Interaction between silica particles with poly(ethylene oxide) studied using an optical tweezer: insignificant effect of poly(ethylene oxide) on long-range double layer interaction

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Abstract

It is known that the adsorption of nonionic polymers or surfactants reduces the magnitude of zeta potential of colloidal particles and provides the steric repulsion between particles. A question remains as to whether nonionic polymers affect the structure of the electric double layer (EDL). To elucidate the effect of nonionic polymer on EDL, we investigated the long-range interaction forces between silica particles in aqueous solutions with different molecular weights of polyethylene oxide (PEO) having higher affinity to silica by using optical tweezers. For all measurements, long-ranged repulsive interactions were observed. The onset of the interaction force for bare particles and those with low molecular weight PEO remained identical and was consistent with the Derjaguin-Landau-Verwey-Overbeek (DLVO) predictions. This result indicates that the adsorption of nonionic PEO does not affect the charging properties of silica, and the interaction originates from the overlapping of the EDL. With high molecular weight PEO, the onset of interactions shifted to a few hundred nanometers larger than those for bare particles and was quantified using the Alexander-de Gennes model, suggesting the steric interactions originate from the protruding tails and/or loops of the adsorbed PEO layer. Based on the force measurements, we emphasize that the adsorption of nonionic polymer onto the surface of the silica particles does not affect the EDL surrounding the particles. Hence, we corroborate the notion that the reduction of the magnitude of zeta potential in the presence of nonionic polymer is attributable to the shift of the shear plane from the hydrodynamic viewpoint.

Keywords: DLVO/Steric interactions/Optical tweezers/PEO adsorption

1. Introduction

The control of the stability and rheology of dispersions of colloidal particles is essential in many applications, as in industrial products like paint, inks, food products like mayonnaise, chocolate, as well as cosmetics, and pharmaceutical formulations [1–4]. On the other hand, applications for flocculation of particles like water and wastewater treatments are also paramount[5, 6].

The stability and rheology of colloids are regulated by the interparticle forces[7, 8]. Meanwhile, colloidal particles are charged and form an electric double layer (EDL). The sum of attractive van der Waals force and repulsive force due to the overlap of EDL is known as Derjaguin-Landau-Verwey-Overbeek (DLVO) force[9–13]. DLVO force is considered ubiquitous for charge stabilized colloids[6, 9, 14].

In most applications, the adsorbing polymers are usually added to the colloidal dispersions to control the stability and rheology[7, 8]. Polymers at interfaces are significantly important in many industrial applications[8, 15]. In general, polymer adsorption onto the colloidal particles can lead to various effects on the stability and rheology of their suspensions, ranging from steric stabilization to bridging flocculation, shear-thickening, and shear thinning, depending on several factors, including polymer concentration, electrolyte concentration, and polymer conformation at the surface [16, 17]. Hence, the adsorbed polymers can be crucial in controlling the fate of the colloidal particles for different applications.

Electrokinetic techniques are widely used to characterize the surface charging properties of colloidal particles and surfaces [18–26]. From the electrokinetic measurements, so-called zeta potential, which is the electric potential at the plane of shear adjacent to the particles, can be extracted. Zeta potential with DLVO theory has been successfully used to explain the stability of the dispersion of bare colloidal particles[9, 13, 27–29]. The electrokinetic measurements are considered a standard technology, and the electrokinetics of bare particles are well studied. The presence of a polymer layer on the surface may affect the electrokinetic transport properties of the colloidal particle [22]. The adsorption of neutral polymers/surfactants on colloidal particles is reported to reduce the magnitude of zeta potential [7, 30–32]. For example, Garvey et al. [33] reported the rapid drop in the zeta-potential of latex particles with the addition of nonionic poly(vinyl alcohol) (PVA). This decrease is considered to originate from the adsorption of PVA onto the latex particles. Zaman [7] also reported the reduction of the zeta potential of silica particles with the addition of poly(ethylene oxide) (PEO). Meanwhile, Heiningen and Hill [34] reported the temporal decrease in the mobility magnitude of trapped silica microsphere with the adsorption of PEO using optical tweezers electrophoresis. In these studies, the reduction in the zeta potential or mobility magnitude is often interpreted by the outward shift of the location of the shear plane, and the shift is in some cases regarded as the thickness of adsorbed polymer layers [4, 22, 30, 31, 33–36]. Then, the thickness of the polymer layer is quantified from the reduction of zeta potential by assuming that the potential distribution in the EDL near the surface is hardly disturbed by the adsorbed polymer layer. The assumption

seems reasonable but has never been examined.

