

NOTE

High-Frequency Viscosity and Shear Modulus of Sterically Stabilized Colloid Particles as Probed by Torsional Resonance Oscillation

A study of the high-frequency viscosity η'_ω and of the high-frequency shear modulus G'_ω of a sterically stabilized latex is presented. The experimental measurements have been done using a torsional resonator described recently (J. Bergenholtz *et al.*, *J. Colloid Interface Sci.* 202, 430 (1998)). The data of η'_ω compare favorably with recent theoretical predictions and point to a partial draining of the steric layer by the solvent as expected. The high-shear modulus, however, is much lower than predicted by theory. The pair potential calculated from G'_ω by neglect of hydrodynamic interaction has a considerably longer range than expected from the structure of the steric layer. This points to the fact that hydrodynamic interactions are not negligible for these systems and must be included in a quantitative analysis of the high-frequency shear modulus G'_ω . © 1999 Academic Press

Key Words: high-frequency shear modulus; high-frequency shear viscosity; torsional resonator; hydrodynamic interactions.

INTRODUCTION

Rheological investigations of concentrated colloidal suspensions conducted at high frequencies probe interactions of the particles at short separation and thus furnish information difficult to obtain by other methods (1). Thus, the high-frequency shear modulus G'_ω of suspensions of particles stabilized in a well-defined manner has recently attracted much attention (2–14). The modulus G'_ω is affected by the effective pair interaction and by hydrodynamic interactions. Hydrodynamic interactions (HI) were shown by Lionberger and Russel (10, 12) to exert a profound influence on G'_ω in good agreement with data of Shikata and Pearson (9). The high-frequency modulus of charged colloids has been discussed in detail by Wagner (8) and by Bergenholtz *et al.* (13). Here HI seem to play a minor role as compared to the case of hard spheres.

The situation seems to be less clear when considering sterically stabilized colloid spheres. Here the effective volume fraction of concentrated suspensions may exceed closed packing for hard spheres. This is due to an overlap of the stabilizing layers on the surface of the particles and the resulting repulsive force will greatly contribute to the modulus. In comprehensive studies Mewis and coworkers (7) concluded that the dimensionless modulus of sterically stabilized particles defined as $G'_\omega a^3/kT$ (a , radius of bare particle) does not scale with the effective volume fraction ϕ_{eff} which may be determined from rheological data at low concentrations and low shear (cf. Refs. 15 and 16 for a discussion of ϕ_{eff}). Neglecting HI, these data can be used to extract the pair potential via the Zwanzig and Mountain equation (17) as done by Buscall (6) and by Goodwin *et al.* (4). In this approach the local structure of the suspension is approximated by a lattice; i.e., the sharp peak of the pair correlation function $g(r)$ is replaced by a delta function. Wagner (8) pointed out, however, that the neglect of HI in this approach could be canceled out by the error induced by this assumption.

Recently, a theory which comprises both the high-frequency viscosity η'_ω as well as the high-frequency modulus G'_ω was presented by Elliott and Russel (14). This theory includes the effect of equilibrium structure while accounting for the HI by a suitable interpolation between lubrication and the far field limit. The theoretical predictions give the general trends of experimental data (3, 7) but overestimates G'_ω considerably. This discrepancy was traced back by the authors to uncertainties with regard to experimental parameters, e.g., the graft density.

In this note we present data for η'_ω and G'_ω measured simultaneously on a well-defined purely sterically stabilized latex. The latex has been prepared through adsorption of a nonionic surfactant $C_{18}EO_{100}$ (Brij 700) onto poly(styrene) particles without permanent charges as described elsewhere (16). The core particles exhibit a very narrow size distribution so that polydispersity does not have a major impact on the resulting rheological data. The method of preparation leads to particles with well-defined cores having a narrow size distribution coated by a layer of adjustable thickness. Recent experimental studies (11, 16) have shown that such latexes present stable model systems for sterically stabilized colloid dispersions. Special attention has been paid to the effect of permanent or adsorbed charges which would lead to an additional electrostatic stabilization. Here a recent study has delineated the conditions under which this problem can be circumvented (18). Furthermore, the core latex bears no permanent charges and the present system is stabilized solely by steric repulsion.

