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Electromagnetophoretic Measurements of Adsorption Forces of Polystyrene Microparticles on Silica Surfaces in Surfactant Solutions

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An electromagnetophoretic force has been applied for the measurement of the adsorption force of a single polystyrene particle to a silica surface in electrolyte solutions. By the electromagnetophoretic buoyancy, polystyrene microparticles in a fused-silica capillary were made to migrate perpendicular to the wall of the capillary. A switching of the current direction and a gradual increase of the current under a homogeneous magnetic field of 10 T could desorb the single particle from the wall and allowed us to measure the adsorption force from the desorbing current with a sensitivity of pN. By this method, the adsorption forces of polystyrene particles on a bare surface and on a squalane-coated fused-silica surface were measured in the absence and the presence of surfactants such as Triton X-100, cetyltrimethylammonium bromide, and sodium dodecyl sulfate. The observed adsorption forces showed that the roles of the surfactants included not only the reduction of the adsorption force as a spacer, but also the production of a characteristic force due mainly to electrostatic interaction.

For the characterization and separation of colloidal particles including industrial particles, environmental particles, and living cells, innovative techniques for the measurements of physical and chemical properties of individual particles must to be developed in various fields.[1,2] Especially, the characterization of the particle surface is very important; therefore, the measurement of the force between a particle and a surface of substrate is required. Theoretical descriptions of these forces have been widely studied in the frame of DLVO theory,[3–5] and some measurement techniques have been developed.[6,7] A modern method to directly measure the interaction force between a micrometer-sized particle and a substrate surface is the atomic force microscopy (AFM). In AFM, the interaction force between a particle attached on a cantilever and a surface is measured as a function of the particle–surface distance. As an alternative method, the interaction forces between cell–cell and cell–solid surface have been measured by the cell detachment using a flush shear stress.[8,9]

Recently, we proposed the electromagnetophoresis (EMP) of micrometer-sized particles in an aqueous electrolyte solution for the separation and characterization of various particles.[10,11] The basic theory of electromagnetophoresis has been proposed by Kolin in 1953.[12] The general concept of electromagnetophoresis is an application of the Lorentz force for the electrolyte solution, which causes the migration of dispersed particle. When an electric current is applied through a conductive fluid including a less conductive particle in a homogeneous magnetic field perpendicular to the current, a particle in the conductive fluid migrates perpendicular to both the homogeneous magnetic field and the electric current due to the electromagnetophoretic buoyancy by the Lorentz force on the medium.

In our previous report, we proposed a simultaneous measurement technique of the migration velocity and the particle–wall interaction force applying the electromagnetophoretic force to the particles, which was controlled by the current under a high magnetic field of 10 T.[13] The electromagnetophoretic force was controlled in the range of 10^{-12}–10^{-9} N by the current of up to 1 mA under 10 T. By this method, the adsorption force of microparticles such as polystyrene and carbon to a fused-silica surface was measured in a 1 M KCl solution. The adsorption forces of particles with different nature and size were mainly governed by their van der Waals interactions with the silica wall.

Interaction between colloidal particles dispersed in a surfactant solution has recently been investigated.[14,15] The presence of surfactant had a large influence on the stability of particles in a liquid, that is, on the aggregation of dispersed particles and on the adsorption to a solid surface. In the present paper, we report the novel application of the electromagnetophoresis for the measurements of the adsorption force of polystyrene particles on a fused-silica surface in the absence or presence of surfactants, such as Triton X-100, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). Moreover, the effect of surface modification of the silica surface by a nonpolar hydrocarbon, squalane ($C_{30}H_{62}$), on the adsorption force was investigated.

