



Exfoliation Dynamics of Laponite Clay in Aqueous Suspensions Studied by NMR Relaxometry

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ABSTRACT

The interaction between Laponite and other constituents in complex systems greatly depends on its available surface area. We report a study of exfoliation dynamics of Laponite in aqueous suspensions by NMR relaxometry. It showed that Laponite particles exfoliate to the same extent in a concentration range of 0.5-3% w/w. Faster increase of specific wetted surface area of Laponite particles in more concentrated suspensions suggests faster exfoliation of disc-shaped Laponite platelets from the initial layered structure.

Keywords: NMR relaxometry, Laponite, exfoliation, clays.

INTRODUCTION

Synthetic hectorite *Laponite* is one of the most used materials for studies of exfoliating clays due to its high dispersibility in water, narrow size distribution and uniform shape of its individual disc-shaped platelets. A lot of research has been dedicated to such processes in *Laponite* suspensions as gelation¹⁻³, dispersing^{4,5}, sedimentation², dissolution of particles⁶. Alongside the fundamental interest, quantitative research of Laponite exfoliation process is important for a range of Laponite applications. Owing to Laponite unique properties, such as ability

to form gel at low concentrations, high specific surface area, nonspherical particle shape and presence of adsorption centers on its surface, it is used in nanocomposite gels⁷⁻⁹, coatings¹⁰, as a stabilizer in suspensions¹¹ and emulsions¹² and as a carrier for drug delivery¹³. For the majority of such applications interaction of *Laponite* particle surface with the other system components (polymers, drugs, precursors, surface of other materials) is a crucial element for effective design of the target products. Quantitative description of such interactions demands knowledge of the specific surface area of dispersed *Laponite*, which is determined by the degree of Laponite exfoliation.

Apparently, there are few studies of the *Laponite* exfoliation process. The study⁵ is dedicated to the process of orientation disordering of individual *Laponite* platelets after their separation from the tactoids. The other work¹⁴ studied the dependence of *Laponite* particle dimensional parameter on the suspension age using acoustic spectroscopy. The authors made a conclusion that the higher *Laponite* concentration, the less effective is the process of exfoliation. According to the paper, the tactoids exfoliated completely at the concentration of 1.5% w/w within 4 hours, while at the concentration of 4% w/w the majority of the particles consisted of tactoids of two to three platelets. The authors of the light scattering study⁴ determined that *Laponite* exfoliation for concentration of 0.2% w/w lasted more than 10 hours. However, formation of gel clusters in *Laponite* suspensions increases scattering light intensity, so decrease of scattering intensity due to exfoliation becomes indistinguishable, thus limiting the use of light scattering method for such study. In the current work we have studied the process of *Laponite* particles exfoliation by NMR relaxometry, monitoring changes of specific wetted surface area of *Laponite* suspensions over a period of 3 months.

MATERIALS AND METHODS

Laponite suspensions were prepared by dispersing *Laponite* RD powder (BYK Additives & Instruments) in deionized water and subsequent stirring for 24 hours. To prevent dissolution of *Laponite* in water⁶, pH of deionized water was adjusted to 10 by addition of NaOH. To prevent exposure of *Laponite* to CO₂¹⁵, the samples were kept in tightly sealed containers. The prepared suspensions remained homogeneous over the whole period of the study.

¹H-NMR relaxometer operating at 13 MHz (Acorn Area particle analyzer, Xigo Nanotools, USA) was used to determine specific area of wetted surface of dispersed objects in suspension. The measured parameters are time of spin-spin (T_2) or spin-lattice (T_1) relaxation of hydrogen protons. T_1 is measured by the inversion recovery method and T_2 is measured by the Carr-Purcell-Meiboom-Gill method. According to the two-phase fast-exchange model, the spin relaxation time T_i depends linearly on specific area of wetted surface of the dispersed phase S_{NMR} ^{16,17}:

$$\frac{1}{T_i} = \frac{1}{T_{fi}} + \left(\frac{1}{T_{bi}} - \frac{1}{T_{fi}} \right) l C \rho S_{\text{NMR}} = a_i + k_i C \quad \dots(1)$$

where T_{fi} is the spin relaxation time of hydrogen protons in free, or bulk, water, T_{bi} – spin relaxation time of hydrogen protons in water bound to the particle surface, i is 1 (spin-lattice) or 2 (spin-spin), l – thickness of bound water layer (estimated as 1 nm^{16,17}), ρ is water density, C – *Laponite* concentration (solid mass/ water mass),

