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Viscosity renormalization in colloidal suspensions

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We report on systematic measurements of the viscosity of concentrated colloidal silica suspensions as a function of the volume fraction of particles and of the ionic strength. The experimental results are rescaled on a universal curve using a direct renormalization procedure which is described; the scaling ratios are interpreted in terms of an effective volume fraction which depends on the electrostatic repulsion between the particles. The master curve is compared with models existing for the viscosity of hard spheres suspensions.

I. INTRODUCTION

In spite of many recent works including theoretical, experimental, and numerical approaches, the prediction of the viscosity of concentrated hard sphere suspensions is still poorly achieved. The difficulty comes mainly from the fact that the hydrodynamic interactions between the particles decrease very slowly with the distance r (as r^{-1}). Accordingly, in order to predict the viscosity of a suspension with a volume fraction of particles larger than 10%, it is necessary to take into account both the many-body hydrodynamic interactions and the spatial distribution of the particles. Only, a few theoretical and numerical results are available at large volume fractions.¹⁻⁶ Experimentally, the results are generally interpreted in terms of a power law variation which expresses a divergence of the viscosity η when the volume fraction of the particles, Φ , approaches a maximum packing fraction Φ_m ,

$$\eta = \eta_0 (1 - \Phi/\Phi_m)^{-\kappa}, \quad (1)$$

where η_0 is the viscosity of the solvent. The exponent κ is taken equal to 2 or to $[\eta]\Phi_m$, where $[\eta]$ is the intrinsic viscosity of the suspension.⁶⁻⁸

In colloidal suspensions where the radius of the particles is smaller than 10 μm , colloidal interactions (van der Waals, electrostatic, and steric interactions) have to be included in addition to hydrodynamic interactions.⁹ Two different situations are encountered depending on the sign of the net colloidal interaction. When attraction prevails, aggregates of particles grow and modify the rheological properties. When the interaction is repulsive, the particles remain dispersed but the suspension viscosity may be several times the viscosity of a hard sphere suspension at the same volume fraction.

In the present paper, we investigate the viscosity of well characterized silica sols consisting of small particles (18 nm in diameter) which bear a high surface charge density. The repulsive electrostatic interaction between the particles is large, but as the suspensions are concentrated, the concentration of counterions associated to the surface charges is fairly high, leading to a partial screening of the electrostatic repulsion. It must be mentioned that neither a colloidal crystal or an organized structure responsible for a zero shear and zero frequency elastic modulus forms in the

suspension, contrary to what happens when the particles are large (100–1000 nm) or when their surface charge density is low.¹⁰

The paper is organized as follows. In Sec. II, we report on systematic measurements of the suspension viscosity as a function of the volume fraction in particles and of the concentration of a foreign salt which is added to the suspension. In Sec. III, we demonstrate that the results can be interpreted using a direct renormalization procedure which is described; we relate the scaling ratios that result from data reduction to the ionic strength in the suspension. In Sec. IV, we discuss the master curve obtained by this procedure in relation to the power law variation.¹

II. EXPERIMENT

A. Samples

The silica sol used is TM Ludox colloidal suspension manufactured commercially by Dupont de Nemours. All the samples are prepared from the same stock Ludox suspension without any purification. Using electronic microscopy, we have determined the mean diameter of the particles (18 nm) and the mean standard deviation (4 nm). An accurate determination of the initial volume fraction, which will be useful in the following to interpret the viscosity data, is first required. Accordingly, we have measured the density of the sol using a density-meter, ρ_S , and the density of the particles by drying and weighting a known volume of the stock dispersion, $\rho_P = 2.16 \pm 0.02 \text{ g/cm}^3$; from ρ_S and ρ_P , we deduce the volume fraction in the stock suspension, $\Phi = 0.345 \pm 0.02$. All the experiments are performed by diluting the stock suspension with deionized water (quality MilliP) containing the amount of a foreign salt (NaCl, NaBr, KCl, CaCl₂, MgCl₂) which is required to get the desired concentration C_S .

