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A simple model for adsorption kinetics at charged solid–liquid interfaces

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Abstract

The kinetics of adsorption of charged nano particles or molecules to a charged surface are modeled on the basis of a simple model that takes into account, (1) the transport step from bulk solution to the subsurface layer and (2) the attachment–detachment step that is involved in the transfer of the particle from the subsurface to the adsorbed state. The transport step is based on the presence of a diffusion layer. Passing through the electric double layer is made part of the attachment–detachment step. The configuration part of the attachment–detachment step is based on either a kinetic model that leads to the Langmuir equation in the equilibrium situation, or one that takes into account the 'specific' lateral interactions too and that leads in the equilibrium state to the Frumkin–Fowler–Guggenheim (FFG) equation. In the FFG model the activation energy due to specific lateral interactions is assumed to be proportional to the equilibrium lateral interaction energy. The effect of the electrostatic interactions and the corresponding activation energy barriers for adsorption and desorption are considered to be an additional part of the attachment–detachment step. The electrostatic potential of the activated state for attachment–detachment is made proportional to the equilibrium surface potential at a given adsorbed amount. The Gouy–Chapman model is used to calculate the (smeared-out) surface potential from the known (smeared-out) overall surface charge density, that is to say, from the known bare surface charge plus the effective charge contribution due to particle adsorption. As a result of this treatment the adsorption kinetics are not only a function of the particle concentration and the surface coverage, but also of the surface charge, the particle charge and the salt concentration. The model is illustrated with some calculated results. The first illustrations are based on the Langmuir model extended with electrostatic interactions and show, for a given particle concentration and transport rate constant, the effects of salt concentration, surface charge and particle charge on both the adsorption and desorption kinetics. The next illustrations are based on the FFG model extended with electrostatics and the effect of the specific lateral interactions on the adsorption kinetics of charged and uncharged particles is shown.

Keywords: Solid–liquid interface; Frumkin–Fowler–Guggenheim equation; Attachment–detachment step

1. Introduction

The characterization of the dynamics of adsorption at a solid–liquid interface is of great importance in many applications. In general, ad-

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sorption is the process whereby matter dispersed in solution accumulates at an interface. Adsorption kinetics of any substance, be it a small molecule, an ion, a particle, a polymer or a colloid, can therefore be described in similar terms. Here we will speak about (nano) particle adsorption, indicating with 'particle' the adsorbing species that can either be a molecule or a nano particle. A generally accepted physical model of adsorption kinetics, originally proposed by Baret [1,2] and reviewed by Dukhin et al. [3], consists of two main steps. The first step is the *transport* of particles from bulk solution to the subsurface layer. The subsurface layer is bounded to the surface and defined as the place from which attachment to the surface can take place without further transport towards the surface. The transport of particles can be due to one or more contributions, such as, convection, diffusion or a combination of both. The second step can be described as the transfer of the adsorbing species from the soluted state in the subsurface layer to the adsorbed state. This step can be indicated as the *attachment* step, it is caused by the attraction exerted by the surface on the adsorbate. In principle, this step will be affected by an activation energy barrier that can slow down the rate of attachment. For the desorption kinetics a similar two step process, composed of *detachment* and *transport*, can be envisaged. In the case of positive adsorption from a dilute solution the barrier for detachment is considerably higher than that for attachment.

Both the transport steps and the attachment–detachment steps proceed simultaneously; a steady state occurs if the transport flux matches the rate of attachment–detachment. Depending on the rates of the processes two limiting cases can be distinguished. If the transport step is much slower than the attachment–detachment step the adsorption process is transport controlled. If the attachment–detachment step is much slower than the transport step, the adsorption process is attachment–detachment controlled. If the rates of both steps are similar, the adsorption process is controlled by both mechanisms and one may speak about a mixed transport/attachment–detachment controlled process.

The transport process in the case of a well stirred solution near an interface is determined by a stagnant layer over which diffusion has to take place according to the second law of Fick. The diffusion of particles is caused by the concentration gradient between the bulk and the subsurface layer. The classical description of this situation is due to Ward and Tordai [4], several specific cases of adsorption are reviewed in [3]. Convective transport depends on the concentration of the particles and the local fluid velocity [5]. Flow fields due to convective diffusion [6], as encountered in stagnation point flow used in reflectometry studies [7–9], have been reviewed for different collectors by Van der Ven et al. [10,11]. For most cases a stagnant diffusive boundary layer with a thickness depending on the diffusion coefficient arises near the interface. Both for diffusion and convective diffusion the concentration gradient over the diffusion layer is important. At the bulk side of this layer the bulk concentration is imposed, at the surface side the subsurface concentration. The usual approach is to define the subsurface concentration as the concentration of adsorbing particles in a layer adjacent to the surface with a thickness of about one particle diameter.

The attachment–detachment process gives rise to two fluxes, one forward, the other backward, the net flux being the algebraic sum of the two. In the most simple case of homogeneous rigid particles that interact with the surface, but not laterally, the forward flux will respond to the subsurface concentration and the fraction of surface that is un-occupied and the backward flux will be proportional to the fraction of the surface that is covered. Langmuir's classical treatment [12] to arrive at his famous isotherm equation is based on this treatment. For rigid particles that also interact laterally both the attachment and the detachment step will, in principle, be affected by the lateral interaction too. Non-homogeneous particles may have to undergo a re-orientation before they can attach. For flexible particles or polymers attachment and detachment may also involve changes in shape, structure and/or conformation (e.g. unfolding of a polymer chain, see e.g. [13,14]).

An additional complication that often arises is that the particles and the interface are charged.

With a charged aqueous interface an electric double layer develops and, in principle, both the diffusion of a charged particle to this interface and the attachment–detachment process will be affected by the electrical double layer. The pioneering and subsequent work in this field by Dukhin et al. [15–17] is reviewed in [3,18]. More recent work on the adsorption kinetics at charged interfaces can be found in [19–21]. According to Dukhin et al. [3] the main effect of the electrostatic interactions is that the subsurface concentration is affected. In the first place, this concentration is modified by a Boltzmann factor accounting for the presence of the electric potential of the subsurface layer. In the second place, a correctional term is added that accounts for the deviation of the transport due to the presence of the diffuse layer. The latter deviation is most important when the interface and the adsorbing particle have the same charge sign, so that the particle flux is decelerated (electrostatic retardation) and the double layer is in a quasi-equilibrium state. In the case of opposite charges the particle flux is accelerated, the double layer is close to its equilibrium state and the correction can be neglected.

In the present paper, the main focus will be on the kinetics of adsorption of charged nano particles on a charged interface. In contradistinction with Dukhin et al. [3], the effect of the electrostatics on the kinetics of double layer formation will be neglected. The influence of the electrostatics will be attributed entirely to the rates of attachment and detachment. This simplified treatment already gives good insight in the way in which electrostatics affect the adsorption kinetics. For the development of the model first the situation is considered in the absence of electrostatics, then the electrostatic interactions are incorporated.

2. Kinetic adsorption model in the absence of electrostatic interactions

In the model localized monolayer adsorption of particles from a dilute solution to flat interface will be considered. The two main steps in the adsorption process, (1) transport of particles towards or from the surface and (2) attachment to or detachment from the surface will be considered.

Transport to and from the surface depends on the hydrodynamic conditions of the adsorption cell. For diffusion and convective diffusion, diffusion of particles through a diffusion layer near the surface will be determining the rate of transport. This rate depends on the concentration gradient. The concentration of the adsorbing particles in the bulk solution is homogeneous and denoted as c_b. From the boundary of the bulk solution the particles can diffuse freely to the subsurface layer adjacent to the surface and *vise versa*. The concentration in the subsurface layer is denoted as c_s, and thus a concentration difference $(c_b - c_s)$ exists over the diffusion layer. A (pseudo) steady state situation of transport of particles through the diffusion layer can be described as the material flux J per unit area to or from the subsurface layer:

$$J = k_t(c_b - c_s) \tag{1}$$

where k_t is a transport rate coefficient. Eq. (1) is an approximation that applies to adsorption from dilute solution, i.e. when the time to reach the equilibrium adsorption is long compared with the time to establish a steady-state diffusion layer. Under this condition the concentration gradient near the subsurface will equal the concentration gradient over the diffusion layer. The value of k_t depends on the type of flow. For instance, for a stagnation point flow (convective diffusion) $k_t = K_t D^{2/3}$, where D is the diffusion coefficient of the adsorbing particles and K_t is a constant that depends on the hydrodynamics of the cell, the flow conditions and the units in which J and c are expressed. For a given condition, the magnitude of K_t can be estimated by measuring the adsorption rate of neutral molecules or particles with a known diffusion coefficient [8].

