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Abstract

A novel technique employing an Uzigirs dip cell arrangement is used in conjunction with Laser Doppler Electrophoresis for the determination of the surface zeta potential for a UF, NF, and RO membrane. To the authors best knowledge this is the first study employing Laser Doppler Electrophoresis and Electro-osmotic Flow Mapping for membrane surface charge determination. High correlation of the regression fit (R^2>0.95) for a carboxylated polystyrene latex particle electrophoretic mobility was achieved at low electrolyte concentrations (1mM and 10mM NaCl), but the reliability and accuracy of the extrapolated zeta potential values were problematic at higher concentration due to high measurement uncertainty (>10% in some cases). Changes in the applied electric field increased the phase resolution of 50mM NaCl electrolyte solutions between 0.5-2.0V. However, the effects of Joule heating at higher voltages compromised 50mM NaCl sample integrity. When compared with the established Tangential Streaming Potential method, Laser Doppler Electrophoresis measurements provided similar zeta potential values and trends indicating that this new methodology can indeed be employed for membrane characterization purposes; however, further research needs to be conducted in order to optimize this new technique and set appropriate operating limits.

Keywords: Membrane characterization; Electrokinetic charge; Laser Doppler Electrophoresis; Streaming potential; Zeta potential

1   Introduction

Membrane applications are found across a wide range of industries including pharmaceutical, biotechnology, water purification, petrochemical, food, dairy, and textiles [1-3]. Within industry, membranes play an integral role in processes used to separate microorganisms, particles, organics or mineral solutes from various solutions [4-6]. Membrane separation mechanisms are primarily dependent on steric (size) and Donnan (charge) effects. Examining membrane charge phenomena provides a deeper knowledge of interactions that occur during the Donnan effect, leading to a better understanding of the resultant membrane separation performance.

Semipermeable membranes acquire an electric surface charge in aqueous solutions leading to the rearrangement of the ions in solution to maintain electroneutrality [4]. In addition to the dissociation of surface functional groups, membranes acquire charge by the adsorption of charged species from the feed solution in contact with the membrane surface. Typical materials adsorbed are ions, polyelectrolytes, ionic surfactants and macromolecules [7, 8]. The spatial distribution and concentration of dissolved solutes at the membrane-solution interface is structured, resulting in the formation of an electrical double layer (EDL) [9-11]. The shear plane separates the stationary phase from the mobile phase of the electrical double layer and is a critical component to all models of the electrical double layer. The electrical potential at the shear plane is known as Zeta (ζ) potential [11]. Zeta potential is a quantifiable

electrokinetic parameter used to evaluate membrane surface charge characteristics, as the membrane surface potential itself is not readily measured. A more detailed review of the electrical double layer and zeta potential is found in **Section 2.1**.

Measuring zeta potential is not only important for gaining an insight into the separation mechanisms for charged solutes, but also for membrane fouling, membrane ageing, membrane cleaning, and membrane functionalization [12-16]. Streaming potential, sedimentation potential, electro-osmosis, and electrophoresis comprise the four standard electrokinetic measurement techniques from which zeta potential is derived, see **Figure 1** [17]. Due to the simplistic nature of the technique, membrane surface zeta potential is generally characterized using the streaming potential technique. Advances in Dynamic Light Scattering and Laser Doppler Electrophoresis (LDE) technology have now enabled the determination of the zeta potential of surfaces through electro-osmotic flow mapping using an Uzgiris dip cell arrangement [18, 19]. This novel methodology has yet to be exploited for membrane surfaces.

The main objective of this study is to further develop the understanding of membrane surface charge in relation to zeta potential. Specifically, LDE is investigated and compared to the more established Tangential Streaming Potential (TSP) method for determination of zeta potential. The effects of solution chemical composition (pH and salt concentration) on the surface charge properties of three commercial membranes spanning ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) is determined. To the authors best knowledge this is the first study of membrane zeta potential determination using LDE and electro-osmotic flow mapping. This paper aims to provide a holistic overview of the measurement technique and commentary on the reliability reproducibility of this novel method.

2   Theoretical background

2.1   *Zeta potential*

The Gouy-Chapman-Stern-Grahame model is used to describe charge distribution in the electrical double layer in which the electrical potential decreases within the solution as a function of the distance away from the surface, see **Figure 2**. The electrical double layer consists of two primary regions:

- the immobile stern layer where ions bind at the solid-liquid interface and the charge distribution is governed by the geometrical restrictions of ions, molecule size and interactions between the ions, surface and the adjoining dipoles,
- the diffuse layer, which is also called the Gouy-Chapman layer, where ions are free to move by thermal motion and the plane of shear separates the two layers.

The first layer is known as the inner Helmholtz plane (IHP) and consists of partially dehydrated ions either adsorbed chemically or bound by electrostatic forces (counter-ions) to the membrane surface. The next layer is known as the outer Helmholtz plane (OHP) and consists of hydrated ions of opposite charge that effectively compensate for the charge of the IHP. Extending from the OHP into the bulk solution is the diffuse layer, which allows for the diffusion of ions through Brownian motion. Three different potentials are assigned in **Figure 2**, namely:

- The surface potential (ψ_o)

- The potential at the IHP (ψ_{IHP})
- The potential at the OHP (ψ_{OHP})

Typically, the potential decreases linearly from the IHP to the OHP. The zeta potential (ζ) is defined at the shear plane, the point where the movement of the diffuse layer will cause some of the counter-ions to be sheared away, i.e. the layers inside this point are adsorbed and fixed in place.

2.2 Zeta potential measurement techniques

2.3 Tangential streaming potential

Streaming potential measurements used to determine membrane zeta potential are either transversal or tangential [20]. Flow travels through the membrane pores during transversal measurements, while flow travels along the active layer of the membrane surface during tangential measurements. TSP is the most commonly used technique to measure membrane zeta potential [21]. An abundance of information regarding TSP applications for membranes is available in the literature; therefore, only a brief overview will be provided.

TSP can be summarized as follows. An arrangement of two identical membrane active layers facing one another and separated by spacers forms a discrete channel. A hydrostatic pressure gradient is applied forcing a background electrolyte solution tangentially through the void of the channel. As the counter ions in solution rearrange, due to the charge density of the membrane surface, excess counter ions are drawn towards the low-pressure side of the channel under the shear flow action. The differential between counter ions from one end of the channel to the other is responsible for an induced electrical current or streaming current [22].

The streaming potential coefficient, $\emptyset_{st}$, is calculated from the measurable potential difference formed by the streaming current.

$$\emptyset_{st} = \Delta V / \Delta P \qquad \qquad \textbf{Eq. 1}$$

Where ΔV is the electric potential difference and ΔP is the applied pressure gradient. Zeta potential ζ is extrapolated from streaming potential using the Smoluchowski equation

$$\zeta = \emptyset_{st} \frac{\eta}{\varepsilon \varepsilon_o} K_B \qquad \qquad \textbf{Eq. 2}$$

where ε is the dielectric constant of the dispersant, ε_o is the permittivity of free space, η is the apparent viscosity, and K_B is the conductivity of the solution [23]. In order to have correct zeta potential values when using the Smoluchowski equation, the surface conductivity contribution has to be accounted for. The equation can be analytically solved when the surface has a low electrical potential (<25 mV) and the liquid moves across the streaming potential channel (or membrane pores) with laminar flow at a concentration high enough to prevent the electrical double layer overlapping (capillary radius higher than the Debye length). However, surface conductivity becomes a problem at low electrolyte concentrations and/or when the surface is highly charged [7].

2.4 Laser Doppler Electrophoresis

The primary mechanism of LDE is dependent on the frequency of scattered laser light as a function of particle velocity - Doppler shift. LDE has been used to determine Brownian motion of particles in solution, as well as particle translational diffusion coefficients [24]. Additionally, many colloidal particles possess surface charge in suspension. Subjecting colloidal particles to non-Brownian motion, including electric fields, leads to a Doppler shift inclusive of both translational diffusion and the induced electrophoretic mobility. The direction and velocity of the motion is a function of particle charge, the suspending medium, and the electric field strength.

Zeta potential ζ is related to electrophoretic mobility U_E by the Henry equation,

$$U_E = \frac{2\varepsilon\varepsilon_o\zeta F(\kappa a)}{3\eta} \qquad \textbf{Eq. 3}$$

where ε is the dielectric constant of the dispersant, ε_o is the permittivity of free space, and η is the apparent viscosity. $F(\kappa a)$ is the Henry function; where κ is the inverse of the Debye screening length or electrical double layer thickness, and a is the particle radius [19, 25]. Approximations can be made for $F(\kappa a)$; $F(\kappa a) = 1.0$ (Debye approximation) for non-polar solvents and $F(\kappa a) = 1.5$ (Smoluchowski approximation) for polar solvents [26]. $F(\kappa a)$ is dependent on the size of the colloid and the supporting electrolyte conditions [11]. For this investigation the Smoluchowski approximation was used, applicable to particles >100nm in aqueous solution with ionic strengths >10^{-3}M.

The frequency shift of Phase Analysis Light Scattering (PALS) associated with changes in particle electrophoretic velocity v is given by,

$$\Delta v = 2U_E\frac{sin(\theta/2)}{\lambda} \qquad \textbf{Eq. 4}$$

where, λ is the laser wavelength, and θ is the angle of scatter [19, 27].

