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Adsorption of Poly(diallyldimethylammonium chloride) on Colloid Silica from Water and Salt Solution

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ABSTRACT: The adsorption of poly(diallyldimethylammonium chloride) (PDDA) on colloid silica was investigated as a function of pH, concentration of NaCl, and molecular weight of the polymer. The results obtained indicate that PDDA adsorbs on the colloid surface from water in a flat configuration via the stoichiometric formation of salt linkages between the quaternary ammonium ions in the polymer and the deprotonated silanol groups of the colloid. In the presence of NaCl, however, the adsorbed polymer has a loop configuration, and salt-linkage formation does not follow a stoichiometric relationship. Gel permeation chromatographic studies of the polymer remaining in the supernatant solution after the adsorption also indicate that the polymer adsorbs in a flat configuration from water and in a loop configuration from salt solution. These adsorption characteristics were discussed in connection with the charge and conformation of PDDA in water or salt solution and also with the surface charge of colloid silica.

Although there are numerous studies[1-13] on the adsorption of polyelectrolytes from aqueous solution onto colloid particles, very little has been reported on the stoichiometry[14-16] of salt-linkage formation between oppositely charged colloid and polyion. Recently, Corry[14] demonstrated that the adsorption of low molecular weight poly(L-lysine) on negatively charged polystyrene latices from aqueous solution is stoichiometric at low levels of surface polymer coverage. We also showed that trimethylammonium glycol chitosan iodide (TGCI) [or 6-*O*-(2-hydroxyethyl)-2-(trimethylamino)chitosan iodide] stoichiometrically forms salt linkages with acidic groups of colloid silica[15] and of a carboxylic type ion exchanger.[16] However, these previous papers are limited to describing the evidence for the stoichiometric salt-linkage formation.

The purpose of the present study is to elucidate how the stoichiometry of salt-linkage formation is influenced by the charge and conformation of polyion in aqueous solution and also by the surface charge of colloid particles. Poly(diallyldimethylammonium chloride) (PDDA) was chosen as an adsorbate since the polyelectrolyte properties have been investigated in detail.[17,18] Colloid silica, a nonporous and spherical particle of amorphous silica, was selected as an adsorbent in view of the available information[15,19] on the electrochemical characteristics. The adsorption of PDDA onto silica from water or NaCl solution was investigated under different conditions of pH, ionic strength, and molecular weight of the polymer. The molecular weight distribution (MWD) of the polymer remaining in the supernatant solution after the adsorption was also investigated by gel permeation chromatography (GPC). It became apparent that PDDA adsorbs onto the colloid surface from water in a flat configuration through the stoichiometric formation of salt linkages between the quaternary ammonium ions in the polymer and the deprotonated silanol groups of the colloid. In NaCl solution, however, salt-linkage formation does not follow a stoichiometric relationship because of the adsorption of the polymer in a loop configuration. These adsorption characteristics were discussed by comparing them with those of previous studies[15,17-19] dealing with the polyelectrolyte or colloidal behavior in aqueous solution.

Experimental Section

Materials. Colloid silica was prepared by the method of Heston et al.[20] The diameter of the silica particles was 16 ± 4 nm, as established by electron microscopic analysis. Measurement of the surface area by Brunauer–Emmett–Teller (BET) nitrogen adsorption gave a value of 264 m^2/g. The pH value (3.42) at the point of zero charge was evaluated by potentiometric titration. Silica gel (325 mesh, 554 m^2/g of BET surface area)[21] was also used as a porous adsorbent for comparison with the polymer adsorption characteristics of colloid silica.

The nonfractionated polymer, PDDA(nf), was the same sample as used previously:[17,18] $[\eta]^{25}$ (1 N NaCl), 1.62 dL/g. The fractionation of PDDA(nf) was made by passing through a column of Sepharose CL-6B. A 0.5 N NaCl solution was used as the eluent. The high and low molecular weight fractions obtained were also used in the adsorption experiments that are respectively abbreviated PDDA(hf) and PDDA(lf). The weight-average (M_w) and number-average (M_n) molecular weights for each polymer sample were estimated by GPC: $M_w = 1.56 \times 10^6$ for PDDA(hf), 8.11×10^5 for PDDA(nf), and 3.30×10^4 for PDDA(lf); $M_n = 6.83 \times 10^5$ for PDDA(hf), 7.28×10^4 for PDDA(nf), and 1.60×10^4 for PDDA(lf).

