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PAA/PEO comb polymer effects on rheological properties and interparticle forces in aqueous silica suspensions

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Abstract

The effects of a poly(acrylic acid) (PAA)–poly(ethylene) (PEO) comb polymer dispersant on the rheological properties and interparticle forces in aqueous silica suspensions have been studied under varying pH conditions. The comb polymer was found to adsorb more strongly under acidic than basic conditions, indicating that the PAA backbone of the copolymer preferentially adsorbs onto silica surfaces with the PEO “teeth” extending out from the surface into the solution. In the presence of low concentrations of copolymer, the silica suspensions were stable due to electrostatic repulsions between the silica surfaces. At higher copolymer concentrations and under neutral and basic conditions, where the copolymer interacted only weakly with silica, the suspensions showed a transition from a dispersed to weakly flocculated state and attractive forces were measured between silica surfaces. Under acidic conditions, the silica dispersion also destabilized at intermediate copolymer adsorbed density and then was restabilized at higher adsorbed coverage. The silica suspensions were stable at high copolymer coverage due to steric repulsions between the particles. The destabilization at intermediate coverage is thought to be due to polymer bridging between particles or possibly depletion forces.

Keywords: Polyelectrolyte; Comb polymer; Silica; Rheology; AFM

1. Introduction

Colloidal routes to materials assembly underpin the fabrication of ceramic [1], photonic band gaps [2], and even cementitious materials [3,4]. They offer the ability to reliably produce materials through careful control of initial suspension “structure” and its evolution during the assembly process [5]. A distinguishing feature of all colloidal systems is that the contact area between particles and the dispersing medium is large. As a result, interparticle (or surface) forces strongly influence suspension behavior. Long range van der Waals forces are ubiquitous, and therefore must be balanced by electrostatic, steric, or other repulsive interactions to tailor suspension behavior [6]. Polymer species are often added to colloidal suspensions to impart the desired stability by adsorbing and forming a steric barrier to aggregation [7].

The stabilization of a colloidal dispersion can be enhanced using amphipathic molecules consisting of segments that can adsorb strongly and other segments that have a higher affinity for the dispersion medium. These molecules adsorb in conformations which increase the thickness of the steric barrier compared to that imparted by polymers which adsorb in a flat conformation on the surface. Graft or comb copolymers, which consist of a backbone of one type of monomer and side chains of another, can be designed to optimize this behavior and show great promise as colloid stabilizers [8–11]. Comb polymers comprising of neutral poly(ethylene oxide) (PEO) teeth attached at frequent intervals along a poly(acrylic acid) (PAA) backbone have recently been explored as dispersants for cement-based materials [12]. PAA has carboxylic acid groups which become appreciably ionized above their pK_a value of 5 [13], thereby promoting significant interactions with oppositely

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charged or neutral oxide surfaces, and yielding a strong anchoring block. Alternately, they undergo a strong coulombic repulsion when interacting with like-charged colloidal surfaces. It is postulated that the neutral PEO teeth extend away from the particle surface and regulate the adsorbed layer density and thickness.

The influence of PAA/PEO copolymers on colloid stability has received scant attention to date, yet some inferences may be drawn from the related work on the interactions between pure PAA and PEO with oxide surfaces. Low-molecular-weight PAA was found to stabilize zirconia dispersions by a combination of electrostatic and steric forces [14]. The conformation of the adsorbed molecules and thus the steric component of this stabilization depended strongly on the pH [14,15]. Adsorbed PEO layers were found to impart steric stabilization to silica dispersions [16]. Some evidence was also found for depletion interactions in the presence of significant concentrations of unadsorbed PEO [16]. At low PEO coverage of silica, attractive bridging forces were measured between silica surfaces, while at higher coverage, repulsive steric interactions were observed [17].

