

Research Article

Adsorption of Polyanion onto Large Alpha Alumina Beads with Variably Charged Surface

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Adsorption of strong polyelectrolyte, poly(styrenesulfonate), PSS, of different molecular weights onto large α -Al₂O₃ beads was systematically investigated as functions of pH and NaCl concentrations. The ultraviolet (UV) absorption spectra of PSS at different pH and salt concentrations confirmed that the structure of PSS is independent of pH. With the change of molecular weight from 70 kg/mol (PSS 70) to 1000 kg/mol (PSS 1000), adsorption amount of PSS increases and proton coadsorption on the surface of α -Al₂O₃ decreases at given pH and salt concentration. It suggests that higher molecular weight of PSS was less flat conformation than lower one. The adsorption density of PSS 70 and PSS 1000 decreases with decreasing salt concentrations, indicating that both electrostatic and nonelectrostatic interactions are involved. Experimental results of both PSS 70 and PSS 1000 adsorption isotherms onto α -Al₂O₃ at different pH and salt concentrations can be represented well by two-step adsorption model. The effects of molecular weight and salt concentration are explained by structure of adsorbed PSS onto α -Al₂O₃. The influence of added SDS on the isotherms is evaluated from the sequential adsorption. The SDS uptake onto α -Al₂O₃ in the presence of hemimicelles can prevent the adsorption of PSS at low concentration so that adsorption of PSS reduces with preadsorbed SDS.

1. Introduction

Removal of organic pollutant is important for water and wastewater treatment in environmental concerns. Among numerous removal techniques for organic pollutants from water, adsorption is one of the most commonly used technologies that can be applicable for developing countries by using cheap adsorbents [1–3]. Recently, the removal of organic contaminants by adsorption from aqueous solutions using solid surface modified with ionic surfactant or polymers (polyelectrolyte) has attracted intense studies [4–10]. Therefore, adsorption of surfactant and polyelectrolyte from aqueous solution on solid surface has been a topic of a lot of researches [11–14]. The adsorption of surfactants and polymers was carried out individually or in mixtures (simultaneous or sequential adsorptions). In general, adsorption of surfactants and polymers in aqueous media can be additive, cooperative, or competitive [15]. Esumi et al. [16] reported the

adsorption of poly(styrenesulfonate) (PSS) with anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant hexadecyltrimethyl ammonium chloride (HTAC) from their binary mixture on positively charged surface of α -Al₂O₃. The results indicated that adsorbed amount of PSS decreased with increasing SDS concentration due to stronger adsorption of SDS, while in the PSS-HTAC system adsorption of PSS was enhanced due to the formation of a complex of PSS-HTAC. The effect of order of addition of ionic surfactants was intensely study by this work. In addition, the adsorption of PSS with different molecular weights on α -Al₂O₃ was studied by Blokhus and Djurhuus [17]. The adsorption of PSS with different molecular weight was found to increase with increasing ionic strength and adsorption density of PSS was more effective in higher molecular weight than the lower ones. The paper [17] also indicated that the effect of added SDS and showed that SDS was preferentially adsorbed from both simultaneous and sequential adsorptions so that

in all cases SDS displaces preadsorbed PSS from the solid surface. Very recent study demonstrated that the presence of PSS and PDADMAC (polydiallyldimethylammonium chloride) effectively prevented different surfactants adsorption on high surface area alumina and silica by blocking charged adsorption sites [18]. Only PSS appears to irreversibly adsorb onto metal oxides surface because of multisite adsorption and kinetic limitations while the adsorption of surfactant is almost completely prevented at concentration higher than critical micelle concentration (CMC).

As mentioned above, polyanion PSS was chosen in various studies for coadsorption with surfactant because it has a high charge density statistically distributed along the backbone of polymer and the benzenesulfonate groups that are strong ultraviolet (UV) chromophores [19]. The individual adsorption of PSS and surfactants or mixture adsorption on metal oxide has been addressed through different measurements of adsorption density, zeta potential, fluorescence spectrophotometry, electrospin resonance (ESR), and attenuated total reflection techniques with ultraviolet or infrared spectroscopy [16–19]. Furthermore, Wolterink et al. [20] indicated that the charge regulation of metal oxide upon adsorption of strong electrolyte was obtained theoretically and experimentally. The self-consistent field (SCF) calculation showed the large effect of pH and the small effect of the salt concentration to the adsorbed amount while the proton coadsorption was dependent on both pH and salt concentration. However, the measured adsorption isotherms of PSS on hematite did not show a high affinity character as theoretical calculations because of fast flocculation and nonequilibrium polymer conformation. The effect of salt concentrations and the influence of added ionic surfactant have not been investigated experimentally in the paper [20]. It is preferable to make a study using relatively large metal oxide beads which are free from flocculation and can be directly used for analysis of transport phenomena of polymer and surfactant.

In this paper, the results of adsorption isotherms of PSS onto large α -Al₂O₃ beads with variably charged surfaces are analyzed thoroughly. The adsorption isotherms of PSS of different molecular weight onto α -Al₂O₃ as functions of pH and NaCl concentrations are fitted by general isotherm equation [21]. Proton adsorption upon the uptake of different molecular weights of PSS is evaluated at different salt concentrations. The structures of adsorbed PSS are proposed on the basis of adsorption isotherm and effect of surface charge. The effect of the presence of SDS on the adsorption of PSS will also be investigated.

