Zeta-Potential

Definition

The zeta potential ζ is a measure of the electrical charge developed when a solid surface is brought into contact with an aqueous solution. More specifically, when a solid surface is brought into contact with an aqueous solution an electrical charge is generated at the interface. As a result, local free ions in the solution tend to rearrange themselves such that a thin region of non-zero net charge density exists near the interface. The arrangement of the charges at the solid–liquid interface and the balancing counterions in the liquid is usually referred to as the electrical double layer (EDL). There is a thin layer of counterions immediately next to the charged solid surface, called the compact layer. The counterions in the compact layer are immobile due to the strong electrostatic attraction. Counterions outside the compact layer are mobile. This part of the EDL is called the diffuse layer. The zeta potential is the electrostatic potential at the boundary dividing the compact layer and the diffuse layer.

Cross References

- ► Temperature Effects on the Zeta Potential
- ► Measuring Zeta Potential, Methods

Zeta Potential Measurement

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Synonyms

Electrokinetic potential; Surface potential

Definition

►Zeta potential is defined as the electrical potential at the shear plane of the electric double layer. Measurement techniques are based on indirect readings obtained during electrokinetic experiments. Typically, the magnitude of the zeta potential varies between $0-200$ mV where both negative and positive values are possible depending on the electrochemistry of the solid-liquid interface.

Overview

►Zeta potential refers to the electrokinetic potential at the shear surface of the electric double layer. Along with surface conductance, zeta potential is an important parameter in the study and modeling of a variety of electrokinetic phenomena relevant to microfluidics and Lab-on-a-Chip devices. The zeta potential of a solid-liquid interface depends on a number of factors including the ion concentration, ion valence, pH level and temperature of the solution. For this reason each solid-liquid interface has its own unique zeta potential that must be measured. Zeta potential measurements are based on indirect readings using one of the following electrokinetic phenomena: electro-osmotic flow, electrophoresis and streaming potential. In terms of microfluidics, electro-osmotic and streaming potential techniques are used in the study of microchannels and capillaries while electrophoresis based methods are used to study charged particles such as fluorescent beads, DNA and proteins.

This document is organized in the following manner: first, a brief introduction to the electric double layer and its significance to electrokinetic phenomenon. Second, the principles behind zeta potential measurements based on the three types of electrokinetic phenomenon are discussed, with special attention to the advantages and disadvantages of each method. Finally, a few key research results for each of the methods are presented. The purpose of this entry is to provide the reader with a brief introduction to the fundamentals of zeta potential measurements, for a more detailed description of zeta potential measurements, electric double layer and electrokinetic phenomenon the reader should consult the various texts that discuss these topics in depth [1–4].

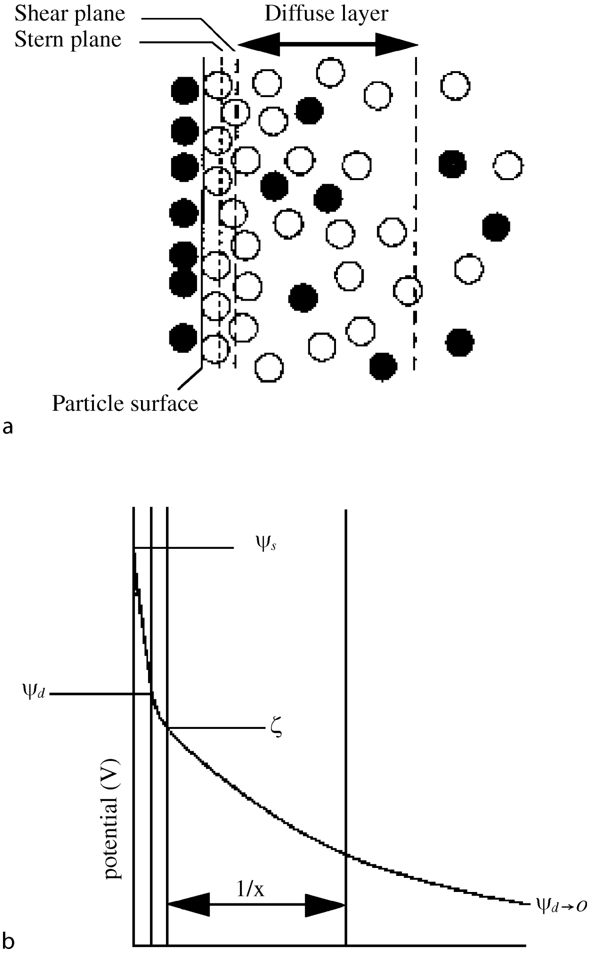
Basic Methodology

Electric Double Layer and Zeta Potential

In most cases, when a solid surface comes in contact with an aqueous solution an electric charge develops at the interface. The surface charge influences the nearby ions creating a non-uniform electric charge distribution near the interface known as the electric double layer (EDL) [1–4]. Several mechanisms cause this effect including ionization, ion adsorption and ion dissolution.

