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Experimental examination of the Booth theory on the first-order electroviscous effect in ionic colloidal dispersions

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The viscosities of aqueous dispersions of three kinds of colloidal silica and an ionic polymer latex, having a particle radii of $(0.04-0.5)\times 10^{-6}$ m, were measured at sodium chloride concentrations, C_s, of $5\times 10^{-5}M$ to $10^{-3}M$. The first-order electroviscous effect was estimated from the experiments and compared with the Booth theory. The effect decreased with increasing particle radius a as expected from the theory. Furthermore, the function $Z(\kappa a)$ ($1/\kappa$ is the Debye screening length), introduced by Booth to express the deformability of the counterion cloud under a shear field, was estimated from the observed effect, at several κa values between 0.9 and 15. The Z versus κa plot thus obtained for colloids with various a values at various C_s's was well represented by a single curve, and decreased monotonically with increasing κa, whether κ or a was varied. This suggests that Z really is a function of the product κa. In other words, it was shown that the deformability of the counterion cloud is determined by the ratio of the Debye screening length to the particle radius. On the basis of the present finding and previous studies, it was concluded that the Booth theory gives satisfactory agreement with experiment for large κa and small charge numbers.

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I. INTRODUCTION

Dispersions of ionic colloidal particles exhibit characteristic viscosity behavior as a result of electroviscous effects [1]. Usually the electroviscous effect is classified into first-, second-, and third-order effects, depending on its origin. The first-order (primary) effect arises from the deformation of the counterion cloud under a shear field. The second-order (secondary) effect is caused by an electrostatic interparticle interaction. The increment in the viscosity due to a change in the size or shape of the particle (or a solute) is referred to as the third-order (tertiary) effect. In the present paper, we are concerned with the first-order effect.

It is currently accepted that the first-order effect arises from a deformation of the counterion cloud. Counterions of an ionic colloidal particle are distributed around the particle by a balance of diffusional and electrostatic forces. In a shear field, the counterion cloud is subjected to a frictional force from the dispersion medium. Excess energy is thus dissipated, causing an increase in the viscosity.

A theoretical expression for the effect was proposed by von Smoluchowski [2], for very thin counterion clouds ($\kappa a > 10, 1/\kappa$ is the Debye screening length, a is the particle radius). Subsequently, Booth [3] developed a theory which removed this limit. He calculated the viscosity for dispersions of charged spheres as a power series in the ζ potential, or the effective charge number Q to the second-order term. The first-order term was found to be zero. When expressed in terms of Q, the reduced viscosity η_{sp}/ϕ [the specific viscosity η_{sp} is defined by $(\eta-\eta_0)/\eta_0$, where η and η_0 are the viscosities of the dispersion and medium. ϕ is the volume fraction of the colloid] at $\phi=0$ (hereafter designated by K_{theor}) is given by

$$K_{\text{theor}}=\tfrac{5}{2}[1+q^*(Qe^2/\epsilon akT)^2Z(\kappa a)]\ , \tag{1}$$

with

$$q^*=(\epsilon kT/\eta_0 e^2)\left[\sum_{i=1}^{N} n_i Z_i^2 w_i^{-1}\Big/\sum_{i=1}^{N} n_i Z_i^2\right] \tag{2}$$

and

$$\kappa^2=(4\pi e^2/\epsilon kT)\sum_{i=1}^{N} n_i Z_i^2\ , \tag{3}$$

where e is the elementary charge, ε is the dielectric constant of the dispersion medium, k is the Boltzmann constant, T is the temperature, N is the number of ionic species, and n_i, Z_i, and w_i are the number concentration, valency, and mobility of the ion of species i, respectively. The first term in Eq. (1) corresponds to the contribution from the hydrodynamic effect, formulated by Einstein [4], and the first-order electroviscous effect is given by the second term. The quantity q^* reflects the mobilities and composition of the small ions, and is independent of the salt concentration. The deformability of the counterion cloud is expressed by the function $Z(\kappa a)$, which increases monotonically with decreasing κa. It should be noted

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that the theory fails in the limit of $\kappa a \rightarrow 0$ (low salt concentrations and small particles), because $Z(\kappa a)$ tends to infinity in this limit. Furthermore, the theory should be more accurate for relatively small values of Q, or the ζ potential, because of the neglect of higher-order terms than the second. Sherwood [5] and Watterson and White [6] extended the Booth theory to larger values of the ζ potential. These theories agree with the Booth theory for small ζ potentials, and give smaller viscosities at larger ζ potentials.

