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Rheological behavior of moderately concentrated silica suspensions in the presence of adsorbed poly(ethylene oxide)

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Abstract: Adsorption and flocculation properties have been investigated for a well-characterized aqueous system of precipitated nanometric silicabeads in the presence of a high molecular-weight poly(ethylene oxide). Particular attention was given to the evolution of these properties with increasing concentration. In addition, the corresponding consequences on the rheological behavior in the homogeneous domains of the phase diagram of the systems were studied. Important rheological effects can actually be obtained with such systems, even at moderate values of the volume fraction of the dispersed phase ($5 \cdot 10^{-3} \leqq \Phi \leqq 5 \cdot 10^{-2}$).

According to the adsorption level, the number of particles per macromolecular chain, and the free polymer equilibrium concentration, quite different phenomena were observed such as rheopectic shear-induced gelation, Newtonian flow or thixotropic shear-thinning.

Key words: Colloid – polymer – adsorption – rheology

Introduction

Controlling the bulk rheological properties of disperse systems is of considerable importance in a number of industrial and biological fields and it is also of fundamental interest to understand their relation with the phase behavior of the system and with both direct and hydrodynamic interparticle forces that develop at the microscopic scale. The rheology of simple suspensions is now rather well-documented [1] and its strong interrelation with colloidal stability has been clearly shown [2]. Various behaviors are observed and can be related to fundamental parameters of the system: Hamaker constants, size, shape, concentration, surface charge density of the particles, ionic strength, dielectric permittivity and viscosity of the solvent.

In dilute suspensions, rheological measurements are not very sensitive to structural change because the particle volume fraction is too low to make a significant contribution when compared to solvent viscosity: particles undergo Brownian motion and Newtonian flow. Their concentration and shape are factors which determine the extent of hydrodynamic interactions. These interactions, together with colloidal effects (attractions or repulsions) drive the interparticle forces during the flow and, consequently, determine the various structural and rheological characteristics. At sufficiently large volume fractions, the deviation from a Newtonian behavior becomes more and more pronounced owing to the presence of aggregated structures which trap the solvent, so raising the effective volume fraction of the dispersed phase and the relative viscosity at low shear. Thus, approach to the maximum packing fraction results in a solid-like viscoelastic behavior.

In aqueous media, since bare particles are electrostatically stabilized, interparticle interactions at a given concentration can be changed by varying the ionic strength: reducing the ionic strength has the effect of increasing the order in the system due to higher electrostatic repulsions, whereas raising the ionic strength induces coagulation. Both processes have dramatic consequences on rheological properties. These effects have been investigated by many authors as also has the effect of shear on the kinetics of coagulation [3–5].

The rheology of mixtures of particles with polymers is still more complex. It is well known that the addition of polymer to colloidal dispersions modifies the interparticle forces. It results in various physico-chemical effects: destabilization as well as stabilization of the system can be improved according to experimental conditions. A lot of work has been devoted to sterically-stabilized suspensions at full particle coverage by grafted or adsorbed polymer layers of thickness δ. In the absence of electrostatic repulsions, when the layer is dense and thin with respect to the particle radius a, sterically-stabilized particles behave like hard-spheres of radii $a + \delta a \approx a$ [6], whereas more complicated soft sphere models have been developed to account for the rheology of suspensions stabilized with thick polymer layers [7]. In those systems, formation of weak microscopic aggregates through incipient flocculation can be followed as a function of solvent quality or temperature: it results in the appearance of yield stresses that can be related to the energy of cohesion of the flocs [8, 9]. In the same way, the addition of free polymer to sterically-stabilized systems generally induces an increase of rheological parameters that has been attributed to the occurrence of depletion flocculation [10]. Depletion effects have been investigated, too, for bare particles with nonadsorbed polymers [11].

