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Hydrodynamic size and electrophoretic mobility of latex nanospheres in monovalent and divalent electrolytes

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HIGHLIGHTS

- ► Hydrodynamic radius and electrophoretic mobility were measured by two commercial devices (Malvern ZetaSizer 3000 and ZetaNano).
- ► Latex sulfate nanospheres of 530 nm diameter were investigated as function of ionic strength and particle concentration.
- ► Electrophoretic mobility at very low ionic strength agrees with the theoretical prediction.
- ► The aggregation rates at high ionic strength are discussed.

GRAPHICAL ABSTRACT
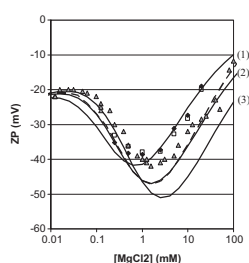
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ABSTRACT

The hydrodynamic size and electrophoretic mobility of sulfate latex nanospheres are given as a function of ionic strength for KCl and $MgCl_2$ and at different volume fractions. The results were obtained from Doppler velocimetry and Dynamic Light Scattering using a Malvern ZetaSizer Nano (ZetaNano) at 173° scattering angle and a Malvern ZetaSizer 3000HSA (Zeta3000) at 90° scattering angle. Although the instrumentation is similar, we observed differences in the hydrodynamic radii. The reason for these discrepancies are most probably due to the conversion of the detected light intensity into particle radius since the particles have a diameter of about 530 nm (measured by TEM) quite close to the lasers' wavelength (633 nm). From the study, we found in particular that the hydrodynamic radius decreases upon addition of monovalent or divalent salt. This behavior is generally attributed to the presence of a hairy layer on the particle's surface. We also found that the electrophoretic mobility decreases logarithmically with increasing particle concentration, as predicted for nearly salt-free conditions. The change in viscosity at higher ionic strength and the shift in the shear plane position are shown to play a role in the aggregation behavior.

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1. Introduction

The stability and electrokinetic properties of colloidal dispersions made of charged monodisperse latex spheres have been extensively studied over the years [1–12]. In the earlier papers there has been a lot of discussions about the non-ideality of such systems. The presence of a mobility maximum in the electrophoretic mobility as a function of electrolyte concentration plots has often been attributed to an anomalous behavior ([1,6] and references within), whereas more recent studies have attributed this behavior to the constant charge nature of these systems [11–13]. There has also been extensive discussions about the surface properties of such latexes [1,6,8,20] to explain the discrepancies between electrophoretic mobilities and dielectric spectroscopy data or the evolution of the hydrodynamic radius as function of ionic strength. Similarly, the early stage of aggregation of these latexes has been

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studied [3,13]. In [3], for example, the same type of sulfate latexes as the ones used in the present study are investigated. The authors come to the conclusion that the DLVO-theory can be used to model the aggregation behavior for these latexes provided that the characteristic length scales (Debye length, energy barrier position) are located at a few nm from the particle surface. This condition is only met for very low charge densities (of at most $\simeq 2\,mC/m^2$). For more charged latexes (as the ones in the present study), a deviation from the DLVO-theory is expected, since the energy barrier position is located at less than 1 nm from the surface in most cases.

The interpretation of aggregation rates at the initial stage of aggregation depends on two important parameters: the particle electrokinetic potential and the Hamaker constant of latex across water. In an earlier studies [10,12], we showed that in order to model correctly the electrokinetic response of the present sulfate latexes we needed to introduce either a Stern layer conductance [10] or shift the shear plane at a distance of 0.25 or 0.5 nm from the particle surface [12]. Either of the two adjustments lead mathematically to the same changes, in particular a decrease of the electrophoretic mobility and the electrokinetic potential in the range of 1–100 mM of added salt (see [12]). The most common interpretation of these adjustments is the hairy layer model that postulates that a layer of polymer chains extend from the particle surface [6]. This is supported by experiments on heat-treated samples, which exhibit a constant hydrodynamic radius as a function of ionic strength, being interpreted as a collapse of the hairs onto the particle's surface. The extend of these hairs can be measured quite accurately [16]. The second parameter, the Hamaker constant of latex across water can likewise be estimated [16]. Its value varies in the literature from 0.9 to 1.3×10^{-20} J [5,14]. As stated in [20] these differences in values can be attributed to inhomogeneities at or close to the particle surface, in particular the presence of nanobubbles on these hydrophobic surfaces. Meanwhile one should keep in mind, while studying the early stage of aggregation, that there might be a combination of aggregate creation in the primary and secondary energy minimum which can lead to a misinterpretation of aggregation rates. Behrens and Borkovec [15] have demonstrated that for large particles (as the ones of the present study) secondary aggregation should be taken into account: a transient period of fast aggregation into the secondary minimum (typically 15 s for 350 nm radius particle and a surface potential of −20 mV and an ionic strength of 10 mM) will be followed by primary aggregation at a lower rate than expected for the initial aggregation in the absence of a secondary minimum. As the degree of aggregation that is reached within the transient time is roughly proportional to the particle concentration, we will in this study try to minimize the effects of secondary aggregation by taking a small particle concentration.

