Colloid Polym Sci 276: 349–355 (1998)

ORIGINAL CONTRIBUTION

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Evaluation of the dynamic properties of polymer latex particles interacting with quartz interface by evanescent wave dynamic light scattering

Received: 2 August 1997
Accepted: 17 December 1997

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Abstract The diffusion behavior of polymer latex particles in dispersion near the quartz interface has been estimated by evanescent wave dynamic light scattering (EVDLS) technique. The diffusion coefficient of the particles was measured as a function of the distance between the particle and interface. The apparent diffusion coefficient estimated by EVDLS was small for particles near the interface and increased upon increasing the distance from the interface, and then saturated at a certain value which is close to the value expected for free-motion. The range of the distance over which diffusion was affected by interaction with the interface depended on the added salt concentration. This means that the diffusion of the particle is influenced by an electrostatic interaction between the particle and quartz interface in addition to the hydrodynamic effect near the wall. This range was found to be more than 800 nm at 0 M salt condition but about 400 nm at 10^{-4} and 10^{-3} M salt conditions. Hence it is appropriate to say that the hydrodynamic effect reaches up to 400 nm and the electrostatic effect is longer ranged, more than 800 nm, for the system studied here. The EVDLS technique is a very powerful tool for quantitative estimations of the dynamic behavior of the particle near the interface and for estimation of the range where the wall effect is dominant. EVDLS will give us an answer to the question of "where is the 'interface' and where is the 'bulk'?".

Key words Evanescent wave – dynamic light scattering – particle-wall interaction – colloidal particle – time-correlation function

Introduction

The interaction between polymer surfaces is the most important basic factor which defines a structure, function and kinetic characteristics of various polymer substances such as polymer material, polymer colloid, polymer solution, liposome and living cell. The behavior of polymer molecules and polymer particles at the interface must differ from that in the bulk phase reflecting characteristics of special circumstance, i.e. "interface". However, it has been very difficult to extract the information for the polymer only near the interface from data obtained by convenient experimental techniques which usually contain mostly the data for bulk and very little contribution of the data near the interface. The scattering techniques have been often used for the study of dynamic and static properties of polymer particle in dispersion and solution. Dynamic light scattering (DLS) technique has been extensively used to study the diffusion behavior of polymer molecules and polymer particles in solution and dispersion to determine the size of them [1–5]. DLS is also very useful

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tool to investigate the interaction between polymer particles like latex particle: the time correlation function obtained by DLS should be a single exponential for free-particle (Brownian particle), but some deviation is observed for particles interacting with other particles and this deviation is a good measure of the interparticle interaction and the solution or dispersion structure [6, 7]. One can find many papers on DLS analysis in the literature.

The interparticle interaction, especially electrostatic interaction, is still important and an interesting topic in the area of colloid and interface science. The famous, traditional theoretical work by Derjaguin and Landau [8], Verwey and Overbeek [9] (DLVO) theory has been believed to be valid for any conditions, but in the recent years some interesting phenomena have been found which cannot be easily explained by DLVO theory [10, 11]. Although the traditional approach is electro "static", there are some reasons to believe that some kind of "dynamic" effect should be taken into account [11, 12]. However, if one takes a dynamic effect into account, both theoretical treatment and experimental procedure of interparticle interactions become very complicated and difficult since both of the two particles move even if only two-body interaction is considered. But if we can obtain information between particle and "wall" or interface, the situation becomes simpler since it is not necessary to consider the "motion" of the wall. This is, of course, a favorite situation. However, for this propose, a new technique to obtain the dynamic characteristics of polymer particles near the interface, i.e. those interacting with wall by interparticle forces such as an electrostatic force should be necessary.

