Rheology of Aqueous Suspensions of Polystyrene Particles with Bimodal Radius Distribution

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Rheological behavior was examined for aqueous suspensions of a mixture of monodisperse polystyrene (S) particles having different radii, 42 nm and 103 nm. The bare volume fraction of the particles, $\phi$, was almost identical in all suspensions examined ($\phi=0.42-0.43$), and the mixing ratio of the small particles, $w_s$, was varied. The particles had an electrostatic shell due to the surface charges, and the shell thickness was different for the small and large particles in respective unimodal suspensions. Thus, the viscoelastically effective volume fraction $\phi_{\text{eff}}$ (including the shell volume) of the particles, being larger than $\phi$, changed with $w_s$. In the linear viscoelastic regime, the suspensions exhibited terminal relaxation attributable to Brownian motion of the particles, and the terminal relaxation time $\tau$ and zero-shear viscosity $\eta_0$ first decreased and then increased with increasing $w_s$. These viscoelastic features were compared with predictions of the Shikata-Niwa-Morishima (SNM) model considering the Brownian motion of hypothetical unimodal particles with a radius being equal to an average of the radii of the large and small particles. The $w_s$ dependence of $\tau$ and $\eta_0$ of the aqueous S suspensions was well described by this model, given that the change of $\phi_{\text{eff}}$ with $w_s$ was accounted. Under steady flow, the suspensions of the S particles exhibited shear thinning of the viscosity. This thinning, attributable to nonlinearity of the Brownian stress, was less significant for the bimodal suspensions (in particular for the suspension with $w_s=0.25$) than for the unimodal suspensions ($w_s=0$ and 1). This difference resulted from a difference of the strain $\gamma_{\text{col}}$ required for particle collision under flow: $\gamma_{\text{col}}$ was the largest for the bimodal suspension with $w_s=0.25$ thereby inducing the weakest thinning in this suspension. In fact, the unimodal and bimodal suspensions exhibited an universal relationship between the normalized viscosity and normalized strain $\gamma/\gamma_{\text{col}}$ (with $\gamma$ being the strain effectively imposed through the flow) irrespective of the $w_s$ value.

1 INTRODUCTION

Rheological properties of suspensions are determined by the inter-particle potential and hydrodynamic interaction. Recently, an increasing interest is placed on the properties of so-called ideal suspensions in which the particles have the short-ranged, hard-core potential. Such ideal suspensions, typically prepared in non-aqueous media, exhibit linear viscoelastic relaxation attributed to the Brownian motion of the particles. Under large strain/fast flow, these suspensions exhibit damping/thinning due to the nonlinearity of the Brownian component of the stress.

On the basis of this knowledge, we recently extended our rheological research to aqueous suspensions of monodisperse poly(methyl methacrylate-co-styrene) (MS) particles. These particles had an electrostatic shell due to the surface charges, and their rheologically effective volume fraction $\phi_{\text{eff}}$ including this shell volume was larger than the bare volume fraction $\phi$. The MS suspensions exhibited linear viscoelastic relaxation of the Brownian stress that was qualitatively similar to the relaxation of the ideal, hard-core silica suspensions having the same $\phi_{\text{eff}}$ ($=\phi$ for the ideal suspensions). Thus, in the linear viscoelastic regime, the electrostatic shell of the MS particles worked approximately as a part of the effective hard-core radius. However, the fast viscoelastic relaxation mode distribution was narrower for the MS suspensions than for the silica suspensions, suggesting some softness of the electrostatic shell at short time scales (where the MS suspensions exhibited large moduli). More prominent effects of this shell softness were observed in the nonlinear regime: The damping against large step strain and thinning under fast flow were less significant for the MS suspensions than for the hard-core silica suspensions having the same $\phi_{\text{eff}}$.\)
The strain/flow-induced particle collision, that tends to randomize the particle distribution to reduce the Brownian stress and enhance the damping/thinning, is less significant for the MS particles having the soft/penetrable shell.

Considering these similarity and difference between the MS and silica suspensions, we have further examined rheological properties of aqueous suspensions of a mixture of surface-charged, large and small polystyrene (S) particles. Linear/nonlinear properties of these aqueous bimodal suspensions should reflect the Brownian motion of the large and small particles under influence of the electrostatic shell of respective particles. From this point of view, we have compared the properties of our bimodal soft-shell suspensions with those of bimodal hard-core silica suspensions examined by Shikata et al.16,17 We found that the effective radii of respective soft-shell particles changed with the mixing ratio and this change strongly affected the properties. Details of these findings are summarized below.