2. Experiments

2.1. Materials. High purity (99.5%), alpha alumina beads with an average diameter of $300 \pm 12 \mu\text{m}$ and a density of 3.82 g/cm^3 were purchased from Hiraceramics, Japan, and were used in the present study. X-ray diffraction (XRD) was collected on a Bruker D8 Advance X-ray diffractometer. The analyses confirmed that the alumina beads contain mainly α -phase. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method using a surface area analyzer (Micromeritics, Gemini VII 2390) and found to

TABLE I: Critical micelle concentration (CMC) of SDS at 22°C.

NaCl (M)	CMC (mM)
0	6.0
0.001	5.5
0.01	5.0
0.05	2.5
0.1	2.0
0.2	1.0

be $0.0041 \pm 0.0016 \text{ m}^2/\text{g}$. This value is comparable to that by geometric consideration. The alpha alumina was treated before measurements as follows: the original α -Al₂O₃ was washed many times with 0.1M NaOH before rinsing by ultrapure water to reach neutral pH. After that, α -Al₂O₃ was dried at 110°C and was reactivated by thermal treatment at 550°C for 2 h. Finally, material was cooled in a desiccator at room temperature and stored in a polyethylene container.

A streaming potential technique was applied to evaluate the surface charging behavior by characterizing the zeta potential of α -Al₂O₃ beads without adsorption. A Zeta CAD (CAD Instrument, France) was used in this study. The details of experimental procedure of streaming potential with Zeta CAD was described in our previously published paper [22]. The treated α -Al₂O₃ has a point of zero charge (PZC) or isoelectric point (IEP) about 6.7.

Sodium poly(styrenesulfonate), PSS, with molecular weights of 70 and 1000 kg/mol was delivered from Aldrich Chemical Co., Inc., with a degree of polymerization of 340 and 4850, respectively. Sodium dodecyl sulfate, SDS (with purity higher than 95%), from Wako Pure Chemical Industries was used. The critical micelle concentration (CMC) of SDS at 22°C was experimentally determined by conductometric and potentiometric measurements and shown in Table I. The chemical structures of PSS (a) and SDS (b) are shown in Figure 1. Ionic strength and pH were adjusted by the addition of NaCl (Wako Pure Chemical Industries) and HCl and NaOH (volumetric analysis grade, Wako Pure Chemical Industries). Other chemicals were obtained from Wako. Ultrapure water, produced from Elix Advantage 5 (Millipore) with electric conductivity around $0.6 \mu\text{S/cm}$, was used in preparing solutions and in all measurements.

2.2. Adsorption Isotherm. Adsorption of PSS onto α -Al₂O₃ was carried out in 100 mL Erlenmeyer flasks at room temperature, controlled by an air conditioner ($22 \pm 2^\circ\text{C}$), using a depletion method. For each adsorption experiment, 0.5 g of the treated α -Al₂O₃ was mixed with 25 mL of NaCl aqueous solutions at different concentrations by a shaker for 1 h. Then, PSS with concentrations from 0.05 mg/mL to 0.6 mg/mL was prepared and pH was adjusted to original value. After shaking for 3 h, the pH was measured again and, if necessary, readjusted by 0.01 M HCl or 0.1 M HCl and 0.1 M NaOH using a Socorex Acura 825 micropipette with minimum volume of $1 \mu\text{L}$. More than 12 h later the samples were equilibrated by vigorous shaking. Then, the pH was checked and, if necessary, readjusted again. This procedure

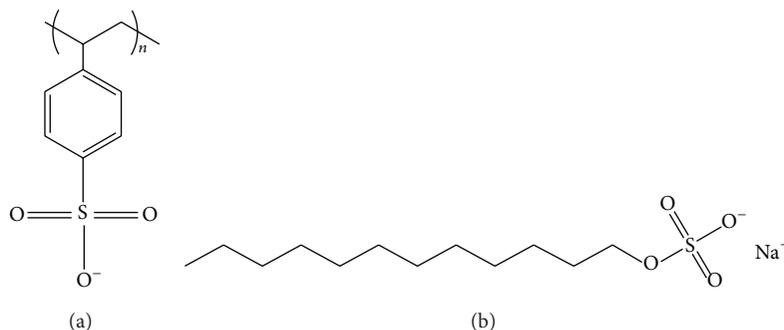


FIGURE 1: The chemical structures of PSS (a) and SDS (b).

was repeated until no further changes in pH were attained. When equilibrium process was achieved, the $\alpha\text{-Al}_2\text{O}_3$ was separated from the solutions. The adsorption density of PSS (Γ_{PSS}) onto $\alpha\text{-Al}_2\text{O}_3$ was obtained by the difference in the concentration of PSS solutions before and after adsorption by spectrometric method. By recording the added amount of HCl or NaOH to keep the pH constant after PSS addition, the surface charge adjustment of alpha alumina has been obtained. The surface charge adjustment was combined with initial surface charge of alpha alumina by chromatographic method [22] to calculate the equilibrium surface charge expressed as $\Gamma_{0,\text{PSS}} = \sigma_{0,\text{PSS}}/F$ with F the Faraday constant.