"Evanescent wave" is a very interesting wave: it is produced by total reflection of an electromagnetic wave at the interface [13]. Evanescent wave exists at the other side of the total reflection plane in the region of the order of magnitude of wavelength from the wall. In other words, evanescent wave is a special kind of light which exists only near the interface. This means that if one uses evanescent wave as a light source, only the information near the interface can be extracted. The existence of evanescent wave has been known for many years, but it is only in recent years that applications of the evanescent wave to interfacial study are tried. There are not so many works using evanescent wave at this stage, but one can find a few papers on the application of evanescent wave to scattering study; Lan et al. [14] applied evanescent wave to study hydrodynamic effects near the wall to the Brownian motion of latex particles. Van de Ven et al. used DLS measurement using evanescent wave for colloidal dispersion [15]. Lin et al. applied evanescent wave light scattering for the study of block copolymer at the air/water interface [16]. For the direct determination of the interaction potential between the particle and the glass wall in dispersion, the evanescent wave light scattering microscope (EVLSM) or total internal reflection microscope (TIRM) technique has been developed by Prieve et al. and applied to latex systems [17, 18] and liposome systems [19]. The combination of evanescent wave and fluorescence technique (total internal reflection fluorescence (TIRF)) has been applied to the study of kinetics of specific reactions, such as protein adsorption, antigen–antibody binding, enzymatic processes with lipid monolayer [20].

In this study, Evanescent wave dynamic light scattering (EVDLS) has been applied to latex systems to investigate the dynamic behavior of the polystyrene latex near the quartz surface and the electrostatic interaction between the particle and interface. EVDLS is, in principle, a novel technique combining the evanescent wave and dynamic light scattering techniques. By EVDLS, the diffusion behavior of the polymer particle near the interface can be clarified, which should reflect the particle–wall interaction, qualitatively.

Theory

The evanescent wave is generated by the total reflection of the incident electromagnetic wave at the interface [13]. Suppose the situation that the incident laser beam comes from the side of medium 1 whose refractive index is n_1 and hits the interface with medium 2 whose refractive index is n_2, the total reflection occurs when the incident angle is larger than the critical angle θ_c (Fig. 1). At this condition, the evanescent wave is produced in medium 2. The evanescent wave exists only near the interface; in the range of the order of the wavelength from the interface. The evanescent wave has special characteristics; the intensity of the evanescent wave decreases exponentially as a function of the distance from the interface at which the total internal reflection occurs (Eq. (1))

$$I_{ev}(z) = (E_\xi(z))^2 = I_0 \exp(-2z/\xi) , \quad (1)$$

where z is the distance from the interface, I_0 the initial intensity of the evanescent wave at the interface (i.e. at $z = 0$), and ξ is the decay rate called "penetration depth", which is defined by Eq. (2) as a function of the wavelength and the incident angle of the laser beam:

$$\xi = \lambda_0 / 2\pi n_1 (\sin^2\theta_i - \sin^2\theta_c)^{0.5} , \quad (2)$$

where λ_0 is the wavelength of the incident laser, θ_i the incident angle, and θ_c the critical angle of the reflection. This equation means that the penetration depth ξ can be controlled by changing the incident angle; the larger the incident angle the smaller the ξ. Hence, we can detect the scattering of evanescent light by latex particle near the interface and also collect the scattering from the

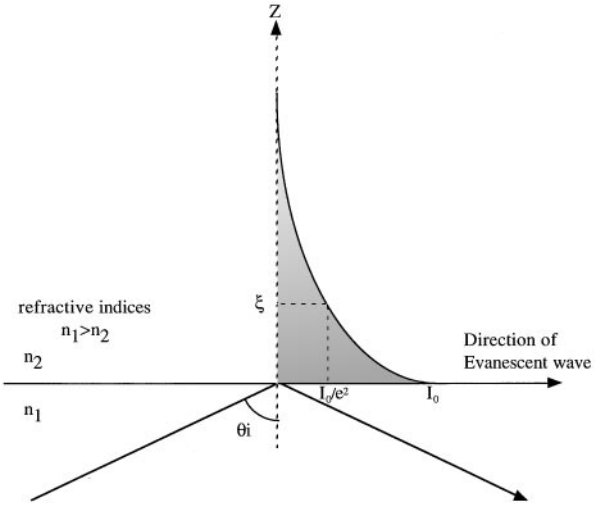

Fig. 1 The principle of evanescent wave. The evanescent wave is generated by total reflection of laser light when the incident angle of the beam, θ_i, is larger than the critical angle, θ_c, for the interface of the media whose refractive indices are n_1 and n_2 ($n_1 > n_2$). The intensity of the evanescent wave at $z = 0$ (z is the distance from the interface) is I_0 and it decays exponentially with increasing z by Eq. (1) in the text. This decay is characterized by the penetration depth ξ, which is a function of θ_i. The evanescent wave propagates parallel to the interface

