

Evaluation Methods for the Zeta Potential of Solid Surfaces

Relevant for: interpretation of zeta potential, streaming potential, streaming current

The measurement of the streaming potential is the classical approach towards the zeta potential of macroscopic solids. The streaming current is an alternative parameter to assess the surface zeta potential. State-of-the-art instruments for surface zeta potential analysis provide the same quality of these measuring parameters. Their relation to the surface zeta potential, however, introduces preferences and restrictions for their applications.

1 Introduction

The zeta potential is an important property of charged solid-liquid interfaces and an indicator for the actual surface charge of a solid in contact with an electrolyte solution. For macroscopic solid surfaces, the zeta potential is determined by the measurement of the streaming potential and alternatively of the streaming current. With SurPASS 3 both streaming potential and streaming current are measured with the same data quality. However, the evaluation of the surface zeta potential from streaming potential measurements may be affected by surface conductance of the sample, while the streaming current approach requires knowledge about the geometry of the flow channel. This report explains the fundamental equations for evaluating the surface zeta potential from streaming potential and streaming current measurements.

2 Surface zeta potential analysis

2.1 Helmholtz-Smoluchowski equations

The fundamental equations that relate electrokinetic phenomena like the streaming potential and the streaming current to the zeta potential have been derived by Marjan von Smoluchowski and Hermann von Helmholtz.

For solid materials with a planar surface the application of Equation 1 for the zeta potential calculation is most appropriate.

$$\zeta = \frac{dI_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon_{rel} \times \varepsilon_0} \times \frac{L}{A}$$

Equation 1

Here the measured streaming current coupling coefficient $dI_{str}/d\Delta p$ is related to the cell constant L/A of the

flow channel (the gap between adjacent solid samples). L is the length of the rectangular slit channel formed between two planar surfaces and A is its cross-section, $A = W \times H$, with channel width W and gap height H . Figure 1 shows a schematic representation of the arrangement of solids with planar surfaces indicating the dimensions of the flow channel. In Equation 1 η and ε_{rel} are the viscosity and dielectric coefficient of the electrolyte solution, and ε_0 is the vacuum permittivity. For dilute aqueous solutions the viscosity and dielectric coefficient of water are used.

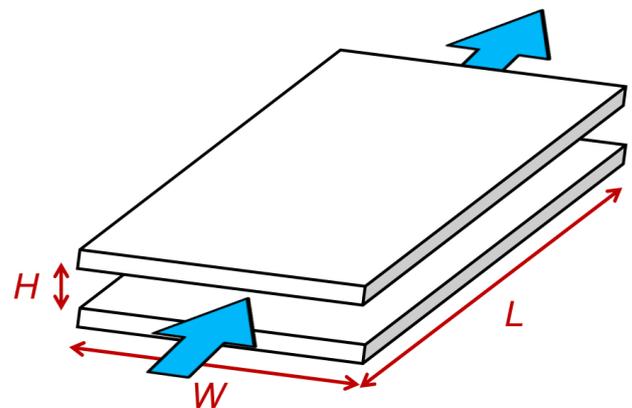


Figure 1: Schematic representation of the rectangular slit channel between adjacent solid samples with a planar surface. L , W and H are the length, width and height of the flow channel. The arrows indicate the direction of liquid flow during the measurement.

The application of Equation 1 requires the exact knowledge about the geometry of the flow channel, i.e., the cell constant L/A . For the rectangular slit channel, the length L and width W are determined by the solid sample size. The gap height H is calculated from the measured volume flow rate of liquid passing through the flow channel driven by the applied differential pressure.

Equation 1 is well-established for zeta potential investigations of planar solids, but is not suitable for the zeta potential evaluation of sample types, where the

cell constant L/A of the flow channel is unknown like planar solids of irregular shape, fibers, textiles and granular samples.

