

INTERACTION BETWEEN POLY (ETHYLENE OXIDE) AND SILICA NANOPARTICLES IN DILUTE SOLUTIONS*

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Abstract A mixed system that includes poly(ethylene oxide) (PEO) and silica (SiO_2) nanoparticles is prepared using two mixing methods. The interaction between PEO and the SiO_2 nanoparticles in the dilute basic solution is investigated using the dynamic light scattering (DLS) and isothermal titration calorimetry (ITC) techniques. The DLS results show qualitatively that SiO_2 nanoparticles interact with both random coils and aggregates of PEO through hydrogen bonding, and PEO- SiO_2 complexes are formed. The degree of disaggregation of aggregates of PEO is readily adjusted by changing the concentration of SiO_2 nanoparticle suspensions. Moreover, the ITC results also certify quantitatively the interaction between PEO and SiO_2 nanoparticle, and give the evidence of formation of PEO- SiO_2 complex.

Keywords: PEO; SiO_2 nanoparticles; Hydrogen bonding; Disaggregation; Mixing method; Depletion interaction.

INTRODUCTION

Polymer-inorganic nanoparticle complexes formed *via* covalent and noncovalent interactions have been extensively studied in recent years due to their potential industrial and biomedical applications^[1–6]. Hydrogen bonding complexes have attracted more attention, compared with those formed from other noncovalent interactions, such as electrostatic and hydrophobic interactions^[7–9]. Aside from being a very simple and feasible method for developing new structures and properties different from those of the two components, hydrogen bonding complexes are also used as model compounds which provide molecular-level or nanoscale information on the interaction between polymer and inorganic nanoparticles.

Polyethylene oxide (PEO) is one of the most studied water-soluble polymers and has a chemical structure of $(\text{CH}_2\text{CH}_2\text{O})_n$. Moreover, it possesses many unique and complicated properties, such as good solubility in water and organic solvents^[10], remarkable biocompatibility^[11], ability to adsorb easily on surfaces^[12–14], effective prevention of protein adsorption^[15], and so on. Furthermore, the clustering behavior of PEO is an interesting phenomenon^[16–19]. When PEO is dissolved in water, it forms characteristic clusters (also named aggregates) that coexist with the PEO random coils. Reasons such as the presence of impurities^[20], crystallization of the PEO chains^[21], chain-end effects^[22] and formation of hydrogen bonds^[18] have been proposed to explain the formation of clusters in solutions. However, no consistent conclusion has been figured out on clustering behavior. It should be mentioned that the aggregation behavior of PEO can lead to an unusual rheological property. One important application is reducing friction drag in flow^[23].

PEO commonly binds with colloidal silica (SiO_2) through hydrogen bonds between surface hydroxyls and

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ether oxygen. Kitchener *et al.*^[24] found that the PEO adsorption amount on flame SiO₂ is higher compared with that on precipitated SiO₂ at pH = 6. This finding indicates that the PEO adsorption on SiO₂ particles crucially depends on the synthetic routes. Eremenko^[25] reported the effect of pH level and ionic strength on the adsorption behavior of PEO on aerosil SiO₂. He found that the amount of PEO adsorbed on SiO₂ decreased with increasing pH values and was very weakly dependent on ionic strength at pH ≤ 7. Stuart *et al.*^[8] studied the adsorption of colloidal SiO₂ on PEO brushes, which can be controlled by adjusting the pH level of the system, and found that many SiO₂ nanoparticles are adsorbed on PEO brushes at low pH values. This result was also confirmed by Beek^[26]. Moreover, theoretical analyses have been performed using both mean field and scaling theories^[27–30].

