

Particle adsorption on mica determined by the streaming potential method

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Adsorption of colloid latex particles on mica was correlated with the streaming potential changes. Measurements were carried out using the parallel-plate channel formed by two mica sheets separated by a teflon spacer. The coverage of particles was determined directly by an optical microscope counting procedure. Two limiting series of experiments were performed: (i) neutral particles on negatively charged mica and (ii) positively charged particles on neutral mica. In the former case the neutral charge of particles was obtained by pH adjustment, whereas in the latter case by adsorption of cationic surfactant (DTACI). The experimental data were interpreted in terms of a theoretical model postulating that the streaming potential change was due to flow damping over the interface and by charge transport from the double-layer surrounding adsorbed particles. Opposite to previous approaches no assumption of the slip (shear) plane shift upon particle adsorption was made. The experimental data allowed one to determine empirically the universal correction function that can be exploited for adsorption kinetics measurements of arbitrarily charged colloid and bioparticles (proteins).

1. INTRODUCTION

Adsorption or deposition (irreversible adsorption) of colloids and bioparticles at solid/liquid interfaces is of large significance in many practical processes, e.g., various filtration procedures, chromatography etc. Learning about mechanisms and kinetics of particle adsorption phenomena is also relevant for polymer and colloid science, biophysics and medicine enabling one

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to control protein and cell separation, enzyme immobilization, thrombosis, biofouling of membranes and artificial organs etc.

Studying adsorption of colloids and bioparticles at solid surfaces is rather tedious because of the lack of direct experimental methods of surface coverage determination. Usually indirect optical methods are applied like ellipsometry [1-2], reflectometry [3-5], total internal reflection fluorescence [6-7] or the radiotracer techniques using labelled particles [8-10]. One also often uses the concentration depletion method [11-12] whose precision is rather limited. The disadvantage of the above methods is that they become accurate enough for higher coverage range, preferably close to the saturation coverage.

Other class of indirect methods, more sensitive for low coverage range is based on measurements of streaming potential changes induced by particle adsorption. Many experiments of this type involving protein solution were performed in the circular [13] or parallel-plate channel arrangement [4,14-15]. Although the streaming-potential method performs well for low coverage where other methods fail, it can only be used as a relative method due to the lack of well-established theory connecting streaming potential changes with particle coverage. As a consequence, adsorption kinetics can only be studied quantitatively if independent measurements of surface coverage are carried out. This may decrease accuracy of the data obtained because the surface coverage and streaming potential measurements are done under different conditions. Recently Hayes [16] used this procedure (based on scanning electron microscope measurements of particle coverage) for determining zeta potential of aminopropylsilane modified glass surface covered with 90 nm of diameter silica particles. The results were interpreted in terms of empirical models postulating a gradual shift of the slip (shear) plane with particle coverage.

Experimental results concerning streaming potential measurements of mica covered *in situ* by precisely controlled amount of colloid particles were reported in [17-19]. The surface concentration of adsorbed polystyrene latex particles was determined by direct optical microscope counting that allowed one to correlate this quantity with the streaming potential changes. However, these experiments have been carried out for charged particles. This complicated the theoretical interpretation of the data since the electrokinetic effects stemming from the interface and particles occurred simultaneously.

Therefore, the goal of this work is to perform model experiments for the two limiting cases (i) uncharged particles at charged mica surface and (ii) charged particles at uncharged mica surface. The particle charge was neutralized by pH change, whereas the charge of mica was reduced practically to zero by adsorption of a cationic surfactant. The superposition of the results obtained for these limiting cases allows one to formulate a unequivocal relationship between

the amount of adsorbed substance and the streaming potential for arbitrary charged particles and interfaces.

2. THE THEORETICAL MODEL

Consider a parallel-plane channel formed of insulating walls bearing surface charge density σ_1 and σ_2 , respectively (see Figure 1). Assume that due to, for example, hydrostatic pressure difference, there appears a steady, laminar flow of the electrolyte in the x direction of the channel. This produces a convective current, often referred to as the streaming current, of ions accumulated in the electrical double-layer near the walls. The magnitude of this streaming current can be calculated from the constitutive dependence [17]

$$I = \iint_S \rho_e \mathbf{V} \cdot d\mathbf{S} = \iint_S \rho_e(y, z) u(y, z) dydz \quad (1)$$

where S is the channel cross-section perpendicular to the x axis, $d\mathbf{S}$ is the surface element vector, $\rho_e = e \sum_{i=1}^N z_i n_i^b$ is the electric charge density, e is the elementary charge, z_i is the valency of i -th ion, n_i^b is the bulk concentration of this ion, and $u(y, z)$ is the tangential component of fluid velocity.