Here, we investigate the effects of PAA/PEO comb polymers on the behavior of aqueous colloidal silica suspensions under varying pH conditions. The PAA/PEO adsorption behavior on silica depended strongly on pH, which in turn influenced the rheological behavior and colloid forces in suspension. Stress viscometry measurements were carried out to characterize the macroscopic flow behavior of the suspensions while direct force measurements were made by the colloidal probe AFM technique [18,19] to determine the microscopic interactions between silica surfaces in PAA/PEO solutions. Under acidic conditions, copolymer additions induced the destabilization of the suspension at intermediate adsorbed copolymer layer densities followed by restabilization at higher copolymer coverage. Interparticle force measurements suggested that this destabilization was due to bridging effects, while the subsequent restabilization at higher coverage was attributed to steric forces. Under neutral and basic conditions, copolymer adsorption was reduced, leading to a flocculated system at high copolymer concentrations. The origin of the attractive interactions measured between silica surfaces under these conditions likely stems from either bridging or depletion effects.

2. Materials and methods

2.1. Materials

A silica powder (Alfa Aesar, Ward Hill, MA) with an average particle diameter of 2.18 µm (by volume) and 0.12 µm (by number) and a specific surface area of 7.1 $m^2\,g^{-1}$ served as colloidal phase in this study. This powder was utilized in both the adsorption isotherm and rheological measurements. Monodisperse silica spheres with a diameter of 4.8 µm (Bangs Laboratories, Indiana) were used as a colloidal probe in the direct force measurements. The silica substrates used in these experiments were microscope cover slides (Fisher Scientific). Their surface roughness was about 0.3 nm across a 10 × 10 µm region, as probed by atomic force microscopy.

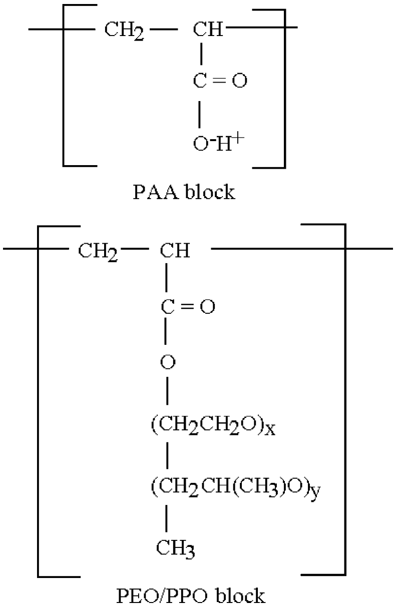

Fig. 1. A schematic illustration of the representative structure of the PAA/PEO copolymer used in this study. It consists of a chain of PAA monomers to some of which PEO/PPO chains have been grafted via an imidized linkage onto the carboxyl group. The polyelectrolyte has a molecular weight of 15,200 $g\,mol^{-1}$.

The polyelectrolyte dispersant studied was a carboxylated acrylic ester-grafted copolymer (ADVA flow, W.R. Grace & Co., Cambridge, MA). A representative structure of the copolymer is shown in Fig. 1. The average molecular weight of the PAA backbone and PEO-based teeth is roughly 2000–8000 $g\,mol^{-1}$ and 700–3000 $g\,mol^{-1}$, respectively, which yields a total average molecular weight of approximately 15,200 $g\,mol^{-1}$.

Colloidal silica suspensions were prepared using distilled, deionized water, while all solutions used in AFM experiments were prepared using Milli-Q water. Electrolyte salts and other reagents used were analytical grade and were used without further purification.

2.2. Adsorption isotherms

Concentrated silica suspensions (48 vol%) were prepared by adding an appropriate amount of silica powder to aqueous stock solutions (10^{-3} M KCl) of varying PAA/PEO concentration, adjusting the pH appropriately, and mixing for 5 min. After initial mixing, the suspensions were magnetically stirred for 24 h. Each suspension was then centrifuged, and a representative aliquot of the supernatant solution was analyzed using a total organic carbon (TOC) analyzer (Phoenix 8000, Tekmar–Dohrmann) to determine the remaining PAA/PEO concentration in solution. The adsorption behavior on silica was determined by comparing these data against known calibration curves.

