

Point of Zero Charge and Surface Charge Density of TiO₂ in Aqueous Electrolyte Solution as Obtained by Potentiometric Mass Titration*

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Mass titration method was developed as a suitable tool for determination of the point of zero charge (p.z.c.) and surface charge density (σ_0) of metal oxide colloid particles at different ionic strengths. In the course of mass titration, subsequent portions of a metal oxide powder are added to an aqueous electrolyte solution, and pH of the equilibrated dispersion is measured. The pH of the system changes gradually and approaches a constant value of pH_∞ , which is in the case of a metal oxide free of impurities equal to the point of zero charge pH_{pzc} . Counterion association shifts the pH_{pzc} either to the acidic region (preferential adsorption of cations) or to the basic region (preferential adsorption of anions). Mass titration therefore enables detection of the difference between association affinities of counterions (cations and anions), which is important information about the equilibrium within the electrical interfacial layer. Such an analysis is not possible by the conventional acid-base potentiometric titration of the dispersion, since the location of the p.z.c. is based on the common intersection point (c.i.p.) of the data obtained at different ionic strengths. It is shown that c.i.p. may be used for locating the p.z.c. only in a »symmetric case«, when affinities of the anions and cations to associate with oppositely charged surface groups are equal. Analysis of the mass titration was performed on the basis of experimental data obtained with colloidal titania dispersed in an aqueous sodium chloride solution, and also by numerical simulation based on the Surface Complexation Model and the 2-pK mechanism of surface reactions. Increase in the NaCl concentration shifted the point of zero charge to the basic region, while the isoelectric point was shifted to the acidic region, indicating higher association affinity of chloride ions compared to sodium ions.

Keywords
mass titration
point of zero charge
surface charge density
counterion association
titan dioxide
sodium chloride

INTRODUCTION

Potentiometric mass titration was originally developed by Noh and Schwartz¹ as a method for determination of the point of zero charge (p.z.c.) of pure metal oxides (in the absence of acidic or basic impurities). The method is simple. One should add subsequent portions of a metal oxide powder to the electrolyte solution (or water) and

measure the pH of the dispersion. The pH of the system changes gradually and approaches a constant value pH_∞ . In the case of a pure metal oxide powder (absence of acidic or basic contamination), pH_∞ is equal to the point of zero charge pH_{pzc} . Mass titration was successfully applied for determination of the point of zero charge of colloidal particles² with low³ and high specific surface areas (activated carbon).⁴ Mass titration was also propos-

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ed for the point of zero charge determination of metal oxide mixtures. The point of zero charge of a metal oxide mixture corresponds to the pH where the net surface charge of the heterogeneous mixture is zero, while one oxide bears a positive and the other a negative charge. For calculation, one needs to know the specific surface areas, mass fractions of components, and points of zero charge of both metal oxides.^{5,6} The mass titration method was extended by Kallay and Žalac⁷ for determination of the point of zero charge of contaminated samples. The pH_{∞} value of contaminated dispersion is higher (basic impurities) or lower (acidic impurities) compared to the point of zero charge. Interpretation of the mass titration provides information on the fraction of impurities in the powder and also on the point of zero charge.⁸ Mass titration was found extremely suitable for determination of the temperature dependency of the point of zero charge. One simply measures the temperature dependency of pH of a sufficiently concentrated metal oxide dispersion in the absence of impurities. The mass titration method was further developed for determination of surface charge density.⁹ The advantage of this method is that experiments can be performed at extremely low ionic strengths.

The common method for determination of the point of zero charge is the potentiometric acid-base titration of a dispersion.^{10,11} Comparison with blank titration in the absence of the dispersed solid oxide phase yields relative values of the surface charge densities. Absolute values of the surface charge densities are then obtained by setting the zero value at the common intersection point (c.i.p.) for different ionic strengths. However, this method neglects the influence of counterion association on the point of zero charge. It assumes the same association affinity for both counterions (anions and cations), which is practically never the case. One still obtains the c.i.p. but this point may be far from the p.z.c.¹² For these reasons, potentiometric acid-base titration cannot be used for examination of the p.z.c. dependency on the electrolyte concentration.

The aim of this article is to examine the possibility of applying mass titration for determination of the effect of electrolyte concentration on the point of zero charge in order to deduce the difference in surface association affinities of cations and anions. The effect of electrolyte concentrations on the mass titration of colloidal dispersions of TiO_2 particles was examined by numerical simulation and experimentally. From mass titration data, the surface charge densities and the point of zero charge at different ionic strengths were obtained. The results were compared with »electrolyte titrations« (increase of the ionic strength in concentrated dispersions)¹³ and with electrokinetic measurements.

Surface Complexation Model

The basic process at a metal oxide surface in aqueous environment is the surface charging due to interactions

of active surface sites with the potential determining ions. For metal oxides, the potential determining ions are H^+ and OH^- ions. Within the Surface Complexation Model (SCM), the 2-pK mechanism^{14,15} may be used for numerical simulation and interpretation of experimental data. Accordingly, surface charge is a result of the two-step protonation of the surface groups produced by hydration of the metal oxide surface



where K_1^\ominus and K_2^\ominus are thermodynamic equilibrium constants of the corresponding surface reactions. Generally, a thermodynamic equilibrium constant K^\ominus is defined¹⁶ in terms of equilibrium activities (a) of species J involved in the chemical reaction

$$K^\ominus = \prod_{\text{J}} a_{\text{J}}^{\nu_{\text{J}}} \quad (3)$$

For interfacial species S activity may be defined¹⁷ in terms of surface concentration Γ (amount of surface species per surface area), so that

$$a_{\text{S}} = y_{\text{S}} \frac{\Gamma_{\text{S}}}{\Gamma^\ominus} = y_{\text{S}} \{\text{S}\} \quad (4)$$

where y_{S} is the activity coefficient, and $\{\text{S}\}$ denotes the relative value of surface concentration of S with respect to the chosen standard value. There is no recommended value for the standard surface concentration, but $\Gamma^\ominus = 1 \text{ mol m}^{-2}$ seems to be a suitable choice. Consequently, $\{\text{S}\}$ becomes the numerical value of surface concentration of species S expressed in moles per meter square: $\{\text{S}\} = \Gamma_{\text{S}} / \text{mol m}^{-2}$. The activity coefficient of surface species S (y_{S}) is defined through the difference in chemical potentials of real (μ^{real}) and ideal (μ^{id}) states at the surface

$$RT \ln y_{\text{S}} = \mu_{\text{S}}^{\text{real}} - \mu_{\text{S}}^{\text{id}} = z_{\text{S}} F \varphi \quad (5)$$

where F denotes the Faraday constant, z_{S} is the charge number of surface species S and φ is the electrostatic potential affecting their state at the interface. Ideal state corresponds to the zero value of the electrostatic potential φ being equal to that in the bulk of the solution. Equation (5) considers only electrostatic effects as responsible for the nonideal behavior. Such an approximation is correct since electrostatics plays a major role. For example, if the potential affecting state of a positively charged surface group ($z = +1$) changes from 180 mV to -180 mV, the activity coefficient at room temperature will be changed due to the electrostatic effect by 6 orders of magnitudes, *i.e.*, approximately from 10^3 to 10^{-3} . Equation (5) can be rewritten as:

$$y_{\text{S}} = \exp(z_{\text{S}} F \varphi / RT) \quad (6)$$

In the case of the two-step protonation (2-pK mechanism) described by reactions (1) and (2), the activity coefficients of charged interfacial species $\equiv\text{MO}^-$ and $\equiv\text{MOH}_2^+$ involved in surface reactions are:

$$y(\equiv\text{MO}^-) = \exp(-F\varphi_0 / RT) \quad (7)$$

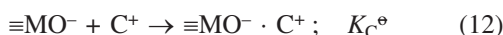
$$y(\equiv\text{MOH}_2^+) = \exp(-F\varphi_0 / RT) \quad (8)$$

where φ_0 is the (inner) surface potential affecting their state at the interface. The activity coefficient of neutral $\equiv\text{MOH}$ species is equal to 1. Accordingly, thermodynamic equilibrium constants for the first (1) and second (2) steps of protonation are defined on the basis of equations (3–8) as:

$$K_1^\ominus = \exp(F\varphi_0 / RT) \cdot \frac{\{\equiv\text{MOH}\}}{\{\equiv\text{MO}^-\} \cdot a_{\text{H}^+}} \quad (9)$$

$$K_2^\ominus = \exp(F\varphi_0 / RT) \cdot \frac{\{\equiv\text{MOH}_2^+\}}{\{\equiv\text{MOH}\} \cdot a_{\text{H}^+}} \quad (10)$$

