CHAPTER 5

Deposition of polystyrene particles in a parallel plate flow chamber under attractive and repulsive electrostatic interactions

ABSTRACT

In this paper, the deposition of negatively charged polystyrene particles in a parallel plate flow chamber to negatively and positively charged collector surfaces is compared at different shear rates (10 - 200 s\(^{-1}\)) and ionic strengths (10 - 80 mM KNO\(_3\)). The observation of adhering particles was done in situ during the deposition process with the aid of an image analyser and the adsorption and desorption of each particle was monitored individually using a special tracking algorithm. Initial deposition rates \(j_0^{\text{EXP}}\) were higher to positively charged glass than to negatively charged glass collector surfaces, depending on shear rates and ionic strength. All observed experimental deposition rates were, however, smaller than the Smoluchowski-Levich (SL) approximate solution of the convective-diffusion (CD) equation. Initial deposition rates were also calculated using an exact numerical solution of the CD equation, which were two times higher than the experimentally observed deposition rates for positively charged glass, and about equal or lower for negatively charged glass. The desorption rates \(j_{\text{des}}(t)\) of polystyrene particles on positively charged glass were near zero under all conditions, whereas the desorption rates from the negatively charged glass were considerable and finally balancing the adsorption rates \(j_{\text{ads}}(t)\).
From the residence time dependent desorption probability per unit time $\beta(t-\tau)$, it could be
determined that polystyrene particles on negatively charged collector surfaces have the highest
probability of desorption within the first 5-10 min after deposition. Five parameters could be
independently extracted from the experiments that together fully describe the deposition
process, including the initial deposition rate $j_0$ (from an extrapolation of the initial adsorption
rate to $t = 0$), the blocked area $A_{\text{kin}}$, the initial desorption probability $\beta_0$, the final desorption
probability $\beta_\infty$, and the relaxation time $1/\delta$ (from the experimentally observed residence time
dependent desorption probability $\beta(t-\tau)$). Experimental results were subsequently compared
with those from a proposed adsorption-desorption model for deposition kinetics, using the
parameters derived as an input, and with a Monte-Carlo simulation of the deposition process. A
high degree of similarity between experimental, adsorption-desorption model, and the Monte
Carlo simulation results was observed, which indicates the consistency of the applied
experimental methods and theoretical models.

5.1 INTRODUCTION

Particle deposition from flowing suspensions onto collector surfaces is of importance in a
broad field of applications ranging from chromatographic separation, pulp and paper making to
microbial deposition onto carrier materials in bioreactors and surfaces in the human body.
Several types of flow devices, such as the stagnation-point flow chamber [1,2], the rotating disc
system [3,4], and the parallel plate flow chamber [5,6], have been designed in order to study
particle deposition to solid surfaces under controlled mass transport conditions.

Conceptually, the parallel plate flow chamber is one of the simplest systems. In a parallel
plate flow chamber mass transport is slow and mainly through convective-diffusion [6], while
an analytical solution of the convective-diffusion (CD) equation for the parallel plate
configuration is difficult to obtain. Therefore, numerical and approximate solutions like the
Smoluchowski-Levich (SL) approximation [7] have been proposed. In the SL approximation it
is assumed that the collector surface acts as a perfect sink, i.e. all particles sufficiently close to
the surface adhere irreversibly. In general, however, experimentally observed deposition rates
are much smaller than predicted by the SL approximation [8,9] unless the repulsive
electrostatic interactions between the collector surfaces and the depositing particles are
reduced by increasing the ionic strength of the suspending fluid.

Numerical solutions of the CD equation can be obtained for the parallel plate flow chamber
in two dimensions while taking into account the electrostatic particle-surface interactions.
Therefore numerical solutions yield a better estimate of the initial deposition rate, where the SL
approximation only yields a theoretically limiting value. However, numerical solutions mostly
yield a critical value for the ionic strength, below which the deposition rate is zero, and above
which the deposition rate is non-zero and nearly independent of ionic strength. Experiments
show a more gradual dependency of ionic strength [8].