The effect of surface polymer coverage has been less investigated. The problem is that partial coverage often induces strong, irreversible flocculation through bridging or charge-neutralization mechanism with consequent rapid settling of the corresponding aggregates. Attempts to follow the rheological characteristics as a function of coverage have been carried out either with low-molecular weight nonionic polymers [12, 13] for which the extent of aggregation remains limited, or by subjecting the system to a high shear rate which breaks the macroscopic flocs prior to measurement [14]. More recently, Otsubo studied the rheological behavior of silica suspensions flocculated by a high molecular weight polyacrylamide in glycerine and glycerine-water mixtures [15]. He showed that, under given conditions, infinite networks can be formed by spontaneous or shear-induced irreversible polymer bridging of the particles [16], and he tried to apply percolation theory to the properties of the elasticity threshold in those systems [17].

However, the exact effect of the adsorbed layers on the rheological behavior of suspensions has never been investigated systematically as a function of the characteristic parameters that determine the relative range of colloidal attractions or repulsions, i.e., molecular weight of the polymer, particle and salt concentration. In previous papers, we investigated the adsorption and flocculation properties of poly(ethylene oxide) (PEO) on dilute aqueous silica suspensions. At pH $\geqq 8$, this system operates in nearly equilibrium conditions, which allowed us to examine the structures of the aggregates in the successive stages of the bridging process by balancing the effects of electrostatic repulsion and bridging attraction [18, 19].

The following study concerns the same kind of systems at slightly higher concentration. The evolution of the steady-shear viscosity is presented in relation to the adsorbed amount of a high molecular-weight PEO in silica suspension in the absence of added salt. Much of the work is preliminary and only the effects of suspension concentration and polymer coverage are investigated. Up to now, few studies have dealt with moderately concentrated suspensions: in this paper, we show that they can offer the opportunity of studying adsorption and rheological effects.

Experimental

Materials

A commercial suspension of precipitated silica beads (NYACOL 2050 from P&Q Corporation) was used. From photon correlation spectroscopy, the particles appeared fairly monodisperse with a mean hydrodynamic radius of 17 nm. After dilution and continuous washing with water in an ultrafiltration cell, the suspension was concentrated up to 60 gl^{-1}. In such conditions the external ionic strength of the supernatant was 10^{-3} M or less and the pH was about 8.5 ± 0.5.

The polymer was a commercial, high molecular weight PEO (WSR 301 from B.D.H.). It was characterized through light-scattering ($\overline{Mw} \approx 2 \cdot 10^6$,

$\langle \overline{Rg^2} \rangle_z^{1/2} \approx 1100\,\text{Å}$) and viscometry ($[\eta]_{30\,^\circ\mathrm{C}} = 8\ \mathrm{dlg^{-1}}$) in pure water. From viscometric determination, the overlap concentration C^* was found to be about $3\ \mathrm{gl^{-1}}$ a rather high value in view of the average molecular weight. This indicates the polydispersity of the sample.

Sample preparation and holding

The polymer solution and the silica suspension were mixed at one time. All physico-chemical or rheological determinations were perfectly reproducible when carried out after 12 h of slow agitation followed by 3 h of rest in order to respect the adsorption kinetics and to allow the mixture to release air entrapped during the preparation.

Adsorption and flocculation

Methods for adsorption and flocculation measurements have been described elsewhere in the case of dilute systems [18]. Only the time of centrifugation was increased as a function of polymer and particle concentrations in order to perform good separation of the supernatant. This becomes more and more difficult as the viscosity of the medium increases and above silica concentrations of $60\ \mathrm{gl^{-1}}$, adsorption measurements were not reliable, especially at high added polymer concentrations Cp, when the medium was very viscous and the depletion method very unaccurate. Since our aim in this work was to master the exact adsorption level, we limited ourselves to a silica concentration range between 0 and $40\ \mathrm{g\,l^{-1}}$.

The flocculation of our systems was followed by observation of light transmission on the supernatant.

Rheological measurements

Viscometric determinations of hydrodynamic layer thicknesses were performed for dilute suspensions in the same conditions as described previously [18].

