



Rheological properties of colloidal gels formed from fumed silica suspensions in the presence of cationic surfactants

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ABSTRACT

Rheological responses of colloidal gels formed from fumed silica suspensions in aqueous KOH solution at pH 11 by the addition of cationic surfactants, such as dodecyltrimethylammonium chloride ($C_{12}TAC$) and hexadecyltrimethylammonium chloride ($C_{16}TAC$) have been investigated as functions of silica and surfactant concentrations. Stable and aggregated fumed silica suspensions with negative charges cause gelling by adding the cationic surfactants through electrical neutralization of their micelles. The resulting critical strain and storage modulus of the gelled silica suspension increase with an increase in the surfactant concentration, irrespective of the cationic surfactant. This means that the higher the surfactant concentration is, the more effective the electrical neutralization interaction through the micelle of the cationic surfactant is. Moreover, the resulting gels can be classified into the strong-link gel and the weak-link one in the presence of $C_{12}TAC$ and $C_{16}TAC$, respectively, from a comparison of the silica volume fraction dependences of critical strain and storage modulus with the fractal gel model.

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1. Introduction

Aqueous suspensions of fumed silica particles were widely employed in academic and application fields [1,2]. They were formed by some aggregates of the silica particles and their aggregated structures were explored by small angle neutron scattering [2,3]. The aqueous suspensions of fumed silica particles were useful to polish the surfaces of silicone oxides in the chemical and mechanical polishing (CMP) technique due to their higher purity [4]. In the CMP process, the presence of coagulates formed from the aggregated fumed silica particles produced some scratches on the corresponding surfaces. In order to understand the formation mechanism and the physical properties of coagulates or a gel formed from the fumed silica aggregates, which are negative electrostatically stabilized at pH 11 [5], we performed to form a gel by the addition of KCl, where K^+ ion is preferentially adsorbed at the negative silica surfaces due to the structure-breaker ion in the Hofmeister sequence [6–8], and to study its rheological property as functions of concentrations of silica and KCl. In previous paper [5], we reported that colloidal gels formed from aggregates of the fumed silica particles could be regarded as the weak-link gel from the comparison of the silica volume fraction dependence of the critical strain and the storage modulus with the power-law predicted by the fractal gel model [9–12]. In the weak-link

gel, the bonding between the silica particles in the aggregates, namely intrafloc link, is stronger than that between the fumed silica aggregates (interfloc link) to form a gel network by electrical neutralization. Moreover, such a gelation mechanism is different from that for that of colloidal silica particles in the presence of KCl [13], where isolated particles initially aggregate to form fractal flocs, which correspond to intraflocs and the resulting intraflocs gradually gather to gel, leading to that intrafloc links are stronger than interfloc ones.

If cationic surfactants with alkyl groups were used as gel agents for the same fumed silica suspensions, it could be expected that electrical neutralization accompanied with the micelle formation of the cationic surfactants more effectively forms a gel at their concentrations much less than simple monovalent electrolytes. Moreover, such an association of the hydrophobic alkyl chain should strongly depend on the alkyl chain length and it could cause changes in gel-structure and rheological properties. In this paper, we investigate dynamic viscoelastic responses of the fumed silica suspensions at pH 11 in the presence of cationic surfactants, such as dodecyltrimethylammonium chloride ($C_{12}TAC$) and hexadecyltrimethylammonium chloride ($C_{16}TAC$) as functions of concentrations of silica and surfactant. Alkyl ammonium ions correspond to a kind of the structure-breaker ion [2–4] and their higher affinity adsorption should occur at the negative silica surfaces at pH 11. Among the dynamic viscoelastic responses of the fumed silica suspensions by adding the cationic surfactants, the critical strain at which the linear viscoelastic response region ends and the storage modulus in the linear viscoelastic response region will be mainly

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focused as a function of silica volume fraction at fixed cationic surfactant concentrations in terms of the power-law scaling behavior based on the fractal gel model.

2. Experimental

2.1. Samples

Aqueous fumed silica suspension (original silica suspension) was kindly supplied from Cabot Microelectronics Co. (Tsu, Japan). The original silica suspension contains 25 wt% solid contents, its pH is kept 11, and its specific density is 1.16. The average size and zeta potential of the silica particle in the original silica suspension was determined to be 170 nm and -50 ± 5 mV, respectively [5]. A dispersion medium, which was employed to prepare the original silica suspensions, was also kindly supplied from Cabot Microelectronics Co. The dispersion medium was also used as a solvent for the cationic surfactants.

C_{12} TAC and C_{16} TAC purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) were used after purification by re-crystallization in acetone. For aqueous solutions of the purified C_{12} TAC and C_{16} TAC, their critical micelle concentrations (CMC) were determined by a fluorescence spectroscopy technique using pyrene as a probe [14–16], which is preferentially aggregated in the hydrophobic parts of the corresponding surfactants.