The adsorption of polymers on the particles and the conformation of polymers on surfaces have been extensively studied using different experimental methods, such as nuclear magnetic resonance, small-angle neutron scattering, reflectometry, the depletion method, dynamic light scattering (DLS) and isothermal titration calorimetry (ITC)^[31–35]. However, no consistent results have been obtained from these different experimental methods. In addition, previous studies only focused on understanding the depletion, bridge flocculation behavior, adsorption kinetics and the flocculation of colloidal SiO₂ suspensions with PEO^[36–41]. More work focused on the change of single PEO chains in the mixing solution. However, a systematic study on interaction between SiO₂ nanoparticles and aggregates of PEO in dilute solutions is less reported. Therefore, we concentrate on interaction of PEO-SiO₂ mixed system through both qualitative and quantitative methods, particularly on the interaction of PEO aggregates and SiO₂ nanoparticles in dilute solutions. Definitely, it is helpful to understand the interaction between polymer and inorganic nanoparticles and aggregated state of PEO chains under addition of SiO₂ nanoparticles.

EXPERIMENTAL

Materials

The two PEO samples, namely, PEO-200K ($M_w = 196000$ g/mol; $M_w/M_n = 1.03$) and PEO-20K ($M_w = 19600$ g/mol; $M_w/M_n = 1.05$), purchased from Polymer Laboratories were used without further modifications. The LUDOX[®] HS-40 colloidal SiO₂ suspension (pH = *ca.* 9.8, radius = *ca.* 12 nm) was purchased from Sigma-Aldrich. Deionized water with 18.2 MΩ-cm resistivity and sodium hydroxide from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China) were also used.

Preparation of SiO₂ Nanoparticle Suspension

The colloidal SiO₂ nanoparticles were diluted in a NaOH aqueous solution *via* the weighing method to form a series of suspensions with different concentrations from 0.0005 g/mL to 0.004 g/mL but with the same pH level of 9.6. Then, the dilute suspensions were sonicated for 45 min and filtered using a 0.22 μm filter to remove dust prior to the experiments.

Preparation of Polymer Solution

The PEO sample was dissolved in a NaOH aqueous solution at a pH level of 9.6 and stirred at 320 r/min for 24 h at room temperature. Then, the polymer solution was filtered to remove the dust prior to the experiments.

Mixture of Polymer Solution and SiO₂ Suspension

Two mixing methods were employed. For Method I, a polymer solution with a fixed concentration was mixed with SiO₂ suspensions of different concentrations. The mixtures were stirred at 320 r/min for 24 h at room temperature. For Method II, a certain amount of polymer was dissolved in SiO₂ nanoparticle suspensions of different concentrations, and the solutions were stirred at 320 r/min for 24 h at room temperature. All mixtures were filtered using a 0.45 μm filter to remove the dust prior to the experiments.

Light Scattering Measurements

The DLS measurement was performed by using a Zetasizer Nano-ZS90 (Malvern, Britain) instrument. All samples were kept in equilibrium state at a predetermined temperature for 3 min before the data collection and were then measured at 25 °C. A 4 mW He-Ne laser ($\lambda_0 = 632.8$ nm) served as the light source. The normalized

autocorrelation functions $g^{(2)}(q)$ of the intensity of the light scattered by the particles were measured at a scattering angle θ of 90° and analyzed using the CONTIN software as follows:

$$g^{(2)}(q, \tau) = g^{(2)}(q, 0) \int \exp(-\tau / \tau_r) G(\tau_r) d\tau_r \quad (1)$$

where q is the scattering vector, τ is the time, and $G(\tau_r)$ is the distribution function of the relaxation time τ_r . The apparent hydrodynamic radius R_h of the particles in the solution was calculated using the Stokes-Einstein relationship

$$R_h = k_B T / 6\pi\eta_0 D \quad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature, η_0 is the viscosity of the solvent, and D is the translation diffusion coefficient.

Zeta Potential Measurement

The DLS measurements of all samples were directly used to determine their zeta potentials with the Zetasizer Nano-ZS90 (Malvern, Britain) at 25°C .