All high-frequency measurements reported here have been done using a torsional resonator which is available commercially. Recently, this device has been used successfully to measure η'_ω and G'_ω of electrostatically stabilized latexes (13, 20). Hence, the present data of η'_ω and G'_ω as functions of the effective volume fraction present a set of experimental data suitable for testing theory on a quantitative base.

EXPERIMENTAL

Materials. The poly(styrene) core latex was prepared and purified as described recently (16). The analysis of the core latex showed that the radius a is 72.5 nm (number-average determined by transmission electron microscopy). The polydispersity is small (6.3% standard deviation). Adsorption of the surfactant was achieved through stirring 250 ml of the purified core latex (20 wt%) with 7.0 g Brij 700 (Aldrich) for several days. Afterward the excess surfactant was removed through serum replacement with 0.002 M KCl solution. The latex could be concentrated without problems to 50 wt% through centrifugation.

The determination of the hydrodynamic radius of the coated particles was achieved through capillary viscosimetry. In the dilute regime, the effective volume fraction ϕ_{eff} may be determined from the relative viscosity η/μ by use of an expression derived by Batchelor (19)

$$\frac{\eta}{\mu} = 1 + 2.5\phi_{\text{eff}} + 5.9\phi_{\text{eff}}^2 \quad [1]$$

where μ denotes the viscosity of the solvent. The thickness Δ of adsorbed layer of a surfactant or a polymer can be obtained from ϕ_{eff} ,



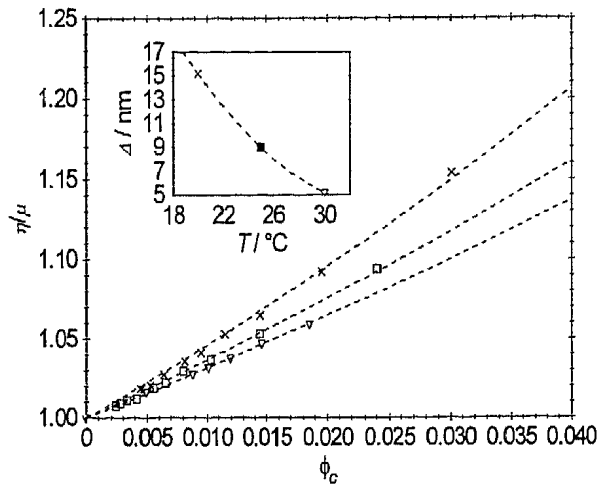


FIG. 1. Reduced zero-shear viscosity η_0/μ (μ , viscosity of the solvent water) vs the volume fraction of the cores ϕ_c of the dilute latex at three different temperatures. Triangles, 30°C; squares, 25°C; crosses, 20°C. The dashed lines show the fit of the experimental data according to Eq. [1]. (Inset) Hydrodynamic thickness Δ derived from these data according to Eq. [2] as function of temperature.

$$\phi_{\text{eff}} = \phi_c \left(1 + \frac{\Delta}{a} \right)^3 = \phi_c \cdot k, \quad [2]$$

where ϕ_c and a denote the volume fraction and the radius of the uncovered latex particles, respectively. Special attention had to be paid to the fact that Δ thus obtained depends quite strongly on temperature. Figure 1 displays plots of η_0/μ as functions of ϕ_c . The dashed lines give the fit of the experimental according to Eq. [1]. The inset demonstrates the dependence of Δ on T . All further measurement to be reported here were done at 20°C with strict control of temperature.

The hydrodynamic thickness Δ of the adsorbed layers follows from these measurements as 15.2 nm. A recent comparison of Δ thus obtained with structural data derived from small-angle X-ray scattering showed that both methods agree in good approximation (16). The value of Δ may therefore be used as a quantitative measure of the extension of the steric layer on the surface of the particles (cf. Table 1).

Torsional resonator. All measurements have been done using a torsional resonator (Rheoswing, Physica) described recently (13). An oscillating rod with a resonance frequency of 8.9 kHz in air is immersed in the dispersion. The shear wave generated penetrates at least 6 μm into the liquid (pure water); in case of the latexes the depth of penetration increases up to about 50 μm , depending on modulus and viscosity of the particular system. It is hence ensured that the method probes the viscoelastic properties of the bulk phase. On the other hand, the measuring cell is much larger than this penetration depth and no disturbance may result from the walls of the container. The small amplitudes of the torsion of the cylinder (ca. 50 nm) ensures that the maximum strain is small and that the measurements are taken in the linear viscoelastic regime.

