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# Relaxation Time of Proton Adsorption from Solution onto Magnetite and Anatase: Classical and New Theoretical Approach\*

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The pH dependence of relaxation time of proton adsorption was analyzed by the classical Theory of Activated Adsorption and Desorption (TAAD) and the recently developed Statistical Rate Theory of Interfacial Transport (SRT). It was found that both models predicted different behaviour of relaxation time as a function of pH. Since SRT and TAAD give an identical result for relaxation time of adsorption of uncharged species, it is suggested that the surface potential is a key factor in ion adsorption kinetics. Additionally, only the order of magnitude of the ion adsorption rate constant can be estimated from the analysis of experimental data because the surface potential and the total concentration of adsorption sites are not known exactly.

## INTRODUCTION

The surface charge, as a key factor determining the behaviour of oxides in solution, depends directly on the amount of protons adsorbed.<sup>1</sup> Nowadays, potentiometric titration is a standard technique to measure hydrogen ion adsorption and hence the surface charge of oxides. Unfortunately, proton adsorption is frequently a very fast reaction and its kinetic study is difficult.

The kinetics of such fast processes as proton adsorption on metal oxides can be investigated using the relaxation method, which is based on the application of a slight perturbation to a system being in chemical equilibrium and observing how fast the system evolves to a new equilibrium state. The change in concentration con-

nected with the shift of equilibrium can be measured by means of an appropriate detection technique.

A comprehensive review of the relaxation method and its application in investigating the kinetics of ion adsorption from solution onto oxides was published by Hachiya, Moriyama and Takeda.<sup>2</sup>

From relaxation measurements one can determine the relaxation time  $\tau$ , which is defined by the following differential equation:

$$\frac{d\Delta x}{dt} = -\frac{1}{\tau} \Delta x \quad (1)$$

where  $\Delta x$  denotes temporary concentration displacement from equilibrium. It is assumed that this displacement is

\* Dedicated to Professor Nikola Kallay on the occasion of his 65<sup>th</sup> birthday.

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very small. It follows from Eq. (1) that the rate of relaxation is proportional to the swing from equilibrium.

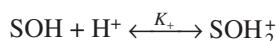
In order to analyze relaxation time, the classical theory of activated adsorption and desorption (TAAD) was used.<sup>2-4</sup> Recently, we have developed a new approach to interpreting adsorption kinetics, including ion adsorption from solution.<sup>5,6</sup> It is based on the statistical rate theory of interfacial transport (SRT) introduced by Ward<sup>7</sup> and developed by Rudzinski and Panczyk.<sup>8</sup>

We have demonstrated that relaxation time measurements can be interpreted successfully using both TAAD and SRT in the case of proton adsorption onto hematite.<sup>6</sup>

In this paper, we will extend our research by the analysis of the kinetics of proton adsorption onto magnetite and anatase.

## THEORY

The surface of oxides in solution is covered by hydroxyl groups SOH that can adsorb hydrogen ions (S means the surface metal atom):



where

$$K_+ = \frac{[\text{SOH}_2^+]}{[\text{SOH}][a_{\text{H}}]} \cdot \exp\left\{\frac{e\psi_0}{k_{\text{B}}T}\right\} \quad (2)$$

where [SOH] and [SOH<sub>2</sub><sup>+</sup>] are concentrations of surface species, *a*<sub>H</sub> is the bulk concentration of protons,  $\psi_0$  is the surface potential, and *K*<sub>+</sub> is the equilibrium constant. All concentrations are expressed as the number of moles per system volume, mol/dm<sup>3</sup>. The concentration of ions at a charged oxide surface with potential  $\psi_0$  is given by the Boltzmann distribution

$$a_{\text{surface}} = a_{\text{bulk}} \exp\left(-\frac{e\psi_0}{k_{\text{B}}T}\right)$$

Equation (2) can be rewritten in the form of the Langmuir adsorption isotherm:

$$\theta = \frac{K_+ a_{\text{H}} \exp\left\{-\frac{e\psi_0}{k_{\text{B}}T}\right\}}{1 + K_+ a_{\text{H}} \exp\left\{-\frac{e\psi_0}{k_{\text{B}}T}\right\}} \quad (3)$$

where the surface coverage  $\theta = [\text{SOH}_2^+] / N_{\text{Total}}$ , and *N*<sub>Total</sub> is the total concentration of adsorption sites in the system in mol/dm<sup>3</sup>.