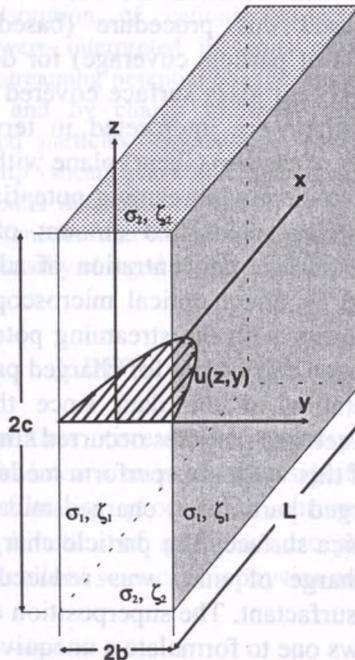


Fig. 1. A schematic view of the laminar flow in the parallel-plate channel

An analytical expression for $u(y,z)$ in the form of series expansion was derived in [15, 17] for a rectangular channel of arbitrary cross-section $2b \times 2c$. It was also shown in [17] that close to the channel walls, the local fluid flow reduces to simple shear, described by the equation

$$V = G^0 h i_x \quad (2)$$

where G^0 is the local shear rate depending on the position on the wall (but independent of the x coordinate) and h is the distance from the wall.

On the other hand, the local charge density ρ_e is connected with the local electric potential ψ via the Poisson-Boltzmann equation

$$\nabla^2 \psi = -\frac{4\pi}{\epsilon} \rho_e \quad (3)$$

where ϵ is the dielectric constant of water.

By considering Eqs (2-3) one can evaluate the double integral in Eq.(1) explicitly which results in the expression [18]

$$I = \frac{\epsilon c}{\pi} \langle G_y^0 \rangle \zeta_1 + \frac{\epsilon b}{\pi} \langle G_z^0 \rangle \zeta_2 = \frac{\zeta_1}{R_o} \left[1 - \left(1 - \frac{\zeta_2}{\zeta_1} \right) \frac{16\alpha}{\pi^3} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^3} \tanh \frac{(2n+1)\pi}{2\alpha} \right] \quad (4)$$

where ζ_1, ζ_2 are the zeta potentials of the channel walls (equal to the electric potential ψ in the slip plane), $\langle G_y^0 \rangle, \langle G_z^0 \rangle$ are the local shear rates averaged over the x,z plane and the x,y plane, respectively, $\alpha = b/c$, $R_o = \pi b/2\epsilon u_{ch}$, $c = \pi \eta / (\epsilon (\Delta P/L) bc)$ is the dynamic resistance of the channel, $\Delta P/L$ is the hydrostatic pressure gradient along the channel and η is the fluid dynamic viscosity.

Eq.(4) represents the general solution valid for arbitrary channel shape (including the case of a square cross-section channel).

In practice, instead of I , one is measuring the potential difference E_s (called the streaming potential) between the inlet and the outlet from the channel and the channel ohmic resistance R_c . Then, equating I with E_s/R_c (ohmic current) one can express Eq.(4) as

$$\zeta_c = \zeta_1 \left[1 - \left(1 - \frac{\zeta_2}{\zeta_1} \right) \frac{16\alpha}{\pi^3} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^3} \tanh \frac{(2n+1)\pi}{2\alpha} \right] = \zeta_1 f(\alpha, \zeta_2/\zeta_1) = \frac{E_s R_o}{R_c} \quad (5)$$

where ζ_c can be treated as the effective zeta potential of the channel and $f(\alpha, \zeta_2/\zeta_1)$ is the universal correction function.

For thin channels, when $\alpha < 0.1$, Eq.(5) reduces to

$$\zeta_c = \zeta_1 \left[1 - \frac{16\alpha}{\pi^3} + \frac{16\alpha}{\pi^3} \frac{\zeta_2}{\zeta_1} \right] = \frac{E_s}{R_c} \frac{\pi \eta}{\varepsilon b c} \frac{\Delta P}{L} \quad (6)$$

By introducing the specific conductivity of the solution $\lambda = L/(4R_c bc)$ one can convert Eqs.(5-6) to the well-known Smoluchowski expression [20], i.e.,

$$\zeta_c = \frac{4\pi\eta\lambda}{\varepsilon} \frac{E_s}{\Delta P} \quad (7)$$

If adsorbed particles are present at the interface the streaming current is changed because the local charge density and hydrodynamic field are perturbed. The change in the streaming current can be formally expressed as

$$\Delta I_p = I_p - I = \iint_S (\rho^* \mathbf{V}^* - \rho \mathbf{V}) \cdot d\mathbf{S} \quad (8)$$

where I_p is the streaming current for particle covered surface, I is the current for bare surface given by Eq.(1), ρ^* , \mathbf{V}^* are the perturbed (due to adsorbed particles) electric charge density and fluid velocity in the S plane, respectively. These quantities obviously depend on particle coverage and distribution over the surface. Therefore, it is impractical to evaluate the surface integral in the general case because this would require a solution of the Poisson-Boltzmann and Navier-Stokes equations for multibody problems. Due to lack of appropriate coordinate systems and nonlinearity of the Poisson-Boltzmann equation no results of general validity were found yet.