$$a_i = 1/T_{fi}, k_i = (1/T_{bi} - 1/T_{fi}) l \rho S_{\text{NMR}}.$$

In the case of suspensions of exfoliating materials, S_{NMR} is equal to the specific external surface area S_{ext} , which is equal to the full specific area of completely exfoliated particles S less internal surface area S_{int} enclosed within stacks of particles. Measurement of relaxation times of hydrogen protons T_1 and T_2 in the suspensions of exfoliating materials allows to make a conclusion about the degree of exfoliation of particles by calculating relative specific surface area:

$$\frac{S_{\text{ext}}(\tau)}{S_{\text{ext}}(\tau_{\text{max}})} = \frac{\frac{1}{T_i(\tau)} - \frac{1}{T_{fi}}}{\frac{1}{T_i(\tau_{\text{max}})} - \frac{1}{T_{fi}}} \quad \dots(2)$$

where τ is the age of the suspension, τ_{max} – the maximum age of the suspension, for which T_i was measured. If at the maximum age of the suspension *Laponite* particles exfoliated to the fullest possible extent, i.e. $S_{\text{ext}}(\tau_{\text{max}}) \approx S$, then the ratio

$S_{\text{ext}}(\tau)/S_{\text{ext}}(\tau_{\text{max}}) = S_{\text{ext}}/S$ and equals exactly to a fraction of individual platelets in the suspension, and

ratio $S_{\text{int}}/S = 1 - S_{\text{NMR}}/S$ – to that of tactoids.

RESULT AND DISCUSSION

Dependence of inverse spin-spin (T_2) and spin-lattice (T_1) relaxation times of hydrogen protons on *Laponite* concentration in suspensions of age 92 days is shown in Fig. 1. The intercepts of the

dependences with the ordinate axis are equal to the inversed spin relaxation time in bulk water and the slopes are proportional to the specific surface area of the particles in the suspension (Eq. 1). The linearity of the dependences demonstrates that the specific surface area of *Laponite* particles is constant in the concentration range of 0.5% - 3% w/w. It means that the aged suspensions *Laponite* tactoids exfoliate to the same extent for the wide concentration range. This conclusion is consistent with the previous findings^{16,17} based on the similar experiments. On the contrary, dependence of T_2 on *Laponite* concentration for suspensions of age of 1 day (Fig.1, open symbols) non-linear, meaning that for non-aged suspensions the specific surface area and the degree of particle exfoliation are concentration dependent. By fitting the data for the aged suspensions to the equation (1), the following coefficients were calculated:

$$a_1^{-1} = T_{1r} = 2.78 \pm 0.07 \text{ s}, k_1 = 7.6 \pm 0.6 \text{ s}^{-1}, a_2^{-1} = T_{12} = 2.5 \pm 0.9 \text{ s}, k_2 = 146 \pm 10 \text{ s}^{-1}.$$

The sensitivity of the inverse relaxation time to a specific area of *Laponite* is 19 times larger for spin-spin relaxation (k_2/S_{NMR}) compared to spin-lattice (k_1/S_{NMR}). Therefore, for examining *Laponite* exfoliation rates the inverse time spin-spin relaxation was chosen for further calculations. Figure 2 shows a dependence of relative specific area of *Laponite* in the suspensions, calculated by the equation (2).

Table 1 shows the characteristic time of exfoliation, when specific external area of the particles in the suspension reaches 90% of the maximum possible specific area; and percentage of the internal area enclosed within tactoids after preparation, which included 24 h of stirring. The data of table 1 shows that the fraction of tactoids

Table 1: Exfoliation dynamics for *Laponite* suspensions in water

Laponite concentration, % w/w	0.5	1	1.5	2	3
Time, needed for 90% exfoliation, days	21	18	11	2	< 1
Percentage of the internal area enclosed within tactoids after 24 hours of stirring, %	28%	31%	24%	14%	3%

