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ORIGINAL CONTRIBUTION

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Direct estimation of the electrostatic interaction between colloidal particle and chemically modified glass surface by the evanescent wave light scattering microscope method

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Abstract The profile of the interaction potential between polystyrene latex particle and chemically modified glass surface was estimated directly by the evanescent wave light scattering microscope (EVLSM) method; this enables us to measure the distance between particle and surface as a function of time in the order of less than a millisecond. The minimum of the potential profile, which is the result of an electrostatic repulsion and an apparent attraction by gravity between the particle and surface, was clearly observed. To change the electrostatic nature, the glass surface was chemically modified by treatment with a silanization reagent and a vinyl monomer with a sulfonate group. As the absolute value of the zeta potential of the glass surface became larger, the position of the potential minimum on the interaction potential profile shifted away from the glass surface, reflecting an increase of electrostatic repulsion between the particle and the wall. The ionic strength dependence of the potential profile was also clearly observed. In conclusion, EVLSM is a powerful tool for the quantitative estimation of particle-wall interactions.

Key words Evanescent wave · Surface modification · Light scattering · Polystyrene latex · Electrostatic interaction

Introduction

In our laboratory, interfacial phenomena and surface structures have been studied in detail by various methods such as X-ray reflectivity (XR) [1–4], atomic force microscopy (AFM), and evanescent wave light scattering microscope technique (EVLSM) [5]. XR measurement is used for structural analysis of the surface and interface in a multilayer system, such as a polymer film and Langmuir-Blodget (LB) lipid monolayer in the order of angstroms. AFM can give us not only 2D surface images, by direct measurement of the intersurface force between scanning tip and investigated objects, but can also be used to estimate particle-wall interaction forces using a particle attached to a cantilever [6]. Using a special property of the evanescent wave, that exists only near the surface [7, 8], EVLSM has been used to estimate the interaction potential between the colloidal particle and glass wall in dispersion systems [9, 10]. Recently, EVLSM has been used for various measurements, such as particle-wall interactions and radiation pressures [11–13]. We constructed an EVLSM apparatus independently [5] following the principle of Prieve et al. [9].

The character of interactions between colloidal particle and macroscopic surface was defined as a function of surface charge densities of the particle, the wall, and the ionic strength of the system. In a previous paper, we have studied the effects of particle charge density and of ionic strength of the dispersion medium on the particle-surface interaction [5, 10]. In this study, we have investigated the interaction potential between polystyrene latex particles and a chemically modified glass surface, using EVLSM to clarify the effect of the charge density of the surface on the interaction.

Chemical modification of the surface was introduced to change the electrostatic nature of the glass surface; sulfonate groups were fixed chemically onto the surface. The relationship between the position of the potential minimum and the surface zeta-potential of the chemically modified glass surface was investigated in detail. Since the effect of gravity is invariant, the shift of potential minimum evaluated by EVLSM reflects the effect of electrostatic forces alone.

Experimental

Brief review of the EVLSM technique

The evanescent wave is a special wave generated by total reflection of light at an interface [14]. Sir Isaac Newton described its existence in his book *Opticks* [15]. Prieve et al. [9, 11–13] proposed an application of the evanescent wave to particle-wall interaction studies. Details of the principle of EVLSM have been described in our previous papers [5, 9].

A schematic illustration of the EVLSM apparatus constructed in our laboratory is shown in Fig. 1. All components were set on a vibration-isolated table. A He-Ne laser ($\lambda = 632.8$ nm) was used in this work. The trapezoidal prism was designed and made of optical glass, BK-7, for the special purpose of generating an evanescent wave. The sample container was made from a glass tube and a glass bottom plate with adhesive, and was attached to the prism with index matching oil.