Effective surface charge is reduced by association of anions A^- and cations C^+ from the bulk of solutions (reactions A and C, respectively):



By introducing the activity coefficients into expressions for thermodynamic equilibrium constants of counterion surface association reactions (11) and (12), and taking into account that interfacial ion pairs behave as oriented dipoles with charged ends being exposed to different potentials, φ_β and φ_0 , one obtains:

$$\gamma(\equiv\text{MO}^- \cdot \text{C}^+) = \exp\left(\frac{F(\varphi_\beta - \varphi_0)}{RT}\right) \quad (13)$$

$$\gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-) = \exp\left(\frac{-F(\varphi_\beta - \varphi_0)}{RT}\right) \quad (14)$$

Accordingly, the corresponding thermodynamic equilibrium constants are:

$$K_{\text{C}}^\ominus = \frac{\exp(F(\varphi_\beta - \varphi_0) / RT) \cdot \{\equiv\text{MO}^- \cdot \text{C}^+\}}{\exp(-F\varphi_0 / RT) \cdot \{\equiv\text{MO}^-\} \cdot a_{\text{C}^+}} = \frac{\exp(F\varphi_\beta / RT) \cdot \{\equiv\text{MO}^- \cdot \text{C}^+\}}{\{\equiv\text{MO}^-\} \cdot a_{\text{C}^+}} \quad (15)$$

$$K_{\text{A}}^\ominus = \frac{\exp(-F(\varphi_\beta - \varphi_0) / RT) \cdot \{\equiv\text{MOH}_2^+ \cdot \text{A}^-\}}{\exp(F\varphi_0 / RT) \cdot \{\equiv\text{MOH}_2^+\} \cdot a_{\text{A}^-}} = \frac{\exp(-F\varphi_\beta / RT) \cdot \{\equiv\text{MOH}_2^+ \cdot \text{A}^-\}}{\{\equiv\text{MOH}_2^+\} \cdot a_{\text{A}^-}} \quad (16)$$

Surface Charge Densities, Zero Charge Conditions and Surface Potential

Total surface concentration of active surface sites Γ_{tot} , within the 2-pK model, as described by reaction equations (1), (2), (11) and (12), is equal to:

$$\Gamma_{\text{tot}} = \Gamma(\equiv\text{MOH}) + \Gamma(\equiv\text{MOH}_2^+) + \Gamma(\equiv\text{MO}^-) + \Gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-) + \Gamma(\equiv\text{MO}^- \cdot \text{C}^+) \quad (17)$$

The corresponding surface charge densities in 0-plane (σ_0) and in β -plane (σ_β) are:

$$\sigma_0 = F(\Gamma(\equiv\text{MOH}_2^+) - \Gamma(\equiv\text{MO}^-) + \Gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-) - \Gamma(\equiv\text{MO}^- \cdot \text{C}^+)) \quad (18)$$

$$\sigma_\beta = F(\Gamma(\equiv\text{MO}^- \cdot \text{C}^+) - \Gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-)) \quad (19)$$

while the net surface charge density σ_s , *i.e.*, the effective charge directly bound to the surface per surface area being equal in magnitude but opposite in sign with respect to the so-called surface charge density of diffuse layer σ_d , is equal to:

$$\sigma_s = -\sigma_d = \sigma_0 + \sigma_\beta = F(\Gamma(\equiv\text{MOH}_2^+) - \Gamma(\equiv\text{MO}^-)) \quad (20)$$

At low ionic strength (I_c) and also at low surface potentials (pH close to pH_{pzc}), the association of counterions is negligible, so the surface charge density in 0-plane could be approximated by:

$$\sigma_0 \approx F(\Gamma(\equiv\text{MOH}_2^+) - \Gamma(\equiv\text{MO}^-)); \quad I_c \rightarrow 0 \text{ or } \varphi_0 \rightarrow 0 \quad (21)$$

The zero charge condition at the surface is expressed by three quantities, *i.e.*, by the point of zero charge (p.z.c.) corresponding to $\sigma_0 = 0$, by the isoelectric point (*i.e.p.*) corresponding to the electrokinetic potential $\zeta = 0$ (and $\sigma_s = 0$), and by the point of zero potential (p.z.p.) corresponding to $\varphi_0 = 0$. In the absence of specific adsorption of ions and in the case of negligible or symmetric association of counterions, all three points coincide and correspond to the state in which all electrical properties diminish ($\sigma_0 = \sigma_s = 0$, $\varphi_0 = \zeta = 0$). This electroneutrality condition is characterized by the so called pristine point of zero charge^{18,19,20,23} (pH_{ppzc} or pH_{eln}) being related to the protonation equilibrium constants by:

$$\text{pH}_{\text{eln}} = \frac{1}{2} \log(K_1^\ominus K_2^\ominus) \quad (22)$$

Electroneutrality condition can be experimentally achieved at low electrolyte concentration, and in such a case:

$$\text{pH}_{\text{eln}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzp}}; \quad I_c \rightarrow 0 \quad (23)$$

Since affinities of binding the cations and anions are not necessarily the same, the shift in pH_{pzc} , pH_{iep} and pH_{pzp} with respect to pH_{eln} might be expected at higher electrolyte concentrations.²¹ For example, in the case of preferential adsorption of anions ($K_{\text{A}}^{\ominus} > K_{\text{C}}^{\ominus}$), p.z.c. is shifted to higher pH values and i.e.p. is shifted to lower pH values compared to pH_{eln} so that: $\text{pH}_{\text{pzc}} > \text{pH}_{\text{eln}} > \text{pH}_{\text{iep}}$. It may be shown that the point of zero potential pH_{pzp} lies between pH_{iep} and pH_{pzc} values ($\text{pH}_{\text{pzc}} > \text{pH}_{\text{pzp}} > \text{pH}_{\text{iep}}$), and is close to pH_{eln} , which depends on the characteristics of the interface.^{22,23}

In the case of the 2-pK mechanism, the surface potential at 0-plane is, according to Eqs. (1) and (2), equal to:

$$\varphi_0 = \frac{RT \ln 10}{F} (\text{pH}_{\text{pzp}} - \text{pH}) - \frac{RT}{2F} \ln \left(\frac{\{\equiv\text{MOH}_2^+\}}{\{\equiv\text{MO}^-\}} \right) \quad (24)$$