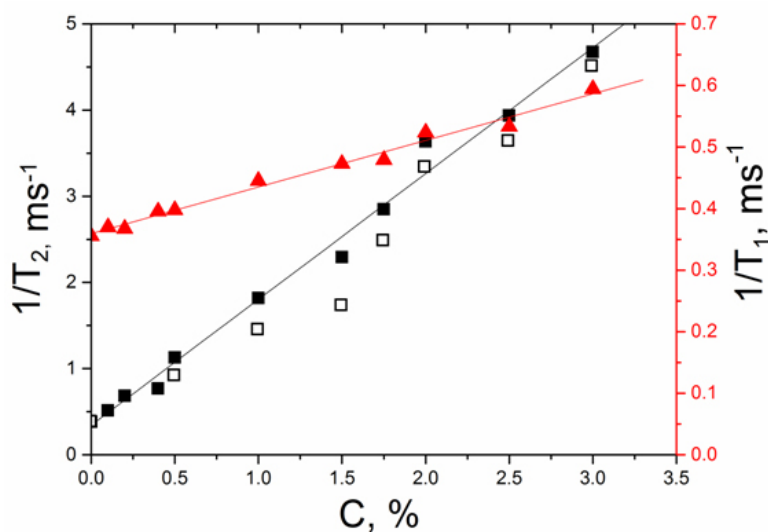


Fig. 1: Dependence of spin-spin (T_2 , squares) and spin-lattice (T_1 , triangles) relaxation times of protons of hydrogen on concentration of *Laponite* in suspension. Closed symbols indicate 92 days old suspensions and open symbols indicate 1 day old suspensions

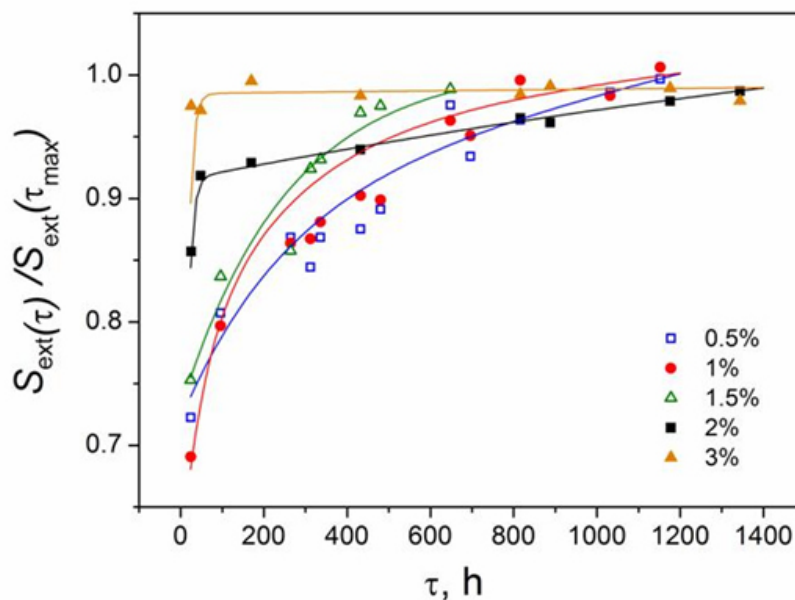


Fig. 2: Dependence of relative specific surface area of Laponite on the suspension age for different concentrations of Laponite. The lines serve as a guide to the eye

in suspension can be up to 31% after preparation. Surprisingly, for the suspensions with high *Laponite* concentrations (2% – 3% w/w) the specific surface area was close to the maximum possible area soon after preparation, suggesting much faster exfoliation rate for more concentrated suspensions compared to the less concentrated suspensions (Fig. 2). Such unexpected effect may be caused by the structure of *Laponite* platelets and the mechanism of their exfoliation. *Laponite* tactoids are known to exfoliate as follows. When the powder is dispersed in water, sodium ions intercalated between the platelets become hydrated, the initially layered structure weakens and is pushed apart into individual platelets or thinner tactoids by osmotic pressure. At the same time, it is also known that *Laponite* platelets have negatively charged lateral surface and positively charged edges at pH 10¹⁸, which are responsible for gelation of *Laponite* suspensions due to “edge-to-face” interactions resulting in “house-of-cards” gel structure¹⁹. We suggest that at the initial stages of exfoliation, before gelation, positively charged edges of randomly moving tactoids or platelets provide additional electrostatic attraction force on negatively charged surfaces of neighboring tactoids, facilitating exfoliation of layers already weakened by osmotic pressure. The possibility of such interaction

increases with increasing concentration of *Laponite*. This collective effect would increase the rate of exfoliation for more concentrated suspensions.

CONCLUSIONS

In summary, the investigation of *Laponite* exfoliation process by NMR relaxometry showed prolonged increase of specific wetted surface area of *Laponite* particles in aqueous suspensions, indicating continuing tactoid disintegration into platelets over extended periods of time - up to three weeks for 1 % w/w suspension. Surprisingly, the suspensions with higher *Laponite* concentrations demonstrated much faster exfoliation dynamics compared to the less concentrated suspensions. These results should be taken into account in the applications that are based on interactions with exfoliating clay particles surface and depending on the available surface area of the exfoliating materials.

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