Adsorption (2010) 16: 405–412
DOI 10.1007/s10450-010-9234-1

Electrical interfacial layer at TiO_2/poly(4-styrene sulfonate) aqueous interface

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Received: 4 March 2010 / Accepted: 28 April 2010 / Published online: 19 June 2010

Abstract The interfacial properties of the system titanium(IV) oxide/poly(4-styrenesulfonate) (PSS) over a broad pH region in the presence of different alkali metal chlorides of different concentrations were investigated by means of electrokinetic, adsorption and surface potential measurements. Adsorption and electrokinetic data were obtained with colloid TiO_2 particles, while surface potential data were obtained using a single crystal rutile electrode with the 001 plane exposed to the liquid medium. The electrokinetic and surface potentials of TiO_2 were measured in the absence and presence of PSS. Since the presence of PSS did not significantly affect surface potentials, it was concluded that negative PSS molecules adsorbed at the surface by forming an outer-sphere surface complex rather than inner-sphere complex. The adsorption decreases significantly with pH, while the electrokinetic potential in the presence of PSS is negative in the whole investigated pH region. Amount of adsorbed PSS molecules is limited by the electrostatic repulsion which suppresses further adsorption, *i.e.* above critical potential of −50 millivolts. In the acidic region, where the surface is originally positively charged the amount of adsorbed PSS molecules is high since negative PSS molecules should at first compensate original positive charge and in the second step reverse the charge to reach the critical potential. In the basic region the surface charge is already negative so that small amount of adsorbed PSS molecules creates critical potential that prevents further adsorption.

Keywords Titanium oxide · Poly(4-styrene sulfonate) · Surface potential · Adsorption · Zeta potential

1 Introduction

The fact that polyelectrolytes are macromolecules that, when dissolved in water, have a large number of repeating charged groups linked to the backbone leads to an increased interest in studying the adsorption of such chained molecules on the metal oxide surfaces. These processes are interesting both from theoretical (Fleer et al. 1993; Netz and Joanny 1999; Chibowski and Krupa 2000) and applicational (Guldberg-Pedersen and Bergström 2000) points of view. It is known that *e.g.* polymers as long chain molecules can form thick adsorbed layers and therefore are particularly suited as stabilizers (Vincent 1974). Therefore, several studies on complexation of polyelectrolytes at the metal oxide aqueous interface can be found in the literature (Gebhardt and Fuerstenau 1983; Bonekamp and Lyklema 1986; Vermöhlen et al. 2000). Among other systems, the adsorption of poly(4-styrene sulfonate), PSS, on hematite was studied (Klein Wolterink et al. 2006). PSS was often chosen as a model system since it is a strong polyelectrolyte which means that it is fully (negatively) charged over the whole investigated pH range. Since PSS is a charged macro-ion, its adsorption at the interface is influenced by electrostatics developed by binding of potential determining ions and background electrolyte ions to the surface of the adsorbent, as well as by the charge put to the interface by the macro-ion itself. Accordingly, to better understand adsorption of macro-ions one should take into account the structure of the electrical interfacial layer (EIL) at the solid liquid interface.

Equilibrium at the solid-liquid interface is the subject of numerous experimental and theoretical investigations. The

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Dedicated to Professor Andrzej Waksmundzki on the 100th anniversary of his birth.

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interpretation of surface equilibria based on only one type of experimental data (*e.g.* only adsorption data) may lead to erroneous conclusions regarding *e.g.* the mechanism of binding and the structure of the Electrical Interfacial Layer (EIL). The introduction of other, additional experimental techniques could provide useful information leading to a more accurate determination of *e.g.* adsorption equilibrium constants (Kovačević et al. 1998, 2000), but also to valuable indications about the location of adsorbed species within the EIL and the binding mechanism. Such an approach is exemplified in this article for the adsorption of PSS on titanium oxide. Additionally to the commonly used adsorption and ζ-potential measurements, the recently introduced surface potential measurements by means of single crystal electrodes (Kallay et al. 2005) were performed on this system. It was expected that surface potential data will help in elucidating whether PSS molecules are bound directly to the surface as an inner complex or as an outer complex that does not directly affect the value of the surface potential. On the other hand, the electrokinetic data provide information on the total charge bound to the surface.