Adsorption Experiment. The sample suspension was prepared by dispersing 0.4 or 0.8 g (as dry weight) of the adsorbents into 200 mL of distilled water or an NaCl solution. The suspension was adjusted to pH 3–8 with 0.1–1 N NaOH or HCl and stirred at 25 ± 0.1 °C in a nitrogen atmosphere until the pH was equilibrated. The PDDA solution (100 mL), adjusted to the pH of the suspension itself, was added into 100 mL of the suspension. The PDDA-added suspension was then stirred at 25 ± 0.1 °C under nitrogen until the adsorption equilibrium was reached. The adsorption from salt solution required more than 6 h to attain equilibrium, while that from water was complete within 5 min (see ref 22). After the adsorption equilibrium was established, the amount of polymer adsorbed was determined by measuring the concentration of the polymer remaining in the supernatant solution by total organic carbon analysis[21] and by colloid titration.[23]

GPC Measurement. The molecular weight distribution (MWD) of the original PDDA or of the polymer remaining in the supernatant solution after the adsorption was examined by GPC. The remaining polymer was isolated by lyophilization of the supernatant liquid. The samples for GPC were prepared by dissolving ca. 0.2 mg of polymer into 1 mL of 0.5 N NaCl solution. The GPC measurements were performed with a Hitachi 635A liquid chromatograph equipped with a Shodex RI detector (Model SE-11) and with a coupled-column system[24] consisting of Shodex OH pak B-806 and B-804 columns, using 0.5 N NaCl solution as the eluent. The GPC curves obtained were analyzed by comparing them with a calibration curve according to the method of Cazes.[25] The calibration curve, determined with standard samples of poly(ethylene oxide), was expressed as $\log M = -0.2537V + 11.31$, where V and M denote elution volume and molecular weight, respectively.

Results and Discussion

The following units were used for expressing the amount (A_p) of polymer adsorbed, the initial (C_i) and equilibrium (C_e) concentrations of polymer, and the adsorbent concentration (C_a): moles of monomer units per 1 g dry silica

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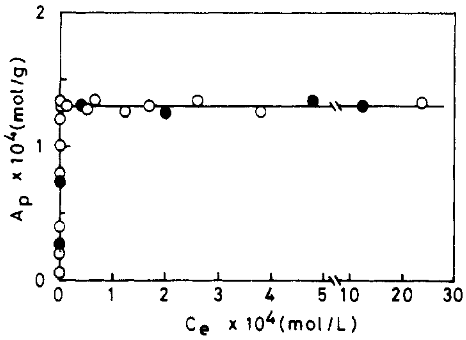

Figure 1. Adsorption isotherm of PDDA(nf) from water onto colloid silica. Adsorption conditions: C_a, 1 g/L (○) and 2 g/L (●); C_i, 5×10^{-6}–2.5×10^{-3} mol/L; pH 6.4.

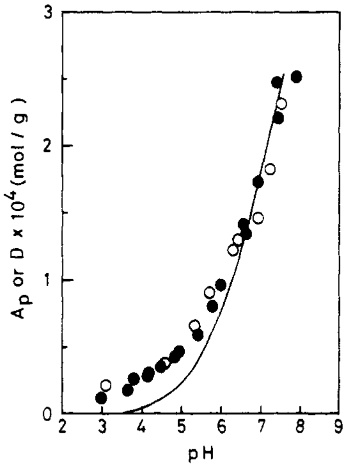

Figure 2. Dependence of A_p and D on pH. The curve of A_p vs. pH (○) for PDDA(nf) was obtained from the adsorption experiments in the absence of salt under the conditions of $C_a = 2$ g/L and $C_i = 1 \times 10^{-4}$–1×10^{-3} mol/L, while that (●) for TGCI was cited from ref 15. The D vs. pH curve (full line) was determined by the potentiometric titration with NaOH for colloid silica suspended into 1 N NaCl solution (see ref 15).

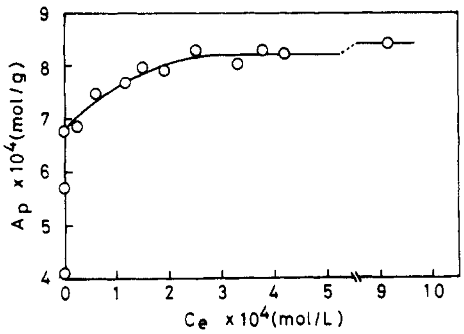

Figure 3. Adsorption isotherm of PDDA(nf) on colloid silica from 0.2 N NaCl solution. Adsorption conditions: C_a, 1 g/L; C_i, 4×10^{-4}–1.76×10^{-3} mol/L; pH 6.4.

