



Dendrimer induced interaction forces between colloidal particles revealed by direct force and aggregation measurements



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ABSTRACT

Interaction forces and aggregation rates were determined in order to characterize colloid stability of negative carboxyl latex particles in the presence of oppositely charged poly(amido amine) (PAMAM) dendrimers of three different generations G4, G7 and G10. The force profiles were measured by the atomic force microscopy (AFM) based on multi-particle colloidal probe technique. Close to the isoelectric point, the measured force profiles were more attractive than the pure van der Waals interactions. This behavior was rationalized in term of an additional electrostatic patch-charge contribution whose magnitude increases by increasing the dendrimer generation. The aggregation rates were calculated from these results using the classical theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO) as well as including the additional attractive term and a radially symmetric force field. The calculated aggregation rates were compared to the ones obtained directly from time-resolved dynamic light scattering (DLS) measurements using exactly the same latex particles as in the AFM study. The results from these two methods were in good agreement in the case of dendrimers of lower generation, while at higher generation, significant differences were found. In the latter case, the stability ratio in the slow aggregation regime extracted from direct force measurements was much higher than the one measured experimentally by DLS. Despite the fact that the additional attractive term was included in the calculation, the discrepancy between the two different stability ratios suggests that the assumption of radial symmetric interaction is weak.

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1. Introduction

The classical theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO) [1,2] constitutes the milestone in describing the stability of a colloidal system which is governed by the interplay between repulsive double layer and attractive van der Waals interactions. For a homogeneously charged surface, the DLVO theory has been verified with different techniques such as total internal reflection microscopy [3,4], colloidal probe [5,6] and surface force apparatus [7,8].

At the beginning of the 70s, Kasper [9] and Gregory [10] suggested that polyelectrolytes might adsorb on oppositely charged surfaces in a heterogeneous way creating a patchy charge distribution. The basic idea was that even if the overall charge of the surfaces is neutral, it is unlikely that each surface charged site can be neutralized by the polymer segments. Consequently, although the surface may have an overall charge close to neutrality, there are “patches” or “islands” of opposite charge between regions of uncoated substrate [11]. From these patch interactions,

an additional attractive force of electrostatic origin was originated [12,13]. Intuitively, when two patchy surfaces approach to each other, the patches formed by the polymer segments adsorbed on one of the surfaces experience an attractive force with the corresponding uncoated portions present on the other surface.

Dynamic light scattering (DLS) experiments aiming to study the stability of colloidal suspensions of particles covered with polyelectrolyte showed stability ratios smaller than unity in the fast aggregation regime at low ionic strength. An additional attractive patch-charge interaction was suggested to be responsible for the acceleration of the aggregation processes in this case [14–17]. Direct evidence of such interaction was observed with multi-particle colloidal probe technique based on atomic force microscope (AFM) for amidine latex and sulfate latex particles coated with polystyrene sulfonate (PSS) and poly(amido amine) dendrimers (PAMAM) respectively [18–23].

Although the importance of surface charge heterogeneities originating from the adsorption process were emphasized with these two different techniques, the results could not be compared directly since the size of the particles used for AFM measurements was more than 10-times higher than the ones applied in the DLS experiments. Direct comparison of forces and aggregation rates was not possible earlier, because of the different size of particles

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as well as the different geometry in the force measurements. We have recently reported for the first time direct comparison of stability ratios determined with DLS and AFM individually using the same colloidal polystyrene latex particles in the presence of multivalent ions [24,25]. As a compromise between the two methods, a particle size of around one micrometer in diameter was suitable to use them in both types of experiments.

PAMAM dendrimers are highly branched macromolecules with an ethylenediamine core and they attract significant interest due to the growing number of applications in fields such as medicinal chemistry, materials science and catalysis [26]. Accordingly, they have been in focus of various kinds of investigations by several research groups worldwide [27–31]. Due to their particular molecular structure and monodispersity, they are perfect candidate to form patchy surface by their adsorption as it has been shown previously by AFM images [32,33].

In the present study, interaction forces measured by the multi-particle colloidal probe technique based on AFM [34] were determined in the system containing negatively charged carboxyl latex particles with a diameter of 1 μm covered with PAMAM dendrimers of different generations. Aggregation rates were calculated from the obtained force profiles and compared to the ones determined in time-resolved light scattering measurements. Using the same particles in both study allowed us to discover the origin of the interaction forces responsible for particle aggregation in the present systems.

