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Interaction Forces Between Silica Surfaces in Aqueous Solutions of Poly(Ethylene Oxide)s

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An understanding of forces responsible for the stability of dispersions of colloidal particles when interacting with each other in aqueous solutions is of great interest academically and industrially. When water-soluble polymers are adsorbed onto colloidal particles, various effects on the stability of their suspensions can be expected ranging from steric stabilization to bridging flocculation. The possibility of detailed characterization of such systems using direct measurements of interaction forces between particles can help in further improvement of existing technologies of solid-liquid separation.

An atomic force microscope (AFM) colloidal probe was used to measure the interaction forces between a silica sphere and a silica substrate in the presence of water-soluble polymers. Poly(ethylene oxide) (PEO) with three different molecular weights (7,000, 43,000, and 63,000), each with a very narrow molecular weight distribution, were used in this study. The interaction forces measured with the AFM over an extended time scale are discussed in terms of the adsorption kinetics measured through in-situ FTIR/IRS measurements.

INTRODUCTION

Polymers can be used as dispersants or flocculants either to stabilize or aggregate particulate suspensions (Israelachvili, 1991). This is of great importance in many industrial areas such as slip casting, filler preparation (Drelich and Miller, 1995), cosmetics (Gans, 1990), paints and inks (Schroeder, 1998), oil production, and water purification. Considering the complexity of the interactions between polymer-covered surfaces and the technological importance for the control of colloidal suspension stability, these interactions have been the subject of many studies (Klein et al., 1986, 1984; Wong et al., 1992; Biggs, 1995, Milling, 1996; Braithwaite et al., 1996). Different techniques

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such as photon correlation spectrometry (Cohen Stuart et al., 1984), microcalorimetry (Korn et al., 1980), and infrared spectroscopy (Eisenlauer et al., 1980) have been used to characterize polymer adsorption in general.

In addition, a number of tools have been developed to measure directly the interaction forces between surfaces. The surface force apparatus (SFA) first introduced by Tabor and Winterton (Tabor, 1969) and developed further by Israelachvili and co-workers (Israelachvili, 1973; Israelachvili and Adams, 1978) has been used with good success. However, the SFA technique can only be applied to a limited number of surfaces (mainly mica) because of its operating principles. More recently, the use of the atomic force microscope (AFM) (Binnig et al., 1986) for measuring inter-particle forces was demonstrated by Ducker et al. (1991). Since then the AFM has become a popular tool for studying the interactions between surfaces (Parsegian et al., 1996; Luckham, 1996; Butt et al., 1995). When a colloidal particle is attached to an AFM tip, the force between this "colloidal probe" and a macroscopic surface can be measured as a function of separation distance. With the AFM, it is possible to investigate any surface, including particulate and fibrous materials.

Poly(ethylene oxide) (PEO) is an uncharged homopolymer which has been successfully used as a dispersant for latex (Cowell and Vincent, 1983) and flocculant for clays. The dispersing or flocculating effect of PEO depends on its conformation at the surface. Many parameters such as surface charge density, surface chemistry, electrolyte concentration, molar mass and adsorption time influence the adsorption of the polymer and its conformation. PEOs are available in a wide molecular weight range with narrow molecular weight distributions. Its adsorption behavior on silica has been studied extensively (Kawaguchi et al., 1984; Killman et al., 1985; van der Beek and Cohen Stuart, 1988; Dijt et al., 1990, 1992; Scheutjens et al., 1986; Mathur and Moudgil, 1997). The interaction forces between PEO covered mica surfaces in 0.1 M KNO_3 were studied by Klein and Luckham (Klein et al., 1986, 1984) using the SFA. At full coverage of polymer the interaction was repulsive at all separations and could quantitatively be explained by scaling theory for the interactions between adsorbed polymers (de Gennes, 1982, 1987). It was found that the range of interaction scaled with the molecular weight of the adsorbed polymer and commenced at separation distances in the range of 5–6 times the radii of gyration (R_g) of the polymer in solution.

