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SHORT COMMUNICATION

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Suspension viscosity of colloidal crystals and liquids in exhaustively deionized aqueous suspensions coexisting with ion-exchange resins

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Abstract Viscosities of exhaustively deionized aqueous suspensions of colloidal silica spheres are measured with coexisting ion-exchange resins using an Ubbelohde-type viscometer. The reduced viscosities of small silica spheres (56.3 nm in diameter) with and without resins decrease as the sphere concentration increases. However, the former are larger than the latter especially at low sphere concentrations. The reduced viscosities of other silica spheres, 81.2, 103, 110 and 136 nm in diameter, with resins decrease as the sphere concentration increases, whereas those without resins increase especially at low sphere concentrations. The significant effect of the extent of deionization upon the viscometric properties supports the important role of the extended electrical double layers formed around the colloidal spheres.

Key words Viscosity · Colloidal silica spheres · Deionization · Electrical double layers

Introduction

Colloidal spheres show some extraordinary behavior in structural and dynamic properties in deionized suspension. For example,

1. Extraordinary behavior in the diffusion and sedimentation coefficients has been reported [1–13].
2. Broad, single peaks in the scattering function in light, X-ray and neutron scattering measurements of salt-free polyelectrolytes have been observed and the existence of a liquidlike structure was supported [8, 14–18].
3. Crystal-like suspension structures of deionized colloidal spheres have been investigated experimentally and have been explained by the effective soft-sphere model [8, 19–33].
4. Extraordinary viscosity and viscoelasticity behaviors have been observed for salt-free colloidal particles [34–38].

Great attention should be paid to achieving the exhaustively deionized state of colloidal suspensions in order to study salt-free colloidal suspensions. Generally speaking, the deionization of colloidal suspensions with ion-exchange resins is not fast. In our experience it takes more than 3 or 4 weeks before achieving the completely deionized state for the sample suspensions even when the stock suspensions have been deionized in advance for more than 3 years with resins. The viscosity of an aqueous colloidal suspension increases significantly as the deionization proceeds. It is clear, therefore, that viscosities of the colloidal suspensions reported hitherto are not so reliable and are low compared with those of exhaustively deionized suspensions.

In this work viscosities were measured for aqueous suspensions of colloidal silica spheres deionized as exhaustively as possible using an Ubbelohde-type viscometer and coexisting with ion-exchange resins and shielded from exposure to air.

Experimental

Materials

Colloidal silica spheres, CS-45, CS-61, CS-82, CS-91 and CS-121, were kindly donated by Catalyst & Chemicals Ind. Co. (Tokyo).

Table 1 Properties of colloidal silica spheres

Spheres	Diameter (nm)	d (nm)	δ/d	Charge density (μC/cm^2)
CS-45	56.3	7.6	0.13	0.30
CS-61	81.2	11.5	0.14	0.60
CS-82	103	13.2	0.13	0.38
CS-91	110	4.5	0.040	0.48
CS-121	136	10.9	0.080	0.40

Their characteristic properties are compiled in Table 1. The sphere diameters (d) and the standard deviation (δ) from the mean diameter were measured using an electron microscope. δ/d denotes the polydispersity index of the spheres. The charge densities were determined by conductometric titration with a Wayne–Kerr autobalance precision bridge, model B331 mark II (Bogner Regis, Sussex) or with a Horiba conductivity meter, model DS-14. These spheres were carefully purified several times with 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, AG-501-X8(D), 20–50 mesh] for at least 3 years, since newly produced silica spheres always release a considerable number of alkali ions from the sphere surfaces for a long time. The amount of resin added was always much in excess compared with the ionic impurities in the suspension. The resins used in this work were further purified by decantation and filtration in water in order to remove fragments of the resins as completely as possible. The water used for the purification and solution preparation was deionized using a Milli-Q reagent grade system (Milli-RO5 plus and Milli-Q Plus, Millipore, Bedford, Mass.).

Viscosity measurements

Viscosity measurements were made at 25 ± 0.05 °C in a system sealed from air. The shear rate of the Ubbelohde viscometer (Fig. 1) for water at the glass wall of the capillary tube was 120 s^{-1}. A G3-size sintered-glass filter was attached at the end of the capillary tube to prevent the resins entering the capillary.