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Experimental

Sample Preparation. The polystyrene particle was purchased from Funakoshi (Polybeads, Tokyo, Japan). The diameters of polystyrene particles were 10 µm (9.14 ± 0.71 µm), 15 µm (14.6 ± 1.7 µm), and 20 µm (22.0 ± 2.7 µm). In addition, the polystyrene particle with the diameter of 3 µm was used for the measurement of migration velocity. Surfactants used in the present experiments were Triton X-100, cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), as nonionic, cationic, and anionic surfactants, respectively, these are all GR grade of Nacalai tesque (Kyoto, Japan). The polystyrene particles were dispersed in 1.0 M KCl aqueous solution with pH 5.4 containing 0.01% (v/v) Triton X-100, 0.2 mM CTAB, or 0.2 mM SDS, respectively. Concentrations of the surfactants in solutions were all less than the critical micelle concentrations (CMC). The density of the aqueous solutions was $1.05\,\mathrm{g\,cm^{-3}}$, nearly equal to that of polystyrene. Thus, the effect of the buoyancy was neglected in our experiments. The viscosity of 1 M KCl solution was 0.88×10^{-3} Pa s,[16] and the electric conductivity measured by a conductivity meter (CM-40V, TOA, Tokyo, Japan) was $0.112\,\mathrm{S\,cm^{-1}}$ at 25 °C. Polystyrene particles were dispersed in the medium by sonication. Because the final concentration of particles was 4.5×10^6–5.7×10^5 particles $\mathrm{mL^{-1}}$, the amount of surfactants was enough to cover all polystyrene particle surfaces.[17–19]

Silica Surface and Its Modification. The adsorption force of polystyrene particles was investigated for a bare fused-silica and a surface-modified fused-silica using squalane. The square fused-silica capillary (Polymicro Technologies, Phoenix, AZ) had a $100 \times 100\,\mu\mathrm{m}^2$ inner section and a $300 \times 300\,\mu\mathrm{m}^2$ outer section with 2 cm length. In order to make the inner surface of the fused-silica capillary nonpolar, the surface was coated with squalane by the following procedure. First, a fused-silica capillary was filled with toluene solution of 3% (v/v) chrolotrimethylsilane and left for 5 h. After washing by methanol, water, and acetone, the capillary was filled with toluene solution of 5% (v/v) squalane and left for 5 h, and then washed with methanol and water.

Apparatus. The magnetic field was generated by a helium-free superconducting magnet (JMTD-10T100HH1, JMT, Japan), which had a room temperature bore of 100 mm diameter and gave a homogeneous magnetic field up to 10 T. The capillary cell was set on the cell holder in the homogeneous magnetic field in the bore. Both edges of the fused-silica capillary cell were connected with PTFE tubes equipped with Ag/AgCl electrodes, and the sample solution was introduced into the tube by a syringe pump that was set out of the bore. A potentiostat device (HSV1K-60, Metronix) was used to provide the electric current, and the current was measured by an ammeter (Digital-multimeter R6551, ADVANTEST, Japan). The migration behavior of the particles was observed by an optical microscope with a CCD camera (ME421, ELMO, Japan) attached. The CCD images were displayed on a monitor and were also recorded on videocassettes.

Measurements of Adsorption Force. Figure 1 shows a schematic illustration of the adsorption–desorption behavior of a particle in a capillary cell induced by the electromagnetophoretic force. The measurement procedure of the adsorption force is as follows. When a flowing particle appeared in the observing region, the flow was stopped. The particle was once adsorbed on the cell wall by an electromagnetophoretic force. Then, the direction of applied current was switched in order to desorb it by a reversed electromagnetophoretic force. The current was increased from 0 to 1000 µA within several seconds under a fixed magnetic field of 10 T. During the increase of the current, the particle was desorbed from the wall and migrated to the opposite sidewall to adsorb again on it. The current at the time of desorption was measured as the desorption current, i_D. Thus, the desorption and the adsorption of a particle were repeated by switching the direction of the current to repeat the measurement of i_D. The desorption current was measured for several particles by repeating these adsorption–desorption cycles. Then, we calculated the adsorption force from the averaged desorption current. The applied current was kept at less than 1 mA so as to reduce Joule heat generation. All measurements were carried out in a thermostated room at 25 ± 1 °C.