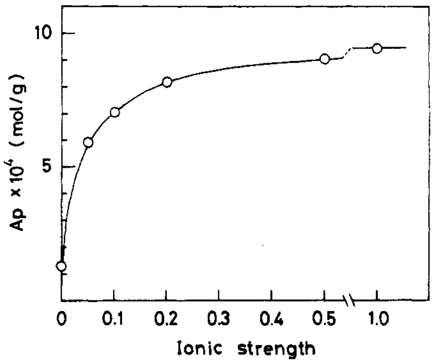

Figure 4. Ionic strength dependence of A_p for PDDA(nf). Adsorption conditions: C_a, 1 g/L; C_i, 2.5×10^{-3} mol/L; pH 6.4. All the values of A_p obtained here could be taken as the adsorption plateau value because C_i is high enough to attain the saturation level of surface polymer coverage.

for A_p, moles of monomer units per liter for both C_i and C_e, and grams of dry silica per liter for C_a. The density (D) of deprotonated silanol groups, which is an indication of the surface charge of colloid silica, was also expressed as moles per 1 g dry silica. This value can be evaluated by counting the number of dissociated protons under conditions where an electrostatic interaction of the protons with the charge of the colloid particles is sufficiently eliminated by the addition of a neutral salt.[15]

Adsorption from Water. In the adsorption of PDDA from water onto silica, aggregation of the adsorbent was observed during the mixing of the colloid suspension and the polymer solution. Nevertheless the values of A_p were reproduced within ±4% for five experiments under the same conditions. A typical adsorption isotherm is shown in Figure 1. The adsorption plateau value (1.30×10^{-4} mol/g) is in fair agreement with the D value (1.24×10^{-4} mol/g) determined at the same pH (6.4). Since the mole number of ionizable groups in PDDA is identical with that of the monomer units, this result suggests that the adsorption takes place through the stoichiometric formation of salt linkages between the quarternary ammonium ions in the polymer and the deprotonated or charged silanol groups of the colloid.

To further investigate the stoichiometry of salt-linkage formation, the pH dependence of A_p was compared with that of D. The result for PDDA is shown in Figure 2, together with that for TGCI, already reported.[15] It is found that at pH > 6 a fair correlation between A_p and D is obtained for both polymers. At pH < 6, A_p is slightly larger than D, which is explained by considering the difference in the methods for evaluating D and A_p. The value of D is obtained by counting the protons dissociated from the silanol groups of the silica particles, while A_p is calculated from the amount of the quaternary ammonium ion bound to the deprotonated silanol groups. Thus, A_p becomes greater than D if the protons are released from the $\equiv SiO^{-+}H$ groups by the ion-exchange reaction with the $^{+}N(CH_3)_2{=}$ ions in PDDA in the course of adsorption. Since at pH < 6 a decrease in pH was observed after the adsorption equilibrium was attained, it is concluded that the salt linkages form between the PDDA cations and the negatively charged silica particles on a stoichiometric basis over a wide range of pH.

From our previous studies[17,18] on the solution properties of PDDA, it has became apparent that in salt-free solutions at different pH values the polymer behaves as a strongly charged rodlike polycation. The stoichiometric formation of salt linkages could be interpreted in terms of the adsorption of the rodlike polyion on the colloid in a flat configuration, as further evidenced below.

Adsorption from Salt Solution. Figure 3 shows an adsorption isotherm at ionic strength 0.2. It is found that the adsorption plateau value (8.41×10^{-4} mol/g) is much larger than that (1.30×10^{-4} mol/g) obtained in the absence of salt. An increase in the level of adsorption caused by the addition of NaCl is further revealed by investigating the dependence of A_p on ionic strength (Figure 4). However, these are in conflict with the results of the electrophoretic studies for both PDDA and colloid silica (Figure 5), which indicate a decrease in the charge of the polyion and of the colloid with increasing ionic strength. It is therefore evident that in the presence of salt the adsorption of PDDA onto silica cannot be treated by

Table I
Values of A_p for Three PDDA Samples at Ionic Strengths (IS) of 0 and 0.2[a]

sample	$A_p \times 10^4$, mol/g IS = 0	 IS = 0.2
PDDA(hf)	1.32 ± 0.02	9.78 ± 0.08
PDDA(lf)	1.29 ± 0.03	7.12 ± 0.06
PDDA(nf)	1.30 ± 0.03	8.41 ± 0.05

[a] Adsorption of PDDA on colloid silica was carried out under the same conditions as described in Figure 4 except for the ionic strength.

considering the stoichiometric formation of salt linkages between the $^+N(CH_3)_2=$ groups in the polymer and the $\equiv SiO^-$ groups of the adsorbent.