The rate of attachment and detachment of a particle from the subsurface to the surface, or *vise versa*, can be modeled considering that, (1) a particle adsorbs with a rate coefficient k_a and desorbs with a rate coefficient k_d; (2) adsorption from dilute solution is proportional to c_s and a function of the fraction of surface that is bare;

and (3) desorption is a function of the surface coverage. The overall rate of adsorption, $(\mathrm{d}\Gamma/\mathrm{d}t)$, or the net flux of molecules from the subsurface to the surface is then given by:

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t}=\Gamma_{\mathrm{m}}\left(\frac{\mathrm{d}\theta}{\mathrm{d}t}\right)=k_{\mathrm{a}}c_{\mathrm{s}}\phi(\theta)-k_{\mathrm{d}}\,f(\theta) \tag{2}$$

where $\theta=\Gamma/\Gamma_{\mathrm{m}}$, Γ is the mass of particles adsorbed per unit area and Γ_{m} is its maximum value, $\phi(\theta)$ and $f(\theta)$ are functions of θ. The parameters k_{a} and k_{d} are Arrhenius-type coefficients. They are related to the activation energy for adsorption and desorption, respectively, and each contains a frequency factor that also accounts for the appropriate units. For neutral particles the activation energies depend on the state of hydration of the surface and the adsorbing particles, the net surface–adsorbate and the net adsorbate–adsorbate interactions. In the presence of adsorbate–adsorbate interactions the rate coefficients will also be a function of θ. The functions $\phi(\theta)$ and $f(\theta)$ will depend on the type of particles, e.g. whether or not the particles can undergo restructuring upon adsorption.

At any time the flux J in the steady-state transport situation expressed by Eq. (1) has to equal $(\mathrm{d}\Gamma/\mathrm{d}t)$ expressed in Eq. (2), this leads to the following expression for c_{s}

$$c_{\mathrm{s}}=\frac{k_{\mathrm{d}}\,f(\theta)+k_{\mathrm{t}}c_{\mathrm{b}}}{k_{\mathrm{a}}\phi(\theta)+k_{\mathrm{t}}} \tag{3}$$

Substitution of the expression for c_{s} in Eq. (2) gives the general rate equation for adsorption:

$$\frac{\Gamma_{\mathrm{m}}\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}\phi(\theta)c_{\mathrm{b}}-k_{\mathrm{t}}k_{\mathrm{d}}\,f(\theta)}{k_{\mathrm{a}}\phi(\theta)+k_{\mathrm{t}}} \tag{4}$$

An alternative form of this equation is:

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}\phi(\theta)}{k_{\mathrm{a}}\phi(\theta)+k_{\mathrm{t}}}\left(c_{\mathrm{b}}-\frac{k_{\mathrm{d}}\,f(\theta)}{k_{\mathrm{a}}\phi(\theta)}\right) \tag{5}$$

When equilibrium is achieved, $(\mathrm{d}\theta/\mathrm{d}t)=0$, c_{b} becomes the equilibrium concentration in the bulk that corresponds with θ, $c_{\mathrm{eq}}(\theta)$, and from Eq. (5) it follows that:

$$c_{\mathrm{eq}}(\theta)=\frac{k_{\mathrm{d}}\,f(\theta)}{k_{\mathrm{a}}\phi(\theta)} \tag{6}$$

where $c_{\mathrm{eq}}(\theta)$ (or $c_{\mathrm{eq}}(\Gamma)$) is the (inverse) equilibrium adsorption isotherm. Substitution of Eq. (6) in Eq. (5) gives a convenient expression for the rate of adsorption when the equilibrium adsorption isotherm is known:

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}\phi(\theta)}{k_{\mathrm{a}}\phi(\theta)+k_{\mathrm{t}}}\{c_{\mathrm{b}}-c_{\mathrm{eq}}(\theta)\} \tag{7}$$

The term $\{c_{\mathrm{b}}-c_{\mathrm{eq}}(\theta)\}$ is the driving force for adsorption. Normalization of the rate of adsorption by the driving force for adsorption gives the effective rate constant:

$$\frac{\Gamma_{\mathrm{m}}(\mathrm{d}\theta/\mathrm{d}t)}{\{c_{\mathrm{b}}-c_{\mathrm{eq}}(\theta)\}}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}\phi(\theta)}{k_{\mathrm{a}}\phi(\theta)+k_{\mathrm{t}}}\equiv k^{\mathrm{eff}}(\theta) \tag{8}$$

which is an experimentally accessible quantity.

The above equations are quite general as long as k_{a}, k_{d}, $\phi(\theta)$ and $f(\theta)$ are not further specified. By introducing appropriate functions for these parameters kinetic models related to, for instance, the Langmuir and the Frumkin–Fowler–Guggenheim (FFG) model [22], can be obtained. Langmuir type adsorption kinetics are obtained if it is assumed that $\phi(\theta)=1-\theta$ and $f(\theta)=\theta$, and that both k_{a} and k_{d} are intrinsic constants:

$$k_{\mathrm{a}}^{\mathrm{int}}=k_{\mathrm{a}}^{0}\theta\,\exp\left[\frac{-\Delta G_{\mathrm{act}}^{0}}{RT}\right] \tag{9}$$

$$k_{\mathrm{d}}^{\mathrm{int}}=k_{\mathrm{d}}^{0}\exp\left[-\frac{(-\Delta G_{\mathrm{ads}}^{0}+\Delta G_{\mathrm{act}}^{0})}{RT}\right] \tag{10}$$

where $\Delta G_{\mathrm{act}}^{0}$ is the net Gibbs energy of activation for attachment and $\Delta G_{\mathrm{ads}}^{0}$ is the standard net Gibbs energy of adsorption. Both $\Delta G_{\mathrm{act}}^{0}$ and $\Delta G_{\mathrm{ads}}^{0}$ are composite parameters that contain contributions form the adsorbing particle and the desorbing solvent. Under these conditions Eq. (4) reduces to

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{int}}(1-\theta)c_{\mathrm{b}}-k_{\mathrm{t}}k_{\mathrm{d}}^{\mathrm{int}}\theta}{k_{\mathrm{a}}^{\mathrm{int}}(1-\theta)+k_{\mathrm{t}}} \tag{11}$$

which leads to the Langmuir equation when $\mathrm{d}\theta/\mathrm{d}t=0$ and $c_{\mathrm{b}}=c_{\mathrm{eq}}$. By using $c_{\mathrm{eq}}(\theta)$ Eq. (11) can also be written as

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{int}}(1-\theta)}{k_{\mathrm{a}}^{\mathrm{int}}(1-\theta)+k_{\mathrm{t}}}\{c_{\mathrm{b}}-c_{\mathrm{eq}}(\theta)\} \tag{12}$$

which is the Langmuir type expression of Eq. (7). When the rate of adsorption and the equilibrium adsorption isotherm are known, the rate constants can easily be obtained by plotting the $1/k^{\mathrm{eff}}(\theta)$ (see Eq. (8)) as a function of $1/(1-\theta)$:

$$\frac{1}{k^{\mathrm{eff}}(\theta)}=\frac{1}{k_{\mathrm{t}}}+\frac{1}{k_{\mathrm{a}}^{\mathrm{int}}}\frac{1}{1-\theta} \tag{13}$$

When the Langmuir model applies a straight line is obtained with intercept $1/k_{\mathrm{t}}$ and slope $1/k_{\mathrm{a}}^{\mathrm{int}}$.