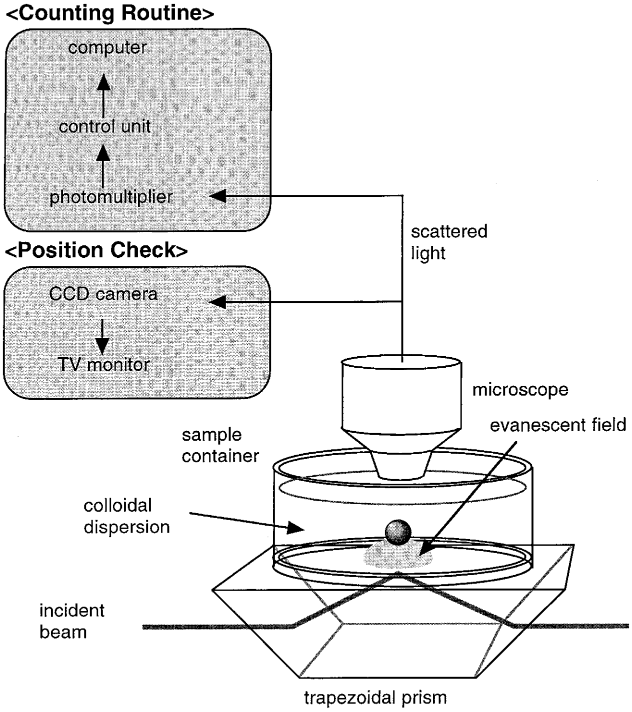

Fig. 1 Schematic illustration of evanescent wave light scattering microscope (EVLSM) apparatus

The incident beam goes into the side wall of the prism. After refraction, it propagates in the prism and then hits the boundary between the colloidal dispersion and the surface of the bottom glass plate of the sample container. The beam is reflected at this interface, and an evanescent wave is produced beyond the boundary, where total reflection occurs. Latex particles near the interface, i.e., in the evanescent field, were irradiated by the evanescent wave and scattered it. The time-fluctuation of scattering intensity from one particle must reflect the time-fluctuation of distance between particle and plane. The scattered light was passed to a photomultiplier (Hamamatsu Photonics, Hamamatsu, Japan) through an optical fiber and counted. The sampling period was 1 ms and 4000 or 8000 data points were collected for each series of measurement. The sampling period used was short enough to show the fast kinetics of particle motion, which cannot be obtained with other methods, such as video observation [16].

Data were collected as scattering intensity in arbitrary units, as a function of time, and converted into an intensity-frequency (number of observations of each intensity) histogram. This histogram was then converted into a potential energy profile, as a function of the distance from the interface/surface [9]. The intensity of scattered light can be translated into the separation distance using Eq. (1).

$$z = \frac{\xi}{2}\ln\left(\frac{I_0}{I_{\mathrm{EV}}}\right), \tag{1}$$

where I_0 is the intensity at the interface, i.e. I_{EV} at $z = 0$, and ξ is the "penetration depth of the evanescent wave", which is a function of the wavelength and incident angle.

When the probability of finding a particle at certain z is represented by a Boltzmann distribution, the potential energy $V(z)$ relative to that at z_0, $V(z_0)$, is given by

$$\frac{(V(z) - V(z_0))}{kT} = \ln\left[\frac{N(I(z_0))I(z_0)}{N(I(z))I(z)}\right], \tag{2}$$

where z_0 is the distance at which the total potential energy is at a minimum, k is the Boltzmann constant, T is the absolute temperature of the system, and $N[I(z)]$ is the observation number at $I(z)$ [9, 17]. The potential is made dimensionless by dividing by kT. The method for determining the absolute separation distance between the particle and the glass surface has described in previous papers [18–20].

Surface modification

Modification of the glass surface was carried out using the procedure of Sun et al. [21] (Fig. 2). 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) was purchased from Tokyo Kasei (Tokyo, Japan). *N*, *N*, *N′*, *N′*-tetramethylethylenediamine (TEMED) and ammonium persulfate (APS) were purchased from Nacalai Tesque (Kyoto, Japan). 3-Methacryloxypropyltrimethoxysilane (MOPS) was purchased from Chisso (Chiba, Japan).

Twelve grams of AMPSA was dissolved in 120 ml Milli-Q grade ion-exchanged water. A concentrated NaOH solution was added to neutralize this acidic solution to pH 7.0; the resulting solution was brought to a total volume of 300 ml with water (NaAMPS solution). The glass plate was washed with KOH saturated ethanol for 2 h before modification. Then the glass plate was placed in a beaker filled with saturated vapor of MOPS for 2 days (step 1). After silanization, the plate was taken out of the beaker and rinsed with water.

About 150 mg APS and 150 μl TEMED were added to the NaAMPS solution; then the silanized glass plate was immersed in the mixed solution (step 2). The degree of surface modification was controlled by the reaction time. After this treatment, the glass plate was rinsed with water and dried.

