



Research paper

Relationship between the fractal structure with the shear complex modulus of montmorillonite suspensions



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ABSTRACT

In this work, we characterized and studied the rheological behavior of montmorillonite suspensions. Our objective was to establish the link between the structure of these suspensions and their rheological behavior.

We have characterized these suspensions using several techniques: X-ray scattering to determine their composition and structure, the light scattering to determine the diffusion coefficient of the clay particles and their size. We also measured their densities and their rheological properties in linear and non-linear viscoelasticity.

The rheological measurements show that the bentonite particles are structured to form a fractal network. We have determined experimentally the moduli and yield stresses. Using Piau model, we have derived its fractal dimension ($D = 1.74 \pm 0.08$). The light scattering measurements allowed us to determine the particles size and the characteristic time of diffusion of the clay particles in the suspension. Finally, knowing the structure of our suspensions and characteristic time, we tried to model their viscoelastic behavior $G^*(\Omega)$ using Chambon and Winter model.

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1. Introduction

The solid-like elastic properties in colloidal gels, which have significant technological and scientific applications (Helgeson et al., 2012; Huh et al., 2007; Drury and Mooney, 2003; Rueb and Zukoski, 1997; Lu et al., 1997) are a result of the three-dimensional stress-bearing structures that are formed by physical or chemical attraction between the individual components of the network (Zaccarelli, 2007; Vermant and Solomon, 2005).

Colloidal aggregates form fascinating structures; despite the apparent disorder of their shape, they possess a remarkable degree of symmetry, and can be well described as fractals (Weitz and Oliveria, 1984). This scale invariance has facilitated the description of their structure and its relationship to the kinetics of their formation (Torres et al., 1991; Weitz et al., 1985). One of the unique features of a fractal structure is that its density decreases as its size grows; as a result, colloidal aggregates ultimately gel to form a very weak solid, comprised of a connected, disordered network that fills all space (Carpineti and Giglio, 1993; Carpineti and Giglio, 1992; Bibette et al., 1992). If the aggregation is predominantly diffusion limited, the average clusters that form the gel are surprisingly uniform in size, resulting in a strong peak in the static light scattering intensity at low angles (Carpineti and Giglio, 1993; Carpineti and Giglio, 1992; Bibette et al., 1992).

Our work concerns water based drilling muds. Our objective is to establish the correlation between the microstructure of the fluid and its rheological properties. In this study, we focused ourselves on clay-water mixtures, which constitute the base of these muds. We studied their rheological behavior and more particularly the linear viscoelasticity for various clay mass concentrations C (2, 4, 5, 6 and 8%).

Our objective being to establish the link between the fractal structure of these suspensions (via the yield stress and the elastic modulus) and the complex shear modulus $G^*(\Omega)$. In this paper, we will show that, starting from the gel fractal dimension and the characteristic time of diffusion of clay particles, it is possible to predict the variation of $G^*(\Omega)$ according to the angular frequency Ω of the water bentonite suspensions. To our knowledge, it is the first time that this type of work is undertaken.

2. Material and methods

2.1. Bentonite

The name bentonite was given by W.C. Knight in 1898, which is an absorbent aluminum phyllosilicate, impure clay consisting mostly of montmorillonite. The bentonite used in this work is a calcium bentonite (B3378) of Sigma. Its chemical composition is SiO_2 —48.35%, Al_2O_3 —12.15%, Fe_2O_3 —8.26%, CaO —6.68%, MgO —5.47%, Na_2O —3.65%, and K_2O —2.39%. It possesses a specific surface of $39.3 \text{ m}^2/\text{g}$, a capacity cationic exchange of 0.88 meq/g , a molecular weight 180.1 g/mol , $\text{pH} = 9$ and a density of 2.4 g/cm^3 .

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2.2. Bentonite suspensions

To prepare the bentonite suspensions for mass concentrations 2, 4, 5, 6 and 8%, the experimental protocol is the following: the bentonite is mixed in the demineralized water during 24 h. After, we made the following observations:

- for the suspension with 2% of bentonite, a sedimentation of the particles was noticed after one day of rest.
- the suspensions with 4, 5, 6 and 8% of bentonite form gel after a 8 h rest. We have focused this work on these concentrations.

The whole of our samples were alkaline suspensions. We measured a pH by pH meter, type 691 metrohm with a glass-rod and a precision 0.01/unit of pH. The pH of these suspensions (2, 4, 5, 6 and 8%) was respectively (9.5, 9.42, 9.35, 9.18 and 9.01).

3. Experimental measurements

3.1. Density of suspensions

In this part, we present the density measurements (ρ) of our suspensions aged during 24 h at 20 °C. The densities of the suspensions are reported in Table 1.

An uncertainty of 0.02 g/cm³ on the density was determined from five measurements on a suspension with 5% of bentonite. In this condition, our measurements are in agreement with the results of Ferreiro and Helmy (1971).