Recently, the use of the parallel plate flow chamber has been combined with real-time in situ
image analysis techniques to monitor not only the kinetics of deposition, but also the
adsorption and desorption rates of particles on a collector surface, the residence times of
desorbing particles, and the direct quantification of blocked areas from the spatial arrangement
of the adhering particles. Using these techniques, Meinders and Busscher [9] described initially high desorption rate coefficients (approximately $10^{-4}$ s$^{-1}$) for polystyrene particles on glass under conditions of electrostatic repulsion that decreased within 2-4 min to a low, but non-zero final value of around $10^{-6}$ s$^{-1}$.

The kinetics of the deposition process was theoretically described by Dabros and Van de Ven [10], taking into account desorption, bond aging, and particle blocking effects. In this Langmuir model, five parameters describe the deposition kinetics that can all be independently derived from deposition experiments using real-time *in situ* image analysis [9]. Blocking effects, as also included in this Langmuirian model, were studied in detail by several experimenters, [11-14] using Monte Carlo simulations, showing that deposition is essentially a random sequential adsorption (RSA) process, in which blocking effects limit surface coverage to 0.547 times the value predicted by the Langmuir model.

The aim of this paper is firstly to establish experimental data for the deposition of polystyrene particles to positively and negatively charged glass surfaces in a parallel plate flow chamber and to compare the deposition data under attractive and repulsive electrostatic conditions with theoretical solutions of the CD equation. Secondly, the experimental results are compared with those from a proposed adsorption-desorption model for deposition kinetics, accounting for residence time dependent desorption, and from Monte-Carlo simulations.

5.2 MATERIALS AND METHODS

5.2.1 Polystyrene particles and collector materials

Monodisperse polystyrene particles (AkA11) with a diameter of 814 nm were kindly provided by Dr. R. Zsom, AKZO Research, The Netherlands. The particles were washed twice by centrifugation in demineralized water and suspended to a concentration of $1 \times 10^9$ per ml in a 10, 45 or 80 mM potassium nitrate (KNO$_3$) solution. Zeta potentials of the polystyrene particles in the different solutions are given in Table 1.

Glass substrata (5.0 x 7.6 cm) constituting the top and bottom plates of the flow chamber, were either cleaned thoroughly to yield a zero degrees water contact angle and a negative zeta potential (see also Table 1), or surface treated after cleaning with 3(2-aminoethylamino)-propyldimethoxysilane (APTS) to yield a slightly positively charged, more hydrophobic surface with zeta potentials and water contact angle as listed in Table 1. To this end, the cleaned glass surfaces were first dried in an oven at 80 °C, after which the surfaces were exposed to a 0.05% (w/v) solution of APTS in trichloroethylene during 10 min. After 10 min, the surfaces were rinsed in trichloroethylene, methanol and Milli-Q water and finally dried overnight in an oven at 80 °C.
Table 1. Zeta potentials in different ionic strength KNO₃ solutions of the polystyrene particles used (by particulate microelectrophoresis) and of the glass substrata (by streaming potential measurements), and water contact angles for these substrata. Note that due to counterion adsorption or desorption of the adsorbed APTS molecules, the positive zeta potentials of glass + APTS gradually became more negative at a rate of approximately 15 mV/h.

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5.2.1 Parallel plate flow chamber, image analysis and experimental conditions

The parallel plate flow chamber and image analysis system have been described in detail before [15,16]. Essential dimensions employed here are the separation distance between the parallel collector plates, constituted by two Teflon spacers (thickness 0.06 cm), and the effective chamber length and width, which were 5.5 and 3.8 cm, respectively.

Deposition on the bottom plate of the flow chamber was observed with a CCD-MXR camera (High Technology, Eindhoven, The Netherlands) mounted on a phase contrast microscope (Olympus BH-2) equipped with a 40 x ultra long working distance objective (Olympus ULWD-CD Plan 40 PL). The camera was coupled to an image analyzer (TEA, Difa, Breda, The Netherlands). In this setup, one image covers an area of 0.017 mm². Live images were Laplace filtered, after time averaging to eliminate moving particles from the analysis followed by subtraction of a background image. Thereafter, particles were discriminated from the background by single grey value thresholding yielding binary black and white images which were subsequently compressed and stored on computer disk. The black and white images were later analyzed by so-called image sequence analysis, in which special attention is given to the establishment of connectivity between the images in order to avoid false detection of particle adsorption or desorption [17].

All experiments were carried out in twofold at different flow rates corresponding to wall shear rates of 10, 100 and 200 s⁻¹, well within the range of laminar flow.