In order to evaluate the effect of preadsorbed SDS on PSS adsorption, SDS was firstly equilibrated with $\alpha\text{-Al}_2\text{O}_3$ at the concentration of 1 mM of SDS in 0.01 M NaCl (pH 4). Thereafter PSS was added in the concentration range of 0.05–0.6 mg/mL at pH 4. Samples were taken for analysis PSS by spectrometry after shaking solutions for 24 h.

2.3. Spectrophotometric Method. The concentration of anionic polymer PSS was measured by spectrophotometry at wavelength 261 nm or 224 nm (according to the results in Section 4.1) using an UV-vis spectrophotometer (UV-1650PC, Shimadzu) with quartz cuvettes with 1 cm optical path length. All standard calibration curves of PSS in different electrolyte concentrations and pH have a correlation coefficient of at least 0.999. Samples were directly measured or appropriately diluted before measuring the absorbance to quantify PSS concentrations by standard calibration curves.

2.4. Potentiometric Method. Potentiometric methods were conducted using a Metrohm 781 pH/Ion meter, Switzerland. The pH of NaCl solutions used in adsorption isotherm and determination of the concentration of proton in solutions was measured by a glass combination electrode (type 6.0258.010 Metrohm). The electrode was previously calibrated with three standard buffers (Metrohm). The critical micelle concentration (CMC) of SDS in different electrolyte concentration was determined with a surfactant ion selective electrode (type 6.0507.120 Metrohm) that is sensitive to ionic surfactants [23, 24]. The electrode potential (E in mV) was measured relative to an Ag/AgCl reference electrode (type 6.0726.100 Metrohm) equipped with a ceramic plug. The CMC of

SDS in pure water and NaCl background solutions can be obtained from the inflection point after the linear range of the curve, presenting E as the function of the logarithm of SDS concentration [25]. The values of CMC are listed in Table 1.

3. General Isotherm Equation

3.1. Theory and Modeling. The obtained isotherms were also fitted by general isotherm equation that was firstly derived by assuming that adsorption on solid-liquid interface occurs in two steps [21, 26]. It was originally derived to describe the adsorption of hemimicelle-forming surfactant. The general isotherm equation is

$$\Gamma = \frac{\Gamma_{\infty} k_1 C (1/n + k_2 C^{n-1})}{1 + k_1 C (1 + k_2 C^{n-1})}, \quad (1)$$

where Γ is amount of PSS adsorbed, Γ_{∞} is the maximum adsorption, and k_1 and k_2 are equilibrium constants for the adsorption of monomers or first layer adsorption and clusters of n molecules. C denotes the equilibrium PSS concentration in the bulk solution.

Although the formation of micelle-like structure is not expected in the case of polyelectrolyte adsorption, polymers can adsorb in a cooperative manner to form cluster. The effect of such structure can be described by the parameter n [27].

3.2. Fitting Procedure. The selected fitting parameters are described in the following. (a) Γ_{∞} can be obtained from adsorption data at high PSS concentrations. (b) The values of k_1 can be predicted from the adsorption data at low concentrations by a limiting Langmuir equation. (c) By using reasonable guesses for k_1 in step (b) and k_2 (with fixed one value of n), the calculation of the adsorption density Γ_{cal} for SDS or proton by (1) was calculated from experimental data points of C . (d) Procedure was repeated with 0.1 step change of n . (e) The trial and error method was used to find the minimum sum of square of residuals for every isotherm, $\text{SS}_{\text{residuals}} = \sum (\Gamma_{\text{cal}} - \Gamma_{\text{exp}})^2$, where Γ_{exp} is the experimental adsorption density of SDS or proton. (f) The minimum $\text{SS}_{\text{residuals}}$ was chosen to find the appropriate values for parameters k_1 , k_2 , and n .