ITC Measurements

The ITC experiment was performed using Macrocal iTC200, according to the relevant data processing methods described in literature^[35]. The 0.0046 g/mL SiO_2 suspension (about 0.8 μL per injection; 30 injections per run) was stepwise added into the cell containing the PEO solution (approximately 200 μL) at 25°C . The heat of dilution for both PEO and silica nanoparticles was measured alone by conducting dilution experiment in respective NaOH solution (pH = 9.6), which was subtracted from total heat of adsorption.

RESULTS AND DISCUSSION

R_h of PEO in Dilute Solutions

Figure 1 shows the R_h distributions of the two PEO samples in the NaOH solution (pH = 9.6) measured *via* DLS. PEO-20K exhibits a single peak at approximately 4.6 nm, which is close to 4.1 nm calculated from the equation of $R_h = 0.0145M_w^{0.571 \pm 0.009[42]}$. Meanwhile, PEO-200K shows two peaks at 12 and 290 nm, respectively. The first peak at 12 nm shows a fast mode corresponding to the random coils of PEO. Based on the above equation, its R_h is about 15.2 nm and exhibits some difference with experimental results, and possible reason is due to the different experimental conditions. Whereas the second peak at 290 nm presents a slow (or interdiffusion) mode corresponding to the aggregates or clusters of the PEO chains in the solution^[43]. However, only a few aggregates exist in the solution. We cannot detect any peak in hundreds nanometer as a number or volume distribution. It is found that both the R_h and the amount of aggregates formed in solution remain very stable during three days.

R_h of SiO_2 Nanoparticle Suspensions

The nanoparticles are usually stable in their stock solutions and possibly aggregate during the dilution procedure. Therefore, all SiO_2 suspensions were filtered using 0.22 μm filters to remove the dust and aggregations prior to the experiments.

The DLS measurements of SiO_2 nanoparticle suspensions with different concentrations are displayed in Fig. 2. Only a single peak at 12 nm was observed in the range of 0.0005 g/mL to 0.004 g/mL, indicating undetectable aggregates in the solution. On the other hand, the zeta potentials of these suspensions keep at -35 mV at pH = 9.6. This result signifies that the surfaces of SiO_2 nanoparticles have lots of negative charges which prevents the aggregation of SiO_2 nanoparticles and leads to good dispersion. In addition, the R_h distributions widen with increasing concentrations, implying possible stronger interactions at higher concentrations due to more particles per volume unit.

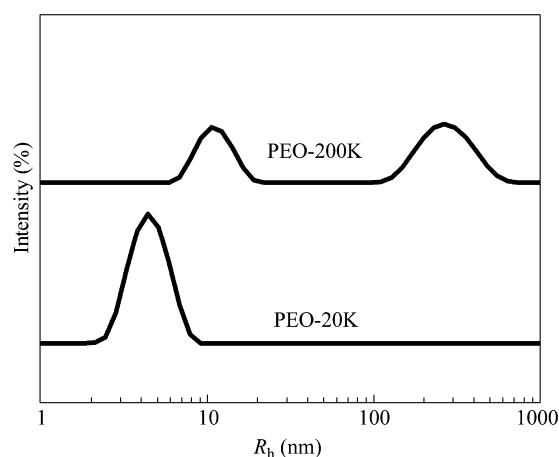


Fig. 1 R_h distributions of PEO-20K (0.005 g/mL) and PEO-200K (0.005 g/mL) in the basic solution at pH = 9.6

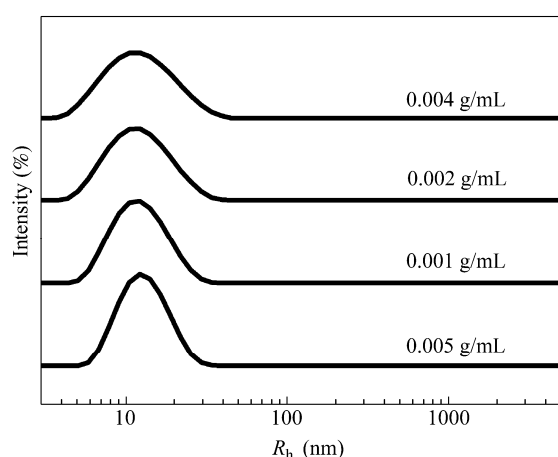


Fig. 2 R_h distributions of SiO₂ nanoparticle suspensions with different concentrations at pH = 9.6