However, one can derive exact solutions in the case of a single spherical particle attached to the surface. The electrostatic field ψ^* around the sphere and consequently the local charge density ρ_e^* can be calculated numerically by solving the Poisson-Boltzmann equation in the bipolar coordinate system [21]. The distribution of the electric potential in the vicinity of an adsorbed sphere obtained from these calculations is shown schematically in Figure 2. The dimensionless parameter κa was 5, where κ^{-1} is the thickness of the electrical double layer and a is the particle radius. This value is typical for colloid particles under the usual experimental conditions [22]. As one can notice, the perturbation to the electric fields around the particle and the interface is limited to an area considerably smaller than the particle surface area. Moreover, as demonstrated by numerical calculations [21], the electrostatic fields stemming from the sphere and the interface become additive in the limit of thin double layers when $\kappa a > 1$.

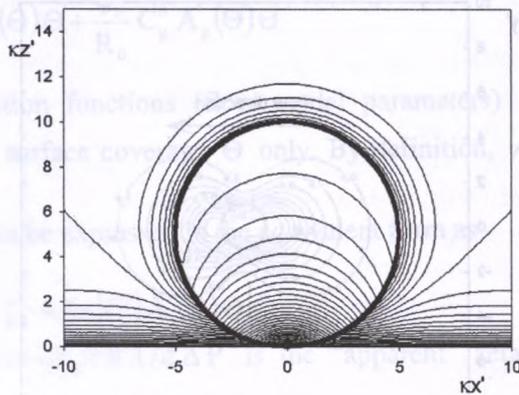


Fig. 2. A schematic representation of the electric potential distribution around a particle adsorbed at a charged interface, $\kappa a = 5$

Except for the electrostatic field, the particle attached to the interface also perturbs the local fluid velocity field. This hydrodynamic problem, i.e., flow distribution around sphere immersed in a simple shear described by Eq.(2), can be solved analytically in terms of Bessel functions [23] or Legendre polynomials in bispherical coordinates [24]. In this way the velocity field V^* can be evaluated explicitly which allows one to calculate also the perturbed velocity gradients at the interface. The calculations demonstrated that the presence of a particles decreases fluid velocity at distances exceeding considerably its radius a . This will result in the decrease in the shear rate at the interface shown in Figure 3 where the contours of the function G^*/G^0 are plotted (G^* is the perturbed wall shear rate). The data presented in Figure 3 were derived by applying the Legendre polynomial expansion method. It is interesting to note that this perturbation is symmetric relative to the flow direction.

Due to decreased flow rate the amount of charge transported from the region attached to the interface, according to Eq.(8) will be considerably decreased independently of the charge of the particle. This means that a neutral particle will also decrease the absolute value of the streaming current that can be exploited for its detection as discussed later on.

Knowing the electrostatic and hydrodynamic fields one can calculate in an exact way via Eq.(8) the incremental change in the streaming current due to one adsorbed particle. Then, knowing the solution for one particle one can construct solutions for dilute multiparticle systems assuming that if the perturbations to the electrostatic and hydrodynamic fields do not interfere and particle distribution remains uniform.

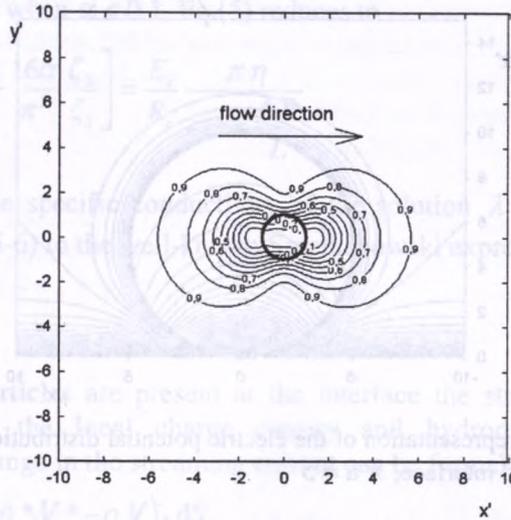


Fig. 3. The contours showing the relative shear rate (tangential flow intensity) at the interface G^*/G^0 in the vicinity of an adsorbed particle

In this way, in the limit of thin double layers when $\kappa a > 1$, one obtains the following analytical expression connecting the streaming current changes with particle coverage $\Theta = \pi a^2 N$ (N is the number of particles adsorbed per unit area)

$$\begin{aligned} \Delta I_p &= \frac{\varepsilon}{\pi} [c \langle G_y^0 \rangle \zeta_1 + b \langle G_z^0 \rangle \zeta_2] C_i^0 \Theta + \frac{\varepsilon}{\pi} \zeta_p [c \langle G_y^0 \rangle + b \langle G_z^0 \rangle] C_p^0 \Theta = \\ &= \frac{\zeta_c}{R_0} C_i^0 \Theta + \frac{\zeta_p}{R_0} C_p^0 \Theta \end{aligned} \tag{9}$$

where ζ_p is the zeta potential of adsorbed particles, $C_i^0 = -10.21$ and $C_p^0 = 6.51$ are the universal constants, being independent of channel geometry, particle dimension, charge (zeta potentials) etc. [17].

In this limiting case the dimensionless constant C_i^0 describes the purely hydrodynamic effect of flow shear rate decrease over the interface as a result of the presence of adsorbed particles, whereas the constant C_p^0 reflects the flow shear rate averaged over adsorbed particles.