Results and discussion

Roughness and thickness of the modified layer

The existence of a modified polymer layer and its homogeneity was examined by XR measurement (RINT TTR-MA, Rigaku, Tokyo, Japan) [1–3, 22]. XR is a relatively new technique for the estimation of the fine structure of a surface. It shows the flatness or roughness of a surface and the thickness of the layer structure. Figure 3 shows the XR profile for the chemically modified glass. A Kiessig fringe was observed, indicating a homogeneous polymer layer on the glass surface. The thickness of the modified layer was calculated to be about 10 nm by the curve fitting of the reflectivity curve. The surface roughness was estimated to be less than 1 nm.

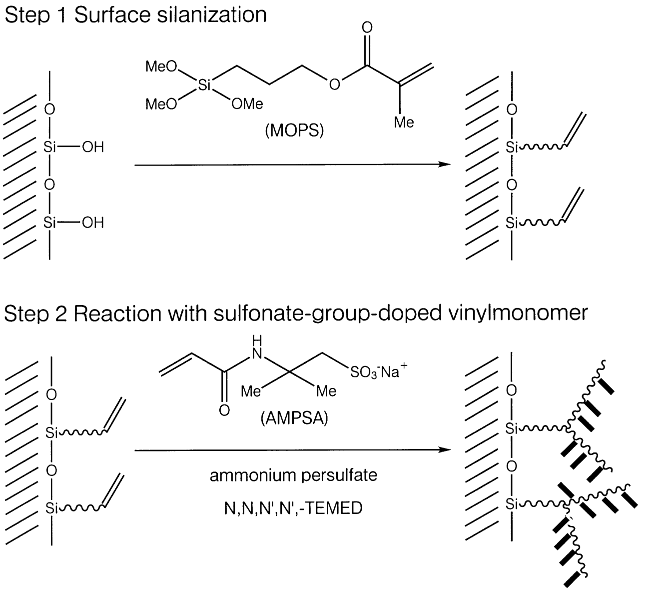

Fig. 2 Scheme of surface modification

Surface zeta-potential of the modified surface

The degree of surface modification was estimated by measuring the surface zeta-potential under no added salt conditions. This measurement was made using a combination of electrophoretic light scattering apparatus (ELS-800, Otsuka Electronics, Osaka, Japan) and a special cell unit, which was developed for zeta-potential measurement of flat surfaces. Hydroxypropylcellulose-coated polystyrene latex (diameter 520 nm) was used as a probe particle for surface measurement. The absolute value of the surface zeta-potential grew with increasing reaction time for step 2. At a reaction time for step 2 of 20 min, 5 h, and 48 h, the surface zeta-potential was estimated to be −7.6 mV, −36.4 mV, and −57.5 mV, respectively, while that for the naked glass surface was estimated to be −48.3 mV.

Interaction potential profile obtained by EVLSM

The raw data set of EVLSM measurement (typical example: Fig. 3 in our previous paper [5]) was a time-series of scattering intensities from one particle, counted by the photomultiplier during one sampling time, i.e. 1 ms in this study.

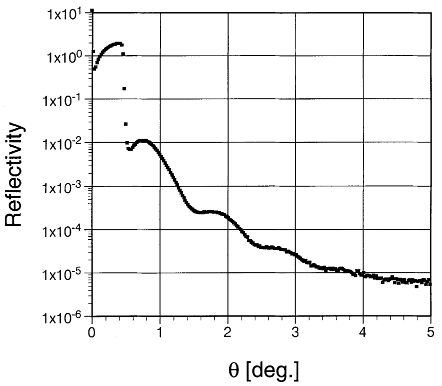

Fig. 3 X-ray reflectivity profile for chemically modified glass. Wavelength of X-ray: 1.54 Å; reaction time: 48 h; $\zeta = -57.5\,\mathrm{mV}$

A histogram of the number of observations at each scattering intensity was drawn using the raw data; Fig. 4 is an example of a histogram for this system. The horizontal axis shows scattering intensity, and the vertical axis is the number of observations. Since the scattering intensity corresponds to the particle-wall distance, as described previously, the shape of this histogram can be converted to the potential profile of the interaction between a latex particle and the glass surface using Eq. (2). Figure 5 shows typical examples of potential profiles obtained by EVLSM. Profile (a) was obtained for the chemically modified glass surface ($\zeta = -57.5\,\mathrm{mV}$), and profile (b) was for the naked glass surface ($\zeta = -48.3\,\mathrm{mV}$). The position of the potential profile shifted away from the glass surface with increasing surface charges, and the distance of the shift was about 150 nm for these examples. The shift was a significant difference, considering that the thickness of polymer layer fixed to the glass surface was estimated as 100 Å, i.e., 10 nm; these results clearly showed the increase of electrostatic repulsion between particles and the glass surface.

