

1-pK and 2-pK model of oxide surface protonation.  
Are they equivalent?

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Simple mechanism of charge formation on metal oxides in electrolyte solution was outlined. Two basic surface protonation models (1-pK and 2-pK) were presented. It was shown that it is impossible to obtain exactly the same results using both of them when we analyzed together surface charge, electrokinetic potential, and isotherms of electrolyte ions adsorption.

## 1. INTRODUCTION

To explain the development of surface charge on metal oxides placed in electrolyte solution so called models of surface complexation (SCMs) were developed [1, 2]. In these models we define a few surface reactions which are responsible for charge formation. The definition of reaction(s) responsible for proton adsorption is a key step in the model formulation. The 1-pK and the 2-pK approaches are basic and the most popular models of surface charging.

In the 2-pK approach we assume two surface protonation reactions [2]:



In the above reactions SOH is an amphoteric surface hydroxyl group which can associate and dissociate proton.

In the 1-pK approach one assumes that surface protonation is described by only one reaction [3, 4]:



We can see that according to the 1-pK model a surface of oxide consists of negative and positive species with half charge which ratio depends on pH of solution.

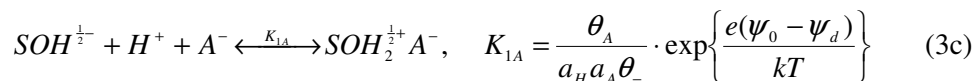
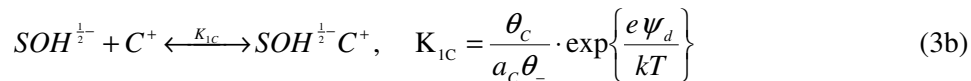
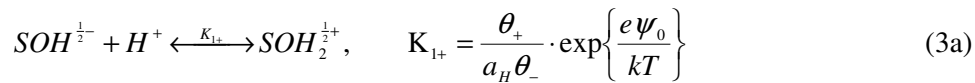
The presented reactions of surface protonation (1-2) are very often connected with reactions describing electrolyte ion adsorption onto oxide. Next the model of electric double layer formed at metal oxide/electrolyte interface is chosen. It can be for example Basic Stern Model (BSM) or Triple Layer Model (TLM). Finally, we obtain the complete model describing oxide/electrolyte interface (e.g. 1-pK BSM or 2-pK TLM).

All the discussed models are often applied to analyze experimental data like potentiometric titration curves, electrokinetic potential, and isotherms of ion adsorption measured for systems metal oxide/simple electrolyte [5]. However they are very often used to analyze more complex adsorption systems including multivalent cations and anions and organic compounds [6, 7].

In this connection the basic question sounds: Is it possible to obtain exactly the same results applying the 1-pK and the 2-pK models? We mean here that both models generate the same surface charge curve, electrokinetic potential, and isotherms of ion adsorption.

## 2. THEORY

According to the 1-pK Basic Stern Model (1-pK BSM) protons, along with the cations and anions of the basic electrolyte, form the following surface complexes [8]:  $SOH_{\frac{1}{2}}^{\frac{1}{2}+}$ ,  $SOH_{\frac{1}{2}}^{\frac{1}{2}-}C^+$  and  $SOH_{\frac{1}{2}}^{\frac{1}{2}+}A^-$  (Fig. 1),



In eqs (3a-c)  $\psi_0$  is the surface potential,  $\psi_d$  is the mean potential at the onset of diffuse layer,  $a_H$ ,  $a_C$ , and  $a_A$  are the bulk activities of protons, cations, and anions, respectively.