Several authors have reported the satisfactory agreement of the Booth theory with experiment [7–11]. It seemed to us, however, that more detailed studies were necessary to confirm the theory. In particular, little attention has been given to the deformability of the counterion cloud, namely the $Z(\kappa a)$ term, in spite of its essential importance in the first-order effect. In the present paper we discuss the function $Z(\kappa a)$ by examining the particle radius dependence of the first-order effect for aqueous dispersions of colloidal silica and an ionic polymer latex.

II. EXPERIMENTAL DETAILS

A. Materials

Four kinds of colloidal silica and a polystyrene-based latex were used. The colloidal silica samples, Seahostar KE-P10, KE-E10, KE-E20, and KE-P30W were kindly provided by Nippon Shokubai Co. Ltd. (Osaka, Japan) as a powder sample (KE-P10), ethylene glycol dispersions (E10 and E20), and an aqueous dispersion (P30W). The N-1000 latex was obtained from Sekisui Chemical Co. (Osaka, Japan) as an aqueous dispersion.

All the dispersions were further purified by dialysis against purified water. For the aqueous dispersions, the dialysis was continued for several weeks, and the completeness of the dialysis was judged by conductivity measurements. The ethylene glycol dispersions were further dialyzed against water for about a month. The content of remaining ethylene glycol in the resulting dispersion of KE-E10 was confirmed to be less than 1 wt. % by applying the metaperiodate method [12]. All the dispersions were then placed in an ultrasonic bath for 10 min to destroy aggregates. After purified ion-exchange resin beads [Amberlite MB-3, Organo, Tokyo, or AG 501-X8(D), Bio-Rad Labs, Hercules, CA] had been added, the dispersions were kept standing for at least a week. Dynamic light scattering measurements showed that the quantity of aggregates in the stock dispersions was negligible. The volume fractions of the stock dispersions were $(2.63-4.80)\times 10^{-2}$. As the purification proceeded, all the colloidal silica dispersions became iridescent. This suggests that an ordered structure [13] was formed in these dispersions due to strong electrostatic interparticle interactions. In the presence of simple salts, however, the iridescence was not observed.

Characteristics of the colloidal silica are shown in Table I. The diameters and their distribution (given as a relative standard deviation) were supplied by the producer, having been obtained by transmission electron microscopy. The surface of a silica particle is covered by silanol groups, and its charge number depends on the dispersion medium. The effective (not analytical) charge number Q was determined by performing electrical conductivity measurements on the purified dispersions under salt-free conditions. The conductivity of water was subtracted from the measured conductivity, and the Q value was estimated from the equivalent conductivity of H^+ at infinite dilution (349.8 $S\,cm^2\,mol^{-1}$ at 25 °C) by utilizing the experimental finding that the transport number of the colloid particle is small [14]. At salt concentrations smaller than $5\times 10^{-4}M$, the Q value agreed with that under salt-free conditions within experimental error. At the ϕ's where viscosity measurements were performed, the value of Q did not vary significantly with ϕ. The Q values extrapolated to $\phi=0$ are shown in Table I.

TABLE I. Properties of the colloidal particles.

	Colloid	Radius, a (10^{-6} m)	σ^a/a (%)	Effective charge number, Q^b (10^3/particle)	Q/a (10^{10}/m)
Silica	KE-P10	0.05	5.9		
	KE-E10	0.04	5.2	0.12	0.30
	KE-E20	0.09	4.3	0.81	0.90
	KE-P30W	0.14	3.5	0.98	0.72
Latex	N-1000	0.50	1.2	94	18.8

[a] σ denotes the standard deviation of particle radius distribution.

[b] Extrapolated values to $\phi=0$ (for silica colloids) and value at $\phi=3\times 10^{-2}$ (for N-1000 latex).

Relevant properties of the N-1000 latex are also shown in Table I. The latex particle had ionizable groups originating from the polymerization initiator on its surface. The analytical charge density and the charge number, determined by electrical conductmetric titration, were 1.6×10^{-6} C/cm^2 and 3.1×10^5/particle, respectively. The effective charge number was determined in the same manner as for the colloidal silica [15]. The fraction of free counterions was 0.30.

