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Research paper

Impact of clay mineral particle morphology on the rheological properties of dispersions: A combined X-ray scattering, transmission electronic microscopy and flow rheology study

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ABSTRACT

The rheological features of aqueous dispersions of three clay minerals, illite, kaolinite and montmorillonite are analyzed using the notion of effective volume fraction that links the morphological properties of the suspended solids to their hydrodynamical behavior. The morphological information obtained from an appropriate treatment of the flow curves is confronted to the results obtained by small and wide angle X-ray scattering and transmission electron microscopy. The excellent agreement obtained by independent measurements proves that rheology can be used as a relevant tool to obtain information about the morphology of clay mineral particles. The fruitfulness of this approach is further evidenced by analyzing the influence of the presence of various clay minerals on the rheology of a concentrated calcareous sand. It was proved that using effective volume fractions, the behavior of various sand–clay mineral mixtures can be easily rationalized.

1. Introduction

The rheological properties of natural clay minerals have been extensively studied for the past century due to their importance in numerous environmental and industrial applications. For instance, the role of clay mineral in seismic response (Barnes et al., 2002; Matsuda et al., 2004; Mochizuki et al., 2005; Saffer et al., 2009; Zhu et al., 2011), subaqueous landslides (Biscontin et al., 2004; Elverhoi et al., 2010; Marr et al., 2002) and continental landslides (Geertsema and Torrance, 2005; Hungr et al., 2001; Khaldoun et al., 2009; Wan and Kwong, 2002) is well recognized, though not fully understood. In terms of industrial applications, the rheological properties of clay minerals play a crucial role in numerous fields. Clay mineral based muds have been used for a long time in oil-drilling operations (Darley and Gray, 1991; Maitland, 2000) where their mechanical properties stabilize the well. In the cement industry, clay minerals present in the sands used for cement manufacturing can have a detrimental effect on the rheological properties of the dispersions that leads to water additions that impair the final mechanical properties (Kroyer et al., 2003).

For all these reasons, numerous studies investigate the rheology of clay mineral dispersions (Baravian et al., 2003; Brandenburg and Lagaly, 1988; Callaghan and Ottewill, 1974; Durán et al., 2000; Heller and Keren, 2001; Keren, 1988; Lagaly, 1989; Lubetkin et al., 1984; M'Ewen and Mould, 1950; Mourchid et al., 1995; Neumann and Sansom, 1971; Ramos-Tejada et al., 2001; Ramsay, 1986; Rand et al., 1980; Ten Brinke et al., 2007; Vali and Bachmann, 1988; Willenbacher, 1996). However, such studies either assess the role of the physico-chemical conditions (pH, temperature, ionic strength…) on the rheological features of the dispersions, or try to find a link between mineralogy and mechanical properties. For this reason, the present understanding is rather confused and very few works have tried to provide a general framework to rationalize the wide spectrum of observed rheological behaviors. Studies have recently concentrated their efforts on well-defined size-selected swelling clay minerals and have shown that particle anisotropy was a crucial parameter involved in the control of flow properties (Michot et al., 2004, 2009; Paineau et al., 2011a,b; Philippe et al., 2011). In the present paper, three different clay minerals, kaolinite, illite and montmorillonite exchanged with calcium, i.e. in conditions close to the most frequently encountered natural ones, have been studied. Some experiments on the sodium-exchanged forms are also presented as this parameter is known to have a strong influence on dispersion rheology. On the basis of an effective approach, these experiments show how morphological parameters can be directly obtained from an appropriate treatment of flow curves. The morphological indicators thus obtained are then confronted with the determination of average aspect ratios by X-ray scattering and transmission electron microscopy measurements. Finally it was shown that the approach

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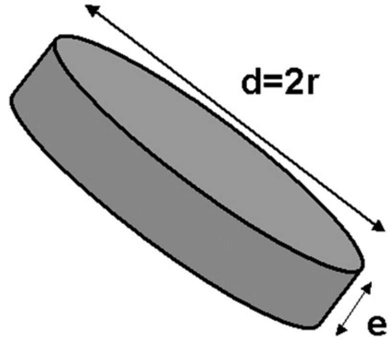

Fig. 1. Schematic representation of a clay mineral particle (aspect ratio = d/e).

developed in the present manuscript can be used to understand the influence of clay minerals on the rheological properties of granular suspensions.

2. Materials and methods

Three clay mineral samples were used in this study: montmorillonite Bleu de Sardaigne (Mt), Illite du Puy (Ilt) and Kaolinite BS3 (Kaol). The raw samples were characterized by X-ray diffraction and infrared spectroscopy. Such analyses revealed the presence of quartz, feldspar, dolomite and calcite as the major impurities. Prior to use, the samples were then purified and homoionized under their sodium and calcium forms (Blachier et al., 2009). A 40 g/L clay mineral dispersion was first decarbonated during 2 h at 90 °C with 1 M sodium acetate solution at pH 5 by addition of acetic acid. After centrifugation, homoionization to Na^+ and Ca^{2+} clay minerals was carried out by exchanging the solid three times in 1 M NaCl or $CaCl_2$ solution. The dispersion was then dialyzed several times in deionized water until the water was chloride free ($AgNO_3$ and conductivity test). Finally, the fraction <2 μm was collected after decantation of the impurities in Imhoff cones. After this purification stage, XRD and FT-IR patterns revealed only trace amounts of feldspar and dolomite, showing the efficiency of the process.