Qualitative Investigation on Interaction between PEO Chains and SiO₂ Nanoparticles via Dynamic Light Scattering (DLS)

The above results show that only random coils exist in the basic solution for PEO-20K, whereas random coils and aggregates coexist in the solution for PEO-200K. Hence, the interactions between the PEO-20K and SiO₂ nanoparticles in the basic solution at pH = 9.6 are first studied using DLS.

(I) Mixture of PEO-20K with SiO₂ nanoparticles via Method I

Figure 3 shows the R_h distribution of the PEO-20K (0.005 g/mL) mixed with SiO₂ nanoparticles at different concentrations. The original peak for PEO-20K (0.005 g/mL) at 4.6 nm nearly disappeared, and new broader peaks appeared at 23 nm and 20 nm for PEO-20K-SiO₂ (0.002 g/mL) and PEO-20K-SiO₂ (0.004 g/mL), respectively (Figs. 3a and 3b). If no interaction occurs between polymer and SiO₂ nanoparticles at pH = 9.6, the PEO-20K-SiO₂ mixtures will keep their original peaks. However, the appearance of a new broader peak indicates that a certain interaction existed between the PEO-20K and SiO₂ nanoparticles.

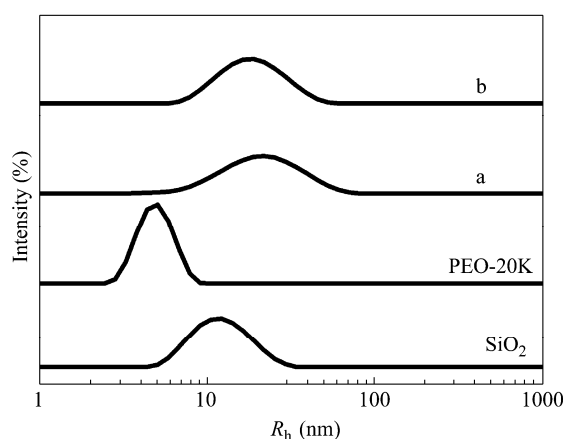


Fig. 3 R_h distributions of PEO-20K mixed with SiO₂ nanoparticle suspensions of different concentrations: (a) mixture of PEO-20K (0.005 g/mL) with SiO₂ (0.002 g/mL) and (b) mixture of PEO-20K (0.005 g/mL) with SiO₂ (0.004 g/mL)

Although the extent of the interaction between the PEO-20K and SiO₂ nanoparticles is unknown, this kind of interaction is known to be mainly from hydrogen bonding, which is also influenced by comprehensive factors

(attractive polymer–particle interactions, repulsive particle–particle and polymer–polymer steric interactions)^[8]. Generally, a hydrogen bond is a direct attractive interaction between an electron-deficient hydrogen atom and a region of high-electron density. This bond is much weaker than covalent or other polar bonds but is stronger than the van der Waals interaction. In the PEO-20K-SiO₂ system, there are many donors and acceptors from segments of PEO-20K and hydroxyls on the surface of silica nanoparticles. Moreover, a relatively moderate interaction mechanism exists at pH = 9.6^[8]. Therefore, SiO₂ nanoparticles can easily interact with PEO-20K in the sodium hydroxide solution *via* attractive interactions, and new PEO-20K-SiO₂ complexes can be rapidly formed.