According to the Theory of Activated Adsorption and Desorption, the rate of hydrogen ion adsorption is expressed by the equation:<sup>2</sup>

$$\frac{d\theta}{dt} = k_a (1-\theta) a_{\text{H}} \exp\left(-\frac{e\psi_0}{2k_{\text{B}}T}\right) - k_d \theta \exp\left(\frac{e\psi_0}{2k_{\text{B}}T}\right) \quad (4)$$

where *k*<sub>a</sub> and *k*<sub>d</sub> are the adsorption and desorption rate constants, and *k*<sub>B</sub> and *T* have their usual meaning. Expressions in the exponents play the role of electrostatic activation energy.

From the above formula, the expression for relaxation time can be obtained:<sup>2,6</sup>

$$\frac{1}{\tau} = k_a \left[ (N_{\text{Total}} \cdot (1-\theta) + a_{\text{H}}) \exp\left(-\frac{e\psi_0}{2k_{\text{B}}T}\right) + \frac{1}{K_+} \exp\left(\frac{e\psi_0}{2k_{\text{B}}T}\right) \right] \quad (5)$$

In Eq. (5), we applied the well-known relation between the adsorption and desorption rate constants *k*<sub>a</sub>/*k*<sub>d</sub> = *K*<sub>+</sub>.

To simplify the interpretation of kinetic data, the linear form of Eq. (5) was mainly used:<sup>2</sup>

$$\frac{1}{\tau} \exp\left(-\frac{e\psi_0}{2k_{\text{B}}T}\right) = k_a \left[ (N_{\text{Total}} \cdot (1-\theta) + a_{\text{H}}) \exp\left(-\frac{e\psi_0}{k_{\text{B}}T}\right) \right] + k_d \quad (6)$$

From Eq. (6), we can determine the values of *k*<sub>a</sub> and *k*<sub>d</sub> as a slope and an intercept of linear regression. However, their values should be treated with caution because the linear equation (6) can overestimate the significance of some data points and underestimate the others.<sup>6</sup>

According to the Statistical Rate Theory of Interfacial Transport, the rate of adsorption depends on the difference of chemical potential of the adsorbing ion in two phases, bulk and surface phases, as follows:<sup>6-8</sup>

$$\frac{d\theta}{dt} = R_{\text{ex}} \left[ \exp\left(\frac{\mu_{\text{b}} - \mu_{\text{s}}}{k_{\text{B}}T}\right) - \exp\left(\frac{\mu_{\text{s}} - \mu_{\text{b}}}{k_{\text{B}}T}\right) \right] \quad (7)$$

where  $\mu_{\text{b}}$  and  $\mu_{\text{s}}$  are the chemical potentials of ion in bulk and in surface phases, respectively, and *R*<sub>ex</sub> is the exchange rate at equilibrium between these two phases, which is a function of the bulk and surface concentration of the adsorbing ion.

In our recent paper,<sup>6</sup> we have shown how one can obtain the formula for the relaxation time in the SRT approach starting from equation (7). The final result is:

$$\frac{1}{\tau} = K_{\text{bs}} a_{\text{H}} (1-\theta) \left[ \left( K_+^{\text{el}} \frac{1-\theta}{\theta} + \frac{1}{K_+^{\text{el}} (a_{\text{H}})^2} \frac{\theta}{1-\theta} \right) \times N_{\text{Total}} + \left( K_+^{\text{el}} a_{\text{H}} \frac{1}{(\theta)^2} + \frac{1}{K_+^{\text{el}} a_{\text{H}}} \frac{1}{(1-\theta)^2} \right) \right] \quad (8)$$

where  $K_+^{\text{el}} = K_+ \exp\left(-\frac{e\psi_0}{k_B T}\right)$ , and  $K_{\text{bs}}$ , in  $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ , is the rate constant for the SRT approach.