2 EXPERIMENTAL

Large and small polystyrene particles (charged latexes) obtained from two batches of emulsion polymerization were utilized. These particles were characterized with dynamic light scattering (DLS; UPA-150, Microtrac) in aqueous suspensions containing concentrated KCl. The DLS data for dilute particles were the same at the KCl concentrations $c_{\text{KCl}} = 0.1$ and 0.01 mol/L, meaning that the surface charges of the particles had negligible effects on the particle motion (more specifically, hydrodynamic radius) at these $c_{\text{KCl}}$. Bare radii of the large and small particles, determined at those $c_{\text{KCl}}$, were $a_l = 103$ nm and $a_s = 42$ nm, respectively. The DLS data also indicated that both particles had narrow distribution in their radii (with the heterogeneity $< 0.05$).

Mother suspensions of the large and small particles having almost identical volume fractions, $\phi = 0.43$ and 0.42, were obtained by allowing water to evaporate from the neat products of the emulsion polymerization (without extra addition of salt). Mixing these unimodal mother suspensions, we prepared three bimodal suspensions. The mixing ratios ($= weight fraction of the small particles in the whole particles$) in the bimodal suspensions were $w_s = 0.25, 0.5,$ and $0.75$.

For these unimodal and bimodal suspensions, linear viscoelastic measurements were made at $25^\circ$C with a tube-type rheometer (V-E system, Virastic Scientific) constructed/operated on the basis of the mechanical impedance analysis.18 The tube diameter and length were 1.03 mm and 61.3 mm, respectively. Steady flow measurements were conducted at $25^\circ$C with a conventional, coaxial rheometer (RFS-II, Rheometrics) in the Couette geometry. The bob and cup radii were 16.0 mm and 17.0 mm, respectively, and the bob height was 33.4 mm.

For the suspensions examined, the bare volume fraction $\phi$ of the S particles increased only a little (from 0.42 to 0.43) with decreasing $w_s$ from 1 (pure small particles) to 0 (pure large particles). However, the surface charge density was different for the large and small particles, as noted from their zero-shear viscosity shown later in Fig. 3. Thus, the electrostatic shell thickness and the corresponding effective volume fraction $\phi_{\text{eff}}$ were different for these particles: $\phi_{\text{eff}}$ decreased from 0.58 to 0.48 with decreasing $w_s$ from 1 to 0. This change of $\phi_{\text{eff}}$, not occurring for the hard-core silica particles, was the key factor determining the changes of the viscoelastic behavior of our bimodal S suspensions with $w_s$.

3 RESULTS AND DISCUSSION

3.1 Overview of Linear Viscoelastic Behavior

For the two unimodal suspensions ($w_s = 0$ and 1) and three bimodal suspensions ($w_s = 0.25, 0.5,$ and $0.75$) of the S particles at $25^\circ$C, Fig. 1 shows dependence of the storage and loss moduli, $G'$ and $G''$ (unfilled and filled circles), on the angular frequency $\omega$. All suspensions exhibit viscoelastic relaxation characterized with the terminal tail, $G' \propto \omega^2$ and $G'' \propto \omega$ (cf. solid curves). For aqueous suspensions of monodisperse MS particles examined previously,13-15 the terminal relaxation is assigned as the relaxation of the Brownian stress due to the particle diffusion over a short distance $\approx \text{particle radius}$. This should be the case also for the similar, unimodal S suspensions as well as for the bimodal S suspensions.

From the terminal tail of the $G'$ and $G''$ data, the zero-
shear viscosity $\eta_s$, the elastic coefficient $A$, the terminal relaxation time (second-order moment relaxation time) $\tau$, and the steady state compliance $J$ are evaluated as: \[ \eta_s = \frac{G'}{\omega^{2n-1}}, \quad A = \frac{G'}{\omega^{2n}}, \quad \tau = \frac{A}{\eta_s}, \quad J = \frac{A}{\eta_s^2} \] (1)

The $\eta_s$, $\tau$, and $J$ of the suspensions evaluated in this way are contributed from both Brownian relaxation and hydrodynamic drug of the particles. These viscoelastic quantities are later related to those defined only for the Brownian relaxation.

In Figs. 2a, 2b, and 2c, respectively, the circles show plots of $\tau$, $J$, and $\eta_s$ of our aqueous S suspensions against the mixing ratio $w_s$ (= weight fraction of the small S particles in the whole particles therein). The bare volume fraction of the particles ($\phi = 0.42-0.43$) is almost identical for the suspensions with various $w_s$. Nevertheless, both $\tau$ and $\eta_s$ firstly decrease and then increase with increasing $w_s$ from 0 to 1, while $J$ does not change significantly on the increase of $w_s$ up to 0.5 but decreases moderately on a further increase of $w_s$.

The minimum of $\tau$, seen for the S suspensions, is never observed for the hard-core silica suspensions. We analyzed this difference in relation to effects of the electrostatic shell of the S particles on $\tau$ (and $\eta_s$). The results are summarized below.