The objective of this research is to clarify if nonionic polymer affects EDL structure. Our idea in this paper is to measure DLVO interaction force at long-range distances in the presence and absence of nonionic polymers. Using optical tweezers allows us to measure the long-range and weak interaction forces between particles for bare and with an adsorbed polymer layer at the different molecular weights. Furthermore, we utilize silica particles and polyethylene(oxide) (PEO), having a higher affinity to silica surfaces, as a model particle and nonionic polymer. The interaction between silica surfaces in the presence of PEO has been studied using different force measurement techniques [7, 20, 32–39]. While many studies reported the effect of adsorbed PEO on the interaction forces between silica surfaces, the discussion is mostly focused on the steric interactions in the presence of PEO at the surface [39–43]. In the present study, the effect of diffuse double layer and steric interactions are differentiated by varying the molecular weight of PEO and background electrolyte concentration. Suppose the force curve with nonionic polymer PEO is similar to that without PEO. In that case, we can postulate that nonionic polymer PEO does not significantly affect EDL structure. Thus, the well-known reduction in zeta potential is due to the shift of the shear plane coming from a hydrodynamic problem with adsorbed polymers. Therefore, this study has aimed to provide a basis for the assumption and improve our understanding of the EDL structure in the presence of nonionic polymer.

2. Materials and Methods

2.1 Materials

The probe particles used in the experiments were non-functionalized silica particles (diameters 2*a*= 10.0 and 5.6 μm, JGC Catalysts and Chemicals, Ltd., Japan) suspended in deionized (DI) water (Elix Advantage 5, Millipore, Tokyo, Japan). Both particle suspensions were prepared by diluting the stock suspension of 0.01 wt.% to 0.0005 wt.%. Poly (ethylene oxide) (PEO) with a molecular weight of 1000 kg/mol and 100 kg/mol were purchased from Sigma Aldrich (Sigma Aldrich: St. Louis, MO). Poly(ethylene glycol) (PEG) with an average molecular weight of 20 kg/mol was purchased from Wako Pure Chemicals Ind., Ltd. Stock polymer solutions (~500 ppm) were prepared by dissolving the powders in DI with vigorous stirring at room temperature for two days and carefully covered to avoid photodegradation. The radii of gyration, R_g, of the polymers were estimated from the molecular weight following the reference [44, 45], as shown in Table 1. All polymer stock solutions were used within two weeks, and stored at 5 °C. A 10 mM KCl solution was added to control the ionic strength of the samples.

2.2 Optical tweezers set up

An optical trapping kit (OTKB/M, Thorlabs) equipped with a single laser (wavelength λ=976 nm) was used in the experiments, as described elsewhere[46, 47]. A 100× oil immersion objective with a high numerical aperture (NA 1.25, WD 0.23 mm, Nikon) was used to tightly focus the laser beam and visualize the colloidal particle.

An air condenser then collected the trapping laser passing through the sample (10×, NA 0.25, W.D. 7 mm, Nikon) and further reflected into the quadrant position detector (QPD) using a dichroic mirror for the back-focal plane detection (OTKBFM, Thorlabs). A piezo-controlled 3-dimension translational stage (NanoMax 300, Thorlabs) was used to position the microscope glass slide using the Thorlabs APT software package. We used a force measurement module (OTKBFM-CAL, Thorlabs) to record the QPD signals. The constant particle displacement was measured by image processing, and the QPD calibration factor was determined to be around 0.16 V/μm[46]. The stage displacement and the *x*- and *y*- displacement of the particle in the optical trap were recorded using a custom-made data acquisition program in LabVIEW software (National Instruments, Austin, TX).

2.3 Force measurement

The force measurement between two particles with different radii, as shown in Fig. 1, was performed in a microscope cell separated by a double adhesive tape and sealed with a vacuum sealant following the reference with slight modifications [48, 49]. The vacuum sealant protects the sample from evaporation during the measurements. A particle A_1 with radius a_1 was optically trapped at a height equal to the radius of a large particle A_2, a_2. The larger particle, A_2, was initially allowed to adhere to the cover glass by drying in a closed environment. Then, the cover glass was used to make the microscope cell. After that, the particle suspension of 0.0005 wt%, 5.6 μm particle was injected into the cell without or with 100 ppm of the polymer [42, 50, 51]. The sample

147 pH was measured to be around 6. The addition of an excess amount of polymer
148 molecule is also expected to be adsorbed onto the large particles pre-adhered on the
149 cover glass. The sample cell was kept for 10 minutes to develop adsorption on the
150 adhered particles and obtain saturation. A free 5.6 μm particle was then held in an
151 optical trap for the measurements. We determined the initial surface-to-surface distance
152 between particles by image processing and converted it from pixels to micrometers
153 using microscope calibration scales.