The streaming current in Equation 1 can be substituted by the streaming potential using Ohm's law, $I_{str} = U_{str}/R$, where R is the electrical resistance inside the flow channel. The zeta potential is then expressed as

$$\zeta = \frac{dU_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon_{rel} \times \varepsilon_0} \times \frac{L}{A} \times \frac{1}{R}$$

Equation 2

By using the definition of electrical conductivity κ ,

$$\kappa = \frac{1}{R} \times \frac{L}{A}$$

Equation 3

Equation 2 is replaced by

$$\zeta = \frac{dU_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon_{rel} \times \varepsilon_0} \times \kappa$$

Equation 4

Since the electrical conductivity κ inside the flow channel cannot be measured directly, it is commonly replaced by the conductivity of the bulk electrolyte solution κ_B . This is a valid approximation for non-conductive samples.

However, if the solid sample contributes to the conductance inside the flow channel, the zeta potential calculated by Equation 4 gets estimated too low. This is due to the fact that the streaming potential, though it "experiences" an increased conductivity (from the electrolyte solution and the conductive sample) inside the flow channel relates only to the smaller (electrolyte) conductivity. The zeta potential calculated according to Equation 4 is therefore underestimated and denoted as the "apparent" zeta potential.

2.2 Fairbrother-Mastin approach

In order to obtain the correct zeta potential, Fred Fairbrother and Harold Mastin simply determined the cell constant L/A according to Equation 3 by measuring the electrolyte conductivity, κ_{high} , and the resistance inside the flow channel, R_{high} , at a higher ionic strength (1),

$$\zeta = \frac{dU_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{1}{R} \times \kappa_{high} \times R_{high}$$

Equation 5

The approach by Fairbrother and Mastin assumes that the additional conductance introduced by the solid sample gets suppressed when the conductivity of the electrolyte solution increases. It is primarily applicable to correct for the influence of surface or interfacial conductance. For other sources of conductance, i.e. electronic or ionic conductance of the solid sample, the assumption of suppressing this additional conductance at high ionic strength may be invalid.

3 Conductive samples

Different sources of sample conductance may contribute to the total conductance inside the flow channel.

3.1 Surface conductance

Common to all solid-liquid interfaces is the occurrence of the so-called surface or interfacial conductance. It arises from the accumulation of a cloud of ions in the vicinity of the solid surface that compensates the surface charge. The ion concentration at the solid-liquid interface is then increased compared to their concentration in the bulk liquid phase giving rise to the increased conductivity in the interfacial liquid layer.

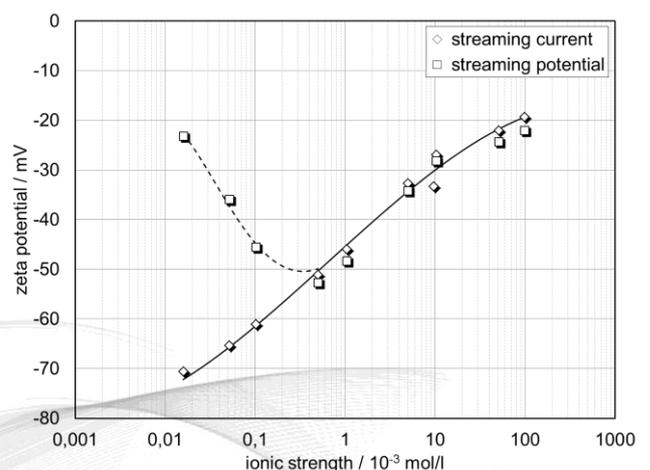


Figure 2: Zeta potential of a glass surface as a function of the ionic strength of a 1:1 electrolyte evaluated from streaming current (Equation 1) and streaming potential (Equation 4) measurements (KCl, pH 5.6).