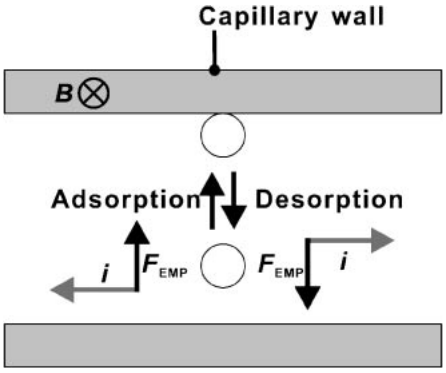

Fig. 1. Schematic illustration of the adsorption–desorption of a particle by electromagnetophoretic force. By applying a current, the particle once adsorbed on the capillary wall was desorbed, and it was adsorbed again to the opposite side wall. Desorption–adsorption cycle was repeated by switching the direction of the current.

Results and Discussion

Electromagnetophoretic Migration of a Particle. Under the situation of a homogeneous magnetic field and an electric current applied orthogonally to an electrolyte solution, the net force of the electromagnetophoretic force, F_{EMP}, on a spherical particle can be written by:[12]

$$F_{\mathrm{EMP}} = 2\left(\frac{\sigma_{\mathrm{p}} - \sigma_{\mathrm{f}}}{2\sigma_{\mathrm{f}} + \sigma_{\mathrm{p}}}\right)\frac{iBV}{S}, \tag{1}$$

where i is the electric current (A), B is the magnetic flux density ($\mathrm{N\,A^{-1}\,m^{-1}}$), V is the volume of the spherical particle ($\mathrm{m^3}$), S is the inner section of the cell ($\mathrm{m^2}$), σ_{f} is the electric conductivity ($\mathrm{S\,m^{-1}}$) of the medium, and σ_{p} is the apparent electric conductivity ($\mathrm{S\,m^{-1}}$) of the particle. The apparent conductivity includes the surface conductivity of the particle. Any electric charges on the surface of particle will produce an electric double layer.[20] Ionic atmosphere around the particles yields the surface conductivity of the particles. Therefore, the apparent conductivity, σ_{p}, reflects the electrostatic surface property of the particle. The apparent conductivity of the particles can be determined from experimentally observed migration velocity using this theoretical equation:

$$v = \frac{4}{9}\left(\frac{\sigma_{\mathrm{p}} - \sigma_{\mathrm{f}}}{2\sigma_{\mathrm{f}} + \sigma_{\mathrm{p}}}\right)\frac{iBr^2}{S\eta C_{\mathrm{W}}{}^2}, \tag{2}$$

where η is the fluid viscosity (Pa s), r is the radius of the spherical particle (m), and C_{W} is the viscous drag coefficient due to

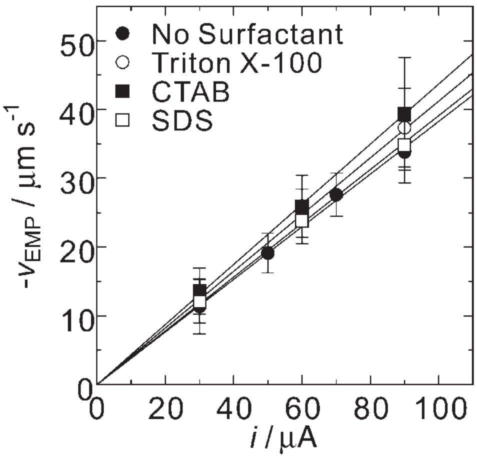

Fig. 2. Electromagnetophoretic (EMP) velocity of polystyrene particles with the diameter of 3 μm in the absence or presence of surfactants, such as Triton X-100, CTAB, or SDS, at various applied currents. The magnetic flux density was 10 T. The aqueous solutions included 1.0 M KCl. From the slopes, the apparent conductivities were determined.