(II) Mixture of PEO-200K with SiO₂ nanoparticles via Methods I and II

Considering that the random coils and aggregates of PEO-200K coexist in the basic solution, two methods for mixing the PEO-200K and SiO₂ nanoparticles were designed. In Method I, the PEO-200K solution with a concentration of 0.005 g/mL is mixed with SiO₂ suspensions at two different concentrations. As shown in Figs. 4(a) and 4(b), new broader peaks appeared at 35 nm and 36 nm for PEO-200K-SiO₂-2 and PEO-200K-SiO₂-4, respectively. These peaks are different from the original peaks of either PEO-200K at 12 nm and 290 nm or SiO₂ at 12 nm. Definitely, the addition of SiO₂ nanoparticles caused the original PEO-200K peak at 12 nm to disappear mostly because of adsorption of PEO chains on the surfaces of the SiO₂ nanoparticles. Furthermore, the aggregation behavior of PEO-200K changed since the original aggregates of PEO were disaggregated. When the interaction between the PEO chains and SiO₂ nanoparticles is stronger than the PEO-200K aggregation itself, the aggregates of PEO start to separate. If the concentration of the SiO₂ nanoparticles is high enough (such as ≥ 0.002 g/mL), the aggregates of the PEO are nearly destroyed, leading to a new peak at 35 nm for the PEO-200K-SiO₂ complexes, as shown in Fig. 4.

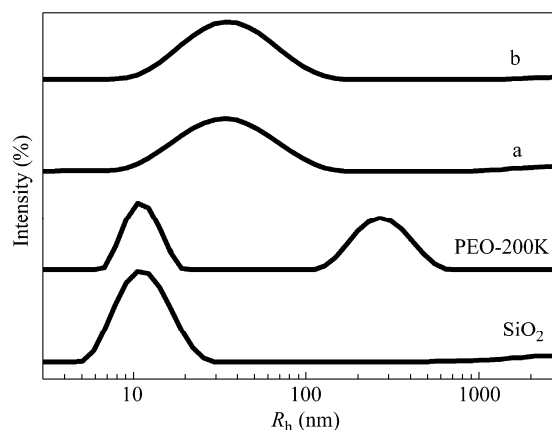


Fig. 4 R_h distributions of the PEO-200K solution mixed with different SiO₂ nanoparticle suspensions *via* Method I: (a) PEO-200K-SiO₂-2 (0.002 g/mL) and (b) PEO-200K-SiO₂-4 (0.004 g/mL). The PEO-200K concentration was 0.005 g/mL.

In Method II, PEO-200K is directly dissolved into the SiO₂ suspension. For the SiO₂ nanoparticle suspensions with concentrations ranging from 0.002 g/mL to 0.004 g/mL, original peak at 290 nm from aggregates of PEO-200K was not observed. Moreover, new peaks appeared with an average R_h of 72 nm as shown in Fig. 5. However, a few residual aggregates (290 nm) are still observed for the mixture with SiO₂ suspensions of 0.0005 g/mL and 0.001 g/mL, and broader peaks can be seen (Figs. 5a and 5b, respectively). Evidently, the broader peaks came from both the PEO-SiO₂ complexes and aggregates of PEO. The latter can be disaggregated *via* hydrogen bonding after adding more SiO₂ nanoparticles. Higher concentrations of SiO₂ suspensions in mixtures provide more SiO₂ interactive sites with PEO-200K, and thus, more SiO₂ nanoparticles can take part in destroying the aggregates. The above DLS results demonstrate that the disaggregation depends on the concentration of SiO₂ nanoparticle suspension, that is, higher concentrations of SiO₂ nanoparticles have

stronger effects on aggregation behavior.

It seems that addition of SiO₂ nanoparticles readily changes the coordinating situation of PEO chains and disaggregates the aggregates of PEO. However, we can adjust the interaction of PEO and silica nanoparticles and further control aggregation state of PEO only through changing the concentration of SiO₂ nanoparticle suspension.