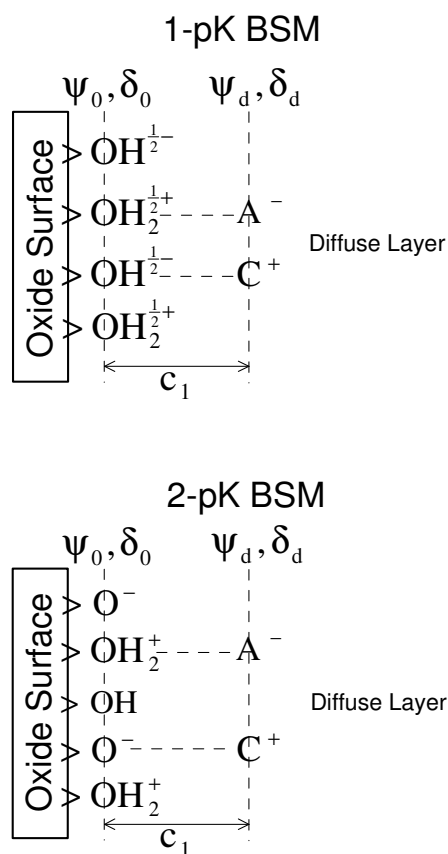


Fig. 1. Schematic presentation of the structure of the Basic Stern Model (BSM) and surface species for the 1-pK and the 2-pK approach. Two planes can be distinguished: the surface plane (0) and the plane of adsorbed electrolyte ions (d) which is also the onset of diffuse layer.  $\psi$  denotes electric potential and  $\delta$  charge located in individual planes.  $c_1$  stands for inner-layer capacitance.

Surface concentration of adsorption complexes was expressed by their surface coverages  $\theta_+$ ,  $\theta_C$ ,  $\theta_A$ . Exponential factors in eqs (3a-c) follows from the presence of electrical field at the interface. The concentration of ions at the

point where electrical potential is  $\psi_x$  is given by Boltzmann distribution

$$a_x = a_{bulk} \exp\left\{-\frac{e\psi_x}{kT}\right\}$$

As can be deduced from Figure 1, the following relations hold between the charges and the potentials within the compact and the diffuse layers,

$$\psi_d = \psi_0 - \frac{\delta_0}{c_1} \quad (4a)$$

$$\delta_d = \sqrt{8\varepsilon_0\varepsilon_r kTI} \sinh\left[\frac{e\psi_d}{2kT}\right] \quad (4b)$$

where  $\varepsilon_r$  is the relative permittivity of water,  $\varepsilon_0$  is the permittivity of the free space and I is the ionic strength of the solution (ions/m<sup>3</sup>). Eq (4b) follows from the Gouy-Chapman theory of the diffuse layer.

Equations (3a-c) can be transformed into following Langmuir-like form,

$$\theta_i = \frac{K_{li}f_{li}}{1 + \sum_i K_{li}f_{li}}, \quad +, A, C \quad (5)$$

where

$$f_{1+} = a_H \exp\left\{-\frac{e\psi_0}{kT}\right\} \quad (6a)$$

$$f_{1C} = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\} \quad (6b)$$

$$f_{1A} = a_A a_H \exp\left\{-\frac{e\delta_0}{kTc_1}\right\} \quad (6c)$$

The equation (5) is very convenient because it expresses amount of adsorption of ion as a explicit function of bulk activities, equilibrium constants, and surface potential and charge.

Using the such defined surface coverages we can calculate surface charge  $\delta_0$ ,

$$\delta_0 = \frac{1}{2}B(\theta_+ + \theta_A - \theta_- - \theta_C), \quad B = e \cdot N_s \quad (7)$$

Where  $N_s$  is an adsorption site density on oxide [*sites/m<sup>2</sup>*]. The above equation is a simple balance of positive and negative surface groups.