The earliest theoretical study on the structure of the EDL was performed by Helmholtz (1879) who proposed that the charged interface is surrounded by two condensed planes of oppositely charged ions. In actual fact, thermal forces tend to spread out the ions creating a diffuse region around the interface. Gouy (1910) and Chapman (1913) independently tackled this problem by applying the kinetic molecular theory to the diffuse region of ions. In their model, the electric potential and charge distributions are described using the well-known Poisson–Boltzman equation of statistical physics. Although the model is based on statistical grounds, it produces accurate results when the surface potential is low or the electrolyte concentration is not too high. The major defect of the Gouy–Chapman model is that the ions are treated as point charges; however, in reality ions have a finite size that limits the distance they can approach a surface. Stern (1924) resolved this issue and proposed a new model that divides the EDL into an inner compact layer and an outer diffuse layer. Inside the compact layer the size of the ions is considered while in the diffuse layer the Gouy–Chapman model is still applied.

As shown in Fig. 1, the Stern layer is approximately one ion radius thick and is defined by the solid surface and the Stern plane. Counterions in the Stern layer experience strong electrostatic forces and are essentially immobilized against the surface. Ions located outside the Stern plane experience a weaker electrostatic attraction and form the mobile diffuse layer of the EDL. The boundary separating these two regions is defined as the shear plane. In the diffuse layer, competing electrostatic and thermal forces creates a non-zero concentration of ions that is a maximum at the surface and decreases gradually with distance until it reaches equilibrium with the bulk concentration. The thickness of the diffuse layer is often characterized by the Debye length λ_d which can vary from several nanometers to micrometers depending on the concentration and properties of the solution.



Zeta Potential Measurement, Figure 1 Schematic representation of the electric double layer using Gouy–Chapman–Stern model [3]

The double layer acts to neutralize the surface charge creating an electrokinetic potential distribution between the interface and the solution. This voltage difference is on the order of millivolts and is refereed to as the surface potential ψ_S. Through the Stern layer the electric potential varies almost linearly to the Stern plane potential ψ_d and then decreases gradually in the diffuse layer until it reaches zero far away from the surface. The electric potential at the shear plane is known as the electrokinetic potential or zeta potential (ζ). Because the zeta potential is located at the fluid flow boundary it is an important parameter for analyzing a variety of electrokinetic phenomenon.

It should be noted that the surface potential and the zeta potential do not always have the same sign [3]. If adsorbed polyvalent or surface active counterions are present the zeta potential may decrease or increase substantially. Thus the zeta potential measurements can not always be extrapolated to determine the surface potential.

In the EDL, the electric potential and net charge density are described by the Poisson–Boltzman equation [1–4].

The Poisson equation describes the electric field within a dielectric medium:

$$\nabla \cdot (\nabla \psi) = \frac{-\rho_{\mathrm{e}}}{\varepsilon_{\mathrm{r}}\varepsilon_0} \tag{1}$$

where ε_0 and ε_{r} are the dielectric permittivity of a vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}$ C/Vm) and the relative dielectric permittivity of the solution. The net charge density, ρ_{e}, is the sum of negative and positive ions ($\rho_{\mathrm{e}} = \sum_i z_i e n_i$). Assuming that the Boltzmann distribution is valid, the ionic concentration in the EDL is given by:

$$n_i = n_0 \exp\left(\frac{-z_i e \psi}{k_{\mathrm{b}} T}\right) \tag{2}$$

where n_i is the specific number of the ith ion, n_0 is the number of ions in the bulk solution, z is the valence of the ion, e is the charge of an electron, k_{b} is Boltzmann's constant and T is the absolute temperature. Combining Eqs. (1, 2) leads to the Poisson–Boltzman equation:

$$\nabla \cdot (\nabla \psi) = \frac{-\sum_i^N z_i e n_0 \exp\left(\frac{-z_i e \psi}{k_{\mathrm{b}} T}\right)}{\varepsilon_{\mathrm{r}}\varepsilon_0} \tag{3}$$

For the special case of a symmetric electrolyte solution ($z : z = 1 : 1$) the Poisson–Boltzman equation reduces to:

$$\nabla \cdot (\nabla \psi) = \frac{2 n_0 z e}{\varepsilon_{\mathrm{r}}\varepsilon_0} \sinh\left(\frac{z e \psi}{k_{\mathrm{b}} T}\right) \tag{4}$$

Applying the non-dimensionalized parameters ($\Psi = ze\psi/kT$, $X = x/L$) to Eq. (4), yields

$$\nabla \cdot (\nabla \Psi) = \kappa^2 L^2 \sinh(\Psi) \tag{5}$$

where κ is the Debye–Hückel parameter and is given by $\kappa = (2z^2 e^2 n_0/\varepsilon_{\mathrm{r}}\varepsilon_0 k_{\mathrm{b}} T)^{1/2}$. As stated previously, the EDL thickness is characterized by the Debye length ($\lambda_{\mathrm{d}} = 1/\kappa$). For most microfluidic applications involving microchannels the appropriate boundary conditions for solving Eq. (4) are $\psi = \zeta$ at the shear plane and the assumption that $\psi \to 0$ as $x \to \infty$. However, this is not the case for nanochannels where over-lapping boundary layers invalidate the assumption of uniform bulk properties far from the wall. Numerical techniques are usually employed to calculate the electric potential and charge distribution from Eq. (3). Analytical solutions are possible for a few cases where simplified assumptions are justified.