The damping of the motion of the rod is due to the impedance Z of the liquid in which the rod is immersed. As a consequence the resonance curve $\Delta\omega$ is broadened and the resonance frequency ω_0 is lowered compared to a measurement in air. The real and the imaginary parts of the liquid impedance $Z = R + iX$ are related to the damping and the frequency shift, respectively,

$$\begin{aligned} R &= K_1(\Delta\omega - \Delta\omega_{\text{air}}) \\ X &= K_2(\omega_{0,\text{air}} - \omega_0), \end{aligned} \quad [3]$$

with K_1 and K_2 being calibration constants. A series of Newtonian liquids,

covering the viscosity range $1 < \eta < 80$ mPas, were used to calibrate the resonator. $K_1 = 69.4 \text{ kg/m}^2$ and $K_2 = 134 \text{ kg/m}^2$ were found at 20°C. An ideal resonator would have $K_2 = 2K_1$. Since the radius of the rod (6 mm) is much greater than the penetration depth of the shear wave, the plane wave approximation applies and R and X may directly be converted into the shear and the loss modulus of the liquid:

$$\begin{aligned} G' &= (R^2 - X^2)/\rho \\ G'' &= \eta' \omega = 2R \cdot X/\rho. \end{aligned} \quad [4]$$

The following analysis requires that the frequency of oscillation is high enough so that η'_∞ and G'_∞ are obtained. Thus the time scale of diffusive motion of the latex particles must be long compared to the frequency of the measurements. This leads to the condition that $\omega/2\pi \gg D_s^2/a^2$, where D_s^2 denotes the short-time self diffusion coefficient. For the present system the minimum frequency can be estimated to be ca. 0.5 kHz which is far below the measuring frequency of 8.9 kHz. The torsional resonance device hence probes the high-frequency limits of G' and G'' .

RESULTS AND DISCUSSION

The present investigation aims at a set of η'_∞ and G'_∞ as a function of the effective volume fraction for a purely sterically stabilized latex. An important prerequisite is the stability of the latex at elevated volume fraction. Previous investigations (11, 16) had demonstrated that the adsorption of the nonionic surfactants with long hydrophobic tails is strong enough to sustain shearing at effective volume fractions up to 0.5. It must be kept in mind that the present experiment probes the rheological behavior of the latex at very small strain. Possible complications occurring at high strain, e.g., shear-induced flocculation, are thus avoided. Hence, even if the steric layer on the surface of the particles is not affixed by chemical bonds, the present latex provides a good model system for purely sterically stabilized particles.

The latex investigated here could be concentrated by centrifugation without the formation of coagulum. In addition to this, crystallization takes place at an effective volume fraction of ca. 0.55 which leads to characteristic iridescent colors. Due to the strong scattering of light, however, the phase diagram could not be determined with the precision necessary for evaluating ϕ_{eff} from the critical volume fraction where crystallization sets in (15). The crystallization at $\phi_{\text{eff}} \approx 0.55$ demonstrates nevertheless that the latex must be stable at least up to this point since small impurities or the onset of coagulation would immediately interfere with the process of ordering.

The method of preparing the core latex avoids carefully chemically bound charges on the surface of the particles. The ionic strength of the serum in which the particles are embedded furthermore screens the residual influence of a

TABLE 1
Results of the Analysis of the Sterically Stabilized Latex
by High-Frequency Torsional Resonance Oscillation

c_L (g/kg)	ϕ_c	ϕ_{eff}	$G'_\infty a^3/k_B T$	η'_∞/μ
263.6	0.2507	0.4437	-0.03	2.67
288.0	0.2743	0.4855	0.37	2.95
312.6	0.2982	0.5278	1.08	3.38
338.2	0.3232	0.5721	2.23	3.77
363.9	0.3484	0.6167	5.84	3.99
396.4	0.3803	0.6731	8.41	5.09

Note. c_L , weight concentration of latex + adsorbed surfactant; ϕ_c , volume fraction relative to cores; ϕ_{eff} , effective volume fraction calculated from Eq. [2]; $G'_\infty a^3/k_B T$, reduced high-frequency modulus of latex (a , radius of core); η'_∞/μ , reduced high-frequency viscosity (μ , viscosity of solvent).