The charge generated in plane “d” by adsorption of electrolyte ions is given by,

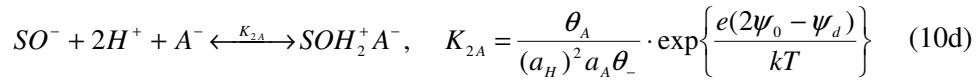
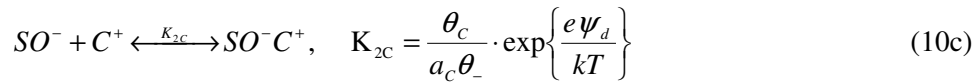
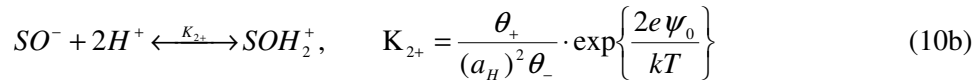
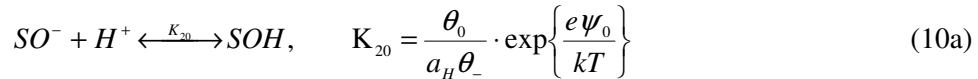
$$\delta_1 = B(\theta_C - \theta_A) \quad (8)$$

The charge in diffuse layer  $\delta_d$  can be calculated from the condition of electroneutrality for the whole system  $\delta_0 + \delta_1 + \delta_d = 0$ ,

$$\delta_d = \frac{1}{2}B(\theta_- + \theta_A - \theta_+ - \theta_C) \quad (9)$$

Calculations of  $\delta_0$ ,  $\delta_1$ , and  $\delta_d$  from eqs (7-9) applying eq (5) is not straightforward because  $\theta_+$ ,  $\theta_C$ ,  $\theta_A$  depend on surface potential and charge ( $\psi_0$  and  $\delta_0$ ). Nevertheless application of special procedure [8] enables us to obtain surface coverages, surface potential and charge for given values of equilibrium constants, inner-layer capacitance  $c_1$ , and bulk activities of ions.

In the 2-pK BSM model we assume occurrence of the following surface reactions (Fig. 1),



Mass action equations (10a-d) can also be written in the form which is more convenient for us,

$$\theta_i = \frac{K_{2i} f_{2i}}{1 + \sum_i K_{2i} f_{2i}}, \quad i=0,+ ,A,C \quad (11)$$

where,

$$f_{20} = a_H \exp\left\{-\frac{e\psi_0}{kT}\right\}, \quad f_{2+} = f_{20}^2 \quad (12ab)$$

$$f_{2C} = a_C \exp\left\{-\frac{e\psi_0}{kT} + \frac{e\delta_0}{kTc_1}\right\} \quad (12c)$$

$$f_{2A} = a_A (a_H)^2 \exp\left\{-\frac{e\psi_0}{kT} - \frac{e\delta_0}{kTc_1}\right\} \quad (12d)$$

Expressions for surface charges in the case of the 2-pK BSM are following,

$$\delta_0 = B(\theta_+ + \theta_A - \theta_- - \theta_C) \quad (13)$$

$$\delta_1 = B(\theta_C - \theta_A) \quad (14)$$

$$\delta_d = B(\theta_- - \theta_+) \quad (15)$$

To solve equation system (11) we can apply similar procedure as for the 1-pK BSM [8].

### 3. RESULTS AND DISCUSSION

Comparing two models describing the same system first we try to fit results generating by a model to experimental data. Next we can try to apply another model to the same data and see if the second one works better. If both models give satisfactory and very similar results we can ask the question whether applied models are actually equivalent?

To check if 1-pK and 2-pK produce the same results we will compare the equations for surface charge, diffuse layer charge, and cation and anion surface

coverage ( $\theta_c$  and  $\theta_A$ ). These quantities are experimentally obtainable from potentiometric titration, electrokinetic measurements, and electrolyte ion adsorption, respectively.