154 Force measurement was performed by translating the adhered large particle via the
155 piezo-controlled stage at a speed of 0.02 μm/s using custom software in LabVIEW
156 (National Instruments, Austin, TX). We assume no hydrodynamic interaction takes
157 place at this slow translation speed. As the larger particle approaches the trapped
158 particle, the trapped particle is displaced laterally from its equilibrium position, Δx,
159 which is detected by the QPD. The force is obtained from the lateral displacement
160 measurement, $k\ \Delta x$, where k is the trap stiffness. The trap stiffness k was fixed at
161 2.35×10^{-5} N/m in all force measurements. Force measurements were repeated for at
162 least five different pairs of particles. All measurements were performed at room
163 temperature, 20 °C.

164 **3. Results and Discussions**

165 **3.1 Interaction forces between silica particles in KCl solutions**

166 The double-layer forces between bare silica particles in electrolyte concentrations
167 were measured to validate the methodology. Figure 2 shows the experimental results of

direct force measurements between silica particles in dilute KCl concentration. When the adhered particle approached the trapped particle at a constant speed of 0.02 μm/s, a repulsive force was observed for both KCl concentrations due to the overlapping of the EDL, and the onset of repulsion decreased with the increasing electrolyte concentration.

To further evaluate the experimental force curve, the total interaction force between the two colloidal particles was analyzed using the DLVO theory, wherein the interparticle forces were governed by the electrostatic double-layer (EDL) force and the van der Waals (VDW) attraction force:

$$F_T = F_{\mathrm{EDL}}(h) + F_{\mathrm{VDW}}(h) \quad (1)$$

The EDL interactions for a sphere-sphere geometry with different sizes can be described as follows:

$$F_{\mathrm{EDL}}(h) = \frac{128\pi N_{\mathrm{A}}\, c_s\, k_B T\, \gamma^2}{\kappa}\left(\frac{a_1 a_2}{a_1+a_2}\right) e^{-\kappa h} \quad (2)$$

where $\frac{a_1 a_2}{a_1+a_2}$ is the effective radius following Derjaguin's approximation with a_1 and a_2 are the particle radii, h is the surface-to-surface distance, N_A is Avogadro's number, c_s is the electrolyte concentration in mM, $k_B T$ is the Boltzmann constant multiplied by absolute temperature, T, γ is given by $\gamma = \tanh(ze\psi/4k_B T)$ where e is the elementary charge, z is the valence of ions, ψ is the surface potential, and $1/\kappa$ is the Debye length. Meanwhile, the attractive VDW interaction is given as

$$F_{VDW}(h) = \frac{-\mathrm{A}_H}{6h^2}\left(\frac{a_1 a_2}{a_1+a_2}\right) \quad (3)$$

where the A_{H} is the Hamaker constant between silica particles in an aqueous solution. The A_{H} was set to 2.0×10^{-21} J; this value is within the reported values of the Hamaker constant of silica in water [13, 52]. The theoretical DLVO force curve was compared to

190 the experimental data with ψ as a fitting parameter, and the κ was calculated directly
191 from the electrolyte concentration of the solution.

192 In Fig. 2, the experimental and theoretical curves showed good agreement. From
193 the fit of DLVO theory to the measured curves, the absolute surface potential was
194 obtained to be around 65.7±1.2 mV and 50±1.7 mV for 0.1 mM and 0.5 mM KCl
195 solutions, respectively. As the salt concentration increases, the onset of the double layer
196 forces decreases at a surface-to-surface distance of around 250 nm and 150 nm for 0.1
197 mM and 0.5 mM KCl due to the thinning of the diffuse double layer. The measured
198 force curve and surface potential between silica particles using optical tweezers were
199 consistent with the theoretical predictions and agreed with previous studies [13, 27].
200 Hence, this agreement indicates that our methodology is sound for measuring long-
201 range interactions between two particles.