Steady-shear apparent viscosities of more concentrated samples (η_a) were measured over a large range of shear rates ($\dot{\gamma}$) by using two types of Contraves rheometers with coaxial cylinders: LS 30 for $10^{-2}\ \mathrm{s^{-1}} < \dot{\gamma} < 130\ \mathrm{s^{-1}}$ and Rheomat 115 for larger values of $\dot{\gamma}$ up to $5000\ \mathrm{s^{-1}}$. The temperature of the sample was maintained at $30 \pm 0.2\,^\circ\mathrm{C}$. In case of time-dependent viscosity values (rheopectic or thixotropic samples), sufficient time was elapsed in order to reach the equilibrium value.

For each sample, the viscosity of the suspending medium η_s was also measured after a centrifugal separation performed in the same way as for adsorption determinations (see above). It allowed the final results to be expressed in terms of relative viscosity $\eta_r = \eta_a/\eta_s$, a parameter which reflects the contribution of the adsorbed polymer to the viscosity of the dispersed phase. As for adsorption, accurate values of η_s could only be obtained when the silica concentration was less than $50\ \mathrm{g\,l^{-1}}$: this definitely imposed the concentration range over which rheological properties could be directly linked to the polymer adsorption behavior. Another restriction in the use of η_r is that it supposes implicitly that the value of η_s is constant with shear rate: strictly speaking, the meaning of η_r is not clear when the flow of the suspending medium is not Newtonian. So, in this preliminary work we deliberately discarded very high added polymer amounts for which equilibrium concentrations in the supernatant were such that η_r was not constant in the range of shear rate investigated (0 to $5000\ \mathrm{s^{-1}}$). Finally, we note that between 0 and $60\ \mathrm{gl^{-1}}$, the flow of bare particles of silica in pure water is Newtonian with viscosities hardly higher than that of the solvent ($\eta_r = 1.4$ for $60\ \mathrm{gl^{-1}}$ and $I = 10^{-3}$ M).

Results and discussion

Adsorption and flocculation

In dilute suspensions ($\leqq 10\ \mathrm{g\,l^{-1}}$), adsorption isotherms display the classical "high-affinity" shape with a maximum adsorbed amount $\Gamma_{\max}$ of $1.35\ \mathrm{mg\,m^{-2}}$. Between 10 and $60\ \mathrm{g\,l^{-1}}$ the high affinity character becomes less pronounced as the particle concentration is raised. Therefore, the isotherms are more and more rounded but the maximum adsorbed amount remains unchanged (Fig. 1). This is an effect of surface to volume ratio since the polymer is polydisperse [20] the initial slope of the curves being, as expected, inversely proportional to this ratio. For the high molecular

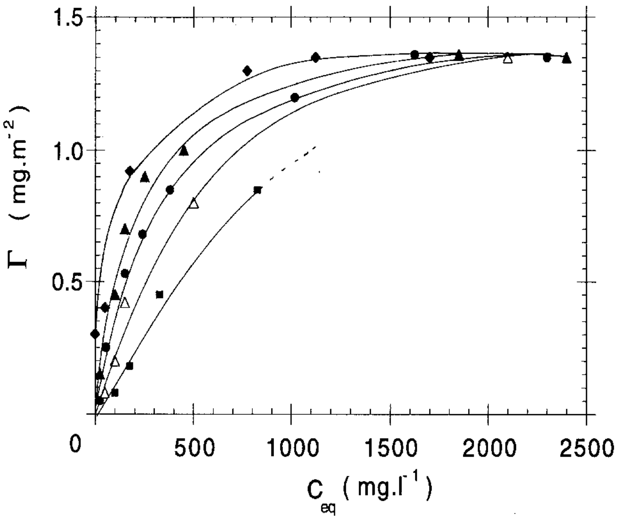

Fig. 1. Adsorptions isotherms of PEO WSR 301 onto Nyacol silica beads in water (pH = 8.5, $I = 10^{-3}$ M) as a function of silica concentration in $g \cdot l^{-1}$: 10(◆); 20(▲); 30(●); 40(△); 60(■)

