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The viscosity of colloidal spheres in deionized suspension

The importance of charge density and monodispersity of polystyrene spheres

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SUMMARY

Reduced viscosities (specific viscosity divided by concentration) of polystyrene spheres (diam. ca. 120 nm) show the quite different concentration dependencies when their charge densities (c.d.) and monodispersities (m.d.) are different. A sharp peak, which corresponds to the transition between liquid-like and crystal-like structures, is observed for spheres having low c.d. and high m.d. The rigidities and yield stresses of crystal-like structures, which are evaluated from the steady-flow viscometry, are sensitive to c.d. and m.d. The way the viscometric properties are influenced by c.d. and m.d. of spheres demonstrates that the electrostatic intersphere repulsion and the elongated Debye-screening length around sphere are both essential for the appearance of the extraordinary crystal-like and liquid-like structures in deionized colloidal spheres.

INTRODUCTION

Keen attention has been paid to the extraordinary properties of deionized colloidal suspensions such as formation of the crystal-like and liquid-like structures(1-17). The extraordinary properties are due to the expanded Debye-screening length and electrostatic repulsion between colloidal spheres.

Recently, this author measured the viscosities of colloidal spheres in deionized ("salt-free") suspensions with the use of an Ostwald-type viscometer and a rotational viscometer(18-20). Extraordinary viscosity behaviour was observed; (1)the reduced viscosity (specific viscosity, η_{sp} divided by concentration(c)) of liquid-like colloidal suspensions was much higher than would be expected by Einstein's prediction and decreased sharply with increasing concentration. (2)A sharp peak showing the transition between liquid-like and crystal-like structures was observed for deionized spheres. (3)The sharp increase in shear stress (S) with increasing shear rate (q) was observed for the crystal-like structures, and from which the elastic modulus was evaluated. (4)The log η for the crystal-like suspensions increased linearly as log q decreased with a slope of -1 at small q values. In this report, the significant influences of surface charge densities (c.d.) and the monodispersities (m.d.) of colloidal spheres on the viscosity properties are investigated in detail using four kinds of polystyrene spheres having similar sizes (109-126 nm in diameters) but different c.d. and m.d. values.

EXPERIMENTAL

Materials

Monodisperse polystyrene spheres, D1B76, were purchased from Dow

Chemical Co. N100 was a product of Sekisui Chemical Co. (Osaka). S065 spheres were prepared by emulsifier-free emulsion polymerization of styrene with $K_2S_2O_8$ as an initiator in water at 70 °C in a nitrogen atmosphere. Monodisperse polystyrene spheres containing sulfonate groups, SS-29 were synthesized by emulsifier-free emulsion copolymerization of styrene, divinylbenzene, and potassium styrenesulfonate with $K_2S_2O_8$. Diameters and other characteristics of the spheres are listed in Table 1. The values for the diameters and their dispersions (standard deviations) were estimated using an electron microscope. The c.d. values of strongly acidic- (sulfate or sulfonate ions) and weakly acidic-groups (carboxylic acid moeities) were determined by the conductometric titration with a Wayne-Kerr autobalance precision bridge (model B331, mark II, Bognor Regis, Sussex). Previously, the c.d. was determined for the strongly acidic groups only. However, in this work conductometric titration curves were reexamined and the concentrations of strongly acidic- and weakly acidic-groups were determined separately(4). These spheres were carefully purified several times using an ultrafiltration cell (model 202, membrane: Diaflo XM300, Amicon Co.). Then the samples were treated on a mixed bed of cation- and anion-exchange resins (Bio-Rad, AG501-X8(D), 20-50 mesh) for at least ten days. The resulting suspension was believed to contain only the macroions (spheres), their counterions (H^+), and H^+ and OH^- from the water dissociation. Water used for the purification and for solution preparations was deionized by using cation- and anion-exchange resins (Puric-R, type G10, Organo Co., Tokyo) and purified further by a Milli-Q reagent grade water system (Millipore Co., Bedford, MA).

