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ORIGINAL CONTRIBUTION

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Effect of polyethylene oxide on the viscosity of dispersions of charged silica particles: interplay between rheology, adsorption, and surface charge

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Abstract In this study a systematic investigation on the adsorption of polyethylene oxide (PEO) onto the surface of silica particles and the viscosity behavior of concentrated dispersions of silica particles with adsorbed PEO has been performed. The variation of shear viscosity with the adsorbed layer density, concentration of free polymer in the solution (depletion forces), polymer molecular weight, and adsorbed layer thickness at different salt concentrations (range of the electrostatic repulsion between particles) is presented and discussed.

Adsorption and rheological studies were performed on suspensions of silica particles dispersed in solutions of 10^{-2} M and 10^{-4} M $NaNO_3$ containing PEO of molecular weights 7,500 and 18,500 of different concentrations. Adsorption measurements gave evidence of a primary plateau in the adsorption density of 7,500 MW PEO at an electrolyte concentration of 10^{-2} M $NaNO_3$. Results indicate that the range of the electrostatic repulsion between the suspended particles affects both adsorption density of the polymer onto the surface of the particles and the viscosity behavior of the system. The adsorbed layer thickness was estimated from the values of zeta potential in the presence and absence of the polymer and was found to decrease with decreasing the range of the electrostatic repulsive forces between the particles. Experimental results show that even though there is a direct relation between the viscosity of the suspension and the adsorption density of the polymer onto the surface of the particles, variation of viscosity with adsorption density, equilibrium concentration of the polymer, and range of the electrostatic repulsion cannot be explained just in term of the effective volume fraction of the particles and needs to be further investigated.

Key words Suspensions viscosity · Polymer adsorption · Rheology · Highly concentrated silica suspensions · Steric stabilization

Introduction

Stabilization of colloidal suspensions by the adsorbed polymers is of considerable importance in the preparation and processing of concentrated colloidal dispersions. These materials find applications as coatings, cosmetics, clays and ceramics, electronic pastes, food, paper, paints, sludges, and effluents. In preparation of these systems, solids are dispersed in the suspending fluid as fine particulates and remain separated from each other through electrostatic, steric, or electrosteric stabilization. Even though the role of polymers and polyelectrolytes in controlling the stability-flocculation behavior of colloidal suspensions has been widely known for many years, most of the past research has been performed on dilute systems. During the past forty years, theories have been developed to describe the adsorption and conformation of polymers at the solid-liquid interface and also, theories have been developed to explain particle-particle interactions in the presence of polymers [1, 2]. Several important factors such as Brownian motion of the particles, particle size, particle size distribution, particle shape, volume fraction of the particles, the viscosity of the suspending media, and the range of particle-particle interactions govern the suspension properties [3, 4]. The calculations as well as experimental studies show that the effect of interparticle forces on suspension properties becomes increasingly important as the particle size is decreased [3]. Control of the range of interparticle interactions is of significant importance in terms of stability, flow properties, and packing of sub-micron-sized particles. In order to improve the material properties to minimize the inhomogeneities in the packing of particles and the distribution of the pores, interparticle forces in the suspension should be manipulated during processing and forming [5, 6]. In addition to Brownian and hydrodynamic interactions, there are several other types of interactions between the suspended particles that determine the stability and state of a colloidal dispersion. These are: van der Waals attractive forces, electrostatic repulsive forces, steric (due to the adsorbed polymers) and electrosteric (polyelectrolytes) forces, depletion forces (due to the presence of free polymers), and structural (hydration) forces (short range). The combination of van der Waals attractive forces and steric forces form the basis for the theory of steric stabilization [7].

Fine particles tend to attract each other due to van der Waals attractive forces. Brownian motion of the particles resists this force tending to keep the particles in the dispersed state. However, if the former dominates, particles will aggregate into flocs and trap the suspending fluid, leading to a high viscosity sample. Van der Waals attractive forces can be neutralized through the addition of like charges, and adsorbing or grafting polymer molecules onto the surface of the particles. In the first case, stabilization occurs due to electrostatic repulsion, while in the second case, stabilization occurs due to steric repulsive forces.

Dispersion stabilization

Electrostatic stabilization

Aqueous colloidal dispersions may be stabilized against adhesion and flocculation of the particles through electrostatic repulsion due to the adsorption of the ions at the particle surface. In electrostatically stabilized dispersions, each particle is surrounded by a layer of ionized surface groups and the associated diffuse part of the ionic cloud of counterions. Competition between van der Waals attractive forces and electrostatic repulsive forces between the suspended particles plays the most important role in the stability of the system. Based on the DLVO theory, the total potential energy of interaction for electrostatically stabilized suspensions can be defined as:

$$V_T = V_{el} + V_d \ , \tag{1}$$

where V_T is the total potential energy of interaction, V_{el} is electrostatic potential, and V_d is the London-van der Waals attraction potential [8–10]. All suspensions are subjected to London-van der Waals attractive forces. In the absence of electrostatic repulsion, the particles will stick together due to these forces and if the magnitude of the attraction is high, flocs or aggregates will be formed. Between two spheres of the same size, these forces can be expressed as:

$$V_d = -\frac{A}{6}\left[\frac{2a^2}{h^2 - 4a^2} + \frac{2a^2}{h^2} + \ln\left(\frac{h^2 - 4a^2}{a^2}\right)\right] \ , \tag{2}$$

where A is the Hamaker constant, a is the radius of the particle, and h is the center-to-center separation distance [11, 12].

When the particles come close together, the ionic concentration between the particles rises due to the overlap of the ionic cloud around the particles and causes repulsion. The electrostatic potential between two spherical particles in a 1:1 electrolyte can be expressed as:

$$V_{el} = \frac{32\pi a\varepsilon\varepsilon_o (kT)^2 \tanh^2\left(-\frac{ze\psi_s}{4kT}\right) e^{-\kappa(r-2a)}}{z^2 e^2} , \tag{3}$$

where ε is the relative permittivity of the dispersion medium, ε_O is the permittivity of free space, z is the counter ion valence, e is the electron charge, k is the Boltzmann constant, and T is the absolute temperature. For a symmetrical electrolyte the screening efficiency (reciprocal Debye length), κ, is given by [13]:

$$\kappa = \left(\frac{\varepsilon\varepsilon_O kT}{e^2 I}\right)^{-1/2} = 3.3\sqrt{I} \ , \tag{4}$$

where I is the ionic strength.