Equations related to the FFG model can be obtained if $\phi(\theta)=1-\theta$, $f(\theta)=\theta$, and it is assumed that both the activation energy for attachment and detachment are linearly dependent on θ. In this situation, k_{a} and k_{d} can be defined as:

$$k_{\mathrm{a}}=k_{\mathrm{a}}^{0}\exp\left[-\frac{(\Delta G_{\mathrm{act}}^{0}+\alpha\Delta G_{\mathrm{lat}}^{0}\theta)}{RT}\right] \tag{14}$$

$$k_{\mathrm{d}}=k_{\mathrm{d}}^{0}\exp\left[-\frac{\{-\Delta G_{\mathrm{ads}}^{0}+\Delta G_{\mathrm{act}}^{0}-(1-\alpha)\Delta G_{\mathrm{lat}}^{0}\theta\}}{RT}\right] \tag{15}$$

where $\Delta G_{\mathrm{lat}}^{0}$ is the standard net lateral interaction energy in the adsorbed layer and $\alpha\Delta G_{\mathrm{lat}}^{0}$ is the standard net activation energy due to lateral interactions. Hence, it has been assumed that the standard activation energy due to lateral interactions is proportional $(0\leq\alpha\leq1)$ to $\Delta G_{\mathrm{lat}}^{0}$ The equation for the adsorption kinetics now reads:

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{int}}\exp[-\alpha\Delta G_{\mathrm{lat}}^{0}\theta/RT](1-\theta)c_{\mathrm{b}}-k_{\mathrm{t}}k_{\mathrm{d}}^{\mathrm{int}}\exp[-(1-\alpha)\Delta G_{\mathrm{lat}}^{0}\theta/RT]\theta}{k_{\mathrm{a}}^{\mathrm{int}}\exp[-\alpha\Delta G_{\mathrm{lat}}^{0}\theta/RT](1-\theta)+k_{\mathrm{t}}} \tag{16}$$

where $k_{\mathrm{a}}^{\mathrm{int}}$ and $k_{\mathrm{d}}^{\mathrm{int}}$ are defined in Eqs. (9) and (10), respectively. For $\mathrm{d}\theta/\mathrm{d}t=0$ the bulk concentration equals the equilibrium concentration and the FFG equation results. By using the equilibrium isotherm Eq. (16) can also be expressed as:

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t}=\frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{int}}\exp[-\alpha\Delta G_{\mathrm{lat}}^{0}\theta/RT](1-\theta)}{k_{\mathrm{a}}^{\mathrm{int}}\exp[-\alpha\Delta G_{\mathrm{lat}}^{0}\theta/RT](1-\theta)+k_{\mathrm{t}}}\{c_{\mathrm{b}}-c_{\mathrm{eq}}(\theta)\} \tag{17}$$

Eq. (17) is the FFG equivalent of Eq. (7), it reduces to Eq. (12) for $\Delta G_{\mathrm{lat}}^{0}=0$. According to Eq. (17) the reciprocal effective rate constant (see Eq. (8)) for the FFG case equals:

$$\frac{1}{k^{\mathrm{eff}}(\theta)}=\frac{1}{k_{\mathrm{t}}}+\frac{1}{k_{\mathrm{a}}^{\mathrm{int}}\exp[-\alpha\Delta G_{\mathrm{lat}}^{0}\theta/RT]}\frac{1}{1-\theta} \tag{18}$$

The slope of the plot of $1/k^{\mathrm{eff}}(\theta)$ versus $1/(1-\theta)$ is decreasing for lateral attraction and increasing for lateral repulsion. To obtain the two rate constants and α an iteration procedure is required (N.B. the value of $\Delta G_{\mathrm{lat}}^{0}$ and hence, whether the slope of Eq. (18) will be increasing or decreasing, follows already from the equilibrium isotherm).

3. Kinetic adsorption model in the presence of electrostatic interactions

Let us now consider monolayer adsorption of charged (nano) particles from a dilute solution on a charged flat SL interface. It will be assumed that the ionic strength of the solution is dominated by the presence of a symmetrical indifferent electrolyte. Under such conditions particle adsorption in the diffuse electric layer of the SL interface can be neglected, the kinetics of double layer formation is determined by the indifferent electrolyte and relatively fast and the Debye length has a value much smaller than the thickness of the diffusion layer. Under the latter condition the time of particle transport through the diffuse electric layer is negligible as compared with that through the diffusion layer. Furthermore, it will be assumed that the presence of the particles does not perturb the double layer of the adsorbing surface, and we neglect the double layer of the particles themselves. Together these assumptions imply that the double layer is considered to be in equilibrium at all times relevant for the particle adsorption process and independent of the presence of the particles in the diffuse part of the double layer. The above assumptions set limits to the particle types and sizes for which the model can be applied. Perturbation of the diffuse layer by the particles will be small for low effective particle charge and the particles should not be too large. Low effective (electrokinetic) charges are more easily realized for gel type particles, in which part of the charge is compensated within the particle, than for rigid particles.

Because diffusion transport of the particles through the diffuse electric layer is assumed to be fast compared with the transport through the diffusion layer, the entire effect of the electrostatic interactions has to be attributed to the attachment and detachment step. In fact, passing through the electric double layer is made part of the attachment–detachment step and the electrostatic potential of the activated state for attachment–detachment becomes important. Here, it will be assumed that this potential is related to the electrostatic potential of the SL interface. For the calculation of the surface potential it will be assumed that the surface charge is homogeneously distributed (smeared-out) over the entire surface, also when the particles contribute to that charge. Since the particles can not be treated as point charges, their charge will be distributed over their surface (non-penetrable particle) or volume (penetrable particle). In general, upon attachment only a fraction of the particle charge (related to the contact area) contributes to the overall surface charge density. The rest of the particle charge will be neutralized in the electric double layer by the supporting electrolyte. Therefore, if the charge number of the nano particle is z_p, only the fraction qz_p will be effective in changing the surface charge, where q ranges from 0 to 1. For instance, for particles like surfactant ions $q = 1$, for impermeable nano particles $q < 1$ and for permeable nano particles $q \ll 1$. To some extent this approximation also allows us to calculate the surface potential without incorporation of further discrete layers of charge near the surface.

Because the double layer is assumed to be in the equilibrium state, the (smeared-out) surface potential, ψ_0, can be estimated from the (smeared-out) overall surface charge density, σ, by using the Gouy–Chapman equation Eq. (22):

$$\psi_0 = \frac{2RT}{zF} \operatorname{arcsinh}\left(\frac{\sigma_0 + qz_pF\theta\Gamma_m/M}{\sqrt{\varepsilon_0\varepsilon cRT}}\right) \quad (19)$$

where σ_0 is the charge of the bare surface, $qz_pF\theta\Gamma_m/M$ is the surface charge contribution due to the adsorbed particles, M is the particle mass, ε_0 and ε are the permitivities of vacuum and water, respectively, c is the concentration of the supporting $(z–z)$ indifferent electrolyte, F is the Faraday constant, R the gas constant and T is the absolute temperature.