Table 1. Properties of spheres used

Sphere	Diameter (nm)	Monodispersity (nm)	Charge density(μC/cm^2) Strong acid	Weak acid
D1B76	109	±3 excellent	2.1	0.71
S065	110	±5 good	1.9	1.1
N100	120	±7 good	6.8	1.2
SS29	126	±5 good	5.5	2.7

Viscosity Measurements

An Ostwald-type viscometer was used at 25 ± 0.05 °C. The shear rate for water near the glass wall of the capillary tube was 310 s^{-1}. The viscometer was cleaned as completely as possible by chromic acid mixture followed by rinsing thoroughly with pure water. A rotational viscometer (Rotovisco RV20, Haake Co., Karlsruhe) was used at 25 ± 0.05 °C to obtain steady flow viscosities. S values were measured as a function of q, and the viscosities were evaluated from the S divided by the corresponding q. The local shear elastic modulus (rigidity, G) of colloidal crystal was obtained from the slope of the plots of S against qt/2 using the rotational viscometer.

RESULTS AND DISCUSSION

Concentration Dependence of the Viscosity of Deionized Colloidal Spheres

The plots of the reduced viscosity, η_{sp}/c against c are shown in figure 1 for S065, SS29, D1B76, and N100 spheres in deionized suspension. Surprisingly, the concentration dependences are quite different though the diameters of the four spheres are similar to each other; the η_{sp}/c values of S065 and SS29 spheres increased with increasing concentration, whereas

N100 decreased. Furthermore, a sharp peak was observed for the deionized D1B76 spheres.

The η_{sp}/c - c profile of D1B76 spheres was quite similar or almost the same to that of D1B22 spheres reported previously(18); both the absolute values of η_{sp}/c and the peak concentrations were quite similar between them. The diameter and the c.d.'s of strongly and weakly acidic groups of D1B22 were 109 ± 3 nm, 2.5 $\mu C/cm^2$, and 1.1 $\mu C/cm^2$,respectively. These values are very similar to those of D1B76. As was discussed previously(18), the peak appearance was correlated deeply to the transition between liquid-like and crystal-like suspension structures. For both D1B22 and D1B76 spheres, suspensions of the concentrations near the peaks showed colorful and beautiful iridescence and the size of flickering crystallites became smaller as the concentration increased(21,22). The sharp peak must be due to the transition between liquid-like and crystal-like suspension structures. Changes in the size of the crystallites would also make an important contribution to the transition. From our experiences, crystallites appeared for the polystyrene spheres of low c.d. and high m.d.

In the deionized suspension, the strongly acidic groups only dissociate and the dissociation of weakly acidic ions can be safely neglected. The c.d.'s of strongly acidic groups for D1B76 and D1B22 were 2.1 and 2.5 $\mu C/cm^2$, which are comparatively low. Furthermore, D1 latex series, products of Dow Chemical Co., such as D1C25, D1C27, D1B22, and D1B76 showed the crystallites very often. Then we believe that the m.d.'s of D1B76 and D1B22 spheres are very high, though the more quantitative analysis for the m.d. is quite difficult except the standard deviations of

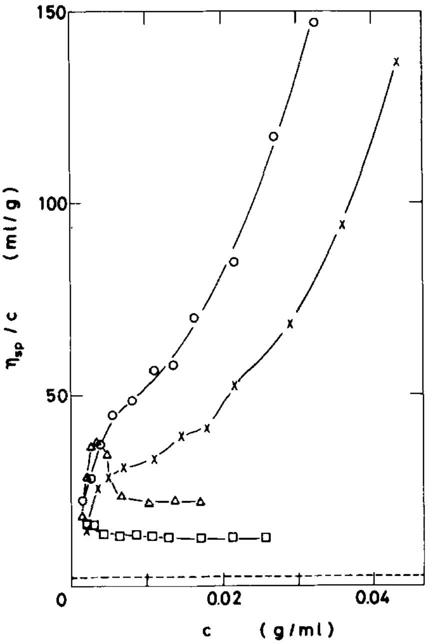


Figure 1. The plots of η_{sp}/c against c for S065(O), SS29(X), D1B76(Δ), and N100(□) spheres at 25°C.
----: Einstein coefficient.