Electrokinetic phenomena arise when the mobile layer of the EDL interacts with an externally applied electric field resulting in relative motion between the solid and liquid phases. There are three types of electrokinetic phenomena relevant to microfluidics: electro-osmotic flow, streaming potential and electrophoresis. In all of these cases, the zeta potential is a key parameter that defines either the fluid flow or particle motion. Since it is not possible to probe the zeta potential directly, measurements are based on indirect readings obtained from electrokinetic experiments. The following discussion focuses on modern methods of measuring the zeta potential using electro-osmotic flow, electrophoresis and streaming potential.

Electro-Osmotic Flow

When an electric field is applied tangentially to the EDL, the mobile ions in the diffuse layer begin to migrate towards the appropriate electrode. Through viscous drag, the motion of the ions causes the surrounding liquid to move generating electro-osmotic flow. The movement also generates an electric current. Since the applied electric field is tangential to the surface, the resulting ion migration does not affect the charge density in the EDL. Thus the body force ($\boldsymbol{F}_{\mathrm{b}} = \rho_{\mathrm{e}} \boldsymbol{E}$) experienced by the fluid is limited to the diffuse layer. Note that it is the external field, $\boldsymbol{E}$, that drives the fluid and not the internal field within the EDL. The resulting velocity profile is *plug* like, where the velocity is zero at the wall (no-slip condition) and rises to a uniform velocity in the bulk. Since the EDL thickness is very small (~ 30 nm) compared to microchannel (~ 50 µm), to an observer it appears as if the fluid *slips* by the surface. The velocity at the edge of the EDL is given by the classic Helmholtz-Smoluchowski equation:

$$u_{\mathrm{HS}} = -\frac{\varepsilon_0 \varepsilon_{\mathrm{r}} \zeta E_x}{\eta} \tag{6}$$

where E_x is the tangential electric field and ζ is the zeta potential. Usually the group of terms, $\varepsilon_0\varepsilon_{\mathrm{r}}\zeta/\eta$, are combined together into a proportionality constant called the electro-osmotic mobility (μ_{eo}) of the solid-liquid interface. Since the velocity only varies in the EDL, the total flow rate is approximated by $Q = u_{\mathrm{HS}} A_{\mathrm{c}}$, where A_{c} is the cross-sectional area of the microchannel. Thus it is possible to determine the zeta potential by measuring the fluid velocity or volume flow rate under electro-osmotic flow.

Volume Method

One of the earliest methods for determining the zeta potential was to measure the volumetric flow rate of a liquid transported in a capillary under electro-osmotic flow. This method seems simple in principal; however, the small flow rates typical of electro-osmotic flow (~ nl/min) make it difficult to obtain accurate measurements. Normally the flow rate is determined by following the progression of a meniscus or bubble in an adjoining capillary which in it self produces a variety of errors [2].

Direct Visualization Methods

Several variations of micro flow visualization have been developed for microfluidic applications such as particle-based flow velocimetry and scalar-based flow velocimetry [5]. In terms of the zeta potential measurement, these visualization techniques such as micro-PIV are used to measure the velocity profile and flow rate under electro-osmotic flow. Once the velocity is known the zeta potential can be calculated from Eq. (6). The main advantage of using a flow visualization technique is that the electro-osmotic velocity can be measured directly and in real time. In general, the small amount of particles or dye used has a negligible effect on the electro-osmotic flow being measured. The only significant disadvantage of this technique is that the extent and cost of the hardware may be prohibitive.