To take into account the effect of the electrostatics on the rate of adsorption, the rate coefficients for attachment and detachment should be written as a product of a non-electrostatic (ne) and an electrostatic contribution:

$$k_a = k_a^{ne} \exp\left(\frac{-\lambda qz_pF\psi_0}{RT}\right) \quad (20)$$

$$k_d = k_d^{ne} \exp\left[+\frac{(1-\lambda)qz_pF\psi_0}{RT}\right] \quad (21)$$

k_a^{ne} and k_d^{ne} can be replaced by their intrinsic values in the absence of lateral interactions, see Eqs. (9) and (10), whereas in the presence of these interactions Eqs. (14) and (15) should be used. The electrostatic contributions to the rate coefficients are expressed as Boltzmann factors, where λ is a proportionality factor, qz_p is the effective (electrokinetic) charge of the particle. For reasons of simplicity it is assumed that the electrokinetic charge is the same as the part of the particle charge that contributes to the surface charge. The parameter $\lambda (0 \le \lambda \le 1)$ in Eqs. (20) and (21) expresses that it is assumed that the height of the electrostatic barrier for attachment is proportional to the value of the surface potential. For simple particles, like a surfactant ion, and a simple exponential decay of the potential as a function of the distance to the surface, the value of λ will be close to 1. This means that the rate coefficient for attachment is modified, whereas the rate coefficient for detachment is about the same as that of the uncharged species (the change of the energy well and the change of the energy barrier just compensate each other). However, in general $(\lambda \ne 1)$, both rate coefficients will be affected. The electrostatic interaction factor, $-\lambda qz_pF\psi_0/RT$, will be negative if the particles and surface have a different charge sign (attraction) and positive when surface and particle have the same charge sign (repulsion). Attractive interactions will accelerate attachment and repulsive interactions will decelerate attachment. The calculation of ψ_0, k_a and k_d as suggested above is fairly crude, but the intention is to capture the basic features of the electrostatic effects on the adsorption kinetics in a simple model.

Based on the above reasoning the attachment–detachment rate becomes

$$\frac{\Gamma_m\,d\theta}{dt} = k_a^{ne}\exp\left(\frac{-\lambda q z_p F\psi_0}{RT}\right)c_s\phi(\theta) - k_d^{ne}\exp\left(\frac{+(1-\lambda)q z_p F\psi_0}{RT}\right)f(\theta) \qquad (22)$$

As before, the transport through the diffusion layer is given by Eq. (1). By equating J to the attachment–detachment rate the expression for the rate of adsorption results:

$$\frac{\Gamma_m\,d\theta}{dt} = \frac{k_t k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta)c_b - k_t k_d^{ne}\exp[+(1-\lambda)q z_p F\psi_0/RT]f(\theta)}{k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta) + k_t} \qquad (23)$$

or, alternatively

$$\frac{\Gamma_m\,d\theta}{dt} = \left(\frac{k_t k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta)}{k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta) + k_t}\right)\left(c_b - \frac{k_d^{ne}\exp[+q z_p F\psi_0/RT]f(\theta)}{k_a^{ne}\phi(\theta)}\right) \qquad (24)$$

Eqs. (23) and (24) can be compared with Eqs. (4) and (5), respectively. In equilibrium $(d\theta/dt) = 0$ and $c_b = c_{eq}(\theta)$ and Eq. (24) leads to:

$$c_{eq}(\theta) = \frac{k_d^{ne}\exp[+q z_p F\psi_0/RT]f(\theta)}{k_a^{ne}\phi(\theta)} \qquad (25)$$

Substitution of this result in Eq. (24) gives

$$\frac{\Gamma_m\,d\theta}{dt} = \left(\frac{k_t k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta)}{k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta) + k_t}\right)\{c_b - c_{eq}(\theta)\} \qquad (26)$$

This equation can be used if the equilibrium isotherm is known, it is the equivalent of Eq. (7). From Eq. (26) it follows immediately that in the case of strong electrostatic attraction, i.e. $k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta) \gg k_t$, that

$$\frac{\Gamma_m\,d\theta}{dt} = k_t\{c_b - c_{eq}(\theta)\} \qquad (27)$$

in other words, the rate of adsorption is determined by the rate of transport (transport controlled). In the case of strong electrostatic repulsion, i.e. $k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta) \ll k_t$, one finds

$$\frac{\Gamma_m\,d\theta}{dt} = k_a^{ne}\exp\left[\frac{-\lambda q z_p F\psi_0}{RT}\right]\phi(\theta)\{c_b - c_{eq}(\theta)\} \qquad (28)$$

or the rate of adsorption is determined by the rate of attachment (attachment controlled). Eqs. (27) and (28) already reveal that when the electrostatic interactions change sign in the course of adsorption, strong effects can be expected on the rate of adsorption. The larger the particle adsorption is, the less attractive or the more repulsive the electrostatic interaction becomes and the slower the adsorption proceeds.

As before it is also possible to normalize the rate of adsorption with respect to the driving force for adsorption and to obtain the effective rate coefficient:

$$\frac{\Gamma_m(d\theta/dt)}{\{c_b - c_{eq}(\theta)\}} = \frac{k_t k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta)}{k_a^{ne}\exp[-\lambda q z_p F\psi_0/RT]\phi(\theta) + k_t} \equiv k^{eff}(\theta, \psi_0) \qquad (29)$$

This equation can be compared with Eq. (8). In general, the equilibrium adsorption isotherm and the rate of adsorption can be measured. Therefore, also in this case $k^{eff}(\theta, \psi_0)$ is experimentally accessible.

The above equations can be further specified if a certain behavior is assumed in the absence of electrostatic interactions. An extension of the Langmuir equation is obtained if: $\phi(\theta) = 1 - \theta$, $f(\theta) = \theta$, $k_a^{ne} = k_a^{int}$ and $k_d^{ne} = k_d^{int}$; an extension of the FFG equation if: $\phi(\theta) = 1 - \theta$, $f(\theta) = \theta$, $k_a^{ne} = k_a^{int}\exp[-\alpha\Delta G_{lat}^0\theta/RT]$ and $k_d^{ne} = k_d^{int}\exp[-(1-\alpha)\Delta G_{lat}^0\theta/RT]$. Below the effects of the electrostatics on the adsorption process will be illustrated with some model calculations.

4. Results of calculations

By substitution of the conditions $\phi(\theta) = 1 - \theta$, $f(\theta) = \theta$, $k_a^{ne} = k_a^{int}$ and $k_d^{ne} = k_d^{int}$ in Eq. (23) the Langmuir model extended with electrostatic interactions is obtained

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t} = \frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{int}}\exp[-\lambda q z_{\mathrm{p}}F\psi_0/RT](1-\theta)c_{\mathrm{b}} - k_{\mathrm{t}}k_{\mathrm{d}}^{\mathrm{int}}\exp[+(1-\lambda)qz_{\mathrm{p}}F\psi_0/RT]\theta}{k_{\mathrm{a}}^{\mathrm{int}}\exp[-\lambda q z_{\mathrm{p}}F\psi_0/RT](1-\theta)+k_{\mathrm{t}}} \tag{30}$$

The initial adsorption rate normalized with respect to the driving force becomes ($\theta \to 0$ and $c_{\mathrm{eq}} \to 0$):

$$\left.\frac{(\mathrm{d}\Gamma/\mathrm{d}t)}{c_{\mathrm{b}}}\right|_{\theta\to 0} = \frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{int}}\exp[-\lambda q z_{\mathrm{p}}F\psi_0/RT]}{k_{\mathrm{a}}^{\mathrm{int}}\exp[-\lambda q z_{\mathrm{p}}F\psi_0/RT]+k_{\mathrm{t}}} \tag{31}$$

which is also equal to the effective initial rate coefficient, $k^{\mathrm{eff}}|_0$. The effects of electrostatics on the adsorption rate, as predicted by Eqs. (30) and (31) are exemplified in Figs. 1–3. For the calculations the following parameters have been used, particle characteristics $M = 20\,000$, $z_{\mathrm{p}} = -10$, $q = 0.3$; adsorption characteristics $\Gamma_{\mathrm{m}} = 1.6$ (mg m^{-2}), $c_{\mathrm{b}} = 30$ (mg dm^{-3}), rate constants $k_{\mathrm{a}}^{\mathrm{int}} = 2 \times 10^{-5}$ (m s^{-1}), $k_{\mathrm{d}}^{\mathrm{int}} = 1 \times 10^{-7}$ (kg m^2 s^{-1}) and $k_{\mathrm{t}} = 4.6 \times 10^{-6}$ (m s^{-1}), at room temperature $RT = 2.4 \times 10^3$ (J mol^{-1}), $F = 96\,500$ (C mol^{-1}), $\varepsilon_0 = 8.84 \times 10^{-12}$ (C Vm^{-1}), $\varepsilon_{\mathrm{r}} = 80$. A somewhat arbitrary value $\lambda = 1$ has been chosen, that is to say, the electrostatics affect the rate constant for attachment maximally and the rate constant for detachment minimally. The values intend to represent adsorption of nano particles with a relatively low effective charge density (low q value). The charge density of the flat surface is specified with each figure. The values of the intrinsic rate constants have been given such values that the effects of the electrostatic interactions on the attachment–detachment step can be clearly illustrated.