3.2 Electrostatic Shell Thickness and Ionic Strength

For monodisperse hard-core silica particles, the zero-shear viscosity $\eta_s$ normalized by the medium viscosity $\eta_m$ is universally dependent on $\phi$ irrespective of the particle radius. \cite{1,2} Our previous studies indicated that the $\eta_s/\eta_m$ ratio of surface-charged MS particles does not follow this universal $\phi$ dependence because of the electrostatic shell at the particle surface. \cite{13,14} Instead, these MS particles exhibited universal dependence of $\eta_s/\eta_m$ on the effective volume fraction $\phi_{eff}$ including the shell volume, and this dependence agreed with the universal $\phi$ dependence seen for the hard-core particles. \cite{15,16} In other words, the electrostatic shell works as a part of the effective hard-core radius in the linear viscoelastic regime at long time scales where $\eta_s$ is measured.

For our large and small S particles in respective unimodal suspensions, the $\eta_s/\eta_m$ ratio was larger than that expected from their $\phi$ values (0.43 and 0.42) because of the contribution from the electrostatic shell. This situation is similar to that seen for the MS particles. Thus, we can evaluate the effective $\phi_{eff}$ of the large and small S particles by comparing the $\eta_s/\eta_m$ ratios of these particles and hard-core silica particles.
The results of this comparison are shown in Fig. 3.

In Fig. 3, filled triangles show the universal $\eta_u/\eta_m$ vs $\phi$ curve for the unimodal, hard-core silica suspensions reported by van der Werff et al. and by Shikata and Pearson. The unfilled square and circle, respectively, indicate the $\eta_u/\eta_m$ ratio of our large and small S particles in respective unimodal suspensions plotted on this universal curve. From the abscissa coordinates of this plot, the effective $\phi_{\text{eff}}$ of the large and small S particles are evaluated to be 0.48 and 0.58, respectively. For the previously examined MS particles, the $\phi_{\text{eff}}$ values obtained in this way agreed well with those calculated from the electrostatically determined Debye-Hückel screening length (shell thickness). This should be the case also for our S particles.

From the above $\phi_{\text{eff}}$ values, the electrostatic shell thickness $\tilde{\xi}$ of the large and small S particles in respective unimodal suspensions (with $\phi = 0.43$ and 0.42, respectively) can be evaluated as

\[
\tilde{\xi} = \left( \frac{\phi_{\text{eff}}}{\phi} \right)^{\frac{4}{3}} - 1
\]

where $a$ is the bare radius of the particles. The shell thickness, representing the magnitude of the electrostatic screening, is determined by the ionic

$$a = \begin{cases} 3.85 \text{ nm (for large particles),} \\ 4.77 \text{ nm (for small particles)} \end{cases}$$

Fig. 3 Plots of normalized zero-shear viscosity $\eta_u/\eta_m$ of unimodal suspensions of the large and small S particles against the effective volume fraction $\phi_{\text{eff}}$ (unfilled symbols). The $\phi_{\text{eff}}$ values were determined in a way that the $\eta_u/\eta_m$ vs $\phi$ plots for these particles (having the electrostatic shell) are superimposed on the universal $\eta_u/\eta_m$ vs $\phi$ plots obtained for unimodal hard-core silica particles (filled triangles).
Within the context of this model, we can evaluate the Brownian relaxation time $\tau_b$ of the bimodal suspension of our $S$ particles as a time required for diffusion of the hypothetical particle of the average radius $<a_{\text{eff}}>$ over a distance identical to a root-mean-square radius $<a_{\text{eff}}^2>^{1/2}$:

$$\tau_b = \frac{K \eta_b <a_{\text{eff}}^2>^{1/2}}{k_B T}$$  \tag{4}

Here, $k_B$, $T$, $\eta_b$, and $K$ are the Boltzmann constant, absolute temperature, high-frequency viscosity, and a proportionality constant, respectively, and the subscript "eff" attached to $a$ represents the effective radius including the electrostatic shell thickness. This $\tau_b$, being defined purely for the Brownian motion of the particles and not contributed from the bare hydrodynamic drug, is expressed as

$$\tau_b = \frac{A}{\left(\frac{\eta_a}{\eta_b} \right)^3 - 1.54}$$  \tag{3}

where $A$ is the elastic coefficient (cf. Eq. 1). Thus, our terminal relaxation time $\tau$ (Eq. 1) and the Brownian $\tau_b$ are linked through a relationship,

$$\tau = \frac{\tau_b \eta_b}{\eta_a} \quad \text{with} \quad \eta_a = \eta_b - \eta_s$$  \tag{5}

