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ORIGINAL CONTRIBUTIONS

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Importance of the electrical double layers for the rheological properties of colloidal liquids

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Abstract Rheological studies of the colloidal liquids of silica spheres in the exhaustively deionized aqueous media are reported. Diameters of the spheres are between 5 nm and 60 nm. The suspensions showed "liquid" or weakly "structured liquid". The shear viscosities in the highly deionized system are substantially higher than those expected from Einstein's equation. When sodium chloride is added, the shear and the dynamic viscosities decrease sharply, which suggests that the electrical double layer plays an important role for the rheological properties. The ratio of the viscosity observed divided by the viscosity calculated from Einstein's equation shows a maximum value for the spheres of 45 nm in diameter. It is highly plausible that the viscosity of the suspension is influenced substantially by the ratio of the thickness of the electrical double layer and sphere sizes. The effective volume fraction of sphere including the electrical double layer, which is estimated from the viscoelasticity, shows a drastic increase when the effective volume fraction reaches around 0.74 corresponding to the closest packing in hexagonal lattice. The importance of electrical double layers is clear for the rheological properties of colloidal liquids.

Keywords Colloidal liquids · Deionization · Rheology · Electrical double layer

Introduction

Generally speaking, the colloidal spheres are coated with electrical double layers on their surfaces in a polar solvent such as water [1–12]. The simple ions in the diffuse region of the double layers are distributed according to a balance between the thermal diffusive forces and the forces of electrical attraction with the unlikely charged colloidal spheres. The thickness of the double layers is approximated with the Debye-screening length D_l,

$$D_l = \left(\frac{4\pi e^2 n}{\varepsilon k_B T}\right)^{\frac{-1}{2}}, \qquad (1)$$

where e is the electronic charge, ϵ is the dielectric constant of solvent, k_B is Boltzmann constant, and n is the concentration of free-state cations and anions in suspension, and is given by $n = n_c + n_s + n_0$, where n_c is the concentration (number of ions per cm^3) of diffusible counterions, n_s is the concentration of foreign salt, sodium chloride in this work, and n_0 is the concentration of both H$^+$ and OH$^-$ ions from the dissociation of water. In order to estimate n_c, the fraction of free counterions (β) must be known, since most counterions are bound tightly with the ions of the colloidal surface [3, 13–16]. Note that β of silica spheres of 45 nm in diameter, for example, is estimated to be 0.47 [15, 16].

According to the effective soft-sphere model [17–23], which is a simple but very convenient assumption especially for the deionized colloidal suspension, crystal-like ordering is formed when effective diameter (d_{eff}) of spheres including the Debye-screening length are close to or larger than intersphere distance (l), i.e., d_{eff} [$=$diameter of sphere (d_0) + $2D_{\mathrm{l}}$]$>l$. In crystal-like structures, the spheres fluctuate around their equilibrium positions. When d_{eff} is comparable to or shorter slightly than the l value, the distribution of the spheres is usually liquid-like and the spheres move vigorously with translational diffusion. The effective concentration in volume fraction is much higher than the stoichiometric one due to the contribution of the extended electrical double layers. When d_{eff} is shorter than l, a gas-like distribution is observed. Note that the observed intersphere spacing (l) is always close to the mean intersphere distance (l_0) calculated from sphere concentration, and l_0 can be safely replaced with l.

In our previous work, viscosities of colloidal dispersions in the deionized ("salt-free") state were measured with the use of an Ostwald-type and a rotational viscometer [24–30]. Several extraordinary properties were observed; (1) the reduced viscosity (specific viscosity, η_{sp} divided by sphere concentration, c) of liquid-like dispersions was much higher than those expected from Einstein's prediction and decreased sharply when sodium chloride was added [24, 25], (2) a sharp peak was observed in the reduced viscosity-concentration curves, which showed the phase transition between "liquid" and "solid" (or "crystal") structures [24, 25], and concentration dependency of the reduced viscosity of the deionized dispersions was sensitive to the type of colloidal particles [26, 27]. (3) a linear and sharp increase in shear stress was observed when shear strain increased for the crystal-like dispersions, and from which the elastic modulus was evaluated [28, 29], (4) log η (shear viscosity) of the crystal-like or solid-like dispersions increased linearly as log $\dot{\gamma}$ (shear rate) decreased with a slope of minus unity [28, 29]. Furthermore, (5) the absolute values of the viscosity of the deionized suspensions were highly sensitive to the ionic impurities [30].

