear flow test) and exhibited the characteristics of a gel (in the oscillatory test), owing to the extensive aggregation of the kaolinite particles. The dispersions with  $X_s \geq 0.105$  mg dispersant/m<sup>2</sup> displayed shear-thinning behaviour (in the shear flow test) and viscoelastic fluid characteristics (in the oscillatory test). This behaviour is typical of dense dispersions of plate-shaped colloidal particles, which are well stabilised by electrostatic repulsion. The rheological properties of well-stabilised dispersions were analysed and readily interpreted by redefining the kaolin platelets as new effective hard particles, the thickness of the plate-like particle with its ionic double layer being considered as effective thickness. This enabled an effective volume fraction to be calculated that describes the combined effect of the solids volume fraction and the dispersant addition on dispersion rheological properties. The study showed that excluded volume interactions are essential to understanding the effect of ionic strength on the rheological properties of well-stabilised highly concentrated dispersions.

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## 1. Introduction

In most practical applications, such as ceramics processing or paper coating, highly concentrated stable kaolin dispersions of controlled fluidity and stability are needed, which must be obtained by adding dispersants to the system (Yuan et al., 1998; Penner and Lagaly, 2001; Murray and Kogelb, 2005). Their rheological behaviour, even for well-stabilised dispersions, is very complex and closely related to the dispersion microstructure, at rest and under stress, which largely results from excluded volume effects (Moan et al., 2003; Bossard et al., 2007). Jogun and Zukoski (1996) studied the rheological behaviour of well-stabilised kaolinite dispersions using a mixture of sodium hydrogen phosphates as a dispersant, as a function of solids volume fraction  $\phi$ . At  $\phi < 0.2$ , the dispersions were Newtonian. As the dispersions became more concentrated, plastic and viscoelastic behaviours were observed, because the translational and rotational motion of the particles was limited through excluded

volume interactions. More recently (Moan et al., 2003) scanning electron cryomicroscopy observations have shown that very concentrated dispersions are organised in quasi-continuous neighbouring domains of aligned, close-packed particles. As a result, their rheological properties (yield stress, storage modulus,  $G'$ , etc.) increased sharply with  $\phi$  (Bossard et al., 2007; Moan et al. 2003; Jogun and Zukoski, 1996, 1999) because excluded volume interactions also increased as the average interparticle distance decreased. In contrast, increasing ionic strength,  $I$ , reduced the thickness of the diffuse ionic layer, increased the translational and rotational freedom of particles and domain, and reduced the elastic properties of dispersions (Bossard et al., 2007). This effect can be considered equivalent to an increase in effective average interparticle distance.

Sodium silicates are among the most widely used inorganic deflocculants in raw clay and kaolin dispersions, either as sole or major constituents of the deflocculant mixture, due to their high efficiency (Worrall, 1986; Manfredini et al., 1987; Rossington et al., 1998, 1999; Garrido et al., 1988; Lagaly, 1989; Rand et al., 1988; Diz and Rand, 1990; Yildiz et al., 1998; Andreola et al., 2001; Andreola and Romagnoli, 2006). Like other anionic dispersants, sodium silicates act mainly in the following ways (Worrall, 1986; Lagaly, 1989): they

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contribute sodium ions to the solution, replacing calcium gegen ions with sodium ions; they change the edge charge from positive to negative by polyanion adsorption; and they increase the dispersion pH, which produces negative edge charges. Condensation reactions between silanol groups of silicates and surface hydroxyls of kaolinite (Andreola et al., 2007; Diz and Rand, 1990) are a specific silicate action, this probably being the most important action in dispersion experiments of homoionic kaolinite (Na-kaolinite) under acidic conditions. The high colloidal protective effect (on clay mineral particles) stemming from the separation of colloidal silica by hydrolysis of sodium silicate is also considered to contribute significantly to dispersion stability (Andreola et al., 2001, 2007). Other important phenomena, with relation to dispersion stability and rheological behaviour, are the dissolution of the clay mineral constituents, this being highly dependent on the dispersant (Zaman et al., 2003; Zaman and Mathur, 2004; Yuan et al., 1998); the reactions between the sodium silicates and the dissolved or desorbed ions from the particles (Andreola et al., 2007); and the protonation and deprotonation of aluminol groups, localised at the edges and in the alumina octahedral sheets (O-faces), which take place under acid and alkaline conditions, respectively (Tombácz and Szekeres, 2006).

Thus, when sodium silicate is added to a kaolin dispersion, the above processes change the particle surface characteristics and solution properties (pH and ionic strength,  $I$ , etc.). These changes should also be influenced by the solids volume fraction but, unfortunately, no studies are available in the literature on this subject for highly concentrated dispersions.

The present study was undertaken, first, to determine the combined effect of the silicate addition and solids volume fraction on the characteristics of solutions obtained from highly concentrated kaolin dispersions (ionic concentration of the main elements, pH, and electrical conductivity, EC), and on the electrokinetic and rheological properties of these dispersions. This information is needed to understand the role of sodium silicate in the deflocculation and properties of these dispersions. Secondly, it intended to interpret and to analyse the rheological properties of well-stabilised kaolin dispersions, based on excluded volume effects. For this purpose, the thickness of plate-like particles with an ionic double layer was considered as effective thickness, and an effective volume fraction was calculated in order to describe the combined effect of the volume fraction and the dispersant addition on the rheological properties of highly concentrated kaolin dispersions.