On the basis of Eqs. 4 and 5, we can calculate $\tau$ from $\tau_b$, $\eta_b$, and the Brownian viscosity $\eta_s$, all being predictable from the SNM model. Specifically, we can choose the unimodal suspension of the small particles ($w_s = 1$) as a reference system to describe the $\tau(w_s)$ of the other suspensions ($w_s < 1$) in terms of the measured $\tau_s$ of this reference suspension. The result is compactly written as (cf. Eqs. 4 and 5)

$$\tau(w_s) = \tau_s Q_s(w_s) Q_{\text{a}}(w_s) Q_{\text{b}}(w_s)$$  \tag{6a}

with

$$Q_s(w_s) = \frac{<a_{\text{eff}}^2>}{a_{\text{eff},s}^2}, \quad Q_{\text{a}}(w_s) = \frac{\eta_a}{\eta_a}, \quad \text{and} \quad Q_{\text{b}}(w_s) = \frac{\eta_b/\eta_a}{\eta_b/\eta_a}.$$  \tag{6b}

Here, the subscript "s" attached to $a_{\text{eff}}, \eta_s$, and $\eta_b$ stands for the quantities in the unimodal suspension of the small particles. The $Q_s(w_s)$, $Q_{\text{a}}(w_s)$, and $Q_{\text{b}}(w_s)$ factors, respectively, represent the changes of $\tau(w_s)$ in the bimodal suspensions prepared by mixing these two unimodal suspensions, the ionic strength decreases as the mixing ratio $w_s$ for the small particles is increased from 0 to 1. This fact becomes the key in the analysis of the rheological behavior described below.

### 3.3 Analysis of Relaxation Time and Zero-shear Viscosity

For bimodal hard-core suspensions of silica particles with the radius ratio $a_l/a_s < 4$, Shikata et al.16,17 found that $\eta_s$ exhibits a shallow minimum while $\tau$ decreases monotonically (without exhibiting the minimum) on an increase of $w_s$. For explanation of this behavior, they considered that the terminal relaxation of those bimodal suspensions is equivalent to a Brownian relaxation of hypothetical monodisperse particles with a radius being equal to an average of the radii of the particles therein. The Shikata-Niwa-Morishima (SNM) model, formulated on the basis of this consideration, well described the $w_s$ dependence of the $\eta_s$ data obtained for the bimodal silica suspensions.31

In contrast, for our bimodal suspensions of the surface-charged $S$ particles (with $a_l/a_s = 2.45 < 4$), the minimum is observed for both $\eta_s$ and $\tau$; cf. Fig. 2. This behavior, in particular the minimum of $\tau$, can be related to the change of the ionic strength $I$ with $w_s$. We here utilize the SNM model to quantify this point.

Within the context of this model,20 we can evaluate the Brownian relaxation time $\tau_b$ of the bimodal suspension of our $S$ particles as a time required for diffusion of the hypothetical particle of the average radius $<a_{\text{eff}}>$ over a distance identical to a root-mean-square radius $<a_{\text{eff}}^2>^{1/2}$.

Here, $\text{subscript} 'l' \text{ and 's' stand for the large and small particles in respective unimodal suspensions.}$

As noted from Eq. 3, the ions (originally included in the emulsion polymerization batches of the particles) are more concentrated in the unimodal suspension of the large particles than in the suspension of the small particles to exhibit a stronger screening effect (smaller $\xi$) in the former. Consequently, in the bimodal suspensions prepared by mixing these two unimodal suspensions, the ionic strength decreases as the mixing ratio $w_s$ for the small particles is increased from 0 to 1. This fact becomes the key in the analysis of the rheological behavior described below.
with the particle radius polydispersity, high-frequency viscosity, and the Brownian contribution to the zero-shear viscosity. These factors are separately evaluated below.

### 3.3.1 Radius Polydispersity Factor $Q_a(w_s)$

The averages $\langle a_{\text{eff}} \rangle$ and $\langle a^2_{\text{eff}} \rangle$ included in the $Q_a(w_s)$ factor (Eq. 6b) are the number-averages. These averages are evaluated from the bare radii $a_l$ and $a_s$ of the large and small particles and the electrostatic shell thickness $\xi(I)$ as

$$\langle a_{\text{eff}} \rangle = n_s \{a_s + \xi(I)\} + (1 - n_s) \{a_l + \xi(I)\},$$

$$\langle a^2_{\text{eff}} \rangle = n_s \{a_s + \xi(I)^2\} + (1 - n_s) \{a_l + \xi(I)^2\},$$

with

$$n_s = \frac{w_s/a_s^3}{w_s/a_s^3 + (1 - w_s)/a_l^3}$$

(number fraction of small particles)