The samples for the measurements were prepared by diluting the stock dispersions. Polyethylene bottles were used as containers, instead of glass bottles, to avoid the ionic impurities which leach from glass walls. The bottles were filled with nitrogen gas to minimize contamination by carbon dioxide from the air.

The water used was purified as described earlier [11], and had a conductivity of $(0.4-0.6)\times 10^{-6}$ S/cm. The sodium chloride used (Merck, Darmstadt, Germany) was of Suprapur grade.

B. Density of the colloids

The density (ρ) of the powdered sample KE-P10 was determined by the pycnometer method. The determination was repeated ten times for vacuum-dried samples, using water and acetonitrile as media. The amounts of small molecules adsorbed onto the dried samples were estimated by Dr. Ogihara, Fukui University, by means of thermogravimetry and differential thermal analysis. By utilizing the results of this analysis, the corrected ρ value was found to be 2.24 g/cm^3. This value is in good agreement with the value reported by Sakka [16]. It was confirmed that the reduced viscosity extrapolated to $\phi=0$ agreed well with Einstein's theoretical value at sufficiently high salt concentrations ($5\times10^{-3}M$ and $10^{-2}M$), when this ρ value was used. The density of the latex was assumed to be the same as that of polystyrene, namely 1.05 g/cm^3. The volume fractions of the stock dispersions were calculated from the dried-out weight.

C. Viscosity measurements

An Ubbelohde viscometer, described elsewhere [9], was used for the viscosity measurements. This was practicable in the light of the negligibly small shear-rate dependence of η under the present experimental conditions. The temperature was controlled at 25±0.02 °C. The viscometer and all the other pieces of apparatus were cleaned very carefully according to the manner described earlier [11], since the viscosities of the dispersions are very sensitive to trace amounts of ionic impurities. The air inside the viscometer was replaced by nitrogen gas. Sedimentation of the colloidal particles during the viscosity measurements was confirmed to be negligible by performing sedimentation velocity measurements.

D. Electrical conductivity measurements

The electrical conductivity was measured by a conductivity meter, type DS-14, (Horiba Co., Kyoto) and a glass cell with platinum electrodes having a cell constant of 1.244 cm^{-1}, at 25±0.05 °C.

III. RESULTS

Viscosities of the colloidal dispersions were measured in the presence of sodium chloride. Figure 1 shows the η_{sp}/ϕ vs ϕ plot for the dispersion of KE-E10 colloidal silica at two sodium chloride concentrations, C_s [17]. The reduced viscosity η_{sp}/ϕ decreased linearly with decreasing ϕ [18]. With increasing C_s, both the absolute value of η_{sp}/ϕ and the slope of the plot decreased. Furthermore, the $\phi\rightarrow0$ limit of η_{sp}/ϕ was larger than Einstein's theoretical value [4] for rigid spheres (2.5) [19] at the lower C_s values. This behavior is obviously attributable to the electroviscous effect. The same trend has been observed for ionic latex dispersions [7,9–11].

The influence of the particle size on the viscosity, at $C_s=5\times10^{-5}M$, is shown in Fig. 2. It can be clearly seen that η_{sp}/ϕ decreases monotonically with increasing particle radius, and the behavior of the N-1000 latex, which had the largest diameter (1×10^{-6} m), is quite close to Einstein's prediction. In Fig. 3, the reduced viscosity η_{sp}/ϕ at very low ϕ (3.5×10^{-3}) is shown as a function of C_s. It should be noted that both an increase in C_s and an increase in the particle radius give rise to a decrease in the viscosity.

IV. DISCUSSION

We now discuss the validity of the Booth theory, on the basis of present and previous experimental results.