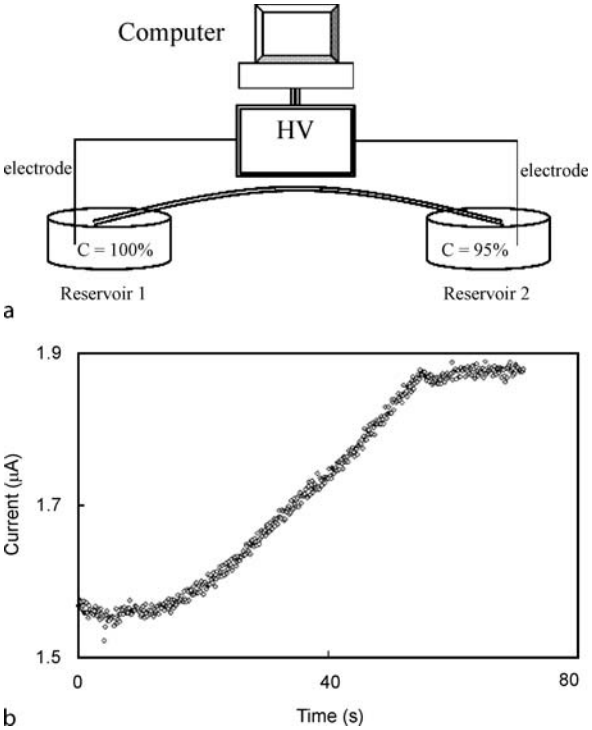
Current-Monitoring Methods

Recently a method has been developed to determine the average flow velocity by measuring the electric current in a microchannel under electro-osmotic flow [6, 7]. The experimental set up is shown in Fig. 2, and consists of a microchannel, a high voltage power supply and a data acquisition system. The microchannel and reservoir 2 are initially filled with an electrolyte solution that has a slightly different concentration than reservoir 1 ($c_1 - c_2 = 5\%$). The concentration difference must be small so that the zeta potential and ionic concentrations are nearly uniform throughout the microchannel.

Immediately after the two solutions are in contact, the high voltage power supply is turned on to induce electro-osmotic flow. As the fluid in reservoir 1 displaces the existing fluid in the microchannel the electric current draw changes. Initially the current is constant and then changes linearly until it reaches another plateau once the initial fluid is completely replaced. The time required for the displacement represents the time required for the solution to travel through the channel length, which can be used to determine the average electro-osmotic velocity:

$$u_{\text{ave}} = \frac{L}{\Delta t} \tag{7}$$

where L is the length of the channel and the zeta potential can be calculated from Eq. (6). The major problem associated with this method is the ambiguity surrounding the displacement time. Small current fluctuations and gradual transitions at the beginning and end of the displacement process may cause errors in measuring Δt.



Zeta Potential Measurement, Figure 2 Schematic of the experimental setup for the current-monitoring technique (*a*) and a typical current time plot (*b*) [7]

To solve this problem, an improved method was developed to determine the zeta potential by using the slope of the current-time relationship [7]. The slope of the current-time relationship is given as:

$$\text{slope} = \frac{\Delta I}{\Delta t} \tag{8}$$

Under electro-osmotic flow the current in the channel is composed of three parts: 1. the bulk conductivity current, $I_{\text{cond,bulk}}$, the surface conduction current, $I_{\text{cond,surf}}$, and the convection current created by the fluid motion, $I_{\text{cond,conv}}$. Typically, the convection current is several orders of magnitude smaller than the other currents and is neglected. Therefore, the total current is given as:

$$I_{\text{total}} = I_{\text{cond,bulk}} + I_{\text{cond,surf}} = \lambda_{\text{b}} A_{\text{c}} E_{\text{x}} + \lambda_{\text{s}} P_{\text{w}} E_{\text{x}} \tag{9}$$

where λ_{b} is the bulk conductivity of the fluid, λ_{s} is the surface conductivity, A_{c} is the cross-sectional area of the channel, P_{w} is the wetted perimeter and E_{x} is the applied electric field. Substituting Eq. (9) and assuming that $\Delta\lambda_s = 0$, Eq. (8) reduces to:

$$\text{slope} = u_{\text{ave}} \frac{E_x A_c (\lambda_{b2} - \lambda_{b1})}{L} \tag{10}$$

The above expression can then be rearranged to solve for u_{ave} and then substituted into Eq. (6) to calculate the zeta potential. In addition, the surface conductivity can be measured using this method. In this case, the reservoirs are filled with the same fluid and the total current is measured. The surface conductivity is calculated from Eq. (9) assuming that the bulk conductivity is already known.

The disadvantages of the current monitoring technique are that

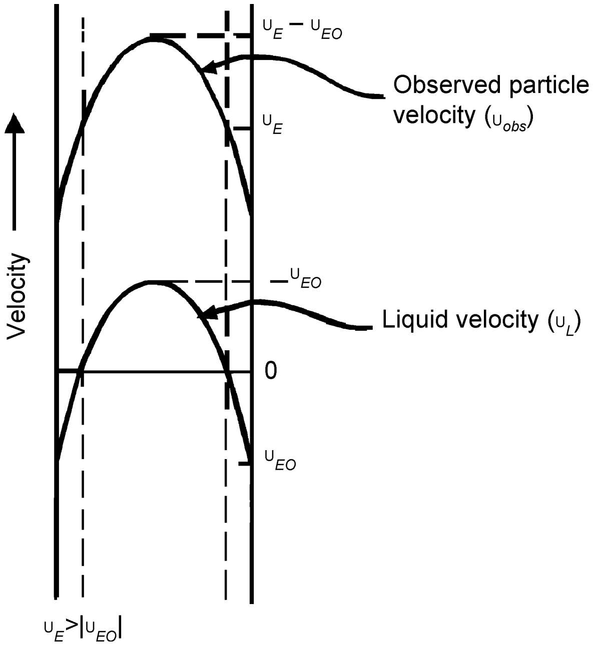
- the electro-osmotic flow is measured indirectly through the current draw,
- the method assumes constant zeta potential between the two fluids,
- the difference in conductivity must be large enough so that the current change is measurable, and
- there is a lack of spatial and temporal resolution since the zeta potential represents an average value.