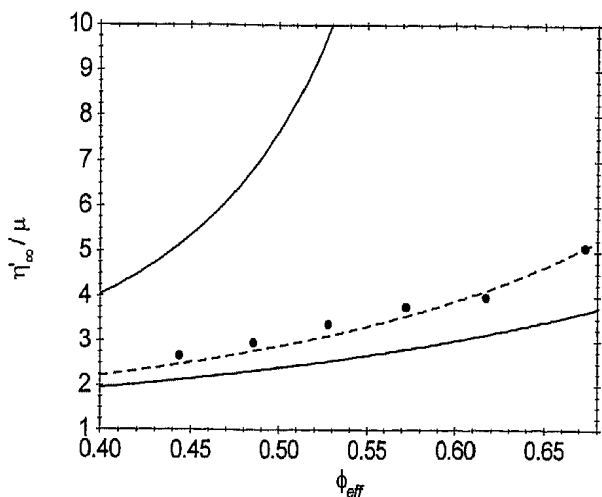


FIG. 2. Relative high-frequency viscosity η'_∞/μ of the steric latex as function of the effective volume fraction ϕ_{eff} (see Eq. [2]). The solid lines give the predicted values (10) for η'_∞ assuming hard spheres with radius a (core radius, bottom curve) and with radius $a + \Delta$ (core radius + hydrodynamic thickness, top curve). The dashed line has been calculated by use of an optimal value of the radius to match the experimental data (radius = $a + 0.24 \cdot \Delta$).

small number of adsorbed charges which cannot be avoided. On the one hand, the concentration of added salt it is low enough to avoid strong adsorption of charges, which would lead to additional electrostatic stabilization. On the other hand, the ionic strength (0.002) is high enough to screen the residual effect of adsorbed ions. This can be shown by a recent analysis of a similar latex immersed in aqueous solutions containing different counterions (18). As mentioned above, the latex exhibits iridescent colors at $\phi_{\text{eff}} \approx 0.55$; i.e., it crystallizes at a volume fraction expected from its hydrodynamic radius. This furthermore underscores the fact that adsorbed charges do not affect the interaction among the particles. If charges would have a nonnegligible influence, crystallization would occur at much lower volume fractions. We therefore conclude that the system under consideration here is purely sterically stabilized, any residual electrostatic repulsion may be ruled out completely.

As shown recently by a comparison of the thickness Δ by hydrodynamic measurements and by small-angle X-ray scattering (16), viscosimetric data present a viable method of determining Δ if the particles have no bare charge. From the factor $k = 1.77$ thus determined (cf. Fig. 1) the thickness of the adsorbed layer follows as $\Delta = 15.2$ nm and a ratio of $a/\Delta = 4.8$. The reduced high-frequency viscosity η'_∞/μ (μ , viscosity of serum) is plotted against the effective volume fraction ϕ_{eff} in Fig. 2 together with the prediction for hard spheres by Lionberger and Russel (10). The bottom curve in Fig. 2 has been calculated using ϕ_c , whereas the top curve has been obtained by use of ϕ_{eff} . The experimental data are located between these two limits which show the theoretical η'_∞/μ for hard spheres with radius a (bottom curve) and for spheres with radius $a + \Delta$. The dashed lines have been calculated by use of an optimal value of the radius to match the experimental data (radius = $a + 0.24 \cdot \Delta$). This immediately points to the fact that the surface layer is partially drained at high frequency as compared to η'_0/μ taken at vanishing frequency (see Fig. 1).

A direct comparison with the theory of Elliott and Russel (14) is difficult since the hydrodynamic correlation length ξ_0 of the present layer is not known accurately. It is interesting to note, however, that the present data virtually coincide with the calculations done in Ref. 14 for spheres with $a/\Delta = 2$ and $\Delta/\xi_0 = 3.6$, i.e., for spheres with a hydrodynamic layer being approximately twice as thick as is the case for the present system. Given the various uncertainties and sources of error when comparing theory and experiment, this can be considered as semiquantitative agreement.