In the present work we used the AFM colloidal probe technique, mentioned earlier, to measure the interaction forces between a silica sphere and a silica flat surface in different PEO solutions for different times of adsorption. Three different PEO solutions of molecular weights 7,000, 43,000, and 630,000 were studied. The approaching and the retracting parts of the force curves were monitored over extended periods of time, up to 24 hours, for any changes in the interaction forces. The measurements reported here were recorded at a scan rate of 1 Hz, which for a scan size of 500 nm, means the surfaces are driven together at a rate of $1 \mu\text{m s}^{-1}$, which roughly corresponds to the Brownian collisions in colloidal suspensions. Hence, the forces measured can be considered representative of the interaction between colloidal particles in solution. The changes in the force curves over time are compared with the adsorption kinetics measured by the FTIR/IRS technique.

EXPERIMENTAL

PEO polymers, with molecular weights of 7, 43, and 630 kg mol^{-1} (hereafter referred as 7k, 43k, and 630k, respectively) were obtained from Scientific Polymer Products, Inc. (Ontario, NY). The polymers were of very narrow molecular weight distribution ($M_w/M_n \sim 1$). Some characteristic properties of the polymers used are summarized in Table 1.

TABLE 1 Characteristics of the PEO molecules used in this study

PEO Sample	Molecular Weight (kg/mol)	Polydispersity (Mw/Mn)	Radius of Gyration (nm)
7k	7,000	1.01	2.4
43k	43,500	1.10	7.8
630k	630,000	1.05	36

Potassium nitrate (KNO_3) was obtained from Sigma Chemicals (St. Louis, MO). Polymer solutions, 0.05% by weight, were prepared as aqueous solutions with 0.25 M KNO_3 as background electrolyte for ionic strength control. Solutions were prepared a day before the experiments and allowed to stay overnight for equilibration. Deionized water (18 m Ω) from a Milli-Q system (Millipore) was used for preparing the solutions. Colloidal silica spheres (4.3 μm diameter) were from Bangs Labs, and the fused silica substrate was obtained from Harrick Scientific.

AFM Force Measurements

Force measurements were conducted using a Nanoscope IIIA atomic force microscope (Digital Instruments, Inc., Santa Barbara, CA). The colloid probe technique of measuring forces with the AFM has been described extensively elsewhere (Ducker et al., 1992) and will not be discussed here.

Standard silicon nitride cantilevers (Digital Instruments, Inc., Santa Barbara, CA) were used for all the force measurements. The spring constant for the cantilevers was reported to be 0.12 Nm^{-1} and the same value was used to convert the force versus deflection curves into force versus separation curves.

The colloidal silica spheres were mounted on the tipless AFM cantilevers using a speed bonder and activator (Loctite Corporation) by means of a micromanipulator and a CCD camera/monitor system. The cantilevers with silica spheres and the silica substrates were cleaned in Argon plasma cleaner just prior to the experiments.

After assembling the cantilever and wafer in the fluid cell, the fluid cell was filled with electrolyte solution and the repulsive silica-silica interaction was measured to check for the cleanliness of surfaces. Subsequently, polymer solution was pumped into the cell and measurements were taken at the stipulated times. All the measurements reported here were done in situ, i.e., in the presence of the polymer solutions. The experiments were done at the natural pH of the solution.

FTIR/IRS Adsorption Density Measurements

FTIR transmission spectra of PEO solutions were collected as a function of concentration in order to calculate the absorptivity of the PEO solution Beer's law. The FT-IR internal reflection experiments were done as a function of time using the closed cylindrical cell with a cylindrical silicon IRE and the Bio-Rad 6000 FTS spectrometer. The areas under the CH_2 peaks were integrated and the surface excess was calculated, according to the FTIR/IRS adsorption density equation, which was first derived by Sperline et al. (1987) and later developed by Miller and co-workers (Kellar et al., 1989, 1990; Free and Miller, 1996)