2 Theoretical

Models that describe the electrical interfacial layer (EIL) at the solid/liquid interface generally differ in the number of postulated layers, *i.e.*, planes that divide these layers. In the so-called general model three layers and four different planes (with corresponding potentials) are postulated (Kovačević et al. 2007). The (inner) surface plane, 0-plane characterized by potential Ψ_0, is a plane that divides solid from liquid. In this plane the charged species are directly bound to the surface. Centers of counterions associated with surface charges, are located in the β-plane. Consequently, the associated counterions are assumed to be exposed to potential Ψ_β. The layer between 0-plane and β-plane is often called inner Helmholtz layer. The part of the EIL, governed only by electrostatic forces and thermal motion is called the diffuse layer, the onset of which is located at the d-plane. The layer between the β- and d-plane, sometimes called the outer Helmholtz layer, is occasionally neglected so that the β-plane is taken as onset of diffuse layer, *i.e.* identical to the d-plane. The distribution of ions in the diffuse layer is affected by the electrostatic potential in the d-plane, Ψ_d, the permittivity of the interfacial region, the thermal energy and the concentration of ions, and is described by Gouy-Chapman theory. The electrokinetic ζ-potential corresponds to the imaginary slip or shear plane that is located within the diffuse layer and close to the d-plane.

The surface charge densities of interfacial planes are related to the corresponding surface concentrations of interfacial ions: the surface charge density of the 0-plane, β-plane and of the diffuse layer are denoted $\sigma_0, \sigma_\beta, \sigma_d$, respectively. The net surface charge density σ_s is equal in magnitude but opposite in sign to σ_d:

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta \tag{1}$$

According to the Gouy-Chapman theory, in the case of (1:1) symmetrical electrolytes the relationship between the surface charge densities (σ_d, σ_s) and the electrostatic potential at the onset of the diffuse layer Ψ_d for planar geometry is given by:

$$\sigma_d = -\sigma_s = -\sqrt{8RT\varepsilon I_c}\,\sinh(-F\Psi_d/RT) \tag{2}$$

or

$$\Psi_d = \frac{2RT}{F}\,\mathrm{ar\,sinh}\,\frac{\sigma_d}{\sqrt{8RT\varepsilon I_c}} \tag{3}$$

where I_c is ionic strength based on (molar) concentration, ε is the permittivity of the medium (solution), while other symbols have their usual meaning. According to the same theory, the relationship between the potential at the onset of diffuse layer and the electrokinetic ζ-potential is given by:

$$\Psi_d = \frac{2RT}{F}\ln\left(\frac{\exp(-\kappa l) + \tanh(F\zeta/4RT)}{\exp(-\kappa l) - \tanh(F\zeta/4RT)}\right) \tag{4}$$

where l is the distance between d-plane and slip plane, corresponding to the thickness of electrokinetic stagnant layer, while κ is the Debye-Hückel parameter given by:

$$\kappa = \sqrt{\frac{2I_cF^2}{\varepsilon RT}} \tag{5}$$

According to the general model, the (inner) Helmholtz layer could be considered a capacitor with two planes; 0-plane and β-plane. The capacitance C_1 is assumed to be constant and is commonly defined as:

$$C_1 = \frac{\sigma_0}{\Psi_0 - \Psi_\beta} \tag{6}$$

3 Experimental

3.1 Materials

All solutions were prepared using deionised and decarbonated water ($\kappa < 3\ \mu\mathrm{S\,cm^{-1}}$). Chemicals used were: poly(sodium 4-styrenesulfonate), $\mathrm{Na^+PSS^-}$ ($M_w = 70000\ \mathrm{g\,mol^{-1}}$, Aldrich), NaCl (Merck), KCl (Fluka), LiCl (Fluka), HCl (Riedel de Haën), NaOH (Riedel de Haën), KOH (Riedel de Haën), LiOH (Riedel de Haën), standard buffers (Fluka). Titanium dioxide particles (P-25, 95% anatase, 5% rutile) were a product of Degussa (Germany) having a specific surface area of 50 $m^2\,g^{-1}$. The particles were purified by extended washing. The single crystal (SCr) electrode was made from a rutile single crystal obtained from MaTecK, Germany. The orientation of the surface was 001. The crystal plane was cleaned with a 50% aqueous solution of ethyl alcohol and washed with water. The crystal used for SCr-electrode was almost rectangular 10 × 10 mm, with a thickness of 4 mm. The electric resistance of the SCr-TiO_2 electrode was measured directly and was approximately 5 GΩ. The properties and construction of the SCr electrode are described in more detail elsewhere (Kallay et al. 2005; Preočanin et al. 2006).

3.2 Methods

3.2.1 *Surface potential measurements*

The potential of the rutile single crystal electrode was measured using the Metrohm 827 pH-meter. The pH was measured with a glass electrode (Metrohm, 6.0222.100) using a separate Metrohm 827 pH-meter. The common reference electrode was Ag|AgCl|Cl^- with a salt bridge (Metrohm, 6.0233.100). The glass electrode was calibrated with three standard buffers. In the course of measurements the system was thermostated at 25.0°C and kept under argon atmosphere. Argon from a tank was used. The acidic solutions (200 mL) of sodium, potassium and lithium chloride were titrated with the corresponding base ($c = 0.1$ $\mathrm{mol\,dm^{-3}}$, NaOH, KOH or LiOH), the system being gently stirred with a magnetic stirrer. The ionic strength was controlled by addition of salt solutions (NaCl, KCl and LiCl) and kept constant during titrations. Potentiometric titrations were performed with and without PSS.

