Adsorption of Poly (ethylene oxide) Onto Silica at Different Solids Loadings

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Abstract

The adsorption of poly (ethylene oxide) (PEO) of 7,500 MW, a hydrogen bonding polymer, onto the surface of monodisperse colloidal silica particles was investigated as a function of volume fraction of solids. Adsorption studies revealed the presence of two plateaus, which was attributed to a change in conformation from a flat, "pancake" type, to a more elongated "brush" type conformation of the adsorbed polymer, where the terminal hydroxyl groups remained bound to the silica surface. Adsorption studies also revealed that, within the concentration range studied, there was no effect upon PEO adsorption as a function of volume fraction.

Introduction

Dispersion and stabilization of particles is of fundamental importance in areas such as ceramic processing, formulation of inks and paints, cosmetics, the food industry, pharmaceuticals, and slurry transport. In order to stabilize particulate suspensions, polymers are often used as dispersing agents. Examples include the use of polyacrylic acid (PAA) to stabilize suspensions of alumina¹ and titania², and poly (ethylene oxide) (PEO) to disperse polystyrene latex³ and silica⁴ particles. Such systems are stabilized through steric barriers as a result of polymer adsorption⁵.

As industry strives towards improved products, there is a growing need to operate at ever increasing solids loadings. This is exemplified by the direct casting methods used in the ceramics industry, where increasing solids loadings while maintaining relatively low slurry viscosities, is providing a more cost effective means of producing increasingly complex objects with low structural defects, high uniformity and good mechanical properties⁶.

The challenge, therefore, is to maintain the stability of highly concentrated particulate slurries by improving the effectiveness and efficiency of polymers used as dispersants. The ability of a polymer to stabilize a given particulate suspension is directly related to the level of surface coverage, conformation and orientation of the adsorbed polymer on the particulate surface, as well as polymer molecular weight. The effect of increasing solids loadings upon these parameters, however, is not well known. The adsorption of poly (ethylene oxide) onto colloidal silica spheres, used as a model system, was therefore studied as a function of solids loading in order to gain an understanding of the pertinent polymer properties (such as adsorption density, conformation, etc.) which ultimately control the stability and viscosity of suspensions.

Experimental Section

Materials. All samples used in this investigation were prepared in an electrolyte solution of 0.01 M NaNO₃ containing polyethylene oxide of different concentrations. Ultra-pure water (Millipore) of specific conductivity less than 1 μS/cm⁴ was used to prepare the solutions and Fisher brand NaOH was used to adjust the pH of the samples to the desired value. All reagents were of ACS grade and obtained from Fisher Scientific Co.

Silica powder of 99.9% purity was used in this study and was obtained from Geltech, Inc. This sample was used as received and had a nominal diameter of 0.5 μm, as stated by the manufacturer. Particle size analysis was performed using a Coulter LS230 laser.
Adsorption studies. Figure 1 is an SEM image of the 0.5 μm sample which indicates that the powder is monosized and the particles are spherical in shape. The experimentally measured volume average (d_{50}) particle diameter of the powder was found to be 0.6 μm. Henceforth, all particle diameters referred to in this text are the experimental, rather than the nominal values. Powder density was measured using a Quantachrome Ultrapycnometer 1000 and was found to be 2.1 g cm^{-3}. The BET nitrogen specific surface area of the silica powder was measured with a Quantachrome Nova 1200 and found to be 6.22 m^{2}·g^{-1}.

Poly (ethylene oxide) (PEO) of molecular weight 7,500 was procured from Polysciences Inc. and used as received. Polymer stock solutions were prepared by mixing 4.0 g of polymer with 500 cm^{3} of 0.01M NaNO_{3} solution and stirring for 16 hours using a magnetic stirrer in order to achieve complete dissolution. The solutions were also covered in order to avoid decomposition of the polymer due to exposure from ultraviolet radiation. The stock solutions were then diluted to the desired concentrations using 0.01M NaNO_{3}.