## 2. Experimental

### 2.1. Materials

A sample of commercial kaolin 'F' supplied by the firm AGS was used as-received. Table 1 shows the chemical analysis of the kaolin, determined by X-ray fluorescence. An approximate mineralogical composition (5% quartz, 5% illite, 85% kaolinite, 1% sodium and potassium feldspars, 2% hematite and other iron and titanium compounds, and 2% other minerals) was estimated by rational analysis from the elemental composition and the nature of the mineralogical species present as determined by X-ray diffraction. Organic carbon content, determined using a UIC Coulometrics model CM-150 carbon analyser, was 890 ppm. The specific surface area, determined by nitrogen adsorption (BET method), was  $23.6 \pm 0.1 \text{ m}^2/\text{g}$ . The cation exchange capacity, CEC, determined by standard method ASTM D2187

**Table 1**  
Chemical analysis of clay (wt.%).

| SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO  | MgO  | Na <sub>2</sub> O | K <sub>2</sub> O | LOI <sup>a</sup> |
|------------------|--------------------------------|--------------------------------|------------------|------|------|-------------------|------------------|------------------|
| 47.30            | 36.40                          | 1.36                           | 1.13             | 0.12 | 0.17 | 0.05              | 0.85             | 12.50            |

<sup>a</sup> Loss on ignition at 1000 °C.

**Table 2**  
Cation exchange capacity of clay in cmol (+)/kg (= meq/100 g).

| Ca  | Mg  | Na  | K   | CEC |
|-----|-----|-----|-----|-----|
| 7.1 | 1.4 | 0.2 | 0.2 | 8.9 |

(ASTM, 2004), is reported in Table 2. The particle size distributions below 2 μm, determined by dynamic light scattering (DLS), are shown in Fig. 1. The particle mean size,  $d_{50}$ , obtained from the particle size distribution, was 410 nm. Mean particle thickness,  $h$ , obtained from the X-ray (001) reflections using the Scherrer equation (Moore and Reynolds, 1989), was 21 nm. The mean particle diameter-to-thickness ratio ( $d/h$ ) was thus approximately 20, which is consistent with reported values (Ma and Eggleton, 1999; Yziquel et al., 1999). The values found for CEC and  $h$  were consistent with the experimental relationship between CEC and crystal thickness obtained for different kaolinites (Ma and Eggleton, 1999). The true density, measured using a helium pycnometer, was  $2.65 \text{ g cm}^{-3}$ .

The dispersions were prepared with distilled water, using a Na<sub>2</sub>O/SiO<sub>2</sub> molar ratio of 0.23 as a deflocculant. This additive is extensively used as a dispersant in clay-based slurries (Rossington, et al., 1998, 1999). A total of 42 aqueous kaolin dispersions were prepared, changing the solids volume fraction,  $\phi$ , from 0.20 to 0.47 and the deflocculant content,  $X_s$ , from 0.0705 to 0.225 mg dispersant/m<sup>2</sup> clay mineral surface area. The dispersions were prepared in the following stages: dissolving sodium silicate in water; dispersion of the required quantity of kaolin by stirring for 2 h; and storage in an airtight container for 1 day to complete soluble salt dissolution and kaolin wetting.

### 2.2. Characterisation of solutions obtained from the concentrated dispersions

When the rheological experiments had been completed, the concentrated dispersions were centrifuged and filtered through 0.45 μm membrane filters to obtain the different dispersion solutions. Dispersion pH and electrical conductivity, EC, were measured. The cation concentrations (Ca, Mg, K, Na, Fe, and Si) were determined by inductively coupled plasma emission spectroscopy. The electrical conductivity of all dispersions was high (EC = 0.20–3.5 mS/cm), so that high ionic strength was expected.

### 2.3. Electrokinetic characterisation

The electrokinetic properties of the clay mineral particles were determined by particle electrophoretic mobility,  $\mu_E$ . No relation could be derived between mobility and zeta-potential for the clay mineral particles, as also noted by Lagaly (2006). Thus, mobility rather than zeta-potential values must be reported (Lagaly, 2006). The 'Smoluchowsky zeta-potential', which is proportional to electrophoretic mobility (Lagaly, 2006), is used below only to enable better comparison with other authors' results. In order for the  $\mu_E$  values of the concentrated dispersions to be representative, the solutions used for dilution were obtained by centrifuging and filtering the respective concentrated dispersions.

### 2.4. Rheological characterisation

The rheological tests were determined on a Bohlin CS-50 torque monitoring rheometer. The measuring system consisted of two concentric cylinders (inner rotor and outer stator): rotor diameter was 25 mm, while stator diameter was 27.5 mm. Initial stirring for 60 s in the rheometer broke up any dispersion inner structure that might have formed, thus eliminating residual history effects. The shear stress was then abruptly reduced to zero, this situation being held for 300 s to enable the dispersion to acquire a controlled,

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