Surface potentials Ψ_0 were obtained (Kallay et al. 2007) from the measured electrode potentials of the rutile single crystal electrode E by

$$\Psi_0 = E - E_{\mathrm{cal}} \tag{7}$$

where the value of E_{cal} includes all potential differences in the measuring circle, except the one at the crystal/solution interface. Once the value of E_{cal} is known, surface potentials can easily be obtained from the measured electrode potentials via (7). In fact, one sets the zero value of surface potential at the $\mathrm{pH_{pzp}}$ which is approximated by the electrokinetic isoelectric point $\mathrm{pH_{iep}}$ or by the point of zero charge $\mathrm{pH_{pzc}}$. This approximation is correct at the condition of the low ionic strength when all three zero charge points coincide with the electroneutrality point $\mathrm{pH_{eln}}$ determined by the thermodynamic equilibrium constant of interaction of active surface sites with potential determining ions (Kallay et al. 2007; Pyman et al. 1979; Lyklema 1984; Sposito 1998; Sonnefeld 2001).

$$\mathrm{pH_{pzp}} = \mathrm{pH_{pzc}} = \mathrm{pH_{iep}} = \mathrm{pH_{eln}};\ I_c \to 0 \tag{8}$$

Accordingly

$$E_{\mathrm{cal}} = E(\mathrm{pH_{pzp}}) \approx E(\mathrm{pH_{iep}}) \approx E(\mathrm{pH_{pzc}}) \tag{9}$$

The surface potential of TiO_2 in the presence of PSS was calculated from the measured electrode potential of the rutile electrode E using the fact that adsorption of PSS in the basic solution is negligible (both PSS and TiO_2 surface are negatively charged) and that surface potentials are same as for systems in absence of PSS.

3.2.2 *Electrokinetic measurements*

The electrokinetic (zeta) potential of titanium dioxide particles was measured before and after adsorption of poly(4-styrenesulfonate) by means of a ZetaPlus Zeta Potential Analyser, Brookhaven Instruments Corporation. The instrument uses electrophoretic light scattering and the Laser Doppler Velocimetry method for determination of particle velocity and, from this, the zeta potential. The mass concentration of titanium dioxide particles was 1.6 $\mathrm{g\,dm^{-3}}$ and PSS concentration was 3 $\mathrm{g\,dm^{-3}}$. The experiments were performed at two different ionic strength values ($I_c = 1 \times 10^{-2}$ $\mathrm{mol\,dm^{-3}}$ and 1×10^{-3} $\mathrm{mol\,dm^{-3}}$).

3.2.3 *Adsorption measurements*

Adsorption measurements were performed as follows: titanium dioxide particles ($\gamma = 27$ $\mathrm{g\,dm^{-3}}$) were dispersed in PSS aqueous solution ($\gamma = 3$ $\mathrm{g\,dm^{-3}}$) and the pH adjusted by adding appropriate amounts of acid or base. In order to determine the adsorption isotherm, TiO_2 was separated by centrifugation and the concentration of PSS in the supernatant solution was determined spectrophotometrically (UV-Vis-NIR spectrophotometer Cary 05E, Varian, USA). The absorbance was measured at 263 nm, which is a characteristic band for the sulfonate groups. Calibration curves were obtained by plotting the measured absorbance *vs*. the concentration of corresponding PSS samples.

4 Results

4.1 Adsorption and electrokinetic measurements

The influence of pH on the adsorption of PSS is shown in Fig. 1. As the pH increases the rutile surface is less positive or more negative (Fig. 2). Therefore, at higher pH values the adsorption affinity has to overcome electrostatic repulsion. It should be noted that accumulation of negatively charged species at the surface creates by itself additional negative charge.