In Eq. 7, we have considered that the large and small particles in the bimodal suspensions have the same shell thickness $\xi(I)$ determined by the ionic strength $I(w_s)$. This strength is simply given by

$$I(w_s) = w_s I_l + (1 - w_s) I_s = (1.54 - 0.54 w_s) I_s$$

where $I_l$ and $I_s$ ( = 1.54$I$; cf. Eq. 3) are the ionic strength in the unimodal suspensions of the small and large particles, respectively. The corresponding expression of $\xi(I)$ is

$$\xi(I) = \xi \left[ \frac{I}{I(w_s)} \right]^{1/2} = \xi \left[ \frac{1}{1.54 - 0.54 w_s} \right]^{1/2}$$

Here, we have regarded $\xi(I)$ to be equivalent to the Debye-Hückel screening length ($\xi \propto I^{-1/2}$) and expressed $\xi(I)$ in terms of $\xi$, of the unimodal suspension of the small particles. From Eqs. 7, 8, and 10 as well as the $a_{\text{eff}}$ value (= $a_s + \xi$, with $a_s = 42$ nm and $\xi = 4.77$ nm), the $Q_a(w_s)$ factor was calculated as a function of $w_s$.

### 3.3.2 High-Frequency Viscosity Factor $Q_\eta(w_s)$

The high-frequency viscosity $\eta_\eta$ included in the $Q_\eta$ factor (Eq. 6b) changes with the effective volume fraction $\phi_{\text{eff}}$ of the S particles. In the bimodal suspensions prepared by mixing the unimodal suspensions of the large and small particles, $\phi_{\text{eff}}$ increases with increasing $\xi(I)$. This $\phi_{\text{eff}}$ is conveniently expressed as

$$\phi_{\text{eff}} = \phi \left[ \frac{w_s \left( a_s + 3 \xi(I) \right)^3}{a_s^3} + (1 - w_s) \left( \frac{a_l + 3 \xi(I)}{a_l} \right)^3 \right]$$

(11)

Here, $\phi$ is the bare, total volume fraction of the large and small particles in the suspension, and $\xi(I)$ is the shell thickness given by Eq. 10.

For monodisperse particles having the electrostatic shell, the $\eta_\eta/\eta_m$ ratio (with $\eta_m =$ medium viscosity) is dependent only on the effective $\phi_{\text{eff}}$, and this dependence coincides with the $f$ dependence of $\eta_\eta/\eta_m$ of unimodal hard-core silica suspensions. This coincidence should be observed also for the bimodal S suspensions, as considered in the SNM model.16) For the unimodal silica suspensions, Shikata and Niwa17) showed that the $\eta_\eta/\eta_m$ data are close to the ratios $\{\eta_\eta/\eta_m\}_\text{KD}$ and $\{\eta_\eta/\eta_m\}_\text{MO}$ calculated from the Krieger-Dougherty (KD)20) and Mori-Ototake (MO)21) theories. In particular, excellent agreement is noted between the data17) and an average of these theoretical ratios. (A small but non-negligible difference is observed between the $\{\eta_\eta/\eta_m\}_\text{KD}$ and $\{\eta_\eta/\eta_m\}_\text{MO}$ ratios.)

Considering the above behavior the unimodal suspensions, we can use the KD and MO theories to express $\eta_\eta$ of our bimodal S suspensions in terms of the effective $\phi_{\text{eff}}$ (Eq. 11). The result is summarized as

$$\eta_\eta(w_s) = \eta_m \left[ \frac{n_s}{n_m} \right]_{\text{KD}} + \left[ \frac{n_s}{n_m} \right]_{\text{MO}}$$

(12a)

with

$$\left[ \frac{n_s}{n_m} \right]_{\text{KD}} = \left[ 1 - \phi_{\text{eff}} \right]^{-1.6} \quad \text{and} \quad \left[ \frac{n_s}{n_m} \right]_{\text{MO}} = 1 + \frac{2.5}{\phi_{\text{eff}} - 0.68}$$

(12b)

In Eq. 12b, we have utilized the numerical factors reported by Shikata and Niwa.17) (In ref. 17, the factor...
of 0.71 and the exponent of -1.6 included in \[\frac{\eta_s}{\eta_0}\] were mistyped as 0.63 and -2.22. From Eqs. 10-12, the \(Q_s(w_s)\) factor was calculated as a function of \(w_s\).