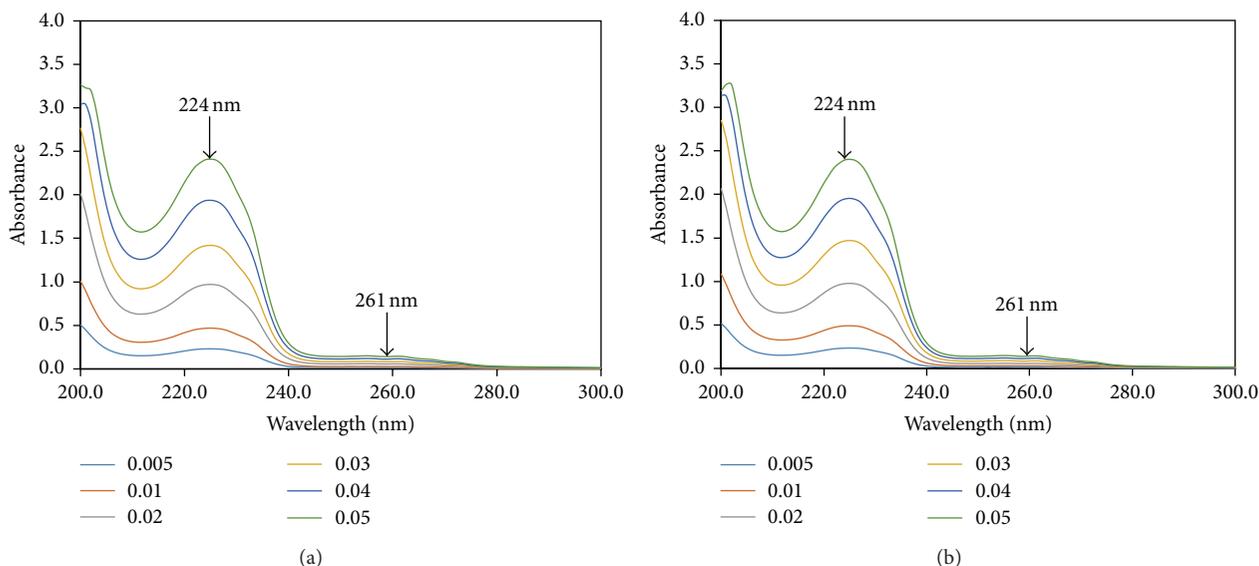


FIGURE 2: UV spectra of PSS 1000 with different concentrations at pH 4 (a) and pH 5 (b) as a function of wavelength in 0.01 M NaCl.

4. Results and Discussion

4.1. Spectra of PSS in the Absence and Presence of SDS. A typical ultraviolet (UV) absorbance spectrum of individual PSS with the concentrations ranged from 0.005 to 0.05 mg/mL is shown in Figure 2. At different pH values, the spectra of PSS in the wavelength region of 200–300 nm have the same shapes with the main absorbance peaks at the wavelength of 224 nm and the secondary peak at 261 nm. Although the intensity of a maxima at 224 nm is greater than that at 261 nm (about 18 times), these peaks are specific wavelengths for benzene sulfonate group. They are in good agreement with the values of maximum absorbance in published papers [17, 19]. Figure 2 also shows that the magnitude of all UV spectra of PSS does not change significantly at a given concentration of PSS. It demonstrates that the dissociation of monomers and structure of PSS is independent of pH [28]. At different salt concentration, the same results are also obtained (not shown here). In other words, PSS can be confirmed as strong polyelectrolyte by UV spectroscopic method.

It should be noted that SDS does not absorb ultraviolet light in the region. The UV spectra of PSS in the presence of SDS are similar to others in the absence of SDS (not shown in detail). Thus, SDS does not contribute to two peaks mentioned above. Adsorbed PSS in the absence and the presence of SDS can be quantified by measuring absorbance at 224 nm and 261 nm peaks with the standard calibration curves (see Experimental Section 2.2). Figure 3 indicates the standard calibration curves of PSS1000 in the absence and the presence of SDS (1 mM and 8 mM) at pH 4 and 0.01 M NaCl. As can be seen in Figure 3, the standard calibration curves of PSS1000 from 0.05 to 0.5 mg/mL with and without SDS have a similar slope with a correlation coefficient of at least 0.999. Again, these curves demonstrate that the effect of SDS to UV method in determining PSS is negligible. These are also helpful to examine the effect of SDS on the process of

TABLE 2: The fit parameters for the adsorption of PSS 1000 and PSS 70 at pH 4 which are maximum adsorbed amount $\Gamma_{\infty, \text{PSS}}$, the equilibrium constants $k_{1, \text{PSS}}, k_{2, \text{PSS}}$ for first layer and multilayer, respectively, and n the number of clusters of polyelectrolyte molecules.

C salt (M NaCl)	Mw (kg/mol)	$\Gamma_{\infty, \text{PSS}}$ (mg/m ²)	$k_{1, \text{PSS}}$ (m ² /mg)	$k_{2, \text{PSS}}$ (m ² /mg) ^{$n-1$}	n_{PSS}
0.01	1000	52	1.1	450	4.5
0.01	70	41	1.0	410	4.2
0.1	1000	60	15	500	4.9
0.1	70	44	10	400	4.6

adsorption and desorption because the concentration of PSS can be directly determined without any separation.

4.2. Adsorption Isotherms of PSS. The adsorption isotherms of PSS with different molecular weight onto large $\alpha\text{-Al}_2\text{O}_3$ beads at two salt concentrations are shown in Figure 4. As can be seen, the adsorption of PSS appears to have the typical high affinity that is close to literature data on adsorption of polyanion PSS on positively charged surface $\alpha\text{-Al}_2\text{O}_3$ [17] or hematite [29]. Although the difference of molecular weight induces the difference in isotherms, the calculated curves fitted by (1) with the fit parameters shown in Table 2 can represent experimental data well. The plateau adsorption increases with increasing the molecular weight of PSS from 70 to 1000 kg/mol at different salt concentrations. At high salt concentration (0.1 M NaCl), the isotherm of PSS 1000 always appears above that of PSS 70. These results are in good agreement with published paper [17] in which absorbed amount for higher molecular weight grows up from 70 to 500 kg/mol. Due to the different structure of adsorbed layer, the conformation for PSS 70 is more flat than PSS 500. However, a further increase from 500 to 1000 kg/mol does not cause an increase of adsorption because the flat conformation

