

The influence of surface potential on the relaxation time of hydrogen ion adsorption from solution onto oxides

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The particles of metal oxides dispersed in electrolyte solution obtain a surface charge due to ion adsorption. The pH of solution is key factor determining its value. Nowadays, potentiometric titration is a standard technique of measuring surface charge of oxides. The adsorption of hydrogen ions on oxides is very fast process which can be investigated by using the relaxation method [1,2]. In this technique small perturbation is applied to a system being in chemical equilibrium. Next, the evolution of the system to a new equilibrium state is monitored. In the case of adsorption of protons the pressure jump is used as a stimulus changing an equilibrium in oxide suspension and measurements of solution conductivity are used to determine changes in ion concentrations. From this type of experiments we can determine a relaxation time τ which depends on ion adsorption kinetics (which can be described by the Theory of Activated Adsorption and Desorption). According to this theory the surface coverage by hydrogen ions θ changes with time as follows:

$$\frac{d\theta}{dt} = k_a(1-\theta)a_H \exp\left(-\frac{e\psi_0}{2k_B T}\right) - k_d\theta \exp\left(\frac{e\psi_0}{2k_B T}\right)$$

where k_a and k_d are adsorption and desorption rate constants, and e , k_B and T have their traditional meaning. Exponential factors represent electrostatic activation energy for ion adsorption on the surface with electrostatic potential ψ_0 [3,4].

During relaxation both the hydrogen ion activity a_H and the surface coverage θ change until reaching new equilibrium values. However, it is commonly assumed that the surface potential ψ_0 is constant during relaxation [2]. This is obvious contradiction because the surface potential is a function of the surface coverage by protons: $\psi_0(\theta)$. Assuming that in reality the surface potential depends on temporary surface coverage by ions we developed a new method of interpretation of relaxation experiments. We compared our results with the conventional approach by analyzing experimental data of adsorption kinetics of hydrogen ions for different metal oxides. Our methodology can be extended for investigating the kinetics of adsorption of any ions.

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- [1] R. D. Astumian, M. Sasaki, T. Yasunaga, and Z. A. Schelly, *Journal of Physical Chemistry*, 1981, **85**, 3832.
- [2] K. Hachiya, Y. Moriyama, and K. Takeda, (N. Kallay, ed.), *Interfacial dynamics Vol. 88*, 2000, p. 351, Marcel Dekker, New York, USA.
- [3] W. Piasecki, *Journal of Physical Chemistry B*, 2006, **110**, 13138.
- [4] W. Piasecki, P. Zarzycki and W. Rudziński, *Croatica Chemica Acta*, 2007, **80**, 345.