The surface potential  $\psi_0$  was calculated using the quasi-Nernst formula proposed by Kallay:<sup>9,10</sup>

$$\psi_0 = 2.303 \cdot \alpha \frac{k_B T}{e} (\text{pH}_{\text{PZC}} - \text{pH}) \quad (9)$$

where  $\alpha \leq 1$  is a parameter and PZC is the point of zero charge of oxide. The above equation is correct in limiting the range of conditions (*e.g.*, low electrolyte concentration should be assumed to assure that the point of zero potential (PZP) coincides with PZC).<sup>10</sup>

## RESULTS AND DISCUSSION

The relaxation time of proton adsorption onto magnetite and anatase was measured in a pressure-jump apparatus with conductometric detection. The details of the experiment can be found in the original papers.<sup>3,4</sup> Additionally, the adsorption isotherm of hydrogen ion was determined by potentiometric titration.

Figure 1 depicts the proton adsorption isotherm and the dependence of relaxation time on pH for magnetite. To fit experimental data, we have used Eqs. (3) and (5) for TAAD and Eqs. (3) and (8) for SRT. The parameter values are collected in Table I.

Fitting the proton adsorption isotherm and relaxation time is not a simple task. It could seem that one has to determine only one parameter in Eq. (3), namely the equilibrium constant  $K_+$ , but in fact we have two additional parameters,  $\alpha$  and  $N_{\text{Total}}$ . The first one determines how surface potential  $\psi_0$  depends on the pH of solution. The second one defines the adsorption site concentration in the system. We can only assume reasonable estimates of these two parameters but it is impossible to give their exact values. This uncertainty has a strong influence on the determined rate constants  $K_{\text{bs}}$ ,  $k_a$ , and  $k_d$ .<sup>6</sup>

As we can see in Figure 1, the fit quality of the adsorption isotherm is quite good. However, the relaxation time calculated using the SRT approach behaves in a re-