The advantage of using this method is in its simplicity, current-time measurements can be performed quickly and with relatively little infrastructure compared to other methods.

It should be noted that there are several additional sources of error for electro-osmotic based measurements. Joule heating must be controlled or temperature fluctuations may cause significant changes in zeta potential, viscosity and other fluid properties. Another source for error is undesired pressure driven flow caused by small head and meniscus (Laplace pressure) differences at the reservoirs. In fact, even modest differences (~ 5 mm of head) can lead to pressure driven flow rates comparable to the electro-osmotic flow being studied. Also electrolysis occurring at the electrodes may create a pH gradient along the channel creating significant errors in the zeta potential measurement. On the other hand, electro-osmotic flow and electro-osmotic pumping are common methods of transporting fluids in microfluidic devices. Therefore, zeta potential measurements based on electro-osmotic flow provide the most accurate representation of on-chip operating conditions.

Electrophoresis

Electrophoresis refers to the movement of a charged surface relative to a stationary liquid. For instances, under an applied electric field a negatively charged particle will migrate towards the positive electrode (anode).



Zeta Potential Measurement, Figure 3 Stationary level, fluid velocity and particle velocity distribution in an electrophoresis cell [1]

For spherical particles the velocity is given as [1]:

$$u_E = \mu_{ep} \boldsymbol{E} \tag{11}$$

where μ_{ep} is called the electrophoretic mobility of the particle. The electrophoretic mobility is related to the zeta potential through:

$$\mu_{ep} = \frac{2\varepsilon_0 \varepsilon_r \zeta}{3\eta} f_1(\kappa a) \tag{12}$$

where a is the radius of the particle, η is the viscosity of the liquid, κ is the Debye–Hückel parameter and $f_1(\kappa a)$ is a correcting function that depends on the shape of the particle. Therefore the zeta potential can be calculated from Eq. (12) if the electrophoretic mobility is known.

The most popular method of measuring electrophoretic mobility is micro-electrophoresis. In micro-electrophoresis, particles are placed in a closed capillary with electrodes at either end. When an electric field is applied the particles migrate towards the electrode and their velocities are measured. Because the capillary walls are charged the applied electric field will also induce an electro-osmotic flow. However, since the capillary is closed a back pressure creates a net zero flow in the tube (see Fig. 3). The particle velocity is a combination of the electrophoretic motion and the fluid flow. To obtain the true electrophoretic mobility the particles must be tracked along the stationary layer where the fluid velocity is zero.

For a circular capillary the liquid velocity across the tube is given by the electro-osmotic flow and the back pressure flow:

$$u = u_{\mathrm{EO}} + u_{\mathrm{BP}} \tag{13}$$

For a pressure driven flow the velocity profile is given by the solution of the Poiseuille equation ($u_{\mathrm{BP}} = -c(a^2 - r^2)$), where c is a constant. The value of c is determined by realizing that the net flow in the capillary is zero, $c = 2u_{\mathrm{EOF}}/a^2$. The velocity profile is then given by:

$$\frac{u}{u_{\mathrm{EOF}}} = 2\frac{r^2}{a^2} - 1 \tag{14}$$

The stationary level is determined by setting u to zero so that $r_{\mathrm{stat}} = a/\sqrt{2}$. The same procedure repeated for a plane cell results in $y_{\mathrm{stat}} = a(1 - 1/\sqrt{2})$. Since the velocity varies significantly across the capillary, locating the stationary level is critical for obtaining accurate results.

Early methods of measuring the particle velocities involved manually tracking them along a reference grid using a microscope. This process was tedious and not very accurate since only a few particles could be tracked at a time. Modern devices use a variety of measurement techniques to increase the accuracy and throughput of the procedure. Current devices use laser Doppler velocimetry (LDV) and phase analysis light scattering (PALS) to measure particle velocity. New developments focus on suppressing electro-osmotic flow through surface modifications of the capillary or by using oscillating electric fields to take advantage of time scale differences between electrophoresis and electro-osmotic flow. It should be noted that electrophoresis is also used as a method of separating charged particles such as proteins and DNA in a variety of biomedical applications. A few examples include gel electrophoresis, isoelectric focusing and capillary zone electrophoresis.