The surface properties of silica sols are known to be largely dependent on the pH.^{11,12} When the pH is lower than 8, the surface of the particles consists mainly of silanol groups; the sol stability when some salt is added is related to an ion exchange mechanism which depends on the nature of the cation. When the pH is larger than 8, a large amount of protons are released by the surface creating a high negative surface charge density. In this case, the sol stability is ruled by the DLVO theory. In our suspen-

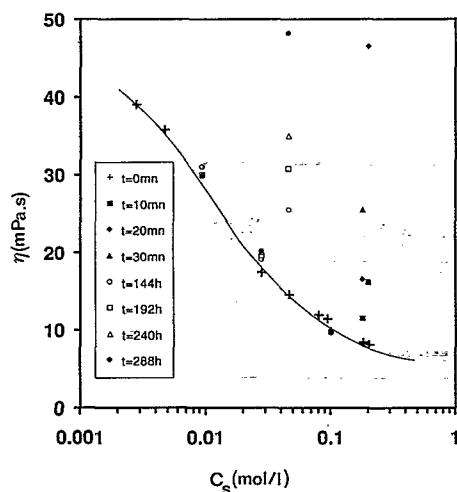


FIG. 1. Evolution of the viscosity of a silica suspension ($\Phi=0.323$) for various NaCl concentrations as a function of the time elapsed from the sample preparation.

sions, the pH is almost constant between 8.8 and 9.0 throughout the whole range of volume fractions ($0.21 \leq \Phi \leq 0.34$) and salt concentrations ($10^{-3} \text{ mol/l} \leq C_S \leq 10^{-1} \text{ mol/l}$) examined; therefore, the particles are highly charged (about $0.5 \text{ OH}^-/\text{nm}^2$) and the DLVO theory is expected to hold.

B. Viscosity measurements

Two rheometers were used to measure the viscosity of the suspensions, a Contraves Low Shear which allows low viscosity measurements in the range of shear rates between 10^{-2} and $5 \times 10 \text{ s}^{-1}$ and a homemade magnetic levitation sphere rheometer¹³ which is well suited to achieve the zero shear limit of systems with viscosities larger than 10 mPa.s . In all the samples, the viscosity depends neither on the geometry of the flow (shear flow or flow around a sphere) nor on the shear rate. This observation is related to the fact that the particles are very small so that the time scale on which the shear acts on the dispersion is much greater than the time scale of Brownian motion (the Peclet number is at most of the order of 10^{-5}).¹⁴

Before measuring the viscosity as a function of the ionic strength, it is imperative to determine the range of stability of the suspension. Accordingly, we have recorded the evolution of the viscosity as a function of the time elapsed from the preparation of the samples. In Fig. 1, the foreign salt is NaCl at various concentrations and the volume fraction is equal to 0.323. When C_S is larger than $2.5 \times 10^{-2} \text{ mol/l}$, the viscosity measured 12 days after the sample preparation has significantly increased thus revealing that aggregates grow slowly in the dispersion. When C_S is larger than 10^{-1} mol/l , the viscosity climbs quickly with time and a gel forms within few hours. In view of these results, we have restricted our study to the range of concentrations lower than 10^{-1} mol/l and we have measured the viscosity immediately after the sample preparation.

Under these conditions, we can assume that our measurements are not affected by the formation of aggregates in the sol.

Next, we have investigated the viscosity of the suspensions when foreign salts other than NaCl are added. First, we have compared the data obtained with different salts involving monovalent cations (NaCl, NaBr, and KCl). In this case, the nature of the salt does not give rise to any specific behavior; the viscosities are all equal and they only depend on the ionic strength. With divalent cations, the short time viscosity and its subsequent evolution do not behave as with monovalent cations. These differences are related to the specific interactions of the divalent cations with the silica surface.¹⁵

In the following, the foreign salt is NaCl. We calculate the pair potential of the particles from the DLVO theory. The potential is the sum of a van der Waals attractive potential and of an electrostatic repulsive potential. The van der Waals potential between two spheres is known exactly,¹⁶

$$V_A = -A/6[2a^2/(r^2 - 4a^2) + 2a^2/r^2 + \log(r^2 - 4a^2)/r^2], \quad (2)$$

where A is the effective Hamaker constant; we have taken¹⁷ $A = 0.63 \times 10^{-20} \text{ J}$. r is the separation between the centres of the particles. The electrostatic potential is calculated using¹⁶

$$V_R = 32\pi\epsilon_0\epsilon_r a (kT/e)^2 \tanh^2(\Psi_S/4) \exp -\Lambda_D h. \quad (3)$$

This expression assumes linear superposition of single sphere potentials. $h = r - 2a$ is the distance between the surfaces of two particles. ϵ_0 and ϵ_r are the permittivity of free space and medium; e is the electronic charge. $\Psi_S = e\psi_S/kT$, where the surface potential ψ_S is of the order of -60 mV in our experimental conditions.^{18,19} Λ_D^{-1} is the Debye length,

$$\Lambda_D^{-1} = (2000e^2 NC/\epsilon_0\epsilon_r kT)^{-1/2}, \quad (4)$$

where N is the Avogadro number and C is the total concentration of the ions in the suspension, expressed in mol/l .

