Dynamic streaming potential analysis

Carina Santner, Dr Thomas Luxbacher, Anton Paar GmbH

Zeta potential is a measure of the electrostatic interaction at the interface between a solid surface and a liquid medium. While electrophoretic light scattering enables the determination of zeta potentials for particles in a dispersion, streaming potential measurements serve as a tool for assessing the zeta potential on solid surfaces. The dynamic streaming potential is an extension of the classic streaming potential measurement and allows for real-time monitoring of the interaction between solutes and solid surfaces. This article aims to understand the principles of the dynamic streaming potential measurement and explores its various applications.

Introduction

Zeta potential is a key parameter in colloid science and electrochemistry. It is established on the surface of any material when it comes in contact with a liquid medium, typically an aqueous solution, and is thus an interfacial property. Put simply, it refers to the electric charge that exists on the surface of small particles when they are suspended in a liquid or on a solid surface that is surrounded by an aqueous solution.

Measuring the zeta potential helps us understand how surfaces perform, how well particles stay dispersed, and how solutes interact with solid surfaces. Knowing the zeta potential of macroscopic surfaces is important in applications like water treatment, creating materials for medical applications or formulating various cosmetic and detergent products. Understanding a material's zeta potential helps to improve its surface for better performance.

In this article, we introduce the dynamic streaming potential, discerning its distinctions from the classic streaming potential, and elucidate the diverse range of applications that offers users a wide range of new possibilities.

Classic streaming potential

Streaming potential is a phenomenon that occurs in fluid-filled capillaries or porous materials when there is relative motion between the fluid and the solid surfaces [1]. Solid materials with a flat surface are placed in a suitable measurement cell in a way to create a rectangular flow channel *(Figure 1a)*.

Subsequently, the channel is filled with an aqueous electrolyte solution, typically a diluted salt solution. This leads to charge formation at the interface between the solid sample and the electrolyte solution. These charges are then compensated by oppositely-charged ions from the diluted salt solution.

When the measurement is started, a pressure gradient Δp is applied to the electrolyte solution, inducing a flow through the capillary in the measurement cell, which is shown in *Figure 1b*. This movement causes the charges, which were established before at the liquid/solid interface, to travel with the flow.

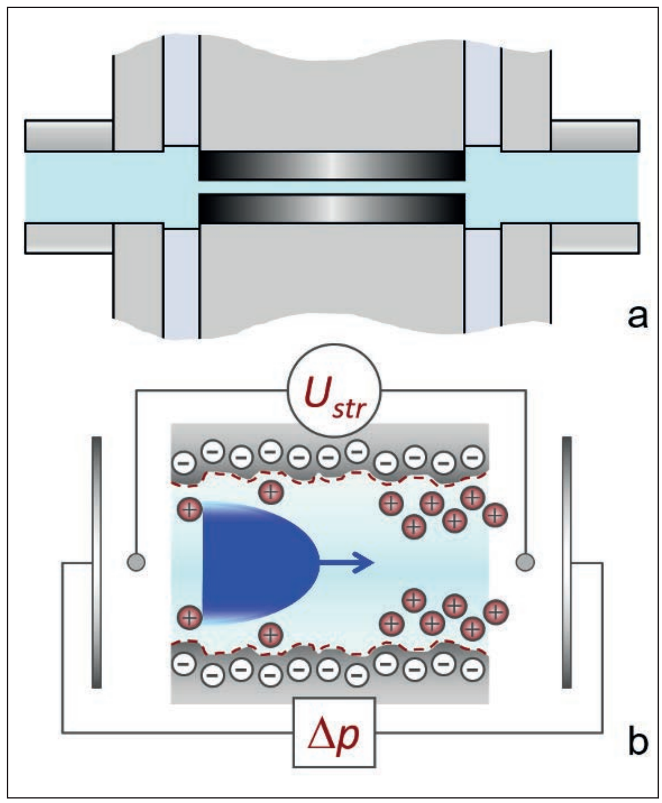

Figure 1: (a) Schematic presentation of the formation of a rectangular flow channel between samples with a flat surface. (b) Generation of streaming potential by liquid flow through a capillary channel enforced by a pressure gradient.