To clarify the effect of the presence of salt on the stoichiometry of salt-linkage formation, the results of viscometric measurements for PDDA were also included in Figure 5. A decrease in the viscosity with ionic strength indicates a reduction of the chain expansion of the polymer. This suggests that in salt solution PDDA behaves as a randomly coiled polycation. It is thus reasonable to consider that such a polyion coil adsorbs in the form of loops or tails, which makes it difficult to stoichiometrically form salt linkages between the oppositely charged ions in PDDA and silica.

It is generally believed that when a polymer adsorbs in a loop or tail configuration, the level of adsorption varies depending on molecular weight.[26] To obtain information about the configuration of PDDA adsorbed, the adsorption experiments with the fractionated polymers were also carried out in the presence and the absence of salt (Table I). The values of A_p at ionic strength 0.2 are in the order PDDA(hf) > PDDA(nf) > PDDA(lf), indicating the preferential adsorption of high molecular weight PDDA. From this result, it can be suggested that the polymers adsorbed from salt solution have a loop configuration. In water, on the other hand, no distinguishable difference in the A_p values for three PDDA samples is observed, indicating that the level of adsorption is independent of molecular weight. This fits in with the characteristic of the polymer adsorption in a flat configuration.[26]

Change in MWD of PDDA Caused by the Adsorption. To obtain further information on the configuration of PDDA adsorbed from water or from salt solution, the polymer remaining in the supernatant liquid after the adsorption was analyzed by GPC technique. GPC analysis of the remaining polymer was also carried out in the adsorption experiments in which silica gel was employed in order to learn the difference in the adsorption behavior of PDDA caused by adsorbent porosity.

The M_w and M_n data of PDDA before and after the adsorption are summarized in Table II, together with the M_w/M_n ratio as an indication of MWD. In the adsorption from water onto colloid silica, the agreement between the molecular weight data of the original and remaining polymers is observed. Since this indicates that the level of adsorption is independent of molecular weight, it is proved that the polymer adsorbed from water has a flat configuration.

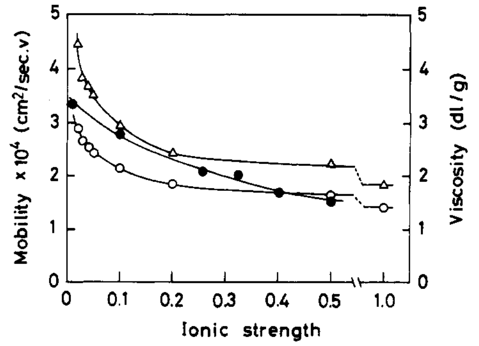

Figure 5. Ionic strength dependence of electrophoretic mobilities for PDDA(nf) (○) and colloid silica (●) and of viscosity for PDDA(nf) (△). Both mobility and viscosity curves for the polymer were cited from ref 17, in which the measurements were done at the polymer concentration range of 0.05–0.2 g/dL with phosphate buffer (pH 7) containing NaCl, and the obtained linear plots of the mobility or viscosity against the concentration were extrapolated to zero concentration. The mobility curve for the colloid particles was also cited from ref 19, in which the electrophoresis was carried out in a buffer solution (pH 8.4) containing NaCl with a Ludox silica AM with surface area 200–235 m^2/g and a diameter of 13.5 ± 0.5 nm.

In the presence of salt, both M_w and M_n of the remaining PDDA(nf) after the adsorption onto colloid silica are lower than those of the original polymer, which shows the preferential adsorption of high molecular weight polymer. Although in the cases of PDDA(hf) and PDDA(lf) such change in the molecular weight data is much smaller because of their narrow MWD (M_w/M_n = 2.1–2.3), the result for PDDA(nf) seems to be strong evidence for the polymer adsorption in a loop configuration from salt solution.

From the results for silica gel, it is found that high molecular weight polymers remain in the supernatant liquid after the adsorption. This can be explained in terms of a steric hindrance effect, which causes the difficulty in penetration of high molecular weight polymers into pores of the gel. Such an influence, owing to porosity of the adsorbent, was not observed in the adsorption of PDDA onto colloid silica. It is thus likely that the PDDA ion adsorbs only on the surface of the colloid particles.

