



# Influence of particle/solid surface zeta potential on particle adsorption kinetics



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## ARTICLE INFO

### Article history:

Received 2 April 2014

Accepted 20 May 2014

Available online 12 June 2014

### Keywords:

Polystyrene/silica

Zeta potential

Electrostatically driven adsorption

Kinetics model

Random sequential adsorption

## ABSTRACT

In this paper we attempt to understand monolayer formation of spherical particles on a solid surface immersed in a suspension and driven by electrostatic interaction force. The study focuses on the theoretical aspects of the particle adsorption and modeling work based on the random sequential adsorption (RSA) approach is done in order to describe the particle adsorption kinetics and the saturation coverage. The theoretical model is then compared with experimental data obtained under conditions similar to those of the modeling work. Studying the adsorption of polystyrene particles on a silicon wafer in an aqueous system was employed to experimentally validate the theoretical framework. It has been shown both theoretically and experimentally that the particle and solid surface zeta potential values do influence the adsorption kinetics but the effect is too negligible to be of any use in accelerating the kinetics. We have shown that the electrostatically driven particle adsorption is a transport limited process and the rate of transport is not a major function of the zeta potential values of the particle and the solid surface. The faster kinetics seen when the ionic concentration of the suspension is increased is because of the blocking effects and not due to faster approach of particles towards the solid surface. Finally, we have made an important addition to the existing models by incorporating the variation in the flux as a function of particle/solid surface zeta potentials, surface coverage and the randomized position of incidence of an incoming particle on the solid surface.

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## 1. Introduction

Formation of a thin layer of particles on a solid surface that is stable on exposure to environmental conditions is important for many practical applications and at the same time poses some interesting scientific questions. Such nano/microscale tailored structures find applications for semiconductor devices [1], layer-by-layer assembly for energy storage devices [2], trace chemical analysis [3] etc. Many methods are reported in literature for forming thin layers of a material on a solid substrate. The popular methods include spin coating, dip coating, Langmuir–Blodgett transfer assembly, etc. [4]. However when only a monolayer of particles is desired on the solid substrate, most of the above mentioned methods prove to be unsuccessful since the driving force for the assembly in those is capillary interaction that does not diminish when a monolayer has been deposited [5,6]. Coating via convective assembly does generate monolayers however it requires the particle suspension to have a high particle volume fraction (~1–30%) for the time scale of operation to be practical and is energy intensive

[7]. The deposition speed required for monolayer formation of nanoparticles from a dilute suspension tends to be very low in accordance to the equation proposed by Nagayama [8]. Self-assembly on the solid surface from particles stabilized in a suspension affords an inexpensive route for formation of the desired monolayers. Since the particles in the suspension are stabilized by virtue of mutual repulsion, a monolayer is guaranteed due to the repulsion between adsorbed particles and an approaching particle. This method would be applicable for suspensions with low volume fractions since the driving force would be the interaction energy between the particles in the suspension and the solid surface and the Brownian motion of the particles towards the solid surface driven by the interaction energy gradient. The driving force for the adsorption method discussed in this work is the electrostatic attraction between the particles and the solid surface. It is important to adjust the pH and the ionic strength of the suspension such that the particles and the solid surface have an opposite surface charge [9–11]. The solid surface with the adsorbed particles is usually analyzed under the scanning electron microscope [12] or the atomic force microscope [13,14] and kinetics data is obtained. Conflicting literature however exists with regards to the nature of the kinetics curve that should be expected. The adsorption of

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surfactants at a liquid/air interface is usually very accurately described by the Ward–Tordai equation [15,16]. The equation is however valid only if the flux of the approaching species towards the solid surface gets entirely adsorbed on the solid surface. The Ward–Tordai equation will not be expected to accurately describe particle adsorption kinetics since it does not take into account blocking effects, electrostatic and van der Waals interactions that would be of importance for the transport of the particle towards the solid surface. The literature for particle adsorption kinetics is conflicting, both square root time and linear time dependence for surface coverage has been reported. The square root time dependence is in accordance with the RSA models that assume constant flux and some experimental data supports this theory [17]. Linear dependence of surface coverage on time has also been reported [11,13,18,19]. With these facts in mind, we felt it is necessary to obtain a better in-depth understanding of the electrostatically driven adsorption of particles at a solid surface in a suspension. We are further motivated to answering the question whether the magnitude of zeta potential for the particles and of the solid surface can be used to tune the adsorption dynamics. If this were true, it would mean that just fine-tuning the pH of the suspension at fixed ionic strengths could minimize the time required for attaining saturation coverage. It has also been reported that the rate of adsorption at later stages is reduced relative to the earlier stages [20] but this has yet to be quantified systematically. In this paper we develop a model describing the adsorption kinetics by coupling the energetics, transport equations and the random sequential adsorption logic.