2.5   Electro-osmotic flow mapping

Electro-osmosis is the motion of a liquid through an immobilized set of particles in response to an applied electric field [25]. Tracer particles are used in a series of measurements under electro-osmotic flow to determine membrane surface zeta potential. A membrane sample is fixed to the sample holder, placed onto an Uzgiris dip-in electrode, and positioned into a cuvette. As an electric field is applied, the subsequent motion of tracer particles dispersed within the electrolyte solution is measured using PALS.

Electro-osmotic flow mapping relies on the characterization of the flow field in the half space outside the slipping plane. Therefore, measurements are mapped at numerous displacements y_i, in the order of 100s of microns, normal to the membrane surface [18]. The slipping plane of the surface under test is assumed to coincide with the test surface and the plane of $y = 0$.

Assuming Stokes flow and zero backpressure the linearized Navier-Stokes equation is given as

$$\rho v = \eta \left[\frac{\delta^2 v}{\delta x^2} + \frac{\delta^2 v}{\delta y^2} \right] \qquad \textbf{Eq. 5}$$

where $v(t, x, y)$ is the component of fluid velocity parallel to the boundary, ρ is the fluid density, and η is the apparent viscosity. The x co-ordinate is parallel to the boundary, whereas the y co-ordinate is perpendicular; therefore, continuity implies that v is not a function of x because there is no flow perpendicular to the boundary. The equation simplifies to a one dimensional homogenous diffusion equation:

$$v = k \left[\frac{\delta^2 v}{\delta y^2} \right] \qquad \textbf{Eq. 6}$$

where $k = \eta / \rho$ (kinematic viscosity). Initial conditions are set as $v(0, y) = 0$ with the boundary condition $v(t, 0) = v_{eo}$, where v_{eo} is the fluid velocity at the boundary. However, the homogenous initial conditions and Dirichlet boundary conditions are problematic on the half line $(0, \infty)$ but have a Green function solution with the closed form:

$$v(y, t) = \int_0^\infty \frac{1}{\sqrt{4\pi k(t-s)^3}} \exp \frac{y^2}{4k(t-s)} v_{eo} ds \qquad \textbf{Eq. 7}$$

and solution:

$$v(y, t) = v_{eo} \left[1 - \mathrm{erf}\left(\frac{y}{2\sqrt{kt}} \right) \right] \qquad \textbf{Eq. 8}$$

where erf is the error function. Furthermore, for $y \geq 750\mu m$ for $t \geq 75ms$ or $y \geq 1.5mm$ for $t \geq 300ms$, the bracketed terms do not apply as $\mathrm{erf}\left(\frac{y}{2\sqrt{kt}} \right) \to 0$. Electrophoretic motion is observed within these time intervals using PALS; therefore, fitting the linearized Navier-Stokes equation to measurements of $v_i(y_i)$ at various displacements y_i can be extrapolated to the y-axis intercept

$$v_{eo} = -\text{Intercept} + v_{ep} \qquad \textbf{Eq. 9}$$

Surface zeta potential ζ is then related to the fluid flow at the slipping plane v_{eo} by

$$\frac{v_{eo}}{E_x} = \frac{\varepsilon \varepsilon_o \zeta}{\eta} \qquad \textbf{Eq. 10}$$

where E_x is the electric field strength, ε is the dielectric constant of the dispersant, ε_o is the permittivity of free space, and η is the apparent viscosity [18].

3 Materials and methods

3.1 Membranes

The three membranes used in this study were:

- Nadir UP010 Polyethersulfone (PES) UF membrane (Microdyn-Nadir GmbH, Wiesbaden, Germany) with a molecular weight cut-off (MWCO) of 10kDa, an operational pH range 0-14, primarily used in the pharmaceutical and dairy industries.

- GE Osmonics DL-Series thin film composite NF membrane (GE Water, USA) with an approximate MWCO of 150-300Da for uncharged organic molecules and an operational pH range 2-10. DL-Series membranes cover a host of industrial applications, some of which include acid purification, antibiotic concentration, whey desalting, and heavy metal removal.
- GE Osmonics AG-Series polyamide thin film composite RO membrane (GE Water, USA) with an operational pH range 1-11, used primarily for desalination of brackish water.

Prior to analysis, the membranes were hydrated for a period of 24 hours in ultra-pure (<1μS/cm) water (Millipore ELIX 5 unit; Millipore UK Ltd., UK) and thoroughly rinsed prior to use.

3.2 Tangential Streaming Potential measurements

TSP measurements were carried out using the Electrokinetic analyzer (EKA) (Anton Paar GmbH, Graz, Austria). Membranes were cut to fit the dimensions of the rectangular measurement cell attachment, (2 sheets 12.5x5.5cm).

NaCl (Fisher Scientific Ltd, UK) was used as the electrolyte for study in this work and three concentrations were employed; namely 1mM, 10mM, and 50mM. These concentrations are sufficient to avoid surface conductivity and justify the use of the Smoluchowski equation (**Eq. 2**). The electrolyte solution was prepared using ultra-pure water and adjusted periodically for acidic or alkaline pH using 0.1M HCl (Fisher Scientific Ltd, UK) and 0.1M NaOH (Fisher Scientific Ltd, UK) as required. Fresh solution was introduced to the system when swapping from acidic to alkaline conditions. Prior to introducing solutions for analysis, the system was thoroughly rinsed with ultra-pure water to ensure any prior solution was removed. Similarly, the electrolyte solutions were introduced and rinsed through the unit to equilibrate the membrane sample. The solutions were well within the electrode polarization limits.

A pressure gradient program of 0-700 mbar over 30-seconds was applied to generate the streaming current and was measured using a pair of AgCl electrodes. For individual pH points, at each NaCl concentration, 10 measurements were made using alternating flow directions to limit electrode polarization. Background electrolyte pH and conductivity were monitored using a pH and conductivity probe. All experiments were carried out at room temperature ($21 \pm 2°C$).

3.3 Laser Doppler Electrophoresis measurements

Electrophoretic mobility and electro-osmotic measurements were carried out using a Zetasizer Nano ZS with the surface zeta potential accessory (Malvern, UK), see **Figure 3**. Membranes were cut to fit the dimensions of the surface zeta cell sample holder (3.5x5mm). Epoxy (Araldite) was used to attach the membrane to the sample holder.

Solutions were prepared and the pH was adjusted as per **Section 3.2**. However, in this case, one drop of 0.2μm carboxylated polystyrene latex tracer particles (Polysciences Inc., PA, USA) was added to each 200mL of prepared electrolyte solution. The surface cell, with attached membrane sample, was washed with 5mL of the corresponding measurement solution to remove any potential debris and pre-equilibrate the surface prior to being placed

into the glass measuring cell containing the measurement solution. In between subsequent measurements, the surface cell was sonicated for 30 seconds in toluene (Fisher Scientific Ltd., UK) in order to remove any electrode debris accumulated during the previous measurement. Following sonication, the electrodes were cleaned using a cotton swab and washed with ethanol (Fisher Scientific LTD, UK). Lastly, the cell was rinsed with ultra-pure water and dried using compressed air.

The Zetasizer was set to forward scatter with the attenuator in position ten. The count rate was adjusted to the optimal 250-500kcps range. The instrument was set to take four distance positions, in 125μm steps, consisting of three measurements (each measurement consisted of 15 sub-runs with a 60 second interval) at each position for each pH and concentration data point. Furthermore, five measurements, consisting of 100 sub-runs with a 60 second interval in between measurements, were used to measure the electro-osmotic mobility of the tracer particles. All measurements were carried out at 25°C.

In comparison with the initial measurement frequency, Doppler shift associated with electrophoretic mobility is relatively small, estimated to be in the order of several tens to hundreds of Hz [24]. Consequently, the Doppler shift is recorded using a heterodyne detection configuration, where a beat frequency is produced by recombining the scattered light (incident beam) with unscattered light (reference beam), see **Figure 4**. Due to the charged nature of the cuvette cell surface, electro-osmotic flow is superimposed on the true electrophoretic mobility of colloidal particles in suspension. More importantly, membrane surface zeta potential measurements should be free of any errors attributed to electro-osmotic flow along the cell wall. Both fast field reversal (FFR) and slow field reversal (SFR) techniques are utilized in this particular application for measuring the effects of electro-osmotic flow on membrane surface zeta potential. Electrokinetic research carried out by Minor et al was successful in demonstrating that particles reached terminal velocity at least an order of magnitude faster than the establishment of electro-osmosis [28]. FFR entails the use of a high frequency alternating electric field to help particles in solution reach terminal velocity quickly, rendering electro-osmotic flow insignificant. FFR measurements provide reliable zeta potential measurement in terms of velocity; however, particle distribution data remains poor due to fast sampling rates. Therefore, SFR is employed to measure mobility distributions of particles in solution by decreasing the frequency of field reversal but the lower frequency results in increased sampling time. Electro-osmotic flow is then taken into account by calculating the difference between mean zeta potential values obtained from both FFR and SFR measurements.

Thus, the measurement sequence for the Malvern instrument is then:

- An FFR measurement to determine mean zeta potential
- An SFR measurement for better resolution of particle mobility (shifted by electro-osmosis)
- Mean zeta potential difference between FFR and SFR is calculated to determine electro-osmotic flow
- SFR distribution is normalized using mean zeta potential data
- Zeta potential for the sample surface is then calculated from the resultant velocity value (v_{eo}) using **Eq. 10**.