Surface charge dependence of the position of the interaction potential minimum

The relationship between the position of the minimum interaction potential and the zeta-potential of the modified glass surface was examined. The surface zeta-potential was varied by changing the reaction time of step 2 in the modification procedure (Fig. 2). The position of the interaction potential minimum was calculated from the potential profile obtained by EVLSM measurements (Fig. 6). The horizontal axis is the zeta-potential of the glass surface and the vertical axis is the distance of the potential minimum from the glass surface; error bars show the standard errors. The position of the minimum shifted away from the interface with increasing absolute value of the zeta-potential of the glass surface. The distance was 1060 nm at about −58 mV, and 780 nm at about −8 mV. The increase in

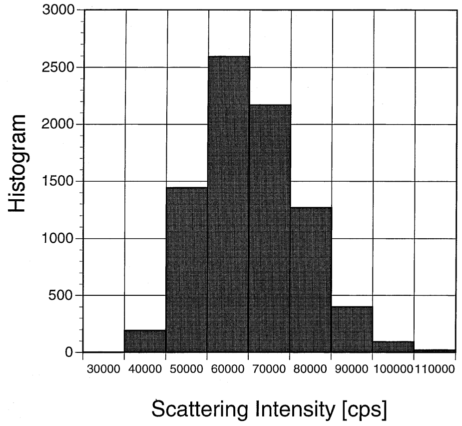

Fig. 4 Example of histogram obtained from EVLSM. Particle: polystyrene latex (diameter = 1000 nm); surface: chemically modified Pyrex glass ($\zeta = -57.5\,\mathrm{mV}$); sampling time: 1 ms; added NaCl concentration: 0 mM

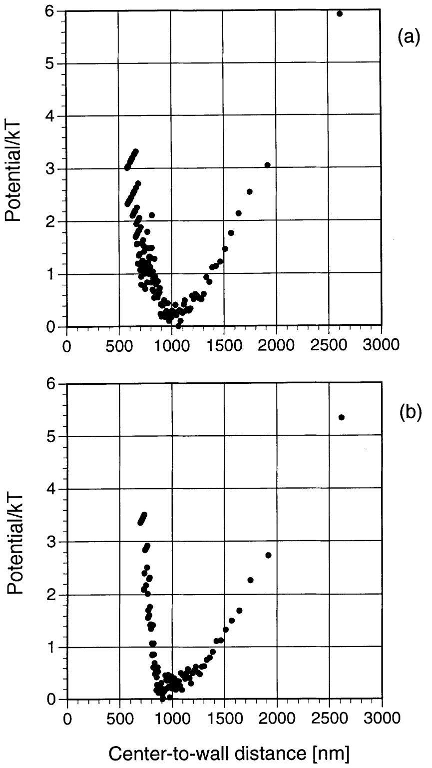

Fig. 5 Examples of potential profile obtained from EVLSM. Particle: polystyrene latex (diameter = 1000 nm); surface: (a) chemically modified and (b) naked Pyrex glass; surface zeta-potential: (a)−57.5 (b) −48.3 mV; sampling time: 1 ms; added NaCl concentration: 0 mM

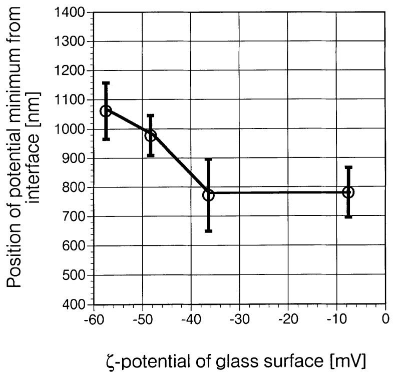

Fig. 6 Position of potential minimum as a function of surface zeta-potential of modified glass. Particle: polystyrene latex (diameter = 1000 nm); surface: naked and chemically modified Pyrex glass; sampling time: 1 ms; added NaCl concentration: 0 mM

the absolute value of the zeta-potential of the glass surface can be attributed to the increase of surface negative charges (sulfonate groups) on the glass surface. The electrostatic repulsion between negative charges on the surface of the particle and of the glass wall grew with increasing surface charges. Meanwhile, gravity did not vary with the modification of the glass surface. Therefore, the position of the potential well, which is formed by particle-surface electrostatic repulsion and gravity, moved a large distance away from the glass surface.