In Fig. 1 the initial adsorption rate normalized with respect to the bulk concentration, $(\mathrm{d}\Gamma/\mathrm{d}t)/c_{\mathrm{b}}|_0 = k^{\mathrm{eff}}|_0$, the rate coefficient $k_{\mathrm{a}}|_0$ (initial value) and the rate constant k_{t} (all in m s^{-1}) are plotted as a function of the surface charge density, σ_0 (in the initial state the particle charge does not yet contribute to the overall charge density). The transport rate is independent of the surface charge and only dependent on the value of the diffusion coefficient. This is briefly indicated in Fig. 1 with the horizontal bars. The actual value of k_{t} used in the calculations is indicated by the thin horizontal line. The initial attachment rate coefficient, $k_{\mathrm{a}}|_0$, follows from Eqs. (20) and (19) for $\theta = 0$. The

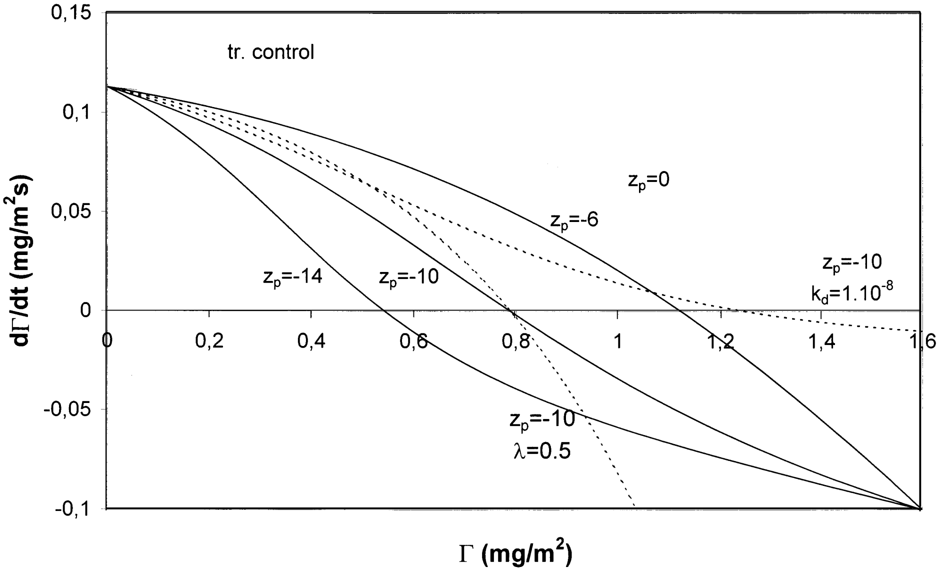

Fig. 1. Effects of electrostatics on the adsorption rate as predicted by Eqs. (30) and (31). Parameters, $M = 20\,000$, $z_{\mathrm{p}} = -10$, $q = 0.3$, $\Gamma_{\mathrm{m}} = 1.6$ mg m^{-2}, $c_{\mathrm{b}} = 30$ mg dm^{-3}, c(salt) = 0.1 M, $k_{\mathrm{a}}^{\mathrm{int}} = 2 \times 10^{-5}$ m s^{-1}, $k_{\mathrm{d}}^{\mathrm{int}} = 1 \times 10^{-7}$ kg m^{-2} s, $k_{\mathrm{t}} = 4.6 \times 10^{-6}$ m s^{-1}, $\lambda = 1$, $RT = 2.4 \times 10^{-3}$ J mol^{-1}, $F = 96\,500$ C mol^{-1}, $\varepsilon_0 = 8.84 \times 10^{-12}$ C Vm^{-1}, $\varepsilon_{\mathrm{r}} = 80$. Results at electrolyte concentrations different from 0.1 M are indicated in the figure.

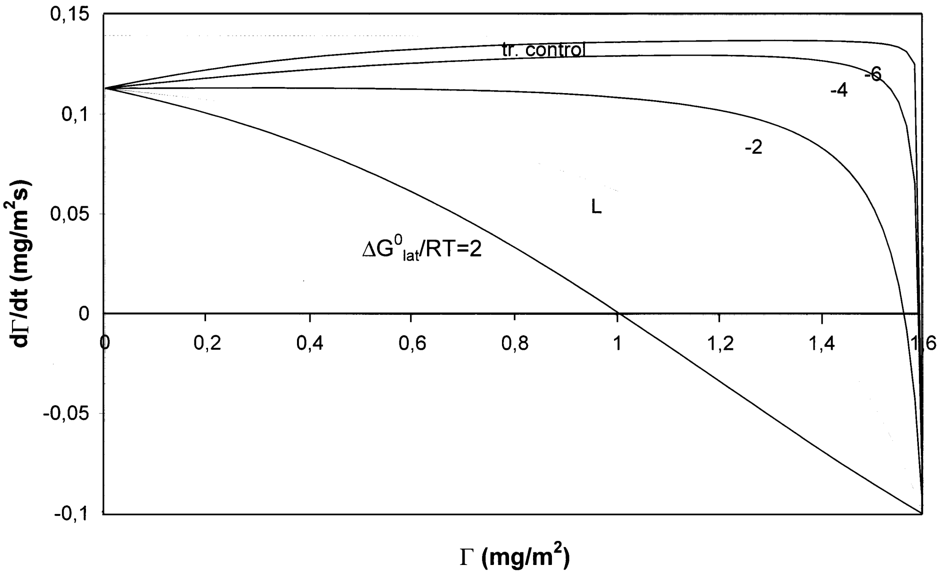

Fig. 2. Evolution of the adsorption rate as a function of the adsorption of charged particles. Influence of the particle charge. Parameters are the same as in Fig. 1 except, $\sigma_0 = 0$. The values of z_p are indicated in the figure. The curve with $z_p = 0$ represents Langmuir type kinetics. Curves with dashed lines are calculated using either $\lambda = 0.5$ or $k_d^{int} = 1 \times 10^{-8}$ kg m^{-2} s, as indicated.

resulting values depend strongly on the surface charge density, they are shown in Fig. 1 by the dashed curves for three indifferent electrolyte concentrations (note the logarithmic *Y*-axis). The intrinsic value of k_a appears in Fig. 1 at $\sigma_0 = 0$. For uncharged particles the chosen values of k_t and k_a correspond to a mixed transport/attachment–detachment controlled rate of adsorption. When the particles are charged the situation can be quite different. When particle and surface have the same charge sign (left side of Fig. 1) the value of $k_a|_0$ strongly decreases with increasing surface charge. The effect being larger if the salt concentration is lower; that is to say, if the screening of the electrostatic field is weaker. For high surface charge densities and low salt concentrations the rates of attachment are so low that in practice no adsorption will be observed. For weakly charged surfaces $k_a|_0$ first approaches k_t and then becomes larger than k_t (for the given conditions). Under these conditions both rate coefficients become important. When the surface charge and the particle charge have opposite signs the $k_a|_0$ becomes larger than k_t. In this situation an increase in the ionic strength decreases $k_a|_0$. However, as soon as $k_a|_0 \gg k_t$ the adsorption process becomes transport controlled and the increase of $k_a|_0$ will hardly be noticed in the rate of adsorption.

The initial value of the effective rate coefficient, see Eq. (31) is shown in Fig. 1 by the thick solid curve, that represent the situation at the high salt concentration. This curve clearly shows that when particles and surface have the same charge sign and the values of the surface charge density are not too low, the adsorption process is attachment controlled, whereas for an uncharged surface, or when particle and surface are oppositely charged, the process is transport controlled.

