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AFM Interaction Study of Poly(ammonium acrylate) Adsorbed on a Si Surface in Aqueous KCl Solution

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Interaction force between solid surfaces in aqueous solvent was investigated using scanning probe microscopy. Only short-range repulsive forces were observed in a poly(ammonium acrylate) (PAA) solution. Their range increased concomitantly with increase of the molecular weight of the PAA. In a PAA solution with 0.1–1 mM KCl, the PAA adsorbed onto the Si substrate. Furthermore, the interaction force was described by DLVO theory, and repulsive force is thought to originate from the steric hindrance of the PAA.

The interaction between solid surfaces in an aqueous solvent can be discussed using Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.[1] However, that between surfaces adsorbing organic polymer cannot be predicted using this classical theory because the electrical double-layer thickness in a solvent is usually much less than that of a polymer adsorption layer.[2] Furthermore, the Hamaker constant and radius of colloids, which are important factors for DLVO theory, cannot be estimated because of polymer adsorption. To analyze these complicated interactions, force curve measurements using scanning probe microscopy have been widely used.[3–6] Biggs measured the repulsive force between ZrO_2 surfaces in poly(acrylic acid) using this approach.[3] The interaction forces are reportedly dependent on the surface coverage of the polymer at the solid–aqueous interface. Kakui et al. investigated the effect of the chemical composition of the polymer for interaction force between solid surfaces in ethanol.[4] We also reported observations of repulsive forces between solid surfaces in poly(ammonium acrylate) (PAA).[5,6] The repulsive force was detected at less than 8 nm. This distance agreed with twice the value of the root-mean-square end-to-end distance of the PAA, which indicates that the PAA adsorbed onto both the substrate and the probe. Moreover, this force originates from the steric hindrance of the polymer adsorbed onto the solid surfaces.

Nevertheless, the effects of PAA properties such as molecular weight and chemical composition and other factors such as the concentration and coexisting ion for the force curve behavior have not been sufficiently evaluated. As described in this paper, the relation between the force curve and the molecular weight of PAA in aqueous KCl solution was estimated.

A 0.1 mass % aqueous poly(ammonium acrylate) solution was prepared from poly(acrylic acid) ($M_w = 5000$, 25000, 250000; Wako Pure Chemical Industries Ltd., Osaka, Japan) and 23 mass % NH_3 aq (Wako Pure Chemical Industries Ltd., Osaka, Japan). The optimum concentration of the polymers was determined in advance using contact angle measurements.[5]

A Si(100) wafer (n-type; Aki Corporation, Miyagi, Japan) was cut into $1 \times 3\,\mathrm{cm}^2$ plates and cleaned using acetone and ethanol. After drying, substrates were immersed in an O_3 atmosphere at room temperature for 1 h to remove organic dirt. The cleaned wafer was soaked in the solutions for 24 h to avoid adsorption–desorption of PAA during force curve measurements. The amount of the aqueous PAA solution was about 60 mL. Force curve measurements were carried out using a scanning probe microscope (SPM; JSPM-5200; JEOL, Tokyo, Japan) with a Si tip ($0.9\,\mathrm{N\,m^{-1}}$ spring constant, $10\,\mathrm{nm}\varphi$ curvature of tip, NSC36/AIBS, Mikromasch, Tallinn, Estonia). The obtained deflection signal vs. z-piezo position was converted into force vs. probe-to-surface separation.[5] The obtained F was normalized by the tip curvature and the viscosity of the liquids.[7]

The potential energy between the tip of cantilever and Si wafer is the total of the van der Waals potential energy (V_{vdW}) and the electrostatic energy (V_{ele}).

$$V_{\mathrm{total}} = V_{\mathrm{vdW}} + V_{\mathrm{ele}} \tag{1}$$

V_{vdW} and V_{ele} are given, respectively, as eqs 2 and 3.

$$V_{\mathrm{vdW}} = -\frac{A_{\mathrm{H}}a}{6D} \tag{2}$$

$$V_{\mathrm{ele}} = -2\pi\varepsilon_0\varepsilon_{\mathrm{r}}{\Psi_0}^2 \cdot \ln[1 + \exp(-D/\lambda_{\mathrm{D}})] \tag{3}$$

Therein, A_{H}, a, D, ε_0, ε_{r}, and Ψ_0 are the Hamaker constant, the curvature of tip, distance, the permittivity of free space, the relative permittivity, and the potential on the surface. Also, λ_{D} is the Debye length as follows.

$$\lambda_{\mathrm{D}} = \sqrt{\frac{\varepsilon_0 kT}{nq^2}} \tag{4}$$

In that equation, k, T, n, and q, respectively, denote Boltzmann's constant, the electron temperature, the electron density, and the electron charge. The summation of the van der Waals potential energy (V_{vdW}) and the electrostatic energy (V_{ele}) is known as DLVO theory.

Previously, the polymer sizes were calculated using the root-mean-square end-to-end distance. However, this calculation was not sufficient to discuss the repulsive force. Therefore, the PAA sizes were estimated using dynamic light scattering (DLS, DLS-6000; Otsuka Electronics Co., Ltd., Osaka, Japan). The obtained results were also verified through comparison with the size estimated using the Stokes–Einstein radius.

Figure 1 presents the relation between the separation distance and the force normalized by the tip curvature. All force curves were measured in ion-exchanged purified water. The pH of all solutions was about 9. This indicates that the effect of the pH was negligible. All force curves show only the repulsive force. For $M_w = 5000$ PAA, the repulsive force was observed as less than 7.5 nm. Ranges observed for repulsive forces increased concomitantly with increasing molecular weight of PAA. To understand the molecular conformation, the PAA size was measured using DLS. The obtained results were also verified through comparison with the size estimated using the Stokes–Einstein radius (Table 1).