4   Results and Discussion

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In this section, the specific attributes of the LDE technique are explored in depth to gain an understanding into the constituents comprising an acceptable measurement. Furthermore, the accuracy, precision, and reproducibility of LDE measurements are discussed by comparison with the TSP method for membrane surface zeta potential determination.

4.1 Tangential streaming potential measurements

Zeta potential data obtained using this method for the AG-Series RO membrane provides an overview of the accepted standard for membrane surface charge determination, see **Figure 5**. A clear distinguishable pattern was evident as zeta potential decreased while electrolyte concentration increased. At lower ionic strength, 10mM NaCl at pH 5.5 had zeta potential measurements ranging -12.18 to -12.81mV with an average zeta potential of -12.45 ± 0.22mV. Fluctuations between the ten measurements comprising each data point were low, producing reliable results with minimal uncertainty (1.8%). At higher electrolyte concentrations, e.g. 50mM and pH 8, surface zeta potential was -8.02 ± 0.74mV (9.2% uncertainty). Although greater uncertainty was observed at higher electrolyte concentrations, the results were within the margins of acceptable statistical error (<10%). The DL-Series NF and Nadir UF membranes were measured in the same manner and the data is presented for comparative analysis with LDE measurements in **Section 4.3**.

4.2 Laser Doppler Electrophoresis measurements

The following section investigates parameters for an acceptable surface zeta potential measurement using LDE. **Figure 6A** shows an ideal phase distribution obtained for the NF membrane at 1mM NaCl and pH 11.1, where the three bands for each of the four displacements y_i are distinct, tightly grouped, and have minimal noise. The polystyrene latex tracer particle electrophoretic mobility was measured at four displacements and extrapolated to the y-intercept, $R^2 = 0.995$, yielding -0.5199μmcm/Vs (intercept error = 0.077 μmcm/Vs), see **Figure 6B**. Applied to **Eq. 9**, the intercept value of -0.5199μmcm/Vs, was added to tracer particle electrophoretic mobility, -3.009μmcm/Vs, producing v_{eo} or velocity at the slipping plane, -2.489±0.097μmcm/Vs. The membrane surface zeta potential was then calculated to be -31.8 ±1.23mV by applying v_{eo} to **Eq. 10**. The calculated zeta potential value is congruent with the expected zeta potential value for GE NF membranes under like conditions [29, 30]. For the same membrane at 1mM NaCl and pH 9.9, a zeta potential value of -29.37 ± 0.47mV was obtained using the TSP method, further confirming the accuracy of the extrapolated zeta potential measurement from LDE.

By contrast, **Figure 7** shows data obtained that is representative of a poor surface zeta potential measurement for the AG-Series membrane at 50mM NaCl and pH 4.3. Phase data presented in **Figure 7A** have non-grouped indistinguishable banding and exhibit a high degree of noise. At first glance, the data seems to be influenced by insufficient transmission of laser light entering the sample. However, as the mean count rate was roughly 350kcps (optimal = 200-500kcps) with the attenuator set to position 10 (30% transmission), sufficient scattered light was detected. Thus, the noisy phase data was related to higher sample conductivities at increased electrolyte concentration. The voltage of the applied electric field at 50mM NaCl was automatically reduced by the equipment's control software to ~2.2V based on the higher conductivity of the electrolyte solution (~6.3mS/cm). For comparison purposes, the applied voltages were ~10V and ~5V for the 1mM and 10mM NaCl electrolyte solutions, respectively. Consequently, electrophoretic mobility data in **Figure 7B** is highly scattered, resulting in $v_{eo} = -1.239 \pm 0.393$μmcm/Vs. The measured surface zeta potential

value of -15.8mV had a high relative uncertainty of 31.8%, as well as a low correlation coefficient ($R^2 = 0.00125$) indicating non-linearity of the regression fit. As the membrane is nearing the isoelectric point under these conditions, -15.8 ± 5.02mV significantly deviates from the expected zeta potential, which should be close to 0mV. The margin of error for electrophoretic mobility was greater than 10% and the correlation of the regression fit was less than 95%.

In an attempt to improve the detection of Doppler shift related to particle electrophoretic mobility under these conditions, the effects of the applied electric field was studied by manually adjusting the voltage (0.5V, 1.0V, 1.5V, 2.0V) in a series of measurements at 50mM NaCl and pH 5.7 for the AG-Series membrane, see **Figure 8**. As the voltage was increased the resolution of the phase plots started to improve; from highly scattered data at 0.5V to slight definition in the bands starting to appear at 1V. Additionally, as the voltage was increased to 1.5V, FFR and SFR profiles began to form. Furthermore, an applied electric field of 2V provided the highest resolution phase plot. However, at 1.5V the effects of Joule heating became apparent and further increases in voltage resulted in tarnishing of the electrode surface. As a result, solution integrity was compromised as an electrochemical reaction was taking place inside the cell, confirmed by visual inspection (colour change), see **Figure 9**. In an effort to increase scattered light detection through transmission, the attenuator position was also manually adjusted; however, the phase data obtained from these experiments was not improved and the error remained much the same.

In conclusion, reducing the voltage of the applied electric field or adjusting the attenuator position did not result in higher resolution phase data or higher distinguishability of electrophoretic mobility between the reference and incident beam. The correlation of the electrophoretic mobility regression fit was outside of the 95% tolerance and the relative uncertainty of the surface zeta potential measurements was greater than 10%, see **Table 1**. Although an applied electric field of 2.0V provided the highest resolution phase data, the effects of Joule heating associated with both voltage and higher electrolyte concentrations rendered the quality of results experimentally compromised. Results obtained from LDE measurements using 50mM electrolyte solutions on the UF, NF, and RO membranes were excluded from the remainder of the study.

4.3 *Reliability and accuracy of measurement*

The primary application for LDE was to construct a zeta potential profile for the membrane surface charge across a range of solution conditions. This was relatively straight forward at low concentration (1mM and 10mM NaCl) but the reliability and accuracy of LDE for zeta potential determination for the higher concentration (50mM) was problematic. Although high particle electrophoretic mobility correlations were achieved (>95%) through the removal of outlying measurement points when necessary, the uncertainty of the final measurement was too large to ignore.

Zeta potential values obtained using LDE were generally in very good agreement with values obtained using TSP measurements, see **Figure 10**. However, the measurement uncertainty of the values obtained using LDE is significantly large when compared to the TSP method (20 to 164% compared to 1.8 to 10.2% respectively). Additionally, uncertainties for the Nadir UF membrane measurements were far greater when compared to the NF membrane. Electrophoretic mobility differences due to the charged nature of the different functional groups associated with polyethersulfone and polyamide membranes could be responsible.

As mentioned in **Section 4.2**, some measurements were obtained that met the statistical criteria for acceptability but these measurements constituted only a small fraction of the overall data points collected in this study. An overview of measurements obtained using both TSP and LDE for all three membranes is shown in **Figure 11**.

Although the error bars are only provided for the LDE measurements, it is clearly evident that many of the points have large errors associated with zeta potential measurements. Certain points overlap in the region of higher and lower electrolyte concentration covering a range of values. Therefore, confidence in the true value for many of these points is low. Closer examination reveals that the range of error is relatively similar for the individual membranes. Membrane surface charge is actually quite low when compared to some other surfaces of different materials, thus, the magnitude of the absolute error for this technique is amplified when compared with a surface that carries higher charge [18]. For all three membranes, a similar general trend for the zeta potential is established alongside the values obtained from the TSP method, but the absolute value carries more uncertainty for similar electrolyte conditions. However, certain points do deviate from the expected zeta potential values, e.g. 1mM NaCl LDE measurements for the Nadir UF membrane.

4.4   Further discussion

4.4.1   Measurement

A study carried out by Corbett et al. [18] successfully employed the use of LDE for surface zeta potential measurement of PTFE and silica samples. The measurement uncertainties in this case were less than (but approaching) 10%. The highly charged nature of PTFE, around ~80mV at pH 9.2, provided a large enough magnitude of measurement value for the uncertainty to remain small. In comparison, the relatively low charge of membranes means that for the same magnitude in absolute error the relative uncertainty becomes larger. Minute differences between measurements can produce significantly greater uncertainties for surfaces that carry low charge. The uncertainty obtained from the experiments in this study are relatively consistent for the three different membranes used. Although the results may be described as statistically weak, the generalized trends obtained for membrane surface zeta potential can be established using this methodology.

Additionally, great care had to be taken during the handling and preparation of delicate membrane samples in contrast with the rigid blocks of solid PTFE samples used by Corbett et al. [18]. Membranes are generally in the region of ~150-200μm in thickness, whereas PTFE block samples are roughly 1.5mm in thickness. The application of the membrane sample to the sample holder should result in a flat surface free of any defects; any slight accidental damage to the membrane surface during preparation may have resulted in erroneous measurements. Furthermore, the variations in material dimensions and composition, the binding agent used, and the size and type of tracer particles could also potentially account for some measurement inaccuracy.