2.3. *Rheology measurements*

Concentrated silica suspensions (48 vol%) were prepared by adding an appropriate amount of silica powder to aqueous stock solutions (10^{-3} M KCl) of varying PAA/PEO concentration, adjusting the pH appropriately, and mixing for 5 min. After initial mixing, the suspensions were magnetically stirred for 24 h. These suspensions were also sonicated for 5 min (pulsed mode) using a Sonic Dismembrator 550 (Fisher Scientific) after 2 h of stirring. The suspensions had pH values ranging from 3.5 to 4.0 and their pH was adjusted to the desired value by adding appropriate amounts of a concentrated stock solution of NH_4OH.

A Bohlin CS50 rheometer with a 25-mm cuvette was used to perform stress viscometry measurements of the suspensions. Prior to the loading of the sample cell, the suspension was sonicated for 5 min with a 1 s on followed by a 1 s off, pulse sequence. The apparent viscosity was measured at a constant temperature of 22 °C for applied stresses ranging between 0.025 to 1200 Pa. A delay time of 30 s elapsed during each applied stress to achieve steady state flow conditions. A solvent trap was used to minimize evaporation.

2.4. *AFM measurements*

The forces of interaction between a colloidal silica sphere and a silica flat in aqueous solutions were measured using an AFM following the method developed independently by Ducker et al. [18] and Butt [19]. A Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) was used with gold-coated silicon nitride cantilevers (Digital Instruments). The spring constants of the cantilevers were measured using the method of Cleveland et al. [20]. The cantilevers were modified by attaching a silica sphere to the tip using Epikote 1004 resin (Shell, USA). The radii of the spheres attached to the cantilevers were measured using a light microscope. The probes and the silica flats used in AFM experiments were cleaned by irradiation with UV light just prior to measurements. The AFM was assembled in a laminar flow hood and all measurements were made at ambient temperature conditions.

The force curves obtained were analyzed using the software “AFM Analysis” [21]. Theoretical DLVO force curves for the interactions between identical surfaces in 1:1 electrolyte were generated (by summing together the van der Waals and electrostatic forces) and fitted to the data by varying the parameters of electrolyte concentration and the diffuse layer potential. For comparison with the fitted electrolyte concentrations, the conductivity of solutions used in AFM measurements was measured.

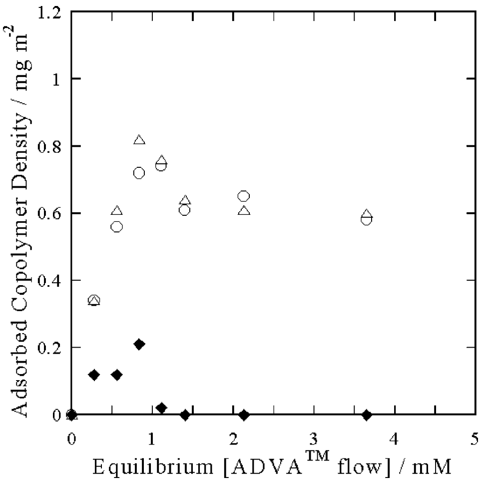

Fig. 2. The adsorption isotherm of PAA/PEO on silica in 48 vol% dispersions under different pH conditions. Two separate experiments were recorded at pH 4 and the data from both the first (○) and second (△) run are shown. The measurements carried out at pH 10 (◆) used suspensions in which 10^{-3} M KCl was present.

3. Results and discussion

3.1. *Adsorption behavior*

The adsorption isotherms for PAA/PEO on silica in aqueous solutions of varying pH are shown in Fig. 2. At pH 4, the amount of copolymer adsorbed rises to a maximum value of 0.7 mg m^{-2} at approximately 8×10^{-4} M PAA/PEO in solution. The apparent variation in the adsorbed copolymer density at higher copolymer concentrations reflects the scatter in the data. Both PAA and PEO have been shown to adsorb strongly onto silica surfaces under such conditions [22]. At pH 4, the silica surfaces and PAA segments are weakly charged, thereby reducing the electrostatic repulsions between them and permitting the build up of an adsorbed layer of modest density [22].