The paper is organized as follows: first we present experimental data to comment on the rate-determining step for the adsorption process, next we present a model to describe the adsorption kinetics considering that the process is transport limited. Finally experimental data to validate the model is presented and we comment on the intricate details of the process.

## 2. Materials and methods

### 2.1. Materials

Acetone (ACS grade, Alfa Aesar), methanol (laboratory reagent, Sigma Aldrich), chloroform (HPLC grade, Spectrum), sodium chloride (NaCl, Spectrum) were used without further purification. Hydrochloric acid (ACS reagent grade, Ricca) and sodium hydroxide pellets (Acros organics) were diluted to obtain 0.1 M solutions for each. Silicon wafers (p-type, <math>\langle 100 \rangle</math>, from Silicon Quest) polished on one side were used as the solid surface for adsorption. Amidine polystyrene particles (Invitrogen) of diameter 200 nm and 500 nm were used for adsorption. All suspensions were prepared using deionized water. The pH of the suspension was adjusted using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solutions. The ionic concentration was adjusted using NaCl crystals.

### 2.2. Substrate preparation

The silicon wafers were cut into  $2 \times 1$  cm pieces using a diamond tipped pen, cleaned with chloroform at  $65^\circ\text{C}$ , then with acetone also at  $65^\circ\text{C}$  and then with methanol at  $75^\circ\text{C}$ . Between solvents, the Si substrates were dried in nitrogen flow. The substrates were then treated in a Samco UV Ozone Stripper to remove organic residue.

### 2.3. Sample preparation

Silicon substrates with adsorbed particles after increasing time intervals were required to obtain the experimental graph for adsorp-

tion kinetics. The particle suspension as obtained was diluted using deionized water to a concentration of 0.2 mg/ml and 0.37 mg/ml. The ionic concentration was adjusted by addition of sodium chloride crystals and the pH was adjusted to the required value. The clean silicon substrates were then dipped in the stagnant particle suspension for fixed interval of time and were taken out, were rinsed with deionized water and were dried under nitrogen flow. More than fifteen data points were collected for obtaining a kinetics curve for any given suspension. One milliliter of suspension was used for every adsorption run. The substrates were dipped vertically in the suspension during the initial run and were dipped horizontally during the repeatability run. This was done to validate the quasi-steady state assumption used in the model.

### 2.4. Characterization

Dynamic light scattering was performed on a Malvern zetasizer nano to quantify the size of the polystyrene particles. A hydrodynamic diameter consistent with that on the product label and as seen under a scanning electron microscope was obtained for both the particle populations. The size of the particles was constant even after a suspension at a pH value of 10 or below was kept stagnant for 24 h and readings were taken without sonication. The coverage of the particles on the silicon wafers was quantified by imaging the wafers under a Zeiss Supra 55 scanning electron microscope. The value of the surface coverage was obtained by processing the images in Matlab. Zeta potential measurement was done according to the principle of laser Doppler electrophoresis on the Malvern zetasizer nano. Fig. 1 shows the zeta potential characteristics of polystyrene particles and that of a silicon surface in an aqueous solution at different pH and ionic strengths.

As can be noted from Fig. 1, electrostatically driven adsorption of polystyrene particles on silicon wafer is possible between pH values of 2 and 10.5.

## 3. Identification of the rate-determining step

The following steps that occur in series govern the rate at which a particle in a suspension adsorbs on a solid surface:

1. Transport towards the solid surface from the bulk.

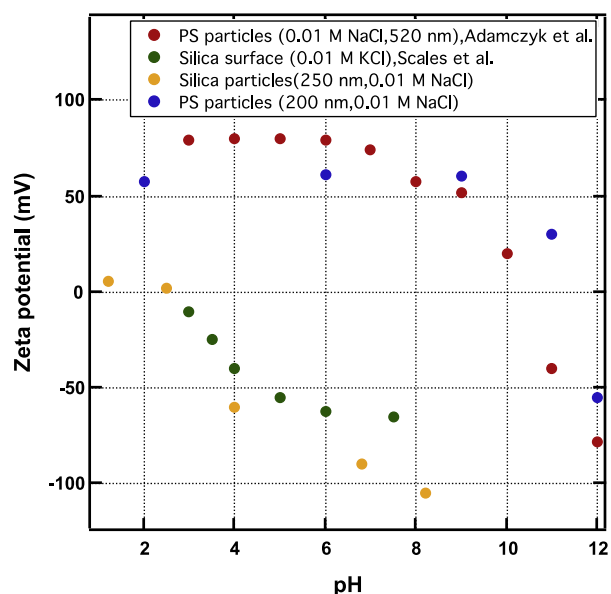


Fig. 1. Zeta potential values for polystyrene and silica particles as a function of the suspension pH and ionic strength [21,22].

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