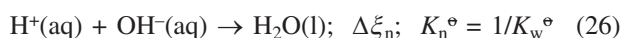
The first term in Eq. (24) is Nernstian while the second one is responsible for the lowering of the magnitude of the slope of the $\varphi_0(\text{pH})$ function. Potential φ_0 can be also approximated²⁴ by the modified Nernst equation as:

$$\varphi_0 = \frac{RT \ln 10}{F} (\text{pH}_{\text{pzp}} - \text{pH}) \cdot \alpha \quad (25)$$

where coefficient α describes deviation from the ideal behavior characterized by $\alpha = 1$. For real metal oxide surfaces, the value of coefficient α is below 1 and depends on the kind of metal oxide,^{25,26,27} but also on the composition of the electrolyte solution.²⁸

Potentiometric Mass Titration Method

Surface charge of an oxide in aqueous environment is the result of surface reactions (1), (2), (11) and (12). In the course of mass titration, when a solid metal oxide powder is added to an aqueous electrolyte solution, the amounts (and concentrations) of H^+ and OH^- ions in the bulk of the solution are changing due to surface protonations (1) and (2), but also due to possible neutralization of H^+ and OH^- ions in the bulk of the solutions:



where K_{n}^{\ominus} and K_{w}^{\ominus} are thermodynamic equilibrium constants of neutralization and water dissociation, respectively. The change of the extent of the reaction is generally defined¹⁶ through the change of the amount of any substance B participating in the chemical reaction, Δn_{B} , and its stoichiometric number ν_{B} as $\Delta\xi = \Delta n_{\text{B}}/\nu_{\text{B}}$.

The solid phase may contain a certain amount of acid (n_{a}) or base (n_{b}) as impurities. The fractions of acid and base impurities (a and b , respectively) in solid metal oxide powder and their difference u will be defined as:

$$a = \frac{n_{\text{a}}}{m}; \quad b = \frac{n_{\text{b}}}{m}; \quad u = a - b \quad (27)$$

where m is the mass of the metal oxide powder. These contributions should be also taken into account when considering the changes in the amounts of free hydronium $\Delta n(\text{H}^+)$ and hydroxyl $\Delta n(\text{OH}^-)$ ions:

$$\Delta n(\text{H}^+) = n_{\text{a}} - \Delta\xi_2 - \Delta\xi_1 - \Delta\xi_{\text{n}} \quad (28)$$

$$\Delta n(\text{OH}^-) = n_{\text{b}} - \Delta\xi_{\text{n}} \quad (29)$$

Note that extents of reactions may have positive but also negative values.¹⁶ In the latter case, the reaction proceeds in the opposite direction, with respect to the direction denoted by the reaction equation. According to Eqs. (27) – (29):

$$\Delta n(\text{H}^+) - \Delta n(\text{OH}^-) = n_{\text{a}} - n_{\text{b}} - \Delta\xi_2 - \Delta\xi_1 = u \cdot m - \Delta\xi_2 - \Delta\xi_1 \quad (30)$$

Changes in the amounts of surface groups are:

$$\Delta n(\equiv\text{MO}^-) = \Delta\xi_1 - \Delta\xi_{\text{c}}; \quad \Delta n(\equiv\text{MOH}_2^+) = \Delta\xi_2 - \Delta\xi_{\text{a}} \quad (31)$$

$$\Delta n(\equiv\text{MO}^- \cdot \text{C}^+) = \Delta\xi_{\text{c}}; \quad \Delta n(\equiv\text{MOH}_2^+ \cdot \text{A}^-) = \Delta\xi_{\text{a}} \quad (32)$$

In the following derivation, the solution in the absence of solid metal oxide will be considered as the initial state (pH_{in}), while the equilibrated dispersion after addition of the solid will be the final state (pH_{f}). Therefore, the mass concentration of the solid is zero in the initial, and γ in the final state. Equations (28)–(32) yield the relationship between the changes in the hydronium and hydroxyl ion concentrations in the bulk of the solution and the mass concentration of the dispersion:

$$\Delta c(\text{H}^+) - \Delta c(\text{OH}^-) = u\gamma - s\gamma (\Gamma(\equiv\text{MOH}_2^+) - \Gamma(\equiv\text{MO}^-) + \Gamma(\equiv\text{MOH}_2^+ \cdot \text{A}^-) - \Gamma(\equiv\text{MO}^- \cdot \text{C}^+)) \quad (33)$$

where γ is the mass concentration of the metal oxide of the specific surface area s . According to Eq. (18), defining surface charge density in the inner plane of the inner layer of the electrical interfacial layer, and Eq. (33), the changes in bulk concentrations of H^+ and OH^- ions are:

$$\Delta c(\text{H}^+) - \Delta c(\text{OH}^-) = u\gamma - \frac{s\gamma\sigma_0}{F} \quad (34)$$

Changes in the concentrations of H^+ and OH^- ions may be obtained from pH measurements according to:

$$\Delta c(\text{H}^+) = \frac{c^{\ominus}}{y} (10^{-\text{pH}_{\text{f}}} - 10^{-\text{pH}_{\text{in}}}) \quad (35)$$

$$\Delta c(\text{OH}^-) = \frac{c^{\ominus}}{y} (10^{\text{pH}_{\text{f}} - \text{pK}_{\text{w}}^{\ominus}} - 10^{\text{pH}_{\text{in}} - \text{pK}_{\text{w}}^{\ominus}}) \quad (36)$$

where y denotes the activity coefficient of H^+ and OH^- ions in the bulk of the solution given by the extended De-

bye-Hückel equation (Davies equation), while c^\ominus is the standard value of concentration ($c^\ominus = 1 \text{ mol dm}^{-3}$).

According to Eqs. (34) – (36) the surface charge density in the 0-plane is equal to:

$$\sigma_0 = \frac{Fu}{s} - \frac{F}{s\gamma} \frac{c^\ominus}{y} (10^{-\text{pH}_\gamma} - 10^{-\text{pH}_{\text{in}}} - 10^{\text{pH}_\gamma - \text{p}K_w^\ominus} + 10^{\text{pH}_{\text{in}} - \text{p}K_w^\ominus}) \quad (37)$$

In order to evaluate the surface charge density σ_0 using this equation, one should know the degree of contamination u . Degree of acid or base contamination may be obtained from the potentiometric acid-base titration of the concentrated dispersion.⁷ If the value of u is unknown, one can still obtain relative values of σ_0 and locate the zero on the basis of the known point of zero charge. Another, and much better, approach is purification of the sample, leading to $u = 0$. To cover both acidic and basic pH ranges, at least two experiments should be performed, one with low and the other with high initial pH.

Equation (37) could be rewritten as:

$$10^{-\text{pH}_\gamma} - 10^{\text{pH}_\gamma - \text{p}K_w^\ominus} = (10^{-\text{pH}_{\text{in}}} - 10^{-\text{pH}_{\text{in}} - \text{p}K_w^\ominus}) + \gamma \frac{y}{c^\ominus} \left(\frac{s\sigma_0}{F} - u \right) \quad (38)$$

It is obvious that the slope of the tangent of curve $(10^{-\text{pH}_\gamma} - 10^{\text{pH}_\gamma - \text{p}K_w^\ominus})$ vs. mass concentration:

$$\frac{d(10^{-\text{pH}_\gamma} - 10^{\text{pH}_\gamma - \text{p}K_w^\ominus})}{d\gamma} = \frac{y}{c^\ominus} \left(\frac{s\sigma_0}{F} - u \right) \quad (39)$$

is in relation with the surface charge density σ_0 and with the degree of contamination u . If addition of metal oxide in dispersion does not change the pH, the value of $(10^{-\text{pH}_\gamma} - 10^{\text{pH}_\gamma - \text{p}K_w^\ominus})$ also remains constant, and the derivative (39) is equal to zero, so that:

$$\frac{s\sigma_0}{F} - u = 0 \quad (40)$$

In the case of a pure metal oxide ($u = 0$), the surface charge density σ_0 is equal to zero and pH_∞ is equal to the point of zero charge, $\text{pH}_\infty = \text{pH}_{\text{pzc}}$.