### 3.3.3 Brownian factor \(Q_b(w_s)\)

The Brownian viscosity and zero-shear viscosity are given by \(\eta_B = A/\tau_s\) and \(\eta_0 = \eta_s + \eta_B = \eta_s + A/\tau_s\), where \(A\) is the (observed) elastic coefficient (cf. Eq. 1), \(\tau_s\) is the Brownian relaxation time (Eq. 4), and \(\eta_s\) is the high-frequency viscosity. From Eqs. 4 and 6, we can write \(\tau_s\) of the bimodal suspensions in terms of \(\tau_s\) of the unimodal suspension of the small particles and the Q factors; \(\tau_s(w_s) = \tau_s \cdot Q_s(w_s) Q_s(w_s)\). Thus, the \(\eta_B/\eta_0\) ratio of the bimodal suspensions included in the \(Q_b(w_s)\) factor (Eq. 6b) is conveniently rewritten as

\[
\eta_B/\eta_0 = \frac{A}{A + \eta_s \tau_s \cdot Q_s(w_s) Q_s(w_s)}
\]

Since \(Q_b(1) = Q_s(1) = 1\) for the unimodal suspension of the small particles (with \(w_s = 1\); cf. Eq. 6), the \(\eta_B/\eta_0\) ratio of this suspension is written in terms of its elastic coefficient \(A\) and the high-frequency viscosity \(\eta_0\), as \(\eta_B/\eta_0 = A/(A_0 + \eta_s \tau_s)\). Combining this result and Eq. 13, we obtain an expression of the \(Q_b(w_s)\) factor for the suspensions with \(w_s < 1\),

\[
Q_b(w_s) = \frac{A_0 (A + \eta_s \tau_s w_s)}{(A + \eta_s \tau_s Q_s(w_s) Q_s(w_s)) A_0}
\]

We evaluated this \(Q_b(w_s)\) factor from the \(Q_s(w_s)\) and \(Q_s(w_s)\) factors (calculated in the way explained earlier), the high-frequency viscosities \(\eta_s\) and \(\eta_s\) (obtained from Eqs. 11 and 12), the Brownian \(\tau_s\) (calculated from Eq. 4), and the \(A\) and \(A_0\) data. For \(\tau_s w_s = K\eta_B[A_0(a+\dot{\xi})]\) with \(a_s = 42\) nm and \(\dot{\xi} = 4.77\) nm, the proportionality constant \(K\) was chosen to match the calculated \(\tau_s\), and the measured \(A/A_0\eta_s - \eta_s\).

Some comments need to be added for this usage of the \(A\) and \(A_0\) data in the evaluation of \(Q_b(w_s)\). In principle, the SNM model can be utilized to calculate \(A\). However, the viscoelastic mode distribution affecting the \(A\) value is considerably narrower for the particles having the soft, electrostatic shell than for the hard-core particles, and the calculation of \(A\) requires us to modify the SNM model by incorporating a factor that accounts for this shell effect on the mode distribution. Unfortunately, no reliable expression of this factor is available. For this reason, we have utilized the \(A\) and \(A_0\), data in Eq. 14 to evaluate \(Q_b(w_s)\) in a semi-empirical way (that is still based on the SNM model).

### 3.3.4 Limitation of Model

The SNM model is originally formulated for hard-core particles. In the previous sections, we have modified/extended this model for soft-shell particles by incorporating the changes of \(\dot{\xi}\) and \(\phi_{\text{ext}}\) with \(w_s\) (cf. Eqs. 10 and 11). However, our modified model accounts for the viscoelastic mode distribution only in an approximate way (through the usage of the \(A\) data). This lack of accurate treatment of the mode distribution results in some limitation of our model.

This limitation is straightforwardly noted from comparison of the relaxation times \(\tau_s\) and \(\tau_s\) of the unimodal suspensions of the large and small \(S\) particles. (Note that these times are not affected by the radius polydispersity.) With the \(\phi_{\text{ext}}\) values of respective suspensions evaluated from the viscosity data (Fig. 3), our model predicts \(\tau_s/\tau_s \cong 1\) (cf. Eq. 6). This calculated ratio is moderately larger than the observed ratio, \(\tau_s/\tau_s \cong 0.5\) (Fig. 2a), meaning that the viscosity and relaxation time of the unimodal soft-shell suspensions are approximately but not exactly described by the single parameter \(\phi_{\text{ext}}\) in a way considered in the SNM model (for the hard core particles). This failure of the single-parameter description is reflected in the difference of the \(\tau_s\) distribution of the soft-shell and hard-core particles. (For a given viscosity value, the relaxation time increases as the mode distribution broadens. This increase is accounted in our model only approximately through the usage of the \(A\) data.)

Despite the above limitation seen for the unimodal suspensions, our model considers the mixing effects in the bimodal suspensions (changes of \(\dot{\xi}\), \(\phi_{\text{ext}}\), and the radius polydispersity with \(w_s\)) in the simplest but reasonable way. Furthermore, the above difference between the calculated and observed \(\tau_s/\tau_s\) values is rather small. Thus, we compared the predictions of our model and the data of the bimodal S suspensions.
to discuss characteristic features of these suspensions. The results are summarized below.