In Fig. 2 the evolution of the adsorption rate is plotted as a function of the adsorption for different values of the particle charge (or equivalently the effective particle charge). The surface is initially uncharged, but becomes gradually charged by the adsorption. The dashed line at the top of Fig. 2 shows the initial situation for $z_p = 0$ and pure transport control ($k_a^{int} \ggg k_t$). The thin solid curve for $z_p = 0$ shows the situation for the given values of k_a^{int}, k_d^{int} and k_t. This curve represents the Langmuir kinetics. The initial rate is lower than the transport rate because of the chosen value of k_a^{int}. Initially the rate of adsorption diminishes weakly, but when the equilibrium adsorption value ($d\Gamma/dt = 0$) is approached the rate decreases strongly because here the detachment rate becomes substantial. The equilibrium value of the adsorption at a particle concentration of 30 mg dm^{-3} equals about $\Gamma = 1.35$ mg m^{-2}. The negative values of $d\Gamma/dt$ beyond adsorption values of 1.35 mg m^{-2} show that pre-saturation of the surface at high values of the particle concentration leads to desorption if the particle concentration is reduced to 30 mg dm^{-3}.

For negative (or positive) values of z_p the shape of the curves deviates from that for Langmuir kinetics. This is due to the electrostatic repulsion, the larger the value of $|z_p|$ is, the slower is the adsorption and the stronger is the change in the shape of the rate curve. For $z_p = -14$ the rate of adsorption is almost immediately affected by the repulsion. Fig. 2 also shows that, for increasing values of $|z_p|$, a decreasing value of the equilibrium adsorption is attained (the value of Γ at $d\Gamma/dt = 0$). The present results apply to a salt concentration of 0.1 mol dm^{-3}, for lower salt concentrations the effects will be even stronger. For particles with a pH dependent charge Fig. 2 gives a qualitative indication of the effect of the pH on the rate of adsorption.

The negative values of the adsorption rate observed at high values of Γ indicate again that desorption will occur if the surface would have been pre-saturated. For instance, an adsorption value of 1.35 mg m^{-2} could have been achieved at a particle concentration of 30 mg dm^{-3} and a very high salt concentration (fully screened electrostatic interactions). A subsequent reduction of the salt concentration to 0.1 mol dm^{-3} and keeping the particle concentration at 30 mg dm^{-3} would lead to desorption with a rate, depending on the particle charge, according to the curves shown in Fig. 2. Also on the desorption side of the plots the shape of the curves deviates more from the Langmuir kinetics when the (effective) particle charge is larger.

At $\Gamma = \Gamma_m$ the adsorption rate becomes equal to $-k_d^{int} = -0.1$ (mg m^{-2} s^{-1}). This can be explained on the basis of Eq. (30). For $\theta \to 1$ the rate of adsorption becomes $-k_d^{int} \exp[-(1-\lambda)qz_pF\psi_0/RT]$, for $\lambda = 1$ this reduces to $-k_d^{int}$. In cases where λ is close to unity, this offers the possibility to obtain k_d^{int} experimentally.

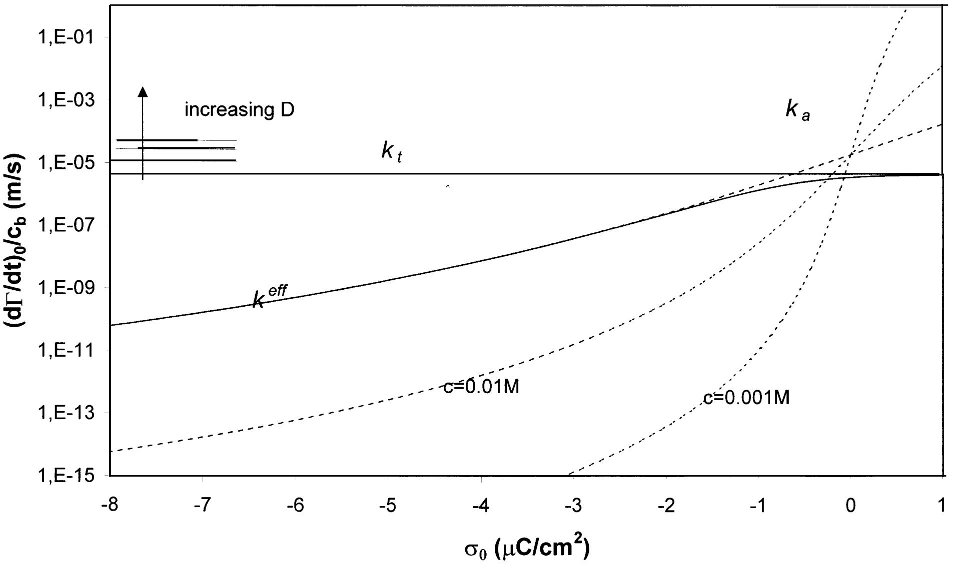

Fig. 3. Evolution of the adsorption rate as a function of the adsorption of charged particles. Influence of the surface charge. Parameters are the same as in Fig. 1. The values of σ_0 (μC cm^{-2}) are indicated in the figure. A curve calculated with $z_p = 0$ is included and represents the Langmuir kinetics (denoted as L). The dashed curves are calculated using either $\lambda = 0.5$ or $k_d^{int} = 1 \times 10^{-8}$ kg m^{-2} s, as indicated.

The effects of λ and $k_{\mathrm{d}}^{\mathrm{int}}$ on the rate of adsorption are illustrated for the case that $z_{\mathrm{p}} = -10$ (dashed curves). A decrease of λ to 0.5 increases the adsorption rate until the equilibrium adsorption value is reached. This is due to the fact that the barrier for attachment lowers by lowering λ. For adsorption values beyond the equilibrium adsorption value the rate of desorption increases strongly with a decrease of λ. This is due to the fact that also the barrier for detachment is lowered. The effective rate coefficient for desorption becomes substantially larger than its intrinsic value. By comparing the two curves at $z_{\mathrm{p}} = -10$ it can be concluded that the desorption part of the curve is most sensitive to the value of λ. This indicates that in order to obtain an estimate of λ a desorption experiment is more suited than an adsorption experiment.

The effect of a decrease of $k_{\mathrm{d}}^{\mathrm{int}}$ by a factor of 10 is shown by the second dashed curve. A decrease of $k_{\mathrm{d}}^{\mathrm{int}}$ for a given value of $k_{\mathrm{a}}^{\mathrm{int}}$ corresponds with a higher rate of adsorption for a given value of Γ. The lower $k_{\mathrm{d}}^{\mathrm{int}}$ is, the higher is the intrinsic affinity and the higher is the value of the equilibrium adsorption. As a result, the slope of the rate curve around $\mathrm{d}\Gamma/\mathrm{d}t = 0$ decreases with decreasing $k_{\mathrm{d}}^{\mathrm{int}}$. In the limiting case of a very high intrinsic affinity $k_{\mathrm{d}}^{\mathrm{int}}$ approaches zero and the rate of adsorption goes asymptotically to zero.