the surface of the capillary wall.[21]

Figure 2 shows the electromagnetophoretic migration velocity of a polystyrene particle whose diameter was 3 μm in the absence or presence of surfactants, such as Triton X-100, CTAB, or SDS. From the results, the apparent conductivities were determined to be 0.0191, 0.0186, 0.0136, and 0.0206 S cm^{-1} for polystyrene particles suspended in a 1.0 M KCl aqueous solution under the conditions of no surfactant, 0.01% Triton X-100, 0.2 mM CTAB, and 0.2 mM SDS, respectively. The apparent conductivity was changed slightly by the adsorption of surfactants on the surface of a particle. The values of the apparent conductivity were used for the calculation of the adsorption force from Eq. 1 with the observed desorption current, i_D.

Desorption Current of Polystyrene Particles. The desorption current of particles was measured after the particles were pinned to the wall by electromagnetophoretic force under the applied current of 1000 μA. Figure 3 shows the histograms for the desorbed numbers of polystyrene particles with 20 μm diameter from the fused-silica capillary surface, when the current was increased by 10 μA steps. The total event numbers were 100 and 121 for 0.01% Triton X-100 and 0.2 mM CTAB systems, respectively. The average value of i_D with no surfactant was 310 μA, as shown in Fig. 3a. On the other hand, the average value of i_D in 0.01% Triton X-100 solution was 163 μA, as shown in Fig. 3b. The value of i_D under this situation was smaller than that with no surfactant. The average value of i_D in 0.2 mM CTAB solution was 300 μA (Fig. 3c), which was agreement with that with no surfactant. The desorption of polystyrene particles in 0.2 mM SDS solution was difficult when the current was less than 1 mA. These results indicated that the desorption current was significantly changed by the adsorption of surfactants on both a particle surface and on the silica wall, and that the desorption current depended on the property of surfactants; smaller for neutral Triton X-100 and larger for anionic SDS.

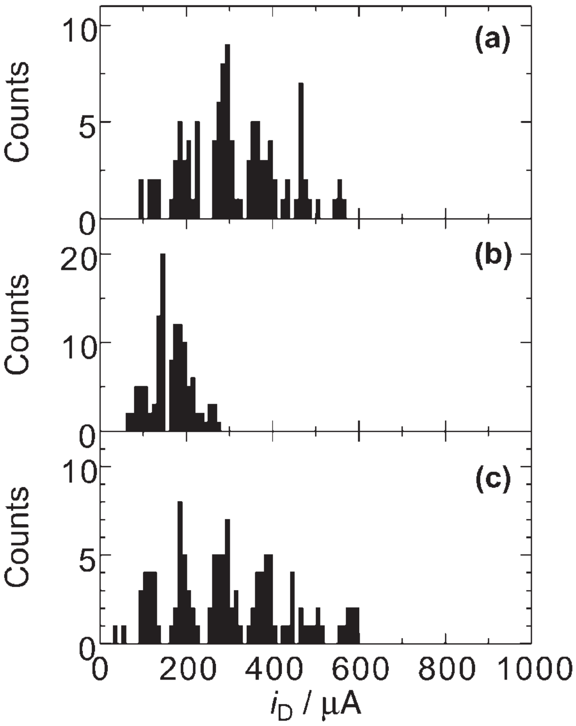

Fig. 3. The histograms of desorption event of polystyrene particles with 20 μm in diameter adsorbed on a fused-silica surface for every increment of the current of 10 μA in a 1.0 M KCl solution containing no surfactant (a), 0.01% Triton X-100 (b), and 0.2 mM CTAB (c). Total numbers of desorption events were 108, 137, and 121 for polystyrene particles with no surfactant, Triton X-100, and CTAB systems, respectively.

