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Characterization of gold nanoparticles with different hydrophilic coatings via capillary electrophoresis and Taylor dispersion analysis. Part I: Determination of the zeta potential employing a modified analytic approximation

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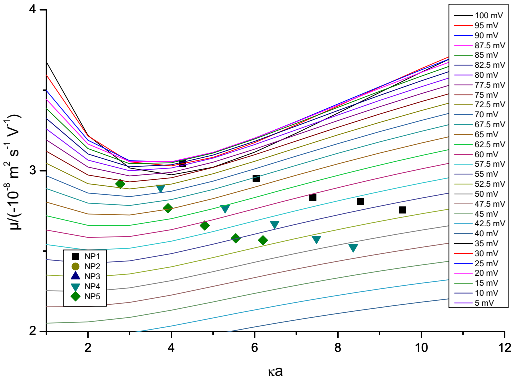
GRAPHICAL ABSTRACT



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ABSTRACT

Taking gold nanoparticles with different hydrophilic coatings as an example, it is investigated whether capillary electrophoresis in combination with Taylor dispersion analysis allows for the precise determination of mean electrophoretic mobilities, electrophoretic mobility distributions, and zeta potentials in a matrix of exactly known composition and the calibration-free determination of number-weighted mean hydrodynamic radii. Our experimental data confirm that the calculation of the zeta potential for colloidal nanoparticles with $\zeta > 25$ mV requires to take the relaxation effect into account. Because of the requirement to avoid particle–wall interactions, a solution of disodiumtetraborate decahydrate (borax) in deionized water had been selected as suitable electrolyte. Measurements of the electrophoretic mobility at different ionic strength and application of the analytic approximation developed by Ohshima show that in the present case of a buffered solution with a weak electrolyte co-ion and a strong electrolyte counterion, the effective ionic drag coefficient should be approximated with the ionic drag coefficient of the counterion. The obtained results are in good agreement with theoretical expectations regarding the dependence of the zeta potential and the electrokinetic surface charge density on the ionic strength. We also show that Taylor dispersion analysis (besides estimation of the

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number-weighted mean hydrodynamic radius) provides additional information on the type and width of the number-weighted particle distribution.

1. Introduction

Colloidal nanoparticles (NPs) that are dispersed in an aqueous medium (electrolyte solution) often are charged in order to warrant colloidal stability [1]. Though also steric repulsion is frequently used for stabilizing NPs in aqueous solution, stabilization by electrostatic repulsion is in particular interesting for obtaining water-soluble NPs with small hydrodynamic radius. Charge is introduced by the adsorption of ions onto the surface and/or the protonation or dissociation of acidic or basic groups bound to the surface [2]. If the surface charge density is very high, counterions (having a charge of opposite sign to that of the NPs) are in part neutralizing these charges via charge condensation, so that the "effective surface charge density" becomes lower than the total charge density [3]. According to the Poisson–Boltzmann approach the effective charge of the NP is compensated by a diffuse layer of counterions around the NP (the ionic cloud [4]), in which the electric potential can be described (in the static case) by the Poisson–Boltzmann equation, considering the electrolyte ions as point charges.

Colloidal dispersions of charged NPs (having a charge of equal sign) are stabilized by electrostatic forces. Consequently, the effective charge Q_{eff}, the electrokinetic surface charge density σ_ζ, and the electric potential at the surface of shear (the electrokinetic potential ζ) are important quantities in the characterization of NPs. These quantities are difficult to be measured experimentally. Typically, the NPs of interest are immersed in an electrolyte of known composition, in which the electrophoretic mobility of the NPs is determined by application of a constant homogeneous electric field or by application of an alternating electric field. The determined electrophoretic mobility μ is then related to the electrokinetic potential ζ (also denoted zeta potential) which is the electric potential near the surface of the NP, where the (relative) velocity of the liquid is zero (surface of shear).