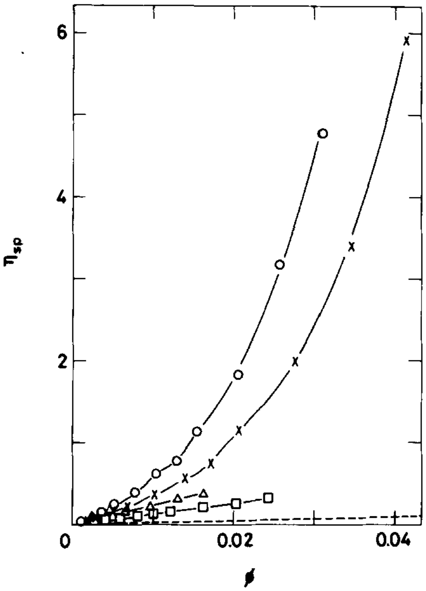


Figure 2. The plots of η_{sp} against φ for S065(O), SS29(X), D1B76(Δ) and N100(□) spheres at 25°C.
----: Einstein coefficient.

diameters cited in table 1.

The m.d.'s of other spheres used in this work are believed to be lower than those of D1B76 and D1B22 spheres. Among three spheres of S065, SS29 and N100, the η_{sp}/c values were in the order S065 > SS29 > N100 (see figure 1). On the other hand, c.d.'s of the strongly acidic groups were in the order S065 < SS29 < N100. Thus, the viscosity increases as the c.d. decreases, when the comparison is carried out among the spheres having similar m.d.'s. This order in the η_{sp}/c values is explained reasonably by the significant role of the Debye-screening length; a colloidal sphere is coated with a thick electrical double layer. The Debye length D_l is calculated from equation (1):

$$D_l = (4\pi Bn)^{-1/2} \qquad (1)$$

Here, B is the Bjerrum length given by $e^2/\varepsilon kT$, where e is the electronic charge, ε the dielectric constant of the solvent, and n is the total concentration of the free-state (diffusible) cations and anions in suspension given by equation (2);

$$n = n_c + n_s + n_o \qquad (2)$$

where n_c is the concentration of diffusible counterions (protons), n_s is the concentration of ions from the foreign salt, and n_o is the concentration of hydrogen and hydroxide ions from the water dissociation. In order to estimate n_c, the fraction of free-state counterions (β) must be known. The β values were determined for colloidal spheres of various sizes and c.d.'s by conductance and electrophoretic mobility measurements, and also theoretically(4,23-25). The n_c-value for the spheres of low c.d. is small, and then the D_l-value is large according to equation (1). Thus, the effective sizes and then effective volumes including the electric double layers of spheres should be large for the spheres of low c.d.

According to the tremendous amount of work on the specific viscosity of colloidal spheres, the following equation is given(26):

$$\eta_{sp} = \eta/\eta_o - 1 = k_1\phi + k_2\phi^2 + \ldots \qquad (3)$$

Here ϕ is the concentration of the colloids by volume fraction. k_1 is the Einstein coefficient,i.e., 2.5. k_2 denotes the electrostatic interaction parameter. Equation (3) shows that the viscosity of colloidal spheres is sensitive to the concentration (ϕ) only irrespective of the diameter of spheres. The dotted lines in figure 1 and figure 2 show the Einstein coefficient (k_1). Clearly, the deviation from Einstein's equation [k_1= 2.5 in equation (3)] is very significant in the deionized suspensions. Qualitatively speaking, the large k_2 obtained for S065 and SS29 spheres implies that the electrostatic repulsive interaction is significant.

By assuming that the simplified relation given by equation (4) holds for the deionized colloids, the effective volume fraction (ϕ_{eff}) of spheres including the Debye length is evaluated:

$$\eta_{sp} = k_1\phi_{eff} \qquad (4)$$

D_l is now calculable using the relation, $\phi_{eff}/\phi = [(d_o + 2xD_l)/d_o]^3$, where d_o is the real diameter of the spheres. D_l values thus evaluated from the initial slopes in figure 2 ($D_{l,obs}$) were 90, 80, and 40 nm, for S065, SS29, and N100 spheres, respectively. On the other hand, the Debye lengths calculated from equation (1), $D_{l,calc}$ were 180, 115, and 100 nm, respectively at 0.5 vol%. Here, we assumed β values to be 0.1 for all the spheres. The orders of $D_{1,obs}$ and $D_{1,calc}$ were the same to each other, though the magnitudes of the formers were smaller than the latters. This strongly supports that the effective hard-sphere model explains the extraordinary properties of deionized colloidal spheres satisfactorily. The inequality between $D_{1,obs}$ and $D_{1,calc}$ is ascribed partly to the strong distortion of the electrical double layers from spherical under the shearing flow of spheres in a capillary tube of the viscometer.