In Fig. 3 the evolution of the adsorption rate is plotted as a function of the adsorption for different values of the surface charge and an effective particle charge $qz_{\mathrm{p}} = -3$. For sake of comparison also the result for $z_{\mathrm{p}} = 0$ is included (Langmuir kinetics, thin solid curve). The behavior is, in general, very similar to that of Fig. 3, increasing the electrostatic repulsion lowers the rate of adsorption. The curve for $\sigma_0 = 0$ equals the curve for $z_{\mathrm{p}} = -10$ in Fig. 2. For a strongly charged positive surface ($\sigma_0 = 3$ μC cm^{-2}) the rate of attachment is strongly enhanced. This leads to a notably higher rate of attachment and a rate of adsorption that is dominated by the rate of transport. For a moderately charged positive surface ($\sigma_0 = 1$ μC cm^{-2}) the initial rate of adsorption is enhanced till the equivalence point is reached. This is the point where the rate curve crosses the curve for $z_{\mathrm{p}} = 0$ (surface charge compensated by the effective charge of the adsorbed particles). Beyond this point the electrostatic repulsion sets in and the adsorption rate becomes much lower than in the absence of electrostatics. When the surface has the same charge sign as the particles (see the curve for $\sigma_0 = -1$ μC cm^{-2}) the electrostatic barrier immediately lowers the initial attachment rate and the adsorption rate is strongly attachment controlled during the entire adsorption process. The intersection points with the Γ-axis indicate the equilibrium adsorption for the given particle concentration, ionic strength and surface charge. By comparing the curves at different values of σ_0 one could also say that, for instance for an oxide surface, the effect of the pH on the adsorption is simulated qualitatively. Pre-‘saturation’ of the surface at low pH (say, corresponding with the curve for $\sigma_0 = 3$ μC cm^{-2}) at the given particle concentration and ionic strength, followed by a change of pH to a high value (say, corresponding to $\sigma_0 = -1$ μC cm^{-2}) and keeping the other conditions the same, leads to the rate of desorption indicated by the curve for $\sigma_0 = -1$ μC cm^{-2} till the equilibrium adsorption value is reached. Fig. 3 also indicates that for particle adsorption to an oxide surface, it can be much quicker to reach a certain adsorption value at a pH favorite for adsorption, followed by some desorption at the desired pH, than by doing the process entirely at the desired pH. For instance, let the adsorption proceed for $\sigma_0 = 3$ μC cm^{-2} till an adsorption value of 0.6 mg m^{-2}, then change the pH so that the surface charge becomes -1 μC cm^{-2} and approach the equilibrium adsorption value for a short stretch along the $\sigma_0 = -1$ μC cm^{-2} curve. When the charge density of both particles and surface are controlled by pH the situation is more complicated, but also in this case it is well possible that the equilibrium adsorption value is most easily reached by a pH variation.

The effects of λ and $k_{\mathrm{d}}^{\mathrm{int}}$ on the rate of adsorption are illustrated in Fig. 3 for the case that $\sigma_0 = 1$ μC cm^{-2}. The effects on the rate of adsorption are qualitatively similar to those presented in Fig. 2 and the effect of a lower $k_{\mathrm{d}}^{\mathrm{int}}$ value needs no further discussion. The effect of lowering of λ has some specific features. For $\sigma_0 = 1$ μC cm^{-2} particle adsorption is electrostatically favored up to the equivalence point, i.e. where the effective particle charge just compensates the sur-

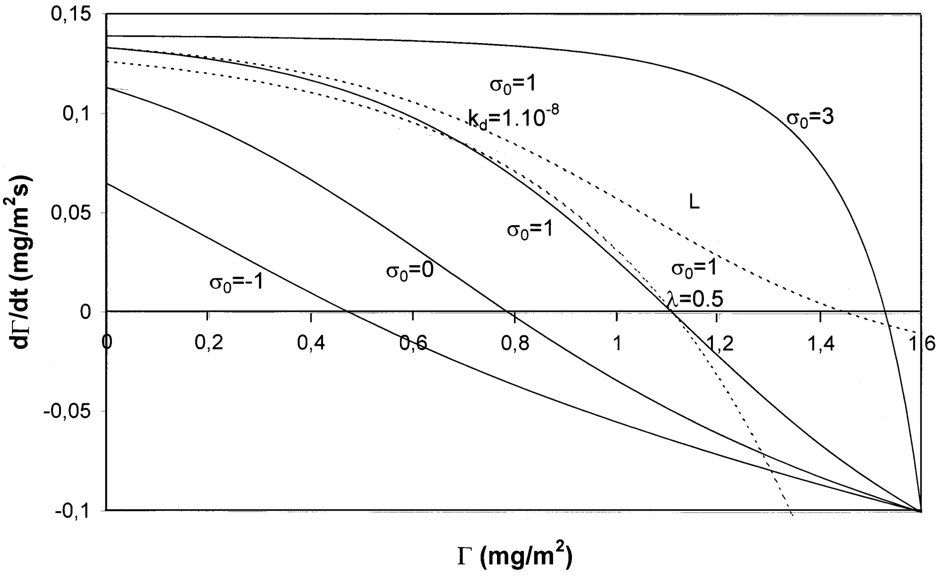

Fig. 4. FFG adsorption kinetics for an uncharged particle as predicted by Eq. (16). Influence of the specific lateral interaction. Parameters are the same as in Fig. 1. The values of $\Delta G^0_{\mathrm{lat}}/RT$ are indicated in the figure. The curve denoted L represents Langmuir kinetics ($\Delta G^0_{\mathrm{lat}}/RT = 0$).

face charge. This point is reached at the intersection of the curves for $\lambda = 0.5$ and $\lambda = 1$ with the Langmuir curve. Before the equivalence point lowering of λ leads to an increase of the barrier for adsorption and hence to a decrease of the rate of attachment. However, the rate of adsorption is also affected by the rate of transport and the effect on the rate of adsorption is not very large. Beyond the equivalence point the electrostatic interactions are repulsive and a lowering of λ now lowers the barrier for attachment. As a result the rate of adsorption for $\lambda = 0.5$ becomes slightly larger than that for $\lambda = 1$. This situation is maintained till the equilibrium adsorption value is reached. For the desorption part of the curve (negative $\mathrm{d}\Gamma/\mathrm{d}t$) it should be realized that a decrease of λ lowers the barrier for detachment and hence the rate of desorption becomes larger for $\lambda = 0.5$ than for $\lambda = 1$ and the differences are substantial.

In order to illustrate the effect of ‘specific’ lateral interactions on the kinetics Eq. (30) has to be replaced by the kinetic FFG model extended with electrostatic interactions:

$$\frac{\Gamma_{\mathrm{m}}\,\mathrm{d}\theta}{\mathrm{d}t} = \frac{k_{\mathrm{t}}k_{\mathrm{a}}^{\mathrm{ne}}\exp[-\lambda q z_{\mathrm{p}} F\psi_0/RT](1-\theta)c_{\mathrm{b}} - k_{\mathrm{t}}k_{\mathrm{d}}^{\mathrm{ne}}\exp[+(1-\lambda)q z_{\mathrm{p}} F\psi_0/RT]\theta}{k_{\mathrm{a}}^{\mathrm{ne}}\exp[-\lambda q z_{\mathrm{p}} F\psi_0/RT](1-\theta)+k_{\mathrm{t}}} \quad (32)$$

where $k_{\mathrm{a}}^{\mathrm{ne}}$ and $k_{\mathrm{d}}^{\mathrm{ne}}$ are given by Eqs. (14) and (15), respectively. Some results based on Eq. (32) are shown in Figs. 4 and 5. The parameters have the same value as before and the values of $\Delta G^0_{\mathrm{lat}}$ are indicated in the figures. For sake of simplicity calculations have been carried out for $\alpha = 1$. The effect of the lateral interactions on the rate of adsorption is shown in Fig. 4 for several values of $\Delta G^0_{\mathrm{lat}}$ and $z_{\mathrm{p}} = 0$ (no electrostatics). The curve for $\Delta G^0_{\mathrm{lat}} = 0$ is the reference curve that applies to Langmuir kinetics (thin solid curve). In general an attractive lateral interaction ($\Delta G^0_{\mathrm{lat}} < 0$) increases the rate coefficient for attachment and hence the rate of adsorption increases. The magnitude of the effect is determined by the value of $\Delta G^0_{\mathrm{lat}}$. By approaching the equilibrium adsorption value the adsorption rate has to approach zero. Due to this behavior a maximum occurs in the rate curves. Although the effect of the lateral attraction is clearly seen in the figure, it should be realized that in practice lateral attraction can easily leads to an adsorption rate that is transport dominated. In the case of lateral repulsion ($\Delta G^0_{\rm lat} > 0$) the barrier for adsorption increases, the rate coefficient for attachment decreases and the rate of adsorption decreases as compared with the situation for $\Delta G^0_{\rm lat} = 0$. In general, it should be noted that for values of $\Delta G^0_{\rm lat} < -4RT$ the equilibrium adsorption isotherm shows a two-dimensional condensation step. This phenomenon will lead to specific kinetic behavior as well, but these complications are not of direct consequence for the results presented here.

