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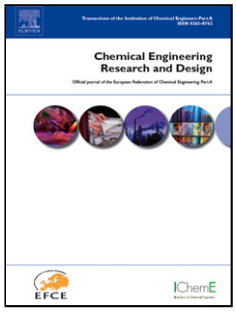

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Laser Doppler electrophoresis and electro-osmotic flow mapping for the zeta potential measurement of positively charged membrane surfaces

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Abstract

Successful characterization of membranes is of paramount importance for the development and improvement of novel membranes and membrane processes. The characterisation of membrane charge is key to understanding charge interactions between the process stream and the membrane and is typically represented by the surface zeta potential. In a previous paper [1], a novel technique employing an Uzigirs dip cell arrangement used in conjunction with Laser Doppler Electrophoresis was used to characterize the surface of several negatively charged membranes. In this paper, positively charged modified PTFE membranes are fabricated and the novel zeta potential measurement technique is utilised to quantify the resultant membrane charge by use of a positively charged amidine tracer particle. The amidine particles were characterised and shown to have a positive zeta potential of 12.4 mV for the experimental conditions used. A comparative analysis was made between the novel laser Doppler electrophoresis measurements and tangential streaming potential measurements for the positive membrane and the agreement was good. The phase plot and mobility-displacement were of good quality for the data set, with the surface equivalent mobility being 0.632 μmcm/Vs with R^2 = 0.977. In addition, a series of experiments were conducted to explore the operating envelope and highlight the pitfalls of the technique, i.e. oppositely charged particles to the surface should not be used. Overall, this work expands the application of the novel zeta potential measurement technique to span all membrane charge types. Thus providing a real benefit to the practicing scientist or engineer by having a reliable, fast and simple zeta potential technique that uses only a very small membrane sample.

Key words: Membrane, charge, zeta potential, positive, electrophoresis

1.0 Introduction

Membrane technology is now embedded across a wide range of industrial applications including water purification, pharmaceutical, biotechnology, petrochemical and textiles to name a few [2-5]. The general role of membranes is to separate, fractionate, concentrate or remove materials such as microorganisms, fine particles, proteins, nucleic acids, sugars, other organics and mineral solutes from various solutions [6-8]. The main separation mechanisms for membrane filtration are steric and Donnan based interactions [9-12]. Steric interactions at membrane surfaces are very well understood and easily measurable [13]. Charge effects are far more complex and a detailed examination of charge behaviour provides greater knowledge of the solute-solution-surface

mechanistic interactions, which leads to a better understanding of the subsequent membrane process performance.

Semipermeable membranes generate an electrical surface charge when contacted by a solution. Ions and molecules from the solution interact with the surface functional groups of the membrane leading to a chemical dissociation from the membrane surface resulting in charge generation. At the same time, ions in the contacting solution may adsorb on to the membrane surface, also generating a surface charge. Typical adsorbed materials include polyelectrolytes, ions, macromolecules and surfactants. The spacial distribution and concentration of these dissolved solutes and ions at the membrane interface is ordered and forms the classical electrical double layer [14-15]. The shear plane separates the stationary phase from the mobile phase of the electrical double layer and is critical to all fundamental models describing the electrical double layer. Zeta (ζ) potential is defined as the electrical potential at the shear plane. The zeta potential is a relatively simple electrokinetic phenomenon often used to quantify membrane surface charge in place of the membrane surface potential which, by comparison, is difficult to measure. Zeta potential measurements are important when determining membrane separation mechanisms, membrane fouling, ageing, cleaning, and functionalization [16-18]. Zeta potential is normally derived from either sedimentation potential, streaming potential, electrophoresis or electro-osmosis, with streaming potential often being the preferred option due to the methods inherent simplicity. A more detailed explanation of streaming potential, used in this study, is provided in the theoretical descriptions and each of the other phenomena is described in detail elsewhere [19-20].