In the next sections we will present the results of our investigation of the correlation between the hydrodynamic radius and electrokinetic charge of sulfate latex nanospheres. The aim of the study is to compare the results of two commercial devices, The Malvern ZetaSizer Nano (ZetaNano) and the Malvern ZetaSizer 2000Hsa (ZetaSizer). The limitations of each equipment will be discussed at hand of the results. Two ranges of ionic strength will be investigated. In Section 2 the results for ionic strengths below 10 mM of added salt, where aggregation is absent are presented. We will in particular show that in the limit of nearly salt-free conditions the behavior of the hydrodynamic radius follows the trend predicted by Ohshima [21,22]. In Section 3 the results for ionic strengths above 10 mM are reported. There, we will briefly discuss the influence of the shift in the shear plane on the aggregation rates. This dependence is often overlooked, as in general it is the Hamaker constant that is taken as an adjustable parameter and adjusted to get the critical coagulation concentration (ccc).

2. Material and methods

2.1. Particles

The measured particles were obtained from Interfacial Dynamics Corporation (IDC). They consist of surfactant-free polystyrene sulfate latex and were used as received as they are sold as "ultraclean" latexes. The radius found by TEM reported by the manufacturer is 265 nm. The sulfate groups are considered to be strong acid and hence the particle's surface charge should not vary as function of pH or ionic strength. This was verified by electrophoretic measurements as detailed in [12]. The manufacturer reports that the surface charge of the particles is $3.9 \times 10^{-2}\,C/m^2$, which was also used in modeling the electrophoretic measurements. The temperature was set at 298 K and the pH of all suspensions was about 7.5.

The samples were made by adding the required amounts of particle stock solution and electrolyte solution. These electrolyte solutions were prepared from pure water (conductivity <1 μS/cm, PureLab) and analytical grade salts ($MgCl_2$ and KCl).

2.1.1. Heat treatment

10 mL of a stock sample (190 mg/L of latex in pure water) was placed in a high density polypropylene (HDPE) sealed bottle and set for 20 s in a microwave oven at 850 W. The sample was then left to cool at room temperature. No traces of coagulum was detected.

2.2. Apparatus

Two commercial devices (zetameters) were used to measure the hydrodynamic radius and the electrophoretic mobility of the samples: the Malvern ZetaSizer 3000 HSa (ZetaSizer) and the Malvern ZetaNano ZS (ZetaNano). Details of the technique can be found at [17]. The main differences and similarities between the devices are that:

Measuring the electrophoretic mobility

- in the ZetaNano, only the scattering beam passes through the capillary cell and the reference beam is routed outside. Analysis of the Doppler shift in the Zetasizer Nano series is done by using phase analysis light scattering. In the ZetaSizer, the two laser beams crossed in the capillary cell and Doppler shift analysis is performed by Fourier transformation.
- the cylindrical capillary cell of the ZetaSizer is made of quartz and platinum electrodes, whereas the U-shaped capillary cell (referred to as U-cell) used for the ZetaNano was the disposable polycarbonate "Size & Zeta potential" Folded Capillary cell DTS1060 which has gold electrodes.

Measuring the hydrodynamic radius

- in both devices the hydrodynamic radius determined by Photon Correlation Spectroscopy (Dynamic Light Scattering) is and is estimated from the particles' diffusivity using the Stokes–Einstein relationship
- the same cells (12 mm square polystyrene cuvettes (DTS0012)) could be used in both devices. This type of cuvette will be referred to as "square cell".
- the scattering angle of the ZetaSizer is 90° and 173° (backscatter) for the ZetaNano
- the U-shaped capillary cell DTS1060 (U-cell) could be used to estimate both the zeta potential and the hydrodynamic radius with the ZetaNano
- Both apparatuses make use of a HE-Ne laser of 5 mW at 633 nm wavelength.