202 **3.2 Interaction forces between silica particles with adsorbed PEO layer**

203 The addition of a PEO in the particle suspension would result in polymer
204 adsorption onto the surface of the silica particle[8, 37, 42, 47, 53–56]. The interaction
205 forces between two surfaces with the adsorbed polymer layers with different molecular
206 weights were measured to evaluate the effect of PEO on the surface properties of the
207 silica particles. Figure 3 presents the experimental results of direct force measurement
208 between silica particles mediated with PEO of different molecular weights at 0.1 mM
209 and 0.5 mM KCl. The force curve is purely repulsive for all particles mediated with
210 PEO. At a low KCl concentration (0.1 mM), the force curve for a low molecular weight

211 PEO (20 kg/mol) converges quite well with the bare particles. Since the layer thickness
212 of the adsorbed polymer, which is assumed to be around $2R_g$-$3R_g$ where R_g of a 20
213 kg/mol PEO is estimated to be 7.6 nm (see Table 1), is thinner than the diffuse part of
214 the double-layer structure, we postulate that the observed repulsion is dominated by the
215 overlapping of diffuse double-layer. This resembles the interaction of silica particles
216 even in the presence of the small molecule polymer adsorbed at the surface, and thus
217 the force is governed by the overlapping of diffuse double-layer and is electrostatic in
218 nature. Furthermore, increasing the molecular weight to 100 kg/mol with R_g estimated
219 to be 17.1 nm (see Table 1), the force curve still converges with those for bare and with
220 20 kg/mol adsorbed PEO layer. Therefore, similar to the interaction mediated with the
221 20 kg/mol adsorbed PEO layer, we consider that the interaction originated from the
222 EDL repulsion, and the adsorption of the nonionic polymer did not affect the surface
223 property of the particles.

224 On the other hand, for a high molecular weight PEO, the onset of the interaction
225 was shifted to a few hundreds of nanometers around to $3R_g$, significantly larger than
226 those for bare particles and with a low molecular weight polymer. With the presence of
227 a high molecular weight PEO, the thickness of the adsorbed polymer layer was
228 expectedly thicker; hence when the two polymer-covered surfaces approach each other,
229 the trapped particle experiences a force from the outer segments of the adsorbed
230 polymer layer. Thus, the shift was attributed to the steric repulsion, and the onset of
231 repulsion can be used to estimate the layer thickness of the adsorbed polymer layer [42].

The effect of double-layer structure and steric repulsion on the interaction between silica particles was further differentiated by increasing the background salt concentration. Increasing the salt concentration suppresses the EDL repulsion due to the charge screening. Figure 3b presents the force curve for bare and adsorbed polymer layers at 0.5 mM KCl concentration. The onset of the interaction force for bare silica particles and those mediated with 20 kg/mol PEO remained identical and shifted to a lower surface-to-surface distance. This observation is in line with those found for 0.1 mM KCl background concentration. Since the layer thickness of the adsorbed polymer is still thinner than the diffuse double layer; thus, the interaction is driven by the overlapping of the EDL, and the adsorption of small molecular weight nonionic polymer does not alter the surface property of the particle. Moreover, a fluctuation in the force curve could be seen at large separation distance and may be a possibility of secondary minimum or depletion force in the presence of polymer. However, this is not the case in our measurements because the polymer size is small and the concentration of polymers is low. Hence, this could be an artifact since these forces are too weak and may be masked by the limitation of the force detection at very low forces. On the one hand, the onset of interaction for silica particles mediated with 1000 kg/mol PEO did not show significant differences from those in 0.1 mM KCl concentration. This implies that the steric interaction is also not affected by the change in the diffuse double-layer [35, 57, 58]. Hence, based on the above discussion, we consider that the adsorption and attachment of the PEO molecule on the surface of the silica particle do not affect the charge group at the surface and imply that the presence of nonionic polymer does not

influence the double-layer structure of the particles.

