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Electro-optics of plate-like silica particle suspension

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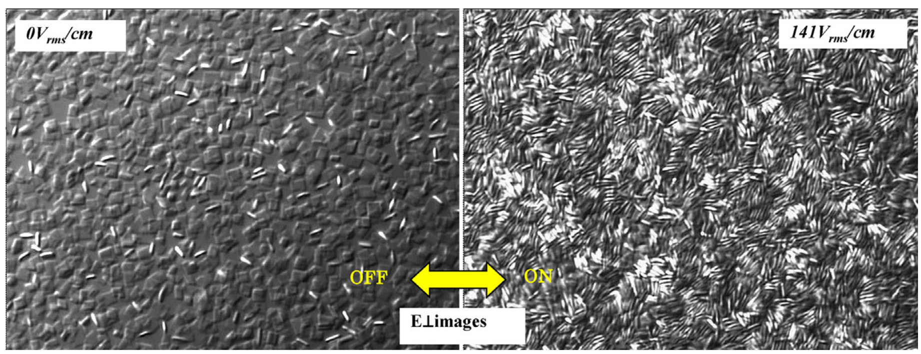
HIGHLIGHTS

- We focused on square plate-like silica particle, i.e., H^+-exchanged ilerite (H-ilerite).
- Ion concentration polarization and relaxation in asymmetric electrical double layer of H-ilerite were examined.
- Electro-optics of H-ilerite suspensions was characterized.
- H-ilerite platelets were aligned to electric field, followed by the formation of face-to-face aggregations.
- When large aggregations were formed, the transmittance change in electro-optics was remarkably enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

We focused on square plate-like silica particle, i.e., H^+-exchanged ilerite (H-ilerite). On the basis of the characteristics of ion concentration polarization and relaxation in asymmetric electrical double layer (EDL) around H-ilerite platelets, electro-optics of H-ilerite suspensions was characterized. The responses of H-ilerite suspension to electric field were assessed by impedance dispersion, microscopic observation and electro-optics optical transmittance of light with the wavelength of 550 nm. As electric field is increased, the relaxation frequency of EDL polarization for H-ilerite systematically shifted from 480 Hz (random orientation) to 126 Hz (alignment to electric field). When electric field of 141 V_{rms}/cm and 10 kHz was switched on, transmittance decreased instantaneously. It was also observed that H-ilerite platelets were individually aligned to electric field in dilute suspension, followed by the formation of face-to-face aggregations of the platelets in concentrated suspension in the presence of AC electric field. When large aggregations were formed, the transmittance change in electro-optics was remarkably enhanced. When electric field was switched off, the transmittance showed fast and slow relaxations. The fast one corresponds to the rotary Brownian diffusion and becomes slow with increasing the volume fraction. The slow one can be related to the release of face-to-face aggregations.

1. Introduction

In the presence of electric field, counter ions in electrical double layer (EDL) around colloids accumulate on one side of the EDL and are deficient on the other side [1]. This is termed ion concentration polarization of EDL. The ion concentration polarization induces dielectrophoresis and pearl chains of colloids that have been widely applied to nanoengineering processes [2,3]. Moreover, the ion concentration polarization for asymmetric EDL around an asymmetric particle causes a torque for rotation and alignment of the particle to electric field. Such an electric response of asymmetric particle induces changes of birefringence and light scattering. This has been well known as electro-optics.

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The electro-optics of colloid suspension has been extensively investigated on a number of colloid systems with a variety of shapes and chemical compositions [4]. Recently, a rapid progress in the study of carbon nanotubes has incited to investigate electro-optics on a variety of rod-like particles with high aspect ratio [5–7]. For anisotropic colloids with plate and disk shapes, for example, smectites and kaolinite, have been examined in 1960–80s [8]. It is true that clay minerals are of much interest in their electro-optic effects but it is difficult to eliminated inhomogeneous properties in their natural origin: (1) wide size distribution and irregular particle shape [9]; (2) coloration and/or contamination with inorganic and organic impurities; (3) positively charged edge and negatively charged face in a platelet; (4) aggregation problems such as bulk aggregation or face-to-edge coagulation in aqueous solution [10]; (5) coexistence of electric polarization (EDL polarization) along long axis and permanent dipole moment along short axis [11]. The heterogeneity of clay minerals prevents from clear understanding of the relation between EDL polarization and electro-optics.

We focus on H^+-exchanged ilerite (H-ilerite), i.e., square plate-like silica particle, because of well-defined shape, colorless transparence, uniform negative surface charge of face and edge and asymmetric EDL. In this study, on the basis of the electric response of EDL polarization characterized under AC electric fields that are high enough to align H-ilerite to electric field, electro-optics of plate-like silica particle suspension are examined precisely.