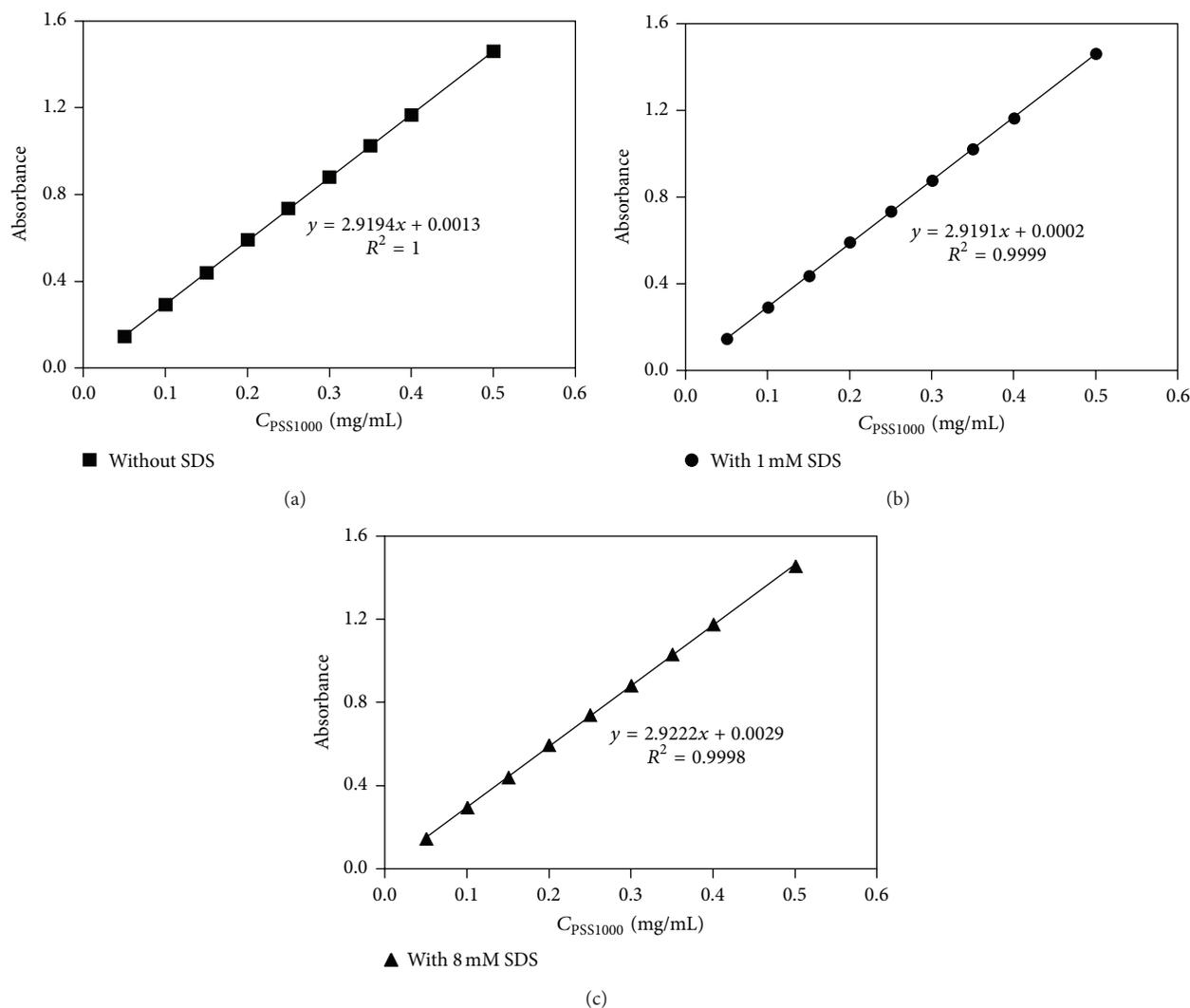


FIGURE 3: The standard calibration curves of PSS 1000 without SDS (a), with 1 mM SDS (b), and with 8 mM SDS (c) at pH 4 and a wavelength of 261 nm in 0.01 M NaCl.

of PSS 500 and PSS 1000 is almost the same. The effect of molecular weight can be evaluated from the difference in the fitting parameters and the isotherms shown in Table 2 and Figure 4 which show that the influence of molecular weight is significant at high salt (Figure 4(b)) rather than at low salt (Figure 4(a)). At two salt concentrations, the higher molecular weight is, the higher value of n is. It suggests that a more flat conformation of adsorbed PSS 70 than that of PSS 1000.

Adsorption amount of PSS with different molecular weights onto $\alpha\text{-Al}_2\text{O}_3$ reaches very high level due to the cooperative manner to form cluster as well as multilayer in the structure of adsorbed PSS. Therefore, the formation of PSS can be described by parameter n of the general isotherm equation. Also, the high adsorption of PSS onto $\alpha\text{-Al}_2\text{O}_3$ can be a result of incomplete dissolution of polymer and its precipitation.

At different salt concentration, the change of pH can be obtained as a function of equilibrium concentration of

PSS. The proton adsorption isotherms upon PSS uptake shown in Figure 5 seem to be remained when the equilibrium concentration of PSS is above 0.10 mg/mL. Polyelectrolyte with different molecular weight caused the difference in charge adjustment especially at low salt concentration (Figure 5(a)) while this is not significant at high salt concentration (Figure 5(b)). Figures 4 and 5 show that the plateau adsorption amounts of polymer appear at about 0.4 mg/mL of PSS but the maximum adsorption amounts of proton are obtained at 0.15 mg/mL of PSS. It is suggested that the first layer of adsorbed polymer can screen the surface charge. The cooperative adsorption to form multilayer does not influence the change of pH or surface charge. Thus, above 0.15 mg/mL of PSS, the multilayer adsorption of PSS seems to be more significant than that at low concentration of polymer. Also, it may be indicated that the charge adjustment could be one factor to evaluate the flat conformation based on molecular weight as mentioned above. However, the adsorption amounts of proton are too small to be compared