$$A = N\epsilon b_{\text{eff}}C + N\epsilon \frac{d_e}{d_p} 1000 \Gamma$$

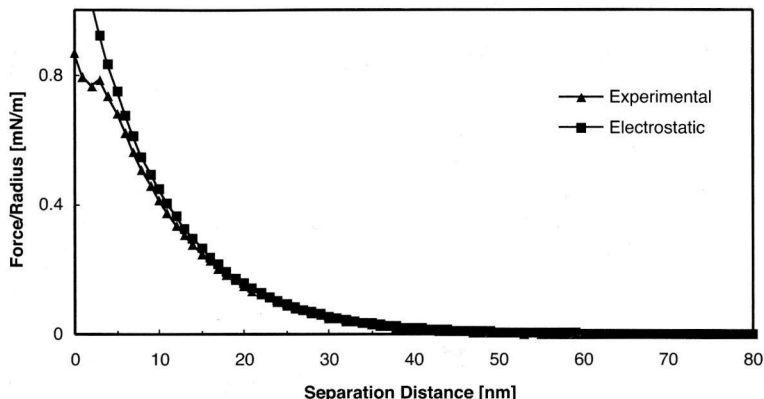


FIGURE 1 Interaction force between two silica surfaces in the presence of 10^{-3} M KCl solution. The experimental data is fitted to a theoretical electrostatic force predicted according to the DLVO theory.

Where: A is integrated absorbance (cm^{-1}), ϵ is absorptivity ($\text{liter}/\text{mole}\cdot\text{cm}^2$), C is concentration (mole/liter), N is number of reflections, d_e is effective path length (cm), d_p is effective depth of penetration (cm) and Γ is the surface excess (moles/cm^2).

RESULTS

Figure 1 shows the interaction force curve between silica surfaces in the presence of 1×10^{-3} M KCl solution. The measured force curve shows complete repulsive behavior both on approach and on retraction. At larger separation distances the force decays exponentially, characteristic of an electrostatic double layer decay length. The results are in nice agreement with the Derjaguin/Landau/Verwey/Overbeek (DLVO) theory for electrical double layer repulsive interactions between silica surfaces, thereby standing evidence that the surfaces are clean. The theoretical curves shown in the figure were calculated by fitting the experimental data according to the Poisson Boltzmann equation assuming constant potential.

The interaction forces between silica surfaces in the presence of PEO solutions, with different molecular weights, are presented in Figures 2–4. The interaction forces are presented for three different adsorption times—5 minutes, 60 minutes and 24 hours. In each case the approaching part and the retracting part of the force curves are presented separately. The approach curve represents the electrostatic or steric forces experienced by the surfaces as they approach each other, whereas, the retraction curve gives an indication of the adhesion forces acting between the surfaces. As mentioned earlier, each force curve presented here is an average of 30 observations taken at different places on the flat silica surface.

Interaction forces between the silica surfaces in the presence of 7k molecular weight PEO solution are shown in Figure 2. Three different curves for adsorption times of 5 minutes, 60 minutes and 24 hours are presented. The interaction forces did not show any changes between 5 and 60 minutes but were significantly different for 24 hours. In the approaching part of the force curve the magnitude and range of attraction were almost identical for adsorption times of 5 and 60 minutes. However, the attraction decreased significantly for forces measured after 24 hours. The retracting force curves