At pH 10, there is little evidence of PAA/PEO adsorption at solution concentrations above 10^{-3} M, with perhaps some adsorption occurring under very dilute concentrations. These measurements were carried out using a background electrolyte concentration of 10^{-3} M KCl. However, as is clear from the conductivity measurements (see Table 1), a constant ionic strength cannot be maintained at high pH. Our observations are in good agreement with previous work, which indicates that PAA and PEO adsorption on silica surfaces decreases with increasing pH, and that above pH 7 PAA completely desorbs [22]. Since little or no adsorption of the copolymer was observed at high pH compared to low pH, this suggests that the PAA backbone of the copolymer preferentially adsorbs onto the silica surfaces in aqueous media. At pH 10, both the silica surfaces and PAA segments are highly negatively charged, providing a strong coulombic repulsion that prevents adsorption.

Table 1
Conductivity of PAA/PEO solutions and equivalent KCl concentrations

PAA/PEO concentration (M)	pH	Conductivity (μS cm^{-1})	Equivalent concentration of KCl (M)
0	4.3	190	1.3×10^{-3}
	6.0	121.9	8×10^{-4}
	9.7	180.3	1.2×10^{-3}
10^{-5}	4.4	130	9×10^{-4}
	7.0	135.3	9×10^{-4}
10^{-4}	4.3	145.1	1.0×10^{-3}
	6.5	193.4	1.3×10^{-3}
	9.7	257	1.7×10^{-3}
10^{-3}	3.9	224	1.5×10^{-3}
	6.5	731	4.9×10^{-3}
	9.9	988	6.6×10^{-3}

3.2. Rheology properties

The apparent viscosity as a function of shear rate for concentrated silica suspensions with varying PAA/PEO concentrations are shown in Figs. 3a–3c for systems at pH 3.5, 7, and 10, respectively. In the absence of copolymer, the suspension viscosity for all pH conditions studied was found to decrease slightly as the shear rate increased up to a rate of about 100 s^{-1} and then increase with increasing shear rate due to shear thickening behavior. At pH 3.5, these suspensions exhibited an increasing shear thinning response as the PAA/PEO concentration increased. At a concentration of 2.5×10^{-4} M, there was a large increase in suspension viscosity at low shear rates. Since a comparable increase in solution viscosity was not observed under analogous copolymer concentrations, the increase in suspension viscosity was attributed to changes in particle interaction. The observed shear thinning behavior likely reflects a change in suspension stability from a dispersed to weakly flocculated state. Above this critical concentration, the suspensions restabilized, as evidenced by a return to the flow behavior observed for lower copolymer concentrations at modest shear rates.

Under neutral pH conditions, the suspension viscosity at low PAA/PEO concentrations decreased slightly as the shear rate was increased up to a rate of about 100 s^{-1}. A modest rise in the degree of shear thinning flow behavior was observed with increasing PAA/PEO concentration, with the suspension viscosity increasing at low shear rates at concentrations above 2.5×10^{-4} M. The maximum increase in the viscosity occurred at 10^{-3} M PAA/PEO in solution. Similar behavior was observed for concentrated silica suspensions, with varying PAA/PEO concentration at higher pH, as shown in Fig. 3c. However, the degree of shear thinning observed at a given PAA/PEO concentration was slightly less under these highly basic (pH 10) conditions. Thus under neutral and basic conditions, the observed flow behavior of these suspensions suggested that the particles were becoming weakly flocculated with increasing copolymer concentration. In sharp contrast to the behavior observed under acidic conditions, suspension restabilization was not observed over the copolymer concentration range studied.

Table 2
Fitted concentrations and potentials from AFM data at pH 3.9

PAA/PEO concentration (M)	Apparent electrolyte concentration (M)	Diffuse layer potential (mV)
0	1.3×10^{-3}	−20
10^{-5}	9×10^{-4}	−76
5×10^{-5}	9×10^{-4}	−77
10^{-4}	1.0×10^{-3}	−66
2.5×10^{-4}	1.5×10^{-3}	−41
5×10^{-4}	2.5×10^{-3}	−43

3.3. Direct force measurements

The interaction force versus separation distance between a colloidal silica probe and flat substrate as a function of varying PAA/PEO concentration are shown in Figs. 4a–4c for systems at pH of about 3.9, 6.7, and 9.6, respectively. In each case, the forces measured in the absence of PAA/PEO additions are not shown, since they are well established [23,24]. Significant differences in the interparticle forces were observed between silica surfaces in the presence of PAA/PEO species at varying concentrations and solution pH, as outlined below.