Figure 4 shows the histograms for the desorbed number of polystyrene particles with 20 μm diameter from the squalane-coated surface in the medium containing 0.01% Triton X-100 or 0.2 mM CTAB. The polystyrene particles in no surfactant or SDS solution could not be desorbed by a current less than 1 mA. The average value of the desorption currents of 20 μm polystyrene particles was 119 and 253 μA in 0.01% Triton X-100 solution and in 0.2 mM CTAB solution, respectively. The desorption current for a hydrophobic wall was larger than that for an uncoated wall.

Adsorption Force of Polystyrene Particles. Table 1 lists the average values of the adsorption forces of polystyrene particles calculated by Eq. 1 using the apparent conductivity and i_D determined from Figs. 4 and 5. As shown in Table 1, the adsorption force on a fused-silica surface was changed by the presence of surfactants. Neither in the absence of surfactant in the squalane-modified surface or in the presence of SDS in the modified and unmodified surfaces, particles were desorbed by the applied current less than 1 mA. Since the electromagnetophoretic force calculated by Eq. 1 at the current of 1 mA was 3700 and 3100 pN in the absence and presence of SDS, respectively, the adsorption force here should be larger than these values. It has been reported that the attractive force of a polystyrene particle with a solid surface and the force between silica particles covered with CTAB layers could be measured by AFM.[22–25] In comparison with AFM method, which

Table 1. Effect of Surfactants on the Averaged Adsorption Force of Polystyrene Particles with 20 μm in Diameter on the Silica Surfaces or on the Squalane-Coated Silica Surface Calculated from Observed Desorption Currents by Eq. 1

Surfactant	Uncoated silica surface	Squalane-coated silica surface
No surfactant	881 ± 314 pN (3.4 nm)[a]	>3700 pN
0.01%Triton X-100	333 ± 96 pN (5.5 nm)[a]	188 ± 39 pN (7.3 nm)[a]
0.2 mM CTAB	587 ± 269 pN (4.1 nm)[a]	560 ± 283 pN (4.3 nm)[a]
0.2 mM SDS	>3100 pN	>3100 pN

a) The values in parentheses are the calculated adsorption distance by Eq. 3 using 5.5×10^{-21} J as the Hamaker constant.

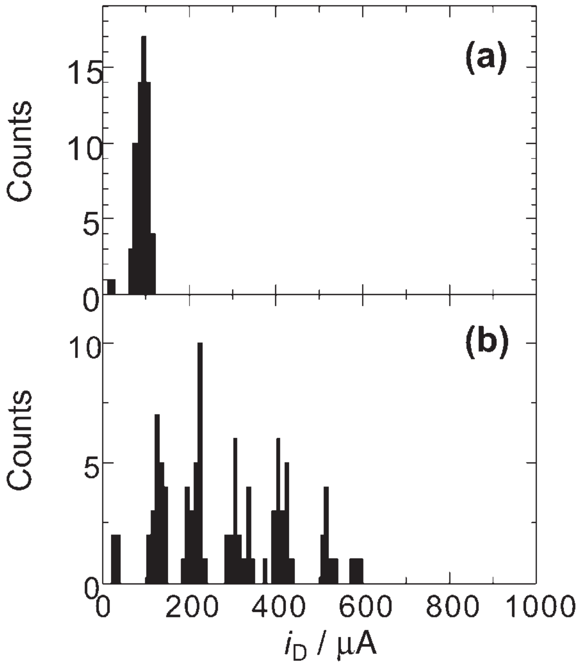

Fig. 4. The histograms of desorption event of polystyrene particles with 20 μm in diameter adsorbed on a squalane-coated silica surface for every 10 μA increment of the current in 1.0 M KCl containing 0.01% Triton X-100 (a) and 0.2 mM CTAB (b). Total numbers of desorption events were 126 and 112 in Triton X-100 and CTAB systems, respectively.