5.2.3 Data analysis

The total number of adhering particles per unit area n(t), the number of adsorbed and desorbed particles per unit area and time jₐₕₜ(t) and jₐₜₜ(t) were directly measured as a function of time by image sequence analysis. n(t) was obtained simply by enumeration of the number of particles in each image, whereas jₐₕₜ(t) and jₐₜₜ(t) were determined from a subtraction of two successive
Deposition of polystyrene particles

images. The initial deposition rate $j_0^\text{EXP}$ was calculated by extrapolating the experimental values of $j_{\text{ads}}(t)$ to $t=0$.

The residence time dependent desorption probability per unit time $\beta(t-\tau)$ is defined as

$$\frac{dn'(t-\tau)}{dt} = -\beta(t-\tau)n'(t-\tau)$$

in which $\tau$ is the time of adsorption, and $n'(t-\tau)$ the number of particles per unit area still adhering to the collector surface $t-\tau$ after their adsorption. By means of a special tracking procedure [17], the residence time of individual particles and their desorption probabilities can be determined for residence times up to the duration of an experiment. Calculation of $\beta(t-\tau)$ included only particles adsorbing at least $t-\tau$ before the termination of an experiment. Therefore, the statistical reliability for the short residence times is better than for the longer residence times, because more particles are involved in the calculation. The experimentally derived values for $\beta$ were fitted to an exponential function [10,16]

$$\beta(t-\tau) = \beta_0 + (\beta_0 - \beta_\infty) e^{-\delta(t-\tau)}$$

in which $\beta_0$ and $\beta_\infty$ denote the initial desorption probability after zero residence time and in a stationary end-point, respectively, while $1/\delta$ is the decay time.

5.2.4 Solutions to the convective-diffusion equation

The convective-diffusion equation in its general form is given by

$$\frac{\partial C}{\partial t} + \nabla J = Q$$

in which $C$ is the particle concentration, $J$ the particle flux vector, and $Q$ a source or sink term [18]. For the parallel plate flow chamber, the deposition rate can be expressed in the dimensionless Sherwood number $Sh_0^{\text{NUM}}$

$$Sh_0^{\text{NUM}} = f_1(y^*) \left( \frac{\partial C^* (x^*, y^*)}{\partial y^*} - F^* (y^*) C^* (x^*, y^*) \right)_{y^*=0}$$

where $f_1$ is a geometry factor, $C^*$ is the concentration $C$ divided by the bulk concentration $C_b$, $y^*$ is the dimensionless distance to the collector surface, made dimensionless by

$$y^* = \frac{y}{a} - 1$$
in which \( y \) is the distance to the surface and \( a \) is the particle radius. The distance \( x \) along the flow channel is expressed in a dimensionless form with respect to the channel half depth \( b \)

\[
x^* = \frac{x}{b}
\]  

Furthermore in Equation (4), \( F^*(y^*) \) denotes the external force vector, and \( C^*(x^*,y^*) \) is the particle concentration profile. \( Sh_{NUM} \) can be obtained after calculation of the concentration profile \( C^*(x^*,y^*) \) by solving the equation in discrete form for a finite number of two-dimensional maze points. The force vector \( F^* \) was obtained by differentiating the particle-surface interaction energy with respect to \( y^* \), taking into account the Lifshitz-Van der Waals interaction energy \( j_{LW} \), the electrostatic double layer interaction energy \( j_{EL} \) [19] assuming constant potentials, and the net potential energy due to gravity and buoyancy \( j_{GR} \) [8]. Consequently:

\[
\varphi_{LW} = \frac{A_{132}}{6y^*}
\]  

in which \( A_{132} \) is the Hamaker constant for interactions of a particle 1 in medium 3 with planar surface 2 (for the present calculations the Hamaker constant was taken \( 0.7 \times 10^{-20} J \));

\[
\varphi_{EL} = \pi \varepsilon \varepsilon_0 a \left( \zeta_1^2 + \zeta_2^2 \right) \left[ \frac{2\zeta_1 \zeta_2}{\zeta_1^2 + \zeta_2^2} \ln \left( \frac{1 + e^{-y^*\kappa a}}{1 - e^{-y^*\kappa a}} \right) + \ln \left( 1 - e^{-2y^*\kappa a} \right) \right]
\]  

in which \( \zeta_1 \) and \( \zeta_2 \) are the zeta potentials of particle and collector surface respectively, and \( \kappa a \) the dimensionless reciprocal double layer thickness;

\[
\varphi_{GR} = \frac{4}{3} \pi a^3 \left( \rho_p - \rho_l \right) g y^* a
\]  

in which \( \rho_p \) and \( \rho_l \) are the density of the particle and the solution, respectively.