particles at different positions from the interface by changing the incident angle, i.e., the penetration depth, ξ. This means that if we perform light scattering experiments with evanescent light scattering geometry (Evanescent wave Dynamic Light Scattering, EVDLS), we can detect the diffusion of latex particles located near the interface as a function of the distance from the interface.

Experimental section

Materials

Polystyrene latex was prepared by soap-free emulsion polymerization of styrene and styrenesulfonate with potassium persulfate as an initiator [21]. The latex suspension was purified by ultrafiltration with Milli-Q grade water and subsequent deionization by ion-exchange resins (Amberlite MB-3, Organo, Tokyo). Ultra-small angle X-ray scattering (USAXS) [22] was carried out to verify the particle size and polydispersity. The latex particle was confirmed to be spherical and 110 nm in diameter. The polydispersity was estimated to be 5%. The surface charge density was determined to be 4.6 μC/cm^2 by conductometric titration. The concentration of the stock latex dispersion was determined by dry-weight method with the density of polystyrene of 1.04. Before EVDLS measurement, the dust and/or aggregates were removed by filtration through a 0.22 μm filter (Millex GV, Millipore, Bedford, MA). Water used for sample preparation and purification was ultra-pure obtained by a Milli-Q system (Millipore, Bedford, MA).

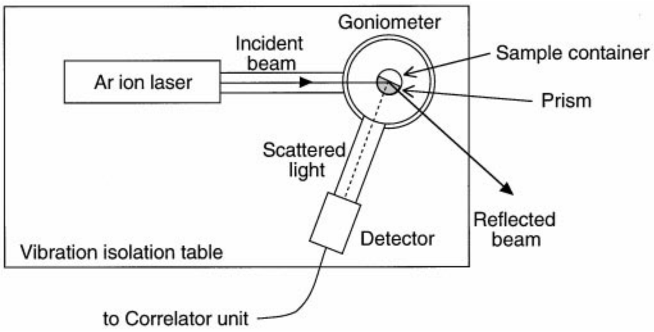

Fig. 2 The schematic representation of EVDLS apparatus. This apparatus is made by modification of conventional DLS apparatus with a combination of specially designed EVDLS cell (Fig. 3). The scattering angle was fixed to be 90°

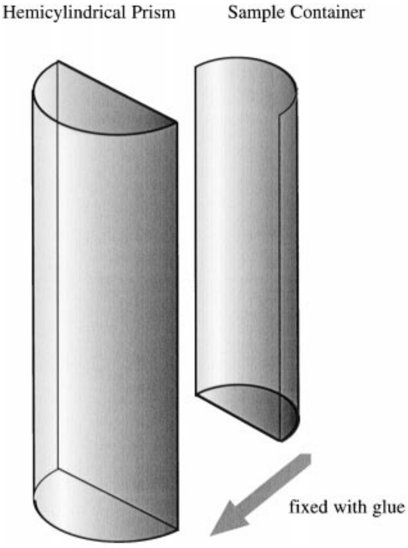

Fig. 3 The light scattering cell specially designed for EVDLS measurements

EVDLS apparatus

The schematic for the EVDLS apparatus used in this work is shown in Fig. 2. The light source was an argon laser (488 nm, 5 W, Model 2020-5, Spectra Physics, Mountain view, CA). The photon correlation spectrometer was a combination of BI-30 goniometer and BI-2030 correlator (Brookhaven, Ronkonkoma, NY). The hemicylindrical prism was specially designed for EVDLS measurement as shown in Fig. 3 and manufactured with fused quartz