For dispersions of silica particles (860 nm in diameter), at electrolyte concentrations of 10^{-4} M and 10^{-2} M $NaNO_3$ (using $A = 1.2 \times 10^{-20}$ J, and surface potential $\psi_0 = -60$ mV), calculations indicate that the repulsive energy at contact is very high (e.g., > 30 kT) for both systems. This is enough to ensure the stability of the system and, under these conditions, the dispersions are stabilized by soft, long-range interparticle repulsive forces. As the electrolyte concentration is increased, the ionic cloud around the particles will be compressed resulting in a decrease in the range of the repulsive forces between the particles. There is an indication of a secondary minimum at 10^{-2} M $NaNO_3$

and the depth of the minima will increase as the salt concentration is increased further. This may cause aggregation of the particles in the secondary minima. The size and strength of the aggregates depends on the depth of the minima (magnitude of the attraction). In the second system, the depth of the secondary minima is about $(-2)k\mathrm{T}$ and there is the possibility for the particles to form very weak aggregates which will break down under shearing motion.

The role of particle-particle interactions between suspended particles on stability and flow behavior of concentrated dispersions becomes more pronounced at higher volume fractions of the particles due to a decrease in surface-surface separation in the system. At a fixed volume fraction of the particles, this effect becomes increasingly important for suspensions of finer particles due to the increase in the surface area per unit volume of solids in the dispersion [14–16].

Steric stabilization

Steric stabilization can be achieved through the addition of the soluble polymers to the suspending media. The polymer molecules can either physically adsorb or chemically bond to the surface of the particles [3, 7, 17–19]. The effect of the added polymer on properties of dispersions varies with polymer molecular weight, polymer conformation, chemistry of functional groups, surface coverage, temperature, and concentration of the solvent. The stability of sterically stabilized suspensions is determined by polymer-solvent interaction parameter χ known as the Flory constant [20], which is defined as [21]:

$$\chi = \frac{1}{2} - \Delta H\left(1 - \frac{\theta}{T}\right) \ , \tag{5}$$

where $\Delta\mathrm{H}$ = enthalpy of dilution, and θ is the theta temperature defined as $\left(\frac{\Delta H}{\Delta S}\right)T$ with $\Delta\mathrm{S}$ being as entropy of dilution. For a sterically stabilized suspension to be stable, χ must be less than 0.5. When $\chi > 0.5$, flocculation will occur in the suspension, and $\chi = 0.5$ corresponds to θ conditions [7, 21, 22]. In sterically stabilized suspensions, the total potential energy of interaction between two polymer-coated particles is defined as:

$$V_T = V_{el} + V_d + V_s, \tag{6}$$

where $\mathrm{V_s}$ is steric repulsion. Both $\mathrm{V_{el}}$ and $\mathrm{V_d}$ have to be modified due to the presence of the adsorbed polymer layer [23]. $\mathrm{V_s}$ is equal to the changes in Gibbs free energy as the polymer-coated particles are brought close together. The steric interaction between two polymer-coated, spherical particles can be approximated as [7]:

$$V_s = V_{s,mix} + V_{s,el}, \tag{7}$$

$\mathrm{V_{s,mix}}$ is the result of the interpenetration and therefore mixing of the polymer segments (osmotic contribution) when the adsorbed layers approach to a distance smaller than twice that of the polymer layer thickness. The following approximation is given for $\mathrm{V_{s,mix}}$ by Napper [7]:

$$V_{s,mix} = \frac{2\pi a\kappa T v_p^2 \Gamma_p^2}{v_s}\left(\frac{1}{2} - \chi\right) S_{mix}, \tag{8}$$

where $\mathrm{v_s}$ is the solvent molar volume, $\mathrm{v_p}$ is the polymer molar volume, Γ_p is the adsorbed amount of polymer (number of chains per unit area), and $\mathrm{S_{mix}}$ is a geometric function that depends on the form of the segment concentration profile in the adsorbed layer normal to the interface. When particles come within the compression domain, an elastic contribution must be added to the steric interaction. The second term, $\mathrm{V_{s,el}}$, in Eq. 7 represents this contribution which is defined as [7]:

$$V_{s,el} = 2\pi a\kappa T\Gamma_p S_{el}, \tag{9}$$

where $\mathrm{S_{el}}$ is a geometric function that depends on the segment concentration profile in the adsorbed layer normal to the interface. Napper [7, 17] has derived analytical expressions for $\mathrm{S_{mix}}$ and $\mathrm{S_{el}}$ for various forms of the segment concentration profiles.

Eqations 8 and 9 indicate that interaction potential in sterically stabilized suspensions is affected by the adsorbed layer thickness and polymer molecular weight. It was observed by Sonntag et al. [24] that the thickness of the adsorbed layer increases with increasing polymer molecular weight. They have also shown that the effect of polymer molecular weight on interaction energy between the suspended particles may vary with polymer molecular weight depending upon the separation distance between the suspended particles. While at large separation distances, the interaction potential increases with increasing polymer molecular weight, at small separation distances, interaction potential is higher for lower molecular weight polymers and there is a steeper rise in energy-distance curve for samples stabilized with a lower molecular weight polymer. This was attributed to the increase in average volume fraction of segments in the adsorbed layer with decreasing polymer molecular weight. More energy is needed for the two particles to approach each other as the segment concentration is increased.

Sterically stabilized suspensions show different behavior depending upon the thickness of the adsorbed polymer layer. Particles can be treated as hard spheres when the layer is thin and small relative to the particle radius, whereas soft sphere behavior is expected for particles coated with thick polymer layers [25]. It is important to note that when the polymer dosage is low, surface coverage will be incomplete (partial coverage) providing weak flocculation through polymer bridging of particles [3]. Also, the presence of free polymer chains in the system can cause depletion flocculation [26] that is accompanied by an increase in the viscosity of the suspension. Using a combination of rheology and small angle neutron scattering techniques, Kawaguchi et al. [27] have shown that non-adsorbed polystyrene chains (PS) induce changes in the structure and the rheological properties of suspensions of fumed silica particles which form gel-like network structures in the suspending fluid.

Most of the past data on rheological properties of sterically stabilized silica are limited to low volume fractions of the particles [25, 28–31]. In addition, in most of these studies, one cannot find all necessary information such as adsorbed layer density and adsorbed layer thickness in a single paper to relate rheological properties of suspensions to physical and chemical characteristics of the system [32, 33]. In this study a systematic investigation on the adsorption of polyethylene oxide (PEO) onto the surface of silica particles and the viscosity behavior of highly concentrated aqueous suspensions of silica particles with adsorbed PEO has been performed. In order to relate the viscosity of the system to the adsorbed layer density of the polymer, adsorption studies were performed on the same samples prepared for rheological experiments. The variation of the shear viscosity with the adsorbed layer density, concentration of the free polymer in the solution (depletion forces), polymer molecular weight, and adsorbed layer thickness at different salt concentrations is discussed. Adsorbed layer thickness was estimated from the values of zeta potential in the presence and absence of the polymer.