Adsorption Mechanism. It has been demonstrated that the stoichiometric formation of salt linkages between oppositely charged ions in PDDA and silica is closely associated with whether the polyion adsorbs in a flat or loop configuration. The adsorption mechanism might be interpreted by considering the behavior of the polyion in aqueous solution and also the surface condition of the

Table II
Changes in Weight-Average (M_w) and Number-Average (M_n) Molecular Weights of PDDA Caused by Adsorption on Colloid Silica (CS) and Silica Gel (SG) at Ionic Strengths (IS) of 0 and 0.2[a,b]

	before adsorption				after adsorption on CS			after adsorption on SG		
sample	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n	IS	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n	$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n
PDDA(hf)	15.6	68.3	2.3	0	15.5	67.9	2.3			
				0.2	15.0	62.5	2.4	17.5	83.1	2.1
PDDA(lf)	0.33	1.6	2.1	0	0.32	1.7	1.9			
				0.2	0.30	1.5	2.0	0.38	2.0	1.9
PDDA(nf)	8.11	7.28	11	0	8.18	7.30	11			
				0.2	6.91	5.60	12	9.76	12.8	7.6

[a] The molecular weights were determined from GPC curves of the original PDDA and the polymer remaining in the supernatant after the adsorption. [b] All the adsorption experiments were carried out under the conditions of C_a = 1 g/L and pH = 6.4, except C_i was varied in each case so that 50% of the added polymer remained in the supernatant after the establishment of adsorption equilibrium.

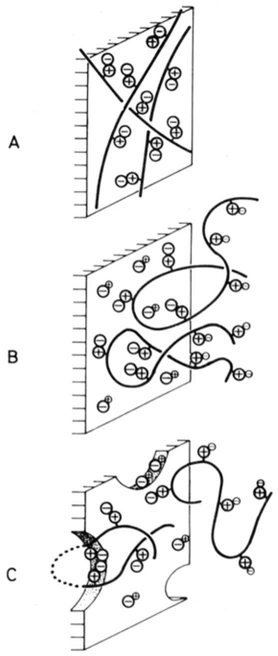

Figure 6. Schematic representations for understanding the PDDA adsorption mechanism: (A) the adsorption on colloid silica in the absence of salt; (B) the adsorption on colloid silica in the presence of salt; (C) the adsorption on silica gel in the presence of salt. The large circled minus sign and circled plus sign represent charged silanol group and quarternary ammonium ion, respectively, while the small circled minus sign and circled plus sign are small anions and cations as counterions, respectively.

adsorbent. The adsorption of PDDA onto colloid silica from water and from salt solution is schematically shown in Figure 6. Additionally, included in Figure 6 for comparison is the scheme for the adsorption onto silica gel from salt solution.

In water, PDDA behaves as a rodlike polycation because of strong mutual repulsion between the polymer-bound quaternary ammonium ions which are dissociated completely in the pH 2 to 12 region.[17,18] The surface of colloid silica is covered with the negatively charged silanol groups in the pH range above the point of zero charge (i.e., pH > 3.42).[15] Thus, the rodlike polycation in water is strongly attracted to the colloid surface and then adsorbed in a flat configuration by forming salt linkages with the surface groups (see A in Figure 6). The present study indicates that the salt-linkage formation follows a stoichiometric relationship. Although at present the exact structure of the salt linkage cannot be described, it is likely that a cationic group bound to the polymer chain forms "a loosely linked ion pair" with an anionic group fixed on the colloid surface, even when they lie considerably far apart.

In salt solution, the charges of PDDA and of colloid silica are reduced by electrostatic interactions with counterions,[17,19] and the polyion assumes a randomly coiled conformation as a result of the weakening chain expansion force.[17] Under such conditions, the attractive force between the colloid and polyion becomes weak. Consequently, the coiled polymer is loosely attached by salt linkages to the colloid surface to form a loop or tail layer (B in Figure 6). Then, the charged silanol and ammonium groups, which do not take part in salt-linkage formation, tend to attract counterions from the solution to keep the electroneutrality. In addition to these electrostatic interactions, an hydrophobic force may play an important part in the adsorption under conditions where the charges of the polyion and colloid are fully eliminated by increasing ionic strength. The sequence of the events described above could bring about the fact that salt-linkage formation between the polyion and colloid does not follow a stoichiometric relationship.

In the adsorption from the salt solution onto silica gel, it is necessary to take into account the steric hindrance effect of polymer chain. When the polyion is attracted electrostatically to the porous surface of the gel, a small coil of the polymer is permeable into pores, but a large one is subject to steric hindrance (C in Figure 6). This could lead to the preferential adsorption of low molecular weight polymer.

Registry No. PDDA, 26062-79-3; NaCl, 7647-14-5; silica, 7631-86-9.

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