This results in an accumulation of charge carriers on one side of the measuring cell and a depletion on the opposite side.

A so-called streaming potential Ustr is generated along the flow channel. The measured streaming potential, in combination with the applied pressure, is then used to calculate the solid surface zeta potential U_{str} of the sample.

Equation 1: Calculation of the Solid Surface Zeta Potential

$$\zeta = \frac{dUstr}{d\Delta p}\frac{\eta \kappa_B}{\varepsilon_r \varepsilon_o}$$

In Equation 1, ε_o is the vacuum permittivity, and εr, η and K_B are the dielectric constant, the electrolyte viscosity and conductivity of the electrolyte solution.

The zeta potential of the sample's surface depends on several factors.

It is strongly pH dependent. Measurements at different pH values give valuable information on the composition of the sample's surface, i.e. the presence of acidic or basic functional groups. The pH dependence of the zeta potential is therefore frequently recorded to understand the nature of surface functional groups and to determine the isoelectric point (pH of the aqueous solution where the zeta potential reverses its sign).

The concentration of ions (ionic strength) in the aqueous phase also has an influence on the zeta potential. That means different electrolyte solutions return different zeta potential values. If more ions are available, the initial surface charge can be compensated more effectively, which results in a minor zeta potential.

When exchanging acid or base for pH adjustment by a different chemical compound (e.g. surfactant, polyelectrolyte, polypeptide, protein), the interaction of such a compound with the material's surface may be investigated.

Dynamic streaming potential

The measurements of the dynamic streaming potential is an extension of the classic surface zeta potential analysis, monitoring the interaction between solutes and solid surfaces in real time. When assessing the dynamic streaming potential, the focus lies on temporal changes rather than static processes. This involves examining variations, such as the accumulation of dissolved substances, as well as the effects of adsorption and desorption on solid surfaces, over time. The principle is quite easy to understand - the adsorbate is added to the electrolyte solution and the changes of the streaming potential are recorded over time.

If the adsorption of substances on a surface is reversible, the process of desorption can be achieved by exchanging liquids, for example. Adsorbed substances desorb from the surface and the initial state of the solid surface is successively approached.

In the assessment of the dynamic streaming potential, the primary emphasis lies on monitoring changes in charge throughout the whole measurement. It is necessary to understand that this emphasis does not imply a change in the sign of the zeta potential, but rather the change of the net charge of the solid surface. Dynamic processes at the solid-water interface can be accomplished by adjusting different factors such as the liquid composition of the electrolyte solution, allowing for flexibility in achieving the desired changes in charge.

Applications

The phenomena of adsorption and desorption play essential roles in various aspects of daily life, spanning activities such as textile laundry, hair washing, and applications within the medical and life sciences.

While certain applications benefit from the desirable adsorption of substances onto surfaces, others necessitate its prevention. Consequently, the evaluation of the dynamic streaming potential proves valuable across numerous industries for examining the adsorption kinetics of substances onto various solid surfaces.

Adsorption processes occur in numerous applications, which are impossible to count in this article. We therefore focus on three examples and discuss selected results in detail.

Cosmetics

Hair care is a versatile area as there are different hair types, different trends and other factors that influence hair health, all of which require specific hair care formulations. Developing such versatile formulations necessitates the understanding of the effect of haircare products on the hair texture directly. Investigating surface zeta potential at the interface between the hair fibre and an aqueous emulsion of the hair care product helps us understand how formulation components of the product interact with the hair surface and allows for precise adjustments of the formulation composition.

By measuring the dynamic streaming potential, when applying a haircare formulation on human hair, the cosmetic chemist gets information about the interaction with the hair structure during application. *Figure 2* shows a typical hair washing cycle. Here, part of a tress of Caucasian hair was first rinsed with an aqueous buffer solution and then shampooed. The shampoo was washed out before a conditioner was applied.