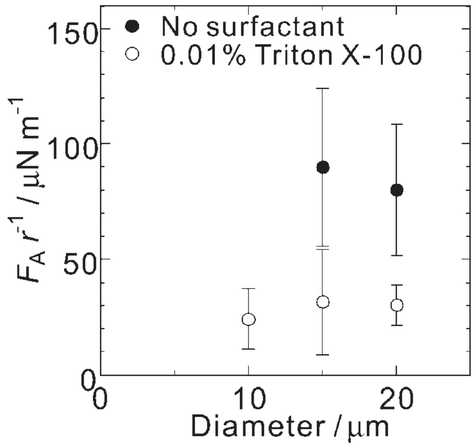

Fig. 5. The adsorption force on a fused-silica surface of polystyrene particles with various diameters in the absence and presence of 0.01% Triton X-100. The adsorption force was normalized divided by the radius of particles.

has the sensitivity of 0.1 nN, our method proved to have a higher sensitivity, of pN order, in the measurement of adsorption force.

DLVO theory explained the interaction force between two surfaces as the combination of van der Waals force and the electrostatic repulsion force. However, in the present experiments, the electrostatic repulsion force should be very small, as the ionic strength of the solution was as high as 1 M. Thermal fluctuations of particles were neglected in the present adsorption–desorption system, because the heat energy of kT (ca. 10^{-21} J) was much smaller than the van der Waals energy characterized by Hamaker constant (ca. 10^{-19} J). Therefore, the adsorption force should be mainly governed by the van der Waals force.

The influence of surface roughness on the interaction force between two surfaces has been studied recently.[26–29] The surface of polystyrene latex spheres included some nanometer-sized asperities and this surface roughness of polystyrene particles affects the van der Waals force in some cases.[26,27,30] However, Suresh and Waltz reported that the size of asperities on polystyrene particles calculated from their experimental results was decreased with increasing ionic strength in the range of 3–7 mM.[27] It can be assumed that the effect of surface roughness on interaction force was small because of 1 M KCl solution used in the present study. Moreover, the fractional surface coverage of asperities is reported to be less than 10%.[26,27] Therefore, we assumed that the effect of surface asperities on the observed adsorption force was not large in our experiments.

The van der Waals force, F_A, between a particle and a flat plate can be represented by,

$$F_A/r = A/6D^2, \tag{3}$$

where r is the radius of the particle (m), A is the Hamaker constant (J), and D is the distance between a flat plate and a particle surface (m).[31] As shown by Eq. 3, F_A becomes smaller when D is larger. Figure 5 shows the normalized adsorption force by the radius, $F_A r^{-1}$, for polystyrene particles with the diameters of 10, 15, and 20 μm on a fused-silica capillary surface in the absence and presence of 0.01% Triton X-100. Triton X-100 reduced the adsorption force most effectively. The 10 μm polystyrene particles were not desorbed under the cur-

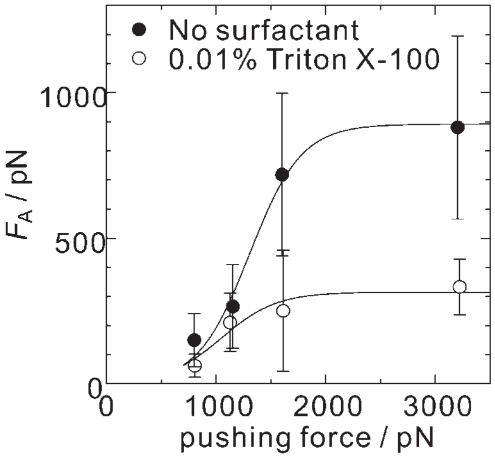

Fig. 6. Effect of pushing electromagnetophoretic force before desorbing the polystyrene particles with 20 µm in the diameter from a fused-silica surface in the absence and presence of 0.01% Triton X-100.

rent less than 1 mA in no any surfactant solution. However, those could be desorbed in Triton X-100 solution. The normalized adsorption forces shown in Fig. 5 were almost constant regardless of the size of particles, as suggested by Eq. 3.