Materials and methods

The silica samples used in this study were of 0.20 μm, and 0.86 μm in diameter (d_{50} value) with specific surface areas of 14.62 m^2/g, and 3.26 m^2/g, respectively. The purity and density of the powders were 99.9% and 2.1 g/cm^3, respectively. Silica samples were provided by Geltech Corporation and were used as received. Polyethylene oxide (PEO) of molecular weights 7,500 and 18,500 was procured from Polysciences Inc. and was used as received. Polymer stock solutions were prepared at concentrations of up to 10,000 ppm in 10^{-2} M and 10^{-4} M $NaNO_3$ solutions and stirred for 16 hours using a magnetic stirrer in order to achieve complete dissolution. The solutions were covered in order to avoid decomposition of the polymer due to exposure to ultraviolet radiation. All experiments were conducted in ultra-pure water of specific conductivity less than 1 μohm/cm.

Silica slurries were prepared by gradually adding silica powder to the electrolyte or electrolyte-polymer solutions. Depending upon the volume fraction of silica used, polymer dosage, and salt concentration, the PEO stock solution was diluted with 10^{-2} M or 10^{-4} M $NaNO_3$ solution to the desired concentration. The required mass of dry silica was then slowly added to the PEO solution while mixing the sample by shaking and vibration. After addition of silica, the suspensions were vigorously shaken by hand and then the pH of the samples was adjusted to 9.5 using NaOH (Fisher brand) solution. After the pH adjustments, samples were sonicated for at least 30 minutes in order to break up any aggregates. The suspensions were then agitated using a Burrell Model 75 Wrist Shaker for a period of 16–20 hours in order for equilibrium to be reached. During equilibration, the pH of the suspensions was checked periodically and readjusted if required.

The viscosities of the samples were determined using a Paar Physica UDS 200 rheometer with a cone-and-plate geometry. All experiments were performed at 25 °C and the sample temperature was controlled to within ± 0.1 °C using water as the heat transfer fluid. In all experiments, a cone of radius 4.30 cm with a cone angle of 0.5° (a gap size of 25 μm) was used. The possibility of sedimentation of the particles and water evaporation from the samples during experiments were examined by performing viscosity measurements as a function of time at a fixed shear rate. Also a cone of radius 3.75 cm with a cone angle of 1.0° (a gap size of 50 μm) was used to check for other possible errors. The results did not change over the time period of experiments and the viscosity values measured with two different cones agreed within experimental error ($\pm 3\%$).

Adsorption of PEO onto the surface of silica particles was determined using a depletion method. After equilibration, the samples were centrifuged for 10 minutes at 15,000 rpm and the supernatant was carefully withdrawn. Supernatant was left in the refrigerator overnight to assure sedimentation of the remaining particles in the solution. The residual PEO concentration was then determined using a Tekmar-Dorhmann Phoenix 8000 Total Organic Carbon (TOC) analyzer.

Electrokinetic studies were performed on two sets of suspensions of 200 nm (diameter) silica particles (0.1% vol) prepared in solutions of PEO-7500 of different polymer concentrations at two different electrolyte concentrations, 10^{-2} M and 10^{-4} M $NaNO_3$, respectively. Zeta potential measurements were carried out using a Brookhaven ZetaPlus instrument. A small portion of the sample was injected into the cell of the instrument and multiple measurements of the electrophoretic mobility of the particles were made at room temperature.

When a charged particle in an electrolyte solution is placed in an electric field, the particle will move toward the oppositely charged electrode. The electrophoretic mobility of the particle may be defined as [34]:

$$\mu_e = \frac{2\varepsilon_o \varepsilon_r \zeta}{3\eta} f_1(\kappa a) \ , \qquad (10)$$

where μ_e is the electrophoretic mobility, ε_O and ε_r are the dielectric constants of the free space and medium, ζ is the zeta potential of the particle, η is the viscosity of the fluid, and f_1 is the shape function. This function changes from 1 (Hückel limit) for small values of κa, to 1.5 (Smoluchowski limit) for large κa values ($\kappa a > 100$). Values of $f_1(\kappa a)$ to be used in Eq. 10 are given by Hunter [34]. For silica particles with an average radius of 100 nm in electrolyte solutions of 10^{-2} M and 10^{-4} M $NaNO_3$, values of κa will be equal to 33 and 3.3, respectively. The corresponding values for $f_1(\kappa a)$ given by Hunter [34] are equal to 1.39 and 1.1, respectively. Using a Brookhaven ZetaPlus instrument, the operator has the option to choose either Smoluchowski's model or Hückel's equation to determine the zeta potential of the sample under consideration. Depending upon the magnitude of κa, the actual zeta potential may differ from the measured values and proper correction has to be made to reduce the corresponding errors. In this work, Hückel's equation was chosen for the default calculation of the zeta potential of PEO coated silica particles in solutions of 10^{-2} M and 10^{-4} M $NaNO_3$ respectively. These values were then divided by 1.39 and 1.1, respectively, to determine the actual zeta potential of the samples at electrolyte concentrations of 10^{-2} M and 10^{-4} M $NaNO_3$, respectively.

When neutral polymers are adsorbed onto the surface of a particle, the shear plane will shift away from the particle surface (depending upon the adsorbed layer thickness) with respect to its position in the absence of the adsorbed polymer [34]. The work of Koopal and Lyklema [35] on the adsorption of polyvinyl alcohol (PVA) onto the surface of AgI indicates that the zeta potential changes by increasing the adsorbed layer density and the initial effect of the polymer is to move the isoelectric point (IEP) to more positive values. The values of the zeta potential can be used to determine the adsorbed layer thickness of the polymer using the following equation [34]:

$$\tanh\left(\frac{ze\zeta}{4kT}\right) = \tanh\left(\frac{ze\psi_\delta}{4kT}\right)\exp(-\kappa(\Delta - \delta)), \qquad (11)$$

where z is the valence of the counterion, e is the elementary charge, ψ_δ is the potential measured in the absence of polymer, δ is the thickness of the stern layer, and Δ is the thickness of the adsorbed layer. With the assumption that ψ_δ is equal to the measured value of zeta potential in the absence of polymer, it is possible to estimate the thickness of the adsorbed layer from the values of zeta potential using Eq. 11.