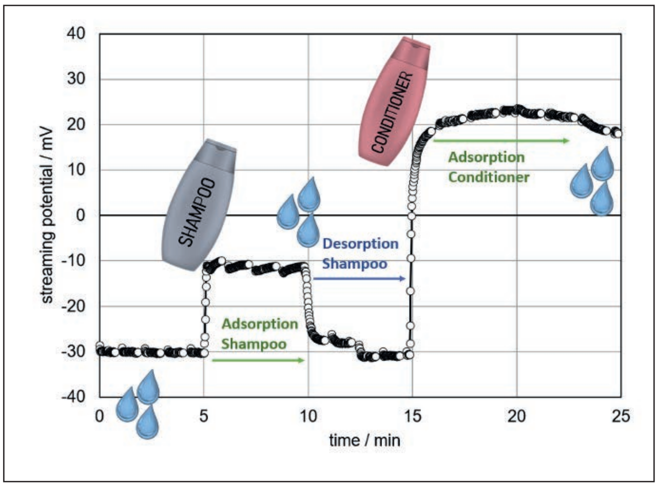

Figure 2: Dynamic streaming potential results for hair treated with shampoo followed by conditioner.

At first, the untreated hair exhibits a negative streaming potential (corresponding to a negative zeta potential). The application of shampoo lowers the magnitude of the zeta potential. Subsequent rinsing of the shampoo returns the streaming potential to its initial values, suggesting the complete desorption of shampoo components. Upon the adsorption of the conditioner, the streaming potential reverses its sign, indicating the conditioner's adsorption. After rinsing the conditioner, the streaming potential reduces in magnitude but remains positive. This suggests that a part of the conditioner becomes irreversibly bound to the hair surface, and some excess amount is removed during the rinsing process.

Textile care

Adsorption processes play a significant role in textile care, particularly in the context of cleaning and stain removal, the application of fabric softeners or the adsorption of specific functionalising materials.

Detergents and stain removers contain surfactants and other chemicals that facilitate the desorption of dirt, oils, and other stain components. The cleaning agents surround the stain particles, making them more water-soluble and allow for easier removal during the washing process. Fabric softeners use cationic surfactants that adsorb onto the fabric's surface. These positively charged molecules reduce the friction between fibres, making the fabric feel softer and smoother. Additionally, they can provide antistatic properties and improve the overall feel of the textile.

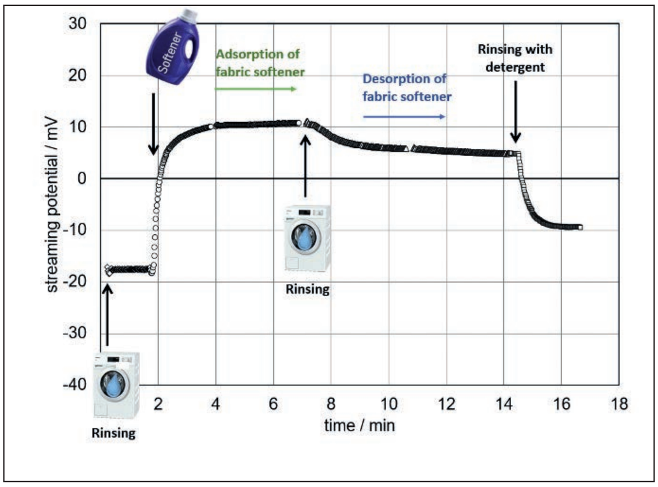

Figure 3: Dynamic streaming potential of cotton/modacrylic fabric during adsorption of fabric softener and subsequent desorption with detergent.