Figure 2 demonstrates the effect of pH on the electrokinetic data in the absence and presence of PSS. In the absence

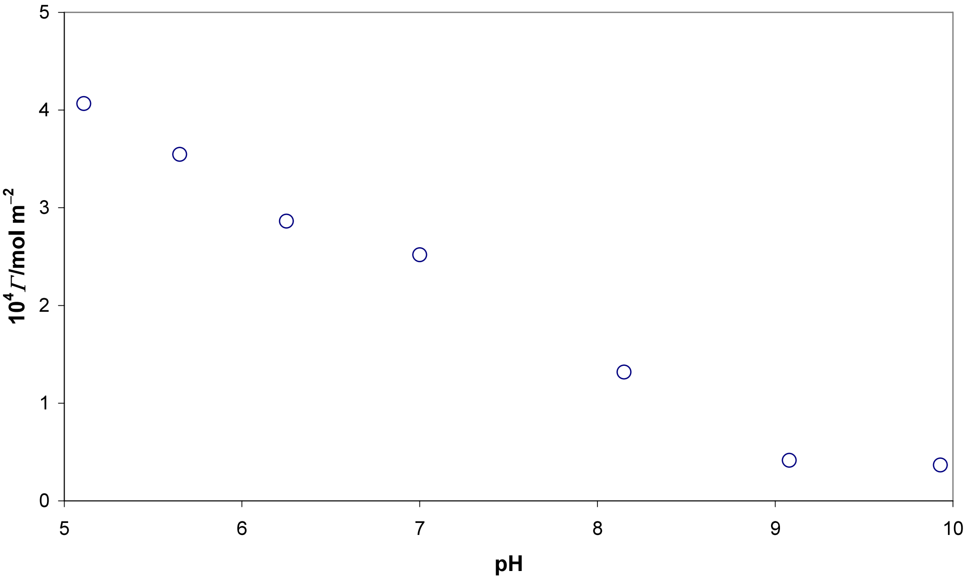

Fig. 1 The effect of pH on the surface concentration of PSS on TiO_2 particles at 25°C; γ (TiO_2) = 27 g dm^{-3}, γ_{in}(PSS) = 3 g dm^{-3}, c_{in}(PSS) = 4.3×10^{-5} mol dm^{-3}, c(NaCl) = 0.001 mol dm^{-3}

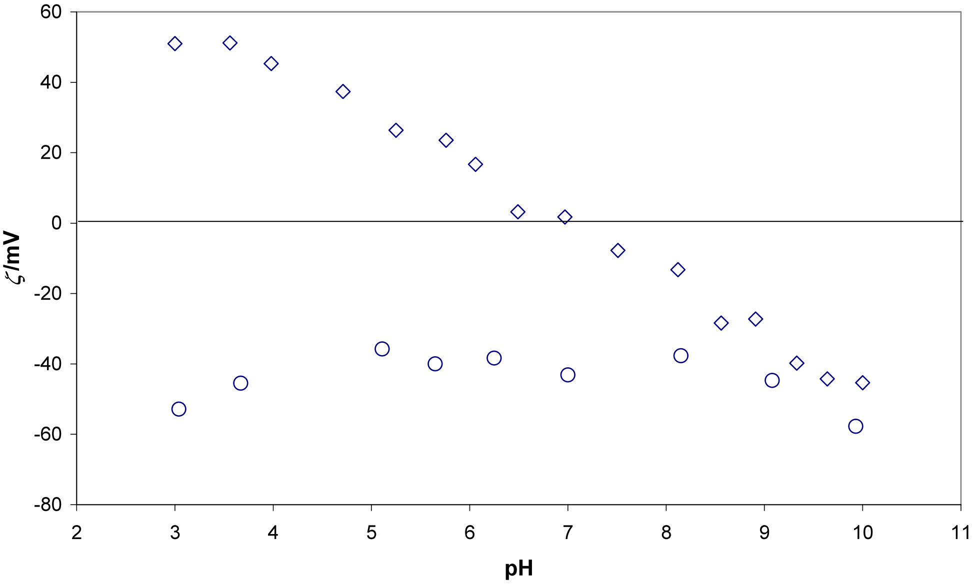

Fig. 2 Electrokinetic potential of TiO_2 particles before (◇) and after (○) addition of PSS as a function of pH at 25°C; γ(TiO_2) = 1.6 g dm^{-3}, γ_{in}(PSS) = 3 g dm^{-3}, c_{in}(PSS) = 4.3×10^{-5} mol dm^{-3}, c(NaCl) = 0.001 mol dm^{-3}

of PSS the isoelectric point of titania particles is at $pH_{iep} \approx 6.6$ in accordance with literature values (Kosmulski 2009) of $pH_{iep} \approx 6.8$. In the region pH > 9 the adsorption of negative PSS molecules is low (Fig. 1) so that electrokinetic potential in only slightly more negative (Fig. 2). In the region 9 > pH > 7 the original surface bears a low negative charge. Therefore, the repulsion is less pronounced and the adsorption is significantly higher. In the acidic region, pH < 6, the adsorption increases further due to the electrostatic attraction between the positive surface and negative PSS molecules.