Advances in Laser Doppler Electrophoresis (LDE) technology and Dynamic Light Scattering (DLS) have now opened up a new methodology to measure surface zeta potential through electro-osmotic flow mapping and using an Uzgiris dip cell [21-22]. In a previous paper [1], this novel method for the determination of membrane surface zeta potentials was applied to measure the surface charge of ultrafiltration, nanofiltration and reverse osmosis membranes. The technique specifically examines the electrophoretic mobility of carboxylated polystyrene tracer microparticles suspended in the contacting electrolyte solution. High quality regression correlations (R^2>0.95) were obtained under most operating conditions and excellent agreement was obtained when comparing zeta potential results to the traditional tangential streaming potential measurement. The methodology has several advantages over traditional surface potential methods. These include:

- Only a very small membrane sample is required when compared to other techniques, for example: The SurPASS instrument for zeta potential measurement uses either a clamping cell or adjustable gap cell with sample areas of 55 x 25 mm and 25 x 5 mm respectively [30]. This measurement uses a sample of 3.5 x 5 mm only. This is particularly useful in the laboratory and early phase development of new membranes.
- The technique can be applied to any class of liquid phase membrane, i.e. microfiltration, ultrafiltration, nanofiltration or reverse osmosis membrane.
- The measurement equipment is more economic when compared to other commercially available devices.
- The measurement equipment is multifunctional, i.e. performs zeta potential measurements for particles and surfaces as well as particle size characterisation.

While the technique offers a simple and economic method for the characterisation of membrane zeta potential, there was one major drawback. Careful consideration is required for the selection of appropriate tracer particles. The sole aim of these particles is to scatter light: chemical functionality

or surface chemistry does not affect the measurement. However, an essential criterion is that the tracer particles do not interact with the sample surface [23]. Due to the requirement for a mobile particle, in this case a negatively charged carboxylated polystyrene latex particle, the technique was limited to the characterisation of negatively charged surfaces only. In this paper, the novel technique for measuring membrane surface zeta potential has been expanded by inclusion of an alternate mobile particle which allows for the measurement of positively charged surfaces, thus allowing the measurement technique to be employed across the full spectrum of membrane charge.

2.0 Theoretical Descriptions

The theoretical descriptions used in this paper have been detailed elsewhere [1] and will only briefly be discussed here to provide appropriate background to complement the methods used.

2.1 Description of Zeta potential

The classical Gouy-Chapman-Stern-Grahame model describes the distribution of charge within the electrical double layer, see Figure 1. There are two clearly defined zones within the electrical double layer;

- the stern layer; which lies between the membrane and the outer Helmholtz plane is immobile, ions from the surrounding liquid bind at the solid interface, and
- the diffuse layer; beyond the outer Helmholtz plane which is mobile, ions move freely by thermal motion.

The plane of shear separates these two layers, with the first layer known as the inner Helmholtz plane (IHP) and the second known as the outer Helmholtz plane (OHP). Extending beyond the OHP into the bulk solution is the diffuse layer, where Brownian motion applies. Three different charge potentials are denoted in Figure 1, namely: the membrane surface potential (Ψ_o), the potential at the IHP (Ψ_{IHP}) and OHP (Ψ_{OHP}). The magnitude of the potential decreases linearly from the IHP to the OHP. The zeta potential (ζ) is measured at the shear plane.

2.2 Zeta potential measurement

Only descriptions related to the techniques in this paper will be discussed here, for further information on other techniques available see [13].

2.2.1 Tangential streaming potential measurements

Zeta potential measurements derived from streaming potential are either transversal or tangential [24]. For transversal measurements flow travels through the membrane pores, while for tangential measurements flow travels parallel to the membrane surface. Tangential streaming potential is the most commonly used method to measure zeta potential [25] and a wealth of information related to this technique is available throughout the literature.

Two identical membrane active layers are arranged to face each other separated by spacers to form a discrete flow channel. An electrolyte solution is pumped through the channel at a given flow rate delivering a fixed hydrostatic pressure gradient. The charge density of the membrane surface causes the counter ions to rearrange and excess ions are drawn towards the downstream (low-pressure) side of the channel by shear flow action. The difference in concentration of counter ions from one end of the channel to the other generates an induced electrical current known as the streaming current. The potential difference resulting from the streaming current is measured and divided by the pressure drop along the channel to form the potential coefficient.

$$\emptyset_{st} = \Delta V / \Delta P \quad (1)$$

where ΔV is the potential difference and ΔP is the pressure gradient. Zeta potential is then calculated from the streaming potential using the Smoluchowski equation.

$$\zeta = \emptyset_{st} \frac{\eta}{\varepsilon \varepsilon_o} K_B \quad (2)$$

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. Note that electrolyte concentrations at or less than 10^{-3} M are commonly used to avoid surface conductivity issues.