From our experiences, spheres smaller than ca. 60 nm in diameter hardly form crystal structures even though the suspensions were deionized exhaustively because of the very vigorous Brownian motion of the small spheres. It should be noted here that the electrical double layers might not be formed firmly when the sphere size is not large enough compared with the simple electrolytes. Static and dynamic light-scattering measurements had been made for colloidal-liquids and -gases of silica spheres (29 nm in diameter) in the exhaustively deionized aqueous suspension and in the presence of sodium chloride in our previous study [31]. A single broad peak appeared for colloidal liquid in the light-scattering curve. It should be noted here that the colloidal crystals are not formed for the 29-nm size spheres at any sphere concentrations. The nearest-neighbored intersphere distances of colloidal liquids, l, agree excellently with the effective diameters of spheres (d_{eff}) including the electrical double layers and also with the mean intersphere distance, l_0, calculated from the sphere concentration, i.e., $l \sim d_{\mathrm{eff}} \sim l_0$. This relation emphasizes the importance of the electrostatic interparticle repulsive interaction.

There are a few reports on the rheological properties of small colloidal spheres (ca. <60 nm) in exhaustively deionized system. Rheological study on the detailed relationship between rheological properties and the thickness of the electrical double layers is important especially for the small spheres, since the small spheres move so vigorously and do not form ordered structures. In this work, an exhaustive deionization was made for the sample suspensions before the measurements for more than 7 years. The sphere size was smaller than ca. 60 nm in diameter. The rheological measurements were carried out carefully since the thickness of the electrical double layers is very sensitive to the ionic impurities and also to the shear forces.

Experimental

Samples

Colloidal silica spheres of CS22p (29 nm) and CS 45 (56 nm) were gifts from Catalyst & Chemicals Ind. Co. (Tokyo). Stock suspensions were deionized with the mixed bed of the ion-exchange resins (Bio-Rad, AG501-X8(D), 20–50 mesh, Richmond, Calif.) for more than 7 years. Water used for the sphere purification and for suspension preparation was purified by a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q plus, Millipore, Co., Bedford, MA). The properties of colloidal spheres used in this study are compiled in Table 1.

Table 1 Properties of spheres used

Sphere	Diameter (nm)	Charge density (μC/cm^2)
Snowtex-S [32]	8 ± 1	0.32
CS22p	29 ± 3	0.30
Snowtex-20L [32]	45 ± 5	0.68
CS45	56 ± 8	0.30
D1C25 [32]	85 ± 6	2.1
D1C27 [32]	91 ± 6	2.8
D1B22 [32]	109 ± 3	3.6
CS91 [29]	110 ± 5	0.48
D1B41 [32]	215 ± 5	1.3
N550 [32]	563 ± 8	6.6
N800 [32]	780 ± 9	1.2

Rheological measurements

A coaxial type rheometer (Rheosol-G2000W-GF, UBM Co., Kyoto) was used. The strains applied to the sample were estimated by subtracting the rotation of the inner cylinder from that of the outer cup. The torque was detected from the twist angle of the torsion wire of 0.3 mm, diameter. The resolution of the torque sensor was in the range from 10^{-6} kgf m to 10^{-4} kgf m. An outer cup (25 mm in diameter and 65 mm in height) was made of stainless steel. The gap between the inner cylinder and the outer cup was 1.5 mm. The latter rotates to apply a shear strain to the sample, and the former detects the torque induced. Before recording the measurements, the outer cup and the inner cylinder were rinsed with deionized water as exhaustively as possible. A simple cover was attached to the cup during the measurements in order to avoid the air contamination. The experiments were completed within a few hours after the sample was set into the cup. All the measurements were made in a room temperature regulated at 25 °C.