4.2 Surface potential measurements

Surface potential measurements were performed in order to elucidate the nature of binding of PSS molecules to the TiO_2 surface. The effect of different salts at different concentrations in the presence and absence of PSS was examined. Results are presented in Figs. 3–5. The surface potentials were obtained from the measured electrode potentials of single crystal electrode by assuming that at low ionic strength the point of zero potential coincides with the isoelectric point. For the 001 rutile crystal plane the isoelectric point was found to be at $pH_{iep} = 5.65 \pm 0.15$ (Bullard and Cima 2006). This value is lower than that obtained with TiO_2 colloid particles exposing different crystal planes to the solution. The inherent problem of using single crystals is that adsorption data cannot be obtained for a single crystal plane, but rather from dispersions of colloid particles of sufficiently large surface area. Experiments in sodium chloride media are presented in Fig. 3;

reproducibility and reversibility of the experimental data were tested and error bars were within the data symbols on Figs. 3–5. In the first run the titration of the SCr rutile electrode was performed by titrating HCl with NaOH in the presence of NaCl at the same ionic strength (*i.e.* NaCl concentration) as in adsorption and electrokinetic experiments; $c(\mathrm{NaCl}) = 1 \times 10^{-3}$ mol dm^{-3}. The surface potential of TiO_2 (in the absence of PSS) is found to decrease with pH, indicating that the surface becomes less positively or more negatively charged. The slope of the $\Psi_0(\mathrm{pH})$ function is found to be lower than the Nernst slope (Kallay et al. 2010; Preočanin et al. 2010). The effect of the slope reduction is slightly more pronounced at higher ionic strength ($I_c = 0.1$ mol dm^{-3}). The next run in the presence of PSS yielded similar results. The same experiments were performed at two higher concentrations of NaCl. The results obtained in presence of NaCl suggested that PSS does not significantly affect the surface potential of rutile. The effect of PSS on the surface potential of rutile is pH dependent and more pronounced at higher pH values. In order to examine whether this finding depends on the type of electrolyte similar experiments were performed in the presence of KCl (Fig. 4) and LiCl (Fig. 5).

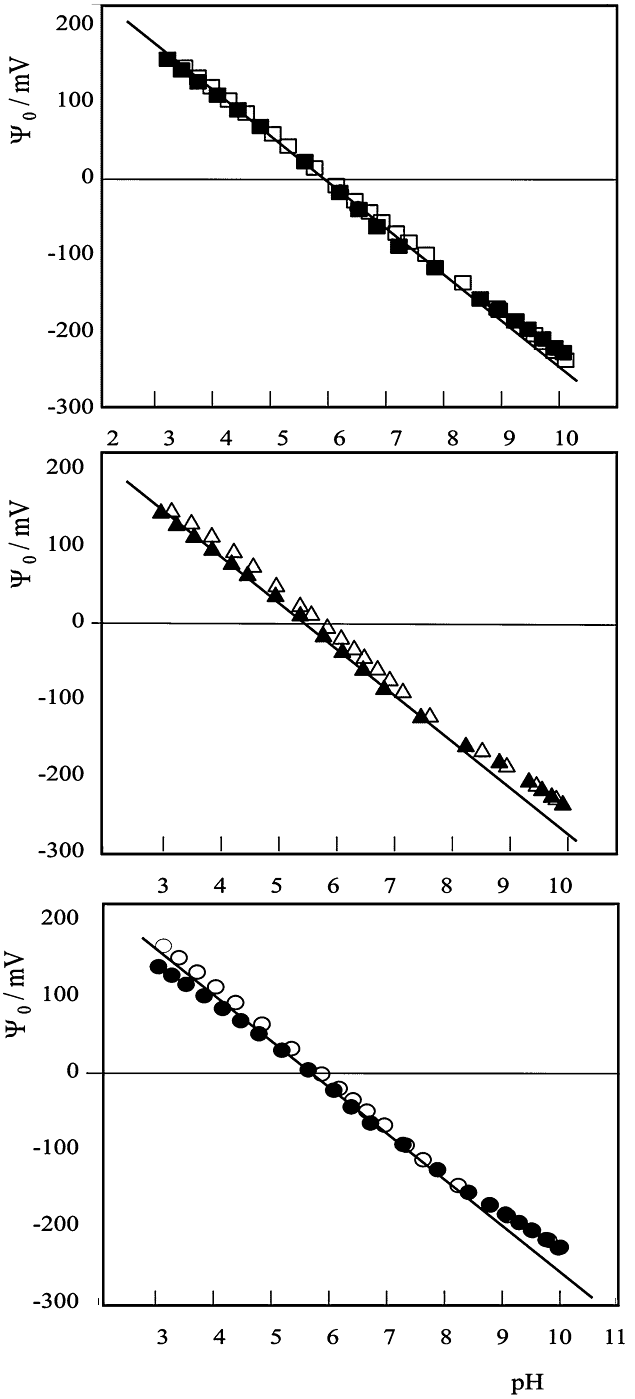

Fig. 3 The dependency of TiO_2 surface potential in NaCl aqueous medium in the absence (*full symbols*) and presence (*empty symbols*) of PSS ($\gamma = 1.0$ g dm^{-3}) for three different NaCl concentrations; $c = 1 \times 10^{-3}$ mol dm^{-3}(■, □), $c = 1 \times 10^{-2}$ mol dm^{-3}(▲, △) and $c = 0.1$ mol dm^{-3}(●, ○), $t = 25$°C. The results are obtained by titration of HCl with NaOH solution and compared with the Nernst slope (*full line*)