2. Materials and methods

2.1. Materials

Microscopic image of H-ilerite with the shape of square plate is shown in Fig. 1(a). We reported preparation of H-ilerite elsewhere [12] but describes in brief as follows. H-ilerite was prepared from layered sodium silicate with the molar ratio of $1Na_2O:8SiO_2:10H_2O$ (Na-ilerite) by exchanging Na^+ ions in the interlayer of Na-ilerite to H^+ ions. Na-ilerite was synthesized from the mixture of colloidal silica with silica gel (Wako, gel Q63), sodium hydroxide (Wako, analytical grade) and water ($1Na_2O:8SiO_2:10H_2O$) in a Teflon-lined autoclave at 115 °C for 3–4 weeks [13]. Suspension of Na-ilerite was rinsed with fresh Milli-Q water several times using centrifugation. Sediment of the suspension (50 g Na-ilerite) was dispersed in 2 L of 0.1 M HCl aqueous solution. The acidic suspension was stirred slowly for 8 h to exchange Na^+ to H^+ in the interlayer of Na-ilerite, followed by repeating it with 2 L of fresh 0.1 M HCl solution again. The sediment of the acidic suspension was rinsed with Milli-Q water repeatedly until the pH of supernatant reached pH ∼ 5. The products obtained before and after the cation-exchanging treatment were identified as X-ray powder diffraction patterns. As a spherical particle, monodispersed silica particle with an average diameter of 1.62 μm was supplied from Nippon Shokubai Co., Ltd. (Fig. 1(b)). Prior to use, silica particles were dispersed in Milli-Q water ultrasonically, followed by rinsing with water repeatedly until the conductivity of supernatant reached that of fresh Milli-Q water. H-ilerite with the average size of 3.5 μm × 3.5 μm × 0.17 μm, that is almost the same volume of a silica spherical particle with the diameter of 1.6 μm (Fig. 1(c)), was obtained using centrifugation. The side length and thickness of the H-ilerite were measured under Normarski-type differential interference optical microscope (Olympus Corporation, BH-2) and an atomic force microscope system (Digital Instrument Inc., Nanoscope III), respectively. Sodium chloride (Wako, analytical grade) was used as a supporting electrolyte without further purification. 0.1 N HCl solution (Wako, analytical grade). For all measurements and sample preparations, Milli-Q water was used in this study.

2.2. Impedance measurements

In order to characterize EDL polarizations and its relaxation of particle in itself, impedance measurements were performed for homogeneous suspension in which sedimentation of particles can be neglected. We used two different electronic measuring units which cover a wide range of applied electric field as reported previously [14]. At a root mean squared values of an electric field strength of 1.41–14.1 V_{rms}/cm (low electric fields), the impedance was measured between two Pt electrodes immersed in a small glass tube of uniform suspensions or its supernatants (Fig. 2(a)) with a impedance and phase analyzer (Solartron Analytical AMETEC Inc., S1260) through an impedance interface (Solartron Analytical AMETEC Inc., 1294) shown in Fig. 2(d). In the range of 14.1–141 V_{rms}/cm (high electric fields), the impedance measurements were performed using another electronic measuring unit shown in Fig. 2(e). AC electric fields with frequencies ranged from 10 Hz to 50 kHz were applied between the two Pt electrodes by a frequency generator (IWATSU ELECTRIC Co., Ltd., SG-4101) through an operational amplifier (Tektronix Co., Ltd., TM502). Current input/voltage output preamplifier (NF Corporation, LI-76) was connected in series with one of the two Pt electrodes, and then current passed through the medium between the two electrodes was monitored as an amplified voltage output. The electric response of the medium to AC electric field is given by complex impedance,

$$\hat{Z} = Z(\cos\,\theta - j\sin\theta) \quad (1)$$

where Z and θ are magnitude and phase components of complex impedance, respectively. The results of impedance measurements presented in this paper are mainly discussed in terms of conductance ($K = 1/Z\cos\theta$). For measurements under low electric field (Fig. 2(d)), equipments and data collection for magnitude and phase of complex impedance were operated via a personal computer. For measurements in high electric field range (Fig. 2(e)), magnitude and phase of complex impedance were estimated from Lissajous curve figured by applied electric field and amplified voltage signal corresponding to the current passed between the two electrodes.

2.3. Optically transparent indium tin oxide (ITO) electrode

ITO NESA glass (IN-100, 10 Ω/cm^2 1t × 100 mm × 100 mm) were purchased from Furuuchi Chemical Corporation. ITO glass was cut into plates with the size of 1t × 15 mm × 15 mm (electro-optical measurements) or 1t × 50 mm × 50 mm (electro-optical device) using a diamond-cut saw with lubricant. After pieces of ITO glass were immersed in detergent solution ultrasonically to remove lubricant and rinsed with Milli-Q water repeatedly, they were blow-dried with inert gas. A pair of ITO glass plates with the size of 1t × 15 mm × 15 mm was used for microscopic observations (Fig. 2(b)) and electro-optical measurements (Fig. 2(c)). A pair of ITO electrodes was separated by double-coated adhesive polyester tape with a thickness of 50 μm (no. 5605) that was kindly supplied from NITTO DENKO Corporation. Two prototypes of electro-optical device were assembled using original ITO electrodes and character-etched ITO electrodes, respectively. Characters were etched on ITO electrodes as follows. Plastic film stickers stamped out with alphabet letters were sticked on ITO coated surfaces. Openings with the shape of letters were filled with zinc powder (The Nilaco Corporation, <180 μm 99.85%), followed by dropping a small amount of 0.1 N HCl solution into the openings to remove ITO. The character-etched ITO electrode plates were immersed in detergent solution ultrasonically to remove glue of stickers and rinsed with Milli-Q water repeatedly, followed by blow-drying with inert gas. The conductivity of H-ilerite suspension intervening between ITO electrodes was equivalent to the resistances of 3000–2000 Ω/cm^2,