In some cases, addition of a metal oxide powder produces a very dense dispersion in which mixing and measurements of pH are difficult so that pH cannot reach a constant value ($\text{pH}_\gamma < \text{pH}_\infty$ or $\text{pH}_\gamma > \text{pH}_\infty$). In such a case, one can still measure the surface charge density in the vicinity of the point of zero charge and the pH_{pzc} value accurately by choosing the initial pH close to pH_{pzc} .

Addition of an electrolyte to a metal oxide dispersion increases the absolute value of the surface charge density,²⁹ so the slope of the $\text{pH}(\gamma)$ function should be steeper and the dispersion reaches the constant pH_∞ value sooner, *i.e.*, at a lower mass concentration. Effects of

ionic strength and of the adsorption of counterions on the mass titration curve are examined in next sections by numerical simulations, and also experimentally.

Numerical Simulations

Effects of the ionic strength, counterion association and choice of the initial pH on mass titration curves and on surface charge densities were examined by numerical simulation of the mass titration. Calculations were based on the Surface Complexation Model assuming the 2-pK mechanism (Eqs. 1–25). Calculations were performed for a pure sample ($u = 0$). Parameters used in calculation correspond to a typical metal oxide aqueous dispersion:

$s = 50 \text{ g m}^{-2}$; relative permittivity of water $\epsilon_r(\text{H}_2\text{O}) = 78.54$; $T = 298 \text{ K}$; total surface concentration $\Gamma_{\text{tot}} = 1.5 \times 10^{-5} \text{ mol m}^{-2}$ ($= 9.9 \text{ sites/nm}^2$); $K_1^\ominus = 9.09 \times 10^7$ ($\lg K_1^\ominus = 7.96$) $K_2^\ominus = 3.16 \times 10^4$ ($\lg K_2^\ominus = 4.50$); capacitance of the inner Helmholtz layer $C_1 = 1.5 \text{ F m}^{-2}$; capacitance of the outer Helmholtz layer $C_2 = \infty$. According to the chosen values of K_1^\ominus and K_2^\ominus : $\text{pH}_{\text{eln}} = 6.23$. Calculations were performed for different ionic strengths: $I_c / \text{mol dm}^{-3} = 10^{-4}$; 10^{-3} ; 10^{-2} ; 10^{-1} .

The following SCM parameters were calculated as a function of pH: surface concentrations of species $\equiv\text{MOH}$, $\equiv\text{MOH}_2^+$, $\equiv\text{MO}^-$, $\equiv\text{MOH}_2^+ \cdot \text{A}^-$, $\equiv\text{MO}^- \cdot \text{C}^+$, surface charge densities at different planes (σ_0 , σ_β and σ_s) and surface potentials (φ_0 , $\varphi_\beta \approx \varphi_d$). Also, the pH of the dispersion as a function of the mass concentration was calculated.

As shown in Figures 1–5, in the course of mass titration, the pH of the metal oxide dispersion changes gradually, approaching the constant value of pH_∞ . The slope of the $\text{pH}(\gamma)$ functions decreases in magnitude, indicating that the absolute value of the surface charge density σ_0 approaches zero. According to Eqs. (38)–(40), when a constant value of pH in mass titration of pure metal oxide ($u = 0$) is achieved, the surface charge density σ_0 is equal to zero and $\text{pH}_\infty = \text{pH}_{\text{pzc}}$. In Figures 1–5, the maximum displayed mass concentration was 500 g dm^{-3} , which in most cases was not high enough to produce a constant pH value of pH_∞ . For that reason, the pH values of dispersions with the mass concentration of 500 g dm^{-3} (pH_{500}) and infinite mass concentration (pH_∞) were denoted by numerical values. According to numerical simulations, the mass concentration at which an approximately constant pH_∞ is reached depends on the electrolyte concentration and equilibrium parameters of the metal oxide *i.e.*, on the equilibrium constants of surface reactions.

Figure 1 represents the effect of ionic strength in the absence of counterion association ($K_A^\ominus = K_C^\ominus = 0$). It is clear that the constant value of pH_∞ is reached sooner (*i.e.*, at lower mass concentrations of the solid) if the ionic strength is higher. However, the difference of pH at 500 g dm^{-3} and pH_∞ is still significant even at the ionic strength as high as $10^{-1} \text{ mol dm}^{-3}$. At infinite mass con-

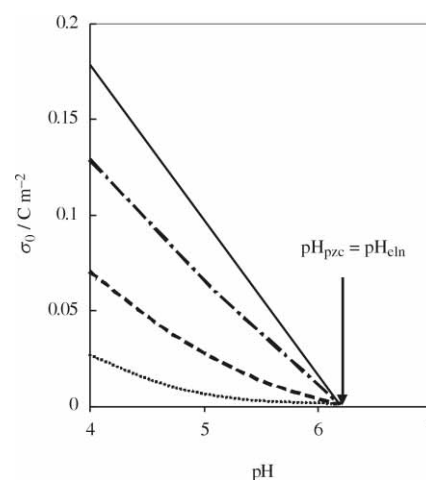
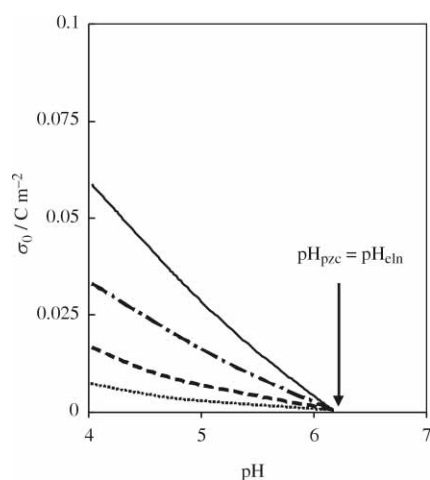
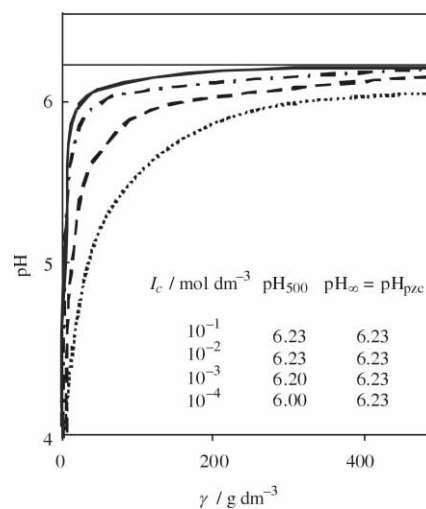
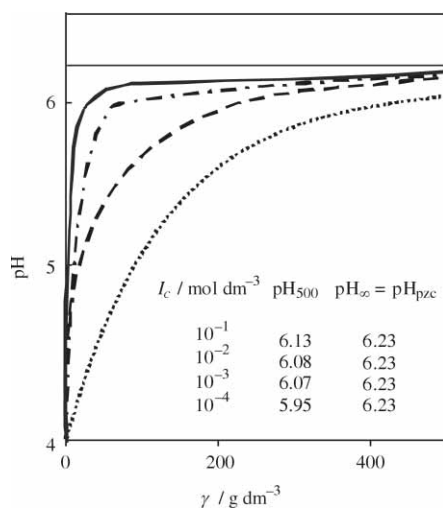


Figure 1. Effect of ionic strength on the mass titration and on surface charge density as calculated for the model metal oxide in absence of association of counterions at the surface ($K_A^\ominus = K_C^\ominus = 0$). $I_c / \text{mol dm}^{-3} = 10^{-1}$ (—); 10^{-2} (---); 10^{-3} (-.-.); 10^{-4} (....). pH_{500} is pH of dispersion with $\gamma = 500 \text{ g dm}^{-3}$. In the calculations 2-pK mechanism of the Surface Complexation Model was assumed, Eqs. (9, 10, 15–22, 24, 25, 37). Result: $\text{pH}_{\infty} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}} = 6.23$.