5 Discussion and conclusions

Adsorption, electrokinetic and surface potential data enable some conclusions regarding the adsorption of PSS molecules on the surface of TiO_2. The comparison of these data should consider differences in the samples. While electrokinetic and adsorption data were obtained with colloid particles, the surface potential data represents properties of single crystal plane. The difference may be in the zero values of electrokinetic and surface potential data, but the general feature remains the same, *i.e.* adsorption of PSS molecules affects electrokinetic behavior, but not the values of the surface potential. Electrokinetic and surface potential data suggest that PSS molecules are adsorbed to the surface, but are not bound directly by forming an inner-sphere complex that would affect the surface potential. The effect of PSS molecules is indirect; negatively charged sites of the adsorbed molecules are near the surface and therefore promoting direct binding of H^+ ions to the surface sites. This conclusion is supported by more or less pronounced increase of surface potential in the acidic region when PSS is added to the system. This trend is opposite to the observed decrease of the surface potential with addition of a simple electrolyte as *e.g.* sodium, potassium and lithium chlorides, nitrates and perchlorates (Preočanin et al. 2007; Preočanin and Kallay 2008). In Fig. 6. the surface potential of rutile for different electrolytes (LiCl, NaCl and KCl) in the absence of PSS ($\gamma(\mathrm{PSS}) = 0$) and in the presence of PSS ($\gamma(\mathrm{PSS}) = 1.0$ g dm^{-3}) at higher ionic strength ($I_c = 0.1$ mol dm^{-3}) are presented. Surface potential of rutile slightly increases with addition of PSS, but it doesn't depend on ionic strength. On the hand, the presence of the simple electrolyte ions (Li^+,