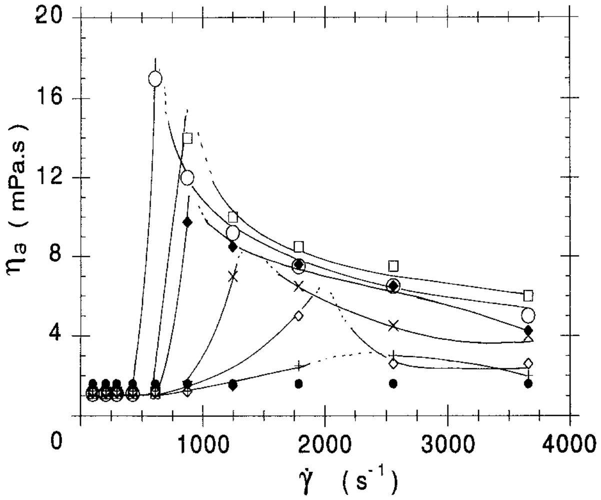

Fig. 2. Viscosity versus shear rate for systems at low coverage Γ in mg m^{-2}: 0.38 (○); 0.45 (□); 0.52 (◆); 0.60 (×); 0.67 (◇); 0.74 (+); 0.8 (●). Silica concentration 30 $g \cdot l^{-1}$, pH = 8.8, $I = 7 \cdot 10^{-4}$ M, $T = 30\,^{\circ}$C. Lines are guides for the eye. Position of the maximum is foreseen from time effects

weight PEO WSR 301 and pH = 8.5, bridging-flocculation of our nearly salt-free suspensions ($I = 10^{-3}$ M) is observed in a sharp range of concentration corresponding to around 0.15 to 0.3 mg m^{-2}, the optimum flocculation concentration (o.f.c.) being at 0.2 mg m^{-2} of added polymer. For coverages higher than 0.35 mg m^{-2}, all systems were homogeneous on a macroscopic scale.

Rheological behavior: general features

Steady-shear viscometric determinations were performed in the domain of the phase diagram which appeared homogeneous on a macroscopic scale, i.e., for coverages higher than 0.35 mg m^{-2} and with the restrictions given in the experimental part.

For very dilute suspensions ($\leqq 5$ g l^{-1}), all the components display Newtonian flow; rheological effects are small but allow the determination of hydrodynamic layer thickness in the same way as previously [18]. A value of 38 nm was measured at complete coverage and pH = 8.5.

Various rheological behaviors are found for more concentrated suspensions according to the polymer-to-particle ratio as depicted in Figs. 2 and 3: rheopectic shear-thickening at coverage levels just higher than the flocculation range, Newtonian flow for moderate adsorption, and thixotropic shear-thinning for plateau values of the amount adsorbed.

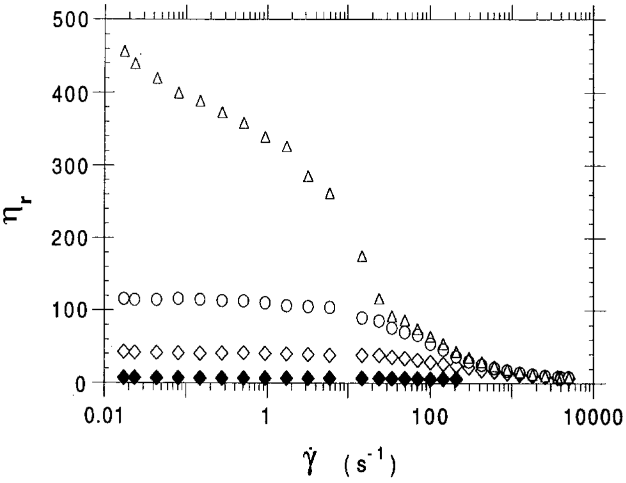

Fig. 3. Relative viscosity versus shear rate for systems at high coverage Γ in mg m^{-2}: 1.22 (◆); 1.32 (◇); 1.35 (○); 1.35 (△). Other experimental conditions: see Fig. 2 and Table 2

Evidence for shear induced bridging at low coverage ($\Gamma/\Gamma_{\max} < 0.6$)