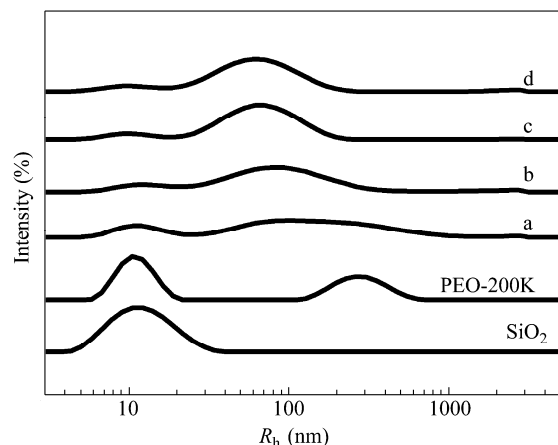


Fig. 5 R_h distribution of the solid PEO-200K dissolved in different concentrations of SiO₂ nanoparticle suspensions *via* Method II: (a) PEO-200K-SiO₂-II-1 with 0.0005 g/mL of SiO₂, (b) PEO-200K-SiO₂-II-2 with 0.001 g/mL of SiO₂, (c) PEO-200K-SiO₂-II-3 with 0.002 g/mL of SiO₂ and (d) and PEO-200K-SiO₂-II-4 with 0.004 g/mL of SiO₂. The PEO concentration was fixed at 0.005 g/mL.

Quantitative Investigation on Interaction of PEO Chains and SiO₂ Nanoparticles *via* Isothermal Titration Calorimetry (ITC)

ITC directly measures the thermodynamic parameters and binding affinities of any type of molecular interaction in solutions^[44, 45]. Furthermore, it provides important information on the surface saturation amount (Γ_{satn}), the segmental heat of adsorption (ΔH_{ads}) and monolayer or multilayer adsorption of the PEO-SiO₂ system in the current study. Together with the above DLS results, it provides details on the interaction between the SiO₂ nanoparticles and PEO.

Figure 6 shows the raw ITC data and the resulting heat evolved per injection of PEO-20K-SiO₂, where 0.003 g/mL of PEO is titrated with 0.0046 g/mL of SiO₂ suspension. The heat evolved per injection finally reached a plateau at zero, indicating a monolayer adsorption^[35]. The density of SiO₂ is approximately 2.2 g/cm³, and its surface area is 220 m²/g, so the surface saturation amount (Γ_{satn}) calculated for PEO-20K-SiO₂ is approximately to be 0.30 mg/m².

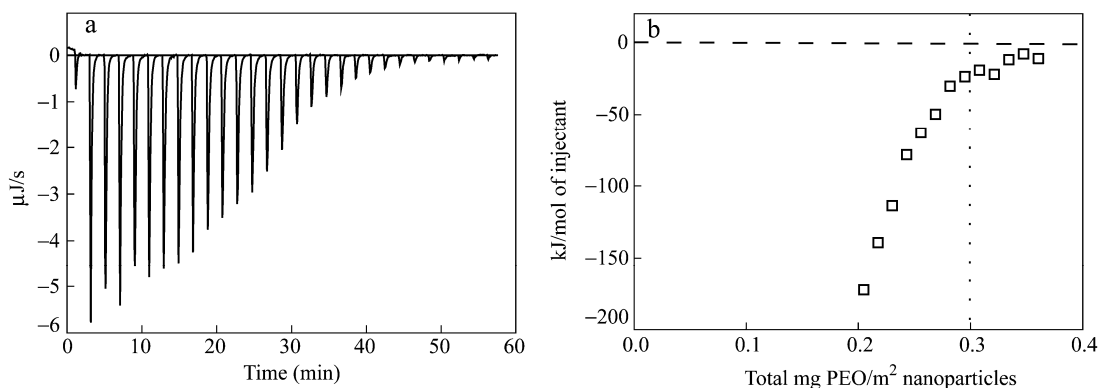


Fig. 6 (a) Raw ITC data for PEO-20K-SiO₂ in the basic solution at pH = 9.6; (b) Heat evolved per injection of PEO-20K-SiO₂ in the basic solution at pH = 9.6