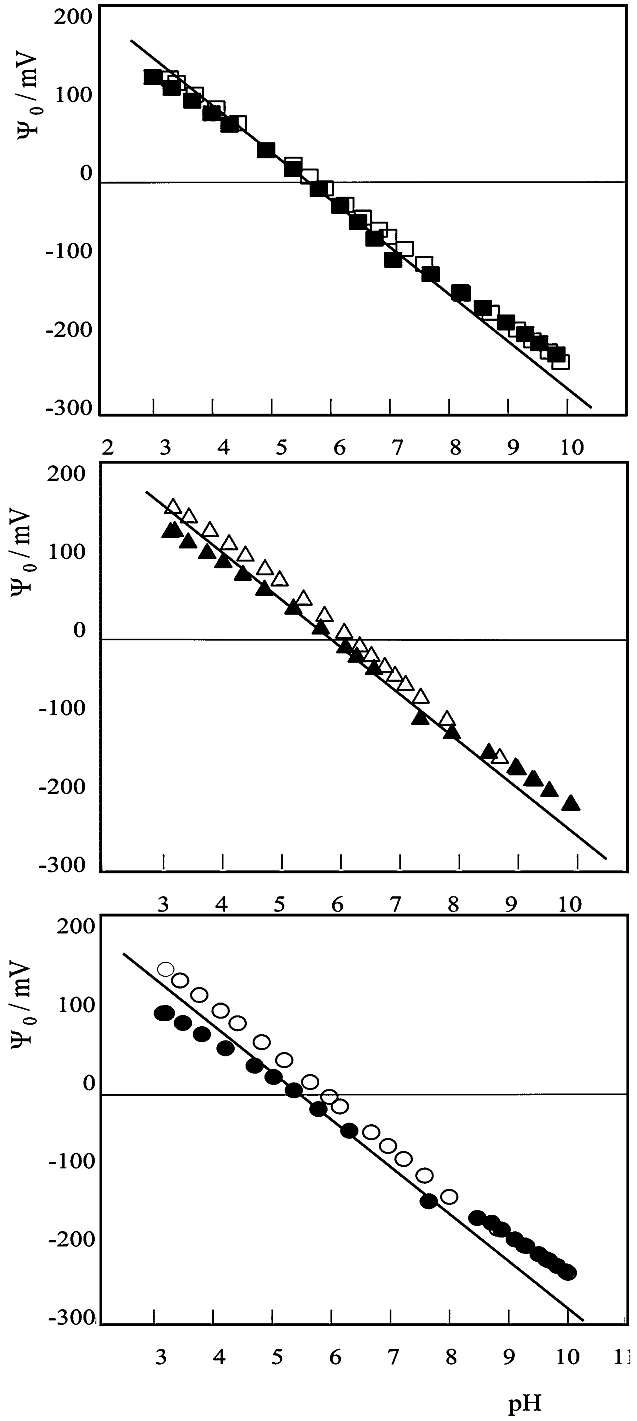

Fig. 4 The dependence of surface potential of TiO2 in the presence of KCl before (*full symbols*) and after (*empty symbols*) adsorption of PSS ($\gamma = 1.0$ g dm^{-3}) for three different KCl concentrations; $c = 1 \times 10^{-3}$ mol dm^{-3}(■, □), $c = 1 \times 10^{-2}$ mol dm^{-3}(▲, △) and $c = 0.1$ mol dm^{-3}(●, ○), $t = 25$°C. The results are obtained by titration with KOH solution and compared with the Nernst slope (*full line*)

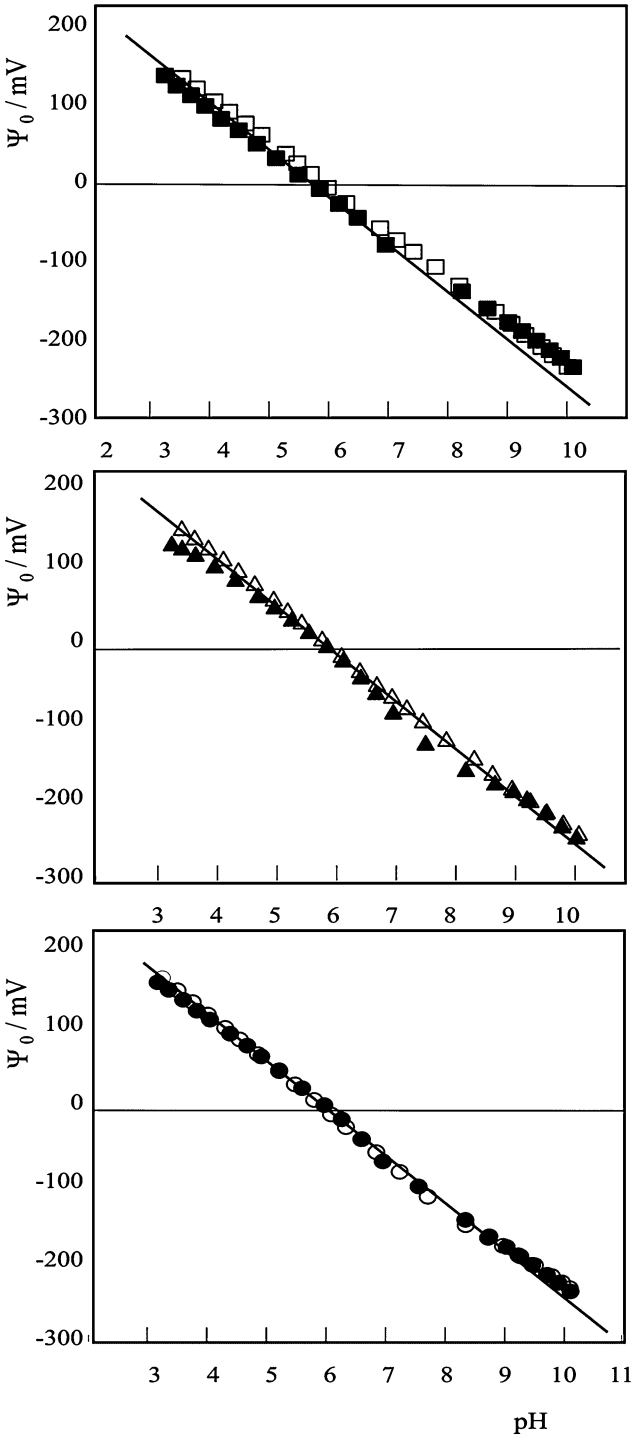

Fig. 5 The dependence of surface potential of TiO2 in the presence of LiCl before (*full symbols*) and after (*empty symbols*) adsorption of PSS ($\gamma = 1.0$ g dm^{-3}) for three different LiCl concentrations; $c = 1 \times 10^{-3}$ mol dm^{-3}(■, □), $c = 1 \times 10^{-2}$ mol dm^{-3}(▲, △) and $c = 0.1$ mol dm^{-3}(●, ○), $t = 25$°C. The results are obtained by titration with LiOH solution and compared with the Nernst slope (*full line*)

Na^+, K^+ and Cl^-) in absence of PSS reduces surface potential depending on ionic strength and type of electrolyte. On the relative scale the effect is more pronounced for KCl than for NaCl and LiCl, which is in accordance with finding that monovalent counterions form inner-sphere complexes at the surface (Předota et al. 2004).