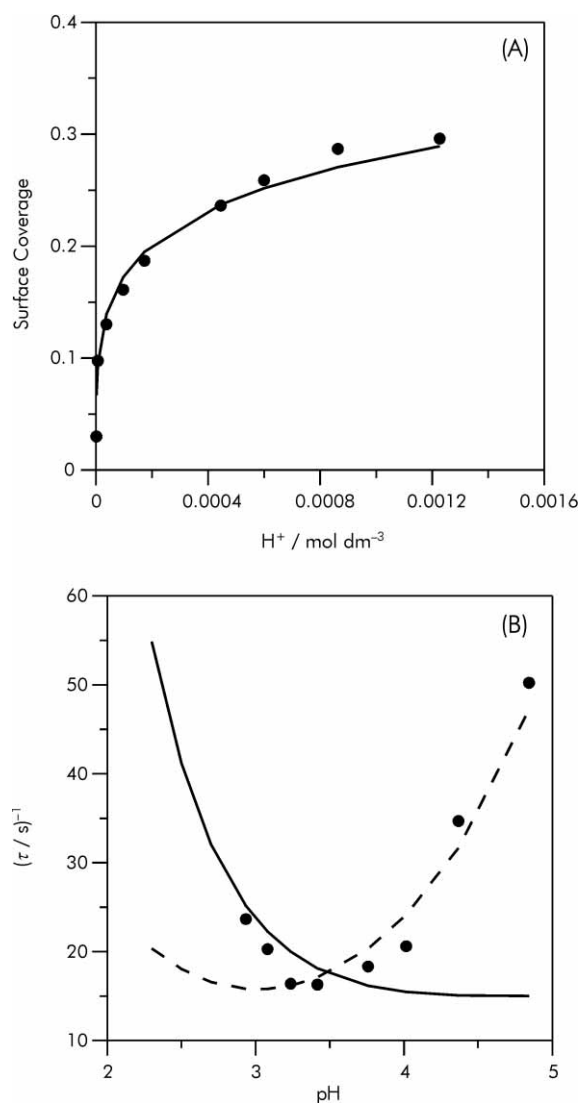


Figure 1. The adsorption isotherm (A) and the reciprocal relaxation time (B) for proton adsorption on magnetite (data from Ref. 4). Kinetic data were fitted using SRT (solid line) and TAAD (dashed line).

verse manner to  $\tau^{-1}$  calculated using TAAD. It seems that the results predicted by both models form the opposite branches of a parabola. TAAD produces a better fit especially for pH above 4. The SRT predictions are better for pH below 3. These observations are in agreement with our earlier findings for hematite.<sup>6</sup>

We have found earlier that in the case of adsorption of neutral species (not ions), both kinetic approaches predict the same relaxation time behaviour.<sup>6</sup> In other words, the addition of electrostatic interactions to kinetic equations has different effects for TAAD and for SRT. Here, we would like to emphasize that parameters  $k_a$  and  $K_{\text{bs}}$  are only scaling factors in equations (5) and (8). It means that the shape of function  $\tau(\text{pH})$  is determined by the expressions in square brackets, which depend on equilibrium quantities only.

TABLE I. Values of parameters used in calculations for magnetite and anatase

Oxide	Magnetite	Anatase
PZC (measured)	7.1	5.8
$K_+$ (Eq. (2))	5.6	3.0
$\alpha$ (Eq. (9))	0.735	0.72
$N_{\text{Total}} / \text{mol dm}^{-3}$	$5 \times 10^{-3}$	$1.4 \times 10^{-2}$
SRT (Eq. (8))	$K_{\text{bs}} = 1650$	$K_{\text{bs}} = 1800$
TAAD (Eq. (5))	$k_a = 7.0 \times 10^4$ $k_d = 1.8 \times 10^{-1}$	$k_a = 3.0 \times 10^4$ $k_d = 3.0 \times 10^1$

Figure 2 shows the isotherm and the relaxation time of proton adsorption for anatase. As before, the isotherm fit is satisfactory but only the TAAD relaxation curve fits the kinetic data. The SRT curve is too steep; however, it has the same trend as the TAAD line. The applied parameter values were given in Table I.

We have to stress again that the numbers given for  $K_{bs}$ ,  $k_a$ , and  $k_d$  in Table I are not unique. They depend on the assumed values of parameters  $K_+$ ,  $\alpha$ , and  $N_{Total}$ . In fact, we can only estimate the order of rate constants. Nevertheless, it is interesting that similar parameters were obtained for hematite in our earlier paper.<sup>6</sup>

The rate constants obtained from linear equation (6) (not presented in the Table) are similar to those estimated from Eq. (5). However, the former equation is simpler to apply but the latter gives better control of the