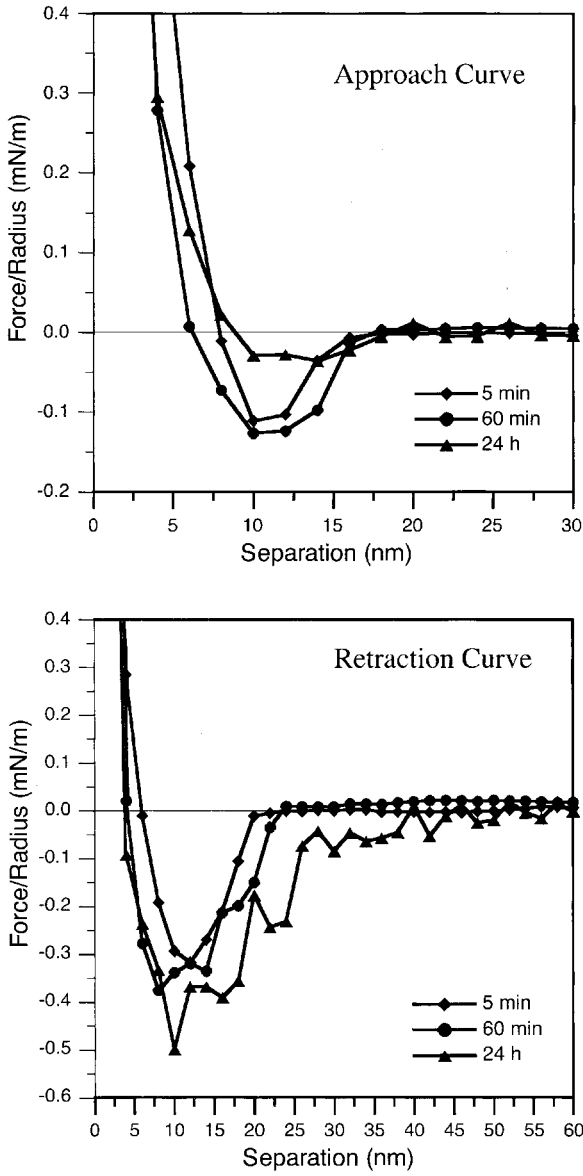


FIGURE 2 Interaction force curves between a silica sphere and a silica flat in aqueous solution of 0.05% PEO (7,000 molecular weight) and 0.25 M KNO_3 , at natural pH. Approach and retraction curves are shown for three different adsorption times—5 minutes, 60 minutes and 24 hours.

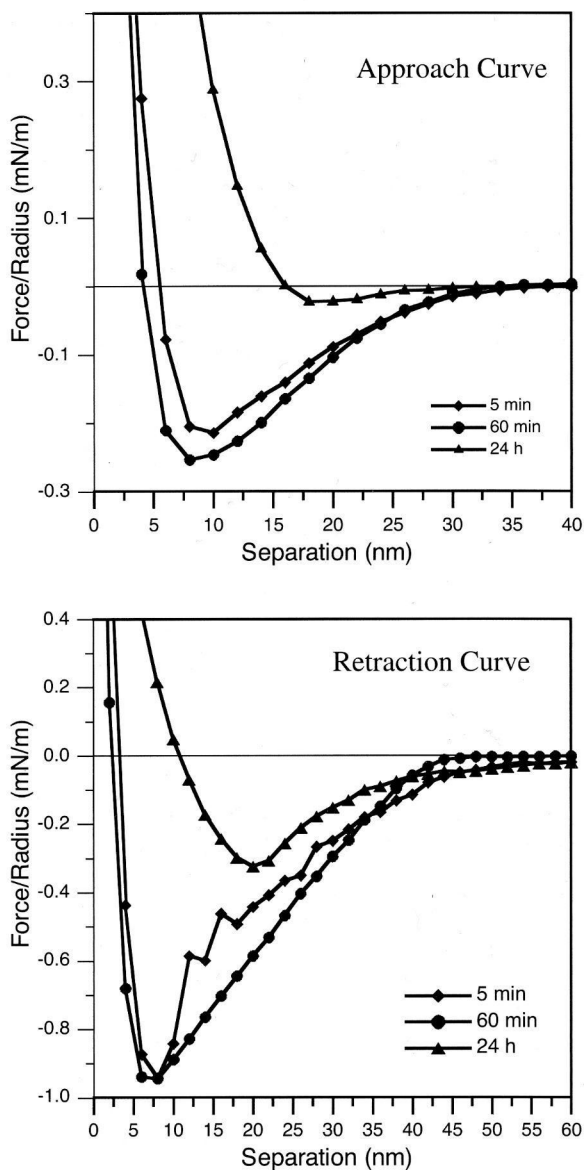


FIGURE 3 Interaction force curves between a silica sphere and a silica flat in aqueous solution of 0.05% PEO (43,000, molecular weight) and 0.25 M KNO_3 , at natural pH. Approach and retraction curves are shown for three different adsorption times—5 minutes, 60 minutes and 24 hours.