2.2.2 Laser Doppler Electrophoresis

Laser Doppler electrophoresis is dependent on the frequency of scattered laser light as a function of particle velocity – known as the Doppler shift. This method has been used to study the diffusion of particles in solution [26]. Many colloidal particles obtain a surface charge in solution and subjecting colloidal particles to non-diffusional motion, from electric fields, leads to a phenomena known as Doppler shift. This includes motion attributed to both diffusion and the induced electrophoretic mobility. The velocity and direction of the resultant movement is a function of the suspending medium, the electric field strength and the particle charge. The zeta potential is defined in terms of electrophoretic mobility U_E by the Henry equation:

$$U_E = \frac{2\varepsilon\varepsilon_o F(\kappa a)}{3\eta} \zeta \quad (3)$$

where $F(\kappa a)$ is the Henry function, κ the inverse of the Debye length and a the particle radius [22,27]. Two main assumptions are usually made for $F(\kappa a)$; either $F(\kappa a)$ = 1.0 (the Debye approximation) or $F(\kappa a)$ = 1.5 (the Smoluchowski approximation) [28]. $F(\kappa a)$ is dependent on the electrolyte used and the size of the colloid. For this work the Smoluchowski approximation was employed, which is applicable to particles greater than 100 nm, aqueous solution, and ionic strength greater than 10^{-3}M.

Phase Analysis Light Scattering (PALS) was measured and the frequency shift resulting from changes in electrophoretic velocity v is given by:

$$\Delta v = 2U_E \frac{sin(\theta/2)}{\lambda} \quad (4)$$

where λ is the laser wavelength and θ is the angle of scatter [22,27].

2.2.3 Electo-osmotic flow mapping

Electro-osmosis is defined as the flow of a liquid through stationary particles in response to an applied electric field. Electro-osmotic flow can be used with mobile tracer particles to evaluate surface zeta potential. The surface in question, in this case a membrane, is fixed to a sample holder and placed in an Uzgiris electrode in a cuvette, see Figure 2. When the electric field is switched on, the motion of the particles is recorded using PALS. Electro-osmotic flow mapping characterises the flow in the half space outside the slipping plane. To do this, measurements are taken at various displacements y_i, normal to the membrane surface [21]. The slipping plane of the surface is assumed to coincide with the test surface at the plane of $y = 0$.

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

$$\rho v = \eta \left[\frac{d^2v}{dx^2} + \frac{d^2v}{dy^2}\right] \quad (5)$$

Where ρ is the fluid density, η the apparent viscosity and v(t,x,y) the component of fluid velocity parallel to the boundary. The y co-ordinate is perpendicular to the boundary and the x co-ordinate is parallel. Continuity implies that v is not a function of x as no flow perpendicular to the boundary is expected. The equation simplifies to:

$$v = k\left[\frac{d^2v}{dy^2}\right] \quad (6)$$

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:

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

and solution:

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

where erf is the error function. For y ≥ 750μm for t ≥ 75ms or y ≥ 1.5mm for t ≥ 300ms, the bracketed terms do not apply as $\mathrm{erf}\left(\frac{\mathrm{y}}{2\sqrt{\mathrm{kt}}}\right) \rightarrow 0$. For surface zeta potential measurements, the main focus is in the y-axis intercept, however, since the measured value consists of both electroosmotic and electrophoretic contributions, an estimate of the tracer velocity v_{ep} itself is also required. Electrophoretic motion is recorded at set time intervals using PALS; therefore, the Navier-Stokes equation can be fitted to measurements of $v_i(\mathrm{y}_i)$ at various displacements and y_i can be extrapolated to the y-axis intercept:

$$v_{\mathrm{eo}} = -\mathrm{Intercept} + v_{ep} \quad (9)$$

The zeta potential ζ is then is then a function of the flow at the slipping plane v_{eo} by:

$$\frac{v_{\mathrm{eo}}}{E_{\mathrm{x}}} = \frac{\varepsilon\varepsilon_o}{\eta}\zeta \quad (10)$$

where $\mathrm{E_x}$ is the electric field strength.

