



Magnetic orientation of nontronite clay in aqueous dispersions and its effect on water diffusion



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ABSTRACT

The diffusion rate of water in dilute clay dispersions depends on particle concentration, size, shape, aggregation and water-particle interactions. As nontronite clay particles magnetically align parallel to the magnetic field, directional self-diffusion anisotropy can be created within such dispersion. Here we study water diffusion in exfoliated nontronite clay dispersions by diffusion NMR and time-dependant 1H-NMR-imaging profiles. The dispersion clay concentration was varied between 0.3 and 0.7 vol%. After magnetic alignment of the clay particles in these dispersions a maximum difference of 20% was measured between the parallel and perpendicular self-diffusion coefficients in the dispersion with 0.7 vol% clay. A method was developed to measure water diffusion within the dispersion in the absence of a magnetic field (random clay orientation) as this is not possible with standard diffusion NMR. However, no significant difference in self-diffusion coefficient between random and aligned dispersions could be observed.

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1. Introduction

Clay dispersions are widely used in for example oil well drilling [1], food packaging [2] and sealing barriers for waste dumps [3] or nuclear waste containment [4]. Colloidal clay dispersions, hydrogels and composites have during the last two decades emerged as possible alternatives to fossil fuel derived polymer solutions and gels [5–7].

Nontronite clay is a naturally occurring aluminosilicate mineral consisting of 0.7 nm thick and typically 25–1000 nm wide plates consisting of two tetrahedral layers of silica sandwiching an octahedral layer that hosts different ions (Al^{3+} , Mg^{2+} and Fe^{3+}). Being rich in Fe(III) ions, nontronite align in both electric [8] and magnetic fields [9–12]. Clay dispersions typically contain aggregates of face-to-face stacked clay plates. However, under certain conditions these can be separated (exfoliated), forming dispersions of individual clay plates. Michot and co-workers found isotropic,

biphasic and nematic phases, and ultimately birefringent gels when increasing the clay concentration in dilute exfoliated nontronite clay dispersions [10].

Due to their extreme surface-to-volume ratios clay plates are very effective for obstructing/slowing down the diffusion of solutes and solvents, an effect that can be tuned by the plate orientation [12–17]. Additional factors that affect the particle diffusion obstruction are shape, volume fraction, size distribution, and aspect ratio [5,18–20]. The aspect ratio is defined as the average diameter divided by the thickness. Furthermore, solute and solvent diffusion is affected by interactions with the clay surfaces [13,21,22].

In a previous study we studied clay alignment and water diffusion in gels made from clay and colloidal silica, taking into account obstruction but also water surface interactions using the following equation [13],

$$\frac{D}{D_0} = \frac{1}{1 + \frac{\alpha}{3}(S + \frac{1}{2})\phi_{\text{clay}}} \frac{1 - \phi_{\text{clay}+\text{bound}}}{1 - \phi_{\text{clay}}} \quad (1)$$

where ϕ_{clay} is the clay volume fraction and $\phi_{\text{clay}+\text{bound}}$ the combined volume fraction of the clay and the surface bound water, and α the

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aspect ratio. The order parameter S is $-1/2$, 0 and 1 , for parallel, random and perpendicular plate orientation, respectively, relative the direction of the diffusive flux.

Detailed studies of water diffusion in clay systems with isotropic/anisotropic microstructure increase the overall understanding of the microstructure–diffusion relationship, solvent/solute surface interactions and aggregation in soft porous materials. This report investigates clay alignment and water diffusion in nontronite clay dispersions and the findings are discussed in terms of clay orientation, particle–particle aggregation and water surface interactions.

2. Experimental

2.1. Preparation and characterization of clay dispersion

A detailed description for the preparation and characterization of nontronite clay dispersions has been reported by us earlier [13]. In short, nontronite clay was obtained from Excalibur Mineral Corp., Peekskill, NY, from the source of Allentown, PA, having the following [23] general formula $[\text{Na}_{0.3}\text{Fe}_2^{3+}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and an estimated unit cell density of 3 g/cm^3 . Clay identity and purity were validated with IR-spectroscopy and X-ray diffraction. The clay was first ground, secondly dispersed in 1M NaCl solution, followed by ultracentrifugation at 35,000g, where the second step was repeated three times followed by redispersion in deionized water. Sample dialysis was performed against deionized water until no change in conductivity was observed, after which the dispersion was placed in Imhoff cones for 72 h to sediment mineral impurities. Dispersions were size fractioned by centrifugation at incrementally higher g-forces, using 6400 and 17,000g. The clay pellet obtained after the last centrifugation was used in this study. A drop of 0.01 vol% clay dispersion was air-dried on a formvar and carbon-coated copper grid (Ted Pella Inc, Redding, CA, USA) prior to transmission electron microscopy (JEOL 1200EX II microscope, JEOL, Tokyo, Japan) at 120 kV to image and estimate the nontronite size distribution. Clay particles had a plate lath shape and the width and length dimensions had a log-normal distribution. Defining the clay plates' diameter as $(\text{length} + \text{width})/2$, a regression analysis from the size distributions obtained from TEM gave a mean diameter of 228 with a standard deviation of 103 nm. Previous studies of exfoliated nontronite clay give an estimated plate thickness of 0.7 nm [9,10] that together with the obtained mean diameter results in a mean clay plate aspect ratio of 326 and standard deviation of 147 nm. Clay gelation was assessed by an inverted tube test, where a 0.5 ml clay dispersion in a 5 mm NMR tube was defined as a dispersion if it flowed when inverting the tube, and a gel if not. Square glass microcapillaries with 1 mm sides (CM Scientific Ltd, Silsden, UK) were filled with 0.3 vol% clay solution and imaged for birefringence with a digital camera (Olympus, FE-360) between crossed polarizers in a 0.72 Tesla magnetic field. The magnetic field was generated in the gap between two rare-earth neodymium permanent magnets and the magnetic field strength was measured with a Hall-sensor.