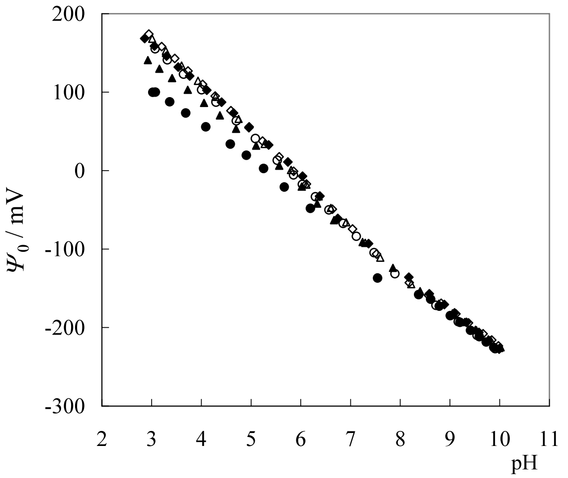

Fig. 6 The dependence of surface potential of TiO_2 in the presence of LiCl (◆, ◇) NaCl (▲, △) and KCl (●, ○) in absence (full symbols) and in presence (empty symbols) of PSS ($\gamma = 1.0$ g dm^{-3}) for $I_c = 0.1$ mol dm^{-3}, $t = 25\,°C$. The results are taken from Figs. 3–5

To examine such effect of PSS on the surface potential a separate experiment was performed. The electrode potential of TiO_2 single crystal electrode, as well as of the glass electrode, was measured as a function of mass concentration of PSS. After addition of PSS to the system, the pH always increased. PSS is a polyelectrolyte that dissociates in the aqueous solution and forms negatively charged groups surrounded with ionic clouds of counterions. Since the affinity of H^+ towards the polystyrene macro-ion is higher than the affinity of Na^+ ions towards the same polyion, H^+ ions would exchange Na^+ ions in the ionic clouds around PSS. Thus the increase in mass concentration of PSS leads to a decrease of the concentration of H^+ ions in the solution (pH increases). On the other hand, it was found that the electrode potential of the TiO_2 single crystal electrode increased with the increase in PSS mass concentration at pH < 3 and decreased at pH > 4. Several influences on the surface potential of TiO_2 could be assumed. The first one is the effect of pH—with the increase of pH, the solution becomes more basic and the surface more negatively charged. The second effect is the adsorption of PSS at the TiO_2 surface—which is more pronounced at higher concentration of PSS in the solution.

Electrokinetic and adsorption data clearly show that negative PSS molecules exhibit high adsorption affinity towards the titania surface which is suppressed by the electrical repulsion. At potentials below −50 millivolts the electrostatic repulsion is so high that adsorption cannot proceed. There are two processes creating electrostatic potential: The first one is surface charging by interaction of potential determining ions, H^+ and OH^-. In the region of a negatively charged surface (pH > 7) the negative PSS molecules still adsorb, and this adsorption process creates additional negative charge. Once this negative charge becomes too high, and a critical value of the potential is reached, adsorption cannot proceed. The amount that produces this critical value of the potential (*e.g.* −40 or −50 mV) is low since the original surface charge was already negative. In the acidic region (pH $<$ 6) the original surface is positively charged, adsorption of negative PSS molecules gradually compensates this positive charge and adsorption proceeds until the reversal of surface charge produces a critical value of the potential affecting the state of adsorbed PSS anions. It is obvious that the amount required for that condition is higher in acidic region and that it increases with lowering of the pH.

Accordingly, one may conclude that PSS macro-ions exhibit high affinity towards the TiO_2 surface, but that adsorption is limited by electrostatic repulsion which is triggered by the original pH-dependent charge of the pristine surface. It is also due to accumulation of negative PSS molecules at the interface. At low pH the initial surface charge is positive so that a substantially higher amount of adsorbed PSS molecules is necessary to compensate the positive charge and to produce negative charge which suppresses further adsorption. Since PSS molecules do not significantly affect the surface potential, their state (*i.e.* the interfacial activity coefficient) *vice-versa* is not determined by the surface potential. Accordingly, it may be concluded that the adsorbed charged groups of PSS molecules are not incorporated in the solid surface, but are rather located at a certain distance from it, which is close to the location of the electrokinetic slip plane. This study is an example that, additionally to *e.g.* surface spectroscopy data, the surface potential measurements by means of single crystal electrodes could be a helpful tool in elucidation of adsorption processes.

Acknowledgements This research was supported by the Ministry of Science, Education and Sports of the Republic of Croatia (project No. 119-119342-2961) and by the COST Action D43.

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