4.4.2   Technique comparison

Ionic strength has considerable impact on membrane surface zeta potential and should be investigated at both low and high concentrations for a more complete understanding of the electrostatic interactions contributing to the sum of the interfacial interactions at the solution-membrane interface. At lower electrolyte concentrations the magnitude of the membrane

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surface zeta potential measurement is large, resulting in the over prediction of electrostatic forces of different polymeric membranes at environmentally relevant ionic strengths. Zeta potential values derived using dilute electrolyte solutions also jeopardize the commonly accepted assumption that the overall membrane surface charge is neutralized or reversed at high ionic strengths [9]. Across both low and high electrolyte conditions the TSP method using an EKA provided more accurate results than the LDE technique. However, the compromised sample integrity, resulting from the effects of Joule heating invalidated the LDE measurements for 50mM NaCl electrolyte solutions. The apparent limitation of LDE to lower electrolyte concentrations hinders the measurement of environmentally relevant electrolyte conditions for membrane surfaces.

In terms of measurement runtime, both TSP and LDE measurements were approximately the same. However, for each measurement point, LDE required the turning of the micrometer stage for each of the four displacements during a single measurement run. TSP measurements using an EKA did not require any further attention after commencing a measurement. As the electrolyte solution was only changed once between alkaline and acidic titrations and the membrane sample remained the same, there was minimal user intervention required between measurement intervals using the TSP method. The recommended full curing time for the binding agent used to attach the membrane to the sample holder for LDE was 24 hours. Additionally, the electrodes on the surface zeta potential cell had to be periodically cleaned using the procedure mentioned in **Section 3.3**. Although the measurement times were roughly the same, the extra sample preparation and interval maintenance associated with the LDE technique significantly increased the amount of time to complete a series of surface zeta potential measurements. A major advantage of LDE is that only a single small test surface is required for the measurement, this is particularly advantageous in membrane fabrication research. Similarly, the equipment itself is cheaper and can be used for other measurements (zeta potential of particles and particle sizing) whereas the TSP measurement equipment is usually single application only.

5   Conclusions

A new technique for the measurement of membrane surface zeta potential using Laser Doppler Electrophoresis (LDE) has been presented. In comparison with the Tangential Streaming Potential (TSP) method, deficiencies in reliability and accuracy using the LDE technique are evident when using high electrolyte concentrations (~50mM NaCl). Nevertheless, the technique has been successfully employed to measure the membrane surface zeta potential of three commercially available membranes (one UF, NF and RO), each with different materials of construction and across a range of experimental conditions (varying concentration and pH). The results obtained from LDE experiments were of similar trend and magnitude when compared to results using the TSP method. As the first study using LDE for determination of membrane surface zeta potential, the apparent issues identified from this work suggests further investigation is required in order to optimize the measurement technique and establish acceptable environmental operating limits for membrane applications.

6   References

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Figure 1: The four zeta potential measurement techniques classified by mobility and potential

Figure 2: Electrical double layer model describing potential as a function of distance from the membrane surface

Figure 3: Uzgiris dip cell arrangement used for surface zeta potential measurements

Figure 4: The heterodyne detection configuration used to record electrophoretic mobility using Doppler shift

Figure 5: Zeta potential profile for the AG-Series membrane from Tangential Streaming Potential measurements

Figure 6: A: Phase plot for a DL-Series membrane (1mM NaCl, pH 11.1) highlighting acceptable Doppler shift detection during surface zeta potential determination using Laser Doppler Electrophoresis. B: Electrophoretic mobility of polystyrene latex tracer particles at four displacements normal to the test surface with uncertainty $< 10\%$

Figure 7: A: Phase plot for the AG-Series membrane (50mM NaCl, pH 4.3) highlighting poor Doppler shift detection for surface zeta potential determination using Laser Doppler Electrophoresis. B: Electrophoretic mobility of polystyrene latex tracer particles at four displacements normal to the test surface with uncertainty $> 10\%$.

Figure 8: Increasing Doppler shift detection through manual adjustment of the applied electric field (AG-Series membrane 50mM NaCl pH 5.7). A: 0.5V; B: 1.0V; C: 1.5V; D: 2.0V

Figure 9: Electrochemical reaction (color change) as a result of Joule heating at increased applied electric field voltages. A: Original solution, B: 1.5V, C: 2.0V, and D: ~2.2V (equipment automatic voltage selection)

Figure 10: A comparison of zeta potential values obtained using Laser Doppler Electrophoresis (LDE) and Tangential Streaming Potential (TSP) for the DL-Series NF membrane

Figure 11: An overview of zeta potential values obtained using Laser Doppler Electrophoresis (LDE) and Tangential Streaming Potential (TSP) at various NaCl concentrations (error bars provided for LDE measurements only, to avoid excessive clutter). A: Nadir UF, B: DL-Series NF, and C: AG-Series RO membranes.
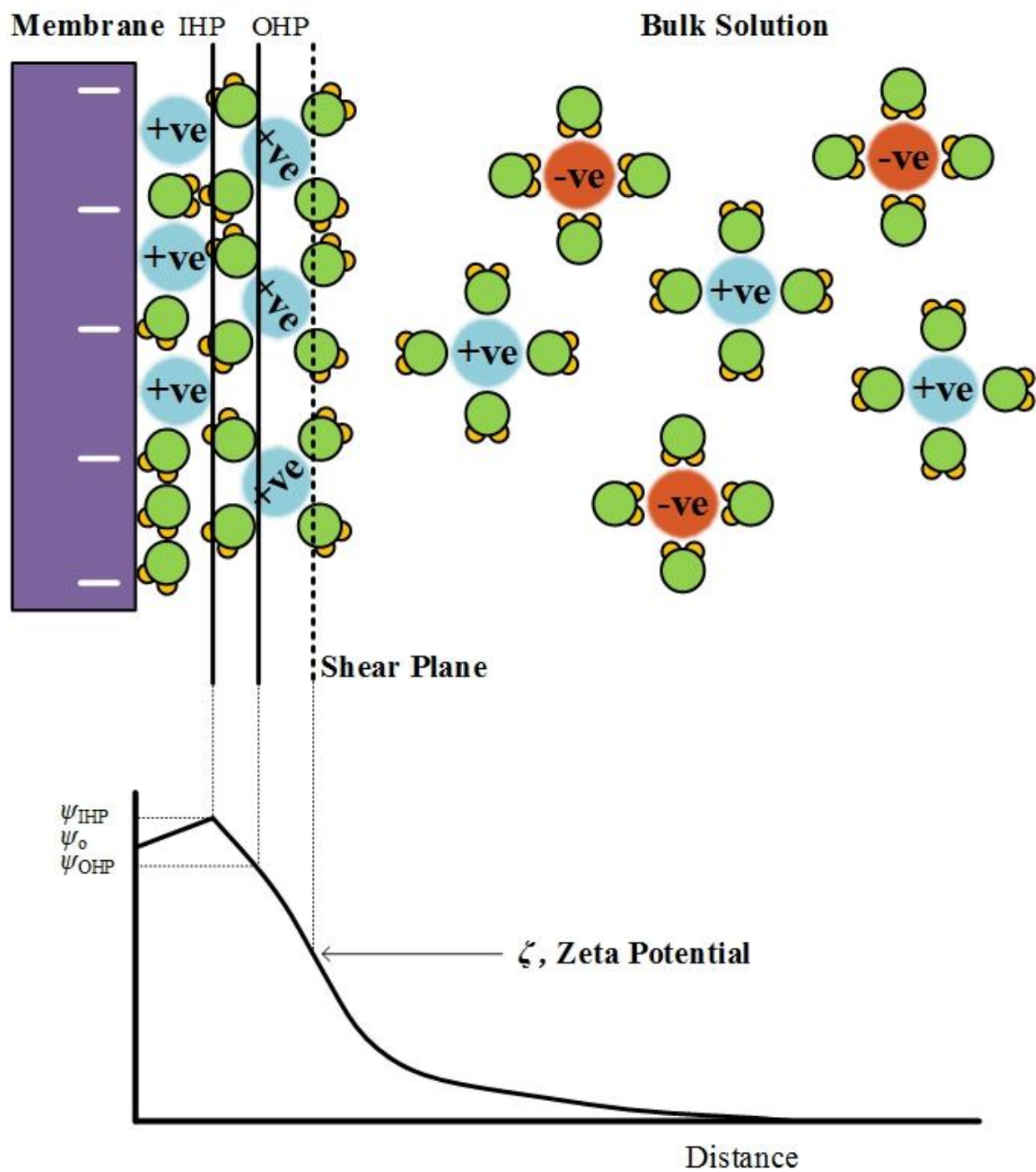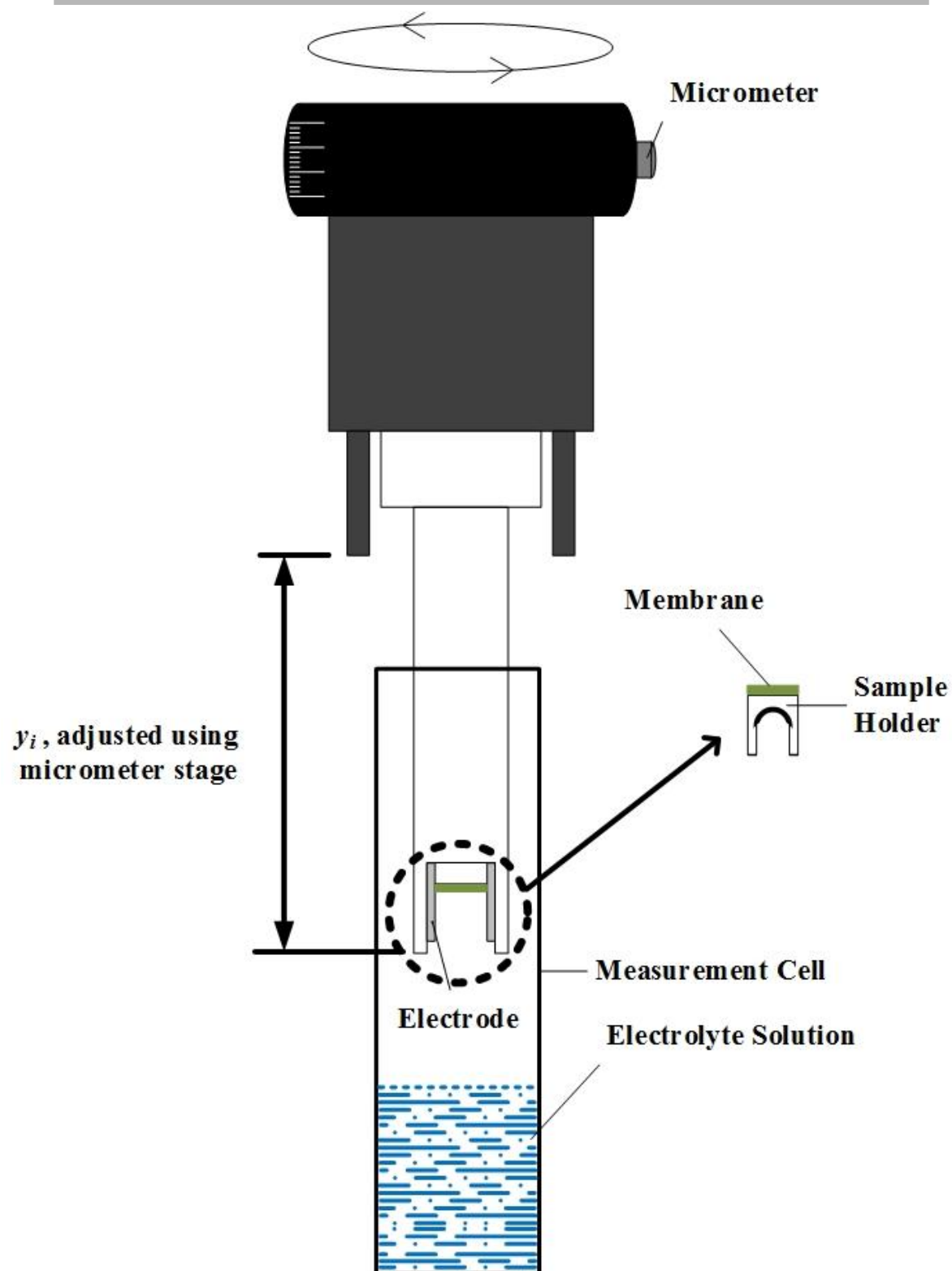
Figure 1