The effect of specific lateral interactions on the rate of adsorption of a charged particle ($z_{\rm p} = -10$) on an uncharged surface is shown in Fig. 5 for the same range of values of $\Delta G^0_{\rm lat}$ as in Fig. 4. The thin solid curve for $\Delta G^0_{\rm lat} = 0$ (no specific lateral interaction) and $z_{\rm p} = 0$ (no particle charge) is included as reference (Langmuir kinetics). Qualitatively the behavior is similar to that of Fig. 4, specific lateral attraction decreases the barrier for attachment. However, the electrostatic repulsion increases the barrier for attachment in this case. As a result the overall behavior deviates less from the Langmuir kinetics than when only electrostatic or only 'specific' lateral interactions would have played a role. The curve for $\Delta G^0_{\rm lat} = -4RT$ is an example of nearly pseudo-Langmuir kinetics. When the lateral interaction is repulsive, i.e. $\Delta G^0_{\rm lat} = 2RT$, the electrostatic and the specific effect enhance each other and the rate of adsorption strongly diminishes.

In the case of adsorption on a charged surface the behavior is somewhat more complicated because the electrostatic interaction may change here from attractive to repulsive, but in general, an attractive lateral interaction will also here increase the rate of attachment and therefore the rate of adsorption. The extent to which this happens depends on the conditions.

In the case of weak electrostatic interactions the Debye–Hückel (DH) approximation can be used instead of the Gouy–Chapman theory. In the DH approximation the electrostatic potential is, for a

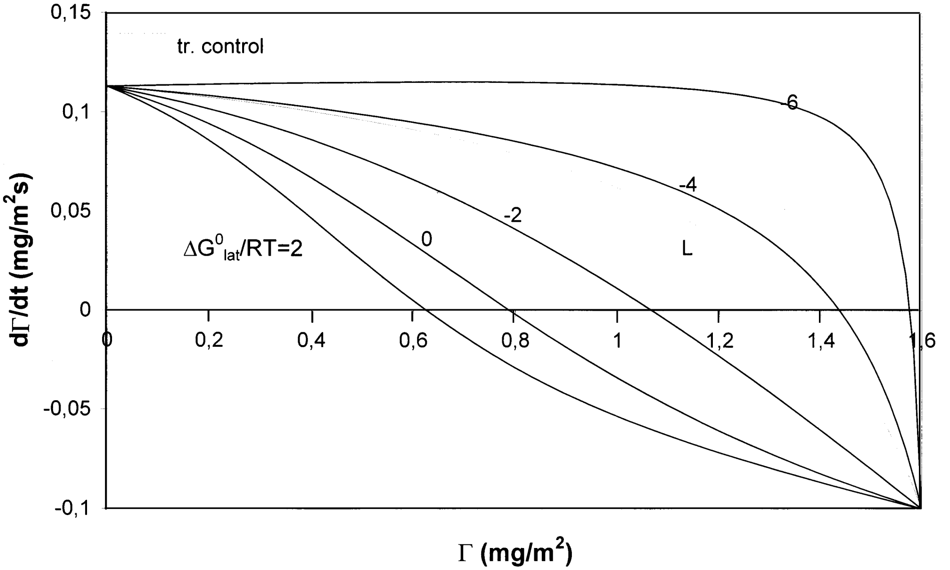

Fig. 5. FFG adsorption kinetics with electrostatics as predicted by Eq. (32). Influence of the lateral interaction. The values of $\Delta G^0_{\rm lat}/RT$ are indicated in the figure. The adsorbing particles have a charge number $z_{\rm p} = -10$, the surface itself is uncharged, $\sigma_0 = 0$, and the value of $\alpha = 1$. Other parameters are the same as in Fig. 1. The curve denoted L represents Langmuir kinetics ($\Delta G^0_{\rm lat}/RT = 0$, $z_{\rm p} = 0$).

given salt concentration, directly proportional to the adsorbed (effective) particle charge and hence, to the adsorption. As a result the activation energy barrier is linearly dependent on both the specific and the electrostatic interaction and a pure FFG type behavior results.

5. Final remarks and conclusions

Although the model of the electrostatic interactions is very simple, the present results are in qualitative agreement with rates of adsorption and the effect of the pH on the rates of desorption as observed for the adsorption of humic acid particles on an iron oxide surface [8,9]. In forthcoming paper, we intend to compare calculations with the present model and these results in more detail.

The present results are also in qualitative agreement with the effect of the pH and the ionic strength on the initial adsorption of IgG and its F(ab′)$_2$ fragments on silica and methylated silica [23]. Ramsden [24] quotes some results for the rate of adsorption of apotransferrin on a $SiTiO_2$ surface that also might be explained on the basis of electrostatic interactions.

The models can also be used to describe the kinetics of surfactant adsorption. In this case the kinetic FFG model and the kinetic FFG model extended with electrostatic interactions seem most promising.

In general, the calculations show that the effect of the electrostatics on the adsorption can be quite large. In the case of electrostatic attraction the tendency is that the rate of adsorption moves towards domination by the rate of transport through the diffusion layer. In the case of electrostatic repulsion the rate of adsorption has the tendency to become dominated by the attachment–detachment step. In general, an electrostatic attraction between surface and particles will diminish in the course of adsorption and for super-equivalent adsorption values convert to electrostatic repulsion. For the rate of attachment–detachment this means a strong change from an enhanced rate (compared with the uncharged situation) to a diminished rate. In the case of a surface that is initially uncharged the adsorption of charged particles leads to electrostatic repulsion all the way and a strong retardation of the adsorption kinetics results. Qualitatively, this results compares well with the predictions according to the models put forward by Dukhin et al. [3] in which the retardation is explained by the retarded transport in the electrical double layer. The advantage of the present model over the far more complicated kinetic models that take into account the retardation in the electrical double layer, is that a simple analytical expression with a fair amount of flexibility is obtained and that the model is able to predict, at least qualitatively, the adsorption process.

A further improvement of the electrostatic model is, for instance, possible by considering different planes of adsorption for the primary surface charge determining ions and the particles under consideration. This would be a first step to take into account the particle size. This type of improvements may make it possible to avoid or to diminish the influence of the adjustable parameter q and it would make the interpretation of λ more easy. However, the predicted trends will only change quantitatively and not qualitatively.

Another improvement could be made by considering explicitly the fact that the local (discrete) potential at the surface in the vicinity of an adsorbed particle will be different from the smeared-out potential. In simple cases this effect is implicitly already accounted for in the present model, for instance, when the discreetness of charge effect can be treated by separating the local potential into a discrete self-atmosphere potential and a smeared-out macro-potential. If it is assumed that the self-atmosphere potential is proportional to the particle loading, the effect is implicitly incorporated in the present model. The part of the self-atmosphere potential that is independent of the adsorption is included in the intrinsic part of the rate coefficients for attachment and detachment. The part of the self-atmosphere potential that is linearly dependent on θ is reflected in the value of $\Delta G^0_{\mathrm{lat}}$ and hence, in the lateral part of the rate coefficients. Therefore, to a first approximation this is not the most serious shortcoming of the present model.

In the case of colloidal particles with a size that largely exceeds the Debye length the present treatment cannot be applied. In this case the initial situation is very similar to considering the kinetics of the adsorption of a colloid particle to a collector surface. For this type of treatment the colloid literature has to be consulted and this will lead to a much more complicated model. The subsequent step of multiple particle adsorption will further complicate the treatment.

The present model already catches the main features of electrostatics on the rate of adsorption of molecules and/or nano particles. Having a simple way to account for the effect of electrostatics on the kinetics of the adsorption is much better than neglecting the effects. Moreover, a simple model has the advantage that it can be relatively easy adapted to situations like, for instance, competitive adsorption, or the calculation of breakthrough curves.

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