For spherical NPs with higher zeta potential ($\zeta > 25$ mV) the relaxation effect, *i.e.* the retarding force due to a deformation of the ionic cloud, must not be neglected [5,6]. Neglecting the relaxation effect in the calculation of the zeta potential will result in an intolerable error in the calculated value for ζ. Taking the relaxation effect into account results in a set of differential equations that cannot be solved analytically, even in the case of a symmetrical 1:1 electrolyte, assuming that the NPs are ideal spheres with a homogeneous surface charge density, and assuming that NP–NP and ion–ion interactions can be neglected [7,8].

Wiersema et al. [9] were the first who succeeded in solving these equations numerically. They calculated a limited set of data for a hypothetical 1:1 electrolyte (and some data for other types of electrolyte) with cations and anions, both having a dimensionless ionic drag coefficient of 0.184 (see Eq. (5)). According to the definition made by Wiersema et al. the ionic drag coefficient is a dimensionless reduced parameter, which is inversely proportional to the limiting equivalent conductance of the ion. As that would have consumed too much computer time (at the time of their investigations), the ionic drag coefficient of the counterion and the co-ion was only varied for one set of scaled zeta potential and reduced radius, although the authors emphasized the importance of this parameter. However, from the few data points presented in their paper one can conclude that a variation in the ionic drag coefficient of the co-ion (here between 0.0655 and 0.74) has only a marginal impact on the electrophoretic mobility, while there is a strong impact when varying the ionic drag coefficient of the counterion.

The aspect "influence of the ionic drag coefficients of the co-ion and the counterion on the electrophoretic mobility" was not considered by O'Brien and White [10] when recalculating electrophoretic mobilities (with an improved algorithm) for varied scaled zeta potential and reduced radius. In all cases, O'Brien and White assumed a solution of KCl as electrolyte.

The analytic approximation presented by Ohshima [11] for the general case includes the calculation of the arithmetic mean of the dimensionless ionic drag coefficients of the co-ion and the counterion. With this analytic approximation, data were calculated for a solution of KCl as electrolyte and compared to those results obtained by O'Brien and White.

Independent of the theoretical approach, the experimental basis of a precise determination of ζ is a precise determination of the electrophoretic mobility in an electrolyte of exactly known composition. In this regard capillary electrophoresis (CE) has come into the focus of interest. CE is a separation technique that permits to separate the NPs of interest from further constituents of the sample and to separate NPs according to differences in size and/or their surface charge density [12–21]. CE has been shown to enable to calculate conversion degrees [22] and to probe NP–protein interactions [23]. In addition, it allows to gain insight into the presence or absence of agglomerates [24,25], to detect fractions with different migration behaviors [26] (*e.g.* in the case of a bimodal distribution) and (as will be shown in the second paper of this series [27]) in favorable circumstances it allows for calculating NP size distributions from recorded electropherograms.

At the same time, CE requires the use of a buffered electrolyte to provide a separation medium of defined pH and to keep the velocity of the electroosmotic flow constant. In principle, buffering needs the use of a weak acid or a weak base, which is in a protonation equilibrium with its conjugate base or acid. Consequently, buffers contain weak electrolytes with an incomplete degree of dissociation or protonation. From this need it can be concluded that in the general case (for buffers employed in CE) the co-ion and the counterion will have very different dimensionless ionic drag coefficients.

The same instrumentation, which is employed for CE, can be also used for Taylor dispersion analysis (TDA), which was recently demonstrated by several working groups [28,29]. TDA allows (independent of capillary electrophoresis) the precise determination of number-weighted or volume-weighted mean hydrodynamic radii (a needed quantity for the correct determination of ζ assuming identity of the sphere radius a (according to the definition given by Wiersema et al. [9]) and the hydrodynamic radius r_H obtained from application of the Stokes–Einstein equation).

For example, Ibrahim et al. [29] succeeded in demonstrating that CE (determination of mean electrophoretic mobility μ) in combination with TDA (determination of mean hydrodynamic radius r_H) permits the determination of mean effective charges (or mean effective charge numbers z_{eff}) for small ions, polyelectrolytes and organic and inorganic NPs. However, although in some instances Ibrahim et al. employed borax dissolved in water as background electrolyte, they did not discuss the influence of the electrolyte ion mobilities on the results obtained.