2.2. Preparation of silica suspensions in the presence of cationic surfactants

To prepare a silica suspension with a desired silica volume fraction ϕ in the presence of the cationic surfactant, the original silica suspension was mixed in a pre-prepared aqueous cationic surfactant solution with a given concentration in a glass bottle. The resulting silica suspensions were subjected to mechanical shaking and then they were stored in an incubator at 25 °C for two days to obtain a schematic phase diagram of the respective silica suspensions, such as sol, gelled, and two phases separated silica suspensions from visual observation by the addition of C_{12} TAC or C_{16} TAC.

2.3. Adsorption characteristics of cationic surfactants

Adsorption characteristics of the cationic surfactants onto fumed silica particles were determined by using a Bromo Phenol Blue (BPB) method, which is an extracting and color development method by adding chloroform to aqueous solution containing BPB and a cationic surfactant. The BPB method is a kind of a qualitative analysis to confirm the presence of the cationic surfactants in a supernatant aqueous solution centrifuged from the silica suspension. If the cationic surfactants were present in the supernatant

solution, the chloroform layer after the extraction should become blue in the color, where the peak at 440 nm is detected in a visible spectrum.

2.4. Rheological measurements

Small-deformation oscillatory measurements of the gelled silica suspensions in the presence of C_{12} TAC and C_{16} TAC were performed using a Paar Physica MCR 300 rheometer with a CP50-1 cone-plate geometry (cone diameter = 50 mm and cone angle = 1°) at the angular frequency (ω) of 0.1 to 100 rad/s under the linear response, which was determined from a plot of the storage (G') and loss (G'') moduli against the strain (γ) at $\omega = 1$ rad/s and 25 °C. From the plot of the shear stress as a function of the strain, the critical strain (γ_c), namely the limit of linearity, was determined.

3. Results and discussion

Five peaks observed in a fluorescence spectrum of an aqueous solution of C_{16} TAC in the presence of pyrene are 373.5, 380.0, 384.0, 390.0, and 394.0 nm, which are coded the peak 1, 2, 3, 4, and 5, in the order of the wavelength, respectively. Similar peaks were observed in the fluorescence spectrum of an aqueous solution of C_{12} TAC in the presence of pyrene. The ratio of the intensities I_1 and I_3 at the peaks 1 and 3, namely I_1/I_3 is well known to be the most sensitive probe for determining of CMC for various surfactants [14–16]. From the plots of the I_1/I_3 value as a function of surfactant concentration, the CMC values of C_{12} TAC and C_{16} TAC were obtained to be 1.1 and 0.1 mM, respectively. The less CMC concentration of C_{16} TAC than C_{12} TAC is attributed to the longer hydrophobic tail connected to the head group of the former surfactant than the latter one. Similar results have been reported for various surfactants [17]. The resulting CMC values are one order magnitude less than those in pure water [17]. This is attributed to the presence of KOH in the dispersion medium to adjust pH and in general the CMC value in the presence of added salt becomes lower than that in the absence of the salt [17].

Addition of the respective cationic surfactants into the silica suspensions causes changes in the phase state and three different phase states appear as mentioned above. Figs. 1a and 1b show schematic phase diagrams of the silica suspensions in the presence of C_{12} TAC and C_{16} TAC, respectively. The silica suspensions at C_{12} TAC concentration ranges from 1 to 3 mM cause gelation for ϕ from 1 to 8%, whereas the silica suspensions at C_{16} TAC concentration ranges from 1 to 3 mM form a gel above at $\phi = ca. 5.0\%$. The concentration of C_{12} TAC required for gel formation is close to its CMC, whereas the C_{16} TAC concentration required for gel formation is beyond the corresponding CMC, indicating that gelation occurs above at CMC and their concentrations are much less than that of KCl [5]. This is attributed to the greater adsorption affinity

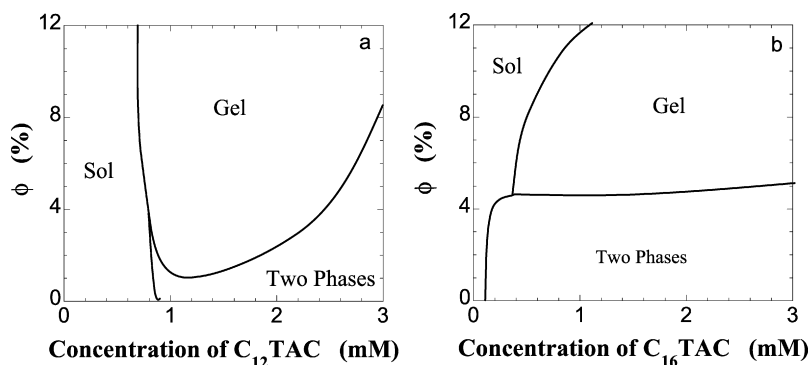


Fig. 1. Schematic phase diagram with three different states, such as sol, gel, and two phases silica suspensions in the presence of C_{12} TAC (a) and C_{16} TAC (b).

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