Eq.(9) remains valid as long as the flow perturbations stemming from individual particles remain additive which is fulfilled for low coverage only. For higher θ one can introduce, however, correction functions in analogy to the flow model parameter A_f used for describing 3D flows in packed bed columns or filtration mats [25-26]. Then, Eq.(9) can be formally expressed as [20]

$$\Delta I_p = \frac{\zeta_c}{R_0} C_i^0 A_i(\Theta) \Theta + \frac{\zeta_p}{R_0} C_p^0 A_p(\Theta) \Theta \quad (10)$$

where the correction functions (flow model parameters) $A_i(\Theta)$, $A_p(\Theta)$ are dependent on the surface coverage Θ only. By definition, $A_i = A_p \rightarrow 1$ when $\Theta \rightarrow 0$.

Eq.(10) can also be expressed in the equivalent form as

$$\zeta_a = C_p^0 A_p(\Theta) \Theta \zeta_p + [1 - |C_i^0| A_i(\Theta) \Theta] \zeta_c \quad (11)$$

where $\zeta_a = I_p R_0 = 4E_{sp} \pi \eta \lambda / \epsilon \Delta P$ is the "apparent" zeta potential of the channel.

From Eq.(11) one can easily deduced that for uncharged particles, when $\zeta_p = 0$

$$\frac{\zeta_a}{\zeta_c} = \frac{I_p}{I} = \frac{E_{sp}}{E_s} = 1 - |C_i^0| A_i(\Theta) \Theta \quad (12)$$

On the other hand, for uncharged channel (when $\zeta_c = 0$), one has

$$\frac{\zeta_a}{\zeta_p} = C_p^0 A_p(\Theta) \Theta \quad (13)$$

Eqs.(12-13) suggest that the correction functions $A_i(\Theta)$, $A_p(\Theta)$ can be determined by measuring experimentally the dependence of the apparent zeta potential of the channel ζ_a on particle coverage Θ . Note that these functions do not depend on any parameters characterizing the channel shape, its surface properties or flow rate. This observation has a considerable practical impact indicating that the $A_i(\Theta)$, $A_p(\Theta)$ functions determined directly for colloid particles can be used for other experimental systems, e.g., proteins, when direct observation of particles is not feasible. The only limitation is the requirement that the double layer thickness should be much smaller than particle radius that is usually fulfilled for protein adsorption due to high (physiological) electrolyte concentrations.

The primary goal of our experimental work discussed below was to determine the correction function empirically.

3. EXPERIMENTAL

Material and Methods. Natural ruby mica sheets supplied by Dean Transted Ltd. England were used without any pre-treatment. Thin sheets were freshly cleaved for each experiment.

Two samples of positively and negatively charged polystyrene latices (L+39, L70, respectively) were synthesized according to the method described in [27,28] without using a surfactant. In the case of L+39 latex, the 1,2-azo-bis-(2-methyl propamidinium) dichloride (ABA) initiator was used [27] whereas the L70 latex were produced using the persulfate initiator [28]. The latex suspensions were charge stabilized by the ionic groups stemming from the initiators. The melamine latex sample (M25) was produced in a polycondensation reaction of melamine and formaldehyde carried out at 80 °C in the presence of formic acid. After synthesis, the latices were purified by steam distillation under decreased pressure and by prolonged membrane filtration until the conductivity of filtrate reached the value of water used for washing. In the case of the melamine latex, a repeated decantation and sedimentation procedure was applied for an effective cleaning of the sample.

The averaged size of particles determined by ZM Coulter Counter was 1.13 μm for L+39 latex, 1.52 μm for the M25 latex and 0.87 μm for the L70 sample.

The zeta potential of latex particles was obtained by microelectrophoresis using the Brookhaven Zeta-Potential Analyzer (Zeta Plus). The pH of latex suspension was adjusted by addition of the phosphate (PB) buffer. At pH close to 7.0 the apparent isoelectric point of the L=39 and M25 latex was attained as discussed later on.

Streaming potential of mica, bare and covered by latex particles was determined using the apparatus shown schematically in Figure 4. The cell, described previously in detail [4, 16-17], consisted of two polished teflon blocks one of them containing two rectangular, inlet and outlet compartments. Two thin mica sheets were placed on the teflon blocks separated by a teflon gasket of the thickness of 0.025 cm serving as a spacer. The parallel plate channel of the dimensions: $2b \times 2c \times L = 0.025 \times 0.33 \times 6.0$ cm was formed by clamping together the teflon blocks with two mica sheets and the spacer, using a press under constant torque conditions. The whole set-up was placed inside the earthened Faraday cage to avoid any disturbances stemming from external electric fields.

The streaming potential E_s , occurring when an electrolyte was flowing through the cell under regulated and constant hydrostatic pressure difference, was measured using the two Ag/AgCl electrodes. These electrodes were located in two glass tubes having a direct contact with inlet and outlet compartments of

the cell. A series of streaming potential measurements was done for at least five various pressures forcing the flow through the cell. Keithley 6512 Electrometer having the input resistance of more than $200\text{ T}\Omega$ was used for potential measurements. The high resistance allowed potential measurements to be carried out at practically zero current conditions.