Hamakar constant in the fused-silica–water–polystyrene system was 5.5×10^{-21} J.[31] In this case, the distance, *D*, in the absence of surfactant was calculated as 3.4 nm by Eq. 3 using F_A/r of 107 µN m^{-1} determined from the present study as shown in Fig. 5. Under the condition of 1.0 M KCl, the repulsion force caused by the adsorption of solvated cations on a silica surface is effective at the distance less than about 3–4 nm.[4,32] Thus, the polystyrene particle is thought to be adsorbed at this manner in this situation. Furthermore, it is expected from this calculation that any force larger than $F_A/r = 107$ µN m^{-1} will be attributable to some additional chemical interaction and that any smaller force may be due to the increase in the distance, *D*. The values of separation distance calculated from adsorption force are shown in parentheses in Table 1.

Effect of Adsorbing Force. Figure 6 shows the effect of the pushing electromagnetophoretic force for 20 µm polystyrene particles to the fused-silica wall in the absence and presence of 0.01% Triton X-100 before desorption of the particles. The applied current values for pushing were 250, 350, 500, and 1000 µA, and the magnetic field was 10 T. When the pushing force was increased, the desorption force was also increased. indicating that the adsorption force of the particle depended on the pushing force. In the presence of Triton X-100, the adsorption force was less increased than in the system of no surfactant. Since the adsorption force depends on the adsorption distance, *D*, as shown in Eq. 3, this result indicates that the particle can not approach the silica surface due to the hindrance of the adsorbed Triton X-100, while in the absence of surfactant, the particle can approach closer to the silica surface by removing hydrated potassium ions from the silica surface. The limiting values of *D* estimated by the observed forces and by Eq. 3 are 3.4 and 5.5 nm in the absence and presence of Triton X-100, respectively. When the pushing force is weak, the particle cannot go closer due to the steric interaction of polymer chain and ions adsorbing on the polystyrene surface.

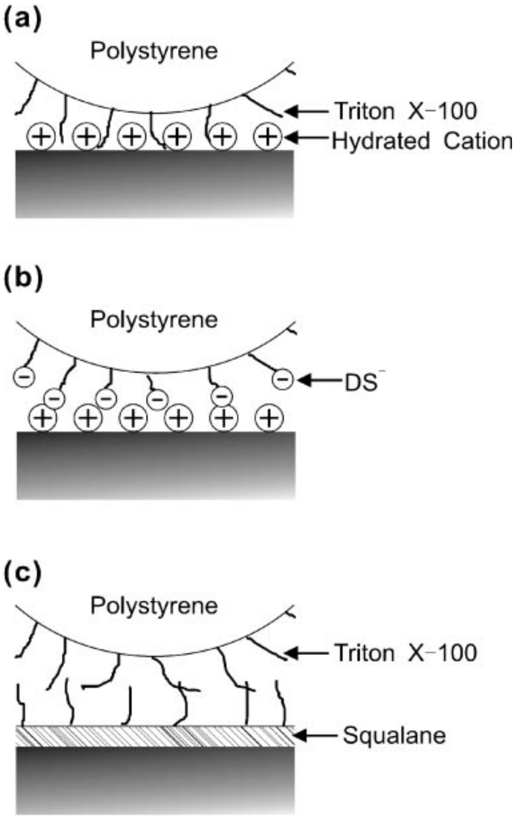

Fig. 7. Schematic illustrations of the adsorption state of a polystyrene particle revealed from the force measurement on a fused-silica surface and a squalane-modified surface in 1.0 M KCl solution. Displayed situations are on the fused-silica surface in Triton X-100 solution (a), on the fused-silica surface in SDS solution (b), and on a squalane-modified surface in Triton X-100 solution (c).