3.0 Materials and methods

3.1 Chemicals used

All chemicals used were of analytical grade or better unless otherwise stated. Methanol (HPLC grade), absolute ethanol, toluene, HCl, NaCl, NaOH, NH_4OH and 3-Aminopropyltriethoxysilane (APTES) were purchased from Fisher Scientific UK Ltd. and ultra-pure (< 1 µS/cm) water was produced from a Millipore ELIX 5 unit (Millipore UK Ltd., UK).

3.2 Membrane preparation

The membrane used was a hydrophobic PTFE microfiltration membrane typically used for filtration and sterilization in medical applications. The membrane has a pore size in the range 45-60 µm and a thickness of 2 mm (Porex Ltd, Aachen, Germany). APTES was coated onto the PTFE membrane via hydrolysis and condensation, using HCl and NH_4OH as catalysts as previously described elsewhere [29]. HCl (0.01 wt%) was added to a mixture of APTES, Ethanol and ultra-pure water (6:89:5), and stirred at 25 °C to ensure dissolution. Following this, 2 wt% NH_4OH was added into the mixture for condensation. The mixture was poured onto the membrane which is held in a mould. The reaction was left to occur at 25 °C for 12 hours. The PTFE membrane was then washed in distilled water and dried for a minimum of 8 hours.

3.3 Streaming Potential

Tangential streaming potential measurements were conducted using an Electrokinetic analyser (EKA) (Anton Paar GmbH, Graz, Austria) using cut flat sheet membranes (2 sheets, 12.5x5.5cm). The electrolyte for this study was aqueous NaCl at concentration of 1 mM. The electrolyte was prepared using ultra-pure water and pH adjusted periodically using 0.1 M HCl and 0.1 M NaOH as required. For methanol – water systems, 1 mM NaCl was dissolved in the mixture and stirred until the NaCl is completely dissolved in the solution. In all cases, fresh electrolyte solution was used for each experiment; even when changing from acidic to alkaline conditions. In this way the concentration of ions in the system is maintained consistent as much as possible. Before loading solutions to the equipment, the system was washed thoroughly with ultra-pure water. Similarly, on entering fresh electrolyte solution to the equipment, a thorough rinse through was conducted to equilibrate the membrane sample. A pressure gradient from 0-700 mbar over 30-seconds was used to produce a streaming current which was recorded using a pair of AgCl electrodes. 10 measurements were made at each pH value using alternating flow directions. Electrolyte pH and conductivity were measured using a pH and conductivity probe. For aqueous solutions, a Fisherbrand pH electrode was used, for alcohol-water solutions a Jenway non-aqueous pH electrode was used. All experiments were conducted at room temperature (25 °C ± 1 °C).

3.4 Laser Doppler Electrophoresis measurements

Electrophoretic mobility and electro-osmotic experiments were conducted using a Zetasizer Nano ZS with the surface zeta potential accessory (Malvern, UK) using the methodology described previously [1]. Electrolyte solutions were prepared as described previously but with the addition of 1 drop of 0.5 µm negatively charged carboxylated polystyrene latex particles (Polysciences Inc., PA, USA) or 0.5 µm positively charged amidine particles (Fisher Scientific Ltd., UK) per 200 mL of electrolyte solution. Membranes were prepared by cutting to shape (3.5 x 5 mm) in order to fit the surface cell and were attached using epoxy (Araldite) resin. Membranes were washed with 5mL of the electrolyte solution to remove any particulate debris before then being submerged into the cuvette. The surface cell was sonicated for 30 seconds in toluene prior to subsequent measurements to remove any debris. This was repeated as necessary until the toluene remained clear. The membrane was then washed with ethanol followed by water and was then dried using compressed air.

The Zetasizer conditions use were: forward scatter with the attenuator in position 10, count rate set to the optimal 250-500 kcps range, four distance position measurements in 125 µm steps, three measurements at each location (each measurement consisted of 15 sub-runs with 60s interval), repeat measurements for each pH, and a further three measurements consisting of 100 sub-runs with a 60s interval to measure the electro-osmotic mobility of the tracer particles. All measurements were conducted at 25 °C.

4.0 Results and discussion

4.1 Characterisation of the tracer particles

The two tracer particles used in this study, latex and amidine, were characterised for surface zeta potential using the Zetasizer Nano ZS and the results are shown in Table 1. As expected, the latex particles demonstrate a strongly negative zeta potential at -52.8 mV. This is in contrast to the Amidine particles that demonstrate a positive zeta potential of 12.4 mV. However, the amidine particles are clearly not as highly charged as the carboxylated latex with only 23% of the charge magnitude. Thus, both particles are confirmed to exhibit the required state of charge for the experimentation.

