

Quantification of the Charge Density on Silica Substrates under Identical Solution Conditions Using Multiple Analytical Techniques

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Statement of Purpose:

The measurement of surface charge density (σ) of a material in an aqueous environment is of substantial importance in diverse fields of biotechnology. Estimates of σ values for materials with ionizable groups that are non-conductive to direct measurement by electro-chemical techniques are often accomplished indirectly through zeta (ζ) potential measurements through different mathematical models. However, even with identical substrates, reported values of σ have been found to widely vary with different techniques and models applied [1]. The objective of the current study was thus to assess the reliability as well as the effects of using different techniques and models on σ determined for glass and quartz (100) in 10 mM potassium phosphate buffer (PPB) solution.

Materials and Methods:

Surface models: Measurements of single quartz crystals with a (100) surface plane (MTI Corporation) and glass (Chemglass Life Sciences) were made in 10 mM PPB at 25°C over a pH range of 4.0-9.0.

Techniques to characterize the ζ -potential of the interfacial system: Three separate techniques were used for ζ -potential measurements on flat quartz (100) surfaces and glass surfaces. The ζ -potentials were estimated from:

- The force measured by the positively charged tip of known σ using atomic force microscopy (AFM, Asylum research);
- The mobility of negatively charged silica particles by electrophoresis (EP, Malvern Instruments) technique;
- The streaming potential (SP, Anton-Paar) technique, which does not utilize a probe but uses flow to create charge separation.

The probes and flow behavior for each method were well-characterized and the measurements were based on established methodology [2-4].

Mathematical model to estimate the σ of samples: Two models were used to estimate the σ of the samples from the ζ -potential measurement for each interfacial system.

Model 1: Assuming a Gouy-Chapman-Stern layer model to account for the activity of ions from the surface in the solution, fractional dissociation (f) is given by:

$$f = \frac{C_s(\text{SiO}^-)}{C_s(\text{SiOH}) + C_s(\text{SiO}^-)} = \frac{10^{(pH + pQ - 2pK_d)}}{1 + 10^{(pH + pQ - 2pK_d)}} \quad (1)$$

Model 2: Assuming simple dissociation kinetics and the activity of ions in the bulk and surface being identical:

$$f = \frac{C_s(\text{SiO}^-)}{C_s(\text{SiOH}) + C_s(\text{SiO}^-)} = \frac{10^{(pH - pK_d)}}{1 + 10^{(pH - pK_d)}} \quad (2)$$

where C_s denotes the density of the functional groups on the surface, pQ is defined as the acidity coefficient and is a function of the surface potential, pK_d is the logarithmic measure of the acid dissociation constant associated with the surface, and pH refers to the logarithmic measure of the proton concentration in solution. Surface parameters, such as point of zero charge (pzc) and pK_d were obtained from the ζ potential measurements.

Assuming the density of silanol groups as 1 site/32 Å² [1], the σ of the glass and quartz surfaces could be determined from the ' f ' values by:

$$\sigma = \frac{1 \text{ silanol site}}{32 \text{ Å}^2} \times \frac{10^{20} \text{ Å}^2}{\text{m}^2} \times \frac{1.602 \times 10^{-19} \text{ C}}{\text{charged site}} \times f \times \frac{(\text{charged site})}{(\text{silanol site})} \quad (3)$$

$$= 0.501 \times f \text{ (units: Coulombs/m}^2\text{)}$$

Results and Discussion:

Figure 1(A, B) shows the ζ -potential measurements for the quartz (100) and glass surfaces in 10 mM PPB for each of the analytical techniques, and the expected ' f ' for the models used. Even though there was no significant differences between the ζ -potential measurements for a given substrate by each technique, the model applied to convert these values to estimate σ significantly affected the results. For example, in case of the quartz (100) surface at pH 7.4, less than 10% ionization was obtained by model 2 while according to model 1, 70% ionization was achieved. Similarly, in case of the glass surface, at pH 7.4, 100% ionization was predicted by model 1, and about 80% ionization was predicted by model 2.

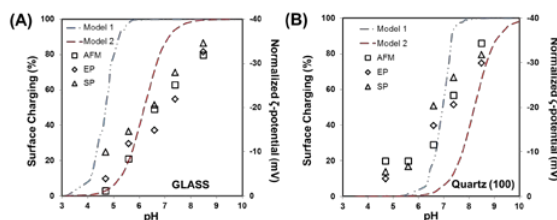


Figure 1: ζ -potential measurement for (a) glass ($pzc = 2.92 \pm 0.31$, $pK_d = 6.19$) and (b) quartz (100) ($pzc = 3.94 \pm 0.25$, $pK_d = 7.84$) in 10 mM PPB (pH 4.0-9.0) using AFM, EP, and SP techniques ($n = 3$ mean \pm 95% C.I.). The data points indicate the measurements obtained from each of the techniques (right Y-axis). The ζ -potentials were normalized to $-\log$ of ionic concentration of PPB. Red and blue trend lines (left-Y axis) represent ' f ' (%) of the substrates, based on the surface constants derived from the ζ -potentials measurements (right Y-axis).

Concluding Remarks:

We conclude that even when different techniques do not significantly impact the magnitude of the ζ -potential measurements, the underlying assumptions as well as the model applied in estimating σ from the measured ζ -potential values do significantly impact the magnitude of the calculated values. Therefore, care must be taken to ensure that the appropriate assumptions, model, and technique are used when estimating σ from ζ -potential measurements.

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References: [1] Behrens SH, Grier DG. J. Chem. Phys. 2001; 115:6716-21. [2] Zimmerman B, et al. J. Eng. Fiber. Fabr. 2011; 6:61. [3] Corbett JCW, et al. Colloid. Surface. A. 2012; 396:169-76. [4] Lützenkirchen J, et al. Adsorption. 2010; 16: 249-58.