The comparison of theory and experiment is much less gratifying when considering the high-frequency shear modulus G'_∞ . Figure 3 displays the

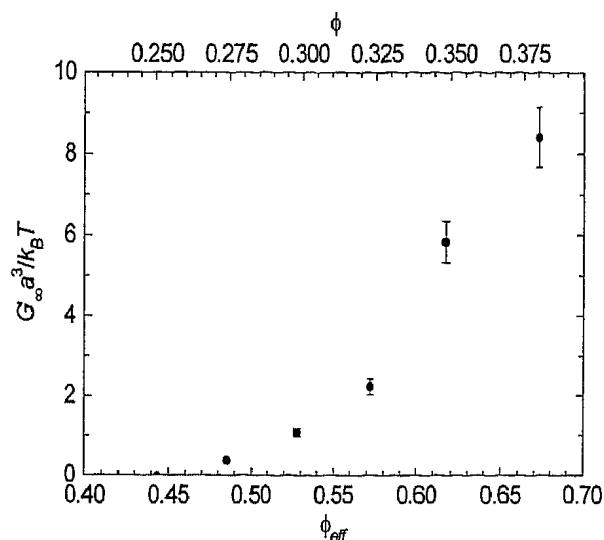


FIG. 3. High-frequency shear modulus G'_∞ scaled with the radius a of the core particles vs the effective volume fraction ϕ_{eff} .

experimental data scaled by the cube of the radius a of the core particles. Comparing these data with the respective calculations done in Ref. 14 for spheres of comparable a/Δ (cf. Figs. 9a and 9b of Ref. 14), it is immediately evident that the experimental result is smaller by at least one order of magnitude. This discrepancy is far beyond experimental uncertainty. It shows that the dependence of the high-frequency shear modulus G'_∞ on the effective volume fraction is not fully understood yet.

It is interesting in this context to evaluate the pair potential $V(r)$ of the latex spheres by neglect of hydrodynamic interaction. Following the Zwanzig-Mountain theory (17) the high-frequency modulus G'_∞ for a system with particle density N/V may be rendered as (4, 6, 11)

$$\frac{G'_\infty}{kT} = \frac{N}{V} + \frac{\phi_m N_m}{5\pi\sigma_c kT} \left(\frac{d^2 V(r)}{dr^2} \right), \quad [5]$$

where N_m is the number of next neighbors, $\sigma_c = 2a$, and ϕ_m is the maximum volume fraction of the spheres. Mewis and D'Haene (7) showed that their results were compatible with $\phi_m = 0.64$, which corresponds to dense random

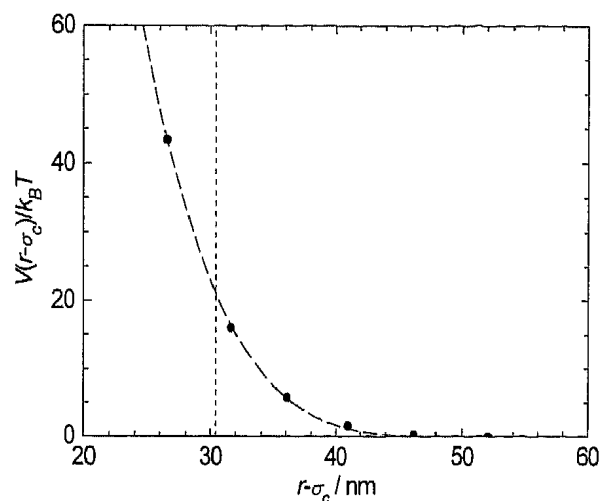


FIG. 4. Pair interaction calculated from Eq. [7] through neglect of hydrodynamic interaction. The short-dashed line indicates the outer diameter of the sterically stabilized particles. The long-dashed line serves as a guide for the eye. See text for further explanation.

close packing. Under these premises the average distance R_m to the center of gravity of next neighbors is given by

$$R_m = \sigma_c \left(\frac{\phi_m}{\phi_c} \right)^{1/3}. \quad [6]$$

Hence, from measurements of G'_z at different volume fractions ϕ_c the second derivative of $V(r)$ may be evaluated according to (11)

$$F(R_m) = \frac{1}{\sigma_c kT} \frac{d^2 V(r)}{dr^2} \approx \frac{5\pi}{\phi_m N_m} \left(\frac{G'_z}{kT} - \frac{6\phi_c}{\pi\sigma_c^3} \right). \quad [7]$$

With $N_m = 12$ this curve leads to $V(r)$ by integrating twice. The resulting pair potential is displayed by the solid line in Fig. 4. The dashed line indicates the maximum range of steric interaction deduced from the hydrodynamic thickness Δ .