ELECTROPHORESIS
Solid phase moves
Liquid is stationary

ELECTRO-OSMOSIS
Liquid phase moves
Solid is stationary

Applied electrical field
causes motion

ζ-potential

Movement results in
an electrical potential

STREAMING POTENTIAL
Liquid phase moves
Solid is stationary

SEDIMENTATION POTENTIAL
Solid phase moves
Liquid is stationary

15
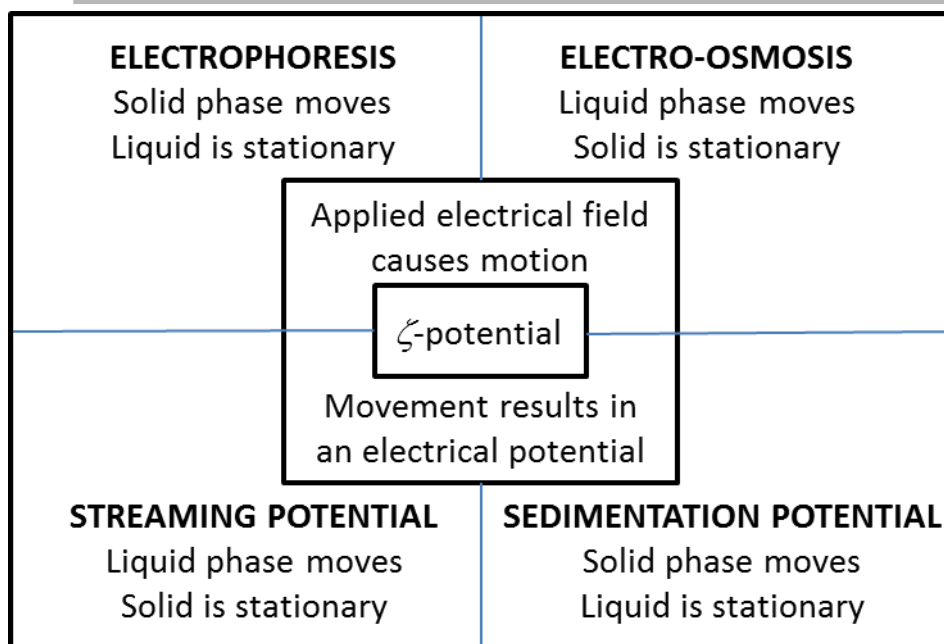
Figure 2

Figure 3

Figure 4
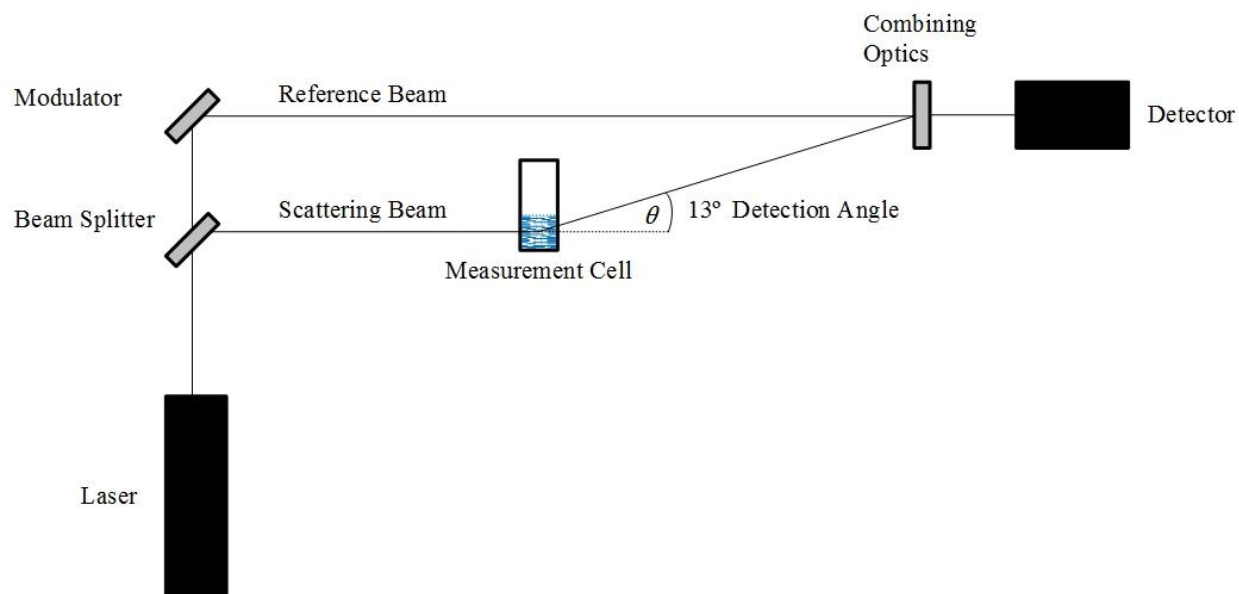
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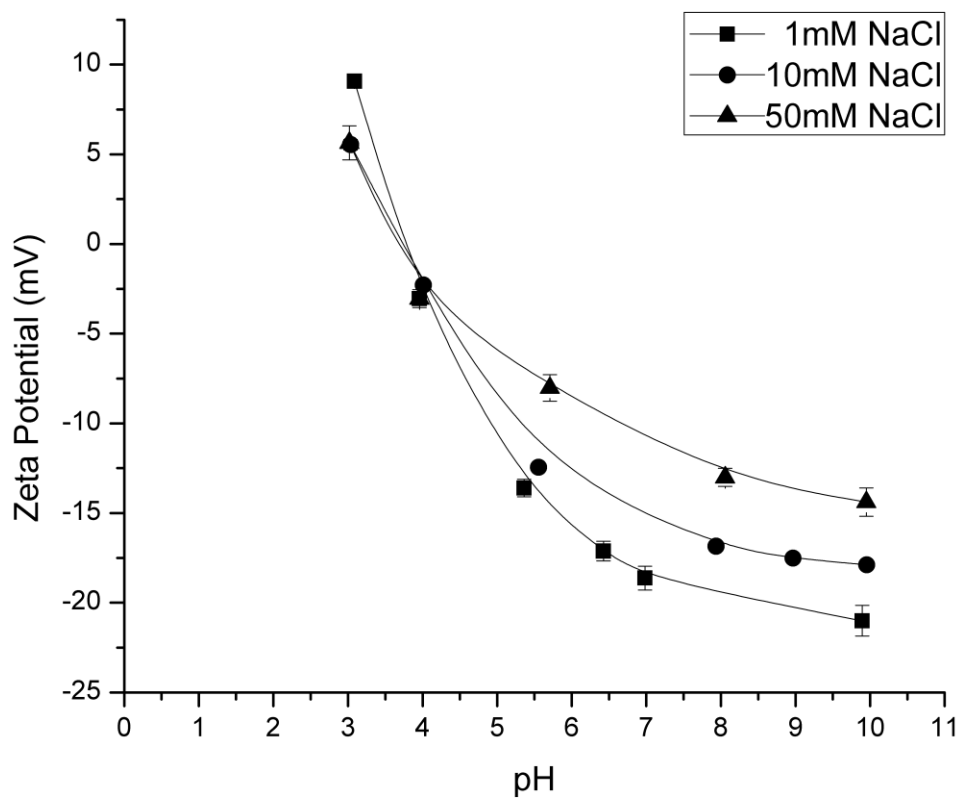
Figure 6A/B
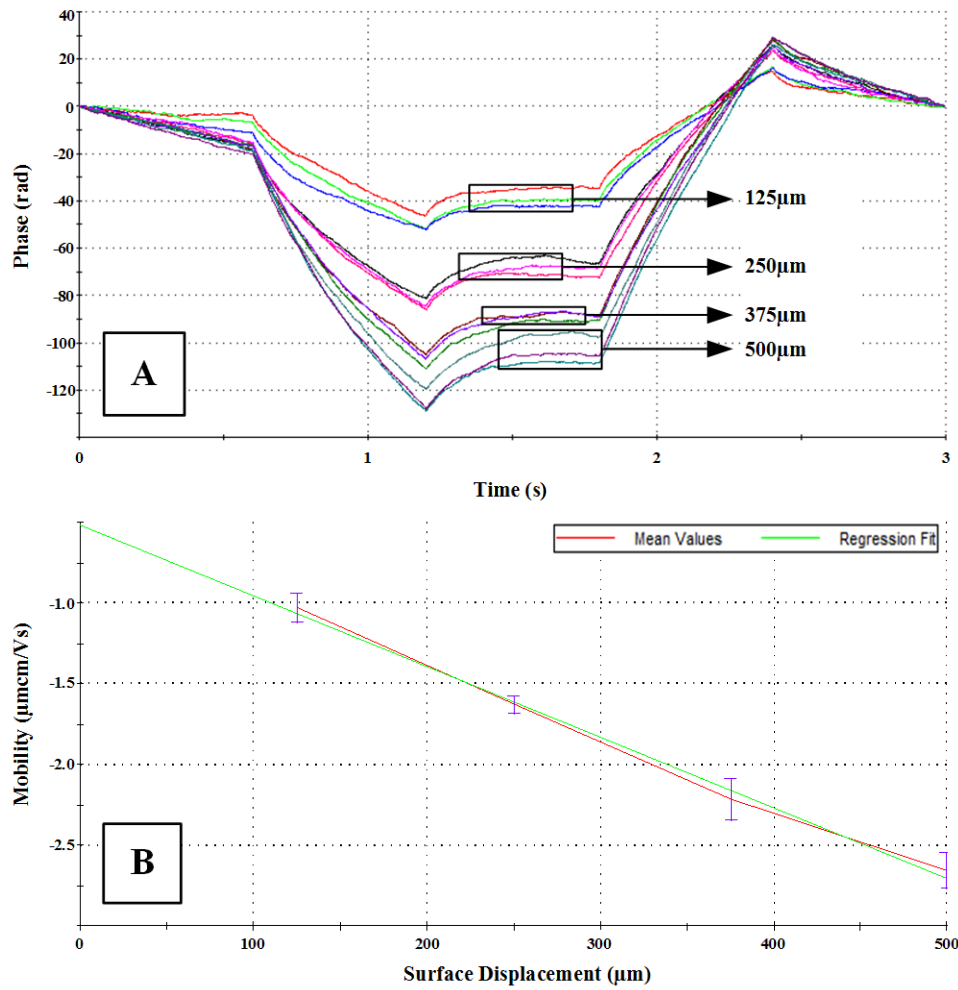
Figure 7A/B
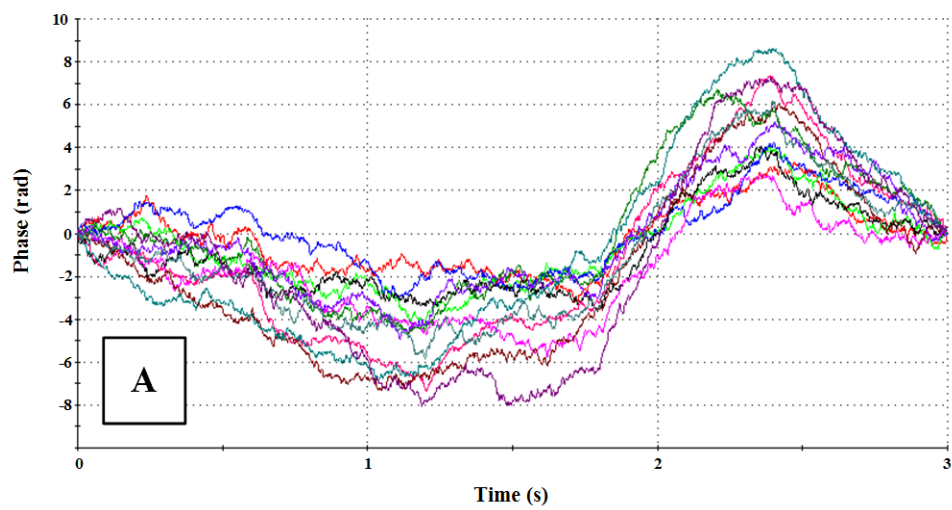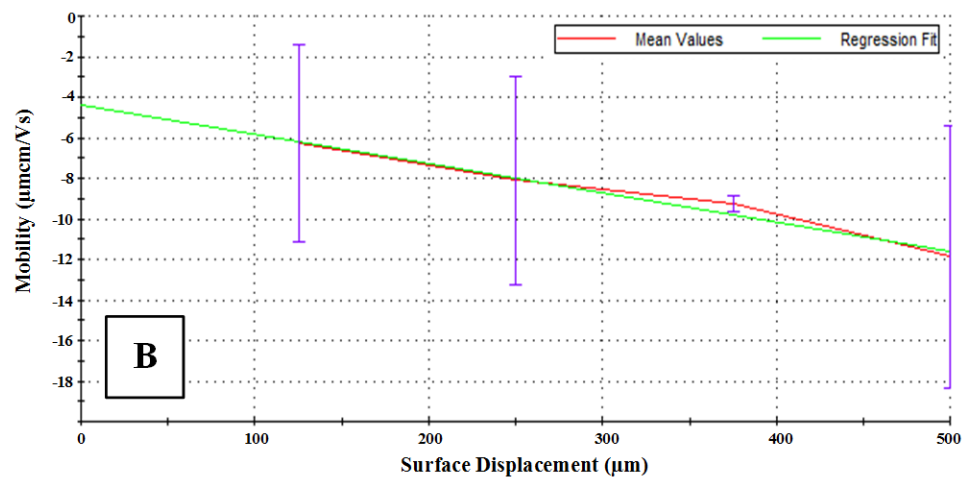
Figure 8A-D