In the specific application shown in *Figure 3*, the adsorption of the fabric softener and the consecutive desorption process using an anionic surfactant is investigated by measuring the change of the streaming potential over time. [2] A plug-shaped sample of a cotton-modacrylic fabric was first rinsed with an aqueous buffer solution before exposure to a dilute emulsion of a fabric softener (at t = 2 min). The cationic active in this softener formulation adsorbs on the fabric surface, reverses the sign of the streaming potential and approaches adsorption equilibrium after approx. 2 min. Rinsing the softener-treated fabric with the initial buffer solution removes reversibly-bound cationic compounds, thus lowering the positive charge. The desorption of softener is enhanced by treating the fabric with an anionic surfactant. The final streaming potential is negative but at a lower magnitude than the initial value for the untreated fabric. This may indicate some remaining active softener or an adsorbed layer of the anionic surfactant.

Protein adsorption

The research field of protein adsorption on surfaces appears to be as popular as ever. It refers to the process by which proteins adhere to the surface of a material. This phenomenon is significant in various fields, including biology, medicine, and materials science. When a material comes into contact with a biological fluid, such as blood or saliva, proteins in the fluid can bind to the material's surface.

The adsorption of proteins onto surfaces is a dynamic and complex process influenced by various factors, including the physicochemical properties of the material, the nature of the proteins, and the surrounding environment. Proteins can undergo conformational changes upon adsorption, and the extent and pattern of adsorption can impact the performance and biocompatibility of the material.

In medical applications, understanding protein adsorption is crucial for the development of biomaterials, implants, and medical devices. The interaction between proteins and surfaces can influence cell adhesion, tissue response, and the overall biocompatibility of the material.

In the adsorption study shown in *Figure 4*, the process of bovine serum albumin (BSA) adsorption onto a titanium dental implant surface was evaluated. [3] Initially, the surface's zeta potential was recorded at -80 mV. As BSA began to adsorb, there was a noticeable decrease in the net charge, leading to a shift in the zeta potential towards less negative values, reaching -52 mV after 20 min.

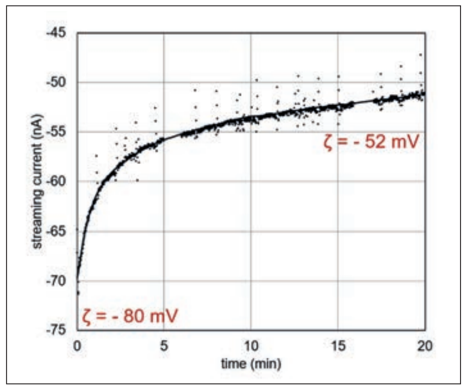

Figure 4. Time-dependent assessment of the streaming potential of BSA adsorbing onto a titanium dental implant

The compatibility of implant materials like stainless steel or titanium with the human body relies on the implant surface's biocompatibility. The biocompatibility is influenced by various surface attributes. The charge on the surface governs the electrostatic attractions that are crucial for binding proteins, necessary for integrating materials like dental implants into bone, the so-called 'osseo-integration'. Thus, a deep understanding of these surface characteristics is essential in creating and evaluating biomaterials for implants.

Conclusion

In this article, we introduce the measurement of the dynamic streaming potential. The combination with the classic streaming potential method for the zeta potential analysis and the recording of adsorption isotherms gives a better understanding of adsorption phenomena at the solid-water interface. The applications detailed in this report demonstrate that the dynamic streaming potential analysis offers valuable insights into various systems, such as those related to detergents and textiles, or hair care products. The user gains a comprehensive understanding about what happens during practical application and related interactions. This approach facilitates a comprehensive understanding of the entire system and its interplay, enabling optimisation of products within these contexts.

References

Luxbacher, T., The ZETA Guide. Principles of the streaming potential technique. Anton Paar GmbH, 2014

Luxbacher, T., et al., Proceedings of the 7th International Textile, Clothing and Design Conference, ed. Dragcevic Z., University of Zagreb, 2014

Lorenzetti, M., et al., Biomed. Mater. 10 (2015) 045012