### 3.4 Comparison with Experiments

The relaxation time $\tau$ of the S suspensions predicted from our model (Eq. 6) was calculated from the $Q_B(w_T)$, $Q_\eta(w_T)$, and $Q_M(w_T)$ factors evaluated in the previous sections. From this $\tau$, the prediction for $\eta_b$ was simply obtained as $\eta_b = A/\tau$ (where the $A$ data were again utilized for the reason explained earlier).

In Figs. 2a and 2c, these model predictions are indicated with the solid curves. Despite the limitation of our model (due to the approximate treatment of the viscoelastic mode distribution), we observe satisfactory agreement of the model prediction and the data including the location of the minima of $\tau$ and $\eta_b$. This agreement suggests that the minima of $\tau$ and $\eta_b$ of our bimodal suspensions reflect the change of the radius polydispersity with $w$. (represented by the $Q_M(w_T)$ factor) as well as the change of the ionic strength, the latter resulting in the changes of the high-frequency viscosity and Brownian viscosity (represented by the $Q_\eta(w_T)$ and $Q_M(w_T)$ factors). The increase of the $\eta_b$ data for $w_T > 0.5$ is also contributed from a mild increase of the terminal relaxation intensity (observed in Fig. 2b as the moderate decrease of $J$).

In relation to the above agreement of the model and experiments, we confirmed that a similar degree of agreement was obtained for Eq. 6 with the $Q_M(w_T)$ factor being replaced by a polydispersity factor defined for the bare radii, $Q'_M = <a^3>/a^3$. This result reflects a fact that the electrostatic shell thickness ($\leq 4.77$ nm; cf. Eqs. 2 and 10) is considerably smaller than the bare radii $a$ and $a^3$, thereby contributing to the effective radius only moderately.

Here, we should emphasize that the changes of the radius and its polydispersity alone cannot result in the
observed minimum of $\tau$: The dashed curve in Fig. 2a, accounting only for these changes (i.e., Eq. 6 with $Q_\sigma(w) = Q_\sigma(w) = 1$), indicates a monotonic increase of $\tau$ with decreasing $w$. This fact demonstrates an interesting difference between the particles having the electrostatic shell and hard-core radius. The electrically neutral, hard-core particles have $Q_\sigma(w) = Q_\sigma(w) = 1$ irrespective of the $w$ value (if $\phi$ is the same for the unimodal and bimodal suspensions) thereby exhibiting no minimum of $\tau$. In contrast, for our S particles having the electrostatic shell, Eq. 6 gives the minimum of $\tau$ as a compromise of the increase of the $Q_\sigma(w)$ factor (dashed curve in Fig. 2a) and the decrease of the $Q_\sigma(w)$ and $Q_\sigma(w)$ factors. Thus, the minimum of $\tau$ (and $\eta_\sigma$) of our S particles reflects a delicate balance of the independently controllable factors, the particle radius distribution and electrostatic interaction. This balance is not only of scientific interest but also of practical importance for tuning the processability of aqueous suspensions utilized as coating materials.

3.5 Non-Newtonian Flow Behavior

3.5.1 Overview

For the unimodal and bimodal S suspensions at 25°C, Fig. 4a shows plots of the steady state viscosity $\eta(\dot{\gamma})$ against the shear rate $\dot{\gamma}$. All suspensions exhibit shear-thinning, but the magnitude of thinning changes with the mixing ratio for the small particles, $w_\sigma$.

For clearer observation of this thinning feature, Fig. 4b examines dependence of the Brownian contribution to the viscosity $\Delta \eta(\dot{\gamma}) = \eta(\dot{\gamma}) - \eta_{\text{visc}}$ normalized by its zero-shear value $\Delta \eta_{\text{visc}} = \eta_{\text{visc}} - \eta_{\text{visc}}$ on the normalized shear rate $\dot{\gamma}\tau_s$. Here, $\tau_s = A/\eta_{\text{visc}}$ is the Brownian relaxation time, and $\eta_{\text{visc}}$ is the high frequency viscosity in the linear regime evaluated from Eqs. 11 and 12. The normalized rate $\dot{\gamma}\tau_s$ is equivalent to a strain effectively imposed by the flow. (For the flow imposed over a period of time $t$, the nominal strain is given by $\dot{\gamma}t$. However, the relaxation in the suspensions erases the strain at $t > \tau_s$. Thus, the effectively imposed strain is given by $\dot{\gamma}\tau_s$.)

The normalized plot shown in Fig. 4b confirms that the thinning at a given $\dot{\gamma}\tau_s$ value is the weakest for $w_\sigma = 0.25$. This result can be related to the thinning mechanism for the Brownian particles, as discussed below.