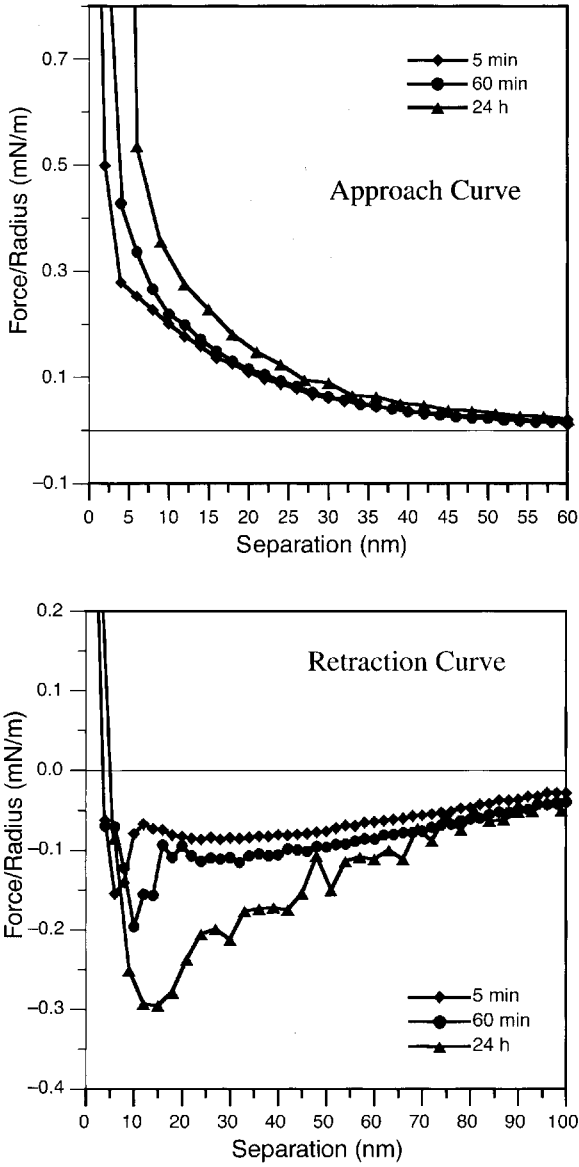


FIGURE 4 Interaction force curves between a silica sphere and a silica flat in aqueous solution of 0.05% PEO (630,000, molecular weight) and 0.25 M KNO_3 , at natural pH. Approach and retraction curves are shown for three different adsorption times—5 minutes, 60 minutes and 24 hours.

showed some interesting changes as well. The range and magnitude of the pull off (adhesive) forces did not show significant changes between 5 and 60 minutes but differed significantly after 24 hours. Both the range and magnitude showed a significant increase.

The force curves obtained for the adsorption of 43k PEO solution are presented in Figure 3. Again, the approach part of the force curves was similar for 5 minutes and 60 minutes. The attractive force was identical in both the cases, both in range and in magnitude. But the magnitude of the attraction force was larger in this case than for the 7k PEO system. The retraction part of the force curves showed a different trend. While the range and magnitude of the adhesive forces were more or less same for 5 and 60 minutes, the magnitude of the adhesive force decreased after 24 hours. This is in sharp contrast with the 7k PEO case where the magnitude and range of adhesive forces increased after 24 hours.

Interaction forces observed for the 630k PEO solution are presented in Figure 4. The force curves are significantly different from the previous two cases. For the approach curve, a repulsive force was observed for all equilibration times. Even though the force curves exhibited the same behavior for different times of adsorption, there were some subtle differences. The distance at which the repulsive forces start, and the distance of closest approach for the two surfaces, was different for different times. The retraction force curve, however, differed significantly, with the range and magnitude of the adhesion increasing significantly with time.

DISCUSSION

The approaching part of the force curves showed a significant attraction for the PEO solutions with molecular weights 7k and 43k (Figures 2, 3) for smaller incubation times, i.e., 5 minutes and 60 minutes. This attractive component can be attributed to bridging. This may seem surprising, since usually bridging is only found for unsaturated surfaces (Fleer et al., 1993), but our experimental conditions are well within the plateau region of the adsorption isotherm of PEO on silica. The first reading here is reported for 5 minutes of adsorption but reflectometer experiments by Dijt et al. (1990) showed that under appropriate flow conditions, the maximum adsorption of PEO on silica is reached within 40 seconds.

Even with the PEO adsorption layers presumably saturated, there is no sign of steric repulsion before constant compliance is reached and it appears that it is still possible for the polymer chains adsorbed at one silica surface to attach to another silica surface. This might be explained as follows. Upon approach, the concentration of polymer segments between the surfaces increases. Due to the flexibility of the PEO chains, fast reformation of the adsorbed layers can take place and additional adsorption of polymer segments is possible, with some of the newly formed PEO/silica contacts formed are bridging contacts. From the fact that attraction occurs on approach and the interaction forces are the same at different places, we can conclude that on the time scale of the experiments, the conformation of the polymers can indeed adapt to the changing conditions. Similar explanation can be applied to the long range adhesion observed in the retraction force curves. The bridging contacts will try to overcome the retracting force thereby stretching the polymer chains. So before the surfaces are totally retracted apart the polymer chains first need to be stretched to break the bridging contacts. However, for longer times of adsorption, although there is no necessary increase in the adsorbed amount of PEO, the polymer chains are given enough amount of time to organize and reorganize at the surfaces there by leaving little scope for any bridging contacts. Accordingly, after 24 hours