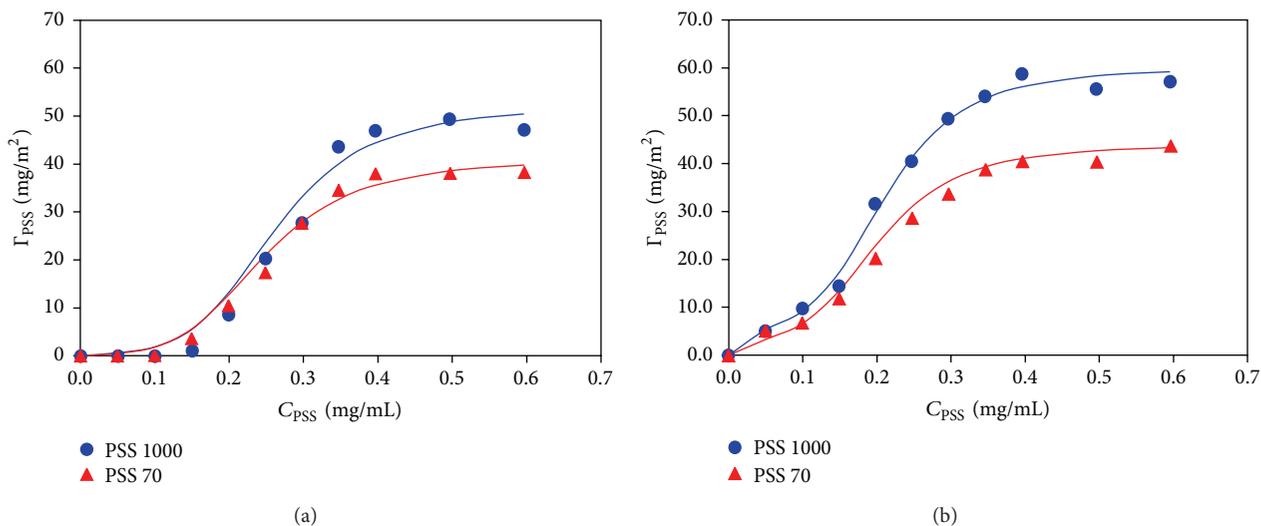


FIGURE 4: Adsorption isotherms of PSS onto α -Al₂O₃ of different molecular weight at pH 4 in 0.01 M NaCl (a) and 0.1 M NaCl (b) as a function of the equilibrium PSS concentration. While the points are experimental data, the solid lines fitted the results by general isotherm equation.

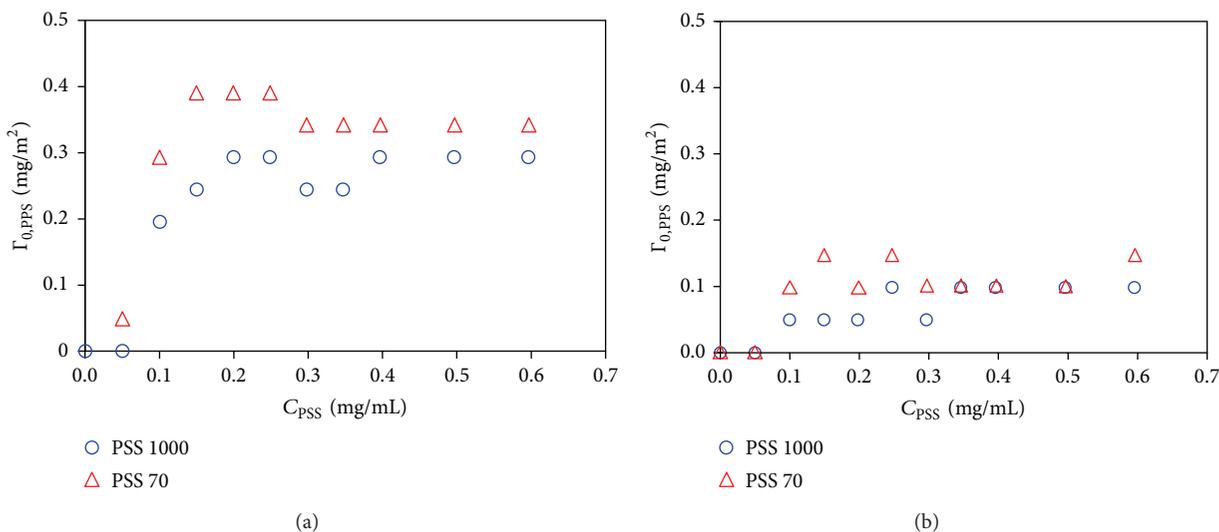


FIGURE 5: Proton adsorption isotherms upon the adsorption of PSS onto α -Al₂O₃ of different molecular weight at pH 4 in 0.01 M NaCl (a) and 0.1 M NaCl (b) as a function of the equilibrium PSS concentration.

with adsorption amounts of PSS (lower than 100 to 200 times). Therefore, it is difficult to explain this effect. Thus, we can suggest that although the proton adsorption isotherms upon PSS adsorption have to be considered, the initial surface charge of α -Al₂O₃ probably seems to be more important for contribution to adsorption.

