

Polyelectrolyte assisted charge titration spectrometry: Applications to latex and oxide nanoparticles

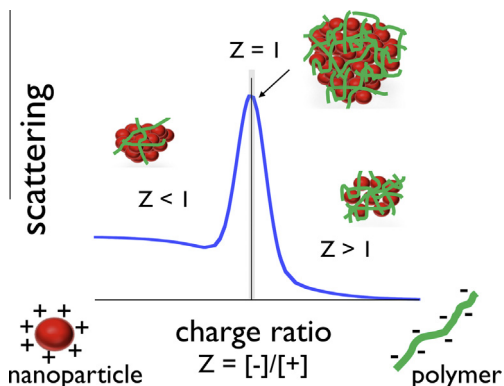


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GRAPHICAL ABSTRACT



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ABSTRACT

The electrostatic charge density of particles is of paramount importance for the control of the dispersion stability. Conventional methods use potentiometric, conductometric or turbidity titration but require large amount of samples. Here we report a simple and cost-effective method called polyelectrolyte assisted charge titration spectrometry or PACTS. The technique takes advantage of the propensity of oppositely charged polymers and particles to assemble upon mixing, leading to aggregation or phase separation. The mixed dispersions exhibit a maximum in light scattering as a function of the volumetric ratio X , and the peak position X_{Max} is linked to the particle charge density according to $\sigma \sim D_0 X_{Max}$ where D_0 is the particle diameter. The PACTS is successfully applied to organic latex, aluminum and silicon oxide particles of positive or negative charge using poly(diallyldimethylammonium chloride) and poly(sodium 4-styrenesulfonate). The protocol is also optimized with respect to important parameters such as pH and concentration, and to the polyelectrolyte molecular weight. The advantages of the PACTS technique are that it requires minute amounts of sample and that it is suitable to a broad variety of charged nano-objects.

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1. Introduction

Electrostatic Coulomb forces are ubiquitous in soft condensed matter [1,2]. Interaction pair potentials created by elementary charges of the same sign at interfaces or along macromolecules

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are long-range and repulsive. These interactions depend on physico-chemical parameters, such as the dielectric constant of the continuous phase, the solute concentration, the pH, the ionic strength and the temperature. Electrostatic forces between like-charged systems are especially relevant to insure repulsion between colloidal objects. At low ionic strength, electrostatic repulsions are for instance sufficient to induce long-range ordering and colloidal crystal phases [3]. In aqueous dispersions, the ionizable groups at the colloid surface exert Coulombic forces toward the counterions, leading to their condensation and to the formation of the electrical double layer [1]. The counterion condensation occurs for charge density σ above a certain threshold [4]:

$$\sigma > \frac{2}{\pi D \ell_B} \quad (1)$$

where D is the diameter of the colloid and ℓ_B is the Bjerrum length (0.7 nm in water). As a result, particles in solution satisfying Eq. (1) behave as if they would have an effective charge Z_{eff} different from its structural charge Z_{str} [4,5]. The counterion condensation for colloids bears strong similarities with that derived for polymers and known as the Oosawa-Manning condensation [6]. Following Belloni [4] the effective charge can be approximated by the expression:

$$Z_{\text{eff}} = \frac{2D}{\ell_B} \quad (2)$$

For a particle of charge density $\sigma = +1e \text{ nm}^{-2}$ and a diameter of 10 nm, the effective charge $Z_{\text{eff}} = +28e$ represents around 10% of the total ionizable groups ($Z_{\text{str}} = +314e$). As the condensed counterions are firmly attached to the surface and move with the colloid during diffusion, experiments such as electrophoretic mobility measurements [7–12] or small-angle scattering experiments in the concentrated regime [13–15] enable access to the effective charge only.

Potentiometric, turbidity or colloid titration techniques, as well as conductometry are commonly used to determine the structural charges of colloids. Potentiometric or acid-base titration coupled with conductometry was successfully applied to microgels [16], polymer micelles [17] and metal oxide nanoparticles [18–21]. However the technique requires large sample quantity, which depending on the particle synthesis is not always possible. To determine the charge density of iron oxide particles for instance, Lucas et al. used potentiometric titration with dispersions containing 5–10 g of iron oxide dry matter [18]. Colloid titration is another method that was introduced by Terayama some 50 years ago [22]. This technique was applied to titrate ion-containing polymers in aqueous solutions. Colloid titration is based on the reaction between oppositely charged polyelectrolytes in presence of a small amount of dye molecules that serves as an indicator of the endpoint reaction between the two polymers [23,24].