Results and discussion

Shear flow properties

The steady shear viscosities of 55% vol suspensions of silica particles (0.86 μm in diameter) suspended in an aqueous solution of 0.01 M $NaNO_3$ containing 7,500 MW PEO of different concentrations are shown in Fig. 1 which represents the viscosity as a function of shear rate at different levels of polymer dosage. As can be observed, all samples exhibit shear thinning behavior at intermediate shear rates and Newtonian behavior at shear rate levels higher than 300 s^{-1}. It appears that over the range of polymer concentrations studied, the degree of shear thinning behavior is approximately the same for all samples prepared using different dosages of PEO indicating the same degree of stability for the systems under consideration. Even though there is no indication of shear thickening behavior at 55% vol over the shear rate and polymer concentration ranges studied this may not be the case at higher polymer concentrations. The effect of polymer dosage on the viscosity of the suspension is more significant at lower shear rates which is due to the fact that, at low deformation rates, interparticle forces are dominant and control the viscosity behavior of the system.

Effect of polymer dosage and adsorption density of the polymer

The effect of PEO 7,500 dosage on shear viscosity of aqueous suspensions of 0.86 μm (diameter) SiO_2 particles at 55% vol (10^{-2} M $NaNO_3$ at a pH value of 9.5) is shown in Fig. 2 which represents plots of viscosity as a function of polymer dosage at shear rate levels of 1 s^{-1}, 10 s^{-1}, 100 s^{-1}, and 1000 s^{-1}. It can be observed that the viscosity of the suspension initially decreases to a minimum with increasing polymer dosage and then starts to increase with further addition of polymer to the suspension. There is a secondary minimum in the viscosity of the system at higher polymer concentrations. Even though one may attribute the change in viscosity to the effect of polymer on the stability and phase separation of the suspension, more research has to be performed before a definite conclusion can be made. It can be seen from Fig. 2 that the variation of viscosity with polymer dosage is more significant at lower levels of shear rate. While there is a considerable improvement in the fluidity of the system through the adsorption of the polymer onto the surface of the particles, it appears that the applied deformation rate also plays a very important role on the level of viscosity reduction.

To study the role of adsorption density of the polymer on rheological properties of silica suspensions, the adsorption of polyethylene oxide (PEO) of molecular weight 7,500 onto the surface of silica particles was

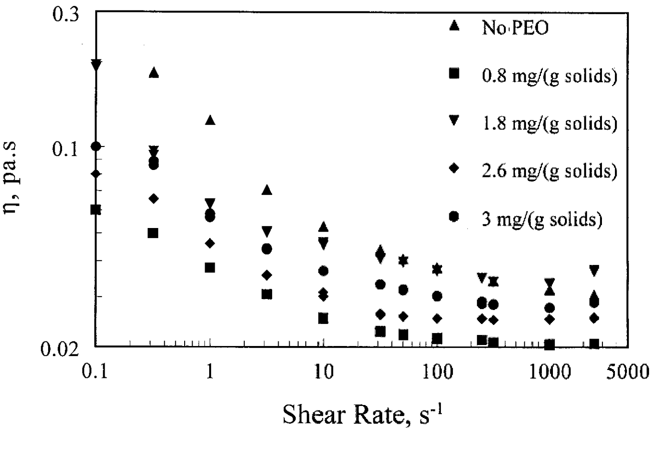

Fig. 1 Variation of viscosity with shear rate and polymer dosage for 0.86 μm size silica particles dispersed in a solution of 10^{-2} M $NaNO_3$ and PEO (MW = 7,500) at 55% volume (25 °C and pH = 9.5)

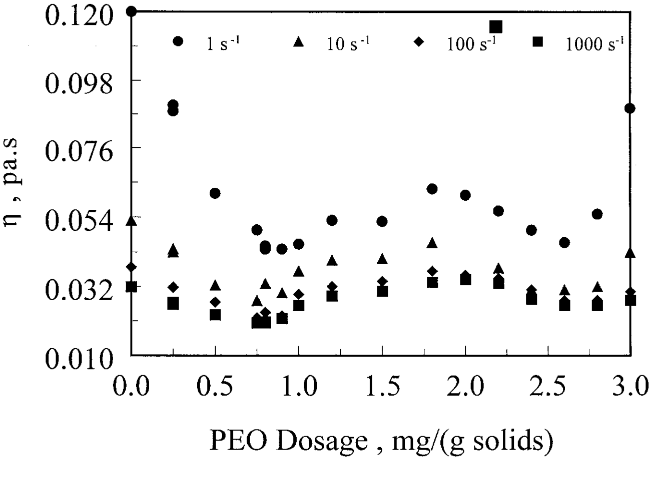

Fig. 2 Variation of viscosity with PEO concentration for 0.86 μm size silica particles dispersed in a solution of 10^{-2} M $NaNO_3$ and PEO (MW = 7,500) at 55% volume at four levels of shear rate (25 °C and pH = 9.5)

investigated. The adsorption isotherm is reported in Fig. 3 which is a composite plot for the viscosity (at 1 s^{-1}) and adsorption density of 7,500 molecular weight PEO onto 55% vol silica suspensions (0.86 μm in diameter) as a function of equilibrium concentration of the polymer in the suspending fluid. It is observed from this figure that a primary plateau is reached at an adsorption density of about 0.34 mg/m^2. Adsorption density increases with further increase in PEO concentration until nearly a second plateau is reached at an adsorption density of 0.68 mg/m^2 which corresponds to an approximate PEO dosage of 2.8 mg/(g solids). Similar behavior has been reported in the literature [36] for the adsorption of a hydroxy-terminated PEG of molecular weight 400 onto the surface of a macroporous silica gel with a mean porosity diameter of 300 nm and the particle size ranges between 40 and 100 μm. These authors observed similar behavior in their adsorption studies of low molecular weight PEO and suggested that once a critical surface concentration is reached, the affinity of the terminal hydroxy groups for the silica surface may allow the polymer molecule to partly ''stand up'', thereby allowing for the adsorption of more PEO onto the surface of the particles. Also, it is possible that the partial polydispersity of the polymer may cause this kind of behavior. It can be observed from Fig. 3 that the first minimum in viscosity corresponds to the start of first plateau in adsorption density and the second minimum in viscosity corresponds to the start of second plateau in adsorption density of the polymer on the particle surface.

The stability of colloidal particles suspended in a polymer solution is affected by both adsorption of the polymer onto the surface of the particles and also the concentration of free polymer chains in the solution. In spite of the importance of the role of free polymers on the viscosity behavior and stability of colloidal suspensions, the subject has not received considerable attention, particularly at high volume fraction of the particles. Several investigators [27, 37–42] have shown that free polymers at sufficiently high concentrations can induce flocculation in a stable suspension. Feigin and Napper [41] and Clark and Lal [43] observed that, above a critical concentration of the free polymer, stability will be imparted in the system if the concentration of the free polymer chains is further increased. In a concentrated suspension, if the spacing between the particles is less than the mean size of the polymer chains, the probability for the polymer chains entering the space between the particles is small and the fluid between the particles is essentially pure solvent. Free energy of the system will decrease as a result of the approach of colloidal particles which will cause the solvent molecules to be pushed out into the bulk medium. Once the particles have approached sufficiently close to exclude the polymer chains, closer approach occurs spontaneously causing flocculation of the particles [7].