Results and discussion

Figure 1 shows the shear viscosity of exhaustively deionized suspensions of CS22p and CS45 spheres at $\phi = 0.033$ as a function of shear rate ($\dot{\gamma}$). It is clear that the η-values increased as the shear rate increased, the so called "dilatancy". This fact indicates that the thickness of the electrical double layer is large in this highly deionized state resulting in the shear thickening phenomena. In the case of CS45 spheres, the rate of increase in the viscosity decreased with shear rates, which suggests that the electrical double layers deformed from spherical to flame-like [29] by high shear rates. The effective volume fraction (ϕ_{eff}) including the electrical double layer was estimated using Eq. 2 from the rheological measurements in this work [33, 34].

$$\eta = \eta_0 (l + k_E \phi_{eff}). \qquad (2)$$

Here, η is the viscosity of colloidal suspension from the present measurements of viscoelasticity, η_0 is the viscosity of dispersion medium (0.00089 Pa s for water at 25 °C), k_E is the Einstein's coefficient (2.5 for sphere) and ϕ_{eff} is the effective volume fraction of colloidal sphere.

The dynamic viscosity (η') of CS45 spheres is shown in Fig. 2 as a function of angular frequency (ω). At small strains, η' decreased as the angular frequency increased. At large strains, however, η'-values were small and independent of ω. These results suggest that the suspension of CS45 spheres forms weakly "amorphous-solid" at low strains and the structure melts away to "liquid" in a high oscillating shear.

Figure 3 shows a typical example of the viscosities (η) of the deionized and salt-containing aqueous suspensions of CS45 spheres as a function of shear rate. The solid line indicates the calculation from Einstein's equation [33, 34]. The broken line is the water's reference value. Clearly, the η-values of the exhaustively deionized suspension are several tensfold larger than those from Einstein's prediction. The η-values were insensitive to $\dot{\gamma}$, which indicates clearly these suspensions being the Newtonian liquid, though the suspensions showed dilatancy at lower sphere concentrations (refer to Fig. 1). When the salt concentration increased, the ob-

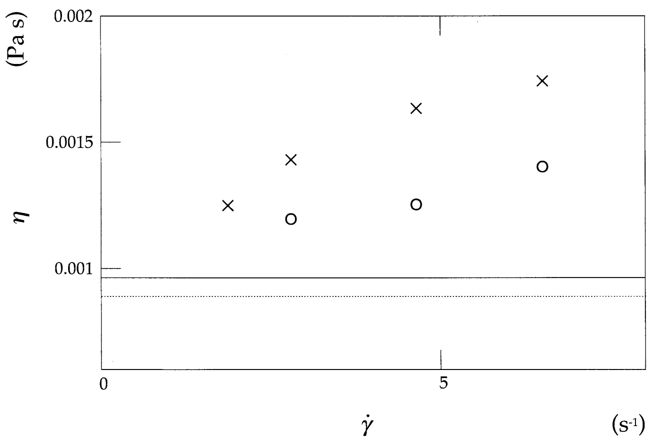

Fig. 1 Shear viscosity of colloidal suspensions as a function of shear rate at 25 °C. $\phi = 0.033$. *Open circle* CS22p, *cross* CS45. *Continuous line* indicates prediction from Einstein's equation for $\phi = 0.033$. *Dotted line* indicates water