Usually in the calculation of interaction potentials, it is assumed that collector and particle surfaces are perfectly homogeneous with respect to the force vector, most notably with respect to the electrostatic charge properties of the interacting surfaces. The theoretical result [8] that a critical ionic strength exists above which deposition is maximal and below which deposition is almost absent is likely due to this assumption. In order to account for the more gradual behaviour observed experimentally, electrical charge heterogeneities were introduced over the collector surface, yielding a theoretical distribution of the zeta potential (\( \zeta \)) of the collector surface according to a Gaussian probability \( p(\zeta) \)

\[
p(\zeta) = \frac{1}{\sigma \sqrt{\pi}} e^{-\left( \frac{\zeta - \zeta_0}{\sigma} \right)^2}
\]
in which \( \zeta \) denotes the zeta potential of the collector surface, \( \sigma \) a surface charge spreading factor in mV, and \( \zeta_0 \) is the zeta potential at which \( p(\zeta) \) is maximal. By varying the spreading factor \( \sigma \), different solutions of the convective-diffusion equation could be calculated as a function of ionic strength that showed this gradual increase of the deposition rate with ionic strength observed experimentally, as can be seen in Figure 1. Figure 1a shows three different spreading functions used to mimic heterogeneities in collector surface charge. Figure 1b shows the numerical solutions of the CD equation, \( j_0^{\text{NUM}} \), as a function of ionic strength for these charge spreading factors, calculated for a shear rate of 200 s\(^{-1}\), on a negatively charged collector surface. It can be seen that the step-like behaviour of \( j_0^{\text{NUM}} \) seen for small charge spreading factors changes to a smoother transition upon increasing the collector surface charge heterogeneity. Approximate solutions to the convective-diffusion equation Equation (4) exist as well and include the Smoluchowski-Levich solution, which is based on the assumption that attractive interaction forces between colloidal particles and a collector surface are counterbalanced by increased viscous forces near an interface while other external forces are neglected. Consequently, the SL solution

\[
Sh_{0}^{\text{SL}} = \frac{1}{\Gamma^{\left(\frac{4}{3} - 9x^*\right)}} \left(\frac{2Pe}{\pi^3}\right)^{\frac{1}{3}}
\]  

(11)

in which \( Pe \) is the Peclet number, constitutes a theoretical upper limit for mass transport in the parallel plate flow chamber. Note that the dimensionless Sherwood number \( Sh_0 \) and the initial deposition rates \( j_0 \) are related by the following expression

\[
j_0 = Sh_0 \frac{kTc_s}{6\pi\eta a^2}
\]

(12)

where \( c_s \) is the particle concentration in suspension, and \( \eta \) denotes the viscosity of the suspending medium.

5.2.5 Kinetics of deposition: An adsorption-desorption model

The adsorption-desorption model applied here is partially based on the random sequential adsorption (RSA) model. Random sequential adsorption accounts for a non-ideal distribution of deposited particles, rendering a large fraction of the collector surface unavailable for adsorption, even though locally there are no particles present. In the RSA model, the available surface fraction \( \phi(t) \) for deposition is approximated by the polynomial expression

\[
\phi(t) = 1 - \left(4\Theta(t) + 3.308\Theta(t)^2 + 1.407\Theta(t)^3 + O(\Theta(t)^4)\right)
\]

(13)
Figure 1. (a) Gaussian charge spreading over a collector surface for different spreading factors. (b) Numerical solutions of the CD equation, $j_0^{\text{NUM}}$ on a negatively charged collector surface as a function of ionic strength, and a shear rate of 200 s$^{-1}$. 
in which $\Theta$ is the product of the adhering particles per unit area $n(t)$ and the blocked area $A_{\text{kin}}$. This blocked area is an input parameter to the calculation and can be obtained by curve fitting to experimental values of $n(t)$ [9]. In our adsorption-desorption model, $j_{\text{ads}}(t)$ is first calculated from

$$j_{\text{ads}}(t) = j_0 \phi(t)$$  \hspace{1cm} (14)

The value of $j_0$ to be employed is an input parameter to the model and may be arbitrarily chosen from experimental results or theoretical solutions of the CD equation, whereas the uncovered surface fraction $\phi(t)$ is calculated from the surface coverage $n(t)$ measured and Equation (13). All calculations carried out in this paper with the adsorption-desorption model have been based upon using $j_0^{\text{EXP}}$ as an input parameter for the initial deposition rate.