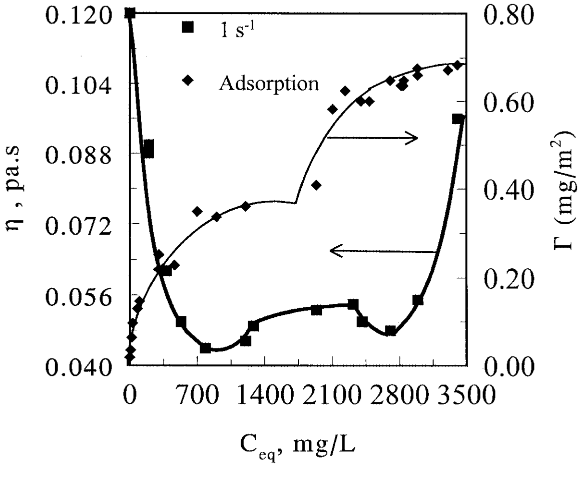

Fig. 3 Variation of viscosity (suspensions of 0.86 μm silica particles at 55% volume) and adsorption density of PEO 7,500 onto the surface of the particles with equilibrium concentration of the polymer (10^{-2} M $NaNO_3$, 25 °C, pH = 9.5)

Increase in the viscosity of silica suspensions with the adsorbed PEO molecules can be explained with changes in the concentration of the free polymer chains in the suspending media. When the first plateau in the adsorption isotherm is reached, most of the added polymer will stay in the solution increasing the concentration of the free polymer chains in the suspending media. This causes an increase in the magnitude of the depletion forces in the system which is accompanied by an increase in the viscosity of the dispersion. Above a critical concentration of the polymer, more polymer molecules will be adsorbed on the surface of the particles, increasing the magnitude of the steric repulsive forces; thus decreasing the viscosity of the suspension. The viscosity of the suspension will reach a minimum when the surface of the particles is fully covered with polymer molecules, which corresponds to the start of second plateau in adsorption isotherm. Further addition of the polymer to the system will cause an increase in the concentration of the free polymer in the suspending fluid and hence increasing the viscosity of the suspension due to increase in the magnitude of the depletion forces in the system.

Effect of polymer molecular weight

The viscosity of silica suspensions was found to vary with polymer molecular weight as indicated in Fig. 4 which is a comparison between the viscosity of suspensions of 0.86 μm silica particles stabilized with PEO of molecular weights 7,500 and 18,500, respectively. Plots in Fig. 4 represent the viscosity (at 1000 s^{-1}) as a

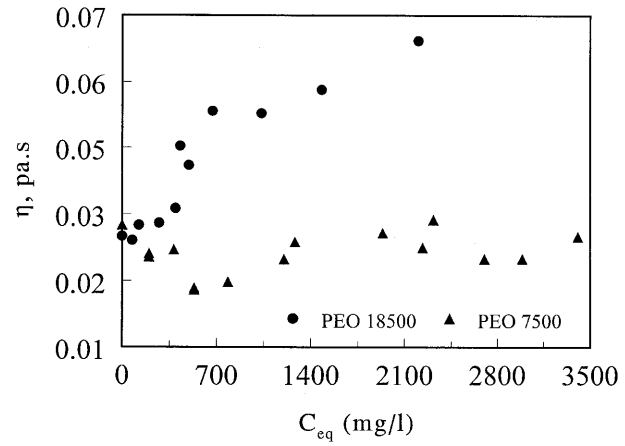

Fig. 4 Variation of viscosity with PEO molecular weight for suspensions of 0.86 μm size silica particles dispersed in a solution of 10^{-2} M $NaNO_3$ at 55% volume (suspension pH = 9.5, 1000 s^{-1}, 25 °C)

function of equilibrium concentration of the polymers in the supernatant. The viscosity response of the suspension to the equilibrium concentration of the polymer (or polymer dosage) varies with polymer molecular weight. While there is a significant decrease in the viscosity of the samples stabilized with PEO 7,500 at a critical concentration of the polymer, this behavior was not observed for the samples prepared with PEO 18,500. The viscosity of the samples decreased slightly with increasing polymer concentration and then increased monotonically as the PEO 18,500 dosage was increased. It is apparent from the rheological data that PEO 7,500 is a more effective dispersant than PEO 18,500, which can be concluded from the significant decrease in the viscosity of the suspension stabilized with PEO 7,500. We point out that the viscosity of the suspending media was determined (using glass capillary) at different polymer concentrations used in this work and indicated no significant change with polymer dosage. From the results of our earlier studies [32], it appears that the viscosity response of a suspension to polymer dosage and polymer molecular weight depends on the state of the colloidal dispersion (e.g., range of the electrostatic repulsion and stability of the system).

Role of ionic strength on polymer adsorption and viscosity

In a concentrated suspension each particle interacts with many neighbors and this occurs when the separation between the particles is comparable with the screening length. Barker and Henderson [44, 45] have developed a perturbation theory for the Helmholtz potential and its derivatives for classical fluids with spherically symmetric interaction potentials of short range. Based on their theory, it can be concluded that in an electrostatically stabilized suspension, the neighboring particles are effectively excluded from a region of radius a_{eff} (a is the radius of the core particle) around it:

$$a_{eff} = a + \frac{1}{2}\int_{2a}^{\infty}\left\{1 - \exp\left[\frac{-V_T(r)}{kT}\right]\right\}dr, \tag{12}$$

The effective volume fraction of the particles, ϕ_{eff}, which takes into account the volume of both particles and the ionic clouds around the particles, can be calculated from the following equation.

$$\phi_{eff} = \phi\left(\frac{a_{eff}}{a}\right)^3, \tag{13}$$

In sterically stabilized suspensions, the adsorbed polymer creates a coating on the surface of the particle with a non-negligible thickness and, therefore, the particles have an effective radius, a_{eff}, that is larger than the radius of the core particles. Techniques such as neutron scattering, osmometry, and glass capillary viscometery can be used to determine the thickness of the adsorbed barrier. The adsorbed layer thickness may also be estimated from the data on zeta potential in the absence and presence of polymer.