III. RESULTS AND DISCUSSION

A. Viscosity data

We have measured systematically the viscosity of the suspensions for various volume fractions and various concentrations of NaCl ranging from 10^{-1} to 10^{-3} mol/l . Figure 2 is a crossplot of the results giving η as a function of Φ for various salt concentrations. As may be seen, the viscosity sharply increases with the volume fraction especially when the foreign salt concentration is low. In the following, we shall relate this behavior to the divergence of the viscosity when Φ becomes close to the packing volume fraction Φ_m . In addition, we observe that the dependence of η on the salt concentration is the strongest in the range of the highest volume fractions.

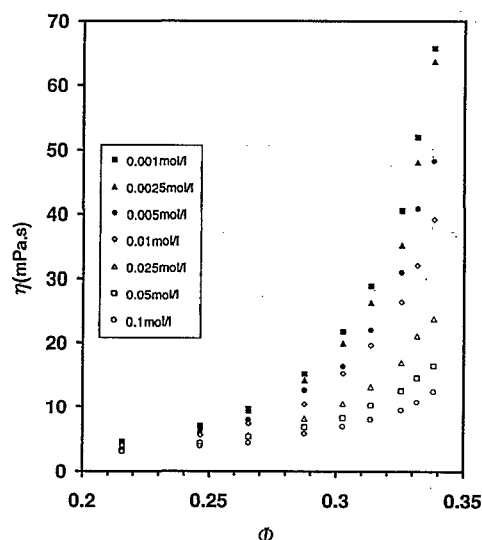


FIG. 2. Crossplot giving the viscosity as a function of the volume fraction at different NaCl concentrations (in mol/l).

B. Direct renormalization

The key idea which supports our data reduction method consists in describing the viscosity variations by a universal law $\eta/\eta_0 = f(\Phi_{\text{eff}})$, where Φ_{eff} is an effective volume fraction proportional to the volume fraction Φ through a coefficient k which depends only on the salt concentration, $\Phi_{\text{eff}} = k\Phi$. The direct renormalization method which is now exposed relies exclusively on the experimental data and, for the moment, does not anticipate any theoretical model yielding values for coefficients k . If the viscosity curves at the different ionic strengths rescale on a universal curve $\eta/\eta_0 = f(k\Phi)$, in a $(\log \Phi, \eta)$ plot they should distinguish themselves one from the other through a $\log(k)$ translation. In practice, the curve which would correspond to $k=1$ is not known experimentally which complicates matter. Accordingly, we proceed in the following manner. We begin by plotting the data using the set of coordinates $(\log \Phi, \eta)$. Then, we take the point corresponding to the highest volume fraction and the largest salt concentration as a reference. We translate the viscosity curve associated with the lower value of salt concentration parallel to the horizontal axis, until it passes through the reference point. The point of highest volume fraction is taken as the new reference, the same procedure is repeated for another salt concentration and so on. The coefficient of translation relative to the concentration C_S is the relative scaling ratio $L(C_S)$ which expresses as $L(C_S) = k/k_0$, where k_0 is associated to $C_S = 10^{-1}$ mol/l; the values of $L(C_S)$ are reported in Table I. The experimental data after

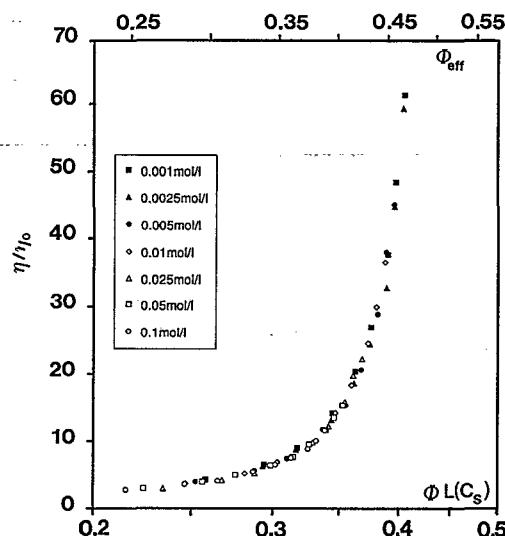


FIG. 3. Master curve giving the variations of the reduced viscosity η/η_0 as a function of the logarithm of the volume fraction. We have plotted the data in function of the two different scales used in the paper, $\Phi L(C_S)$ and Φ_{eff} .

reduction are displayed in Fig. 3. The volume fraction scale is now $\Phi L(C_S)$; for the moment we ignore its physical meaning. Strikingly, the viscosity data collapse successfully on the same curve. Thus, the introduction of an effective hard sphere volume fraction makes it possible to renormalize the viscosity variations on a single master curve.