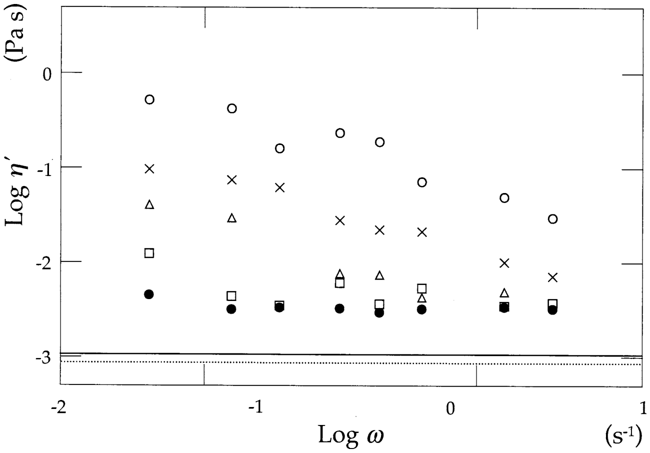

Fig. 2 Dynamic viscosity of CS45 spheres as a function of angular frequency at 25 °C. $\phi = 0.088$. *open circle*: $\gamma = 0.01$, *cross*: 0.06, *triangle*: 0.15, *open square*: 0.6, *closed circle*: 1.5. *Solid line* indicates prediction from Einstein's equation for $\phi = 0.088$. *Dotted line* indicates water

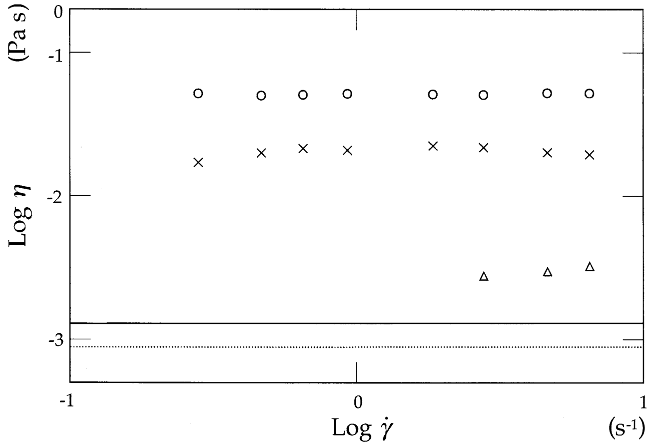

Fig. 3 Shear viscosity of colloidal suspensions of CS45 spheres as a function of shear rate at 25 °C. $\phi = 0.181$. *Open circle*: [NaCl] = 0 M, *cross*: 1.0×10^{-4} M, *triangle*: 1.0×10^{-3} M. *Continuous line* indicates prediction from Einstein's equation for $\phi = 0.181$. *Dotted line* indicates water

served values closely approached to the calculated values especially for high salt concentrations, for example, the ratio η/η_{cal} was 2.1 at $[NaCl] = 10^{-3}$ M. These facts support strongly the important role of the electrical double layers around the colloidal spheres especially in the deionized suspensions.

The ratio of the shear viscosities against those estimated from Einstein's equation are compared in Fig. 4 for CS22p and CS45 as a function of ϕ with results of other deionized colloidal suspensions reported in our previous work [29, 32, 35]. When the sphere concentrations are lower than 0.01 in volume fraction, η/η_{cal} values are close to unity, which means that the interaction among the colloidal spheres are very small. At sphere concentrations higher than 0.01, η/η_{cal} values increased drastically when ϕ increased. When sodium chloride was added, η/η_{cal} decreased substantially as shown in the figure (see the data for CS45 sphere). This observation supports the idea that the thickness of the electrical double layers decreases when the concentration of sodium chloride increases. It is interesting to note here that the ratio η/η_{cal} increased first and then began to decrease when the diameter of the sphere increased. The ratio showed maximum when the diameter of the sphere was around 50 nm. The viscosity ratio for the colloidal crystals [29] (CS91, colloidal silica spheres in water) are also shown in the Fig. 4. The values were very high compared with the corresponding colloidal liquids.