Fig. 5 represents the viscosity data for suspensions of 0.86 μm (diameter) silica particles at 55% vol (suspension pH = 9.5, 1000 s^{-1}, 25 °C) as a function of equilibrium concentration of PEO-7500 at electrolyte concentrations of 10^{-2} M and 10^{-4} M $NaNO_3$. At an electrolyte concentration of 10^{-4} M $NaNO_3$, the viscosity of the suspension decreases through the addition of polymer, reaches a minimum, and then remains almost constant over a wide range of equilibrium concentration of the polymer. Different behavior is observed for the viscosity of the system of 10^{-2} M $NaNO_3$. In this

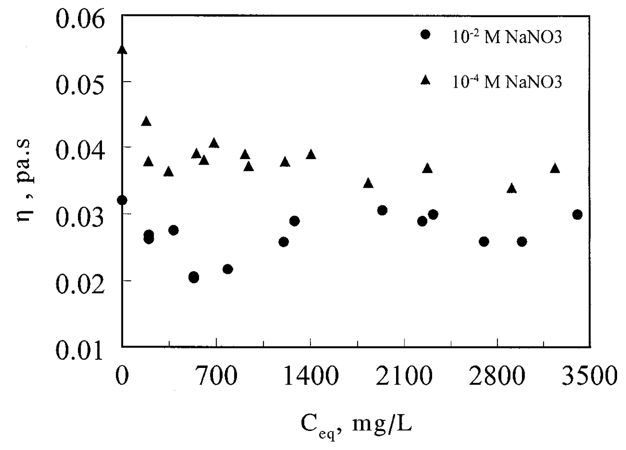

Fig. 5 Variation of viscosity of suspensions of 0.86 μm silica particles at 55% volume with equilibrium concentration of the polymer and salt concentration (1000 s^{-1}, 25 °C, pH = 9.5)

system, the viscosity decreases through the addition of polymer, reaches a minimum at a critical concentration of the polymer, increases with further increase in polymer concentration, goes through a maximum, and then decreases to a secondary minimum at a second critical concentration of the polymer used. It appears from the data that there is an increase in the viscosity of both systems with further increase in the concentration of the polymer in the system. Final increase in viscosity occurs at equilibrium concentrations of the polymer corresponding to saturation adsorption (plateau) on adsorption isotherms.

It can be observed from Fig. 5 that there is a significant decrease in the viscosity of electrostatically stabilized (without PEO) suspensions as the salt concentration is increased from 10^{-4} M $NaNO_3$ to 10^{-2} M $NaNO_3$. The effect of electrolyte concentration (range of the electrostatic repulsion) on the viscosity of electrostatically stabilized suspensions can be explained in terms of effective volume fraction of the particles. At low electrolyte concentrations, the effective volume fraction of the particles is larger due to long-range interparticle interactions. As the electrolyte concentration is increased, there will be a decrease in the effective volume fraction of the particles due to the compression of the double layers around the particles and, therefore, one may expect a decrease in the viscosity of the system. The range of the repulsive forces between the suspended particles is a decreasing function of electrolyte concentration and hence, above a critical concentration of the added salt, the van der Waals attractive forces become dominant which is accompanied by an increase in the viscosity of the suspension due to the formation of aggregates in the system. The above explanation is confirmed by experimental observations of Kaji et al. [46] and Zaman et al. [32] on the effect of electrolyte concentration on the viscosity of colloidal dispersions.

Comparison of the viscosities of the two systems at different equilibrium concentrations of the polymer indicates that the variation of viscosity with equilibrium concentration of the polymer and range of the electrostatic repulsive forces cannot be explained just in term of the effective volume fraction of the particles. The two systems do not exhibit similar trends in viscosity as the adsorption density of the polymer (or equilibrium concentration of the polymer) is increased. In the absence of polymer, the decrease in viscosity with increase in electrolyte concentration can be attributed to the decrease in the range of electrostatic repulsive forces which is accompanied by a decrease in effective volume fraction of the particles.

Fig. 6 represents the zeta potential as a function of the adsorption density of the polymer at two different salt concentrations. When a non-ionic polymer such as PEO is added to the dispersion of charge-stabilized particles, the electrical double layer around the particles and, therefore, the zeta potential may be altered due to the adsorption of polymer molecules onto the surface of the particles. The zeta potential may be influenced by the change in the adsorption characteristics of the ions due to the presence of the polymer and/or shifting the position of the shear plane away from the surface of the particles. It can be observed from Fig. 6 that over the entire range of the adsorption density of the polymer, the zeta potential values indicate a strong negative charge on the surface of the particles. Results indicate that the magnitude of the zeta potential decreases as particles are gradually covered by the polymer. The lowest value of the zeta potential for each system corresponds to the plateau value of the adsorption isotherm. Also, it can be observed that there is a significant decrease in the magnitude of the zeta potential as the salt concentration is increased which is due to the compression of the double layer around the particles with increasing salt concentration.

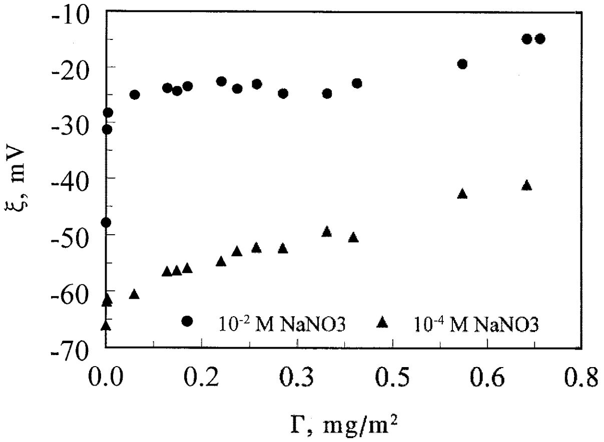

Fig. 6 Variation of zeta potential with the adsorption density of PEO MW 7,500 onto the surface of silica particles at two different salt concentrations (0.20 μm silica particles, pH = 9.5, 25 °C)

The adsorption isotherms at two different salt concentrations for SiO_2-PEO system (2% vol suspensions of silica particles of 200 nm in diameter, suspension pH = 9.5, PEO of molecular weight 7500) are shown in Fig. 7. Results given in this figure indicate that the adsorption density of the polymer for the system of 10^{-4} M $NaNO_3$ concentration is larger than the system of 10^{-2} M $NaNO_3$ concentration. Similar behavior was observed for the adsorption of PEO-7500 onto the surface of silica particles of 1.5 μm in diameter at two electrolyte concentrations. Studies performed by Cosgrove [47] on the adsorption of PPS polyelectrolyte (polystyrene sulfonate) onto the surface of polystyrene particles at different salt concentrations of 0.1 M, 0.5 M, and 1.0 M NaCl indicate an increase in the adsorption density of PPS polyelectrolyte with increasing ionic strength. It is generally believed that increasing the salt