For PEO-200K-SiO₂, the surface saturation amount is approximately to be 0.29 mg/m² (Fig. 7b), and no significant change in Γ_{satn} was observed with increasing PEO molecule weights in the two systems. This result agrees with Wagner's results that the surface saturation amount does not depend on the molecular weight of PEO adsorbed on the particles^[35]. The surface saturation amount is an important parameter that determines the size and size distribution of polymers and nanoparticle in a system^[38]. PEO can adsorb on the surfaces of SiO₂ nanoparticles *via* hydrogen bonding, and the thickness (δ) of the saturated layer on larger nanoparticles equals the free radius of the macromolecules in the solution. According to the ITC results, the molar ratio of the saturation adsorption can be calculated approximately to be 30/1 for PEO-20K-SiO₂ and 3/1 for PEO-200K-SiO₂. Actually, according to the previous DLS measurement, the minimum molar ratio in mixed system is 600/1 and 60/1 for PEO-200K-SiO₂ and PEO-20K-SiO₂ respectively, higher than the above results. Thus, SiO₂ nanoparticles are actually fully saturated with the PEO molecular chains when the interaction between the PEO and SiO₂ nanoparticles reaches an equilibrium state and residual PEO chains exist in the solution. Based on the value of $R_h/R_g = 0.665$ ^[46], the radii of the gyrations of PEO-20K and PEO-200K are about 7 nm and 18 nm, respectively. Thus, the hydrodynamic sizes of the complexes are approximately 19 nm and 30 nm for PEO-20K-SiO₂ and PEO-200K-SiO₂, respectively. These results are nearly consistent with the above DLS results, *i.e.* 20 nm and 35 nm.

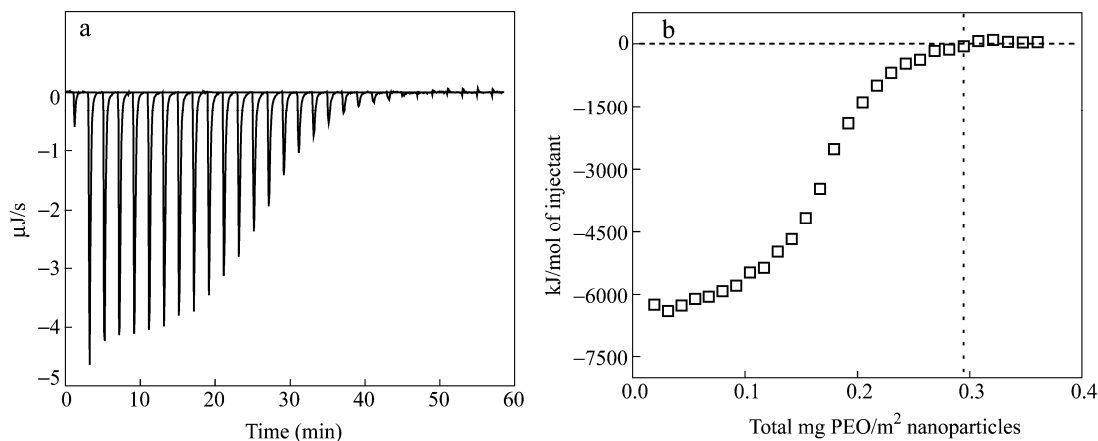


Fig. 7 (a) Raw ITC data for PEO-200K-SiO₂ in the basic solution at pH = 9.6; (b) Heat evolved per injection of PEO-200K-SiO₂ in the basic solution at pH = 9.6