Figure 2. Effect of ionic strength on the mass titration and on surface charge density as calculated for the model metal oxide with significant and symmetrical association of counterions at the surface ($K_A^\ominus = K_C^\ominus = 100$). $I_c / \text{mol dm}^{-3} = 10^{-1}$ (—); 10^{-2} (---); 10^{-3} (-.-.); 10^{-4} (....). pH_{500} is pH of dispersion with $\gamma = 500 \text{ g dm}^{-3}$. In the calculations 2-pK mechanism of the Surface Complexation Model was assumed, Eqs. (9, 10, 15–22, 24, 25, 37). Result: $\text{pH}_{\infty} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}} = 6.23$.

centration: $\text{pH}_{\infty} = \text{pH}_{\text{eln}} = 6.23$. As expected, for a given pH, the surface charge density σ_0 was found to be higher at a higher ionic strength. The common intersection point (c.i.p) coincides with $\text{pH}_{\text{cip}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{eln}}$, which is due to the absence of counterions association.

Figure 2 represents the effect of ionic strength in the case of symmetric counterion association ($K_A^\ominus = K_C^\ominus = 100$). It is clear that the $\text{pH}(\gamma)$ function approaches the constant pH_{∞} value sooner (*i.e.*, at lower mass concentrations of the solid) compared to the system in the absence of counterion association. For relatively high ionic strengths (above $10^{-2} \text{ mol dm}^{-3}$), pH_{500} was found to be practically equal to $\text{pH}_{\infty} = \text{pH}_{\text{eln}} = 6.23$. The surface charge density was significantly increased due to the association of counterions. The common intersection point is again at $\text{pH}_{\infty} = \text{pH}_{\text{eln}} = 6.23$. According to the results

presented in Figures 1 and 2 for negligible ($K_A^\ominus = K_C^\ominus = 0$) and symmetric counterion association ($K_A^\ominus = K_C^\ominus > 0$), the value of pH_{pzc} coincides with the state in which all electrical properties disappear, *i.e.*, coincides with the surface electroneutrality point. In such a case, $\sigma_0 = \sigma_s = 0$ and $\varphi_0 = \zeta = 0$, so that $\text{pH}_{\infty} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzp}} = \text{pH}_{\text{eln}} = \text{pH}_{\text{cip}}$, so the common intersection point may be used for determination of the point of zero charge.

Figures 3 and 4 correspond to the unsymmetrical counterion association ($0 < K_A^\ominus \neq K_C^\ominus > 0$). Due to the high counterion association equilibrium constants, the pH_{∞} is reached earlier, practically at a mass concentration of 200 g dm^{-3} . These results show that $\text{pH}_{\infty} = \text{pH}_{\text{pzc}}$, *i.e.*, that the point of zero charge could be obtained by the mass titration method also in the case of high and unsymmetrical counterion associations. As shown in Fig-

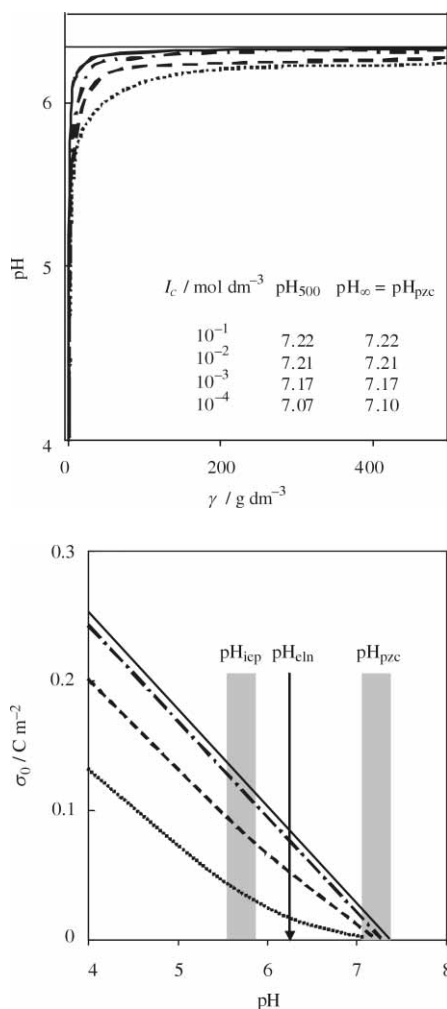


Figure 3. Effect of ionic strength on the mass titration and on surface charge density as calculated for the model metal oxide with preferential association of anions at the surface ($K_A^\circ = 10000$; $K_C^\circ = 100$). $I_c / \text{mol dm}^{-3} = 10^{-1}$ (—); 10^{-2} (— · —); 10^{-3} (---); 10^{-4} (····). pH_{500} is pH of dispersion with $\gamma = 500 \text{ g dm}^{-3}$. In the calculations 2-pK mechanism of the Surface Complexation Model was assumed, Eqs. (9, 10, 15–22, 24, 25, 37). Result: $\text{pH}_{\infty} = \text{pH}_{\text{pzc}} > \text{pH}_{\text{eln}} = 6.23$.

Figure 3, in the case of the preferable association of anions ($K_A^\circ > K_C^\circ$), the point of zero charge is shifted from the original pH_{eln} value to a higher pH value ($\text{pH}_{\text{pzc}} > \text{pH}_{\text{eln}}$) while the isoelectric point pH_{iep} is shifted to a lower pH value. The point of zero potential pH_{pzp} remains close to pH_{eln} . Figure 4, for the case of the preferential association of cations, shows the opposite trend. The results presented in Figures 3 and 4 suggest that the common intersection point c.i.p. cannot be used for evaluation of the point of zero charge in the case of unsymmetrical counterion association, $\text{pH}_{\text{pzc}} \neq \text{pH}_{\text{cip}}$. Differences in pH_{pzc} values at different ionic strengths are not highly pronounced but they are still significant.