First we examine the theory in light of the salt concentration and particle radius dependences. According to Eq. (1), the first-order electroviscous effect is proportional to $(Q/a)^2$ times $Z(\kappa a)$. Note that the quantity κa is the ratio of the particle radius to the Debye screening length. When the properties of the medium and the small ions (simple salts and counterions) are kept constant, Eq. (1) shows directly that the effect decreases with increasing C_s. This prediction has been confirmed experimentally by several authors [7–11,22]. The C_s dependence obtained in the present study is also consistent with previous findings. Furthermore, Eq. (1) also shows that the effect decreases

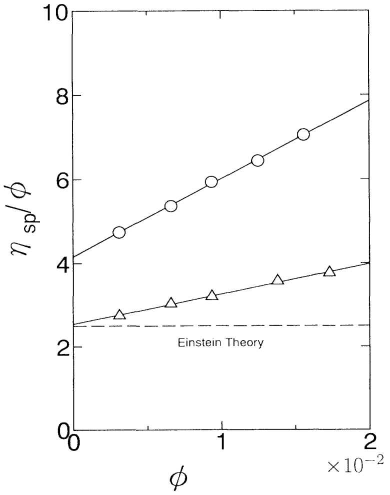

FIG. 1. The reduced viscosity η_{sp}/ϕ plotted against the volume fraction of the colloid, ϕ, for aqueous dispersions of KE-E10 colloidal silica, at sodium chloride concentrations C_s of $5\times10^{-5}M$ (circles) and $5\times10^{-4}M$ (triangles).

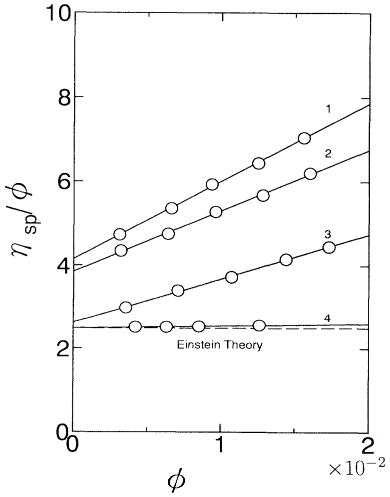

FIG. 2. The η_{sp}/ϕ vs ϕ plot for dispersions of colloids having various particle radii. (1) KE-E10 (0.04×10^{-6} m). (2) KE-E20 (0.09×10^{-6} m). (3) KE-P30W (0.14×10^{-6} m), (4) N-1000 (0.50×10^{-6} m). $C_s=5\times10^{-5}M$.

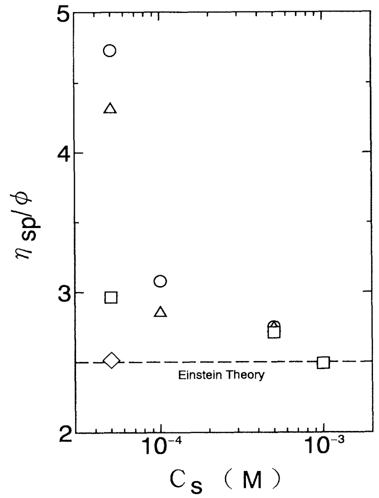

FIG. 3. The η_{sp}/ϕ vs C_s plot for various kinds of colloid dispersion at $\phi=3.5\times10^{-3}$ circle. KE-E10; triangle, KE-E20; square, KE-E30; and rhombus, N-1000.

as the particle radius increases in proportion to $Z(\kappa a)$, when the value of Q/a is kept constant.

To examine this prediction, the Z value was calculated from the experimental value of η_{sp}/ϕ. The mobility w which is included in the q^* term [Eq. (2)], is defined by a velocity of the ion under an unit electric field, and related to the equivalent ionic conductivity of the ion, Λ, by

$$\Lambda = Fw , \tag{4}$$

where F is the Faraday constant [23]. The values of w's are calculated from this relation by using limiting equivalent conductivities at infinite dilution, Λ_0. In aqueous solution at 25 °C, the value of Λ_0 for Na^+ is, for example, 50.10 $S\,cm^2\,mol^{-1}$, and the w value is 5.192×10^{-4} $cm^2\,V^{-1}\,s^{-1}$.

Figure 4(a) shows Z as a function of κa for colloids having various particle radii at very small ϕ (3.5×10^{-3}). The Z vs κa plot at $\phi=0$ for some of the dispersions are shown in Fig. 4(b). The experimental value of η_{sp}/ϕ at $\phi=0$ (hereafter designated by $K_{\rm expt}$), used for the calculation of Z at $\phi=0$, was determined by extrapolating the η_{sp}/ϕ vs ϕ plot to $\phi=0$ using the first-order least squares method. The values of $K_{\rm expt}$ and the corresponding $K_{\rm theor}$ are compiled in Table II. It can clearly be seen from Fig. 4 and Table II that the Z value decreases monotonically with increasing κa, as expected from the theory. It should be noted that the plot could be represented by a single curve; that is, almost exactly the same form was obtained for the Z vs κa plot both when the κ value was varied keeping the a value constant, and when a was changed while keeping κ constant. This finding suggests that Z really is a function of the product κa. In other words, we have shown experimentally that the deformability of the counterion cloud depends solely on the ratio of the Debye screening length to the particle radius. Although various transport phenomena in colloidal dispersions have frequently been described in terms of the ratio κa, to our knowledge no experimental verification has hitherto been made in the manner described above.