For coverages between 0.35 and 0.8 mg m^{-2} (Fig. 2) the viscosity of the mixture is low,

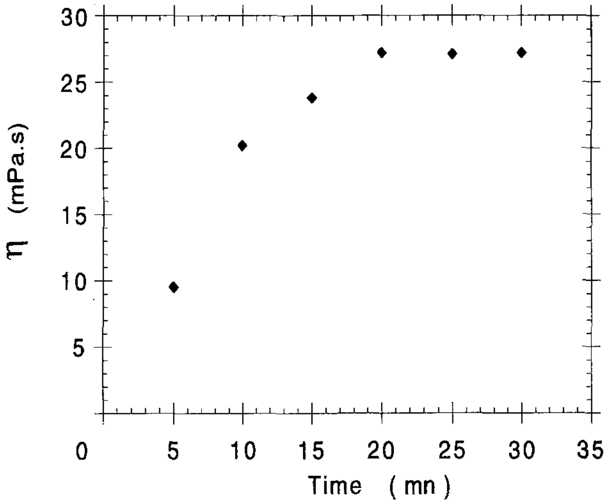

Fig. 4. Example of a rheopectic system for 40 g·l^{-1} silica concentration with $\Gamma = 0.45$ mg m^{-2} and $\dot{\gamma} = 609$ s^{-1}, pH = 8.8, $I = 7 \cdot 10^{-4}$ M, $T = 30$ °C

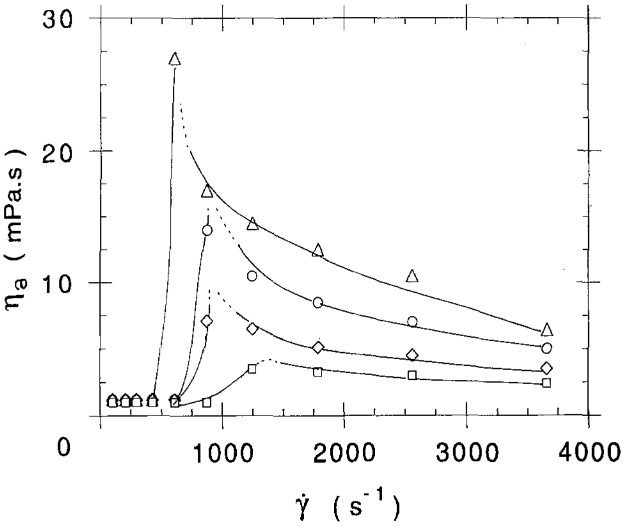

Fig. 5. Viscosity versus shear rate for coverage $\Gamma = 0.45$ mg m^{-2} and different silica concentrations in g·l^{-1}: 10(□); 20(◇); 30(○); 40(△). Other experimental conditions: same as in Fig. 2. Lines are guides for the eye. Position of the maximum is foreseen from time effects

Newtonian, and independent of time as long as the shear rate $\dot{\gamma}$ is below a critical value $\dot{\gamma}_c$. But when the shear rate just exceeds $\dot{\gamma}_c$, the apparent viscosity abruptly increases with shear time (Fig. 4). If the strain is switched off after this increase has been completed, the suspension returns to its original viscosity in the quiescent state. This phenomenon is very spectacular at the macroscopic scale: such fluid samples become soft gels when vigorously shaken and recover their initial flow properties at rest. Qualitatively, the critical shear rate decreases with decreasing coverage (Fig. 2) or with increasing concentration (Fig. 5), while the extent of thickening increases under the same conditions. However, because the transition is very sharp, the exact values of $\dot{\gamma}_c$ and, consequently, the maximum viscosity (which may become infinite) are difficult to determine with an experimental apparatus which only operates at discrete shear rates.