($n = 1.463$ at 633 nm) (Sigma-Koki, Saitama, Japan). The sample cell was a hemicylindrical tube stacked on the reflection surface of the prism. This sample cell assembly was placed into the cell holder of BI-30. The incident laser beam goes into the hemicylindrical prism, and is totally reflected at the interface between the prism and the sample solution. The incident angle was varied from the critical angle (66.1°) to 80°. Then the evanescent wave is generated at the interface and scattered by polystyrene latex particles existing near the interface. The scattering angle was fixed at 90° for all measurements. The scattered light is detected by a photomultiplier and its time fluctuation was converted to the time correlation function of scattered intensity by the correlator and computer.

Analysis

In general [1–5], by DLS measurement the time-correlation function of scattered intensity $g^{(2)}(q,\tau)$ can be obtained and this is related to the time-correlation function of the scattered field by the so-called Siegert relation:

$$g^{(2)}(q,\tau) = B(1 + |g^{(1)}(q,\tau)|^2) . \tag{3}$$

where B is the base coefficient. $g^{(1)}(q,\tau)$ is related to the decay rate Γ by the following relation:

$$g^{(1)}(q,\tau) = \exp(-\Gamma\tau) \tag{4}$$

and Γ is expressed by the translational diffusion coeffcient D by

$$\Gamma = Dq^2 , \tag{5}$$

where q is the scattering vector: $q = 4\pi n \sin\theta/\lambda$ with the wave length of the laser beam λ, and the refractive index of the medium n. The obtained time correlation functions were analyzed by cumulant method [23] and single exponential fitting.

As mentioned already, the evanescent wave decays in intensity exponentially upon increasing the distance from the interface z. In this sense, the time correlation function obtained at a certain incident angle θ_i, i.e., at certain ξ condition, is the "integrated" information for function $I_{ev}(z)$ with the ξ value at that condition. The contribution from $z = 0$ is the largest to $g^{(1)}(q,\tau)$ and the contributions from other z values are decreased exponentially as easily recognized from Eq. (1). To extract the information for a certain z condition, in other words, to evaluate the diffusion behavior as a function of the distance from the interface z, we applied the following technique.

Figure 4 shows the $E_\xi - E_{257.1\,\mathrm{nm}}$ value, i.e., the result of the subtraction of penetration function at several ξ values by that at $\xi = 257.1$ nm. This is expressed by $\exp(-z/\xi) - \exp(-z/257.1)$. We changed the values of penetration depth as 257.1, 386.4, 527.0, 666.7, 863.1 and 1062.2 nm in this study. The minimum value of 257.1 nm was selected as the standard penetration depth and the data under this condition were used for the subtraction procedure in Fig. 4. As seen in Fig. 4, these functions show a maximum at a certain z value ($z_{\max}$) which is characteristic for each combination of two ξ values used for subtraction. This means that these functions mainly reflect the contribution from z value at the maximum although the contribution from other z values are not completely eliminated. In addition, since the maximum position depends on the ξ values, we can extract the infomation at different $z_{\max}$ values by this subtraction procedure. In this paper, we subtract the time-correlation functions at two different ξ conditions and analyzed by a single exponential fitting, and we regarded these time-correlation functions after subtraction as those mainly reflecting the dynamic behavior of latex particles located at that $z_{\max}$.

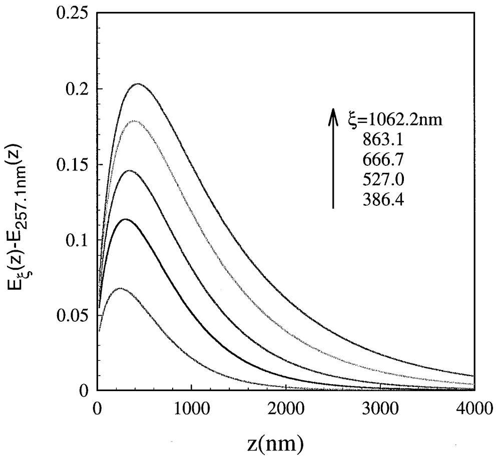

Fig. 4 $E_\xi - E_{257.1\,\mathrm{nm}}$ as a function of z at various ξ. The result of subtraction of the amplitudes of evanescent wave at two ξ conditions shows a maximum whose position depends on the combination of two ξ's. This means that the time correlation function after subtraction mainly reflects the information around the maximum position