Adsorption studies. All adsorption experiments were conducted at pH 9.5 using suspensions with a total volume of 10 cm^{3} contained in 30 cm^{3} polyethylene screw capped bottles. Depending upon the volume fraction of silica and the polymer dosage, the PEO stock solution was diluted with 0.01M NaNO_{3} to the desired concentration and used as the suspending fluid. The required mass of dry silica was then slowly added to the PEO solution while mixing the sample by shaking and vibration. After adding all silica particles, the pH of the suspension was adjusted to 9.5 using 1M NaOH. Adjustment of pH was performed in one direction only.

After addition of silica, the suspensions were vigorously shaken by hand and the pH checked and readjusted, after which they were treated with ultrasonics in order to break up any aggregates, using a Cole-Parmer Model CV-26 water jacketed cup horn probe with Model CPX-600 Ultrasonic Processor set at 500 watts power. The suspensions were then agitated using a Burrell Model 75 Wrist Shaker for a period of 20-24 hours in order for equilibrium to be reached. During equilibration, the suspensions were treated with ultrasonics at regular intervals (for at least 30 minutes) to break up any aggregates which may have formed, and the pH checked and readjusted if required. After equilibration, the samples were centrifuged for 10 minutes at 15,000 rpm and supernatant was carefully withdrawn. The supernatant was then allowed to sit overnight in a refrigerator in order to allow the settling of any remaining particles, as tests had shown that small numbers of particles could still be present after the centrifugation process, the presence of which could adversely affect subsequent analysis.

Residual PEO concentration was measured directly in terms of organic carbon content using a Tekmar-Dohrmann Phoenix 8000 Total Organic Carbon (TOC) analyzer. The TOC analyzer was calibrated using potassium hydrogen phthalate standards of known carbon concentration to give a linear primary calibration curve. Solutions with known masses of 7,500 MW PEO were also analyzed, and within the concentration range studied (0.1-20 mg·L^{-1} carbon), a secondary linear calibration curve was obtained. The multiplication factor to convert from units of mg·L^{-1} organic carbon, to mg·L^{-1} of PEO, was found to match the theoretical value of 1.83 (determined from the amount of carbon in the PEO repeating unit). TOC analyses were performed in triplicate and had an experimental error of not more than ±5%.

Results

Adsorption studies of 7,500 MW PEO were performed using silica spheres at different volume fractions. The adsorption isotherm for a suspension of 50 %vol of 0.6 μm silica particles is illustrated in Figure 2. This shows that polymer adsorption steadily increases until a plateau is reached at approximately 0.34 mg·m^{-2} surface coverage. However, as the equilibrium solution concentration increases above approximately 6,000 mg·L^{-1}, more polymer adsorbs until a second plateau is reached at 1.20 mg·m^{-2} surface coverage. It should be noted that the initial portion of Figure 2 should not be taken as being indicative of a
Typical high affinity type isotherm, generally associated with polymer adsorption, due to the large equilibrium concentration (Ceq) scale used. The Figure 2 inset shows the initial portion of the isotherm has a rounded (as opposed to high affinity) profile, and possibly is a consequence of polydispersity7,8 within the PEO sample used for this study.

Figure 3 shows the adsorption of 7,500 MW PEO on 0.6 μm silica spheres as a function of volume fraction for PEO doses of 2.5 mg·(g solids)-1 and 1.0 mg·(g solids)-1, respectively. Polymer adsorption rises steadily with increasing silica volume fraction until a plateau is reached at approximately 20% solids for both polymer doses used. In Figure 4, the adsorption of PEO onto silica at 2 %vol fraction is shown. As in the Figure 2 inset, polymer adsorption increases until a pseudo plateau is reached at approximately 0.34 mg·m⁻² surface coverage.

**Discussion**

**Adsorption Behavior.** The adsorption of 7,500 MW PEO on 0.6 μm silica as a function of solids volume fraction was studied due to the importance of understanding how increasing the solids loading would impact upon adsorption phenomena. Figure 2 shows the adsorption of 7,500 MW PEO onto 50 %vol SiO₂. It was observed that adsorption increased until a plateau was obtained at approximately 0.34 mg·m⁻², which corresponds to an approximate PEO dose of 1.4 mg·(g solids)-1 (see Figure 2 inset).