The effect of surface conductance on the zeta potential can be assessed experimentally by measuring streaming potential and streaming current at low ionic

strength. Figure 2 shows the dependence of zeta potential for a glass surface on the concentration or ionic strength of an aqueous solution of a 1:1 electrolyte. The zeta potential was calculated according to Equation 1 for the streaming current measurement and Equation 4 for the streaming potential measurement, respectively. At low ionic strength a significant deviation between the reliable and apparent zeta potential arises, which diminishes at an ionic strength of 0.001 mol/l. The difference in the zeta potential data at low ionic strength is explained by the surface conductance. At higher ionic strength (increased electrolyte conductivity) the effect of sample surface conductance is suppressed.

The effect of surface conductance is thus depending on both the ionic strength of the electrolyte solution but also on the distance between adjacent solid surfaces. For an insulating and non-porous solid material the zeta potential data calculated from Equation 1 and Equation 4 coincide at a sufficiently high ionic strength. For solids with a planar surface this threshold is 0.001 mol/l for a distance between sample surfaces of 100 μm . For smaller distances between solids, e.g. in fiber plugs or powder beds, a higher ionic strength may be required to suppress the effect of surface conductance.

3.2 Intrinsic material conductance

Depending on the solid material and the ionic strength of the electrolyte solution, surface conductance occurs in the range of 1-2 nS. Various solid materials exhibit an "intrinsic" conductance that is significantly higher than the surface conductance. In these cases a deviation between the zeta potential calculated by Equation 1 and the apparent zeta potential may still occur even at an ionic strength that suppresses the effect of surface conductance (as shown in Figure 3).

For a metal surface the contribution of the *electronic conductance* to the total conductance inside the streaming channel is obvious. The enormous effect on the underestimation of the apparent zeta potential makes the use of Equation 4 inapplicable. A semiconductor shows smaller electrical conductivity than a metal and the difference between the reliable and the apparent zeta potential is reduced.

Ionic conductance arises for insulating though porous materials when they get soaked in an aqueous electrolyte solution. The same is true for a thin film surface coating that shows swelling in water. In both cases ions enter the porous or swollen sample surface layers resulting in an increased conductance. The presence of ionic conductance has an effect on the apparent zeta potential similar to that of a semiconductor surface. Different from electronic conductance, ionic conductance is strongly depending on the ionic strength of the electrolyte solution and – in case of swelling – also depending on the electrolyte pH.

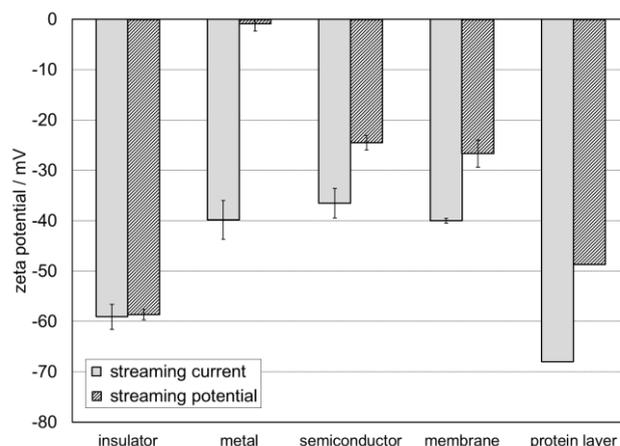


Figure 3: Comparison of zeta potential data evaluated from Equation 1 and Equation 4 for insulator, metal, semiconductor, membrane (porous material) and protein layer (swelling).

A comparison of the zeta potential results evaluated from streaming current and streaming potential measurements helps to elucidate the behavior of such complex solid materials in contact with an aqueous solution.

4 Summary

Referring to the explanations on the applicability of the zeta potential equations above, the following rules for the determination of the reliable zeta potential can be derived. The zeta potential of planar samples is preferably determined from the measurement of the streaming current especially if these samples are electronically conductive (metals). For solids of irregular shape such as fibers, textiles and granular media, the zeta potential evaluation applies the streaming potential method.

5 References

1. **Fairbrother, F. and Mastin, H.** Studies in Electroendosmosis. Part I. *Journal of the Chemical Society* 125 (1924) 2319-2339.

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