Finally, when sheared beyond $\dot{\gamma}_c$, the suspension becomes thixotropic and shear-thinning while the degree of reversibility displays a complex dependence on shear rate and shear time [21]. The rheopexy (Fig. 4) indicates the growth of a macroscopic network structure in the system during flow and the overall behavior is consistent with the competition between its build-up and breakage or reorganization under shear. Such a phenomenon has already been observed by Otsubo et al. for mixtures of polyacrylamide and another type of silica (Aerosil) in glycerine/water solvents; with the smaller Aerosil particles (10 nm diameter) and for a slightly higher range of silica concentration, these authors obtained viscoelastic pastes at critical shear rate values as low as 1 s^{-1}. They interpreted their results as a gelation through shear-induced bridging [15–17] although adsorption, flocculation and hydrodynamic layer thicknesses were not investigated in great detail in these studies.

A similar explanation holds for our system. Obviously, at a given particle concentration, the critical shear rate and degree of thickening are closely related to both adsorption and flocculation properties (Fig. 2, Table 1). At low coverages

Table 1. Results for systems at low coverage under the same conditions as Fig. 2

Cp g l^{-1}	Γmg·m^{-2}	n	$\dot{\gamma}_c$ s^{-1}*)
1.0	0.38	5.0	600
1.2	0.45	4.2	700
1.4	0.52	3.6	900
1.6	0.60	3.1	1200
1.8	0.67	2.8	> 1500
2.0	0.74	2.6	> 1500
2.5	0.90	2.1	–

*) Approximate value

and as long as the number n of particles per macromolecular chain is higher than 2.5, nearly all the available polymer is shared by the "starving" surfaces and from neutron scattering experiments, we know that in this case, particles are organized in necklaces along macromolecular chains at distances governed by electrostatic repulsions [19, 22]. The o.f.c. corresponds to the situation at which necklaces become unsaturated in particles together with still enough vacant surface sites to allow their connection through adsorbed polymer. In the present experimental conditions, polymer concentrations are just above the o.f.c. and the interaction between necklaces is no longer attractive enough to produce spontaneous flocculation because the surfaces, though still unsaturated with segments, are too well covered [23]. So, increasing shear rate, which is well known to increase the rate and energy of aggregation in colloidal systems [5], has the effect of branching the necklaces through physical crosslinks between the outer part of the adsorbed layers and the remaining free spare surface sites on the particles. As a confirmation, we never observed the phenomenon of shear induced bridging when $n \leqq 2$, e.g., for the same particles with PEO of molecular weight lower than 10^6, or for bigger particles ($a = 40$ nm) [21], whereas, at fixed coverage, the phenomenon is enhanced either by increasing particle concentration (Fig. 5) or by diminishing particle size at a fixed concentration [21], giving then easier gelation or stronger gels. The absence of phase separation (contrary to classical situations of shear induced coagulation [5]), results from a subtle balance between bridging attractions and electrostatic repulsions that develop between silica particles at high pH and low ionic strength. The effect of ionic strength will be investigated in a forthcoming study.

Flow at high coverage ($\Gamma/\Gamma_{\max} > 0.6$)

In such conditions the stoichiometry of the system corresponds to less than one particle per macromolecule and when the polymer concentration Cp is increased, the surfaces become more and more saturated with segments, preventing any possibility of bridging [23]. At the same time, the free polymer equilibrium concentration C_{eq} begins to increase while the rounded part and plateau of the adsorption isotherm are reached (Fig. 1).

Data concerning such systems are reported in Table 2; they also include the effective volume fraction Φ_{eff} for polymer covered particles calculated from the Einstein equation:

$$\eta_r = 1 + 2.5\,\Phi_{\mathrm{eff}}$$

for the case of very dilute suspensions ($\Phi_0 \leqq 2 \cdot 10^{-3}$) at the same coverage, together with the corresponding hydrodynamic layer thickness δ_{H} such as:

$$\Phi_{\mathrm{eff}} = \Phi_0 \left(1 + \frac{\delta_{\mathrm{H}}}{a}\right)^3 .$$

The evolution of the relative viscosity with the addition of polymer is presented on Fig. 3 for a 30 g l^{-1} ($\Phi_0 \approx 0.014$) silica suspension. Newtonian flow is observed for the lowest coverages (and consequently for the lowest free polymer equilibrium concentrations). At higher added polymer concentration, pronounced viscometric effects appear in the low shear regime when the non-hydrodynamic forces control the suspension