2. Materials and methods

2.1. Materials

Poly(amido amine) (PAMAM) dendrimers of generations G4, G7 and G10 were purchased from Dendritech (Midland, USA) and used without further purification. Their concentrations were verified by total organic carbon and nitrogen analysis (TOC-V, Shimadzu, Japan). Carboxylated polystyrene latex particles were purchased from Interfacial Dynamics Corporation (Portland, USA). The data sheet provided by the manufacturer showed the following characteristics: diameter of 1 μm , surface charge density of -127 mC/m^2 obtained by conductometry and a polydispersity of 4.5% determined by transmission electron microscopy. The particles were dialyzed against Milli-Q (Merck Millipore, Billerica, USA) water with a cellulose ester membrane having a molecular mass cutoff of 300 kg/mol (Spectrum Rancho, Dominguez, USA) till the conductivity of the surrounding medium reached the value of the Milli-Q water. The particle concentrations were determined with light scattering by comparing the scattering intensity of an unknown sample with a reference one. All the experiments were carried out at a particle concentration of 80 mg/L, while dendrimer concentrations were varied between 1 and 10 mg/L. The measurements were performed at pH 5.8 adjusted with HCl (Merck, Darmstadt, Germany) or KOH (Sigma–Aldrich, Steinheim, Switzerland) solutions and at an ionic strength of 1 mM by adding appropriate amount of KCl (Acros, Geel, Belgium) solution to the samples. In such conditions, the degree of ionization of the dendrimers due to the protonation of the primary amines is roughly 0.65 [35].

2.2. Electrophoresis

The electrophoretic mobilities of the bare particle suspensions as well as in the presence of PAMAM dendrimers were measured with a Zeta Sizer 2000 (Malvern Instruments, Malvern, UK) device in the range of electric fields of 7.5–15 kV/m. In a typical experiment, 0.1–4.0 mL of denrimer stock solution was mixed with

appropriate amount of KCl solution used to adjust the ionic strength. The sample preparation was finished by the addition of 0.5 mL of the latex stock suspension. The final volume was always 5 mL. The samples were equilibrated overnight and the electrophoretic mobilities were determined in plastic capillary cells (Malvern Instruments, Malvern, UK) by averaging 5 individual measurements. The ζ -potentials were calculated invoking the standard electrokinetic model developed by O'Brien and White [36].

2.3. Light scattering

Static and dynamic light scattering experiments were performed with a multi-angle goniometer having 8 fiber-optic photomultiplier detectors (ALV/CGS-8, Langen, Germany) and a solid state laser of a wavelength of 532 nm (Verdi V2, Coherent Inc., Santa Clara, USA). Round borosilicate glass cuvettes were used for stability measurements while static light scattering experiments were carried out in quartz cuvettes. Both were cleaned with a mixture of concentrated H_2SO_4 and H_2O_2 at a volume ratio of 3:1 (piranha solution) at 80 °C for 3 h and afterwards rinsed thoroughly with Milli-Q water and dried in dust-free environment.

The absolute aggregation rate constant of the particles was determined in time-resolved simultaneous static and dynamic light scattering measurements where changes in intensity and hydrodynamic radius were followed with time in an aggregating sample containing 4.5 mg/L latex particle in 1 M KCl solution. Plotting the slopes obtained from intensity versus the ones from hydrodynamic radius measurements, the absolute aggregation rate can be determined from the intercept as detailed elsewhere [37,38]. As published in our previous study carried out with the same particle, an absolute aggregation rate of $2.0 \times 10^{-18} \text{ m}^3/\text{s}$ was obtained for the carboxyl latex particles [25].

Colloid stabilities were investigated in time-resolved dynamic light scattering (DLS) experiments. The total volume of the samples were always 2 mL prepared by mixing calculated amount of KCl and PAMAM denrimer solutions followed by the addition of the particle stock suspension. The aggregation rates k were determined on the basis of calculating the slope of the hydrodynamic radius versus time plots as follows [38].

$$\frac{1}{R_{h,0}} \cdot \left. \frac{dR_h}{dt} \right|_{t=0} = \left[1 + \frac{\sin(2qR)}{2qR} \right] \left(1 - \frac{R_{h,1}}{R_{h,2}} \right) k n_0 \quad (1)$$

In the equation above, $R_{h,0}$ is the initial hydrodynamic radius, q is the magnitude of the scattering vector, $R_{h,2}/R_{h,1} = 1.38$ is the ratio of the hydrodynamic radii of the dimer and the monomer, and n_0 is the initial particle number concentration. The stability was expressed in stability ratio (W) which is the ratio between the fast or diffusion controlled aggregation rate constant determined in 1 M KCl solution and the aggregation rate obtained in the actual measurement. Note that in case of fast aggregation, the stability ratio is close to unity while it increases when the aggregation slows down. A critical coagulation concentration (which separates the slow and fast aggregation regimes) of 190 mM and a fast aggregation rate of $2.7 \times 10^{-18} \text{ m}^3/\text{s}$ were determined for the carboxyl latex particles in the presence of KCl. The latter value close to the absolute aggregation rate obtained from simultaneous static and dynamic light scattering measurements indicating a good estimate for the optical and structural properties of the particles.

2.4. Direct force measurements

Forces between two colloidal particles were measured with a closed loop atomic force microscope (AFM) (MFP-3D, Asylum Research, Santa Barbara, USA) mounted on an inverted optical microscope (IX70, Olympus, Volketswil, Switzerland). The glass

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