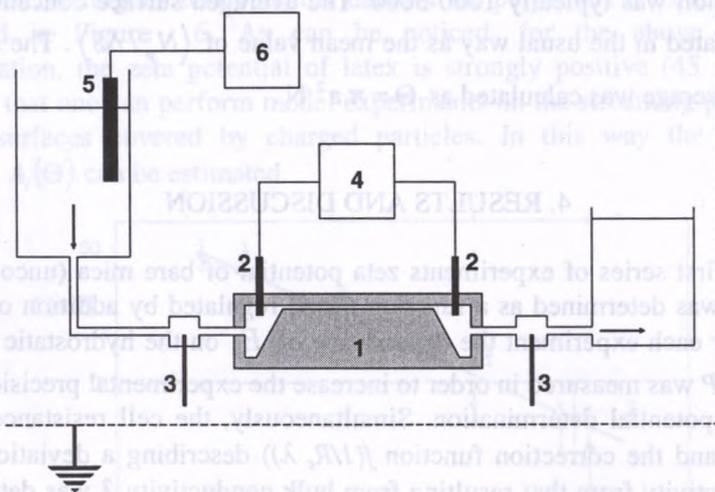


Fig. 4. A schematic view of the experimental set-up used for the streaming potential measurement: 1 – the cell, 2 – electrodes for streaming potential measurements, 3 – electrodes for cell resistance measurements, 4 – electrometer, 5 – conductivity cell, 6 – conductometer

Another pair of electrodes situated outside the teflon cell (along the flow path) was used for determination of the cell resistance R_c . This parameter was determined after the streaming potential measurements for each experiment.

The surfaces covered with particles were produced *in situ* by filling the channel with polystyrene latex suspension having particle concentration typically in the range of $10^8 - 10^{10}$ $1/\text{cm}^3$. The PB concentration in L+39 and M25 latex particle deposition was equal to 3.3×10^{-4} M and $\text{pH} = 5.3$. Particles of L70 latex were deposited from 1.2×10^{-4} M DTACl solution. The fluid flow rate during the deposition experiments was kept as low as possible in order to create the diffusion-controlled transport conditions. The particle deposition time was typically 30 minutes. Then, the cell was washed with pure electrolyte solution without allowing air bubbles to enter the channel. When the outlet solution was free of latex particles the streaming potential measurements were performed using the electrolyte solutions of appropriate composition.

After finishing the experiment the cell was washed with water, opened and mica sheets covered by particles were placed onto special glass cell filled with

water. The wet mica sheets with deposited latex particles were examined under optical microscope. The surface concentration was obtained by determining the number of particles N_p found over equal sized surface areas (of geometrical area ΔS equal typically few thousands of μm^2) chosen at random over the interface. The total number of particles used in surface concentration determination was typically 1000-3000. The averaged surface concentration N was calculated in the usual way as the mean value of $\langle N_p / \Delta S \rangle$. The averaged surface coverage was calculated as $\Theta = \pi a^2 N$.

4. RESULTS AND DISCUSSION

In the first series of experiments zeta potential of bare mica (uncovered by particles) was determined as a function of pH regulated by addition of the PB buffer. For each experiment the dependence of E_s on the hydrostatic pressure gradient ΔP was measured in order to increase the experimental precision of the streaming potential determination. Simultaneously, the cell resistance R_c was measured and the correction function $f(1/R_c \lambda)$ describing a deviation of the cell conductivity from that resulting from bulk conductivity λ was determined. This function incorporates *inter alia* the surface conductivity effects expected to play a role for lower ionic strengths. Knowing $E_s/\Delta P$ and the cell conductivity λ , the zeta potential of the channel ζ_c was calculated from Eq.(6) (with the appropriate correction for temperature dependence of viscosity and of dielectric constant). It was assumed that this value corresponds to the zeta potential of mica ζ_1 . This is justified by the fact that for our channel geometry ($\alpha = 0.076$) the coefficient $16\alpha/\pi^3$ was equal 0.04. This means that according to Eq.(6) that the correction term $-(16\alpha/\pi^3)(1-\zeta_2/\zeta_1)$ is much smaller than unity (if the mica and teflon zeta potentials are comparable).

Using the above procedure, it was found that $\zeta_1 = -103$ mV for pH = 5.3, -104 mV for pH = 6, -126 mV for pH = 7 and -119 mV for pH = 7.8. For sake of convenience the dependence of ζ_1 on pH for bare mica is plotted in Figure 5. The dependence of zeta potential ζ_p of latex particles (L+39 and M25) on pH determined by microelectrophoresis is also plotted in Figure 5. As one can notice, at pH around 7.0, ζ_p is practically reduced to zero. This was exploited in a series of experiments aimed at determining the correction function $A_i(\Theta)$ for particle covered surfaces.