Figure 5 shows the relation between the volume fraction of the colloidal spheres and the effective volume fraction including the electrical double layer calculated by using Eq. 2. The additional data of ϕ_{eff} in our previous work [29, 32, 35] for the deionized suspensions of other large colloidal spheres were added as shown here. The added data were obtained at shear rate in the range from 1.0 s^{-1} to 1,000 s^{-1}, and further from the suspensions which behaved like as Newtonian liquid where the effect of the shear rate on the viscosity can be neglected. For all the suspensions, ϕ_{eff} increased when ϕ increased. The slopes of ϕ_{eff}-ϕ profiles were larger than unity at ϕ lower than 0.003. The slopes decreased gradually with increasing ϕ at $\phi > 0.003$. When ϕ increased to be about 0.01, ϕ_{eff} approached 0.74, it corresponds to hexagonal closest packing, and increased drastically as ϕ

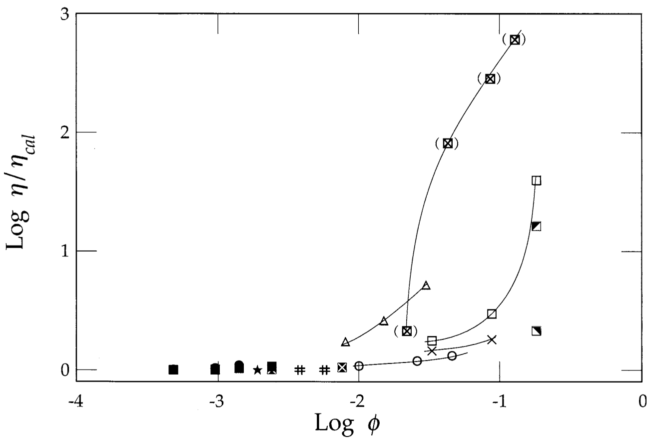

Fig. 4 Shear viscosity divided by viscosity estimated from Einstein's equation as a function of volume fraction at 25 °C. *Open circle*: Snowtex-S [34], *cross*: CS22p, *open triangle*: Snowtex-20L [34], *open square*: CS45, *square with upper-left triangle*: CS45 ([*NaCl*] = 10^{-4} M), *square with upper-right triangle*: CS45 ([*NaCl*] = 10^{-3} M), *filled circle*: D1C25 [34], *filled triangle*: D1C27 [34], *filled square*: D1B22 [34], *white square with* ×: CS91 [29], *black square with* ×: D1B41 [34], *filled star*: N550 [34], *hash*: N800 [34]

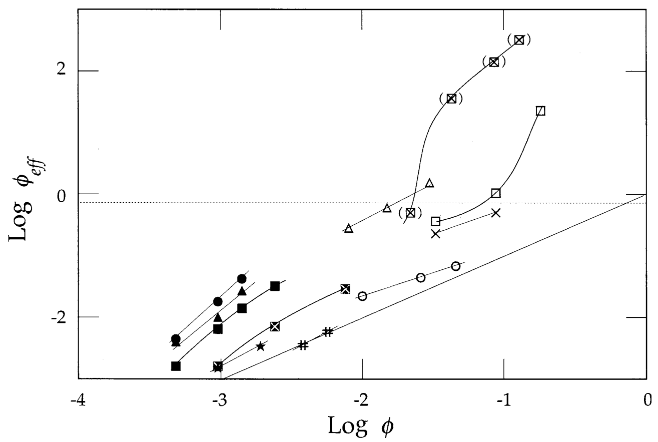

Fig. 5 Effective concentration of colloidal sphere as a function of volume fraction at 25 °C. *open circle*: Snowtex-S [34], *cross*: CS22p, *open triangle*: Snowtex-20L [34], *open square*: CS45, *filled circle*: D1C25 [34], *filled triangle*: D1C27 [34], *filled square*: D1B22 [34], *white square with* ×: CS91 [29], *black square with* ×: D1B41 [34], *filler star*: N550 [34], *hash*: N800 [34]. *solid line*: $\varphi_{eff} = \varphi$, *dotted line*: $\varphi_{eff} = 0.74$

increased. This fact means that a large interaction between spheres was induced among the spheres with an effective diameter including the electrical double layer.

Clearly, the increase in the viscosity of the colloidal suspensions in the course of deionization is due to expansion of the electrical double layers around the spheres in the deionized condition. The thickness of the double layers is estimated by using Eq. 3.

$$\frac{\phi_{\mathrm{eff}}}{\phi} = \left(\frac{d_0 + 2D_{l,\eta}}{d_0}\right)^3. \tag{3}$$

Here, $D_{l,\ \eta}$ indicates the thickness of the layers estimated from viscoelastic measurements.