Subsequently, the desorption rate $j_{\text{des}}(t)$ is calculated, by assigning a residence time dependent desorption probability to all adhering particles according to Equation (2), with $\beta_0$, $\beta_\infty$, and $\delta$ serving as input parameters to the model. The number of particles adsorbing between $\tau$ and $\tau+\text{dt}$ equals $j_{\text{ads}}(\tau)\text{dt}$. The probability of desorption for these particles between $\tau$ and $t$ is dependent on their residence time $t-\tau$ and the fraction of particles still adhering to the collector surface $t-\tau$ after adsorption can be obtained by solving the differential equation Equation (1) using Equation (2) for $\beta(t-\tau)$

$$f(t - \tau) = e^{-\beta_0(t-\tau) - (\frac{\beta_0 - \beta_\infty}{\delta})(t - 1 - e^{-\delta(t-\tau)})}$$ \hspace{1cm} (15)

Multiplication with the desorption probability $\beta(t-\tau)$ and $\text{dt}$ yields the number of particles $f(t-\tau)\beta(t-\tau)\text{dt}$ that eventually desorb at $t$ of those particles $j_{\text{ads}}(\tau)\text{dt}$ that originally adsorbed at $\tau$. This procedure can be extended for all adsorption times $\tau$ prior to $t$, yielding the desorption rate

$$j_{\text{des}}(t) = \int_0^t j(t) f(t - \tau) \beta(t - \tau)\text{d}\tau$$ \hspace{1cm} (16)

Finally, $n(t)$ was calculated from the balance between adsorption and desorption, according to

$$n(t + \text{dt}) = n(t) + \left(j_{\text{ads}}(t) - j_{\text{des}}(t)\right)\text{dt}$$ \hspace{1cm} (17)

The calculational procedure is carried out by a computer program using small progressing time steps $\text{dt}$, in which $j_{\text{ads}}(t)$ and $j_{\text{des}}(t)$ are determined from previous values of $n(t)$ and $j_{\text{ads}}(t)$ respectively. The deposition kinetics thus calculated were compared with the experimental deposition kinetics for a number of experiments.
5.2.6 Kinetics of deposition: Monte-Carlo simulations

Monte-Carlo simulations of the deposition process were carried out by generating a time series of images, starting with the random deposition of $j_{0}^{\text{EXP}}$ particles per unit time and area, while excluding circular blocked areas $A_{\text{kin}}$, obtained from the experimental values of $n(t)$, around generated particles for further deposition. Desorption was simulated by randomly assigning a desorption probability to each particle according to Equation (2), with the experimental $\beta_0$, $\beta_\infty$, and $\delta$ values as input parameters.

The simulated deposition kinetics thus obtained were compared with the experimental deposition kinetics for a number of experiments.