Streaming Potential

If an electrolyte solution is forced through a microchannel under pressure driven flow, charges in the EDL move downstream resulting in an electric current called the streaming current:

$$\boldsymbol{I}_{\mathrm{s}} = \int_{v} \boldsymbol{u}\rho_{\mathrm{e}}\,\mathrm{d}v \tag{15}$$

where $\boldsymbol{I}_{\mathrm{s}}$ is the streaming current, $\boldsymbol{u}$ is the velocity and ρ_{e} is the net charge density. The accumulation of these charges creates a potential difference across the channel known as the streaming potential. This potential, in turn, drives the conduction current in the opposite direction of the streaming current. The conduction current is the sum of the bulk and surface conduction:

$$\boldsymbol{I}_{\mathrm{c}} = A_{\mathrm{c}}\boldsymbol{E}_{\mathrm{s}}\lambda_{\mathrm{b}} + P_{\mathrm{w}}\boldsymbol{E}_{\mathrm{s}}\lambda_{\mathrm{s}} \tag{16}$$

where $\boldsymbol{I}_{\mathrm{c}}$ is the conduction current, A_{c} is the cross-sectional area, $\vec{E}_{\mathrm{s}}$ is the streaming potential electric field, P_{w} is the wetting perimeter, λ_{b} and λ_{s} are the bulk and surface conductivities, respectively. At steady state, $\boldsymbol{I}_{\mathrm{c}} + \boldsymbol{I}_{\mathrm{s}} = 0$ and the general relationship between the streaming potential and *zeta potential* can be derived as:

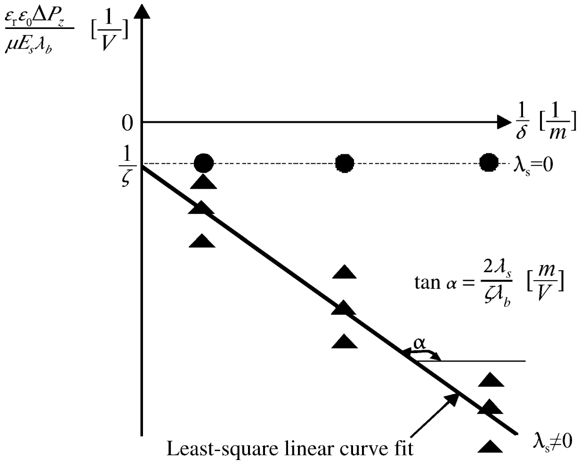
$$\frac{\boldsymbol{E}_{\mathrm{s}}}{\Delta P} = \frac{\varepsilon_0\varepsilon_{\mathrm{r}}\zeta}{\eta\,(\lambda_{\mathrm{b}} + f\lambda_{\mathrm{s}})} \tag{17}$$

where ΔP is the pressure difference, f is a shape factor for the channel and is given as the ratio of the wetted perimeter to the cross-sectional area ($f = P_{\mathrm{w}}/A_{\mathrm{c}}$). One can see that Eq. (17) provides a basis for calculating the zeta potential and surface conductance if the pressure drop and streaming potential are measured. By rearranging Eq. (17) a more convenient form of the streaming potential equation appears:

$$\frac{\Delta P\varepsilon_0\varepsilon_{\mathrm{r}}}{\eta\boldsymbol{E}_{\mathrm{s}}\lambda_{\mathrm{b}}} = \frac{1}{\zeta} + \left(\frac{2\lambda_{\mathrm{s}}}{\zeta\lambda_{\mathrm{b}}}\right)f \tag{18}$$

For a physical system λ_{s} and ζ should remain constant. Eq. (18) shows that there is a linear relationship between the streaming potential measurement and the form factor as shown in Fig. 4. The zeta potential is calculated from the intercept and the surface conductivity from the slope. Therefore, unless the surface conduction is neglected at least two measurements are required to determine the zeta potential and surface conductivity. For practical purposes multiple streaming potential experiments are performed for different form factors to increase the accuracy of the measurements.

A typical experimental apparatus consists of a capillary connected to a pump through a pipe network and a series of transducers strategically placed to measure the pressure drop, flow rate, streaming potential and conductivity. The piping network is designed so that the flow direction can be reversed in the microchannel. Particular attention is required in the preparation and assembly of the apparatus. The potential must be measured with a high impedance electrometer so that the streaming current and therefore the flow in the microchannel are not disturbed. Also, it is important to use electrodes that respond reversibly to current flows (eg. Ag/AgCl).



Zeta Potential Measurement, Figure 4 Plot of the relationship between streaming potential, surface conductance and zeta potential used in the streaming potential method [8]

To prevent the electrodes from polarization streaming potential measurements must not exceed 1 – 2 minutes before the flow should be reversed and measurements taken again. By reversing the flow any errors caused by the asymmetry of the electrode system are also reduced. For a given gap height this procedure should be repeated for several different flow rates. Consequently, in order to obtain an accurate streaming potential plot a number of experiments (∼ 20) must be performed.