It was clearly observed in figure 1 that the η_{sp}/c values of D1B76 spheres having high m.d. and low c.d. were lower than those of S065 and SS29 spheres at relatively high concentrations. This may be ascribed to the steric effect,i.e., the crystal-like structures of highly monodispersed spheres are formed and/or broken much easier than the highly distorted crystal-like structures of polydispersed spheres. A detailed discussion on this effect is in progress in our laboratory especially for the binary mixtures of spheres having different sizes.

It should be mentioned here that the formation of crystallites was not observed for the suspensions of comparatively polydispersed S065 and SS29 spheres, though the iridescent color was observed. The crystal-like structures of S065 and SS29 are considered to be highly distorted. Suspensions of N100 spheres were milky and both the crystallites and iridescent color were not recognized at all.

Steady Flow Viscosity of Deionized Colloidal Spheres

Figure 3 shows the plots of S against q for SS29, S065, D1B76, and N100 spheres and water. S values of SS29, S065, and D1B76 increased drastically at the very small q, and then showed very significant non-Newtonian flow. The first increase in S is ascribed to the deformation of crystal-like structures by the shear strain as was observed for the first time by Mitaku et al.(27,28). For N100 spheres and water, the S-q curves showed a typical feature of Newtonian flow showing liquid-like structures. Nonexistence of the crystal-like structures for the N100 spheres is quite understandable if we take into account the fact that the contribution of the Debye length is not so significant, because both the c.d. and the polydispersity are high.

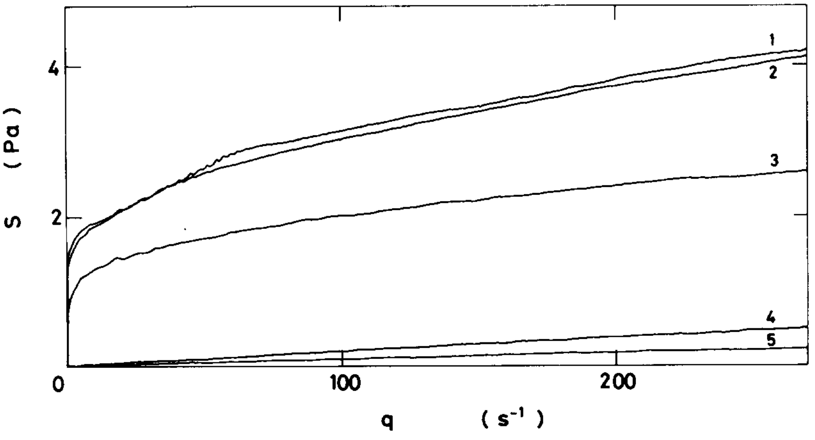
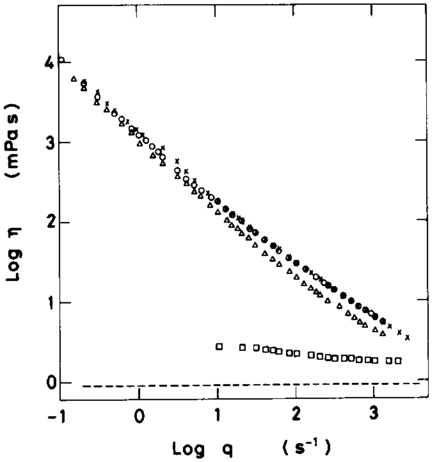


Figure 3. The plots of S against q for deionized spheres at 25°C. Curve 1: SS29, 10.3 vol%, 2:S065, 8.08 vol%, 3:D1B76, 9.77 vol%, 4:N100, 6.06 vol%, 5:water.