3.5.2 Strain required for particle collision

The Brownian stress $\sigma_\tau$ is determined by the anisotropy of the spatial distribution of the particles. In general, this anisotropy increases in proportion to $\dot{\gamma}$ and the Newtonian behavior prevails only under slow flow at $\dot{\gamma} \ll \tau_s$. The proportionality vanishes and the nonlinear thinning occurs under faster flow, and this nonlinearity is enhanced when the particle collision (induced by flow) tends to randomize the particle distribution. Thus, a difference of the magnitude of particle collision in the unimodal and bimodal suspensions quite possibly leads to the observed change in the magnitude of thinning with $w$, (Fig. 4).

This argument suggests that an average strain $\gamma_{\text{col}}$ required for the particle collision is a key quantity governing the thinning behavior of those suspensions. For concentrated unimodal suspensions, $\gamma_{\text{col}}$ is defined as a ratio of the averaged distance between surfaces of neighboring particles at equilibrium to the particle radius. Our bimodal suspensions are modeled as the hypothetical unimodal suspensions having the averaged bare radius $<a> = n,a_1 + (1-n)a_2$, with $n$ being the number fraction of the small particles (Eq. 8). Thus, utilizing the above definition, we estimated $\gamma_{\text{col}}$ in our suspensions as:

$$\gamma_{\text{col}} = \frac{\nu-a}{<a> - a}$$

(15)

Here, $\nu$ is the particle number density, and the average distance between the centers of neighboring particles is given by $<a>$. As shown in Fig. 5, this $\gamma_{\text{col}}$ exhibits a peak at $w_\sigma = 0.25$. Namely, the thinning in the bimodal suspension requires the largest flow-induced strain for $w_\sigma = 0.25$ and thus is the weakest at this $w_\sigma$. This point is quantitatively examined in Fig. 6 where the normalized Brownian contribution to the viscosity $\Delta \eta(\dot{\gamma})/\Delta \eta_{\text{visc}}$ is plotted against the normalized strain, $\dot{\gamma}\tau_s/\gamma_{\text{col}}$. Clearly, $\Delta \eta(\dot{\gamma})/\Delta \eta_{\text{visc}}$ of the unimodal and bimodal suspensions exhibits universal dependence on $\dot{\gamma}\tau_s/\gamma_{\text{col}}$ irrespective of the $w_\sigma$ value. This result allows us to conclude that
the thinning of these suspensions is commonly governed by the particle collision and the difference in the magnitude of thinning of the suspensions reflects the difference in their $\gamma_{\text{on}}$ specifying the onset of flow-induced collision.

Finally, a comment needs to be made in relation to this conclusion. Since the electrostatic shell of the particles is soft and penetrable under large stresses in the nonlinear regime, we have utilized the bare radius $<a>$ in Eq. 15 to estimate the strain required for the collision, $\gamma_{\text{on}}$. However, the results shown in Figs. 5 and 6 hardly changed even for the strain evaluated from the effective radius $<a_{\text{eff}}>$ (Eq. 7). Thus, the existence of the electrostatic shell introduced no uncertainty in our argument about the thinning behavior.

4 CONCLUDING REMARKS

We have examined rheological properties of aqueous, unimodal/bimodal suspensions of the large and small S particles having the radius ratio $a_M/a_T = 2.45$. The bare volume fraction of the particles was almost identical in the suspensions examined ($\phi = 0.42-0.43$). However, the particles had the electrostatic shell (due to surface charges), and the effective volume fraction $\phi_{\text{eff}}$ including this shell volume increased as the mixing ratio $w_T$ for the small particles was increased. This change of $\phi_{\text{eff}}$ with $w_T$ had pronounced effects on the rheological properties.

In the linear viscoelastic regime, the suspensions exhibited terminal relaxation attributable to Brownian motion of the particles, and minima of the relaxation time $t$ and zero-shear viscosity $\eta_0$ were observed at $w_T = 0.25$. This result was well described by the Shikata-Niwa-Morishima (SNM) model considering the Brownian motion of hypothetical unimodal particle having an average radius, given that the increase of the effective $\phi_{\text{eff}}$ with $w_T$ was also accounted. Specifically, the minima of $t$ and $\eta_0$ resulted from a delicate balance of this increase of $\phi_{\text{eff}}$ and a change of the particle radius polydispersity.

Under steady flow, the suspensions exhibited shear thinning attributable to nonlinearity of the Brownian stress. This thinning was the weakest for the bimodal suspension with $w_T = 0.25$. This result was related to the strain $\gamma_{\text{on}}$ required for particle collision under flow: This strain was the largest for $w_T = 0.25$ thereby inducing the weakest thinning at this $w_T$. In fact, the normalized viscosity of the unimodal/bimodal suspensions was universally dependent on the normalized strain $\dot{\gamma}^* / \gamma_{\text{on}}$ irrespective of the $w_T$ value.

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