5.3 RESULTS

5.3.1 Flow experiments

Figure 2 gives examples of the deposition kinetics on a positively and on a negatively charged glass substratum for deposition from a 10 mM KNO$_3$ solution at a shear rate of 100 s$^{-1}$. The surface coverage $n(t)$ and the adsorption rate $j_{\text{ads}}(t)$, are higher for the positively charged glass substratum, whereas the desorption rate $j_{\text{des}}(t)$ is lower. Note also, that the graphs for $j_{\text{ads}}(t)$ and $j_{\text{des}}(t)$ contain considerably more noise than the smooth graphs of the total counts $n(t)$, which is due to the statistical nature of the process of particle deposition in combination with the limited field of view of the microscope. Furthermore, $\beta(t-t)$, the desorption probability as a function of particle residence time, shows that desorption from the positively charged glass is unlikely, since the desorption probability becomes zero after a small initial period. For negatively charged glass however, the probability of desorption is much higher for the entire duration of an experiment, indicating that particles are less strongly bound. From these curves an initial and final desorption probability, $\beta_0$ and $\beta_\infty$, can be calculated together with a relaxation time constant $1/\delta$, which are listed in Table 2 for all experiments carried out, together with the initial deposition rates $j_{0}^{\text{EXP}}$, as derived directly from the adsorption rates $j_{\text{ads}}(t)$, and the blocked area $A_{\text{kin}}$, as calculated from the surface coverage. For positively charged collector surfaces the initial deposition rate $j_{0}^{\text{EXP}}$ does not vary greatly with ionic strength, whereas for negatively charged collector surfaces initial deposition rates increase with increasing ionic strength except for the highest shear rate applied. For both surfaces however, the initial deposition rate increases significantly with shear rate. This is also shown in Figure 3. Significant differences are also noted for the average blocked area $A_{\text{kin}}$, which are highest for measurements at low ionic strength on negatively charged surfaces, yielding values up to 10 times larger than the average for 80 mM experiments. Furthermore, the desorption probabilities $\beta_0$ and $\beta_\infty$ are much lower for the positively charged surfaces as compared to the negatively charged surfaces. Also, for negatively charged surfaces, the initial deposition probability $\beta_0$ is relatively low for all measurements done in 80 mM as compared to other ionic strengths.
Deposition of polystyrene particles

Figure 2. Examples of the deposition kinetics of negatively charged polystyrene particles on a positively (closed symbols) and on a negatively (open symbols) charged glass substratum for deposition in a parallel plate flow chamber from a 10 mM KNO$_3$ solution at a shear rate of 100 s$^{-1}$.

5.3.2 Solutions to the convective-diffusion equation

Figure 3 shows the experimentally obtained initial deposition rates $j_0^{\text{EXP}}$, and numerically calculated deposition rates $j_0^{\text{NUM}}$ as obtained from the convective-diffusion equation accounting for surface charge heterogeneities according to a Gaussian distribution with $\sigma = 25\text{mV}$. Both the experimental as well as the numerically calculated deposition rates are smaller than the deposition rates $j_0^{\text{SL}}$ as obtained from the Smoluchowski-Levich approximate solution of the convective-diffusion equation, which is similar for positively and negatively charged collector surfaces due to the neglect of electrostatic interactions. For positively charged collector surfaces (Figure 3, top) experimental and numerically calculated deposition rates are independent of ionic strength, while numerically calculated deposition rates are higher than the experimentally obtained values by a factor of about 1.6. All deposition rates, experimental, numerically calculated and approximated by the Smoluchowski-Levich approach increase with increasing shear rates. For the negatively charged collector surfaces on the other hand, (Figure 3, bottom), there is a marked increase in the experimentally obtained
Table 2. Experimentally obtained values of five deposition parameters for positively and negatively charged collector surfaces for different ionic strength KNO$_3$ solutions and shear rates. Experiments were carried out in duplo and measurements differed 25% from the mean of the two values for the initial deposition rate $j_0^{\text{EXP}}$, 38% for the blocked area $A_{\text{kin}}$, 43% for the initial deposition probability $\beta_0$, 38% for the final deposition probability $\beta_\infty$, and 19% for the relaxation constant $\delta$, on average over all shear rates and ionic strengths.

<table>
<thead>
<tr>
<th>Substratum charge</th>
<th>shear rate (s$^{-1}$)</th>
<th>ionic strength (mM)</th>
<th>$j_0^{\text{EXP}}$ (cm$^2$ s$^{-1}$)</th>
<th>$A_{\text{kin}}$ ($10^{-8}$ cm$^2$)</th>
<th>$\beta_0$ ($10^{-6}$ s$^{-1}$)</th>
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deposition rates in the range from 10 to 45 mM, followed by a decrease from 45 to 80 mM. A continuous, more gradual increase upon increasing the ionic strength is observed for the numerical calculations.