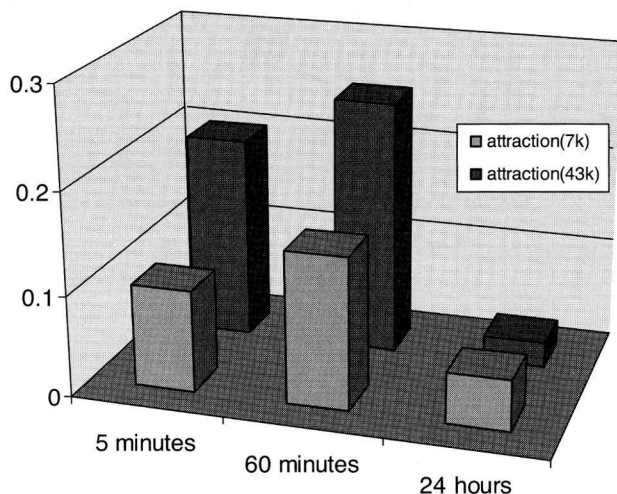


FIGURE 5 Maximum attractive force between silica surfaces for an aqueous solution of 0.05% PEO (7k and 43k), 0.25 M KNO_3 solutions, at natural pH. The data are taken from the force curves shown in Figures 2 and 3.

of adsorption, the magnitude of attraction decreased in both the cases of 7k and 43k molecular weights PEO solutions, as shown in Figure 5.

In order to provide further evidence that the change in interaction forces shouldn't necessarily come from the change in the adsorption density of polymers, in-situ Fourier-transform infrared (FTIR) internal reflection experiments were done to study any changes in adsorption density that might occur during the equilibration time. The infrared spectra are shown in Figure 6. From these spectra the adsorption density of PEO was calculated as explained in the earlier section. The plot of adsorption density as function time is shown in Figure 7. No significant change in adsorption density with time was observed from FTIR experiments, which can suggest the rapid saturation of silica surface with PEO (plateau adsorption density of 0.3 mg/m^2). These results are consistent with the trends reported in the literature (Dijt et al., 1990, have observed a plateau adsorption density of 0.5 mg/m^2 , for a PEO with molecular weight 56,300, from reflectometry experiments); however the absolute values of adsorption density are somewhat smaller. From FTIR measurements it was found that changes in force curves cannot be related to simple increase in adsorption density but also to the rearrangement of PEO molecules in time.

For the PEO system with very high molecular weight (Figure 3), force curves on approach show a steep repulsion starting at greater separation distances. The repulsive interaction increases monotonically at first, before changing the slope at closer distances. This can be explained as follows. The adsorption density of polymers shows a direct dependence on molecular weight. The adsorbed thickness of PEO on silica varies accordingly as $M^{0.56}$ (Kato et al., 1981), where M is the polymer weight. Therefore the thickness of the adsorbed PEO layer on silica is much higher in the case of the high molecular weight PEO (630k) than the lower molecular weight PEO (7k and 43k). This thick adsorbed layer makes any kind of bridging impossible. As the surfaces approach closer, the osmotic pressure between the adsorbed polymers increases steeply, giving rise to the greater steric repulsive forces. This fact is further corroborated by the evidence that the distance of closest approach is much higher for 630k PEO than either of 7k or 43k PEO solutions.