As mentioned in our published paper [22], the surface charge of α -Al₂O₃ is strongly dependent on both pH and ionic strength. Thus, it is necessary to emphasize the effect of electrostatics interaction at different pH and salt concentrations. Figure 6 shows the results from the adsorption of PSS 1000 onto α -Al₂O₃ at pH 4 and pH 5 and at two salt concentrations. As can be seen in Figure 6, the adsorption amount of PSS increases with increasing salt concentration at both pH 4 and pH 5, demonstrating that not only electrostatic but also

nonelectrostatic interactions induce PSS adsorption. These results agree well with experimental data in published paper [17], where only plateau adsorption of PSS at fixed pH 6 as a function of NaCl concentration is reported. However, in this work, we successfully described salt effect of the experimental adsorption isotherms at different pH and by modeling with general isotherm equation (1). Table 3 and Figure 6 show that 10 times increase in salt concentrations induces about 13 times in the values of $k_{1,PSS}$ (with both pH 4 and pH 5), while the values of $k_{2,PSS}$ grow up not significantly. It implies that the monolayer adsorption isotherm of PSS expressed by $k_{1,PSS}$ can be used to evaluate the electrostatic and nonelectrostatic interactions. Electrostatic forces and the salt effect on the adsorption are screened at high salt concentration. If the adsorption is promoted by only electrostatic force, the

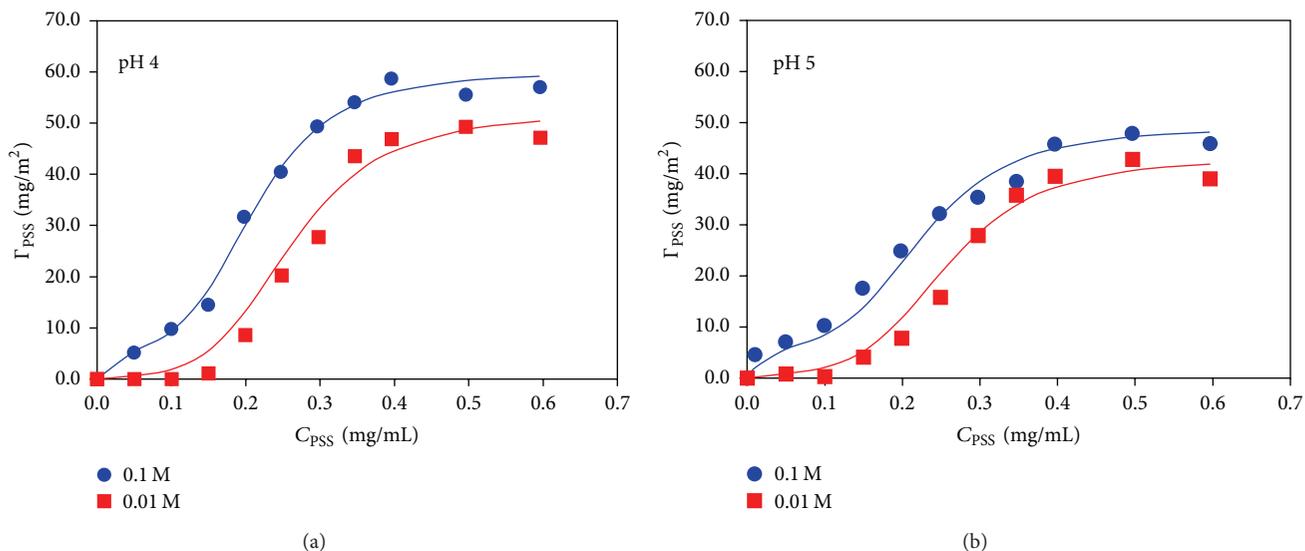


FIGURE 6: Adsorption isotherms of PSS 1000 onto α -Al₂O₃ at pH 4 and pH 5 in 0.01 M NaCl and 0.1 M NaCl as a function of the equilibrium PSS concentration. While the points are experimental data, the solid lines fitted the results by general isotherm equation.

TABLE 3: The fit parameters for the adsorption of PSS 1000 at pH 4 and pH 5 in 0.01 M NaCl and 0.1 M NaCl which are maximum adsorbed amount $\Gamma_{\infty, \text{PSS}}$, the equilibrium constants $k_{1, \text{PSS}}$, $k_{2, \text{PSS}}$ for first layer and multilayer, respectively, and n the number of clusters of polyelectrolyte molecules.

C salt (M NaCl)	pH	$\Gamma_{\infty, \text{PSS}}$ (mg/m ²)	$k_{1, \text{PSS}}$ (m ² /mg)	$k_{2, \text{PSS}}$ (m ² /mg) ^{$n-1$}	n_{PSS}
0.01	4	52	1.1	450	4.5
0.1	4	60	15	500	4.9
0.01	5	43	2	400	4.7
0.1	5	49	25	350	4.9

first layer adsorption or the value of k_1 will be decreased with increasing salt concentration. On the contrary, when nonelectrostatic interaction occurs, the adsorption of highly charged polyelectrolytes is enhanced by addition of salt [30] that is close to our results. Nonelectrostatic interactions which are enhanced by increasing salt concentration can promote the lateral or hydrophobic interactions between PSS molecules [20, 31]. The lateral and hydrophobic interactions can induce more loops and tails as well as the multilayer in the structure of adsorbed PSS on α -Al₂O₃. Therefore, the less flat conformation of PSS and less multilayer of adsorbed structure take place at higher salt concentration than that at low salt concentration. Thus, adsorption amounts increase with increasing salt concentration.