3.3.1. Acidic pH

Long range repulsive interactions were observed over the entire PAA/PEO concentration range studied at pH 3.9. The apparent solution electrolyte concentrations and the silica diffuse layer potentials, estimated from fitting theoretical curves (which assumes a monovalent electrolyte) to the force data for the different PAA/PEO concentrations, are given in Table 2. The fitted electrolyte concentration is very similar to that estimated from the conductance measurements (see Table 1). The diffuse layer potential of the silica was markedly higher than that expected for clean silica surfaces, indicating the adsorption of negatively charged PAA/PEO molecules which was consistent with the adsorption isotherm shown in Fig. 2.

For PAA/PEO concentrations ranging from 5×10^{-5} to 5×10^{-4} M, at small separations (within about 5 to 8 nm) the interaction forces tended to become constant, or attractive, with separation. Since this PAA/PEO concentration is well below the adsorption plateau value, it is likely that the attractive interactions arise from bridging effects. The silica diffuse layer potential decreased at 2.5×10^{-4} M PAA/PEO and then remained nearly constant with increasing dispersant concentration, as shown in Table 2. The ionic strength of the solutions also increased in this concentration range. Since polyvalent PAA species represent a significant fraction of the overall number of ions in solution in this additive concentration, it is no longer reasonable to assume that the solution can be modeled as a monovalent electrolyte in