Results and discussion

Comparison of the time-correlation function obtained by DLS and EVDLS methods

Figure 5 shows a comparison of the time-correlation functions obtained by DLS and EVDLS methods. The latex concentration was 1.0×10^{-2} vol% for DLS and 1×10^{-1} vol% for EVDLS. Of course, we are fully aware that the comparison at the same concentration should be performed, but DLS measurement could not be applied to the higher concentration which was applied for EVDLS

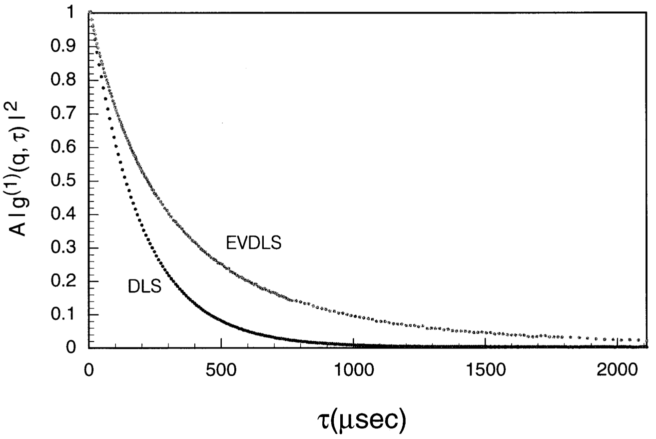

Fig. 5 The comparison of time correlation functions of scattered intensity obtained by DLS and EVDLS ($\xi = 281.3$ nm). Sample: SS-155, diameter: 110 nm, conc.: 1×10^{-2} vol% (DLS), 1×10^{-1} vol% (EVDLS), NaCl = 1×10^{-4} M, scattering angle: 90°

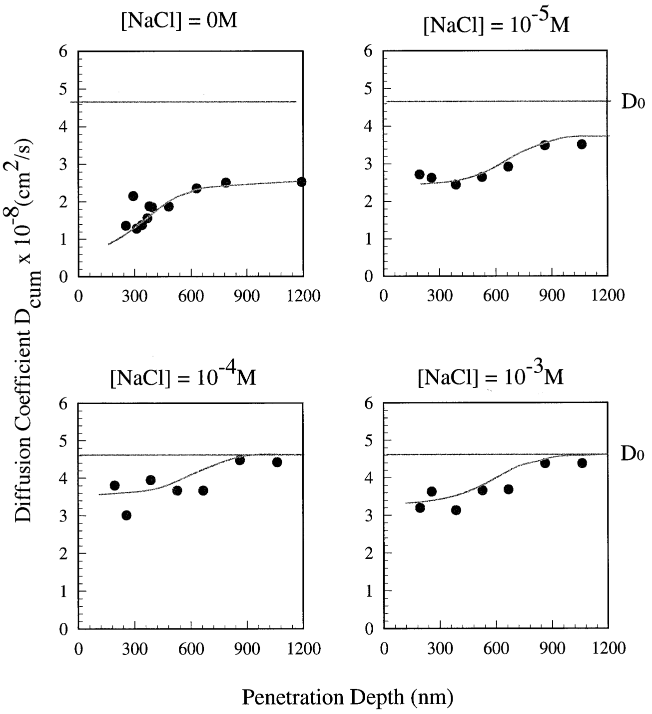

Fig. 6 Apparent diffusion coefficient estimated by Cumulant method as a function of ξ at various salt conditions. The horizontal straight line at $D = 4.46 \times 10^{-8}$ is the D_0 value which is calculated by Einstein–Stokes equation from its size. The tendency of increasing D with increasing ξ is clearly observed and saturates before D_0