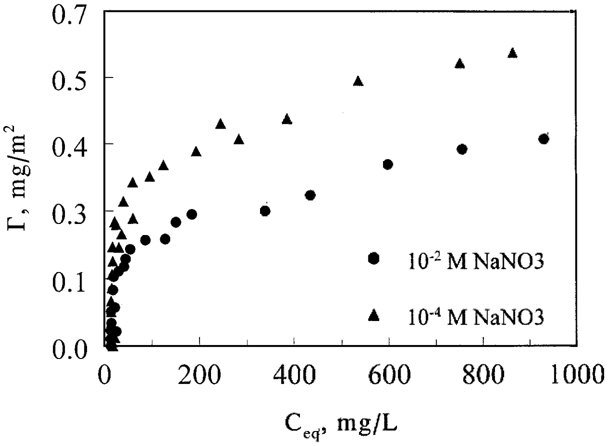

Fig. 7 Adsorption of 7,500 MW PEO onto 0.20 μm (diameter) silica particles at two different salt concentrations (pH = 9.5, 25 °C)

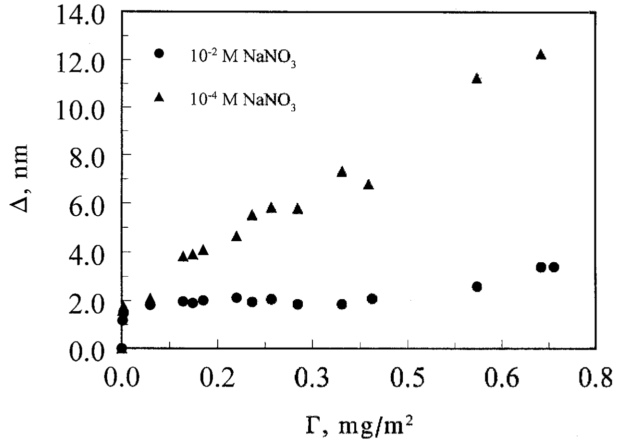

Fig. 8 Adsorbed layer thickness as a function of the adsorbed layer density of PEO on the surface of 0.20 μm silica particles suspended in solutions of 10^{-2} M $NaNO_3$ and 10^{-4} M $NaNO_3$ containing PEO 7,500 MW (pH = 9.5, 25 °C)

concentration will screen out the electrostatic repulsion between the polyelectrolyte chains and hence lead to an increase in the adsorption density of the polymer. However, the results of the current study indicate this may not be the case for neutral polymers. It may be concluded that, over the range of salt concentrations at which the suspension is stable, the tendency of polymer molecules to migrate to the surface of the particles decreases due to compression of the double layers with increasing salt concentration. This causes a decrease in the adsorption density of the polymer onto the surface of the particles.

The adsorbed layer thickness of the polymer, which determines the range of the steric barrier, was estimated at two different salt concentrations using Eq. 11 and knowing the zeta potential in the presence and absence of the polymer. The use of this equation implies that the electrokinetic potential variation is only due to the shift of the shear plane, without any charge variation in the vicinity of the surface. This was verified by measuring the pH of the suspension during the adsorption process where no pH change was detected. The adsorbed layer thickness with the adsorption density of the polymer at two salt concentrations of 10^{-2} M and 10^{-4} M $NaNO_3$ are shown in Fig. 8. There is a significant decrease in the adsorbed layer thickness as the salt concentration is increased. It can be observed that while there is a continuous increase in the adsorbed layer thickness with the adsorption density of the polymer at an electrolyte concentration of 10^{-4} M $NaNO_3$, the behavior is quiet different at the electrolyte concentration of 10^{-2} M $NaNO_3$. In the second system, three regions can be observed for the adsorbed layer thickness as a function of the adsorbed layer density. A sharp initial increase in the adsorbed layer thickness in the first region (up to 0.1 mg/m^2), a gradual increase (almost a plateau) in the second region (up to 0.4 mg/m^2), and another increase in the adsorbed layer thickness in the third region. While the adsorbed layer thickness for the system of 10^{-4} M electrolyte concentration is 12.48 nm at an adsorption density of 0.82 mg/m^2, this value is equal to 3.26 nm at an adsorption density of 0.73 mg/m^2 for the system of 10^{-2} M electrolyte concentration, indicating that the adsorbed layer is very dense in the later case. Even though one may attribute these differences to the effect of the range and magnitude of the electrostatic repulsive forces on the conformation (distribution of tails, loops, and trains) of the polymer on the surface of the particles, more research has still to be performed before a definite conclusion can be made. We would like to mention that the adsorbed layer thickness for the system of 10^{-4} M electrolyte concentration was estimated to be nearly equal to 11 nm using the viscosity data at low volume fraction of the particles obtained with a glass capillary viscometer. In addition, the adsorbed layer thickness of PEO was determined using the relationship developed by Killmann et al. [48] for the adsorption of PEO of a given molecular weight on silica. The adsorbed layer thickness was determined to be 1.86 nm and 1.17 nm for 7,500 MW PEO dosages of 2.5 mg/(g solids) and 0.4 mg/(g solids), respectively. This approach does not take into account the effect of the range of electrostatic repulsion on the adsorbed layer thickness of the polymer. The results of the current study indicate that, in sterically stabilized suspensions, the adsorbed layer thickness decreases with increasing electrolyte concentration. Therefore, it is expected that sterically stabilized systems exhibit a higher fluidity at higher electrolyte concentrations (over the range of ionic strength at which the system is electrostatically stable) as is the case in this study. The unusual viscosity behavior at higher salt concentrations may be attributed to the effect of the range of electrostatic repulsive force on the conformation of the polymer. Change in electrolyte concentration may affect the distribution of tails, loops, and trains of the polymer on the surface of the particles depending upon the equilibrium concentration of the polymer. As a result of the change in conformation of the polymer with electrolyte concentration, there may be a significant change in the viscosity of the system. Results indicate that controlling particle size, volume fraction of the particles, and thickness of the adsorbed layer can control the viscosity of sterically stabilized suspensions.