Initially developed to study protein complexes, isothermal titration calorimetry (ITC) has gained interest in the field of physical chemistry. ITC was also used to survey the condensation of DNA with multivalent counterions [25] and with oligo- and polycations [26–28] and more recently the complexation between polymers, proteins or surfactants. Despite a large number of studies [29–39] the interpretation of the thermograms remains a challenge, as the heat exchanges during titration exhibit rich and numerous features not always accounted for by existing models [33,40]. More recently, ultrafast laser spectroscopy coupled to the generation of the second harmonics or resistive pulse sensing techniques were proposed to measure the surface charge of particles in the nanometer range [41,42].

The technique examined here borrows its principle from methods developed for enzymatic activity measurements [43] and from turbidity titration [44,45]. Earlier reports suggest that the maximum of absorbance or turbidity associated with the precipitation is related to the end-point reaction, and allows an estimation of

the charge density of the titrated colloids. The method applied here differs from turbidity titration in two aspects: (i) light scattering is preferred to UV-spectrometry and (ii) the mixed polymer and particle dispersions are prepared by direct mixing instead of step-wise addition. With newly developed photon counters, light scattering is a highly sensitive technique, which can detect colloidal diffusion down to extremely low concentration. During the last decade, light scattering has been applied to investigate the complexation of oppositely charged species, including surfactant, polymers, phospholipids and proteins [12,46–53]. In most studies however, emphasis was put on the structures that formed and not on the reaction stoichiometry [54]. Here we develop a simple protocol based on the use of light scattering and on the complexation property of particles with oppositely charged polymers. The technique is assessed on different types of organic and inorganic nanoparticles in the 50 nm range, either positive or negative and it is shown that the structural charge and charge density can be determined with minute amount of sample. The technique was dubbed Polyelectrolyte Assisted Charge Titration Spectrometry subsequently abbreviated as PACTS.

2. Materials and methods

2.1. Nanoparticles

Latex particles functionalized with carboxylate or amidine surface groups were acquired from Molecular Probes (concentration 40 g L^{-1}). The dispersion pH was adjusted at pH 9.7 and pH 6 by addition of sodium hydroxide and hydrochloric acid, respectively. The particles were characterized by light scattering and transmission electron microscopy, yielding $D_H = 39 \text{ nm}$ and 56 nm and $D_0 = 30$ and 34 nm . Negative silica particles (CLX[®], Sigma Aldrich) were diluted from 450 to 50 g L^{-1} by DI-water. Particles were dialyzed for 2 days against DI-water at pH 9. Positive silica particles ($D_H = 60 \text{ nm}$) were synthesized using the Stöber synthesis route [55–57]. Silica seeds were first prepared and grown to increase the particle size. Functionalization by amine groups was then performed, resulting in a positively charged coating [56]. Aminated silica synthesized at 40 g L^{-1} were diluted with DI-water and the pH was adjusted to pH 5 with hydrochloric acid. Aluminum oxide nanoparticle powder (Disperal[®], SASOL) was dissolved in a nitric acid solution (0.4 wt% in deionized water) at the concentration of 10 g L^{-1} and sonicated for 1 h. For the PACTS experiments, the dispersions were further diluted to 0.1 g L^{-1} and the dispersion pH was adjusted to pH 4 with sodium hydroxide. In this pH condition, the nanoalumina are positively charged ($D_H = 64 \text{ nm}$) [58].

Fig. 1 displays images of the particles obtained by transmission electron microscopy (TEM). Except for Al_2O_3 which have the form of irregular platelets of average dimensions 40 nm long and 10 nm thick, all other particles are spherical. In Table 1, the hydrodynamic diameters D_H are found slightly higher than the geometric diameters D_0 found by TEM. With light scattering, the largest particles contribute predominantly to the scattering intensity and determine the value for the measured D_H . The dispersity s defined as the ratio between the standard deviation and the average diameter are shown in Table 1 (see Supplementary Fig. 1 for size distributions).

2.2. Polymers

Poly(diallyldimethylammonium chloride) (PDADMAC) of molecular weight $M_w = 13.4$ and 26.8 kDa was purchased from Polysciences Europe and from Sigma Aldrich respectively. The degree of polymerization was determined from the number-average molecular weight M_n by size exclusion chromatography

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