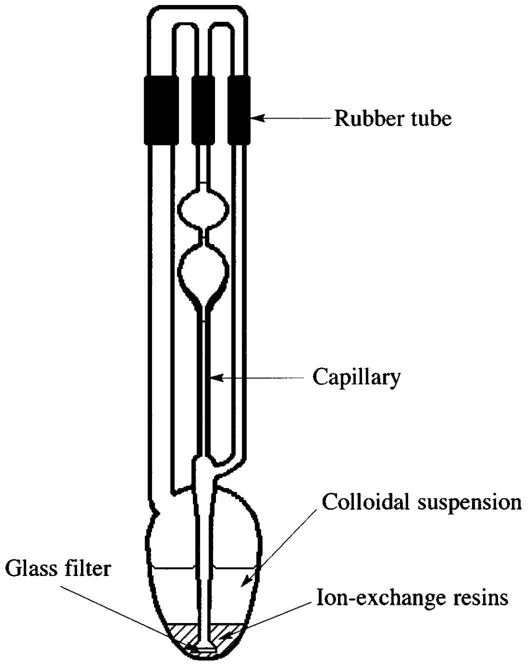

Fig. 1 Schematic representation of the viscometer used

Results and discussion

Plots of the reduced viscosity, η_{sp}/ϕ (η_{sp}: specific viscosity, ϕ: sphere concentration in volume fraction), against ϕ for CS-45 spheres (56.3 nm in diameter) are shown in Fig. 2. All the deionized suspensions had liquidlike distributions in suspension for all the sphere concentrations studied. This is be due to the fact that the thermal movement of the very small spheres is too vigorous to form crystal-like structures. In our experience, colloidal spheres smaller than 50 nm do not form crystal-like structures and they keep their liquidlike distributions irrespective of their concentrations, though the critical size is sensitive to the monodispersity of the spheres and the suspension temperature. The η_{sp}/ϕ values for suspensions with resins were large compared with those without resins, especially at low sphere concentrations and decreased as ϕ increased. This decrease is consistent with the extension of the electrical double layers in the deionized suspensions, since the thickness of the double layers increases as the sphere concentration decreases. If the ϕ values were very small, the reduced viscosities of the suspensions with resins would be larger than those of the suspensions without resins, since the effective diameter of the spheres, d_{eff}, which is given by the diameter plus twice the Debye screening length, i.e., $d_{\text{eff}} = d + 2 \times l_{\text{DH}}$, increases as the sphere concentration decreases.

The thickness of the electrical double layer is approximated by the Debye screening length, l_{DH}, given by Eq. (1).

$$l_{\text{DH}} = (4\pi e^2 n/\varepsilon k_{\text{B}} T)^{-1/2} \; , \qquad (1)$$

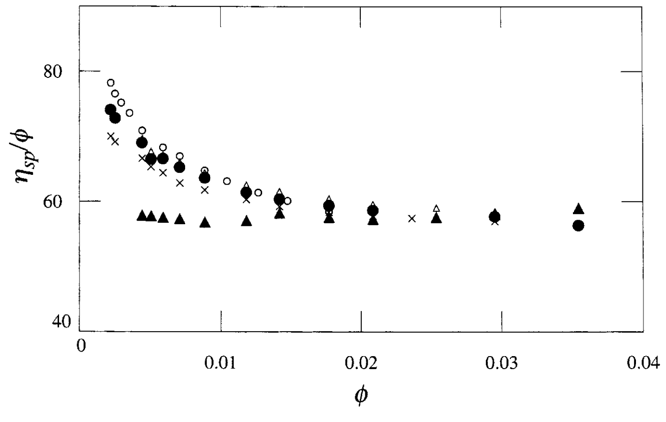

Fig. 2 Reduced viscosity of CS-45 suspensions at 25.0 °C. Three experiments on liquidlike suspensions with resins (○, ×, △). Mean data of the three experiments: liquidlike with resins (●), liquidlike without resins (▲)

where e is the electronic charge and ε is the dielectric constant of the solvent. n is the concentration of "diffusible" or "free-state" cations and anions in suspension. Thus, n is the sum of the concentration of diffusible counterions (n_c), foreign salt (n_s) and both H^+ and OH^- from the dissociation of water (n_o), i.e., $n = n_c + n_s + n_o$. In this work n_o is taken to be 2×10^{-7} mol $\times N_A \times 10^{-3}$ cm^3, where N_A is Avogadro's number. In order to estimate n_c, the fraction of free counterions (β) must be known. Values of β have been determined for many kinds of colloidal spheres of various sizes and charge densities [39–42]. Experimentally, the total stoichiometric number of charges on a sphere was the only factor needed to determine β. Following the effective soft-sphere model, the nearest-neighbor intersphere distance, l, should be close to the d_{eff} value.