Highly concentrated clay mineral dispersions were prepared by osmotic stress to ensure dispersion homogeneity. Dialysis tubes (Visking) with a molecular mass cut off of 14,000 Da (Paineau et al., 2009) were placed in a 75 g/L PEG 20,000 (Roth) solution and experiments were stopped after two weeks. Concentrated clay mineral pastes were recovered and their mass concentrations were determined by mass loss upon drying one night at 105 °C. Clay mineral dispersions were then prepared by dispersing various amounts of these clay mineral pastes in MilliQ Water.

Rheological measurements on clay mineral dispersions were performed using an AR2000 TA Instruments apparatus. The cone and plate geometry used was 6 cm in diameter with a 2° angle and a 59 μm truncature. All experiments were carried out at 25 °C. A pre-

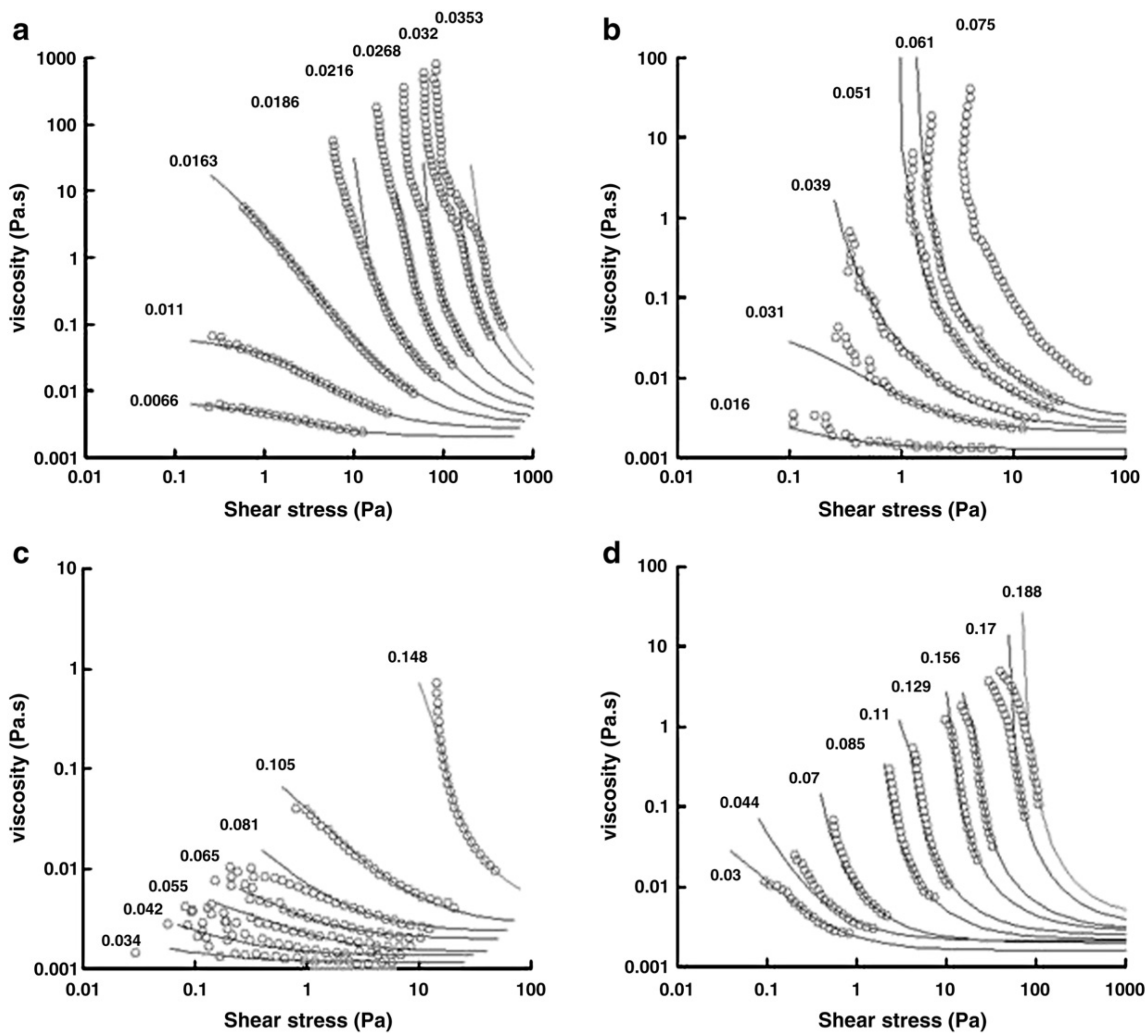

Fig. 2. Viscosity as a function of shear stress for different volume fractions of (a) Na^+-Mt, (b) Ca^{2+}-Mt, (c) Ca^{2+}-Ilt, (d) Ca^{2+}-Kaol. Continuous black lines correspond to the best fit of Eq. (6).