2.2. NMR self-diffusion measurements

The self-diffusion of H_2O water, from here on referred to as H_2O , was measured in clay dispersions in the absence of the rest of the membrane system (See further below) with a Bruker Avance III 500 spectrometer (Bruker, Fällanden, Switzerland) equipped with Mic5 micro-imaging probe and a 5 mm 1H RF coil. Clay dispersions with 0.3, 0.5, and 0.7 vol% clay were prepared in 5 mm NMR tubes and the self-diffusion coefficient was measured both in the direction parallel and perpendicular to the external magnetic field, denoted D_{\parallel} and D_{\perp} , respectively. Using the conventional PGSTE-LED

sequence [24], all diffusion experiments were performed at 23 °C with 50 ms diffusion time, 0.5 ms gradient pulse length, and 160 G/cm maximum gradient strength. Trapezoidal gradient pulses with ramping time of 0.1 ms and stabilization time of 0.1 ms was used. The LED time was set to 10 ms and the gradient strength was calibrated by diffusion experiments on pure H_2O at 23 °C and 25 °C. The estimated self-diffusion coefficients measurement error was $\pm 1 \times 10^{-11} \text{ m}^2/\text{s}$.

2.3. NMR 1D imaging

To understand the effect of clay orientation on water diffusion in nontronite dispersions we intended to study diffusion in the parallel, perpendicular and random states as earlier described in connection to Eq. (1). However, the very strong magnetic field in the NMR spectrometer (14.1 Tesla) does not allow the measurement of the self-diffusion coefficient in the random state, D_{random} , in dilute nontronite dispersions due to the very fast alignment process once the sample is placed inside the magnet. Instead an indirect method was used to measure the diffusion coefficients from the mass transport across a clay dispersion membrane in the presence (D_{am}) and absence (D_{nam}) of a magnetic field. The diffusion process across the membranes is referred to as membrane diffusion, which is in contrast to the self-diffusion as measured by the NMR self-diffusion technique in the clay dispersions.

Compared to the self-diffusion coefficient, the membrane diffusion coefficient was affected by the presence of two cellulose films that kept the clay dispersion inside the membrane. However, as Eq. (2) shows this effect cancels out by normalization in the calculation of D_{random} as,

$$\frac{D_{\parallel}}{D_{\text{random}}} = \frac{D_{\text{am}}}{D_{\text{nam}}} \quad (2)$$

The custom-made membrane system in Fig. 1 was made out of polyether ether ketone (PEEK) plastic. Two regenerated cellulose membranes (Spectrum Labs, Spectra/Por, MWCO 12–14000) were cut from a larger membrane disk and glued with polyacrylate glue to the separating spacer ring, forming a 1.2 mm thick membrane while the hole in the center of the ring had a diameter of 3 mm. The space confined by the spacer ring and the cellulose membranes were filled with 0.7 vol% clay dispersion from a syringe with a needle. The system was assembled according to Fig. 1, after which the upper chamber (donor chamber) and lower (receiver chamber) were rinsed with deuterium oxide water (99.8 atomic% deuterium, from here on referred to as D_2O) and equilibrated with D_2O for 30 min to exchange and remove the H_2O present in the clay dispersion within the membrane. The receiver chamber was then filled with pure D_2O and sealed from the bottom with a polydimethylsiloxane (PDMS) plug. The donor chamber was rinsed and filled with a 1:1 volume mixture of D_2O and H_2O (MilliQ water, Millipore, 18 M Ω cm) and Parafilm M[®] was used to seal the chamber. A 10 mm NMR glass tube was attached to the top of the membrane system, where the rubber ring ensured a mechanically secure fit between the glass tube and membrane system. Both the upper and lower chambers shown in Fig. 1 are cylindrical and 3 mm in diameter and 8 mm in length.

For the imaging measurement the membrane system was placed in a Bruker Avance 600 spectrometer (Bruker, Fällanden, Switzerland) equipped with Diff30 diffusion probe and a 10 mm RF insert coil. Inside the NMR magnet the membrane experienced a temperature of 23 °C and a magnetic field of 14.1 Tesla perpendicular to the plane of the membrane. Allowing for diffusion of $\text{H}_2\text{O}/\text{D}_2\text{O}$ over the membrane, instant 1D-proton intensity profiles were recorded at different time points over 6 h and 12 min using a standard 90/180° spin-echo 1D-image profile pulse sequence with 12 G/cm gradient pulses. Following magnitude calculation of the

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