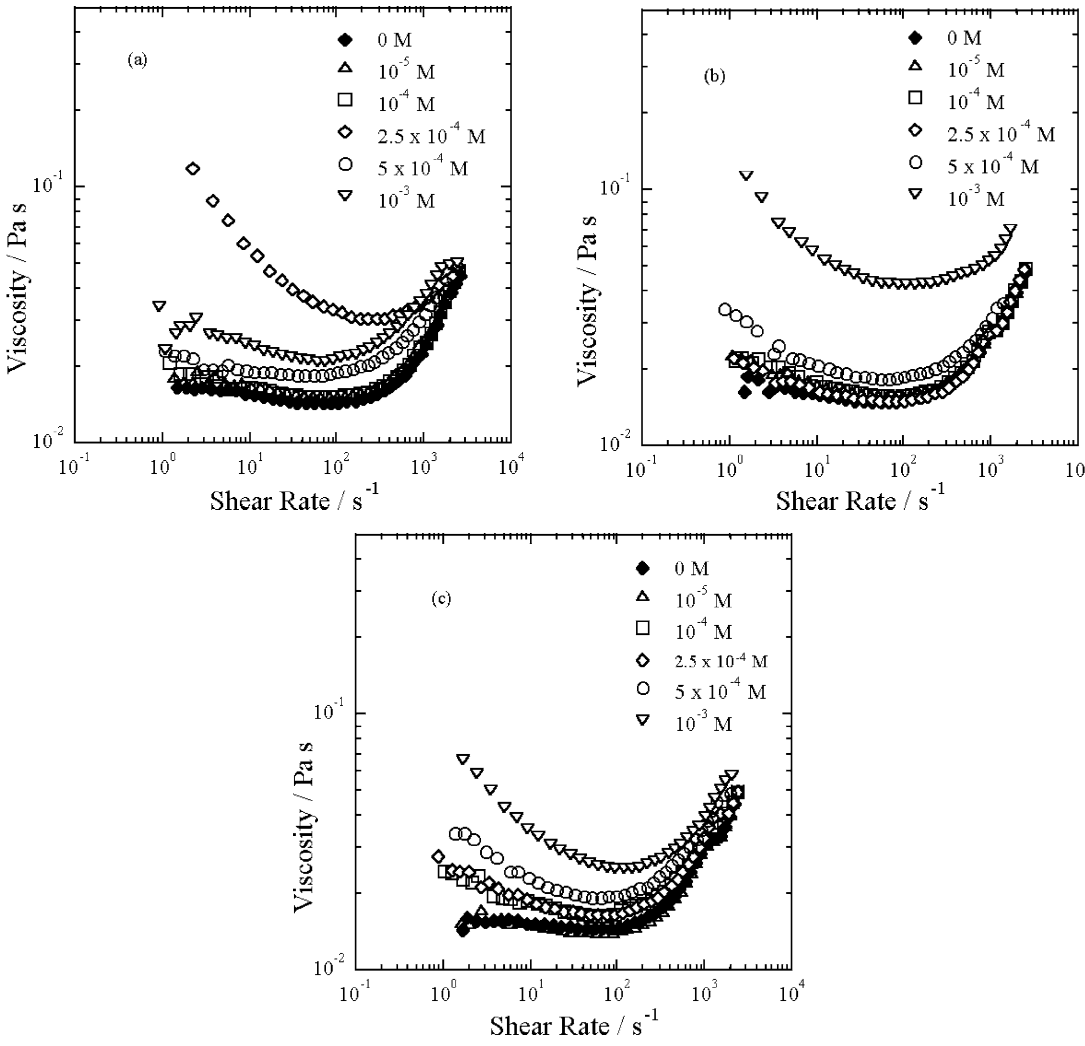

Fig. 3. The apparent viscosity versus shear rate of a silica suspension as a function of PAA/PEO concentration at (a) pH 3.5, (b) pH 7, and (c) pH 10. The silica volume fraction was 48% and the background electrolyte concentration was 10^{-3} M KCl.

calculating the theoretical interaction forces for this system. Thus, the reduction in the silica diffuse layer potential (estimated from fitting the theoretical curves to the force data) probably reflects the higher proportion of polyvalent ions in the solution under these conditions [6].

Above 5×10^{-4} M PAA/PEO, the interactions measured are due mainly to steric effects, since similar interactions forces were measured at an electrolyte concentration (10^{-2} M) high enough to fully screen electrostatic interactions. The adsorbed layer thickness was estimated to be approximately 10 nm. The observation of steric interactions between the surfaces is consistent with the onset of the maximum in the adsorption data observed at this concentration in the adsorption isotherm (Fig. 2).

3.3.2. *Neutral pH*

Long-range repulsive interactions were observed at low PAA/PEO concentrations studied at pH 6.7. These were attributed to electrostatic interactions. The apparent electrolyte concentrations in the electrical double layer (as deduced from fits to the long-range interaction) and the silica diffuse layer potentials are given in Table 3. The trend in the silica diffuse layer potential was similar to that observed at lower pH, but less marked, due to the (presumably) lower adsorption density. The fitted electrolyte concentration was reasonably similar to that estimated from the conductance measurements (Table 1).

At small separations (about 5 nm), the measured interaction forces deviated from those predicted assuming electrostatic forces, with extra repulsive forces being observed (this behavior was most obvious at 10^{-4} M PAA/PEO). These were attributed to the presence of adsorbed material causing steric repulsions. The lower surface coverage under neutral conditions (compared to acidic pH) accounts for the smaller thickness of the adsorbed layer.

At PAA/PEO concentrations of 2.5×10^{-4} M and above, attractive interactions between the silica surfaces were observed. Due to these attractive forces, the surfaces tended