C. Physical interpretation of the scaling ratios $L(C_S)$

A physical understanding of the scaling ratios now requires a proper expression for the effective volume fraction Φ_{eff} . In the following, we consider that our suspensions behave like dispersions of hard spheres with an effective radius a_{eff} ; Φ_{eff} results directly, $\Phi_{\text{eff}} = \Phi(a_{\text{eff}}/a)^3$. We obtain a_{eff} by replacing the colloidal potential between two particles by an hard core repulsive potential at a distance a_{eff} from the particle centers. In practice, the expression of a_{eff} should take into account the detailed shape of the interparticle potential which, in addition to the screened electrostatic repulsion, involves the van der Waals attraction. Since, the van der Waals term is proportional to the particle radius, which is very small in the case of Ludox TM silica particles, we expect that it becomes rapidly negligible as the interparticulate distance increases and that the electrostatic repulsion is dominant far from the particles, even when the Debye-screening length Λ_D^{-1} is small. Therefore, the distance from the silica particle surfaces to the hard core repulsive potential has to be proportional to

TABLE I. This table gives the values of the experimental scaling ratios as a function of C_S and the effective particle radii which result from the effective hard sphere model. The accuracies of $L(C_S)$ and a_{eff}/a are, respectively, 10^{-3} and 2×10^{-3} .

C_S (mol/l)	10^{-3}	2.5×10^{-3}	5×10^{-3}	10^{-2}	2.5×10^{-2}	5×10^{-2}	10^{-1}
$L(C_S)$	1.197	1.194	1.171	1.145	1.087	1.041	1
a_{eff}/a	1.117	1.113	1.107	1.097	1.079	1.064	1.049

the Debye length and the effective radius a_{eff} is equal to $a_{\text{eff}} = a + \alpha \Lambda_D^{-1}$; α is a coefficient which will be determined in the following. To put these arguments on a quantitative basis, using the expression of the pair potential given in Sec. II B, we have calculated numerically the distance h between the particle surfaces for which the net colloidal potential takes on prescribed values (kT , $5kT$, and $10kT$ for instance). With the physical parameters standing for silica sols (see Sec. II B), we find that h is proportional to Λ_D^{-1} with deviations smaller than 10% provided that Λ_D^{-1} is larger than 1 nm. Accordingly, the relation $a_{\text{eff}} = a + \alpha \Lambda_D^{-1}$ holds over the range of ionic strengths investigated in this study and we get the following expression for the effective volume fraction:

$$\Phi_{\text{eff}} = \Phi(1 + \alpha \Lambda_D^{-1}/a)^3. \quad (5)$$

This result is not universal; in particular, it would fail in the case of large particles where the van der Waals attraction extends at long distances.

Let us now calculate the scaling ratios at the various salt concentrations using relation (5). For the moment α is unknown; the Debye length is obtained from the total concentration of the ions in the suspension. These come from the foreign salt added to the suspension and the counterions associated with the particle surface charge. In practice, the counterion concentration in the initial stock suspension, C_i , is not known with precision but it may be fairly large because of the great surface charge density and of the high volume fractions which are investigated. Accordingly, we search the values of α and C_i which give the best agreement between the calculated and the experimental renormalization ratios. We find $\alpha = 0.5$ and $C_i = 0.02 \text{ mol/l}$. Using these values, we are now able to plot the master curve displayed in Fig. 3 in function of the effective volume fraction Φ_{eff} .