Table 2. Results for systems at high coverage under the same conditions as Fig. 3

Cp g l^{-1}	Γ mg m^{-2}	C_{eq} g l^{-1}	Φ_{eff}	δ_{H} nm	$\frac{C_{\mathrm{eq}}}{1-\Phi_{\mathrm{eff}}}$ g l^{-1}	$\eta_{r\infty}$	δ'_{H} nm
2.5	0.9	0.3	0.09	15	0.3	1.52	20
3.0	1.05	0.4	0.11	17	0.5	1.67	22
4.0	1.22	1.0	0.17	22	1.2	2.34	28
5.0	1.32	1.75	0.35	33	2.7	7.05	38
6.0	1.35	2.7	0.47	38	5.1	8.40	38.5
7.0	1.35	3.7	0.47	38	7.0	8.65	39

rheology with occurrence of shear-thinning at higher shear rates. This behavior is displayed as soon as the free polymer molecules entangle with the adsorbed layer, i.e., for:

$$\frac{C_{\mathrm{eq}}}{1 - \Phi_{\mathrm{eff}}} > C^* .$$

The deepness of these transient entanglements increases with C_{eq}, the effect of shearing being to destroy them, leading to much lower high shear viscosity values $\eta_{\mathrm{r}\infty}$.

Effects of particle size and concentration investigated elsewhere [21] show that these results are very general. In the same way, a yield value is observed for the highest added polymer concentrations if $C_{\mathrm{eq}} > C^*$, i.e., when it becomes impossible to distinguish between free and adsorbed macromolecules since the former can reach the surface and exchange their segments with the latter ones. In this regime, which has not been much investigated since it corresponds to the upper limit of the experimental conditions defined above, the medium behaves as a permanent gel when at rest or under very low shear conditions.

A final feature, which appears to be common to all the systems investigated [21] concerns the high-shear limiting Newtonian viscosity $\eta_{\mathrm{r}\infty}$, a parameter characteristic of the objects that flow when disentangled from free non-adsorbed polymer. For example, the Krieger and Dougherty equation:

$$\eta_{\mathrm{r}\infty} = \left(1 - \frac{\Phi'_{\mathrm{eff}}}{\Phi_{\mathrm{m}}}\right)^{-[\eta]\Phi_{\mathrm{m}}} ,$$

with $[\eta] = 2.5$, was used to calculate their volume fraction Φ'_{eff}, and the corresponding hardsphere equivalent layer thickness δ'_{H}, assuming polymer-covered particles (which is the case in dilute medium). For maximum packing volume fractions Φ_{m} between 0.64 and 0.74, δ'_{H} values were found very close to dilute medium values of δ_{H}, the best agreement being obtained for $\Phi_{\mathrm{m}} = 0.72$ (Table 2), a rather high value which indicates the softness of the interparticle interaction [7].

All the above results appear as characteristic of rheological effects induced by adsorbed layers. Unlike grafted [11, 24], adsorbed layers, where structures are less homogeneous, have a looser segment density far from the surface [25]; they undergo no significant compression under shear and can be entangled with free equilibrium polymer chains of the same chemical nature without displaying depletion effects.

Conclusion

In this study, we have shown that the addition of a high molecular weight polymer to a colloidal suspension can induce various important rheological effects, even if the volume fraction of the particles remains rather low ($< 5 \cdot 10^{-2}$). The nature of these effects as well as their magnitude depend on the relative size of the species and are also strongly related to the degree of adsorption of the polymer. Accordingly, several regimes can be distinguished in the homogeneous domain of the phase diagram. In particular, an unusual shear-thickening behavior is observed for nanoparticles when the number of particles per chain exceeds 2, and it has been interpreted as the occurrence of shear-induced bridging. For higher coverages, the role of the free equilibrium macromolecules has been underlined. Their entanglement with adsorbed layers leads to non-Newtonian flow but the behavior at high shear is consistent with that of dilute suspensions at the same coverage.

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