It is immediately obvious that $V(r)$ calculated under these premises extends the range of steric interaction derived from the hydrodynamic thickness of the surface layers: From $\Delta = 15.2$ nm one would expect $V(r) \approx 0$ for $r - \sigma_c > 30$ nm. This is not the case, as clearly seen in Fig. 4, but $V(r)$ extends to considerably higher distances. It must be noted that this effect is outside of the present experimental uncertainty. It is already visible in Fig. 3 where G'_z assumes nonzero values at effective volume fractions ϕ_{eff} far below 0.64, where the spheres are expected to be in direct mutual interaction. Any marked effect of the particle polydispersity can be ruled out since the standard deviation of the size distribution is small. We ascribe this discrepancy to the hydrodynamic interactions which give an additional contribution to the modulus G'_z . The range of hydrodynamic interaction is obviously longer than the range of steric interactions, which explains the discrepancy seen in Fig. 4. This finding is in qualitative accord with the predictions of Elliott and Russell (14). It also demonstrates that extracting the pair potential by using Eqs. [5] to [7] may lead to erroneous results if applied at concentrations far below $\phi_{\text{eff}} = 0.64$.

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REFERENCES

1. Russel, W. B., Saville, D. A., and Schowalter, W. R., "Colloidal Dispersions." Cambridge, UK, 1989.
2. Buscall, R., Goodwin, J. W., Hawkins, R. H., and Ottewill, R. H., *J. Chem. Soc. Faraday Trans I* **78**, 2889 (1982).
3. Frith, W. J. T., Strivens, T. A., and Mewis, J., *J. Colloid Interface Sci.* **139**, 55 (1990).

4. Goodwin, J. W., and Hughes, R. W., *Mater. Res. Soc. Symp. Proc.* **177**, 187 (1990).
5. Buscall, R., *J. Chem. Soc. Faraday Trans* **87**, 1365 (1991).
6. Buscall, R., *Langmuir* **8**, 2077 (1992).
7. Mewis, J., and D'Haene, P., *Macromol. Symp.* **68**, 213 (1993).
8. Wagner, N. J., *J. Colloid Interf. Sci.* **161**, 169 (1993).
9. Shikata, T., and Peason, D. S., *J. Rheol.* **38**, 601 (1994).
10. Lionberger, R. A., and Russel, W. B., *J. Rheol.* **38**, 1885 (1994).
11. Raynaud, L., Ernst, B., Vergé, C., and Mewis, J., *J. Colloid Interface Sci.* **181**, 11 (1996).
12. Lionberger, R. A., and Russel, W. B., *J. Rheol.* **41**, 399 (1997).
13. Bergholtz, J., Willenbacher, N., Wagner, N. J., Morrison, B., van den Ende, D., and Mellema, J., *J. Colloid Interface Sci.* **202**, 430 (1998).
14. Elliott, S. L., and Russel, W. B., *J. Rheol.* **42**, 361 (1998).
15. Meeker, S. P., Poon, W. C. K., and Pusey, P. N., *Phys. Rev. E* **55**, 5718 (1997).
16. Weiss, A., Dingenouts, N., Ballauff, M., Senff, H., and Richtering, W., *Langmuir* **14**, 5083 (1998).
17. Zwanzig, R., and Mountain, R. D., *J. Chem. Phys.* **43**, 4464 (1965).
18. Hartenstein, M., Weiss, A., Seelenmeyer, S., and Ballauff, M., *J. Colloid Interface Sci.* **208**, 266 (1998).
19. Batchelor G. K., *J. Fluid Mech.* **83**, 97 (1977); cf. also Brady, J. F., and Vico, M., *J. Rheol.* **39**, 545 (1995).
20. Bergholtz, J., Horn, F. M., Richtering, W., Willenbacher, N., and Wagner, N. J., *Phys. Rev. E, Rap. Comm.* **58**(4), 4088 (1998).

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