A similar observation was also reported by Giesbers et al. [41] using AFM between the polymer-covered sphere and polymer-covered plate, wherein the approach curve with low molecular weight PEO at 10^{-3} M NaCl is dominated by electrostatic repulsion. Correspondingly, Wei et al. [39] observed a similar tendency in the interaction between latex particles and silica glass surface-mediated with PEO at low polymer concentration. Although reported, the consideration of the surface potential and the commonly observed reduction in the zeta-potential was not addressed. Moreover, the effect of PEO on the surface of silica particles has been studied using electrokinetic measurements[7, 8,33, 36, 37]. It was shown that the absolute magnitude of zeta-potential (ζ-potential) decreases with the increasing adsorbed amount of PEO. As mentioned in the introduction, electrokinetic measurements provide information on the surface properties of the charged particles; however, it is equally reliant on the hydrodynamic properties of the outermost region of the interface. Thus, the observed decrease in the ζ-potential somehow reflects the hydrodynamic properties of the adsorbed PEO layers. Since the long-range force measurements did not exhibit any significant changes in the surface properties of the particles in the presence of the nonionic polymer layer, we attribute that the adsorption of the nonionic polymer has almost no effect on the surface potential and EDL structure of charged silica particles, albeit the commonly reported change in the ζ -potential. Therefore, based on the above discussion, we postulate that the reported decrease in the absolute magnitude of ζ-potential in the presence of PEO was attributed to the shift of the shear plane from the hydrodynamic point of view as

schematically drawn in Fig. 4.

3.3 Steric interactions by large molecular weight polymer

The effect of steric repulsion by large molecular weight polymers was quantified using the Alexander-de Gennes (AdG) model [60, 61]. Following Derjaguin's approximation, the interaction force between two surfaces for the symmetric case of the AdG model is given as follows:

$$F_{\mathrm{symm}}(h) = \frac{8\pi k_B T\, L}{35 s^3}\left(\frac{a_1 a_2}{a_1 + a_2}\right)\left[7\left(\frac{2L}{h}\right)^{5/4} + 5\left(\frac{h}{2L}\right)^{7/4} - 12\right] \quad (4)$$

where $k_{\mathrm{B}}T$, a_1, a_2 and h are defined earlier, and L is originally defined as the thickness of the grafted polymers. In this case, we followed the consideration of Block et al. [62] and considered the PEO as only physisorbed on the surface of the silica particles. Hence, L can be redefined as the thickness of the adsorbed PEO layer [62, 63]. In addition, the parameter s is originally defined as the average distance between two anchoring, grafted chains. Again, since the polymer was treated as physisorbed on the surface of the particles; hence, the steric force was considered to originate from the opposing loops and tails [62, 63]. Therefore, the parameter s may provide information on the average density of tails and loops of the adsorbed polymer [62, 63]. For the fitting, the parameters s and L were kept constant with a value of 75 nm and 198 nm, respectively.

As shown in Fig. 3, the AdG model showed good agreement with the measured force curve without adding the electrostatic forces, implying that the model is sufficient to describe the steric forces generated by the adsorbed polymer layer for both salt concentrations. These findings are fairly intuitive as the adsorbed polymer layers are thicker than the double-layer structure. Hence, the high molecular weight PEO provides a steric repulsion by the adsorbed polymer layer's opposing tails and/or loops.

Additionally, depletion was not observed in this study, as was previously observed [39], probably due to the concentration used in the present study. Depletion usually occurs at overdose polymer concentration, where the concentration of free polymers in the solution is relatively high, thereby increasing the osmotic pressure between the particles upon approach.

According to the AdG model, several pieces of information could be obtained. Firstly, the layer thickness of the adsorbed polymer layer was estimated to be around $2R_g$ - $3R_g$ for both salt concentrations. This observation was rather consistent and within the range of the previous studies, as the range of steric forces can be as several times as R_g [42, 65–67]. Meanwhile, our previous study on the kinetics of PEO adsorption onto silica surfaces showed a hydrodynamic layer thickness of around $1.3R_g$ at 50 ppm for the same molecular weight polymer [47]. Secondly, the parameter *s* was not affected much by the salt concentrations. However, the obtained parameter *s* was slightly higher than those for the grafted polymer case and in molecular dynamics simulations, with a value of around 3-18 nm [36, 68]. This is reasonable as the polymers in this study were only physisorbed onto the surface, and parameter *s* may be from the average density of tails and loops of the adsorbed polymer. On the other hand, Klein and Luckham obtained a value of *s* to be 11.0 nm for physisorbed PEO on mica surfaces[66]. In the case of physisorbed poly(styrene sulfonate), the value of *s* was within 50-60 nm [62, 63], while Mohamad et al.[69] reported the value of *s* around 30-44 nm for the case of pseudo-brush poly(diallyl dimethylammonium chloride) (PDADMAC), which were comparable to our fitted value of *s*. Hence, we attribute the steric interactions were caused by the dangling loops and tails of the adsorbed PEO layer.

