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Comparison between the electrokinetic properties of kaolinite and montmorillonite suspensions at different volume fractions

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ABSTRACT

We have investigated the electrokinetic responses of two different kinds of clay particles, kaolinite and montmorillonite. The dielectric permittivity of kaolinite suspensions is linearly proportional to volume fraction up to volume fractions of 20%, whereas that of montmorillonite is deviating from a linear relationship, for volume fractions below 0.5%. This indicates that the montmorillonite particles experience a particle–particle interaction at these low volume fractions. The complex dipole coefficients of both clays estimated by experimental data are, however, within experimental error in good approximation independent on volume fraction and agree with the theoretical predictions. The relaxation frequency in clay–water system at low ionic strength is almost determined by the relaxation of the double layer for both kaolinite and montmorillonite. For volume fractions larger than 0.5% for montmorillonite, we find that the zeta potential measured by electroacoustic methods starts to depend strongly on volume fraction. It is expected that for these high volume fractions, the dipole coefficients will also become volume-fraction dependent.

1. Introduction

The permittivity and conductivity of clay suspensions have been investigated by numerous authors [1–14]. In a previous article [15], we have investigated both the electrophoretic mobility and the dielectric spectroscopy response of dilute montmorillonite particle suspensions of montmorillonite (0.1% volume fraction). We have found values comparable to what other authors find for this system, using the same techniques. However, we also noted a deviation from our results compared to those of Rasmusson et al. [5], who similarly studied dielectric spectroscopy and electrophoretic mobility responses. These authors used a volume fraction of 0.4% or 0.8% for the size and mobility measurements where they used a AcoustoSizer from Matec Applied Sciences. On the other hand, for the complex conductivity measurements (corresponding to our dielectric spectroscopy measurements), they used 2% or 4% volume fraction [5]. The authors found that the electroacoustic signal (ESA) used to assess the dynamic mobility of the particles was independent of the stirrer speed, implying that the particles were randomly oriented in this experiment. For the lower volume fractions we used in the dynamic mobility experiments (0.025%, 0.05%, and 0.1%), there were similarly no changes in electrokinetic response. The question remains, however, how particles behave during a dielectric spectroscopy (complex conductivity) experiment, where the suspension is not stirred and the volume fraction 10 times higher.

In this article, we would like to investigate into more detail the dependence of the complex conductivity response as a function of volume fraction. We do this for two types of clays: kaolinite and montmorillonite. In order to get the best information about particle interaction, we favored to study a system with as low ionic strength as possible. The Debye length κ^{-1} around the charged particles is then very large, and particle–particle interactions are more likely to occur.

We are going to compare the results we obtain with the results obtained by Rasmusson et al. and other authors that work at different volume fractions.

2. Experimental

2.1. Sample preparation

The kaolinite (China clay) was obtained from VE-KA Industry Keramische Grondstoffen Ltd., the Netherlands. The average size of the primary particle was found to be around 10 μm [16]. This clay sample was prepared by dispersing the powder as received in millipore water. The suspension was ultrasonic shaken for 5 min prior use.

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Montmorillonite were obtained from commercially available Kunipia-F (Kunimine Industry Co. Ltd.). Coarse components, mainly silica sands, contained in the purchased material were removed by sedimentation. To replace the surface cations by sodium ions, we dispersed the clay particles into the 2.0 M NaCl solution for weeks and occasionally replaced the clear supernatant by a new 2.0 M NaCl solution until the substitution was completed. Salt-free stock dispersions were prepared by repeatedly dialyzing the suspension against distilled water until the electric conductivity became less than 1.5 μS/cm. After these treatments, this suspension was stocked after freeze-drying. Dielectric spectroscopy measurements were performed with the suspensions made from the stock freeze-dried montmorillonite diluted with an aqueous solution of sodium chloride of known concentration. The value of pH in the suspension was not purposely controlled, but was measured to be between 5.5 and 6.5 throughout all the experiments. As an equivalent diameter, we measured 382 nm by dynamic light scattering measurements.

2.2. Dielectric spectroscopy

The details of this measurement technique and the theory can be found in [15]. The electrokinetic response of the clay suspensions was measured in the range 10^4–1.5×10^7 Hz using a homemade concentric cylindrical measurement cell [17]. The impedance Z measured by the dielectric spectroscopy device can be seen as the impedance of an equivalent circuit formed by a resistance R and conductance C in parallel. Therefore:

$$\frac{1}{Z} = \frac{1}{R} + iC\omega \tag{1}$$

From the measured R and C, the conductivity and permittivity are calculated according to the following formula [18]:

$$K = \frac{1}{2\pi L}\mathrm{Re}\left(\frac{1}{Z}\right) \tag{2}$$

$$\varepsilon = \frac{1}{2\pi\varepsilon_0 L\omega}\mathrm{Im}\left(\frac{1}{Z}\right)$$

L represents the height of liquid in the cell. This cell was filled at start with 45 mL suspension. Measurements for one sample repeated four times by removing 10 mL from the suspension. The conductivity and permittivity were estimated from the slope of the variation in $1/Z$ as function of the variation in liquid level. "Blank" solutions, i.e., electrolyte solutions of same conductivity as the suspensions were also measured. The conductivity and permittivity of the particles were calculated by subtracting the blank solution response from the conductivity and permittivity responses of the suspensions. Doing so, the effect of electrode polarization was minimized [18]. All measurements were performed at 25 °C.