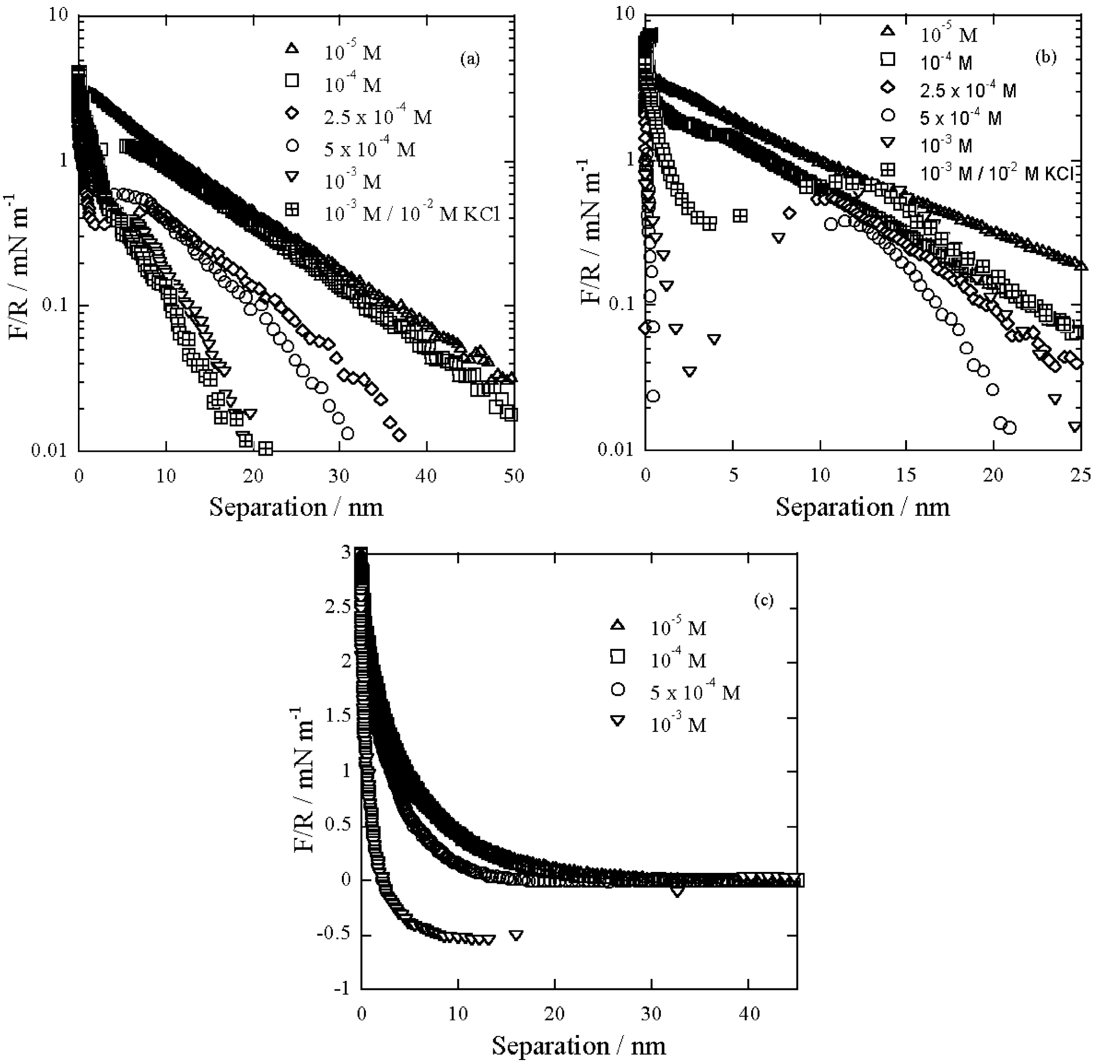

Fig. 4. The forces of interaction between a silica sphere and a silica flat in 10^{-3} M KCl at (a) pH 3.7–4.1, (b) pH 6.6–6.8, and (c) pH 9.4–9.7 plotted as a function of the PAA/PEO concentration. Also shown in (a) and (b) are the interaction forces measured in 10^{-2} M KCl at the highest copolymer concentration.

to jump into closer contact, but not zero separation, suggesting that the adsorbed layer had first to be compressed between the surfaces before they were pushed into contact. Adhesive forces were measured as the surfaces were pulled apart. The interactions measured at 10^{-3} M PEO/PPO did not vary as the electrolyte concentration was changed from 10^{-3} to 10^{-1} M KCl, indicating that the interactions measured largely reflect contributions from polymer interaction effects at these high dispersant concentrations. The attractive forces were perhaps due to molecular rearrangements of the adsorbed copolymer (longer equilibration times were required at these concentrations) or depletion effects. Since steric repulsions were also observed at larger separations, it seems less likely that the attractive forces are due to bridging phenomena. If the forces were due to attractive depletion, the repulsive interaction could in part be due to long range ordering of the nonadsorbed copolymer species.