The parking area occupied by one polymer molecule, S_{exp}, at the plateau values was calculated from the adsorption isotherm using the formula:\(^{9}\)

\[ S_{\text{exp}} = \frac{1}{\Gamma_{\text{max}}} \times 10^{18} \frac{N_{A}}{R_{g}} \]  

where \(\Gamma_{\text{max}}\) is the amount adsorbed at the plateau (mol·m⁻²; converted from units of mg·m⁻² by dividing by polymer MW), 10^{18} is a conversion factor for m² to nm², and \(N_{A}\) is Avogadro’s number \((6.02 \times 10^{23})\). Values of \(S_{\text{exp}}\) are summarized in Table 1. Additionally, the theoretical parking area, S_{theory}, for unperturbed polymer coils was calculated using the radius of gyration, R_g, for 7,500 MW PEO, which was determined from the intrinsic viscosity data published earlier by Bailey and Koleske.\(^{10}\) These values are also summarized in Table 1.

Figure 2 shows that the first plateau is reached at a surface coverage of 0.34 mg·m⁻². This value is in good agreement with the earlier work of Killmann et al,\(^{11}\) who obtained a plateau value of 0.37 mg·m⁻² for the adsorption of 6,000 MW PEO on Stöber silica. Comparison of the values of \(S_{\text{exp}}\) and \(S_{\text{theory}}\) in Table 1 reveals that for the first adsorption plateau, the experimentally obtained parking area is some 20% less than the theoretical value derived from \(R_{g}\) Killmann et al,\(^{11}\).
observed that at monolayer capacity, there was a marked increase in the hydrodynamic layer thickness of PEO (of various molecular weights) adsorbed onto Stöber silica, citing this as evidence for the polymer undergoing elongation or "stretching" perpendicular to the surface. Such behavior is in agreement with the polymer adsorption theory of Scheutjens and Fleer, where the conformation of adsorbed polymers is strongly influenced by the amount adsorbed and the surface coverage, i.e., competition for adsorption sites between polymer segments increases with increasing coverage. This suggests that as the amount of polymer covering the silica surface approaches the (pseudo) monolayer capacity (or first plateau), the adsorbed PEO molecules change from a flat conformation to a somewhat more elongated or "brush type" conformation.

Some idea of the conformation of the adsorbed polymer can also be obtained from examining values of adsorbed layer thickness (d), and comparing them to those for unperturbed coils in the bulk. For an unperturbed polymer coil adsorbing on a surface, the layer thickness would be two times the radius of gyration (2Rg). From the work of Killmann et al., the following equation (derived from photon correlation spectrometry measurements) can be used to determine the PEO layer thickness on silica for a given molecular weight (M):

\[ d = 0.018 M^{0.52} \] (2)

Using Equation (2), one obtains a layer thickness value of 1.86 nm for the present study. In comparison, the corresponding value for an unperturbed coil would be equal to 7.62 nm, or twice the value of Rg (see Table 1). This therefore suggests that at the first plateau, the adsorbed polymer is in a flat, or "pancake" type conformation, and is significantly more coiled compared to the free polymer in the bulk. From the previous discussion, however, the adsorbed polymer also undergoes some degree of elongation perpendicular to the surface.

The various works of Killmann et al., however, did not explore the adsorption region beyond the first plateau. The present study shows that after the first plateau was reached, more PEO adsorption occurred when the equilibrium polymer concentration increased above approximately 6,000 mg L⁻¹ (see Figure 2). This resulted in the observation of a second plateau region at 1.20 mg m⁻² surface coverage, as illustrated in Figure 2. To the best of the authors' knowledge, the only other occurrences in the literature of a "two plateau" adsorption isotherm for PEO on silica surfaces, was in the recent study by Trens and Denoyel. These researchers examined the effect that methyl and hydroxyl end groups on PEO of various molecular weights, had upon their adsorption to fumed silica. They observed similar behavior for the adsorption of hydroxyl terminated (as used in the present study), low molecular weight PEO on fumed silica at high equilibrium concentration. From their adsorption data, these authors showed that the affinity of terminal hydroxyl groups was greater than that of the ethoxy groups, and thus argued that as more polymer adsorbed onto the surface after the first plateau was reached, the adsorbed polymer molecules would partly "stand up", fixed by one or both ends, thereby allowing for the adsorption of more PEO. This change in conformation is illustrated in Figure 5. Although they only considered the case of a polymer with one surface-active terminal group and make no mention of "two plateau" adsorption isotherms as is observed in the present study, this conformational change is also consistent with the work of Fleer et al. They state that a polymer containing both a terminal group and chain segments which have an affinity for the surface, will adsorb in a "pancake type" conformation at low surface coverages, and then change to a "brush type" conformation, attached to the surface by the terminal group, as surface coverage increases.