The present results support the Booth theory at rather large values of κa. However, the theoretical values for Z and the first-order effect are smaller than the experimental ones, and the deviation becomes larger with decreasing κa. Although this discrepancy will be discussed further, we note here that a relatively large value of κa was assumed as a boundary condition in the theory (assumption 5 of Ref. [3]). Furthermore, as we pointed out else-

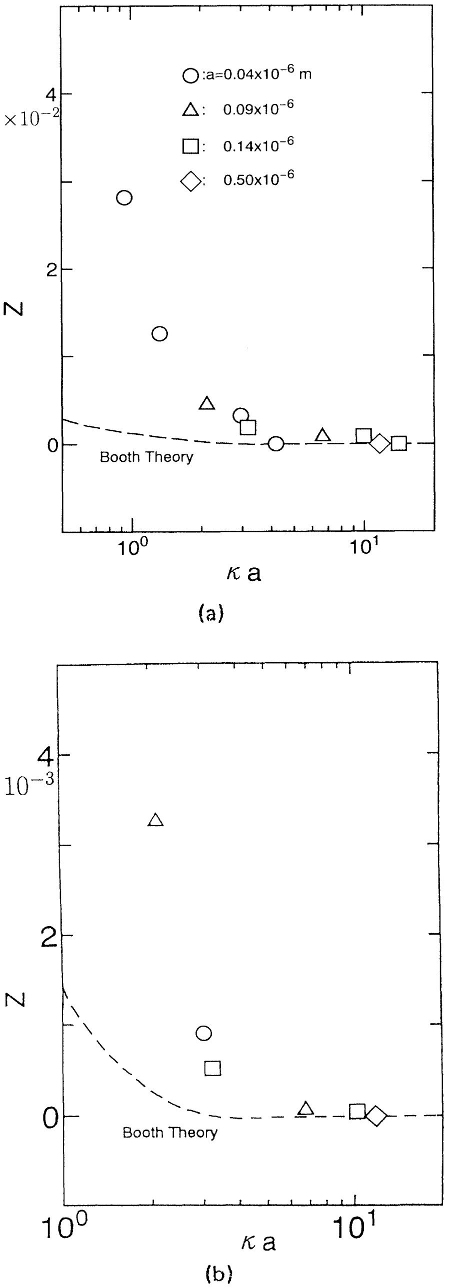

FIG. 4. The Z vs κa plot for dispersions of four kinds of colloids having various particle radii, at various salt concentrations. (a) $\phi=3.5\times10^{-3}$, (b) $\phi=0$.

TABLE II. Experimental and theoretical first-order electroviscous effects for various dispersions.

Sample	C_s (M)	K_{expt}[a]	K_{theor}[b]
KE-E10	5×10^{-5}	4.16	2.6
	5×10^{-4}	2.53	2.5
KE-E20	5×10^{-5}	3.86	2.5
	5×10^{-4}	2.53	2.5
KE-E30	5×10^{-5}	2.64	2.5
	5×10^{-4}	2.52	2.5
N-1000	5×10^{-5}	2.50	2.5

[a] Experimental values of η_{sp}/ϕ extrapolated to $\phi=0$.
[b] Booth's theoretical value.

TABLE III. Influence of the effective charge number on the first-order effect.