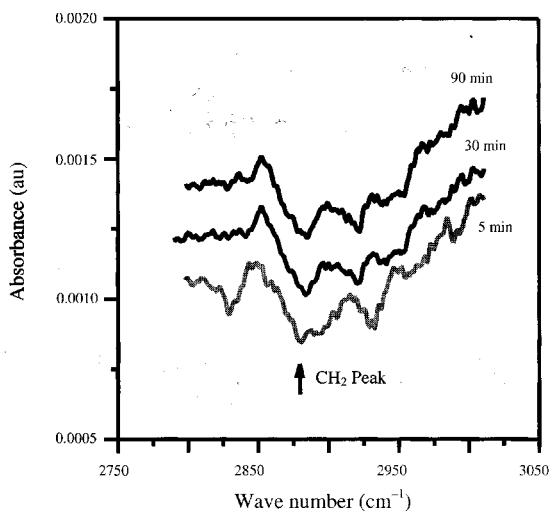


FIGURE 6 In-situ Fourier transformation infrared (FTIR/IRS) spectra taken at the surface of a silicon IRE for an aqueous solution of 0.05% 43k PEO in 0.25 M KNO₃ solution, at natural pH. The spectra, collected for three different adsorption times (5 minutes, 30 minutes and 90 minutes), are shown.

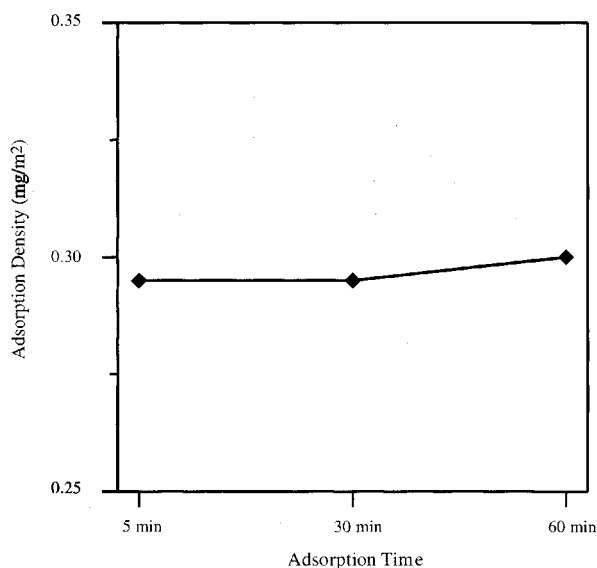


FIGURE 7 The calculated adsorption density values adsorption from an aqueous solution of 0.05% 43k PEO, 0.25 M KNO₃, at natural pH, at the surface of a silicon IRE. The values were calculated integrating the areas under the CH₂ peak of spectra shown in Figure 6.

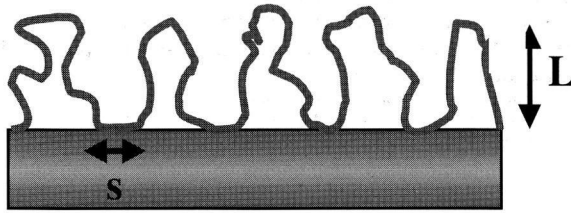


FIGURE 8 Schematic representation of surface polymer configuration assumed in the Alexander-de Gennes' scaling theory

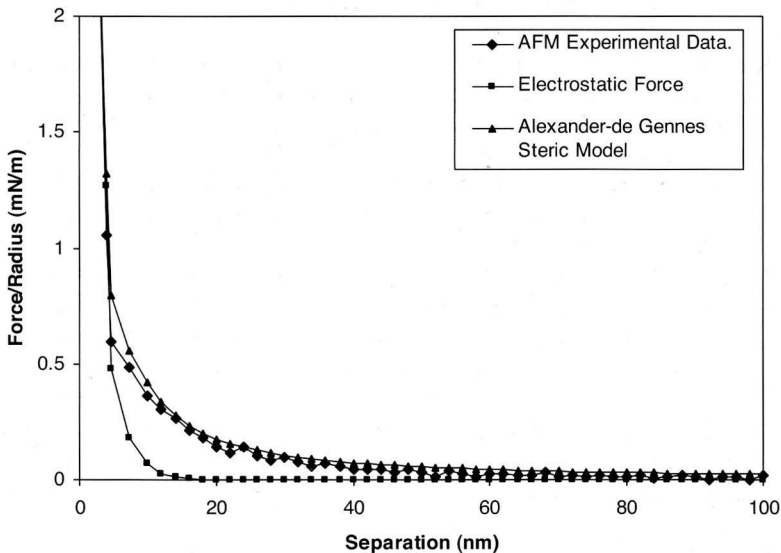


FIGURE 9 The experimental approach curve in Figure 4 fitted with the Alexander-de Gennes' scaling theory. There is an excellent fit at greater separation distances, although a slight deviation is observed at closer separation distances. The parameters used for fitting the curves are summarized in Table 1.