4. Conclusion

The present study provides long-range force measurements between silica particles without and with nonionic PEO polymer layers at different molecular weights. In samples without PEO, the force profiles can be quantitatively interpreted in terms of DLVO theory, provided by the parameters describing the surface properties of the particles. This quantitative comparison between the experimental and theoretical features provides strong support for the applicability of the methodology for the force measurements in the presence of adsorbed PEO layer. In the presence of adsorbed PEO layer, the addition of low molecular weight PEO did not affect the double-layer structure. Based on this observation, we corroborate the notion that the reduction in the magnitude of the zeta potential in the presence of neutral polymer can be attributed to the shift of the shear plane from the hydrodynamic point of view.

Author Contributions

Lester C. Geonzon: Conceptualization; Investigation; Methodology; Software; Data curation; Formal analysis; Validation; Visualization; Writing-original draft; Writing-review & editing. **Motoyoshi Kobayashi**: Supervision; Conceptualization; Methodology; Formal analysis; Visualization; Writing-original draft; Writing-review & editing; Resources; Funding acquisition; Project administration. **Takuya Sugimoto**: Formal analysis; Writing-review & editing; **Yasuhisa Adachi**: Supervision, Formal analysis; Writing-review & editing Resources; Funding acquisition; Project administration.

Conflicts of interest

There are no conflicts of interest to declare.

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Table 1. Estimated radius of gyration of PEO as a function of molecular weight

Molecular weight (kg/mol)[a]	**R_g (nm)**
20	7.6
100	17.1
1000	64.9

a Supplier Information

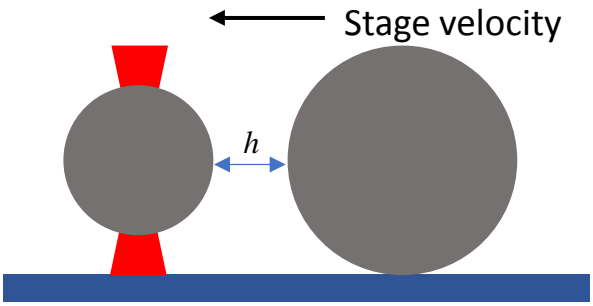

Figure 1. Schematic diagram of the silica-silica interaction. The large particle is adhered to the glass slide and displaced by moving the stage at a speed of 0.02 µm/s.

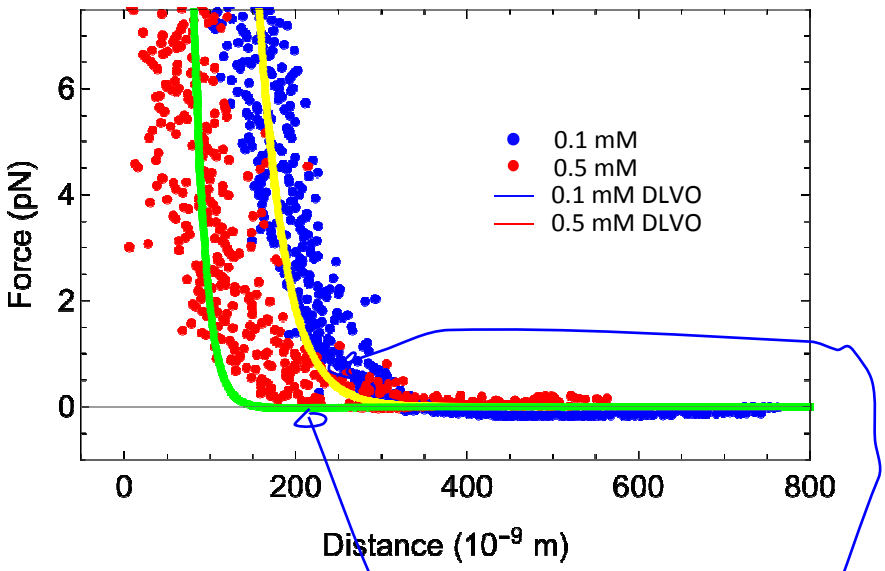

Figure 2. Effect of electrolyte concentration on the interaction between silica surfaces. Solid line: Theoretical curve using for 0.5 mM KCl (red), and for 0.1 mM KCl (blue).