The zeta potential of mica can be modified to a considerable extent by adsorption of cationic surfactants that was exploited in our measurements for

producing a neutrally charged mica surface. This effect is illustrated in Figure 6 where the dependence of zeta potential of mica on the concentration of dodecyltrimethyl ammonium chloride (DTACl) surfactant is shown. The pH value of these experiments was equal to 6. It can be noted that for the surfactant concentration about 1×10^{-4} M, the zeta potential of mica becomes zero. For comparison, analogous zeta potential data for the polystyrene latex L70 are also presented in Figure 6. As can be noticed, for the above surfactant concentration, the zeta potential of latex is strongly positive (45 mV). This suggests that one can perform model experiments on the streaming potential of neutral surfaces covered by charged particles. In this way the correction function $A_i(\Theta)$ can be estimated.

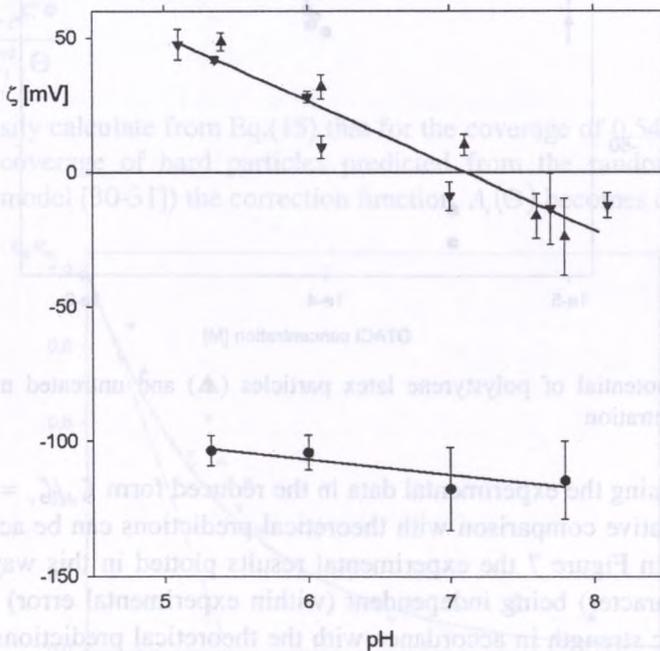


Fig. 5. Zeta potential of latex particles (▲ – L+39, ▼ – M25) and untreated mica (●) vs. pH regulated by the PB buffer

Such measurements for particle covered mica were carried out according to the procedure described above. In the first step particles were adsorbed until the desired surface coverage was attained. After completing the particle deposition procedure, the streaming potential measurement was carried out *in situ*. As mentioned previously, for each experiment the dependence of the streaming potential for particle covered channel E_{sp} on the hydrostatic pressure gradient

ΔP was determined in order to increase the experimental precision. Then, the apparent zeta potential of the channel ζ_a was calculated using Eq.(7).

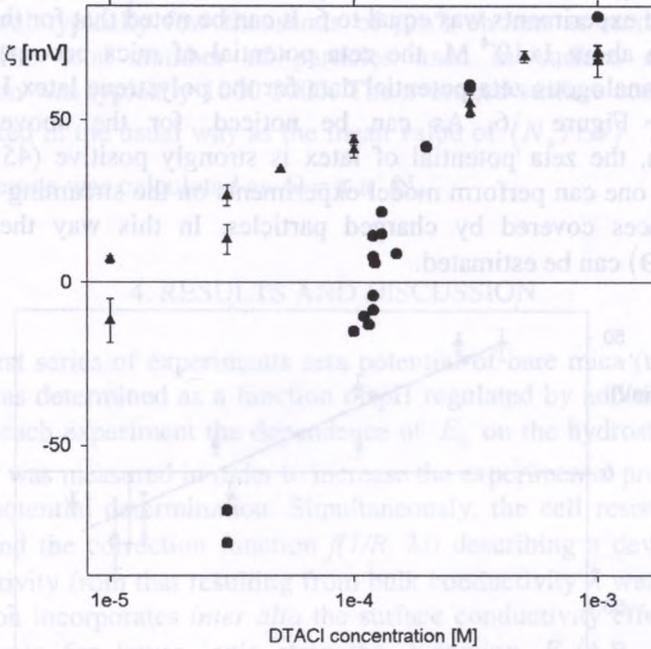


Fig. 6. Zeta potential of polystyrene latex particles (▲) and untreated mica (●) vs. DTACl concentration

By expressing the experimental data in the reduced form $\zeta_a/\zeta_c = E_{sp}/E_s$ on Θ , a quantitative comparison with theoretical predictions can be achieved. As can be seen in Figure 7 the experimental results plotted in this way exhibit a universal character) being independent (within experimental error) of particle size and ionic strength in accordance with the theoretical predictions. It should also be noted that for low coverage range ($\theta < 0.05$) the experimental data are well reflected by the linear model (broken line in Figure 7) derived from Eq.(12) by substituting $A_i(\Theta)=1$. For higher coverage, however, the experimental results shown in Figure 7 deviate from theoretical predictions stemming from the linear model. This can be interpreted, in accordance with previous discussion, as due to the fact that the flow fields stemming from individual particles are no longer additive, so the function A_i becomes smaller than unity. It was found that the experimental dependence of $\zeta_a/\zeta_c, (E_{sp}/E_s)$ on Θ shown in Figure 7 can well be reflected by the interpolation function