Table 3
Fitted concentrations and potentials from AFM data at pH 6.7

PAA/PEO concentration (M)	Apparent electrolyte concentration (M)	Diffuse layer potential (mV)
0	1.2×10^{-3}	−70
10^{-5}	1.1×10^{-3}	−74
5×10^{-5}	1.7×10^{-3}	−69
10^{-4}	2.4×10^{-3}	−60
2.5×10^{-4}	3.4×10^{-3}	−61

Table 4
Fitted concentrations and potentials from AFM data at pH 9.6

PAA/PEO concentration (M)	Apparent electrolyte concentration (M)	Diffuse layer potential (mV)
0	1.2×10^{-3}	−46
10^{-5}	1.1×10^{-3}	−45
10^{-4}	1.7×10^{-3}	−42
5×10^{-4}	2.4×10^{-3}	−36

3.3.3. Basic pH

Long range repulsive interactions were observed at PAA/PEO concentrations up to 10^{-4} M studied at pH 9.6. The apparent electrolyte concentrations in the electrical double layer (as deduced from fits to the long range interaction) and the silica diffuse layer potential for the different PAA/PEO concentrations are given in Table 4. The silica diffuse layer potential did not change significantly, except at the highest copolymer concentration, suggesting that there was little or no adsorption of copolymer on the silica surfaces. At 5×10^{-4} M PAA/PEO, however, extra repulsions were measured at surface separations of about 1 nm, suggesting the presence of a very thin adsorbed layer on the surfaces. The adsorption isotherm at pH 10, although not conclusive, indicates that some polymer may be adsorbed. It is possible that the AFM measurements are much more sensitive in detecting low levels of adsorbed material than can be measured by quantitative assays. After all, adsorbed polymer concentrations are calculated by difference.

At 10^{-3} M PAA/PEO, long range attractive forces were observed. Large adhesive forces were also measured (not shown) as the surfaces were pulled apart. It is difficult to account for the origins of such a long range attraction. Given the presence of a thin adsorbed layer, attractive bridging interactions between the surfaces are possible. Yet it seems unlikely that there would be sufficient adsorption for bridging to occur. Depletion of the copolymer from the solution in between the surfaces as they were compressed together may also have been responsible for the attractive forces measured. Since the diffuse layer potentials measured at high pH were lower than that observed at neutral pH, it is possible that attractive depletion interactions dominated the electrostatic repulsions under these conditions.

Direct comparisons between the rheology and AFM data were not possible as the amount of copolymer adsorbed onto the silica particles in the rheology measurements is unknown. There are similarities, however, in the overall trends in the data. Under acidic conditions, in the rheology measurements, the dispersions were observed to be destabilized and then restabilized as the copolymer concentration was increased. Under neutral and basic conditions as the copolymer concentration was increased, the silica dispersions were destabilized. On the basis of the force measurements, it is proposed that in the absence of copolymer or the presence of small amounts of copolymer the dispersions were stabilized by electrostatic repulsions between the particles. It is speculated that the origin of the stabilization of the dispersions in the presence of high concentrations of copolymer (at acidic pH's) was the result of steric forces due to adsorption of the copolymer. The destabilization of the dispersion in the presence of copolymer under conditions where little or no adsorption occurs is thought to be due to bridging or depletion interactions.

4. Summary

In conclusion, the influence of PAA/PEO comb polymer additions on the stability of colloidal silica suspensions as a function of varying pH conditions was investigated by measuring the adsorption behavior and the macroscopic flow behavior of the suspensions and by measuring the direct interactions between silica surfaces in the presence of such additives. Our observations reveal that the PAA backbone of the copolymer preferentially adsorbed onto the silica surface, resulting in a strong pH dependence. Stress viscometry measurements indicated that under basic and neutral conditions, where the copolymer adsorbs only to a small extent, the silica suspensions were destabilized by the addition of high copolymer concentrations. Under acidic conditions, the silica suspensions were restabilized at higher adsorbed copolymer densities. On the basis of direct force measurements, it is suggested that at low adsorbed copolymer densities electrostatic repulsions dominated the interactions between the particles, while at high adsorbed densities, steric repulsions dominated. The origin of the attractive forces measured at intermediate adsorbed densities may stem from either bridging or depletion interactions.

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