5.3.3 Adsorption-desorption model results and Monte-Carlo simulation

Model calculations and Monte-Carlo simulations were done for a negatively charged collector surface and polystyrene particles suspended in a 45 mM KNO$_3$ solution at a shear rate of 10 s$^{-1}$ or 200 s$^{-1}$ and compared with experimental results. Model calculations and simulations used input parameters $j_0^{\text{EXP}}$, $A_{\text{kin}}$, $\beta_0$, $\beta_\infty$, and $\delta$ from experiments, as summarized in Table 2. The comparison of the results is presented in Figure 4 and demonstrates that Monte-Carlo simulated results correspond well with experimental data as do the results from the adsorption-desorption model. With regard to the desorption rate, it can be observed that
Deposition of polystyrene particles

Figure 3. The initial deposition rate $j_0$ on positively (top) and negatively (bottom) charged glass substratum for the ionic strengths and shear rates employed in the experiments, as obtained experimentally (open symbols), and from a numerical solution of the CD equation (drawn lines), using a spreading factor $s$ of 25 mV. Values obtained from the SL-approximation were 2463, 5322, and 6600 cm$^{-2}$s$^{-1}$ for shear rates of 10, 100, and 200 s$^{-1}$, respectively, and are indicated by the dotted lines.

initially desorption is zero, but the adsorption-desorption model demonstrates that desorption quickly rises to a maximum value in the beginning of an experiment that can easily be missed in a real experiment.

5.4 DISCUSSION

In this paper we compare deposition of negatively charged polystyrene particles to glass under conditions of electrostatic attraction and repulsion. The analysis of the deposition data as carried out here is most extensive and includes the main aspects of particle deposition. The experimental initial deposition rates are considerably smaller than those approximated according to Smoluchowski-Levich, because in reality the perfect sink condition does not
apply. Even on positively charged collector surfaces counter-ion adsorption rapidly destroys the perfect sink configuration as existing for negatively charged particles (see also Table 1). Even though the numerically calculated initial deposition rates based on the convective-diffusion equation show results in better correspondence with experimental data, especially when surface charge heterogeneities are accounted for in the interaction potential, deviations remain. Similar to previous results, [8,18] these deviations are maximal under conditions of electrostatic repulsion at intermediate ionic strength.

The existence of more or less favorable sites on the collector surfaces may also influence other parameters of the deposition process. Blocked areas, for instance are supposed to depend on interparticle interactions [13,19,20] but when surface chemical heterogeneities exist, those may be more influential on the spatial arrangement of the adhering particles than hydrodynamics and interparticle interactions.

The analysis of experimental data obtained by image analysis should always be considered critically, because image analysis bears the risk of inducing artifacts. In this respect, it is reassuring that the desorption probabilities, which are measured based on the times of arrival and departure of adhering particles, and which rely heavily on the establishment of optimal connectivity between images [16,17], are essentially zero on the positively charged collector surfaces, except for a small initial non-zero value.

On the negatively charged collector surfaces, desorption is initially high but decreases within minutes to a low, but non-zero value, similar as observed by Meinders et al. [16], who only studied negatively charged collector surfaces. Also, another point supporting the analysis is provided by the model calculations and Monte-Carlo simulations carried out, yielding results that coincide well with the experiments.

Meinders and Busscher [20], in their analysis of desorption data, contributed a role to collisions between flowing and adhering particles in stimulating desorption on the basis of their observation that desorption probabilities were higher at higher shear rates, i.e. higher particle velocities near the collector surfaces. The present results confirm that on negatively charged collector surfaces and for low ionic strength solutions, the initial desorption probability is higher at high shear rate, but for high ionic strength solutions this is not obvious. The desorption probabilities on the positively charged collector surfaces, however, are considered too small to draw any conclusions from.

Summarizing, colloidal particle deposition on a positively and negatively charged collector surface was compared for a parallel plate flow chamber configuration on an experimental and theoretical basis, including both adsorption and desorption. Whereas previously only data on negatively charged collector surfaces were obtained in the parallel plate flow chamber, this study provides support in the detailed analysis of experimental deposition data, including residence-time dependent desorption, by demonstrating that the analysis indicates minor desorption under conditions of electrostatic attraction as compared with conditions of electrostatic repulsion. Moreover, the independently acquired data show a high degree of internal consistency, underlining the validity of the analysis.
Figure 4. Deposition kinetics according to the adsorption-desorption model and Monte-Carlo simulations as compared with experimental results for 814 nm diameter polystyrene particles in a 45 mM KNO$_3$ solution on negatively charged glass, at a shear rate of 10 s$^{-1}$ (closed symbols) and 200 s$^{-1}$ (open symbols). Circles indicate experimental results, triangles denote the average of 25 Monte Carlo simulation runs, while the drawn lines are obtained from the adsorption-desorption model calculations.
5.5 REFERENCES