Latex[a]	Q (10^3/ particle)	C_s (M)	K_{expt}	K_{theor}	Ref.
1P30	0.3	5×10^{-5}	3.1	2.6	[10]
		10^{-4}	3.0	2.6	
1B76	0.8	5×10^{-5}	2.9 ± 0.1	3.4	[9]
		10^{-4}	2.9 ± 0.2	3.0	
N-100	2.8	5×10^{-5}	3.6 ± 0.1	11.0	[9]
		10^{-4}	3.1 ± 0.1	7.2	

[a] The particle radius is 0.055×10^{-6} m (for 1P30 and 1B76), and 0.060×10^{-6} m (for N-100).

where [10], the Debye screening length loses its original meaning, derived for simple ionic solutions, at no- and low-salt conditions in colloidal and macroionic solutions. Stone-Masui and Watillon [7] who reported a satisfactory agreement between the Booth theory and experiment for $\kappa a > 1$, found that the theory gave a smaller value than their experimental value at $\kappa a=0.73$ [$K_{\text{expt}}=5.1$, while $K_{\text{theor}}=3.7$, for system 4 of Ref. [7] (1968)]. It seems reasonable to conclude that the theory is more accurate at κa values higher than 1.

It should also be noted that the theory is correct at small Q. In Table III we have compiled some of our previous results for dispersions of three ionic latices having almost the same particle radii. For the two latices having relatively small-Q values, the theory agreed well with the experimental results, whereas the theory gave a K_{theor} value much larger than K_{expt} for the latex with the largest Q (the ζ potential at $C_s=5\times10^{-5}M$ was -50.3 mV). Although more detailed studies seem to be necessary, it is likely that the theory is inapplicable to particles with large Q values.

It follows from the discussion so far that the Booth theory gives good agreement with experiment under boundary conditions of large κa and small Q. Although we have focused our attention on the size and valency of the colloidal particles in the present examination, our previous studies of the medium [10] and counterion effects [11] showed that the theory correctly predicted the influence of η_0, ε, and w_i on the first-order electroviscous effect.

However, it has sometimes been reported [8,22] that the experimental effect was larger than the theoretical expectation, even when the boundary conditions were fulfilled. As seen above, a similar trend is observed for the present experimental results. McDonogh and Hunter [8], who have obtained the augmented viscosity for polystyrene latex dispersions, concluded that this discrepancy was attributable to the presence of a gel-like layer on the surface of their sample. Our silica particles can be regarded as rigid spheres at sufficiently high salt conditions, since K_{expt} was very close to Einstein's theoretical value. At the relatively low C_s's where the viscosity measurements were performed, however, the condition of the surface is not fully understood. In addition, the somewhat porous surface of silica [24] might affect the viscosity. Detailed characterization of the surface would be necessary for a more quantitative discussion.

V. CONCLUDING REMARKS

In this paper, the viscosities of aqueous dispersions of colloidal silica and an ionic polymer latex, having particle radii of $(0.04-0.5)\times10^{-6}$ m were measured in the presence of sodium chloride. The deformability of the counterion cloud, which was represented by a function Z in the theory, was estimated from the experimental effect at κa values between 0.9 and 15. Irrespective of the manner of varying κa (namely, whether we changed κ or a independently), the Z value thus obtained decreased monotonically with increasing κa, as predicted by the theory. The Z vs κa plot obtained for colloids with various radii at various C_s's was well represented by a single curve. This suggested that Z was actually a function solely of κa, as described in the theory. In other words, it was suggested that the deformability of the counterion cloud is determined by the ratio of the Debye screening length to the particle radius. On the basis of the present finding and previous studies, the validity of the Booth theory was discussed. It was concluded that under boundary conditions of large κa and small Q, the theory predicts the first-order effect correctly.

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[16] S. Sakka, *Science of the Sol-Gel Method* (Shoufu-sha, Tokyo, 1988), p. 31.

[17] C_s denotes the salt concentration expressed as a molarity.

[18] This behavior has been attributed to a decrease in the second-order electroviscous effect with decreasing ϕ (see Ref. [7], for example). However, the first-order effect should be taken into consideration.

[19] At $\phi\neq0$, the η_{sp}/ϕ value for an uncharged sphere is slightly larger than the Einstein value, due to a hydrodynamic interparticle interaction. Guth and Simha (Ref. [20]) obtained $\eta_{\mathrm{sp}}/\phi=2.5+14.1\phi$. Vand (Ref. [21]) also reported a theoretical expression, but the coefficient of ϕ was calculated to be 7.349. At $\phi=2.\times10^{-2}$, for example, these theories give a reduced viscosity of 2.78 and 2.647, respectively. Our data on N-1000, shown in Fig. 3, are close to the Vand [21] theoretical value.

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