The specific viscosity of a colloidal suspension is given by Eq. (2), i.e., the Stokes–Einstein equation.

$$\eta_{sp} = (\eta/\eta_o) - 1 = k_1\phi + k_2\phi^2 + \cdots\cdots \quad . \tag{2}$$

Here η and η_o are the viscosities of the colloidal suspension and of the solvent, respectively. k_1 is the Einstein coefficient, 2.5. k_2 denotes the interaction parameter. When the effective volume fraction of spheres including the electric double layer, ϕ_{eff}, is used instead of the real sphere concentration, ϕ, and the second- and the higher-order terms on the right-hand side of Eq. (2) are neglected, Eqs. (3) and (4) hold.

$$\eta_{sp} = k_1\phi_{\text{eff}} \tag{3}$$

$$\eta_{sp}/\phi = k_1(d_{\text{eff}}/d)^3 \quad . \tag{4}$$

As is clear in Fig. 2, the η_{sp}/ϕ values are tens of times higher than the Einstein coefficient, $k_1 = 2.5$, which supports the important role of the extended electrical double layers for the viscosity in the deionized suspension. When η_{sp}/ϕ is taken to be 60 at $\phi = 0.01$, l_{DH} and d_{eff} are estimated to be 53 and 162 nm, respectively, using Eq. (4). On the other hand, n_c is estimated to be 6.6×10^{-6} mol/dm^3 when β of the CS-45 spheres is assumed to be 0.2. Furthermore, n_s and n_o are safely assumed to be 0 and 2×10^{-7} mol/dm^3, respectively; thus, d_{eff} and l_{DH} are estimated to be 164 and 385 nm. Clearly, the observed l_{DH} is smaller than that calculated by a factor of 3. This is ascribed to the strong distortion of the electrical double layers from spherical and even strip of the layers under the shear flow of the spheres in the capillary tube of the viscometer [32].

It should be mentioned here that the reduced viscosity of a colloidal suspension is highly sensitive to the extent of deionization of the suspension, since Eq. (4) shows that the reduced viscosity changes linearly with the cube of $d_{\text{eff}}/d\,[= (d + 2l_{DH})/d]$. The observed difference between the reduced viscosities of suspensions with and without resins, therefore, demonstrates that the suspension without resins is contaminated with the ionic impurities repelled from the wall of the glass cell (alkali ions) and with impurities from the air (carbonic acids).

Reduced viscosity versus ϕ plots for CS-61 spheres (81.2 nm in diameter) are shown in Fig. 3. The distribution of the CS-61 spheres with resins changed from liquidlike to crystal-like as ϕ increased. The critical concentration of melting was around $\phi_c = 0.005$. On the other hand, the suspensions without resins kept their liquidlike structure. Furthermore, the η_{sp}/ϕ values of the suspensions with resins were larger than those without resins.

The plots of η_{sp}/ϕ against ϕ are shown in Fig. 4 for CS-82 spheres (103 nm in diameter). The phase transition of the colloidal suspensions from liquidlike to

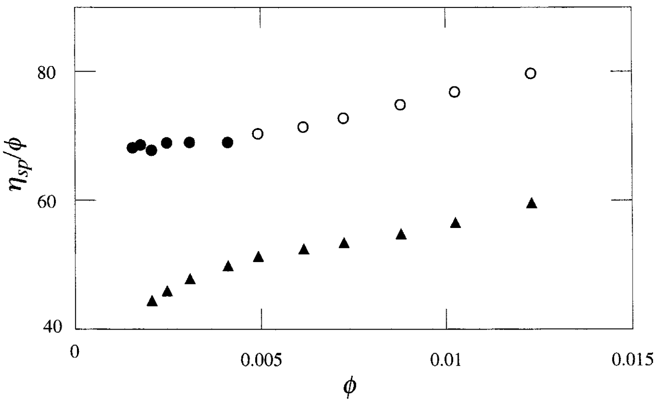

Fig. 3 Reduced viscosity of CS-61 suspensions at 25.0 °C. Crystal-like with resins (○), liquidlike with resins (●), liquidlike without resins (▲)