3.2. Size of the particles

For the suspension containing 2% of bentonite, we have observed a sedimentation. But, a part of the particles remains however in the supernatant fluid. This fluid is a very diluted bentonite suspension which can be used to determine the size of bentonite particles. The particle size was measured on a dynamic light scattering apparatus (DL 135-45) developed by IFP (French Petroleum Institute) and working on very thin suspension layer in order to avoid multi-scattering phenomenon. It is equipped with a laser (having wavelength 633 nm). With this apparatus, we have determined the size of the particles in suspensions mono-layer or multi-layers (Le Pluart et al., 2004; Jozja, 2003) under various conditions.

In dynamic diffusion, the fluctuations in intensity of the scattering light are emitted by scattered and in suspension particles. The signal fluctuation rate is linked to the diffusion coefficient of the scattered particles. The diffusion coefficient is linked to the size of the object which diffuse. It is proved true that the diffusion coefficient of a spherical particle with a radius R_h in a medium of viscosity η and a temperature T will diffuse with the coefficient (Stokes–Einstein equation): $D_m = k_B T / 6\pi\eta R_h$, where k_B is the Boltzmann-constant. Knowing the diffusion coefficient, the hydrodynamic radius R_h can be calculated (the hydrodynamic radius R_h is the effective size of the particle detected from its Brownian motion).

In Table 2 are reported the measurement conditions and the mean value of their size. We note that the particle sizes measured are larger than that of the particle (mono-layer): they are associates of mono-layer particles. The associate particle size depends on the agitation condition. Thus at rest the associates particles have sizes more important

Table 1
Suspensions densities ρ .

Concentration bentonite (%)	2	4	5	6	8
ρ (g/cm ³)	1	1.02	1.05	1.07	1.17

Table 2
Particle sizes under different agitation conditions.

State of sample	R_h (nm)	$D_m \times 10^{13}$ (m ² /s)
Taking of sample after sedimentation	390	6.10
Taking of sample under agitation	230	10.3

than under agitation. In addition, we observed that after stop of agitation, the dimension of these associates of particles increased. A value of their coefficient of diffusion D_m is indicated in Table 2.

3.3. Discussion

In the literature, authors consider that the association of the particles and the formation of the gels are controlled by two important parameters: the particles concentration and the pH of the suspension (Luckham and Rossi, 1999). For the concentrations lower than the concentration of percolation ($\leq 2\%$), we are in the case of dilute suspensions, the bentonite particles are isolated (light scattering observation). This stable state is explained by the absence of interaction between particles because the mutual repulsion of the electrical double layers takes place. The stable dispersion corresponding to minimum free energy, which presents in the form of single platelet or of very fine primary particle (Callaghan and Ottewill, 1974). In light of the work Callaghan and Ottewill (Callaghan and Ottewill, 1974), we deduce that the bentonite suspension 2% presents the same structure.

Under the action of the attractive forces governing the flat surface association, appears the primary clusters of individual particles, followed by the secondary aggregation of these clusters, which sediment under the action of gravity. For clay concentrations $> 2\%$, the particles are sufficiently close to be structured. The three various shapes of association of the particles can then occur. These various modes of organization were described by Van Olphen (1964).

In this work, we obtained gel for concentrations $> 2\%$ (4, 5, 6 and 8%). This result is consistent with those of Darley and Gray (1988). These authors showed that with sodium montmorillonite suspensions for concentrations $> 3\%$, the flocculation causes the formation of continuous gel. Callaghan and Ottewill (1974) assign the formation of the gel to repulsive interactions between the electric double-layers. Brandenburg and Lagaly (1988); Vali and Bachmann (1988); Weiss and Frank (1961) support the idea of a three-dimensional network of sheet shaped aggregates. These aggregates would be composed by platelets agglomerated by flat to flat interactions with a partial covering of their respective surfaces.

De Kretser et al. (1998) arrive at the same conclusion. Pignon et al. (1998), by combining different techniques of analysis to characterize the gel structure of Laponite on various scales, showed that the structure of the dispersions at rest is composed of subunits measuring a few tens of nanometers that combine to form dense aggregates measuring about 1 μm . For large scales, these micrometric aggregates flocculate to form a fractal structure. While being based on work (Tombácz and Szekeres, 2006; Tombácz and Szekeres, 2004; Abend and Lagaly, 2000; Durán et al., 2000; Benna et al., 1999; Pignon et al., 1998; De Kretser et al., 1998; Brandenburg and Lagaly, 1988; Khandal and Tadros, 1988), we can propose that the suspensions of concentrations higher than the percolation concentration (in our case $> 2\%$) and pH higher form fractal structures (in our case > 9) where the association flat to flat is favored.

The SEM (scanning electron micrograph) of our sample (see Fig. 1) shows the microstructure formed from the bentonite suspension 6%. Here, the structure of bentonite floccules and led to the formation of compact irregular aggregates having a multi-layer structure of the face-face type. Similar results were obtained by Stawinski et al. (1990) on the bentonite sediments and on the kaolin at various concentrations of Na⁺ and Ca²⁺.

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