| Plateau | \( R_{\text{max}} \) (mg m⁻²) | \( S_{\text{dep}} \) (nm²) | \( R_g \) (nm) | \( S_{\text{theory}} \) (nm²) |
|--------|---------------------|-----------------|-------------|---------------------|
| first  | 0.34                | 36.6            | 3.81        | 45.6                |
| second | 1.20                | 10.4            | –           | –                   |

Table 1: \( R_{\text{max}} \) Radius of Gyration \( R_g \) and Experimental and Theoretical Parking Areas \( S_{\text{dep}} \), \( S_{\text{theory}} \) for 7,500 MW PEO on 50 vol Fraction of 0.60 μm Silica Particles.
Examination of the values of $\Gamma_{\text{max}}$ and $S_{\text{exp}}$ for the second plateau in Table 1 reveals the adsorbed PEO molecules occupy approximately three-and-a-half times less surface area in comparison to that occupied at the first plateau (10 nm$^2$ compared to 37 nm$^2$). This suggests that PEO undergoes significantly more elongation at surface concentrations beyond the first plateau.

**Effect of Solids.** From the inset of Figure 2, it can be seen that a PEO dose of 2.0 mg·(g solids)$^{-1}$ was sufficient for the first plateau to be reached at 50 %vol of silica. A PEO dose of 2.5 mg·(g solids)$^{-1}$ was therefore used for other volume fractions of silica, under the reasonable assumption that the plateau would also be reached in all cases. Additionally, a PEO dose of 1.0 mg·(g solids)$^{-1}$ was also used in order to be able to observe any effect of volume fraction in the more sensitive “knee” region of the adsorption isotherm. The adsorption as a function of volume fraction at the two PEO doses is illustrated in Figure 3, which shows that the adsorption density increases as a function of volume fraction until a plateau is reached at approximately 20 %vol. Figure 4, however, shows the adsorption isotherm of 7,500 MW PEO on 2 %vol SiO$_2$. From this diagram, it is apparent that a PEO dosage of 2.5 mg·(g solids)$^{-1}$ is insufficient for the (pseudo) plateau to be reached due to a very low number of polymer molecules being present in the system. Indeed, when the (first) plateau value is used in Figure 3 (dashed line), it is apparent that there is no effect of volume fraction on the adsorption of PEO. This is an important observation, as previous experimental protocols for measuring the adsorption of polymers have been the same, in the past, irrespective of the solids loading of the suspension. This approach is valid for fixed (or constant) solids loadings. However, from the present experimental findings, in order to obtain equivalent surface coverages under different solids loading conditions, it is imperative to scale from one volume fraction to another with respect to the residual concentration as opposed to initial polymer dosage, as is mostly practiced. This is an important consideration for many industrial processes where the solids loadings can vary, such as flocculation and dispersion, as practiced in the ceramics and minerals processing industries.

**Conclusions**

The adsorption of PEO onto colloidal silica (SiO$_2$) spheres at different volume fractions was found to show two plateau values, the first of which was found to be consistent with those observed in previous studies employing similar polymer molecular weights (~7,500 MW). The second plateau was observed for higher equilibrium concentration values and was attributed to a change in the conformation of the adsorbed polymer molecules. The experimental evidence suggested that at low surface coverages, PEO was adsorbed in a flat, “pancake” type conformation, before changing orientation to a more elongated, “brush like” conformation at higher equilibrium concentrations, where both terminal hydroxyl groups are still attached to the silica surface.

Adsorption density measurements as a function of the solids loading studied in this work (2 %vol to 50 %vol) showed that there was no effect of volume fraction upon PEO adsorption. Rather, it was demonstrated that in order to obtain equivalent surface coverages at different volume fractions, scaling from one volume fraction to another should be done with respect to the equilibrium ($C_{eq}$), as opposed to the initial ($C_0$), polymer solution concentration.

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