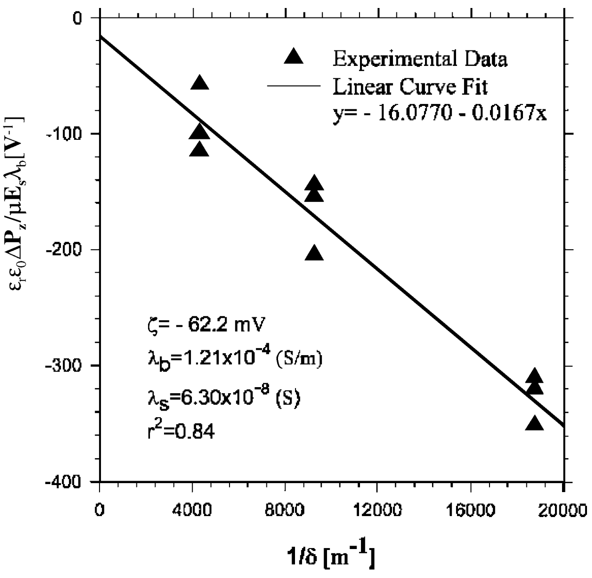
It is important to emphasize the need to measure the surface conductance as well as the zeta potential. If the surface conductance is neglected in Eq. (18) the zeta potential can be severely underestimated. It should also be noted that the equations derived above neglect electrokinetic effects on the flow by assuming a Poiseuille type flow through the microchannel. In actuality the streaming potential creates a reverse electro-osmotic flow in the channel that decreases the overall flow rate. The decreased velocity creates the appearance of an increased fluid viscosity and is known as the electroviscous effect. Generally this effect is prevalent in microchannels less than 50 μm.

Key Research Findings

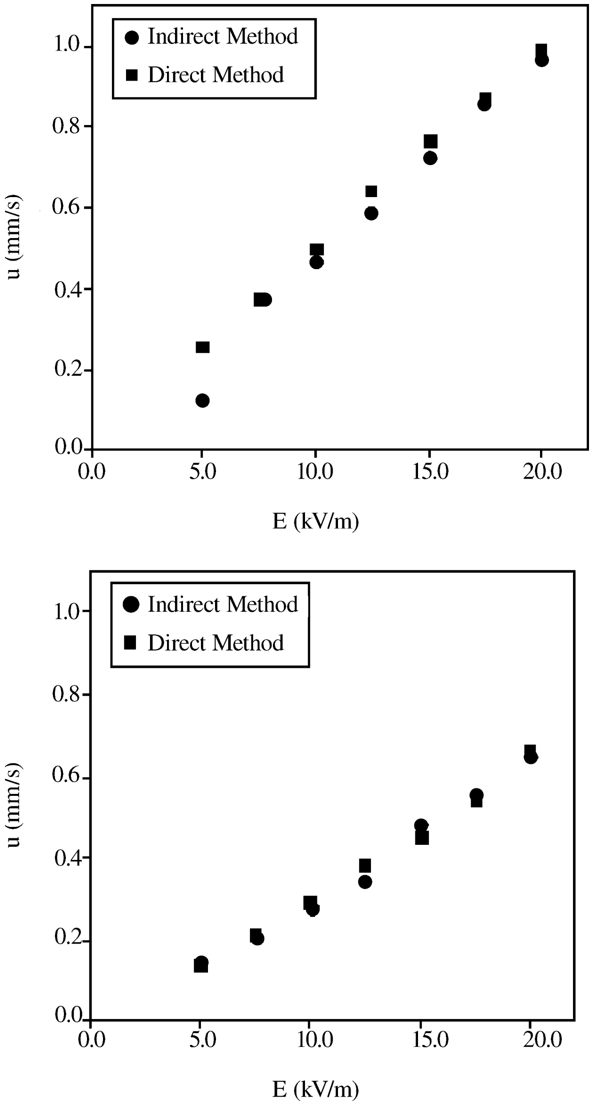
Sanders et al. applied the micro-electrophoresis technique to measure the zeta potential of finely ground glass slides as a function of pH [9]. The results show that for glass particles suspended in a 0.1 M NaCl the zeta potential varies from −20 mV for a pH of 3 to −75 mV for a pH of 10 demonstrating the importance of pH on zeta potential. One problem that arises with this method is whether the zeta potential measured using finely crushed particles corresponds to the zeta potential of the uncrushed solid-liquid interface. The act of grinding may alter the zeta potential of the original material and is still a topic of debate.

Oddy and Santiago used micro-PIV techniques to study small particles in AC and DC electro-osmotic flow [10]. Independent measurements of the particle motion in the two fields can be correlated to determine the electrophoretic mobility of the particle and electro-osmotic mobility of the solid-liquid interface. The electrophoretic mobility of the fluorescent polystyrene particles was found to be −3.76 ± 0.05 μm cm/Vs and the zeta potential of the glass/water interface for a pH of 7 was −115 ± 10 mV.