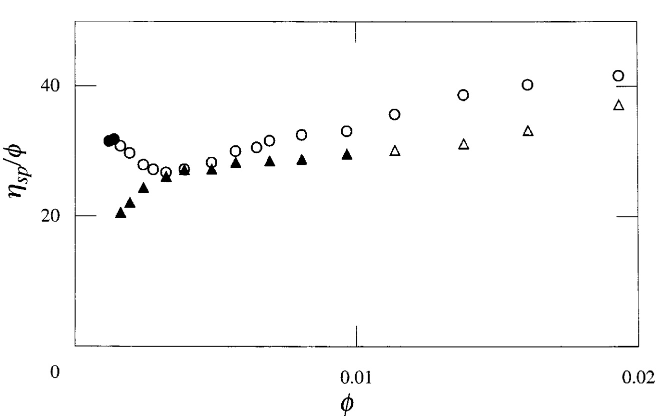

Fig. 4 Reduced viscosity of CS-82 suspensions at 25.0 °C. Crystal-like with resins (○), liquidlike with resins (●), crystal-like with resins (△), liquidlike without resins (▲)

crystal-like structures took place above the critical sphere concentrations, $\phi_c = 0.0015$ and 0.01 with and without resins, respectively, which indicates clearly that the extent of deionization of the former is higher than that of the latter. The reduced viscosities of the former were still higher than those of the latter.

Plots for CS-91 spheres (110 nm in diameter) are shown in Fig. 5. The difference in the reduced viscosity of the suspensions with and without resins was clear only at low sphere concentrations. Interestingly, the viscosities of the former were smaller than those of the latter, which is the opposite behavior compared with the observation for spheres smaller than 110 nm in diameter as described earlier. The values of η_{sp} of the suspensions with and without resins were about 0.001 and 0.005, respectively.

Plots of η_{sp}/ϕ against ϕ for CS-121 spheres (136 nm in diameter) are shown in Fig. 6. The suspensions with resins were crystal-like for all the sphere concentrations examined, which means ϕ_c was smaller than 0.002, i.e., the lowest sphere concentration examined. The ϕ_c value of the suspensions without resins was about 0.0095.

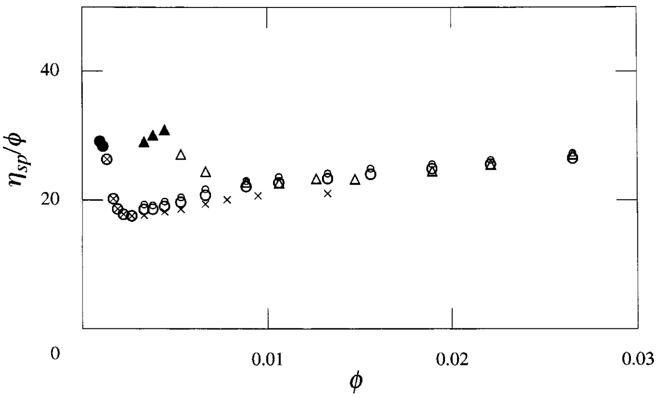

Fig. 5 Reduced viscosity of CS-91 suspensions at 25.0 °C. Two experiments with resins ((○, ×), Mean values of the two experiments: crystal-like with resins (○), liquidlike with resins (●), crystal-like without resins (△), liquidlike without resins (▲)

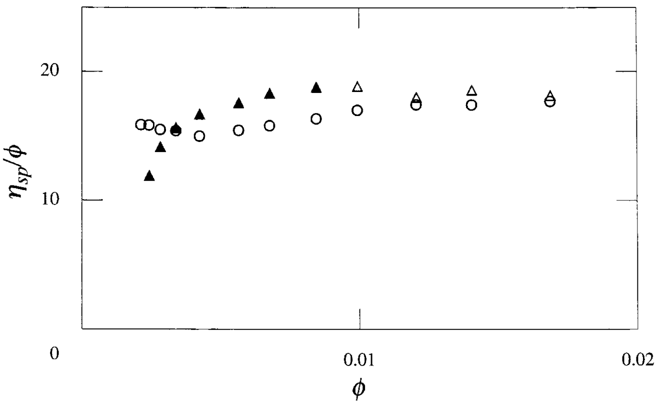

Fig. 6 Reduced viscosity of CS-121 suspensions at 25.0 °C. Crystal-like with resins (○), crystal-like without resins (△), liquidlike without resins (▲)

Conclusion

In this work, the viscosity and the critical sphere concentration of melting of colloidal suspensions were clarified to be highly sensitive to the extent of deionization of the colloidal suspension. This is exclusively due to the extension of the electrical double layers formed around the spheres in the progress of the deionization process. The thickness of the double layers becomes large up to 1.2 μm in the completely deionized aqueous suspension, where $n_o = 2 \times 10^{-7}$ mol/dm^3, $n_s = 0$ mol/dm^3 and $n_c = 0$ mol/dm^3. Thus, great attention should be paid to the extent of deionization when the viscometric properties of aqueous colloidal dispersions are studied.

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