Colloids and Surfaces A 525 (2017) 7–12

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Accurate size determination of polystyrene latex nanoparticles in aqueous media using a particle tracking analysis method

Yusuke Matsuura, Naoko Ouchi, Hidekuni Banno, Ayako Nakamura, Haruhisa Kato*

National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

ARTICLE INFO

Keywords:
Particle tracking analysis
Nanoparticle
Size
Polystyrene latex
Electrolyte
DLVO theory
Zeta potential

ABSTRACT

The size determination of nanoparticles in aqueous solution is important in bio- and nanotechnology. The sizes of particles in aqueous solution are determined by particle tracking analysis (PTA) with the Stokes–Einstein assumption from diffusion coefficient measurements. However, the interactions between particles affect the particle size determined by PTA. In this work, we observed particle/electrolyte concentration-dependent change in the apparent size of polystyrene (PS)-latex particles. Based on the Derjaguin, Landau, Verwey, and Overbeek theory, the change in the observed size of PS-latex particles estimated by PTA in various aqueous electrolyte solutions is caused by the long-range electrostatic interactions between the particles. Accurate size determination of PS-latex particles in aqueous solution was performed after reduction of the electrostatic interaction between particles by varying both the concentrations of the PS-latex particles and the electrolyte in aqueous solution. Zeta potential measurement and DLVO assessment gave a good indicator to reduce the electrostatic interactions between the particles for determination of accurate size of particle by PTA method. The proposed approach makes it possible to compare the determined sizes of various nanoparticles in the liquid-phase by PTA to those obtained by differential mobility analysers in the gas-phase. Although the determined sizes of nanoparticles using different sizing methods are difficult to compare, our investigation would allow researchers to achieve some degree of concordance on the size of nanoparticles using different sizing methods.

1. Introduction

Understanding the dynamics of particle diffusion in aqueous solution is key to understanding many phenomena in biotechnology and nanotechnology, including the mechanisms of drug targeting technologies using small-sized drug carriers [1,2]. Diffusion also plays an important role in chemical reactions and is described by diffusion rate equations [3,4]. To design these systems, understanding particle diffusion processes enables good control of parameters to achieve stable and reliable production of novel products/drugs/chemicals [5]. Diffusion phenomena are also used to determine the sizes of particles in the liquid phase by particle tracking analysis (PTA) [6–8], pulsed field gradient nuclear magnetic resonance (PFG-NMR) [9,10], and dynamic light scattering (DLS) [11,12]. In PTA, the sizes of particles in a suspension are determined by measuring the diffusion coefficients, and then calculating the sizes of the particles from these diffusion coefficients by the Stokes–Einstein relation as well as the PFG-NMR and DLS methods. In principle, these measurements were observed the diffusion coefficients of particles, the calculated size should be compared considering the simple assumption (e.g. size distribution, sphere structure, etc.). In contrast to PFG-NMR and DLS, PTA can be used to visually observe the diffusion of an individual particle in liquid phase. Therefore, it is easier to visualize and understand the Stokes–Einstein assumption of the Brownian motion of particles in liquid phase, i.e., that the smaller particles diffuse faster than larger ones. Furthermore, PTA can determine the number-average particle size directly, although DLS gives the light scattering intensity average diameter and calculates the number-average particle size by particulate assumption, i.e. the particle shape is spherical. This implies that the sizes determined by PTA can easily be compared with those determined by the electromicroscopic (EM) or differential mobility analyser (DMA)-based methods in the gas phase, which are also commonly employed for nanoparticle number-average size determination and the measured mean size of spherical nanoparticles measured by DMA and SEM/TEM were agreed within experimental standard deviation [13]. Indeed, there are many studies on the relationship between particle size and physical properties in liquid phase [14–25]. Therefore, the accurate determination of particle size is necessary to produce well-controlled

---

* Corresponding author.
E-mail address: H-kato@aist.go.jp (H. Kato).

http://dx.doi.org/10.1016/j.colsurfa.2017.04.058
Received 24 February 2017; Received in revised form 22 April 2017; Accepted 25 April 2017

functional materials.

Although the PTA method offers the possibility to compare the determined sizes with those of EM and DMA methods, the interactions between particles affect the observed particle diffusion [26], since the PTA method is based on the observation of diffusion phenomena of particles in liquid phase. The particle interactions are mediated by the solvent and measured as the configurational dependence of the system friction, thus; this effect should increase at higher particle concentrations. According to the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [27,28], the interaction between the particles in a suspension is determined by electrostatic repulsive and van der Waals attractive interactions. The electrostatic repulsion arises from the overlap between the diffuse double layers of the particles and decays approximately exponentially with the distance between the particles. Thus, there are long-range interactions between particles. However, the van der Waals attractive energy decays according to a power law. The time-independent interaction between particles can be described by the net interaction given by the sum of the electrostatic and van der Waals interactions according to the DLVO theory. In PTA, when the electrostatic repulsion is observed, it is important to consider the effects of the interactions between particles on the determination of particle size since the interactions between particles cause significant errors in size determination using diffusion coefficients.