Summary and Conclusions

In this paper, a systematic study of the effect of adsorption of non-ionic PEO onto the surface of silica particles on electrokinetic and rheological properties of aqueous silica suspensions (at 25 °C) has been described. When polymers are added to electrostatically stabilized suspensions, the range of the electrostatic repulsion between the suspended particles affects not only the adsorption density of the polymer, but more significantly also the adsorbed layer thickness which affects the viscosity behavior of stable systems at different salt concentrations. While, at low salt concentration, the adsorbed layer density of the polymer increases monotonically until a plateau is reached, it appears from the data that for systems of shorter-range electrostatic repulsive forces, there is a primary plateau in the adsorption isotherm before the final plateau is reached. This is reflected in the viscosity behavior of such a system as the viscosity of the suspension goes through a minimum with addition of polymer to the system, increases with further increase in polymer dosage, and then goes through a second minimum at higher polymer concentrations. The first minimum in viscosity corresponds to the start of first plateau in adsorption density and the second minimum in viscosity corresponds to the start of second plateau in adsorption density of the polymer on the particle surface. Results indicate that not only the adsorbed layer thickness but also the concentration of free polymer in the suspending media play a significant role on the viscosity of the system. When a plateau in the adsorption isotherm is reached, most of the added polymer will stay in the solution increasing the concentration of the free polymer chains in the suspending media; thus increasing the magnitude of the depletion forces which is accompanied by an increase in the viscosity of the dispersion.

The adsorbed layer thickness was estimated from the values of the zeta potential in the presence and absence of the polymer at electrolyte concentrations of 10^{-2} M and 10^{-4} M $NaNO_3$ and it was found that there is a significant reduction in the adsorbed layer thickness as the salt concentration is increased. Comparison of the viscosity of silica suspensions at two salt concentrations indicates that, in addition to the adsorbed layer density and range of the electrostatic repulsive forces, the conformation of the polymer on the surface of the particles probably has a significant role on the viscosity of the system. However, more investigation has to be performed to clarify the role of the conformation of the polymer onto the surface of the particles on the viscosity of sterically stabilized colloidal dispersions.

Results of this work provide useful information on the roles of electrostatic, steric, and depletion forces on suspension properties that can be applied to develop robust dispersant schemes for engineered slurries.

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References

1. Jimenez J, Rajagopalan R (1998) The European Physical Journal B 5:237–243
2. Jimenez J, Rajagopalan R (1998) Langmuir 14:2598–2601
3. Russel WB, Saville DA, Schowalter WR (1991) Colloidal Dispersions, Cambridge University Press, New York
4. Persello J, Magnin A, Chang J, Piau JM, Cabane B (1994) J Rheol 38(6):1845–1870
5. Aksay IA (1984) In: Advances in Ceramics, vol. 9, Forming of Ceramics. Mangels IA, Messing GL (eds), American Ceramic Society, Westerville, OH, pp 94–104
6. Lange FF (1989) J Am Ceram Soc 72:3–15
7. Napper DH (1983) Polymeric Stabilization of Colloidal Dispersions, Academic Press, Orlando
8. Derjaguin BV, Landau LD, (1941) Acta Physicochim USSR 14:633–662
9. London F (1937) Trans Faraday Soc 33: 8
10. Hamaker HC (1937) Physica 4:1058–1072
11. Derjaguin BV Rabinovich YaI, Churaev NV (1982) Adv Colloid and Interface Sci 16:63
12. Ohshima H, Healy TW, White LR (1982) J Coll Interf Sci 89(2):484–493
13. Derjaguin BV, Churaev NV, Muller VM (1985) Surface Forces, E.D. Shchukin, Moscow
14. Russel WB (1978) J Fluid Mech 85:209–232
15. Russel WB (1980) J Rheol 24:287–317
16. Gadala-Maria F, Acrivos A (1980) J Rheol 24:799–814

17. Napper DH (1977) J Coll Interf Sci 58(2):390–407
18. Napper DH (1984) In: The Effect of Polymers on Dispersion Properties, Tadros TF (ed), Academic Press, London, pp 199–206
19. Tadros TF (1987) In: Solid/Liquid Dispersions, Tadros TF (ed), Academic Press, London, pp 1–16
20. Flory PJ (1953) Principles of Polymer Chemistry. Ithaca Press, New York
21. Van De Ven TGM (1989) Colloidal Hydrodynamics. Academic Press, London
22. Croucher MD Milkie TH (1982) In: The Effect of Polymers on Dispersion Properties, Tadros TF (ed), Academic Press, London, pp 101–124
23. Vincent B (1974) Adv. Colloid and Interface Sci 4: 193
24. Sonntag H, Ehmke B, Miller R, Knapschinsky L (1984) In: The Effect of Polymers on Dispersion Properties, Tadros TF (ed), Academic Press, London, pp 207–219
25. Liu SF, Lafuma F, Audebert R (1994) Colloid Polym Sci 272(2):196–203
26. Prestidge C, Tadros, TF (1988) Colloids and Surfaces 31:325–346
27. Kawaguchi M, Mizutani A, Matsushita Y, Kato T (1997) Langmuir 13(23):6339–6341
28. Kawaguchi M, Ryo Y, Hada T (1991) Langmuir 7(7):1340–1343
29. Kawaguchi M, Kimura Y, Tanahashi T, Takeoka J, Kato T, Suzuki Jun-ichi, Funahashi S (1995) Langmuir 11(2):563–567
30. Otsubo Y (1990) Langmuir 6: 114–118
31. Otsubo Y (1992) J Colloid Interface Sci 153:584–586
32. Zaman AA, Moudgil BM, Fricke AL, El-Shall H (1996) J Rheol 40(6):1191–1210
33. Van Der Werff JC, De Kruif CG (1989) J Rheol 33(3):421–454
34. Hunter RJ (1981) Zeta Potential in Colloid Science. Academic Press, New York
35. Koopal LK, Lyklema J (1975) Faraday Discuss Chem Soc 59:230
36. Trens P, Denoyel R (1993) Langmuir 9:519–522
37. Asakura S, Oosawa F (1958) J Polym Sci 33:183
38. Vincent B (1987) In: Solid Liquid Dispersions, Tadros TF (ed), Academic Press, London, pp 149–161
39. Vincent B, Clarke J, Barnett KG (1986) Colloids and Surfaces 17:51–65
40. Vincent B, Luckham PF, Waite FA (1980) J Coll Interf Sci 73:508–521
41. Feigin RI, Napper DH (1980) J Coll Interf Sci 74:567
42. Feigin RI, Napper DH (1980) J Coll Interf Sci 75:525
43. Clark AT, Lal M (1981) J Chem Soc Faraday Trans II 77:981–996
44. Barker JA, Henderson ID (1967) J Chem Physics 47:2856–2861
45. Barker JA, Henderson ID (1967) J Chem. Physics 47:4714–4721
46. Kaji R, Muranaka Y, Miyadera H, Hishinuma Y (1987) AIChE J 33(1):11–18
47. Cosgrove T (1987) In: Solid Liquid Dispersions, Tadros TF (ed), Academic Press, London, pp 149–161
48. Killmann E, Wild T, Gutling N, Maier H (1986) Colloids and Surfaces 18:241–259