Ionic strength dependence of the position of the interaction potential minimum

The position of the potential minimum was estimated as a function of the concentration of NaCl added to the colloidal dispersion (Fig. 7). The left-hand graph is for the naked glass surface, and the right-hand graph is for chemically modified glass. In both cases, the position of the potential minimum shows a similar tendency; the higher the concentration of NaCl, the closer the position to the surface. At relatively high NaCl concentration, the electrostatic interaction between the surface of the colloidal particle and both types of glass was shielded. An additional factor might be a change in the surface charge of the glass plate. The ζ-potential of glass surfaces varied with added salt concentration [10, 23]. In our previous study of liposome particle-glass wall interactions in buffer solution, we examined the change of ζ-potential as a function of ionic strength. The ζ-potential decreased from −100 mV to −56 mV continuously as ionic strength was changed from ca. −4.0 to −2.0. Although the absolute value of the ζ-potential is different, since the system is different, a similar effect should occur in the present study. Hence, it is fair to think that the position of the interaction potential well moved closer to the glass surface for these two reasons, that is, electrostatic shielding and reduction of the surface ζ-potential of glass.

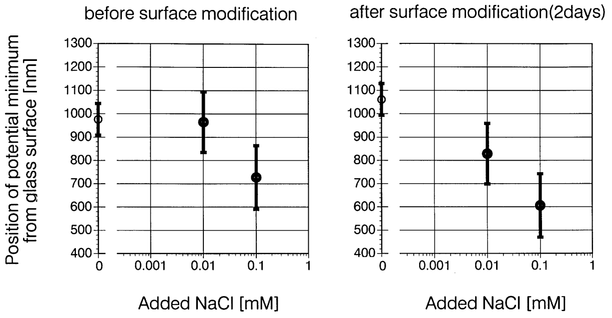

Fig. 7 Position of potential minimum as a function of added NaCl concentration in the system. Particle: polystyrene latex (diameter = 1000 nm); surface: naked and chemically modified Pyrex glass; sampling time: 1 ms; added NaCl concentration: 0 mM, 0.01 mM, 0.1 mM

Advantages of EVLSM and comparison with other techniques

Although EVLSM has been shown to have some disadvantages, such as the relatively large particle size compared to the wavelength and the penetration depth, EVLSM techniques may be widely applicable.

One potential application of EVLSM is an estimation of external forces. In this study, the external force was gravity. Alternatively, other forces such as electric field and magnetic field could also be evaluated by EVLSM; some experiments have already been carried out in our laboratory. In the present polystyrene latex particle-glass system, electrostatic interaction was detected by EVLSM, since it was the dominant factor. Other interactions should be detected, where they are dominant, such as hydrogen-bonding and antigen-antibody interaction, especially in biological systems.

Recently, AFM has been extensively used to measure particle-surface forces, in addition to surface imaging [24]. As already described, it is necessary to glue one colloidal particle to the cantilever as a tip and measure the force directly. In EVLSM, the interaction potential can be estimated *without* fixing the particle; we can measure the interaction for the particle in a *free* state. This is a great advantage of EVLSM over AFM, since the dynamic properties of colloidal particles and/or counterions play an important role in the electro "static" interaction [25].

Conclusions

EVLSM is a powerful tool for estimating electrostatic forces between a colloidal particle and a flat surface. The minimum position of the interaction potential under gravity, between a polystyrene latex particle (1000 nm in diameter) and a flat glass plate, where sulfonate groups were fixed chemically in dispersion, was estimated as a function of the surface zeta-potential of glass and also of ionic strength.

The position of the potential minimum for particle-wall interactions shifted away from the glass surface, as the absolute value of the surface zeta-potential became large with surface modification. After the addition of electrolytes to the colloidal system, the position of the interaction potential well came closer to the naked/chemically modified glass surface. These results can be explained by changes to the electrostatic interaction between the particle and the surface under constant gravity.

EVLSM is considered to be an important method for interfacial studies and is expected to be extensively utilized in the near future. More quantitative discussion of colloidal interaction theories is now in progress.

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