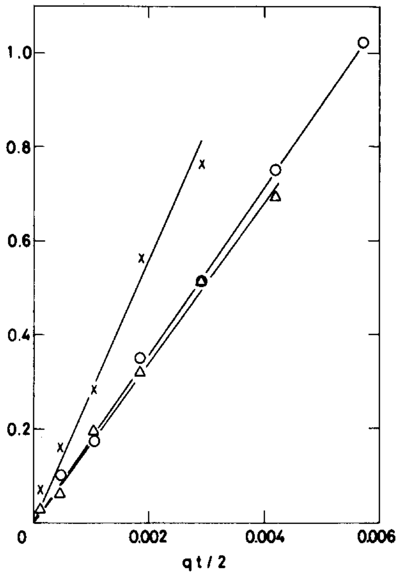


Figure 4. The plots of log η against log q for deionized spheres at 25°C. O:S065, 8.08 vol%, X:SS29, 10.3 vol%, Δ:D1B76, 9.77 vol%, □:N100, 6.06 vol%, ----: water.

Figure 6. The plots of S against qt/2 for deionized spheres at 25°C. O:S065, 8.08%, X:SS29, 10.3 vol%, Δ:D1B76, 9.77 vol%,

Figure 4 shows the plots of log η against log q derived from figure 3. At low q values, log η of S065, SS29 and D1B76 decreased linearly as log q increased with the slope -1.0. This means that the suspensions are truely crystal-like. When q was high, absolute values of the slopes decreased. This implies that the crystal-like structures were melted partly by the flow. For N100 spheres at 6.06 vol% the log η vs. log q plots show the typical rheological feature of liquid-like structures.

Rigidity of Crystal-like Suspensions

It is surprising to observe the initial sharp increase in shear stress at shear rate close to zero. Figure 5 shows the plots of S against q for S065 (curve A), SS29 (B) and D1B76 (C) spheres in deionized suspensions. Clearly, S increased abruptly within 0.1 s^{-1}, and the S-q curves were S-shaped. Furthermore, the values of yield stress, at which the flow starts, were observed clearly. The S-shaped curves imply that the stress-strain relationship for the crystal holds in the range of very small q values when the crystal-like structures do not flow by the shear rate. Since the shear strain is given by an integral, $\int_0^t q dt$, the local shear elastic modulus (rigidity, G) of colloidal crystal is obtained from the slope of the plots of S against qt/2, where t is time.

Figure 6 shows the S vs. qt/2 plots. The linear relationship between S and qt/2 was observed excellently as is clear in the figure. By this procedure, the G values and yield stresses of S065, SS29 and D1B76 spheres were evaluated as is given in table 2. Though the concentrations of the suspensions are different to each other and the experimental errors are rather large, both the G's and yield stresses were in the order S065 ≃ SS29 > D1B76. This order seems to be consistent with the order of the

Debye-screening lengths,i.e., S065 > D1B76 > SS29, if we take into account the fact that the m.d. of D1B76 is higher than those of the other spheres. It should be noted that the G values observed in this work are not far from those of the previous reports as was discussed in a preceding paper(20).

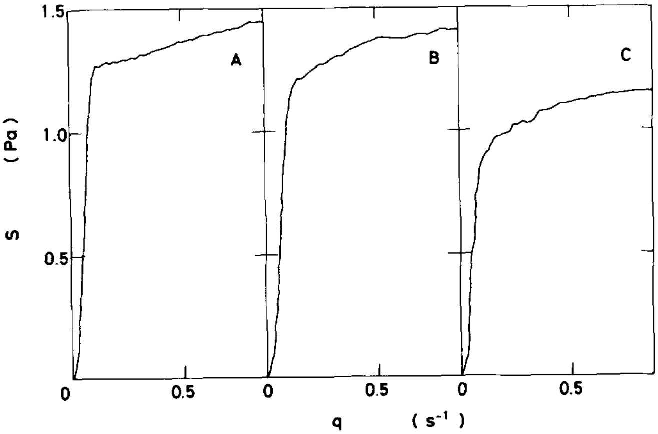


Figure 5. The plots of S against q for deionized spheres at 25°C. A:S065, 8.08 vol%, B:SS29, 10.3 vol%, C:D1B76, 9.77 vol%.

Table 2. Rigidity and yield stress of crystal-like Suspensions of S065, SS29, and D1B76 spheres

Sphere	Concn. (vol%)	G (Pa)	Yield stress (Pa)
S065	8.08	180	1.3
SS29	10.3	280	1.2
1B76	9.77	170, 130*	1.0, 1.3*

*) from reference 16.

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