Eq. (1) of Ref. [15]:

$$\tilde{K} = \check{K}_1(1 + 3\varphi\beta) \tag{3}$$

where $\tilde{K} = K + i\omega\varepsilon_0\varepsilon$, where K is the conductivity, ω is the frequency (rad/s), i is the square root of -1, ε is the relative dielectric permittivity, and ε_0 is the dielectric permittivity of vacuum. K_1, φ, and β indicate the conductivity of electrolyte, volume fraction, and dipole coefficient, respectively. This equation was derived under the assumption that there is no particle–particle interaction. From this equation, we obtain:

$$\varepsilon \equiv \frac{\varepsilon - \varepsilon_1}{\varphi} = 3\left[\varepsilon_1\mathrm{Re}(\beta) + K_1\frac{\mathrm{Im}(\beta)}{\omega\varepsilon_0}\right] \tag{4}$$

$$K \equiv \frac{K - K_1}{\varphi} = 3[K_1\mathrm{Re}(\beta) - \varepsilon_0\varepsilon_1\mathrm{Im}(\beta)]$$

where ε_1 indicates the dielectric permittivity of the electrolyte. The dipole coefficient is then found from the measured conductivity and permittivity by inverting these equations.

β is dependent on two contributions, β_n and β_p which represents the dipole coefficient in the direction perpendicular to the electric field or along it, respectively. In case that (as assumed here) the electric field is weak enough, we have [15]:

$$\beta = \frac{1}{3}\beta_p + \frac{2}{3}\beta_n \tag{5}$$

2.3. Electrophoresis

The electrophoretic mobilities U_s were measured at low frequency by Doppler velocimetry using a Malvern Zetasizer Zeta-Nano. The electrophoretic mobility is plotted for convenience of units using the Smoluchowski formula

$$U_s = \frac{\varepsilon_0\varepsilon_r\zeta}{\eta} \tag{6}$$

which gives a linear relationship between mobility and zeta potential ζ, given the dielectric permittivity and the viscosity. We use: $\varepsilon_r = 78.55$ and $\eta = 0.89$ mPa s.

At high frequency, the suspension's electroacoustic response was measured at 3.3 MHz using the Dispersion Technology device DT-300. The zeta potential obtained from the electroacoustic device was given by the manufacturer [19].

3. Results of dielectric spectroscopy

3.1. Kaolinite suspensions

3.1.1. conductivity and dielectric increment

The conductivity and dielectric permittivity of the studied kaolinite suspensions is shown in Fig. 1a and b as function of volume fraction, for several applied field frequencies. We observe that the conductivity is linear with volume fractions above 9.2%. The dash line in Fig. 1a is meant as a guide for the eye. Under 9.2% volume fraction, the conductivity is almost constant and roughly equal to 0.024 S/m. This conductivity value corresponds to ionic strength of 1.4 mM of KCl, which is quite large, considering the fact that no salt has been added to the suspension. This conductivity derives from the fact that the kaolinite has not been properly cleaned before use, so some ions release from the clay to form a background electrolyte concentration. The linearity between both conductivity and permittivity upon volume fraction indicates that particle–particle interaction can be neglected for kaolinite in the volume fraction range [0–20%].

Raythatha and Sen [6] studied the high-frequency dielectric response of kaolinite (in the MHz regime). They report that the kaolinite sample they study give $\varepsilon - \varepsilon_1 = 0$ for the whole frequency range, below a volume fraction of 9.6%. At 9.6% volume fraction, they find that $\varepsilon - \varepsilon_1 = 25$ at 0.5 MHz. This is also in line with our results at 0.5 MHz, as, we find $\varepsilon - \varepsilon_1 = 29$ for 14% volume fraction. For lower volume fractions, we find $\varepsilon - \varepsilon_1 = 9$ (4%), $\varepsilon - \varepsilon_1 = 11$ (7%), and $\varepsilon - \varepsilon_1 = 16$ (9%). For any frequency, the dielectric permittivity is almost linear with volume fraction (see Fig. 1b), indicating that there is no particle–particle interaction for the low volume fractions.

In order to better study the relation between surface properties of kaolinite and its dielectric response, we will analyze the data in terms of dipole coefficients. These (complex) dipole coefficients are obtained from Eq. (4). Note that the dipole coefficient β is in principle independent on volume fraction when $\varepsilon - \varepsilon_1$ is linearly dependent on volume fraction.