Effects of sol–gel transition of clay colloids on the spectroscopic behavior of cationic dye adsorbed on the clay particles

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A B S T R A C T

Colloidal systems of smectite-type clay minerals have been examined as heterogeneous media of photofunctional molecules. However, behavior of the photoactive molecules adsorbed on the colloidal clay particles has not been systematically investigated in relation to the sol–gel transition of the clay colloids. We investigated effects of the sol–gel transition on the spectroscopic behavior of a cationic rhodamine dye adsorbed on the colloidal particles of synthetic hectorite (Laponite). The adsorbed dye indicated shift of the absorption and emission wavelengths occurring within a few days independent of the sol–gel transition, as well as increase in the fluorescence intensity that took place synchronously to the gelation occurring in a much longer time range dependent on the clay concentration. Observations of the sol–gel transition by fluidity loss at a macroscopic scale and alteration of the profile of autocorrelation function measured by dynamic light scattering (DLS) indicated that the former technique established the completion of the arrest of clay particles but the latter one tended to detect the beginning of the gelation. The increase in the fluorescence intensity of the dye started at the timing similar to that of the commencement of the sol–gel transition indicated by DLS.

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1. Introduction

Smectite-type clay minerals have been investigated as matrixes of photofunctional molecules such as organic dyes for a long time (Auerbach et al., 2004; Ogawa and Kuroda, 1995). Their structure is characterized by stacking of negatively charged aluminosilicate layers together with interlayer exchangeable cations (Theng, 1974). They host the functional molecules in their interlayer spaces to provide specific microenvironments for the guest molecules to regulate their functions. The intercalated molecules have been discovered to exhibit various properties that are not observed in homogeneous systems like solutions. Typical examples are unusual spectroscopic and photochemical behavior of functional dyes (Ogawa and Kuroda, 1995; Shichi and Takagi, 2000; Suzuki et al., 2012; Takagi et al., 2006, 2013). Such interactions between the clay minerals and functional molecules are further modified by changing the aggregation states of the clay particles. For example, porous structures constructed by pillaring and "house-of-cards" type agglomeration of the clay particles allow specific photoprocesses (Ogawa et al., 1992; Ooka et al., 2003; Yariv et al., 1990). Clay films prepared by casting or layer-by-layer assembling provide macroscopic anisotropy of the incorporated molecules (Suzuki et al., 2011; Umemura et al., 2002). In these applications, however, the clay minerals are used as solid matrixes.

Other than the employment of clay minerals in solid-state, colloidally dispersed clay particles have also been examined as the heterogeneous matrixes of functional molecules. The interlayer spaces of smectite-type clay minerals are infinitely swollen in water, by which the clay layers are exfoliated to be colloidally dispersed in water (van Olphen, 1991). Photochemical and photophysical behaviors of functional molecules are influenced by their adsorption onto the colloidal clay particles (Bujdák et al., 2002; Czímerová, 2004; DellaGuardia and Thomas, 1983; Eguchi et al., 2013; Ghosh and Bard, 1984; Ishida et al., 2014; Jacobs and Schoonheydt, 1999; Nakamura and Thomas, 1986; Nakato et al., 2012, 2013; Rao et al., 2011; Villemure et al., 1985; Zitnan et al., 2009). The adsorbed molecules located at the clay–solvent interfaces are influenced by both of the clay surfaces and solvents to which the molecules are exposed, and thus their behavior is different from those in the homogeneous solutions as well as on the clay surfaces and interlayers in solid state.

However, colloidal structures of the smectite-type clay minerals have not reached a comprehensive understanding despite long time debates. The clay colloids exhibit complicated sol–gel and isotropic–nematic phase transitions, both of which are accompanied by modification of the colloidal structures (Paineau et al., 2013; Ruzicka and Zaccarelli, 2011). In particular, the sol–gel transition is a nonergodic process that occurs with the time scale of more than months depending on the concentration of the colloidal clay particles. Various structures have been proposed for the gelled clay colloids such as "house-of-cards" networks (Dijkstra et al., 1995; Jönsson et al., 2008; van Olphen, 1991) that induce fractal structures of the aggregated clay

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particles (Pignon et al., 1997a, 1997b), and attractive and repulsive glasses with the arrest of the clay particles (Avery and Ramsay, 1986; Bonn et al., 1999; Mourchid et al., 1995; Tanaka et al., 2004).

The sol–gel transition of the clay colloids has been investigated mainly by scattering and rheological measurements (Bonn et al., 2002; Brandenburg and Lagaly, 1988; Jabbari-Farouji et al., 2007, 2008a, 2008b; Kroon et al., 1996; Marques et al., 2015; Michot et al., 2009; Mourchid et al., 1995; Mourchid and Levitz, 1998; Nicolai and Cocard, 2001; Pignon et al., 1997b; Ramsay and Linder, 1993; Rand et al., 1980; Ruzicka et al., 2004; Shalkevich et al., 2007; Tanaka et al., 2005; ten Brinke et al., 2007; Tudisca et al., 2012). These techniques indicate macroscopic states of the colloidal clay particles. Among them, dynamic light scattering (DLS) informs effects of the sol–gel transition of the clay colloids on the dynamics of the dispersed particles. Although most of the studies have employed synthetic hectorite known as Laponite, these studies have indicated gradual alteration of the profile of intensity autocorrelation function with the sol–gel transition (Bonn et al., 2002; Jabbari-Farouji et al., 2008b; Kroon et al., 1996; Marques et al., 2015; Nicolai and Cocard, 2001; Ruzicka et al., 2004; Tanaka et al., 2005; Tudisca et al., 2012). The autocorrelation functions of the gelled colloids show reduced time correlation of scattered intensity and more gradual fall down, reflecting suppression of the particle diffusion in the system.