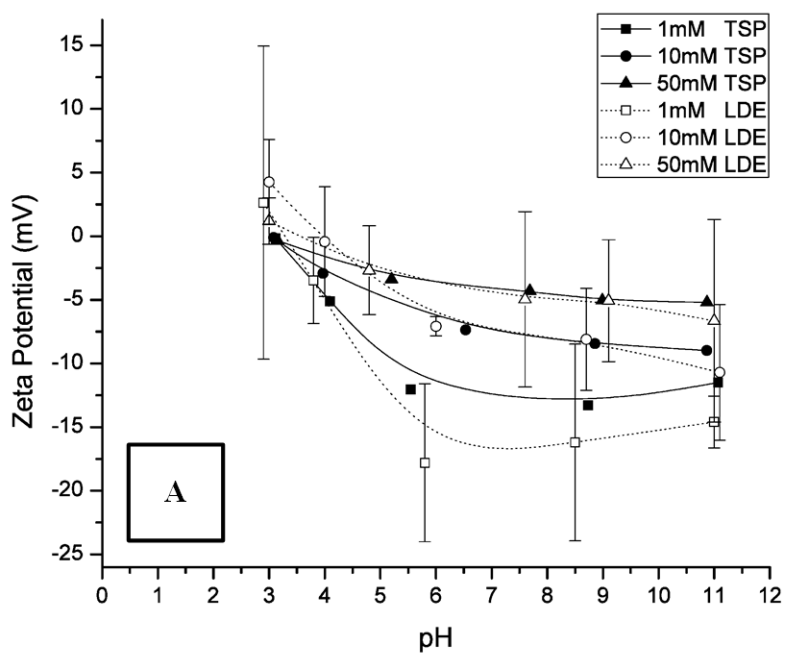**Figure 9**

21
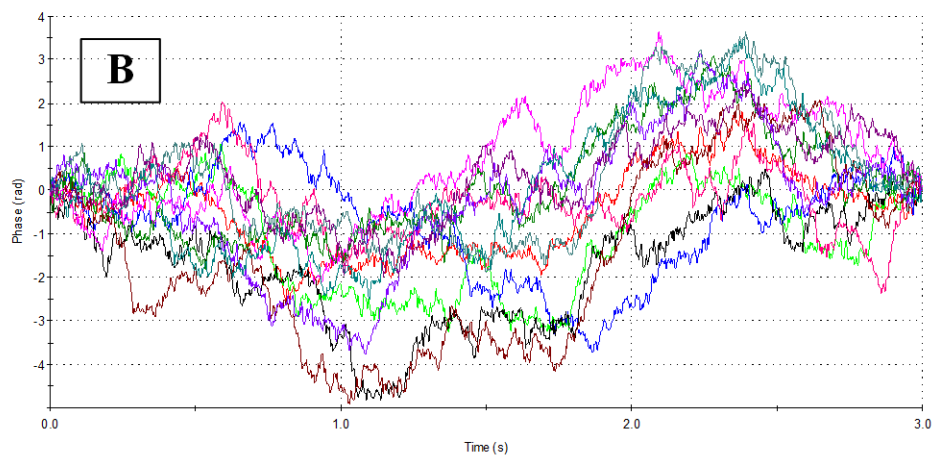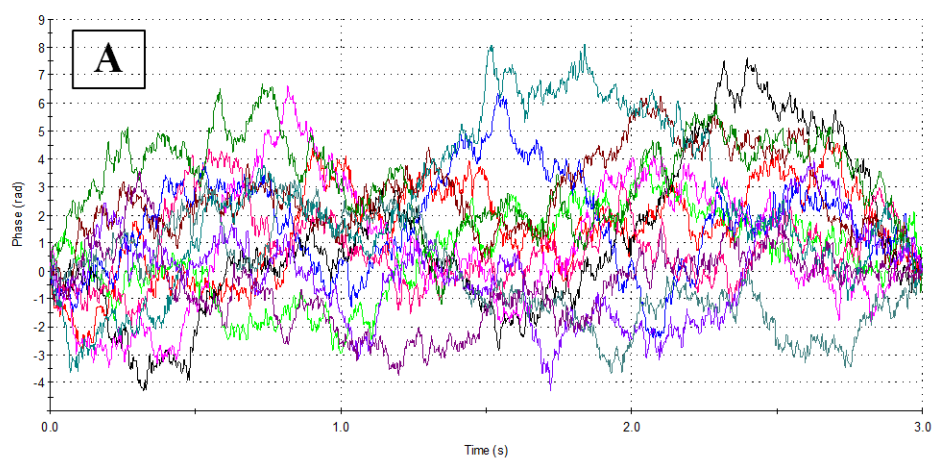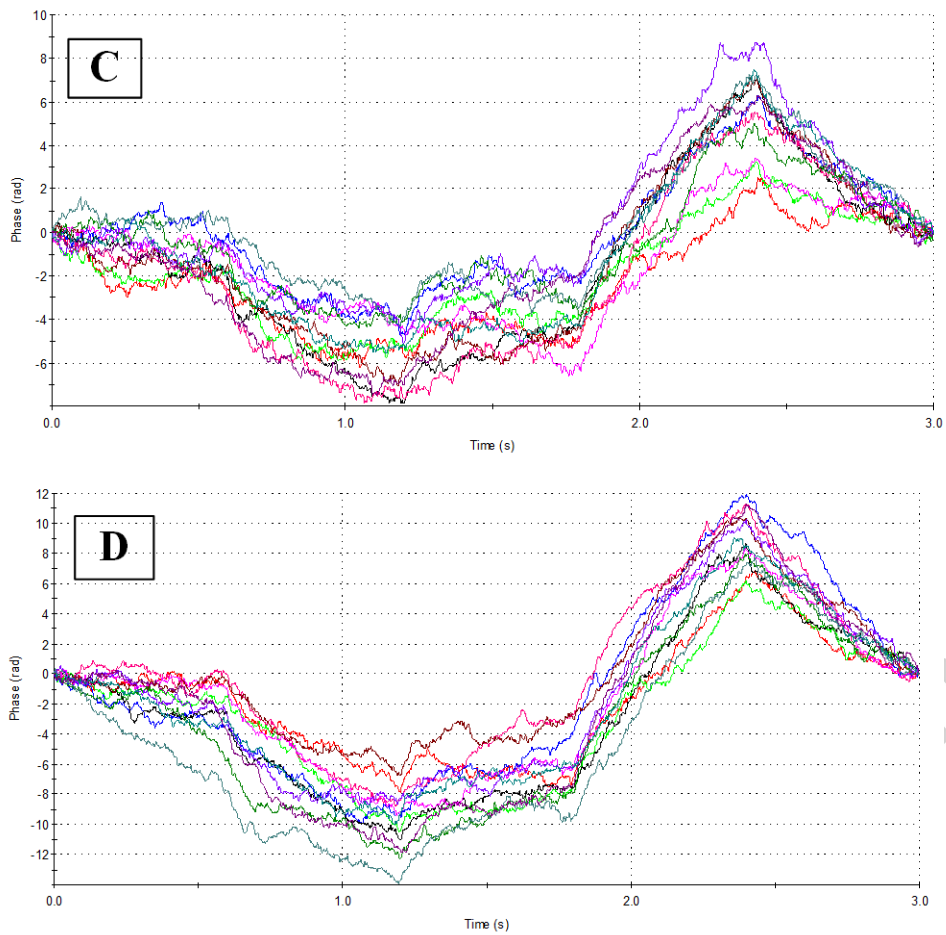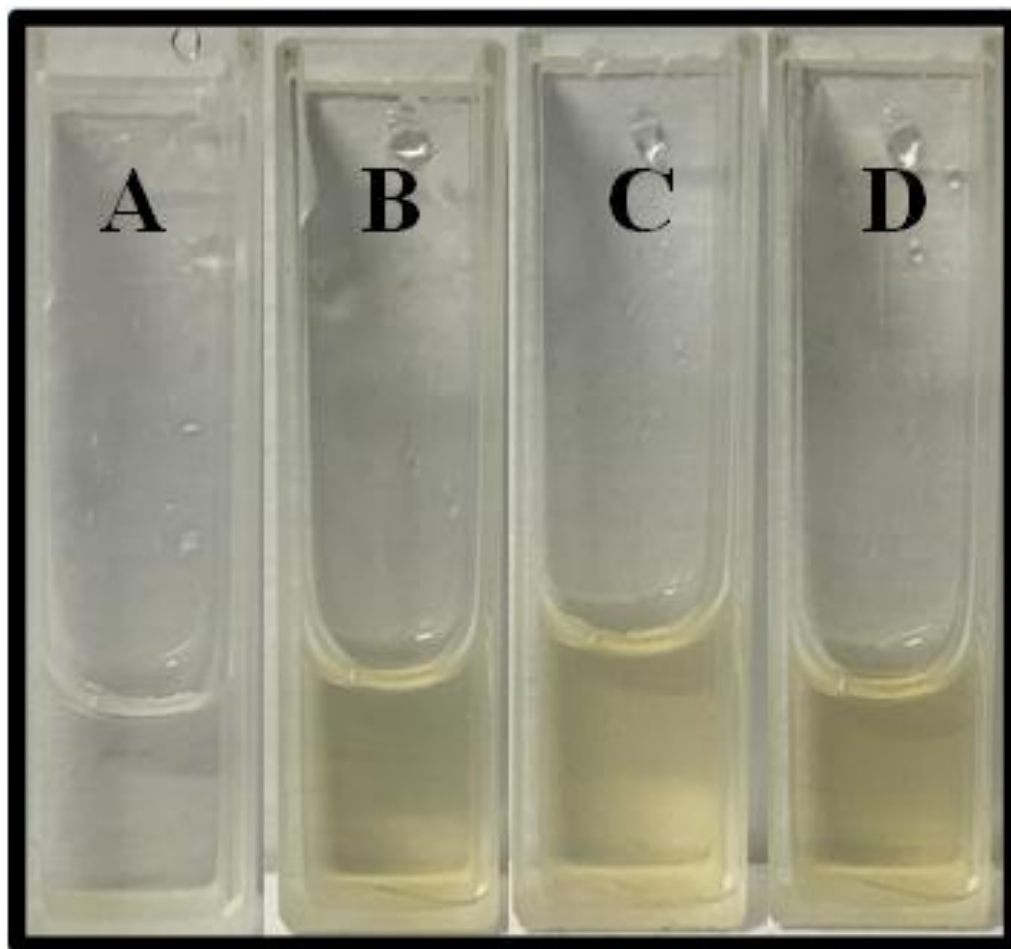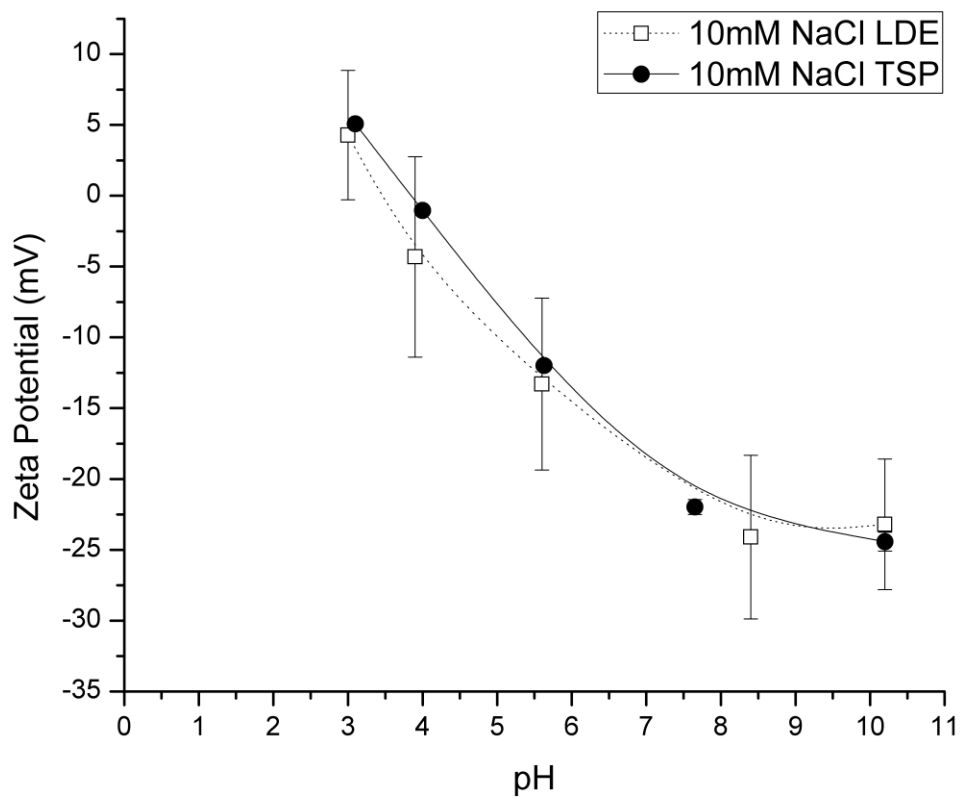
Figure 10
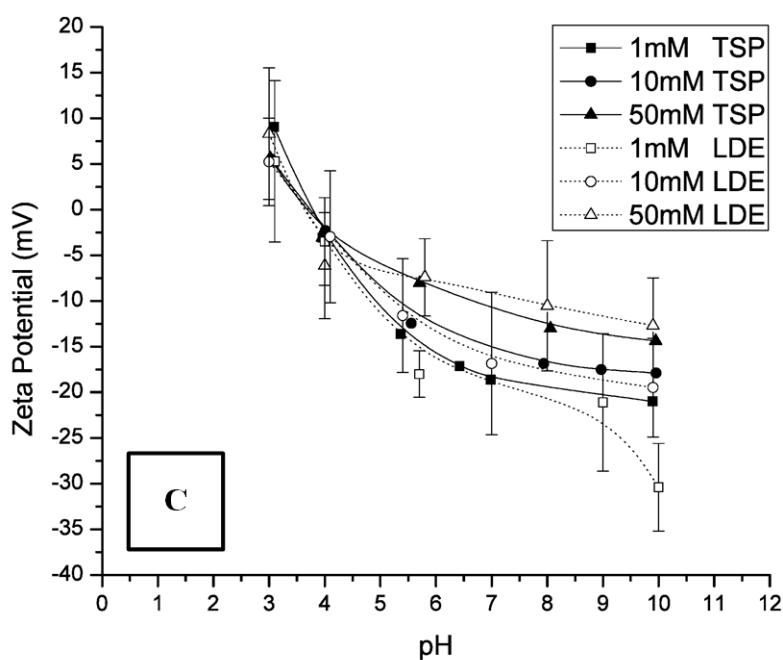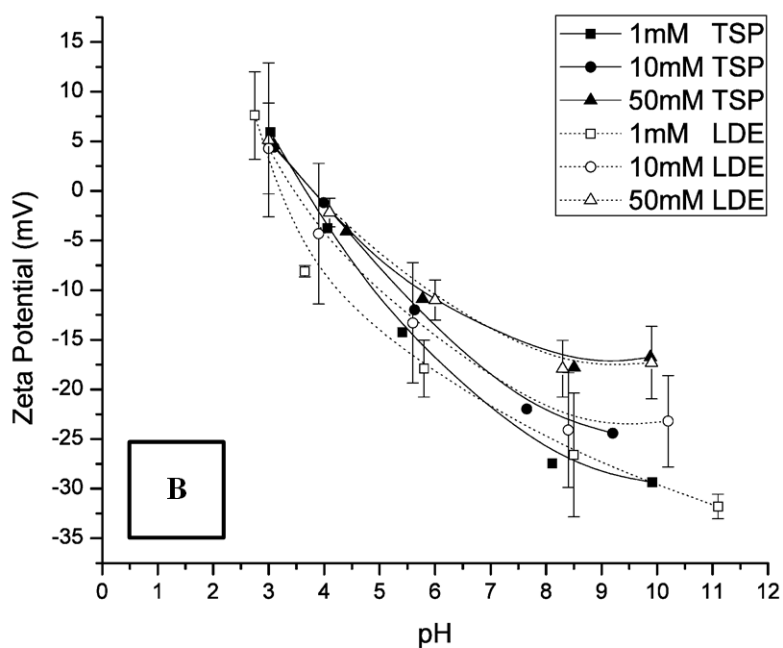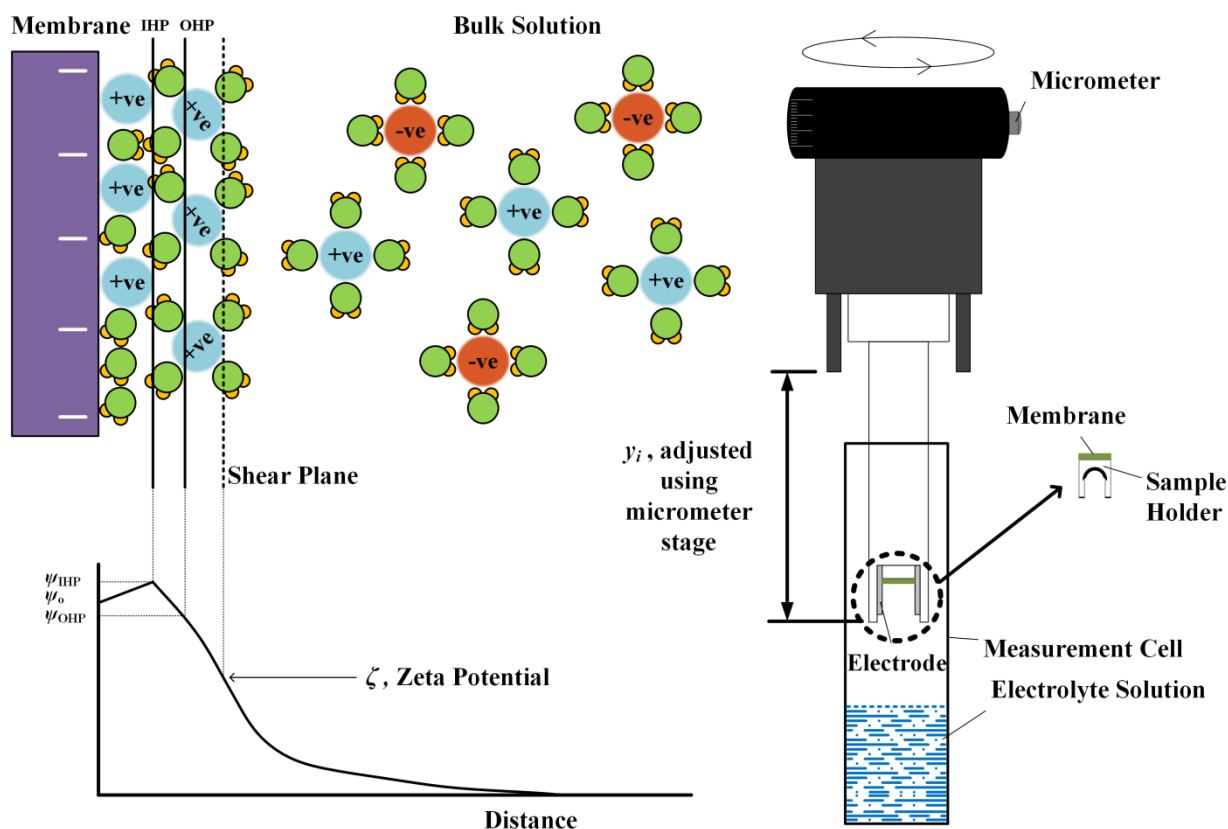
Figure 11 A-C

Table 1: **Uncertainty of zeta potential measurements by adjusting the applied electric field**

Voltage (V)	zP (mV)	R^2	Uncertainty (±mV)	Uncertainty (%)
0.5	-83.48	0.45	105.16	125.97
1.0	-27.21	0.01	4.59	16.88
1.5	-10.93	0.71	4.27	39.09

| 2.0 | -12.48 | 0.50 | 5.36 | 42.97 |

Highlights

- Laser Doppler Electrophoresis was successful for membrane charge characterization
- Joule heating effects were experienced at high electrolyte concentrations
- Statistical parameters were analyzed for Laser Doppler Electrophoresis measurements
- Results were compared to Streaming Potentials and found to correlate well

Graphical Abstract