In this study therefore, a PTA method is developed to determine the accurate size of particles in aqueous solutions. The sizes of polystyrene (PS)-latex particles in pure water and aqueous electrolyte solutions were determined by PTA, free from the effects of interactions between particles. Using the DLVO theory and zeta potential measurements, the experimental PTA results were also investigated by simulating interactions between PS-latex particles in aqueous electrolyte solutions. The proposed approach can reliably determine the sizes of various kinds of particles in the liquid phase by PTA.

2. Experimental

2.1. Materials

A surfactant-free aqueous dispersion of PS-latex particles (STADEX SC-0100-D, JSR Co., Japan) with an approximate sample concentration of 1.0 wt% was purchased. The official value of the size of the PS-latex particles as determined by a differential mobility analyser (DMA) is given as 100 ± 3 nm. The electrolytes were potassium nitrate (KNO_3) and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) (Wako, Japan). Samples for studying the effect of the concentration of the electrolytes on the self-diffusion coefficients of PS-latex were prepared with the same volume fraction as that of the PS-latex particles.

2.2. Particle tracking analysis

PTA was performed with a nanoparticle analysis system (NanoSight LM10, Malvern Instruments, UK) using a 660 nm focused laser beam introduced to the particle suspension through a glass prism. A 60 s video of particle diffusion with a frame rate of 30 fps was collected, and the particle movement, analyzed by NTA 2.3 software (Malvern Instruments). The velocity of particle movement was used to calculate particle size with the two-dimensional Stokes-Einstein equation,

$$\overline{(\Delta x)^2 + (\Delta y)^2} = 4D\Delta t \tag{1}$$

and

$$d = \frac{k_B T}{3\pi\eta D} \tag{2}$$

where Δx and Δy are the displacements of particles in the x and y directions, respectively, during time period Δt; D is the particle diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity (0.89025 cP) [29], and d is the particle diameter. To calculate the size using the equation, the temperature was measured during the measurements. Analysis parameters optimized for the video capture included camera gain, shutter speed, filter settings and minimum required track length.

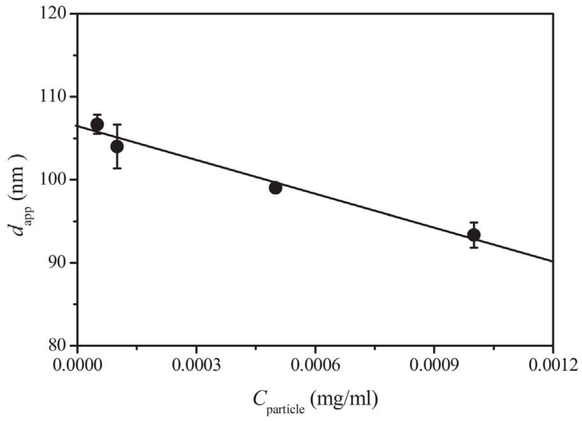

Fig. 1. PTA results of the calculated diameter of the PS-latex particles as a function of the PS-latex particle concentration in pure water.

2.3. Electrophoretic mobility

Electrophoretic mobility measurements were performed at 25.0 ± 0.1 °C using a zeta potential analyser (ELSZ, Otsuka Electronics Co., Ltd., Japan). The zeta potentials were estimated using the simplified Smoluchowski equation. The spherical Smoluchowski approximation can overestimate the zeta potential by up to 20%, depending on the magnitude of the zeta potential [30].

3. Results and discussion

3.1. Particle concentration effects on determination of PS-latex nanoparticle size in pure water

Fig. 1 shows the results for the dependence of the observed apparent diameter d_{app} of the PS-latex particles on the particle concentration ($C_{particle}$) in aqueous solution.

The observed apparent diameter, proportional to the inverse diffusion coefficients of the PS-latex particles, decreased linearly with an increase in the PS-latex particle concentration. This dependence on particle concentration is used to represent the relationship between the observed and the more reliable diameter of particles in terms of the particle concentration in solution [31],

$$d_{app} = d_{calc}(1 + k_P C_{particle}) \tag{3}$$

where d_{app} is the observed apparent particle diameter, d_{calc} is the calculated particle diameter assuming no inter-particle interaction effect, and k_P is a constant. Using the weighted least-mean-squares method with the corresponding uncertainties for the results in Fig. 1, d_{calc} is estimated to be 106.2 ± 2.3 nm by extrapolating the PS-latex particle concentration to zero form Eq. (3). The individual sources of uncertainty and the calculation method of the combined standard uncertainty in the diameter of the PS-latex particles in aqueous suspension are shown in the supplementary information. The k_P value in Eq. (3) obtained by linear regression is -1.32×10^5 mL/mg. The size, d_{calc}, of the PS-latex particles determined by PTA was slightly different from the official values determined by DMA (100 ± 3 nm), indicating that inter-particle interaction effect is not completely removed by only extrapolating the PS-latex particle concentration to zero.