Several theories have been developed to describe the steric forces experienced by surfaces in the presence of adsorbed polymer layers, both qualitatively and quantitatively. Without going into detail, for an adsorbed polymer conformation as shown in Figure 8, the Alexander-de Gennes' scaling theory (de Gennes, 1982, 1987) can be given as

$$\frac{F(D)}{R} = \frac{16\pi kTL}{35s^3} \left[7 \left(\frac{2L}{D} \right)^{5/4} + 5 \left(\frac{D}{2L} \right)^{7/4} - 12 \right]$$

where, k = Boltzmann Constant (J/K), T = temperature (K), L = layer thickness (m), S = mean separation distance between adsorbed polymers (m), and F = force as a function of separation distance 'D' between the surfaces.

In Figure 9, we show the experimental force curves fitted with the theoretical values predicted according to the Alexander-de Gennes' scaling theory. Also, just to bring out the difference the calculated electrostatic force curve based on the DLVO theory is

TABLE 2 The values of the mean separation distance between the adsorbed polymers at the surface 'S', and the thickness of the adsorbed polymer 'L', obtained from fitting the approach curve in Figure 4 with the Alexander-de Gennes' steric model. The geometrical interpretation of 'S' and 'L' values are shown in Figure 8.

Time	L (nm)	S (nm)
5 min	65.7	9.3
60 min	71.4	8.3
24 hours	82.8	6.5

shown in the figure. Here it should be mentioned that as the scaling theory is only applicable to surfaces experiencing steric forces, attempts were not made to fit the force curves obtained in the presence of lower molecular weight solutions, due to the presence of an attractive component in the forces.

It can be seen that the fit to the scaling theory curve is very remarkable indeed, thereby suggesting that the forces being seen are due to steric repulsion. The values for the layer thickness and the mean separation distance obtained through fitting for different times of adsorption are summarized in Table 2. The layer thickness for the polymer adsorbed on two surfaces is close to twice the radius of gyration of the molecule given in Table 1. Once again it can be seen that there are some small reconformations (changes in 'S' and 'L' values) with time.

The retraction force curves in Figure 4, for the 630k PEO system, show great adhesion forces both in range and in magnitude, although there is no attraction seen in the approach curves. In the absence of attractive force it is expected that there is no bridging interaction between the surfaces (i.e., the polymer adsorbed on one surface interacting with the other surface). However, that doesn't necessarily mean that there is no interaction between the adsorbed polymer molecules on both surfaces. Hence, although steric repulsion is experienced between the two approaching surfaces, once they overcome the repulsive barrier and enter the constant compliance region, there is some interaction between the polymer molecules adsorbed on the two surfaces as the dangling tails interact with each other. The adhesion force seen from the retraction curves is a result of these contacts being broken as the surfaces are being pulled apart. The polymers will be stretched completely before eventually giving away, leading to the great range of the adhesion forces. Again, the changes in the range and magnitude of adhesion with time can be attributed to the reconformation of the polymer at the surfaces, as can also be evidenced by the changes in the fitting parameters, summarized in Table 1, with time.

CONCLUSIONS

From the AFM results, it can be concluded that interaction forces between silica surfaces depend on the molecular weight of the polymer and the time of adsorption. For the low molecular weight PEO attractive bridging interactions are observed. The attractive component of the surface force decreases with time, which can be related to adsorption and rearrangement of the PEO layer. The range of the force during approach and retraction increases with molecular weight of PEO, which might be expected assuming some stable conformation of polymer at the silica surface. Increase in the range and magnitude of the pull-off force and steps observed during retraction can be explained by bridging between silica surfaces.

In the case of the very high molecular weight PEO, steric repulsive forces were observed in the approach curves at all times of adsorption. The steric forces corresponded

very well with those calculated based on the Alexander-de Gennes' scaling theory. Adhesion forces of greater magnitude and acting at larger separation distances were seen in the retraction curves.

Any changes in the force curves are attributed to the reformation of polymers at the surfaces and not necessarily due to the changes in adsorption density values, as is evident from adsorption density measurements by FTIR/IRS.

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