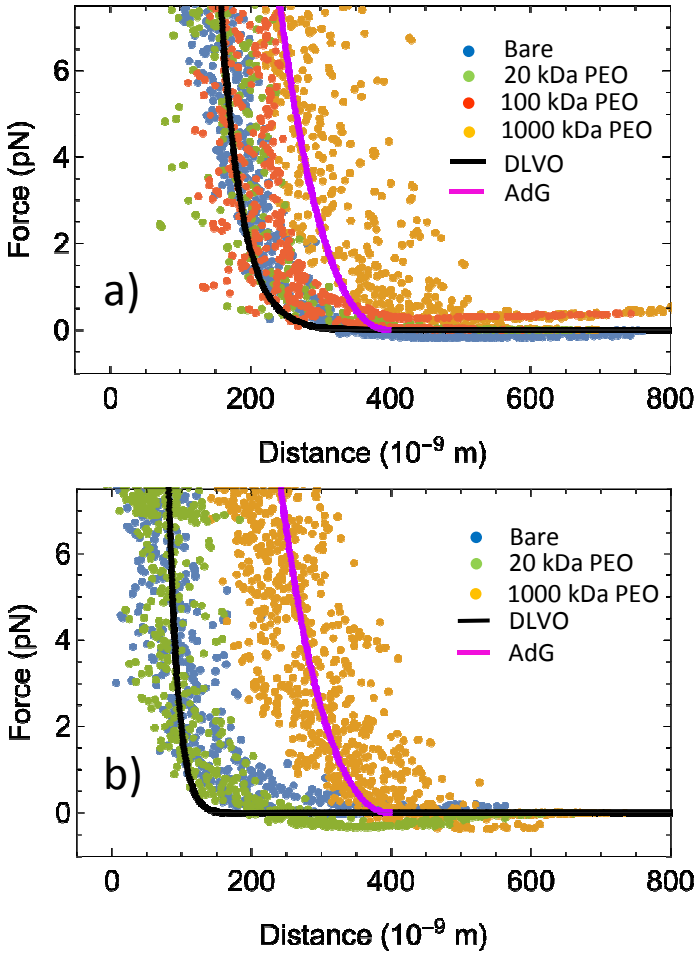

Figure 3. Effect of adsorbed PEO with different molecular weight on the interaction between silica surfaces: a) in 0.1 mM KCl, and b) in 0.5 mM KCl. Solid line: Theoretical curve using DLVO (Black) and AdG model (Orange).

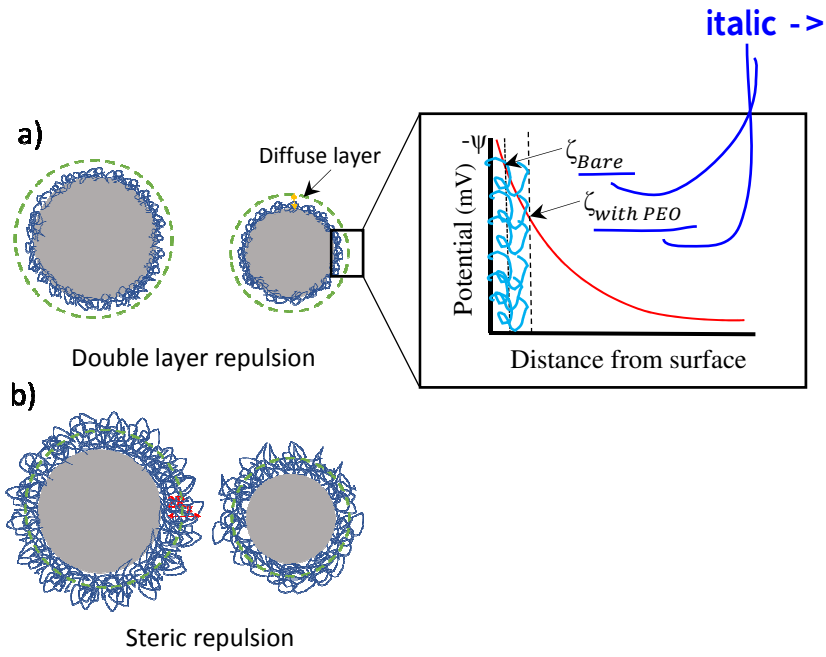

Figure 4. Schematic illustration of the interaction between particles with adsorbed neutral polymer. Inset of Figure 4a is the schematic potential distribution in the presence of PEO.