measurement, and EVDLS measurement could not be done at a lower concentration which was applied for DLS due to the weak scattering intensity. Although conditions on the concentration are different for DLS and EVDLS, these conditions are low enough to expect no contribution of interparticle interaction for scattering data. The time-correlation functions obtained by DLS and EVDLS were largely different as shown in Fig. 5. That by DLS decayed exponentially with typical Γ for its hydrodynamic size, which was calculated to be 111 nm in diameter by using Eq. (5) and the Einstein–Stokes equation. On the other hand, that by EVDLS decays more slowly. Since EVDLS extracts the information about dynamic behavior only near the interface, some effect of interface on the diffusion behavior of latex particle can be expected from these data.

We have measured the time-correlation function at different ξ values for dispersions at different [NaCl] conditions by EVDLS. The "raw" time-correlation functions obtained were analyzed by cumulant and the apparent diffusion coefficients were estimated at different conditions on ξ. The results were plotted against ξ in Fig. 6. As clearly seen, the apparent diffusion coefficient depends on the ξ value; D tends to increase with increasing ξ value. However, the tendency is not so clear and not quantitative enough since the information obtained is an "integrated" one as was described in the experimental section. So, we have applied the new method described in the experimental section to extract the dynamic behavior of latex partices at different z values.

Figure 7 shows the D values thus obtained (D_{diff}) as a function of $z_{\max}$ at four different salt concentrations, i.e., 0, 1×10^{-5}, 1×10^{-4}, and 1×10^{-3} M NaCl. The increasing tendency of D upon increasing the distance from the interface is more pronounced. The D value increased with z and saturated at a certain z value which depends on the salt concentration. The saturated D value is nearly equal to the D value expected for free-Brownian particle of the same size, which is shown by an horizontal straight line at $D_0 = 4.46 \times 10^{-8}$ cm^2/s in Fig. 7, for all the salt concentrations studied here. This means that the particles behave similar to a free-particle without the influence of the interfacial wall above this critical z value. The critical z value, which is indicated by a vertical dashed line in Fig. 7, depends on the salt concentration; this value is more than 800, 600, 400, 400 nm for 0, 1×10^{-5}, 1×10^{-4}, and 1×10^{-3} M salt concentrations, respectively. For 0 M, the D_{diff} value increases monotonically upon increasing $z_{\max}$ in the range studied, but it is suitable to think that this is due to the large value of the critical z beyond 800 nm; the saturated behavior is expected in the large $z_{\max}$ regions which could not be covered in this study. This critical z value decreased with increasing salt concentration and becomes independent beyond 1×10^{-4} M salt concentration. From these facts, the reason for the "slowing down" of the D value near the interface (small z value) can be attributed to an electrostatic interaction between latex