Although the microenvironments and gelation of the clay particles have been extensively investigated, effects of the sol–gel transition on the microscopic conditions of the clay particles typically represented by the spectroscopic properties of the adsorbed dyes have scarcely been investigated. If the gelation influences the microenvironments around the clay surfaces, we should take into account the colloidal state of the clay particles in addition to their molecular-level and nanostructural conditions in order to understand the behavior of functional molecules adsorbed on the clay surfaces. In other words, the sol–gel transition could be utilized as a controlling parameter of molecular functions on the clay surfaces.

In the present paper, we report effects of the sol–gel transition on the spectroscopic behavior of a cationic rhodamine dye adsorbed on the colloidal particles of synthetic hectorite. Rhodamine dyes have been frequently investigated as spectroscopic probes for the surfaces and interlayer spaces of the clay minerals and related inorganic layered compounds, and polarity and rigidity of the clay microenvironments have been realized by the absorption and emission behavior of the adsorbed rhodamine molecules (Bujdák et al., 2003, 2004; Czímerová, 2011; Grauer et al., 1984; López Arbeloa and Martínez Martínez, 2006; López Arbeloa et al., 1995, 1997, 2007; Sasai et al., 2002; Shinozaki and Nakato, 2004; Tapia Estévez et al., 1993, 1994a, 1994b, 1995; Xie et al., 2009). The present study clarifies that the spectroscopic properties of rhodamine 6G (R6G) cations on the colloidal clay particles indicate two types of time-dependent behavior. One is reflected by the absorption and emission wavelengths, and it takes place in a short time range (within a few days) independent of the sol–gel transition. The other is alteration of emission intensity synchronous to the gelation, which occurs in a much longer time range.

2. Materials and methods

2.1. Sample preparation

Laponite RD, a synthetic hectorite (ideal formula $Na_{0.33}Mg_{1.67}$ $Li_{0.33}Si_4O_{12}H_2$, cation exchange capacity 0.75 meq g^{-1} Levitz et al., 2000) supplied by Rockwood Additives Ltd., was used as the source of the clay colloids without further purification. R6G chloride salt purchased from Sigma was dissolved into water to yield a 5×10^{-6} mol L^{-1} stock solution of the dye. Clay powders were added to water (200 mL) and the dispersion was stirred for 30 min. Then, a 50 mL portion of the R6G stock solution was added to the dispersion to yield the clay colloids for the observations. The clay concentration, indicated as [clay] hereafter, was set to 1, 10, 20, 30 g L^{-1}, and the

R6G concentration was fixed to 1×10^{-6} mol L^{-1}. The clay colloids were further stirred for 30 min after the addition of the dye solution, and we started the measurements of the samples. This starting time was defined as 1 h after the sample preparation. The colloid samples were kept in the dark. Small portions were repeatedly taken out from the stored colloids, and subjected to the spectroscopic and DLS measurements. The measured portions were not returned to the stored colloids (thus, the sample volume gradually decreased with repeating the measurements).

2.2. Sample characterizations

Fluorescence spectra were measured with a Jasco FP-6500 spectrofluorometer using a conventional rectangular quartz cuvette of 1 cm path length. For each sample, excitation spectrum for emission at 590 nm was recorded to determine the excitation wavelength, and then emission spectrum was obtained at the determined excitation wavelength to record the wavelength and intensity of the emission maximum. Visible spectra of the colloids were recorded on a Shimadzu UV-2450 spectrophotometer by a transmission method using a quartz cuvette of 1 cm path length. DLS of the colloids was examined by using a DLS-7000 (Otsuka Electronics Co., Ltd., Osaka, Japan) equipped with He-Ne laser with the wavelength of 632.8 nm, which is out of the absorption band of R6G. The scattering angle was set to 90°. The temperature of the bath was maintained at 25 °C by water circulation. We obtained the time correlation function, $g^2(\tau)$, of the measured scattered intensity defined by the following equation:

$$g^2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2},$$

where $I(t)$ is the scattered intensity at time t, and τ is the delay time. We employed the plots of $g^2(\tau) - 1$ against τ because the time correlation function of scattered amplitude, $g^1(\tau)$, is related to $g^2(\tau)$ by the following equation:

$$g^2(\tau) = 1 + \beta|g^1(\tau)|^2,$$

where β is the coherent factor.

3. Results

3.1. Sol–gel transition of the clay colloids

Colloids of Laponite, a synthetic hectorite, show sol–gel transition by standing the colloids under ambient conditions when [clay] is higher than 20 g L^{-1}. Fig. 1 shows variation of the colloid appearances with the lapse of time after the sample preparation. The gelation is detected by the loss of colloid fluidity in a 200 mL tall-form beaker for the colloids with [clay] higher than 20 g L^{-1}. Increase in [clay] reduces the time necessary for the gelation. In the present paper, we define the period required for the fluidity loss in the beaker as the "gelation time", which is estimated as 720 h (1 month) and 72 h (3 days) for the colloids of [clay] = 20 and 30 g L^{-1}, respectively. Although the colloid of [clay] = 10 g L^{-1} does not loose fluidity 2520 h (3.5 months) after the preparation, it shows viscosity increase related to the gelation. In contrast, the colloid of [clay] = 1 g L^{-1} does not indicate the gelation during our observations. The results are in accordance with previous studies, which have reported faster gelation of the Laponite colloids with larger [clay] (Jabbari-Farouji et al., 2007, 2008a, 2008b; Tudisca et al., 2012). This also indicates that the addition of a small amount of R6G in the present study hardly changes the sol–gel transition of the hectorite colloid.