$$\zeta_a/\zeta_c = E_{sp}/E_s = I_p/I = e^{c_i^0 \Theta} \quad (14)$$

The function used previously for positively charged particles [18] reduces exactly to the linear model in the limit of low coverage. A physical justification of its validity stems from the fact that the probability of finding an empty surface area ΔS over the interface uncovered by particles can be approximated by $e^{-(\Delta S/\pi a^2)\Theta}$ [29]. As a consequence, the zeta or streaming potential ratio E_{sp}/E_s is expected to decrease proportionally to this quantity. Eq.(14) implies that the correction function $A_i(\Theta)$ describing the flow damping by the adsorbed particle layer assumes the form

$$A_i(\Theta) = \frac{1 - e^{c_i^0 \Theta}}{|C_i^0| \Theta} \quad (15)$$

One can easily calculate from Eq.(15) that for the coverage of 0.547 (that is the maximum coverage of hard particles predicted from the random sequential adsorption model [30-31]) the correction function $A_i(\Theta)$ becomes close to 0.2.

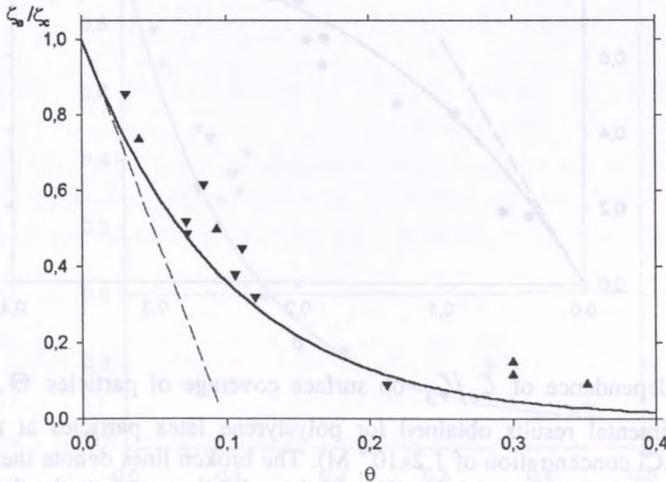


Fig. 7. The dependence of $\zeta_a/\zeta_c = E_{sp}/E_s$ on surface coverage of particles Θ . The points denote experimental results obtained for neutral latex particles (at pH 7). The broken lines denote the initial slope calculated from the linear model Eq.(9) and the solid line presents the data calculated from Eq.(12)

Eq.(17) has a practical impact because once knowing $A_i(\Theta)$ one can determine quantitatively surface coverage of colloid particles or proteins by measuring the streaming current (or potential) ratio, i.e., I_p/I or E_{sp}/E_s for

such a ionic strength that $l/\kappa a$ parameter becomes smaller than unity. Then, for uncharged or slightly charged particles one can determine directly the coverage by using the relationship

$$\Theta = \frac{1}{C_i^0} \ln \left| \frac{I_p}{I} \right| = \frac{1}{C_i^0} \ln \left| \frac{E_{sp}}{E_s} \right| \quad (16)$$

Eq.(16) has a considerable practical significance for determining protein adsorption kinetics because most of them exhibits low zeta potential [4, 13-14]. On the other hand, the multi-body correction function $A_p(\Theta)$ can be estimated empirically by measuring the dependence of ζ_a/ζ_p on particle coverage in the case when the channel zeta potential vanishes (as a result of surfactant adsorption discussed above). The results of such experiments are collected in Figure 8.

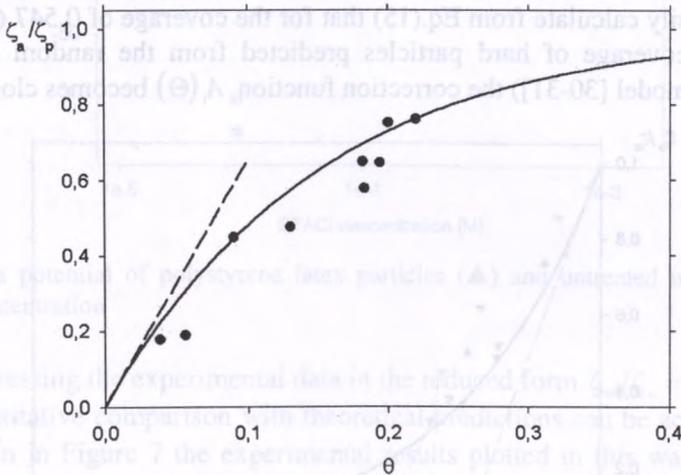


Fig. 8. The dependence of ζ_a/ζ_p on surface coverage of particles Θ . The points denote experimental results obtained for polystyrene latex particles at neutral mica surface (DTACl concentration of 1.2×10^{-4} M). The broken lines denote the initial slope calculated from the linear model, Eq.(9), and the solid line presents the data calculated from Eq.(13)

It should be mentioned that the range of surface coverage that can be studied in this case is limited by insufficient adhesion force between particles and the uncharged interface. Nevertheless, these data allowed one to predict that the correction function $A_p(\Theta)$ can be approximated well by the exponential dependence

$$A_p(\Theta) = \frac{1 - e^{-c_p^0 \Theta}}{C_p^0 \Theta} \quad (17)$$

One can notice in Figure 8 that Eq.(13) with $A_p(\Theta)$ given by Eq.(17) reflects quite satisfactorily the experimental data. Obviously, this function reduces in the limit of low coverage to the theoretically predicted linear relationship (depicted by the dashed line in Figure 8).