It should be mentioned that this determination of α and C_i is very sensitive to small variations. For instance, Fig. 4 gives the values calculated for $L(C_s)$ when α is fixed and C_i is variable. Clearly, the discrepancies between the experimental and the calculated renormalization ratios become large as soon as C_i is taken larger than 0.01 mol/l or smaller than 0.03 mol/l . It is worth noting that the value of C_i which is deduced from the fit ($C_i = 0.02 \text{ mol/l}$) compares well with the value which can be estimated from the surface charge density and the volume fraction ($C_i \approx 0.06 \text{ mol/l}$). Also, it should be noted that C_i is relevant to the stock suspension and that it decreases as the suspension is diluted to get lower volume fractions. However, in practice, the stock suspension is diluted by less than a factor 2 and a rough estimate shows that the effect of the counterion dilution on the viscosity is then negligible. This conclusion is supported by the fact that the implementation of other renormalization procedures involving variable volume fraction ranges changes neither the relative renormalization ratios nor the master curve. In the same manner, Fig. 5 compares the experimental scaling ratios to those which are calculated for $C_i = 0.02 \text{ mol/l}$ and for different values of α . Obviously, $\alpha = 0.4$ and $\alpha = 0.6$ leads to large discrepancies and the best agreement occurs for $\alpha = 0.5$.

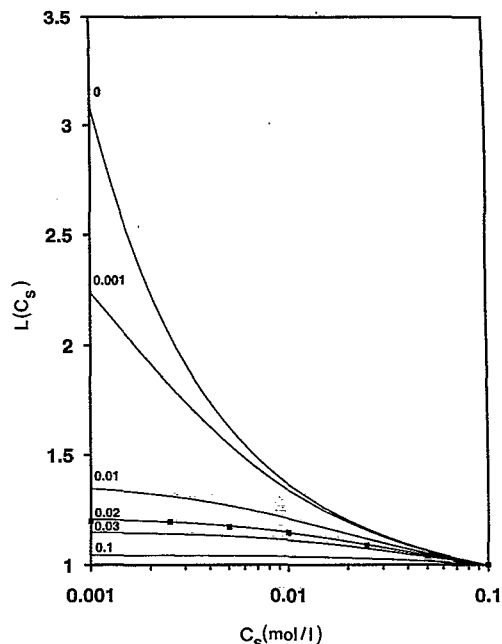


FIG. 4. Comparison between the scaling ratios resulting from the renormalization of the experimental data (■) and the scaling ratios calculated from the hard sphere effective radii of the particles taking $\alpha = 0.5$ and different values for C_i (in full line).

To finish with this discussion, we emphasize that the previous arguments are based on a two-particle colloidal potential and that many-body effects are neglected. Indeed, the colloidal interactions decay very rapidly with distance,

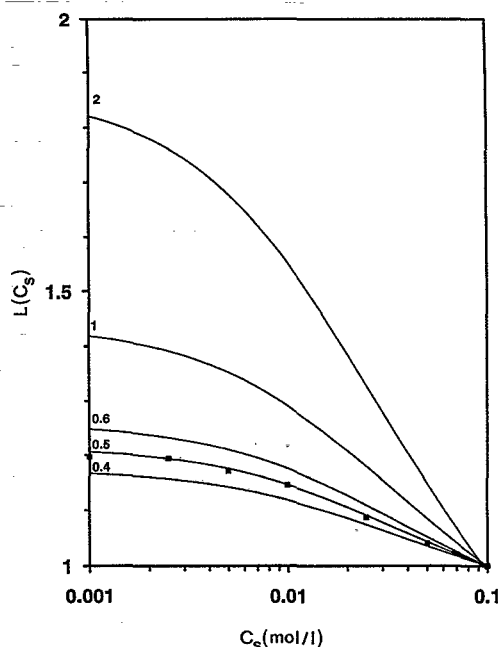


FIG. 5. Comparison between the scaling ratios resulting from the renormalization of the experimental data (■) and the scaling ratios calculated with $C_i = 0.02 \text{ mol/l}$ and different values for α (in full line).

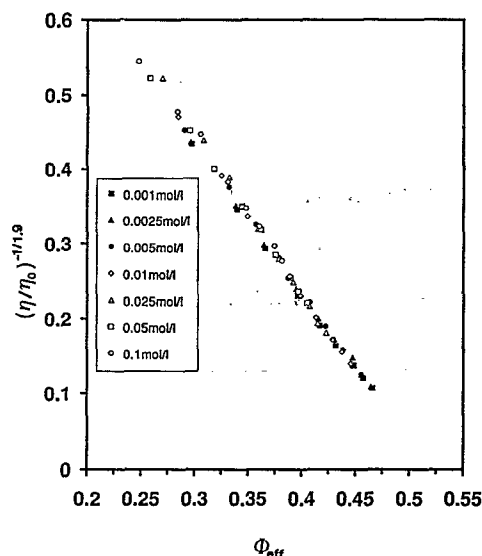


FIG. 6. Representation of the master curve in the set of coordinates $(\eta/\eta_0)^{-1/1.9} = f(\Phi_{\text{eff}})$.

in contrast with the hydrodynamic interactions which are long-ranged; consequently, we can assume that each particle interacts only with its nearest neighbor even though the center-to-center mean distance is small (about $2.4a$ for $\Phi = 0.338$). In addition, the effective radius is always smaller than half this center-to-center mean distance (for $C_S = 0.001 \text{ mol/l}$, the Debye length is the greatest and $a_{\text{eff}} = 1.1a$). In conclusion, we argue that a two-particle colloidal potential suffices to describe the colloidal interactions in the suspension.