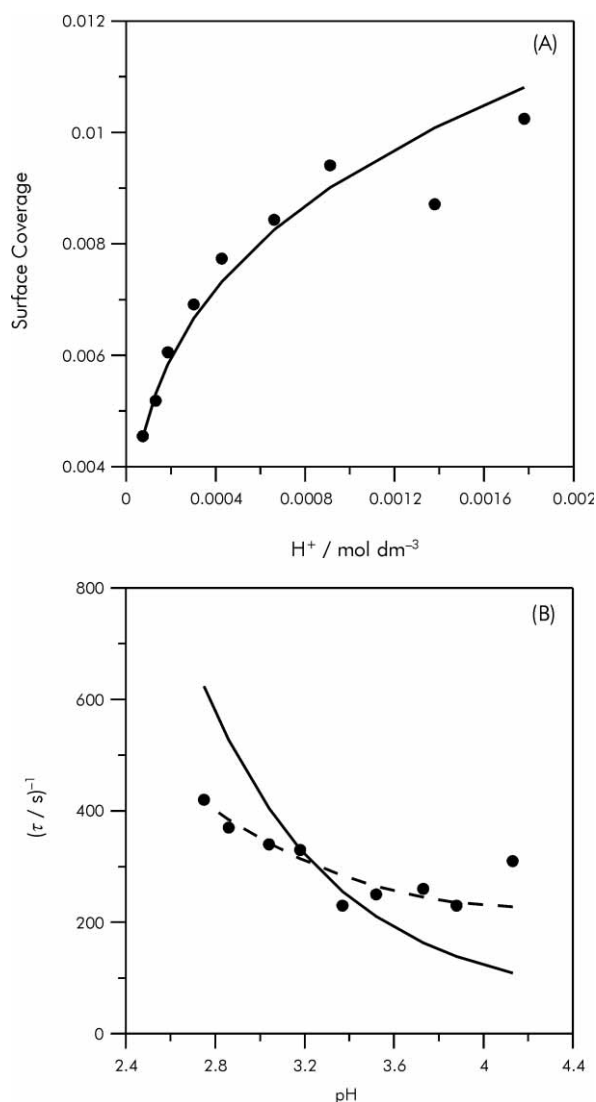


Figure 2. The adsorption isotherm (A) and the reciprocal relaxation time (B) for proton adsorption on anatase (data from Ref. 3). Kinetic data were fitted using SRT (solid line) and TAAD (dashed line).

fitting procedure and enables comparison with the SRT equation (8).

Recently, Kallay and coworkers developed a Single Crystal Electrode enabling direct measurement of the surface potential for hematite and its dependence on pH, showing that the slope is significantly lower than the Nernstian one.<sup>10</sup> Additionally, they demonstrated that slow kinetics of equilibration at the interface may produce hysteresis in the obtained surface potential values.<sup>11</sup> The influence of kinetics on the determination of surface charge for different oxides was recently studied experimentally by Duc *et al.*<sup>12</sup> These new experimental evidences confirm that the proton adsorption kinetics is crucial for correct determination of the properties of the metal oxide/electrolyte interface.

## CONCLUSIONS

Our analysis of the relaxation time of proton adsorption measured for magnetite and anatase confirms the results for hematite, namely that the two theoretical approaches, SRT and TAAD, predict different behaviour of the relaxation time as a function of pH.

In our opinion, to better understand the relaxation of ion adsorption, we should re-examine the role of surface potential in ion adsorption kinetics. Since  $\psi_0$  appears in the exponent in kinetic equations, even a small change in surface potential during relaxation may have a considerable effect on the final result.

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**SAŽETAK****Relaksacijsko vrijeme adsorpcije protona iz otopine na magnetit i anatas:  
klasični i novi teorijski pristup****Wojciech Piasecki, Piotr Zarzycki i Władysław Rudziński**

Ovisnost relaksacijskog vremena adsorpcije protona o pH analizirana je klasičnom teorijom aktivirane adsorpcije i desorpcije (*Theory of Activated Adsorption and Desorption, TAAD*) i nedavno razvijenom statističkom teorijom brzine međupovršinskog prijenosa (*Statistical Rate Theory of Interfacial Transport, SRT*). Utvrđeno je, da oba modela predviđaju različito ponašanje relaksacijskog vremena kao funkcije pH. Budući da SRT i TAAD daju identične rezultate za relaksacijsko vrijeme nenabijenih vrsta, smatra se, da je površinski potencijal ključni čimbenik u kinetici adsorpcije iona. Dodatno, iz eksperimentalnih se podataka može odrediti samo red veličine konstante brzine adsorpcije iona, jer ni površinski potencijal niti koncentracija adsorpcijskih mjesta nisu točno poznati.