Gu and Li [8] used the streaming potential method to study the effects of surface conductance, pH, ionic concentrations and surfactants on zeta potential using the streaming potential technique. A glass slit microchannel was used as the capillary which has a form factor of $f = 1/\delta$, where δ is the gap height. As an example, the streaming potential plot obtained for deionized ultrafiltered (DIUF) water is shown in Fig. 5. Each data point represents the average of 18 readings for a given flow rate and for each gap height three flow rates were studied. Ideally for a given gap height the results for different flow rates should be almost identical. The discrepancy is attributed to the fact that the measured streaming potential $\boldsymbol{E}_\mathrm{S}$ is not exactly proportional to the pressure drop ΔP as specified in Eq. (18). A least-square linear curve fit of the data determines the zeta potential and surface conduction. In particular, the zeta potential for a glass-water interface was determined to be −62.2 mV and −22.7 mV for an electrolyte solution of 1×10^{-3} M NaCl solution. In addition, for glass/water the zeta potential var-



Zeta Potential Measurement, Figure 5 Experimental data from streaming potential measurements for glass/DIUF water in a slit microchannel [8]



Zeta Potential Measurement, Figure 6 Plot of the electro-osmotic velocity as a function of the applied electric field for two buffers (*a*) 1xTAE and (*b*) 1xTBE. Results for both the direct flow visualization method and the current-monitoring method are shown [6]

ied from −40 mV for a pH of 3 to −80 mV for a pH of 10. Sinton et al. [6] utilized both the direct visualization method and current monitoring technique to measure the zeta potential for two buffer solutions commonly used in biochemistry. The direct method employed caged fluorescent dye that upon exposure to an intense ultraviolet light uncages and fluoresces. The fluorescent dye is then tracked through a series of images that are analyzed to determine the velocity field. Electro-osmotic velocity measurements for the two methods are shown in Fig. 6. The results from both methods are in excellent agreement indicating that the simpler current-monitoring method produces accurate measurements.

Future Directions for Research

Zeta potential is a fundamental parameter for modelling and characterizing electrokinetic flows in a variety of microfluidics and Lab-on-a-Chip devices. Because the zeta potential depends on so many factors (pH, concentration, liquid, surface etc.) more measurements are required for a variety of surface-liquid combinations; particularly, biological and biochemical fluids. Since measurements can vary greatly between methods and experiments, multiple tests should be employed to accurately determine the zeta potential. In addition, measurements performed using multiple techniques can be corroborated which will reduce errors between results. The ultimate goal is to develop an accurate database of zeta potential measurements for various solid-liquid interfaces, however this will most likely require the development of new theoretical models and experimental methods to increase the accuracy and throughput of current devices.

Cross References

- Electric Double Layers
- Electric Double Layer Interaction
- Electroosmotic Flow (DC)
- AC Electro-Osmotic Flow
- Electrophoresis
- Electrical Current Monitoring Methods
- Methods for Measuring Zeta
- Inter-Atomic Potential
- Lennard–Jones Potential
- Microscale Flow Visualization
- Surface Conductivity Measurement
- Electrokinetic Flow and Ion Transport in Nanochannels
- Temperature Effects on the Zeta Potential
- Measuring Zeta Potential, Methods

References

1. Probstein RF (1994) Physiochemical Hydrodynamics. An Introduction. New York, John Wiley & Sons, Inc.
2. Hunter RJ (1981) Zeta potential in colloid science: principles and applications. Academic Press, London
3. Masiliyah JH (1994) Electrokinetic Transport Phenomena. AOSTRA, Edmonton
4. Hunter RJ (2001) Foundations of Colloid Science. Oxford University Press, Oxford
5. Sinton D (2004) Microscale flow visualization. Microfluid Nanofluid 1:2–21
6. Sinton D, Escobedo C, Ren L, Li D (2002) Direct and Indirect Electro-osmotic Flow Velocity Measurements in Microchannels. J Colloid Interface Sci 254:184–189

7. Sze A, Erickson D, Ren L, Li D (2003) Zeta-Potential Measurement Using Smoluchowski Equation and the Slope of Current-Time Relationship in Electro-osmotic Flow. J Colloid Interface Sci 261, 402-410
8. Gu Y, Li D (2000) The ζ-Potential of Glass Surface in Contact with Aqueous Solutions. J Colloid Interface Sci 226:328–339
9. Sanders RS, Chow RS, Masilyah JH (1995) Deposition of Bitumen and Asphaltene-Stabilizing Emulsions in an Impinging Jet Cell. J Colloid Interface Sci 174:230–245
10. Oddy MH, Santiago JG (2004) A method for determining electrophoretic and electro-osmotic mobilities using AC and DC electric field displacements. J Colloid Interface Sci 269:192–204

Zinc Oxide

► Piezoelectric Materials for Microfluidics