From eqs (7) and (13) we have,

$$\frac{K_{1+}a_H Y + K_{1A}a_A a_H X - K_{1c}a_c \frac{Y}{X} - 1}{2M1} = \frac{K_{2+}(a_H)^2 Y^2 + K_{2A}a_A (a_H)^2 XY - K_{2c}a_c \frac{Y}{X} - 1}{M2} \quad (16)$$

From eqs (9) and (15) we get,

$$\frac{1 - K_{1+}a_H Y + K_{1A}a_A a_H X - K_{1c}a_c \frac{Y}{X}}{2M1} = \frac{1 - K_{2+}(a_H)^2 Y^2}{M2} \quad (17)$$

And from eqs (5) and (11) we obtain two equations for cation and anion surface coverage,

$$\frac{K_{1c}a_c \frac{Y}{X}}{M1} = \frac{K_{2c}a_c \frac{Y}{X}}{M2} \quad (18)$$

$$\frac{K_{1A}a_A a_H X}{M1} = \frac{K_{2A}a_A (a_H)^2 XY}{M2} \quad (19)$$

Where

$$X = \exp\left(-\frac{e\delta_0}{kTc_1}\right) \quad (20a)$$

$$Y = \exp\left(-\frac{e\psi_0}{kT}\right) \quad (20b)$$

$$M1 = 1 + K_{1+}a_H Y + K_{1A}a_A a_H X + K_{1c}a_c \frac{Y}{X} \quad (20c)$$

$$M_2 = 1 + K_{20}a_H Y + K_{2+}(a_H)^2 Y^2 + K_{2A}a_A(a_H)^2 XY + K_{2C}a_C \frac{Y}{X} \quad (20d)$$

Equations (16-19) mean that we assume that both models (1-pK and 2-pK) give exactly the same results. Additionally we take the same surface potential because it is a measurable quantity [9]. From eqs (4ab) it follows that electric capacitance  $c_1$  should also be the same for the both models.

Assuming that electrolyte activity is constant during experiments we have three variables in equations (16-19): hydrogen ion activity  $a_H$  (or pH), X, and Y. Now we check if it is possible to obtain from the above equations the relation connecting the parameters describing the 1-pK model ( $K_{1+}, K_{1A}, K_{1C}$ ) with the parameters describing the 2-pK model ( $K_{20}, K_{2+}, K_{2A}, K_{2C}$ ). As a first attempt we can try to eliminate from eqs (16-19) three variables  $a_H$ , X, and Y using computer algebra system (e.g. Mathematica). Unfortunately it is fruitless.

On the other hand taking into account eqs (18) and (19) the ratio of equilibrium constants  $K_{1A}, K_{1C}$  and  $K_{2A}, K_{2C}$  can be expressed as follows,

$$\frac{K_{2C}K_{1A}}{K_{1C}K_{2A}} = a_H Y \quad (21)$$

From the above equation it is clear that the parameters  $K_{1A}, K_{1C}$  and  $K_{2A}, K_{2C}$  can not be constant if eqs (18) and (19) are fulfilled. **This obvious contradiction indicates that the 1-pK model and the 2-pK model are not equivalent.**

#### 4. SUMMARY

Two mechanisms of oxide surface charging in electrolyte solution were presented. The 1-pK approach assumes that only one protonation reaction is responsible for that process in contrast to 2-pK model where two consecutive protonation steps are assumed. The above discussion indicates that it is not possible to reproduce results given by one model using the second one. However we can obtain very similar results but they will not be identical.



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## CURRICULUM VITAE



**Wojciech Piasecki** was graduated from the Faculty of Chemistry of UMCS in Lublin in 1995 and obtained his Ph.D. in physical chemistry from the same Faculty in 1999. He was awarded two scholarships by the Foundation for Polish Science: Domestic Grant for Young Scientists and Foreign Postdoc Fellowship. He was a postdoc in the Department of Earth and Planetary Sciences at Johns Hopkins University in Baltimore (2003–2004). From 2000 he is employed in the Institute of Catalysis and Surface Chemistry PAS in Kraków. His main field of interest is the modeling of ion adsorption from electrolyte solution onto metal oxides. He is the author or co-author of over 30 papers.