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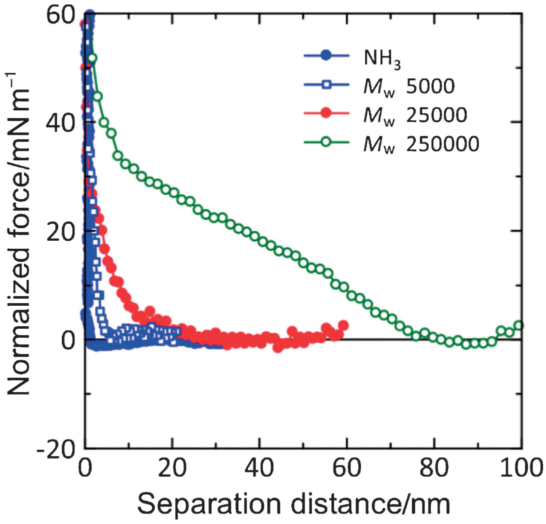

Figure 1. Force curve of the PAA on the Si substrate in ion-exchanged purified water. Average molecular weights of PAA were 5000, 25000, and 250000.

Table 1. Size of the PAA molecules in the aqueous solvent and range observed for repulsive force

M_w	PAA size/nm	Range observed for repulsive forece/nm
5000	7.5	7
25000	16.3	16
250000	55.9	76

The results for PAA sizes of $M_w = 5000$ and 25000 showed fair agreements with the observed repulsive forces. This indicates that the PAA molecules formed a coil and adsorbed onto Si substrate without large deformation. In contrast, the repulsive force of $M_w = 250000$ PAA was slightly larger than the PAA size estimated using the Stokes–Einstein method. Furthermore, $M_w = 250000$ PAA was thought to deform slightly during adsorption on the substrate.

Figure 2a portrays the force curve between the cantilever and the substrate in the $M_w = 5000$ PAA with 0.1–100 mM aqueous KCl solution. The potential energy of the surface between the substrate and the tip of cantilever is also presented in Figure 2b. In 100 mM KCl solution, the attractive force was observed at less than 7 nm. At less than about 5 nm, the interaction force was repulsive. This slight attractive force is considered to originate mainly from van der Waals interaction. Furthermore, the repulsive force was attributed to the steric hindrance of PAA molecules adsorbed onto the solid surface. The PAA size in the 100 mM aqueous KCl solution estimated by DLS was about 7.5 nm, corresponding to the range observed for repulsive force. In the 10 mM KCl solution, the interaction force was not detected at long range because the potential energy was weak at more than 10 nm. At less than 10 nm, the attractive force should be generated at less than 5 nm because of the potential curve. However, the actual measurement shows the repulsive force. The repulsive force is considered to originate from steric hindrance of PAA molecules.

In the 0.1–1 mM KCl solution, long-range repulsive force was observed. These fairly well agreed with the potential energy curve presented in Figure 2b, indicating the interaction between the surfaces in the aqueous solution with a low KCl concentration, as described by DLVO theory. On the other hand, an unknown repulsive force was also observed at about less than 15 and 40 nm for 1 and 0.1 mM, respectively. These forces were not explained using the potential curve illustrated in Figure 2b. Moreover, these distances were larger than PAA sizes. It indicates the interaction between the solid surfaces was also affected by other factors.

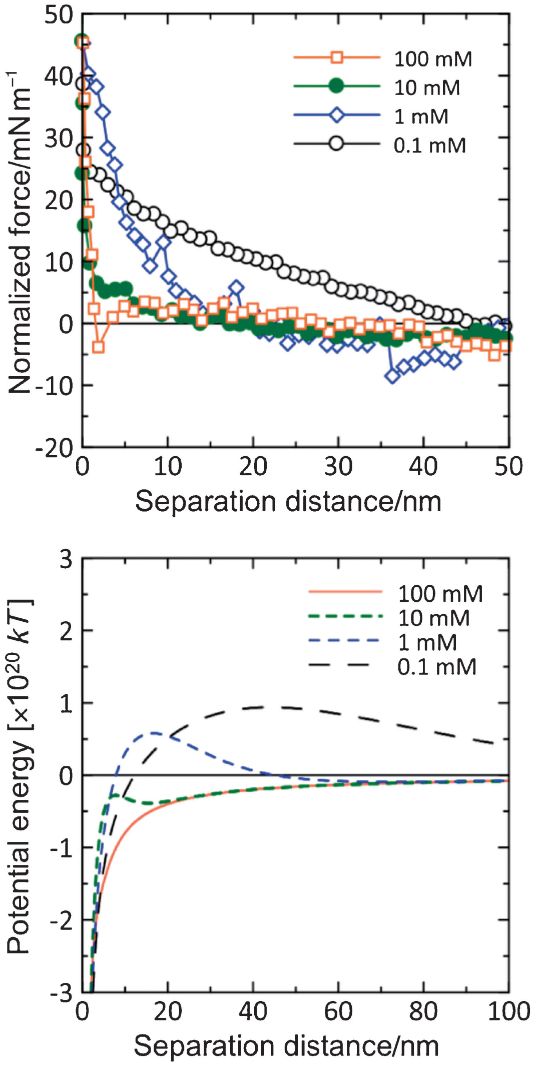

Figure 2. (a) Force curve of the PAA on the Si substrate in the KCl solution and (b) the potential energy calculated using eq 1. Concentrations of KCl were 0.1, 1, 10, and 100 mM.

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