Moreover, the significant difference in the sizes and size distributions of the PEO-200K-SiO₂ systems prepared *via* Methods I and II (Figs. 4 and 5) can be explained by the following reasons^[38]. For Method I, numerous PEO molecular chains exist in the mixed solution, with each SiO₂ nanoparticle rapidly saturated by the PEO chains before it binds with other SiO₂ particles. Compared with Method I, Method II provides the possibility of binding SiO₂ particles before they are fully covered with PEO chains and before bigger particles are formed. As shown in Fig. 5 curves c and d, R_h is about 70 nm, which comes from the interaction among SiO₂ nanoparticles that are not fully covered by PEO-200K. According to Denoyel's study^[47], the segmental heat of adsorption of PEO-200K on SiO₂ nanoparticles *via* Method II can be further calculated by combining the heats of adsorption (-6279 kJ/mol) from the ITC results, as shown in Fig. 7(b). For the current system, the segmental heat of adsorption for PEO-200K on SiO₂ nanoparticles is about $0.55 K_B T$, which is less than the thermal energy $K_B T$. Therefore, the formation of peaks in Figs. 5 curves c and d mainly results from the depletion interaction instead of the bridging process. Our result is also certified by other literature^[35].

From both DLS data and ITC results, we find that the mixing methods have a dominant effect on the size and size distribution of the resultant complexes. A concise schematic illustration is shown in Fig. 8 to illustrate the interaction process between PEO chains and silica nanoparticles under different mixing methods.

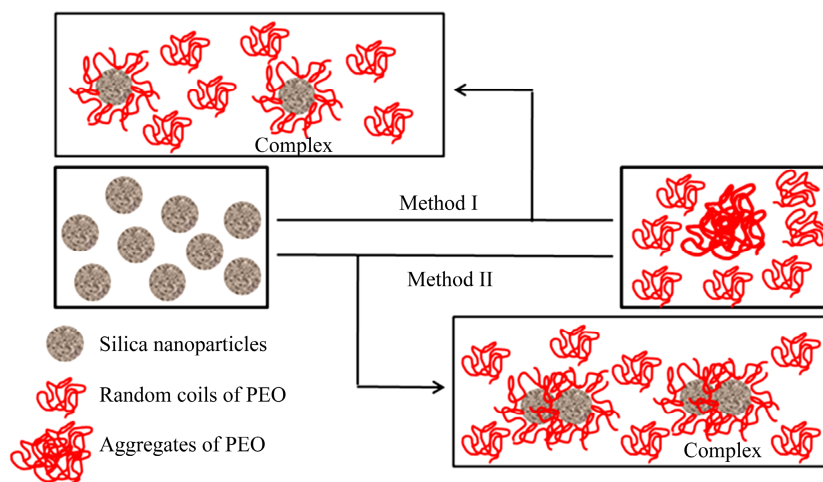


Fig. 8 Schematic illustration of interaction process

CONCLUSIONS

The interaction between PEO chains and SiO₂ nanoparticles in a dilute basic solution was investigated using DLS and ITC techniques. The qualitative results from DLS showed that silica nanoparticles could interact with random coils of PEO, and disaggregate the aggregates of PEO to form steady new PEO-SiO₂ complexes through hydrogen bonding. The concentrations of SiO₂ nanoparticles dramatically affected the interaction between PEO and silica nanoparticles, and the degree of disaggregation in the mixed solution. We can adjust the aggregation state of PEO only through changing the concentration of SiO₂ nanoparticle suspension. In addition, the size and size distribution of the resultant complexes were significantly affected by the type of mixing methods. For our PEO-SiO₂ complexes, it may be developed for providing different aggregation states of PEO to study its effect on unusual rheology of dilute aqueous solutions of PEO which is related with the aggregation state of PEO such as the turbulent drag reduction, and help us to well explain the corresponding mechanism^[23]. Moreover, the ITC results also certify quantitatively the interaction between PEO and SiO₂ nanoparticle, and give the evidence of formation of PEO-SiO₂ complex.

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