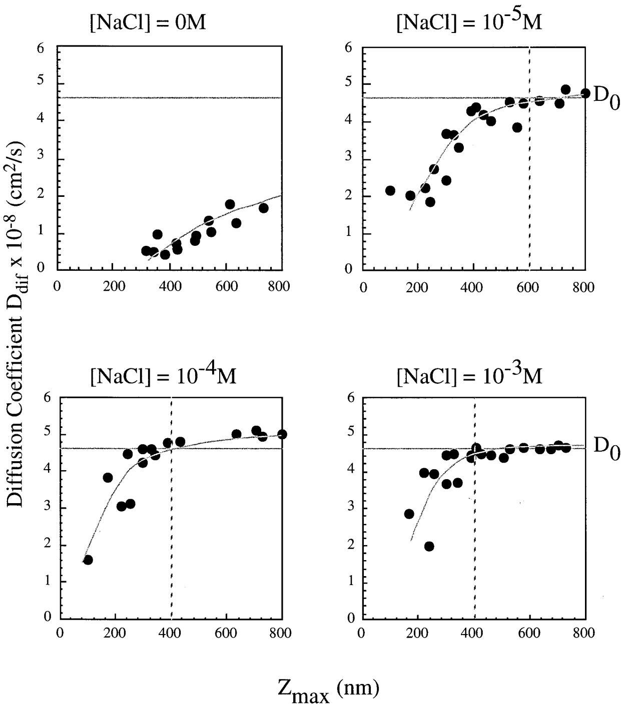

Fig. 7 Apparent diffusion coefficient as a function of $z_{\max}$ at various salt conditions. The horizontal straight line at $D = 4.46 \times 10^{-8}\,\mathrm{cm}^2/\mathrm{s}$ is the D_0 value which is calculated by the Einstein–Stokes equation from its size. The tendency becomes more clear than in Fig. 6 since subtraction procedure extracts the information at $z_{\max}$. The saturation value is very close to D_0 which is indicated by a horizontal straight line. The critical z value at which the D value reaches saturation is indicated by a vertical dashed line, whose position depends on the salt concentration; it decreases with increasing salt concentration

particle and quartz interface in addition to the characteristic hydrodynamic effect near the interface. Although nothing conclusive can be said about the nature of the hydrodynamic effect in at this stage, our physical idea of this effect is a complex water flow near the wall which is caused by particle motion. If only the hydrodynamic effect is dominant, the critical z value should be independent of the salt concentration. But this is not the case. Hence, we can conclude now that the electrostatic interaction between the particle and the quartz wall affects the diffusion behavior of the particle near the interface; it causes the slowing down of the diffusive motion. The range where this effect is effective is more than 800 nm from the interface at 0 M salt concentration, 600 nm at 10^{-5} M, and about 400 nm at 10^{-4} and 10^{-3} M. From this observation, we can say that the slowing down near the interface observed at high salt concentrations can be attributed to the hydrodynamic effect; the hydrodynamic effect is effective upto 400 nm from the interface since this is the effective distance at high salt concentrations where the electrostatic effect is expected to be shielded enough. At low salt concentrations, i.e., 0, 10^{-5} M, the electrostatic effect becomes effective in addition to the hydrodyamic effect which causes the increase of the critical z value.

It should be noted that the range where the wall effect, either hydrodynamic or electrostatic, is fairly large from the interface. It is more than 800 nm at 0 M and about 600 nm at 10^{-5} M NaCl conditions. Since the particle diameter is 110 nm, this is about 8 and more times of the particle size. Quantitative estimations of diffusion behavior near the interface and the range where the wall effect is effective becomes possible by this new technique, EVDLS, i.e., a combination of evanescent wave and dynamic light scattering techniques.

Conclusions

The dynamic behavior, i.e., diffusive motion of polymer latex particles in dispersion near the quartz surface was evaluated as a function of salt concentration by evanescent wave dynamic light scattering technique. The apparent diffusion coefficient of the particles located at different distance from the interface was extracted by a subtraction procedure of time correlation functions obtained by EVDLS for different ξ values. The diffusion coefficient for the particle very close to the interface was found to be fairly small and increases upon increasing the distance from the interface and saturated at the critical distance to the D value expected for free Brownian motion from its geometrical size. The critical distance was dependent on the added salt concentration. This means that an electrostatic interaction between the particle and quartz surface is one of the dominant factors affecting the diffusion near the interface in addition to the hydrodynamic effect. The critical distances were estimated to be >800, 600, 400, and 400 nm for 0, 1×10^{-5}, 1×10^{-4}, and 1×10^{-3} M NaCl concenrations, respectively. Hence, the hydrodynamic effect is effective upto 400 nm and additional effects beyond 400 nm distance should be attributed to the electrostatic interaction. The electrostatic interaction between the particles and the interface was effective beyond 800 nm at 0 M salt concentration. The diffusion behavior and the range of characteristic nature of the interface, i.e., the range of the interaction between particle and interface could be estimated quantitatively by the EVDLS technique. EVDLS will give us an answer to the question of "where is the 'interface' and where is the 'bulk'?".

Acknowledgement This work is supported by Grants-in-aid from the Ministry of Education, Science, Culture and Sports, Japan (No. 07555300, and 08226226).

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