The values of $D_{\mathrm{l},\ \eta}$ and the ratios of the thickness against the diameter D_{l}/d_0 are shown in Fig. 6 as a function of d_0. The calculated value of $D_{\mathrm{l},0}$ from the sphere concentration is also in the figure. $D_{\mathrm{l},\ \eta}$ and $D_{\mathrm{l},\ \eta}/d_0$ values increased when d_0 increased and then decreased passing the maximum at d_0 ~100 nm. $D_{\mathrm{l},0}$ increased gradually as d_0 increased, which means that the spheres left the neighboring spheres as d_0 increased. The cause of low $D_{l,\ \eta}$ values when d_0 is small may be related with vigorous Brownian motion of the small spheres. At d_0 larger than 100 nm, the interaction among the spheres might decrease when the sphere size increased because the expansion of the intersphere distance occurred as the sphere size increased, resulting in the decrease in the shear viscosity. This fact suggests that the interaction among the colloidal spheres could not be neglected completely in the deionized suspensions, even at low sphere concentrations. The difference between the values of $D_{\mathrm{l},\ \eta}$ and $D_{\mathrm{l},\ \eta}/d_0$ increased as d_0 increased. It means that the larger size of spheres induced the smaller ratio of the Debye length to the sphere size. This fact indicates strongly that the electrical double layer has a decisive role for the viscosity.

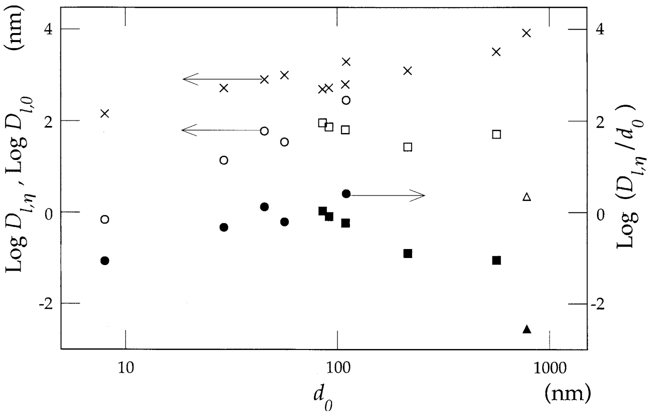

Fig. 6 Thickness of the electrical double layer estimated from viscoelastic measurement $D_{\mathrm{l},\ \eta}$ and that from sphere concentration $D_{\mathrm{l},\ 0}$ and the ratio of the thickness of the layer to the sphere diameter $D_{\mathrm{l},\ \eta}/d_0$ as a function of sphere diameter at 25 °C. *open circle*, *filled circle*: $\phi = 1.4\times10^{-3}$, *open triangle*, *filled triangle*: 5.8×10^{-3}, *open square*, *filled square*: 0.030. *open circle*, *open triangle*, *open square*: $D_{\mathrm{l},\ \eta}$, *cross*: $D_{\mathrm{l},\ 0}$, *filled circle*, *filled triangle*, *filled square*: $D_{\mathrm{l},\ \eta}/d_0$

In this study, it is clear that the effect of the sphere diameter on the viscosity was closely associated with the relation between the thickness of the electrical double layer and the sphere sizes; (1) for the small spheres, a sufficient electrical double layer can hardly form because of vigorous brownian motion of spheres, (2) for the large spheres, the ratio of the Debye length to the sphere size decreases with increase of the sphere diameter.

Conclusions

Rheological measurements for colloidal suspensions of silica spheres smaller than ca. 60 nm in diameter in exhaustively deionized aqueous media were carried out. The suspensions showed liquid or weakly structured liquid behaviors. The shear viscosities in highly deionized system were substantially higher than those expected from Einstein's equation. The ratio of the thickness of the electrical double layers and the size of the sphere is an important factor for the shear viscosity of the suspension.

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