IV. MODELING THE MASTER CURVE

In this section, we discuss the master curve in terms of the power law variation given by Eq. (1). In practice, we plot $(\eta/\eta_0)^{-1/x}$ vs the effective volume fraction Φ_{eff} for different values of x . The result of the best fit is displayed in Fig. 6; the viscosity exponent κ and the packing volume fraction Φ_m are found equal to $\kappa = 1.9 \pm 0.1$ and $\Phi_m = 0.53 \pm 0.03$. The error on κ comes mainly from the experimental error in the determination of η_0 which is about 3%. Concerning Φ_m , the uncertainties which comes from the measurement of the volume fraction in the stock suspension and from the determination of α and C_i add to the error which arises from fitting, making the determination of Φ_m poor. Fitting the master curve without assigning a prescribed value to the solvent viscosity results in larger values for κ and Φ_m and lower mean deviations, $\kappa = 2.1 \pm 0.1$ and $\Phi_m = 0.54 \pm 0.03$. The values obtained for exponent κ in both methods are in good agreement with the exponent 2 expected in concentrated suspensions.^{6,8} Experimentally, this exponent has also been found in electrostatically stabilized lattices^{20–23} and in sterically stabilized silica.^{24–27} Recently, it was demonstrated that the singular scaling $\eta/\eta_0 \approx (1 - \Phi/\Phi_m)^{-2}$ arises from the divergence of the Brownian stress but that interparticle forces produce identical behavior as long as their range remains compara-

ble to the particles size,⁶ which is the case in our experiments where a_{eff} is close to a (Table I). The value of the effective volume fraction at which the viscosity diverges, Φ_m , deserves further discussion. In random arrangements of macroscopic hard spheres, Φ_m ranges from 0.63 in close packings to 0.55 in loose packings with intermediate values depending upon the method of packing.²⁸ In suspensions of Brownian particles, which necessarily involve colloidal interactions, various values of Φ_m are reported in the literature and it is not clear at the present moment how it should depend on the details of the colloidal potential. In suspensions of sterically stabilized spheres, Φ_m has been found to take the same value as in macroscopic random-close-packings.^{24,25} Clearly, our value is significantly smaller. This discrepancy has also been observed in sterically stabilized suspensions where Φ_m varies with the nature and the thickness of the stabilizer layer.²⁷ The strength of the renormalization procedure described in Sec. III is to provide a direct interpretation of the experimental data which does not require the value of Φ_m .

V. CONCLUSION

We have reported on systematic measurements of the viscosity of colloidal silica concentrated suspensions in the range of volume fraction between 0.2 and 0.35 and for foreign salt concentrations between 10^{-3} and 10^{-1} mol/l . The addition of the electrolyte causes large variations of the viscosity specially at high volume fractions. This phenomenon is related to the fact that the particles have an excluded effective volume as a consequence of the electrostatic repulsion. An effective hard sphere model which neglect many-body interactions and which introduces an effective volume fraction proportional to the volume fraction of the particles provides a good interpretation of the viscosity data. These can be renormalized directly on a master curve; the scaling ratios are related on the ionic strength of the suspension, which determines the electrostatic repulsion. Finally, we have discussed the master curve in terms of different models which consider power-law divergence for the viscosity.

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¹⁴ We define the Peclet number as the ratio of the diffusion time $a_{\text{eff}}^2/D_0(\Phi_{\text{eff}})$ to the flow time γ^{-1} , $Pe = \gamma a_{\text{eff}}^2/D_0(\Phi_{\text{eff}})$. $D_0(\Phi_{\text{eff}})$ is the short-time self-diffusivity; we have taken the expression reported in Ref. 6, $D_0(\Phi_{\text{eff}}) = 0.85(1 - \Phi_{\text{eff}}/\Phi_m)$. a_{eff} , Φ_{eff} , and Φ_m are defined in Secs. III and IV.

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