Knowing both correction functions one can attempt to reflect the experimental data obtained for the general case of arbitrary zeta potential of particles and interfaces important from practical viewpoint. In Figure 9 results of such measurements are presented (obtained for the M25 latex for pH= 5.3). As one can notice the theoretical model (solid line in Figure 9) with the above semi-empirical correction functions $A_i(\Theta)$, $A_p(\Theta)$ reflects well the experimental data for the broad range of particle coverage (reaching 0.5).

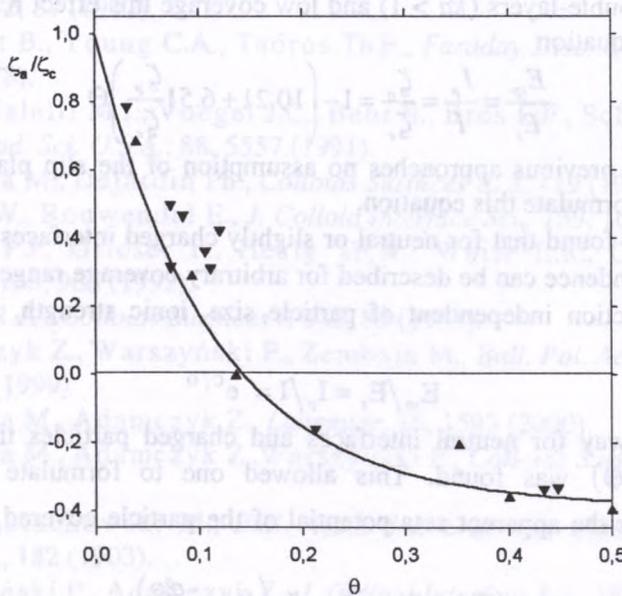


Fig. 9. The dependence of $\zeta_a/\zeta_c = E_{sp}/E_s$ on surface coverage of particles Θ . The points denote experimental results obtained for the latex (melamine and polystyrene) particles at pH=5.3. The solid line represents the theoretical data calculated from the dependence

$$\zeta_a/\zeta_c = E_{sp}/E_s = e^{c^0 \Theta} + \frac{\zeta_p}{\zeta_c} (1 - e^{-c^0 \Theta})$$

This suggests that Eq.(11) can be used for interpretation of results obtained for arbitrary particle and interface charge (zeta potential). Moreover, if particle (protein) zeta potential is known (this quantity is easily accessible by microelectrophoretic measurements as mentioned above) one can determine via Eq.(11) the coverage of particles by measuring the apparent zeta potential of the channel. This means that our experimental method can be exploited for quantitative, on line studies of protein or particle adsorption.

5. CONCLUSIONS

It was confirmed experimentally that the presence of adsorbed particles influences the streaming potential and the apparent zeta potential of interfaces as a result of damping of fluid motion in the vicinity of particles and additional charge transport from the ionic atmosphere surrounding particles.

For thin double-layers ($\kappa a > 1$) and low coverage this effect remains linear, given by the equation

$$\frac{E_{sp}}{E_s} = \frac{I_p}{I} = \frac{\zeta_a}{\zeta_c} = 1 - \left(10.21 + 6.51 \frac{\zeta_p}{\zeta_c} \right) \Theta$$

In contrast to previous approaches no assumption of the slip plane shift was necessary to formulate this equation.

It was also found that for neutral or slightly charged interfaces, the E_{sp}/E_s or I_p/I dependence can be described for arbitrary coverage range by the semi-empirical function independent of particle size, ionic strength, shape of the channel etc.

$$E_{sp}/E_s = I_p/I = e^{c_i \Theta}$$

In a similar way for neutral interfaces and charged particles the correction function $A_p(\Theta)$ was found. This allowed one to formulate the general expression for the apparent zeta potential of the particle covered interfaces in the form

$$\zeta_a = \zeta_c e^{c_i \Theta} + \zeta_p \left(1 - e^{-c_p \Theta} \right)$$

This relationship valid for arbitrary particle and interface zeta potential can be used for determining surface coverage of arbitrary sized particles (colloids, proteins) by measuring experimentally the streaming potential ratio.

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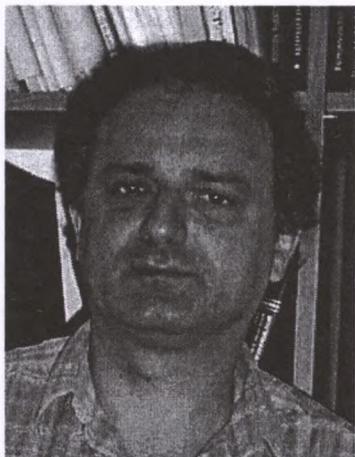


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