Figures 1–4 indicate also, especially at low ionic strengths and at low affinities of counterions association, that the pH_{∞} value can be hardly reached at moderate

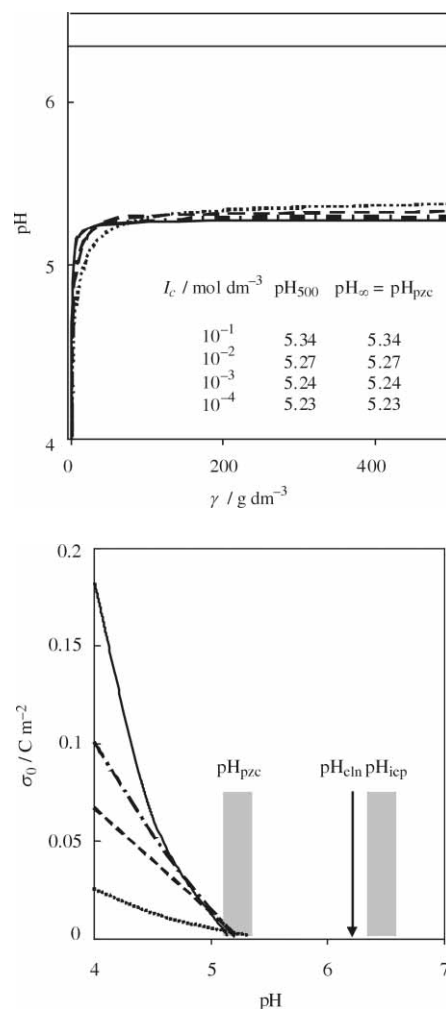


Figure 4. Effect of ionic strength on the mass titration and on surface charge density as calculated for the model metal oxide with preferential association of cations at the surface ($K_A^\circ = 100$; $K_C^\circ = 10000$). $I_c / \text{mol dm}^{-3} = 10^{-1}$ (—); 10^{-2} (— · —); 10^{-3} (---); 10^{-4} (····). pH_{500} is pH of dispersion with $\gamma = 500 \text{ g dm}^{-3}$. In the calculations 2-pK mechanism of the Surface Complexation Model was assumed, Eqs. (9, 10, 15–22, 24, 25, 37). Result: $\text{pH}_{\infty} = \text{pH}_{\text{pzc}} < \text{pH}_{\text{eln}} = 6.23$.

mass concentrations of solids if the initial pH is far from the pH_{pzc} . Figure 5 shows the results of calculations for different initial pH_{in} values. It is clear that if pH_{in} is close to the pH_{pzc} , a lower mass concentration is required to reach $\text{pH}_{\infty} = \text{pH}_{\text{pzc}}$. As expected, the same pH_{∞} was obtained when the initial solutions were more basic or more acidic than the pH_{pzc} . Accordingly, one may conclude that the mass titration experiment should be performed in more than one run. For example, if the initial pH value is significantly lower than pH_{pzc} , the pH_{∞} value will be approached but not reached. In the second run, one starts with the solution of the initial pH closer to pH_{∞} , *i.e.*, the initial pH might be the pH measured in the first run at a high mass concentration. In the third run, one chooses the initial pH even closer to the pH_{∞} . In most real cases, the pH_{∞} will be reached in the second or the third run.

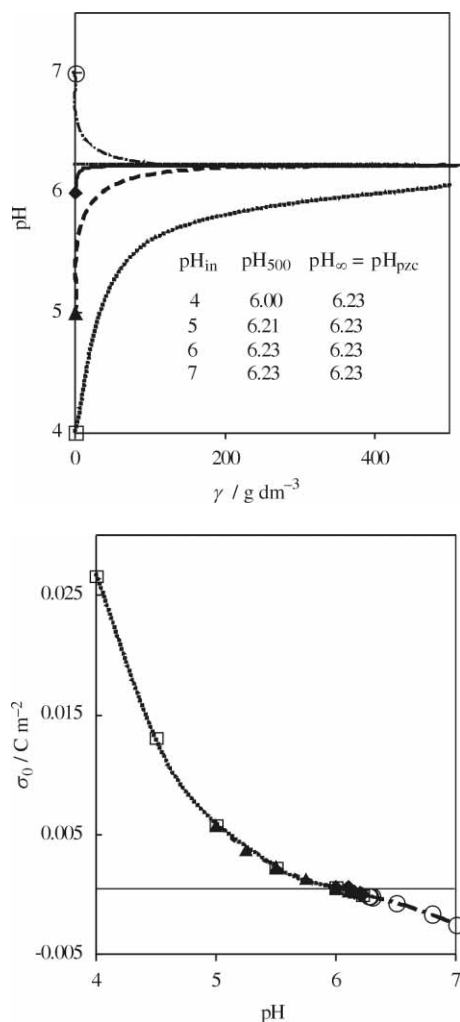


Figure 5. Effect of initial pH (pH_{in}) on the mass titration as calculated for the model metal oxide with significant and symmetrical association of counterions at the surface ($K_{\text{A}}^{\circ} = K_{\text{C}}^{\circ} = 100$). Surface charge density was also displayed. $I_{\text{c}} = 10^{-4} \text{ mol dm}^{-3}$, $\text{pH}_{\text{in}} = 7$ (O, - - -); 6 (◆, —); 5 (▲, - · - ·); 4 (□, ····). In the calculations 2-pK mechanism of the Surface Complexation Model was assumed, Eqs. (9, 10, 15–22, 24, 25, 37). Result: $\text{pH}_{\infty} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{el}} = 6.23$.

Then, an analogical experiment should be conducted, but starting from basic pH of the solution. If the same pH_{∞} is obtained, it proves that $\text{pH}_{\infty} = \text{pH}_{\text{pzc}}$. This procedure can cover a broad pH range, as shown in Figure 5. The results of numerical simulations were supported by experimental findings, presented in the next section.

EXPERIMENTAL

Materials: TiO_2 (P-25, Degussa); $s = 50 \text{ g m}^{-2}$, NaCl (*p.a.*, Fluka), HCl (0.1 mol dm^{-3} , trivalent, Fluka), NaOH (0.1 mol dm^{-3} , trivalent, Fluka), standard buffers (Merck), redistilled and decarbonated water.

Purification: The TiO_2 sample was purified by extended washing as follows. The titania powder was dispersed in water. Mass concentration of the dispersion was about 50

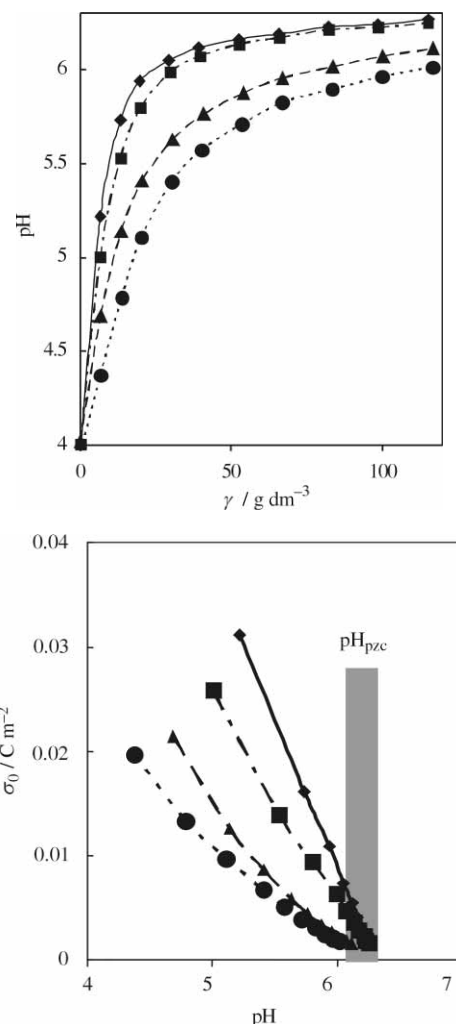


Figure 6. Mass titrations of TiO_2 at different ionic strengths adjusted with NaCl. $I_{\text{c}} / \text{mol dm}^{-3} = 10^{-4}$ (●); 10^{-3} (▲); 10^{-2} (■); 10^{-1} (◆). Temperature: 25 °C. Surface charge densities were calculated from mass titration data by means of Eq. (37).

grams per liter. After mixing, the dispersion pH was about 3.5 due to acidic impurities in the commercial sample. Dispersion was treated with an ultrasonic probe and pH was adjusted by adding a small amount of NaOH to $\text{pH} \approx 7$. After adjusting the pH, the dispersion was close to the isoelectric point, the particles were aggregated and sedimentation occurred. Supernatant was separated from the sediment by decantation. Conductivity and pH of the supernatant were measured. To the sediment, which was in fact a very concentrated dispersion (mud, slurry), redistilled water was added and the dispersion was again treated with ultrasound. If the pH was far from the isoelectric point, no sedimentation occurred. In such a case, the pH was again adjusted with NaOH to $\text{pH} \approx 7$. The procedure was repeated until the supernatant conductivity reached the constant and low value of about $10 \mu\text{S cm}^{-1}$. (Conductivity of redistilled water was about $3 \mu\text{S cm}^{-1}$.) Use of glassware was avoided so that the possible dissolution of silica would not contaminate the TiO_2 surface due to adsorption.