Effect of Surfactants on Adsorption State of Particles. Figure 7 displays the illustration of the adsorption state of polystyrene particles on the silica surface in the presence of surfactants. Triton X-100 reduced the adsorption force. When Triton X-100 was adsorbed on a hydrophobic surface of the particle, the distance *D* should be increased and the adsorption force should be decreased by the hindrance of the surfactant as a spacer, as shown in Fig. 7a. In the case of SDS solution, the adsorption force might become larger due to the electrostatic interaction between the anionic SDS on the particle and the cationic stern layer on a negatively charged silica surface as shown in Fig. 7b.

When the fused-silica surface is modified by nonionic squalane, Hamakar constant is estimated to be 5.9×10^{-21} J, assuming the same situation as for hydrocarbon–water–polystyrene system.[31] As this value is close to that for fused-silica–water–polystyrene system, it is expected that the van der Waals force is not seriously changed by the modification with squalane. On the hydrophobic surface of squalane, no Stern layer of hydrated cation as a spacer is formed and the particles will be able to adsorb more closely. Thus, the van der Waals adsorption force of polystyrene particles becomes larger. On the contrary, the adsorption force is weakened by the presence of Triton X-100 and CTAB. This result should be understood as the result of an increase of the adsorption distance caused by the adsorption of surfactants on both surfaces of a hydrophobic squalane and a polystyrene particle, as illustrated in Fig. 7c. The difference of the adsorption forces between Triton X-100 and CTAB systems should depend on the molecular sizes of the surfactants. Molecular lengths are about 5.1 and 2.3 nm for Triton X-100 ($CH_3(CH_2)_7C_6H_4O(CH_2CH_2O)_{10}H$) and CTAB ($CH_3(CH_2)_{15}N(CH_3)_3Br$), respectively. Triton X-100 molecule is longer than CTAB. This will be the reason why the adsorption distance in Triton X-100 system is longer than that of CTAB, though the actual sizes of the surfactants should be smaller than the estimated lengths, since they are usually entangled. Anyway, the adsorption distances listed in Table 1 increase in the order of no surfactant < CTAB < Triton X-100, suggesting a relationship with the molecular sizes of the surfactants.

In Figs. 3 and 4, fine structures could be found in the histograms, in which every difference is corresponding to about 300 pN. Although the cause of the difference is not clear in the present stage, it may suggest that the rupture of the interaction between the particle and the wall is not continuous phenomena, but discrete and non-continuous phenomena due to the rupture of some individual interactions of hairy polymers on a particle and the active sites on the wall.

Conclusion

We propose a new non-invasive technique for the measurements of desorption or adsorption forces of microparticles to a solid surface in liquids by the use of electromagnetophoretic force. By this technique, the change of the adsorption force of polystyrene particles on a fused-silica surface due to the adsorption of surfactants was observed, on modifying the charge of surfactant and silica surfaces. The adsorption force depended on the size of surfactant molecules. Furthermore, the adsorption force of the particles on the silica surface modified with squalane was increased in the absence of surfactant, but reduced in the presence of Triton X-100 or CTAB. The adsorption force was mainly governed by van der Waals force. The increase of the adsorption force by the squalane modification was attributed to the decrease of the hydrated ions between the particle and the surface, while the decrease of the adsorption force by the surfactants was ascribed to the increase in the adsorption distance expanded by the adsorbed surfactants used as spacers. However, in the case of SDS, the electrostatic interaction between SDS anion and the Stern layer of potassium ions on the substrate increased the adsorption force. From the present study, innovative advantages of the present method were demonstrated; the high sensitivity of pN, order is enough to measure the physical and chemical adsorption forces of microparticles on a substrate surface, and an applicability in any closed liquid system without any contact to the particle as in the case of AFM cantilever. The present technique will be useful to measure the interaction force of a microparticles binding to a solid surface with a single chemical bond or only a few, which is in the range from several pN to sub nN. Therefore, this method will be promising as a nondestructive and noninvasive method of determining the binding properties of the surface of blood cells and any other biological cells.

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