4.3. Effect of SDS on the Adsorption of PSS. The effect of SDS on the adsorption of PSS onto α -Al₂O₃ beads was studied by sequential method (Section 2.2). The adsorption isotherms of PSS 70 in the absence and the presence of SDS are indicated in Figure 7. We can see that the PSS 70 adsorption with preadsorbed SDS seems to be high affinity type when the equilibrium concentration of PSS is higher than 0.2 mg/mL.

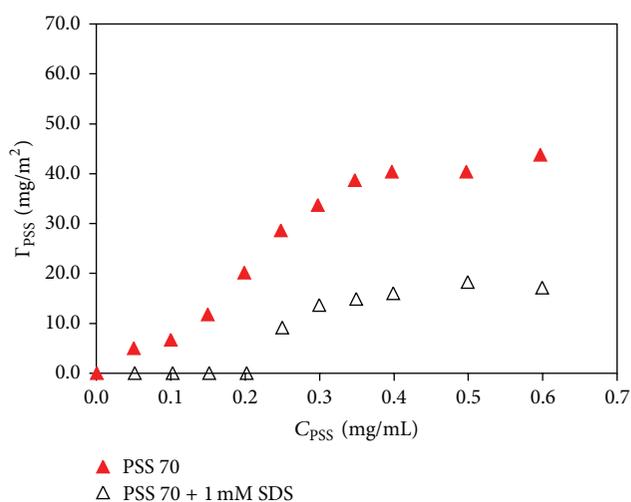


FIGURE 7: Adsorption isotherms of PSS 70 onto α -Al₂O₃ at pH 4 and 0.01 M NaCl without preadsorbed SDS and with preadsorbed SDS (1 mM) as a function of the equilibrium PSS concentration.

A similar trend was also observed for simultaneous adsorption of different molecular weights of PSS on α -Al₂O₃ at low concentration of SDS [17]. At low concentration of SDS than hemimicelle concentration, HMC (HMC of SDS adsorption onto the surface of α -Al₂O₃ is about 1-2 mM) [32], the adsorption of SDS is low so that surface sites for adsorption of PSS are available. In this experiment, the preadsorbed SDS was conducted with 1 mM that was near HMC. Nevertheless, at low concentration of PSS, the adsorption of polyelectrolyte is not significant because the preadsorbed surfactant can prevent the adsorption of polyelectrolyte. It can be suggested that the adsorption of SDS onto alumina is much stronger than that of PSS [16–18].

4.4. Structures of Adsorbed PSS onto α -Al₂O₃. Polyanion poly(styrenesulfonate), PSS, with different molecular weight adsorbed onto α -Al₂O₃ at different ionic strength induced the difference in the structures of adsorbed PSS. As mentioned in Section 4.2, the adsorption amount of PSS 70 is lower than that of PSS 1000 because the conformation for PSS 70 is more flat than PSS 1000. It can be emphasized by the adsorption amount of proton upon the uptake of polyelectrolyte. More protons are adsorbed when the adsorbed PSS has flatter conformation. Even though the adsorption amount of proton is much lower than that of PSS, it is probably useful to explain the structure of adsorbed PSS, suggesting that the less flat conformation can be obtained for PSS 1000 with more loops in adsorbed layer.

An increase in salt concentration also affects the adsorbed structure. By increasing salinity of solution, the adsorption amount increases due to both electrostatics and nonelectrostatic interactions. The electrostatic repulsion among internal segments decreased with increasing salt concentrations. Actually, the adsorption of PSS onto α -Al₂O₃ followed a multilayer manner as deduced from the fitting by two-step model. However, to describe the adsorbed structure of polyelectrolyte on the metal oxide surface, the first layer adsorption is focused. The results from adsorption isotherms of both PSS and proton suggest that more loops in the adsorbed layer of PSS can be formed at high salt concentration than that at low salt concentration.

5. Conclusions

We have investigated the adsorption of poly(styrenesulfonate), PSS, of different molecular weights onto large α -Al₂O₃ beads. The properties of PSS shown as a strong polyelectrolyte were confirmed by UV spectrometry. An increase in molecular weight of PSS from 70 kg/mol to 1000 kg/mol increases the adsorption amount of PSS and decreases proton uptake on the surface of α -Al₂O₃, suggesting that the less flat conformation on the adsorbed structure is expected for higher molecular weight rather than for lower one. The adsorption density of PSS 70 and PSS 1000 increases with increasing salt concentrations, indicating that both electrostatic and nonelectrostatic interactions occur. While electrostatic interactions are screened by increasing salt concentration, nonelectrostatic can induce the lateral and hydrophobic interactions at higher salt concentration. The calculated curves from two-step adsorption model are successfully applied to represent experimental results of both PSS 70 and PSS 1000 adsorption isotherms onto α -Al₂O₃ at different pH and salt concentration. The SDS uptake onto α -Al₂O₃ in the presence of hemimicelles can prevent the adsorption of PSS at low concentration so that adsorption of PSS decreases with preadsorbed SDS.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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