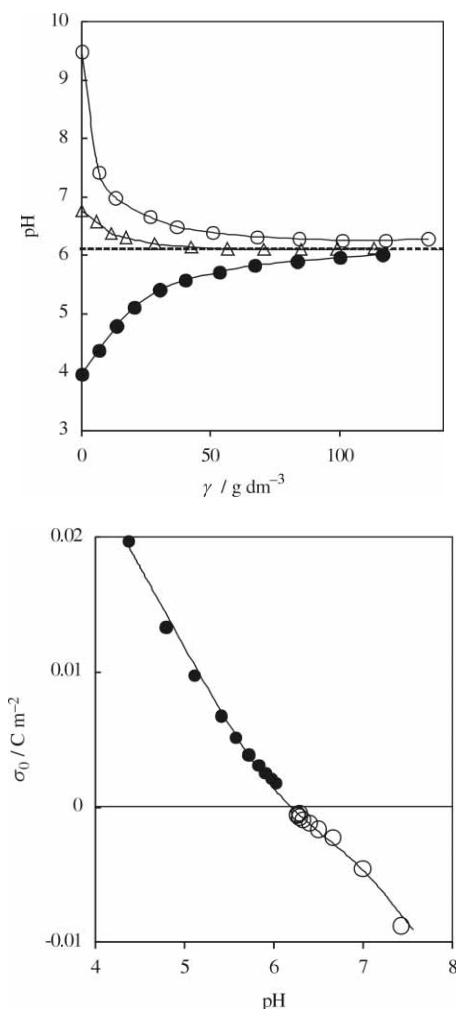


Figure 7. Mass titrations of TiO₂ for different initial pH: pH_{in} = 9.8 (O); 6.7 (Δ); 4 (●). Ionic strength was adjusted with NaCl: $I_c = 10^{-4}$ mol dm⁻³. Temperature: 25 °C. Surface charge densities were calculated from mass titration data by means of Eq. (37).

Experimental Procedures and Conditions: The pH was measured by a combined glass-Ag/AgCl electrode (Metrohm 6.0233.100). The electrode system (glass-Ag/AgCl electrode) was calibrated with three standard buffers. The systems were kept under an argon atmosphere and thermostated at 25 °C. The equilibrium was achieved by the application of ultrasounds (ultrasonic probe) and by stirring the dispersion.

Potentiometric Mass Titration

Potentiometric mass titration was used to determine the effect of ionic strength on the surface charge density and on the point of zero charge of TiO₂. Initial pH of water was adjusted by addition of HCl (pH_{in} = 4) or NaOH (pH_{in} = 9.8). Constant ionic strength (I_c / mol dm⁻³ = 10⁻⁴; 10⁻³; 10⁻²; 10⁻¹) was controlled by NaCl. Weighed amounts of titania powder were added to the aqueous solution of NaCl of predetermined acidity (pH_{in}) in subsequent portions. After each addition and equilibration (5 minutes under ultrasound and 10 minutes of stirring), the pH was measured. Figure 6 represents the mass titrations of TiO₂ at different ionic

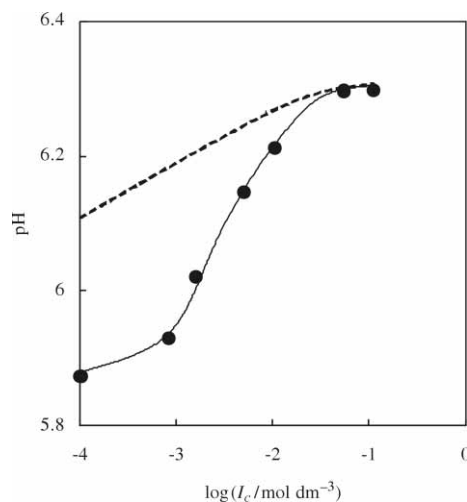


Figure 8. Effect of NaCl concentration on pH_{pzc} (dashed line) and on pH values (●) obtained by electrolyte (NaCl) titration of TiO₂ dispersion ($\gamma = 120$ g dm⁻³) at 25 °C.

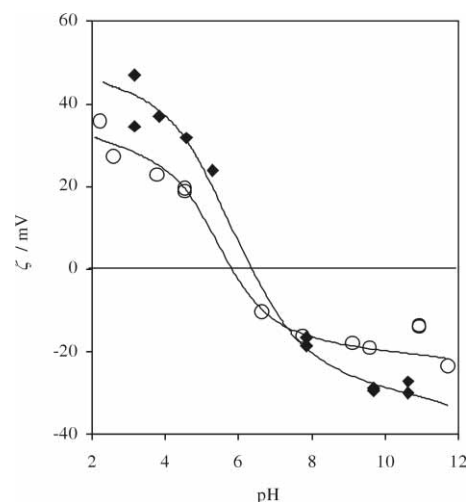


Figure 9. Effect of pH and ionic strength (controlled with NaCl) on electrokinetic ζ -potential of TiO₂ dispersion at 25 °C. I_c / mol dm⁻³ = 10⁻³ (◆), 10⁻¹ (O).

strengths. The maximum mass concentration was 120 g dm⁻³, because the more concentrated dispersions are too dense, and it would be difficult to stir them and measure the pH. The results are in agreement with numerical simulations demonstrated in Figures 1–4. As shown in Figure 6, an approximately constant pH was reached only for the dispersion at higher ionic strengths ($I_c > 10^{-2}$ mol dm⁻³). According to Eq. (40), the point of zero charge for the ionic strengths of 10⁻² and 10⁻¹ mol dm⁻³ was found to be pH_{pzc} ≈ 6.3, or slightly higher. For lower ionic strengths, the pH value did not reach the plateau, so p.z.c. could not be evaluated. Surface charge densities vs. pH were calculated from the mass titration data by means of Eq. (37). As expected, the surface charge densities increased with the ionic strength.

According to numerical simulations (Figure 5), the point of zero charge at low ionic strengths could be determined by choosing the initial pH of the dispersion close to

pH_{pzc} . In order to examine this finding experimentally, mass titrations of titania at low ionic strength (10^{-4} mol dm^{-3}) were performed using three different initial pH values. The results (Figure 7) are in agreement with numerical simulations (Figure 5). Initial pH values were adjusted to be in the acidic region far from and close to the point of zero charge ($\text{pH}_{\text{in}} = 4$ and $\text{pH}_{\text{in}} = 6.7$), but also in the basic region ($\text{pH}_{\text{in}} = 9.8$). At a sodium chloride concentration of 10^{-4} mol dm^{-3} , the point of zero charge of TiO_2 was found to be at $\text{pH}_{\text{pzc}} = 6.1$. Surface charge densities σ_0 were also evaluated. By performing two runs, the first with the initial acidic solution and the second with the initial basic solution, the broad pH region was covered.

Electrolyte Titration

Initial TiO_2 dispersion was prepared by addition of a relatively large amount of purified TiO_2 powder ($\gamma = 120$ g dm^{-3}) to the aqueous HCl solution ($c = 10^{-4}$ mol dm^{-3}). Weighed portions of solid sodium chloride were then added to the initial dispersion so that ionic strength increased from 10^{-4} to 1 mol dm^{-3} . The pH values of the dispersion were measured after each addition of NaCl and after equilibration (5 minutes under ultrasound and 10 minutes of stirring).

Increase in the electrolyte concentration caused an increase in the dispersion pH to pH = 6.3 (Figure 8). Dashed line demonstrates the dependency of pH_{pzc} on the ionic strength determined from the mass titrations. At relatively high ionic strengths of 10^{-2} mol dm^{-3} and 10^{-1} mol dm^{-3} , the point of zero charge is $\text{pH}_{\text{pzc}} \approx 6.3$ (Figure 6). At the low ionic strength of 10^{-4} mol dm^{-3} , the point of zero charge is lower, *i.e.*, $\text{pH}_{\text{pzc}} = 6.1$ (Figure 7). Discrepancy of the data obtained from the electrolyte titration with p.z.c. data from mass titration is due to the insufficient mass content of titania in the electrolyte titration experiments. At higher mass concentrations this discrepancy might disappear, which is hard to prove experimentally because the dispersion is too dense at high mass concentrations. Increase of pH_{pzc} with sodium chloride concentration indicates the preferential association of anions with respect to cations: $K_{\text{Cl}^-}^{\ominus} > K_{\text{Na}^+}^{\oplus}$.

Electrokinetic Measurements

The electrokinetic ζ -potential was measured using an ELS-800 Otsuka instrument. Titania dispersion was prepared by adding a small amount of powder to the aqueous solution ($\gamma \approx 5$ mg dm^{-3}). Ionic strength and pH were controlled by addition of NaOH, HCl and NaCl. The isoelectric point of TiO_2 particles at $I_c = 10^{-3}$ mol dm^{-3} is at $\text{pH}_{\text{iep}} = 6.2$, while at $I_c = 10^{-1}$ mol dm^{-3} $\text{pH}_{\text{iep}} = 5.8$. The shift of the pH_{iep} value to the acidic region indicates preferential association of anions with respect to cations $K_{\text{Cl}^-}^{\ominus} > K_{\text{Na}^+}^{\oplus}$, as deduced from electrolyte and mass titrations. This finding is in agreement with the literature.^{30–34}

DISCUSSION AND CONCLUSION

The effect of ionic strength, in a broad range (10^{-4} mol dm^{-3} ... 10^{-1} mol dm^{-3}), on the mass titration curve, sur-

face charge densities, and point of zero charge of metal oxide colloidal dispersion was examined by numerical simulation, and also experimentally using titania aqueous dispersion. Experimental results agreed with the numerical simulation, thus supporting the idea of applying the mass titration method for examination of equilibrium at solid/liquid interface. Mass titration was found to be a very simple and useful tool for determination of the point of zero charge. To avoid limitations of the method, one should first purify the sample so that the pH of highly concentrated dispersion corresponds to the point of zero charge. The second problem is that in some cases one is not able to prepare enough concentrated dispersion. This problem can be avoided by adjusting the initial pH (of the liquid medium) close to the point of zero charge, prior to addition of the solid phase. Such measurements can produce accurate results, which are important because they indicate the possible preferential association of cations with respect to anions and *vice versa*. The results with titania dispersed in an aqueous sodium chloride solution, indicating the unsymmetrical association of the counterions, are also supported by electrokinetic results; pH_{iep} and pH_{pzc} were shifted in opposite directions with respect to their values obtained at a low ionic strength. It was found that chloride ions exhibit higher affinity towards association with oppositely charged surface groups than sodium ions.

Accuracy of the point of zero charge determination by the mass titration method enables a comparison of pH_{iep} and pH_{pzc} values. In the case of unsymmetrical association, these two values are different and their shifts caused by electrolyte addition are in opposite directions. If these two points coincide at high ionic strength, or if they do not depend on the electrolyte concentration, this means that the association equilibrium constants of the anions and cations with oppositely charged surface groups are equal. In such a case, all zero charge conditions coincide, so that $\text{pH}_{\text{eln}} = \text{pH}_{\text{pzc}} = \text{pH}_{\text{iep}} = \text{pH}_{\text{pzc}}$. This finding is useful for locating the point of zero potential, necessary for evaluation of the surface potentials from the electrode potentials of the corresponding single crystalline electrodes.^{23,28,35} It is suitable for a given metal oxide to find an electrolyte with the same surface association affinities of cations and anions. Such an electrolyte should possess equal pH_{pzc} (mass titration) and pH_{iep} (electrokinetics), and also independence of these two pH values of the electrolyte concentration. It is important to note that the common intersection point in acid-base titrations of a dispersion at different ionic strengths cannot be used as a tool for location of the point of zero charge, since this approach implies the independency of pH_{pzc} on the electrolyte concentration, *i.e.*, it assumes the same association affinities of cations and anions at the surface, which is actually never the case.

The mass titration method can be also used for determination of the surface charge density in 0-plane. To

cover the entire pH range of interest, one should perform several experimental runs at different initial pH values of the solutions to which the samples of solid powder are added. Four runs might be enough, two in the acidic and two in the basic region. This method does not require titration in the absence of the solid phase (blank titration) and the problem of locating the point of zero charge disappears. It is especially useful for determination of the surface charge density in the pH range close to the point of zero charge.

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SAŽETAK

Točka nul-naboja i površinska gustoća naboja TiO₂ u vodenim otopinama elektrolita dobivene potencimetrijskom masenom titracijom

Tajana Preočanin i Nikola Kallay

Masena titracija pokazala se pogodnom metodom za određivanje točke nul-naboja (p.z.c., point of zero charge) i površinske gustoće naboja (σ_0) koloidnih čestica kovinskih oksida. Postupak se sastoji od postupnog dodavanja kovinskog oksida u otopinu elektrolita i mjerenju pH suspenzije. Svakim dodatkom, pH suspenzije

se mijenja dok ne dosegne stalnu vrijednost, pH_{∞} , koja je u slučaju čistog kovinskog oksida jednaka točki nul-naboja, pH_{pzc} . Asocijacijom protuiona pomiče se pH_{pzc} u kiselo područje (jača asocijacija kationa) ili u lužnato područje (jača asocijacija aniona). Rezultati masene titracije pružaju informacije o razlici u afinitetu površinske asocijacije protuiona (aniona i kationa), važnom parametru ravnoteže unutar električnog međupovršinskog sloja. Određivanje točke nul-naboja klasičnom potenciometrijskom kiselinsko-baznom titracijom suspenzije temeljeno je na zajedničkom sjecištu $\sigma_0(\text{pH})$ krivulja (c.i.p., common intersection point) za različite ionske jakosti. Pokazano je da se c.i.p. može koristiti za određivanje točke nul-naboja samo u slučaju kada je asocijacija aniona i kationa sa suprotno nabijenim površinskim vrstama jednaka. Analizirani su eksperimentalni rezultati masene titracije suspenzije koloidnih čestica titanijevog oksida u vodenoj otopini natrijeva klorida, te rezultati numeričkih simulacija temeljenih na 2-pK mehanizmu i modelu površinskog kompleksiranja. Povećanje koncentracije natrijeva klorida pomiče točku nul-naboja u lužnato područje, dok se izoelektrična točka pomiče u kiselo područje, što ukazuje na jaču asocijaciju kloridnih iona sa suprotno nabijenim površinskim mjestima u odnosu na natrijeve ione.