4.2 Zeta potential measurements of the PTFE membrane

The zeta potential of the raw PTFE membrane was evaluated using both tangential streaming potential and laser Doppler electrophoresis, the results are shown in Figure 3. The zeta potential, as measured from tangential streaming potential, illustrates that the PTFE membrane is positively charged in the low pH range and then rapidly becomes negative as pH is increased, with an isoelectric point in the region of pH 5. At higher pH values, greater than pH 7.5, the zeta potential of the membrane stabilises at about -20 mV. These findings are very similar in trend to those of Wang et al. [29] obtained using KCl as an electrolyte rather than NaCl as in this study. The laser Doppler electrophoresis results when using the negative latex particles show very similar behaviour and are almost identical in trend and magnitude to the tangential streaming potential measurement results. This confirms that the technique is indeed capable of zeta potential measurements of negatively charged membranes as proposed by Thomas et al. [1]. The phase plot and mobility-displacement plot for the measurements are shown in Figure 4. The three average phase measurements are illustrated in Figure 4a and are banded and clear at each of the four displacement lengths used, highlighted by black circles overlaid on the plot. The mobility-displacement is shown in Figure 4b and the surface equivalent mobility was calculated as -1.411 µmcm/Vs (-[-2.664]+[-4.075]) with R^2 = 0.994. However, care has to be taken when selecting an appropriate tracer particle for use in this measurement technique. In this case, the membrane is negative at the study conditions and so the tracer particle should also be negative. To highlight this problem, the positive Amidine particle was also used to measure the zeta potential of the membrane. The equipment did take a measurement and did derive a zeta potential as a correlation was able to be made. The results are shown in Figure 3 as green squares. Clearly the derived zeta potential measurement is very different to that of the other two measurements and is never really anywhere close to the same magnitude or trend. This is problematic when using a membrane of unknown charge. The phase plot and mobility-displacement plot for these measurements are shown in Figure 5a and 5b respectively. In this case the phase plot is not as well defined with each of the lines being quite sporadic and showing no clear trend by comparison with Figure 4a. The surface equivalent mobility for this data set is -2.36 µmcm/Vs (-[0.235]+[-2.125]) with R^2 = 0.984. In this case, the positively charged Amidine particles are adsorbing to the surface of the negatively charged membrane and their mobility in solution is clearly compromised as a result. However, the quality of the mobility-displacement plot (Figure 5b) could easily be interpreted as a good result with the R^2 value being reasonably close to unity. Thus, this

data would suggest that avoiding a meaningless result can only be achieved by interpretation of the phase plot when the nature of the surface charge of the membrane is unknown. This would be no issue to an experienced colloid scientist, however, for a less experienced scientist or engineer corroboration of the results obtained from laser Doppler electrophoresis should be made by an alternative technique such as tangential streaming potential and once the nature of the surface is known, laser Doppler electrophoresis can be used with a much higher level of confidence.

4.3 Zeta potential measurements of the APTES-modified PTFE membrane

The PTFE membrane surface charge was adjusted to a positive charge by modification using APTES and the resulting zeta potential derived from tangential streaming potential measurements and laser Doppler electrophoresis are shown in Figure 6. The zeta potential, as measured from tangential streaming potential, illustrates that the APTES-modified PTFE membrane is positively charged at low pH, slowly reduces in charge magnitude as the pH increases and becomes negative beyond a pH of around pH 9. The trend of the zeta potential versus pH is almost linear in fashion. Again, this is very similar behaviour to that observed for a comparable membrane produced by Wang et al. [29]. The zeta potential measurements obtained using laser Doppler electrophoresis and the Amidine particles (positively charged) show very similar behaviour. However, in this case the zeta potential values obtained fall slightly below the values obtained from streaming potential measurements. In essence, the trend is the same but the data is slightly offset and the resulting isoelectric point has moved to around pH 7.8. The phase plot and mobility-displacement were of good quality for the data set (not shown as similar to Figure 4), with the surface equivalent mobility being 0.632 µmcm/Vs (-[-1.494]+[-0.862]) with R^2 = 0.977. Interestingly, the magnitude of the charge for the Amidine particle is significantly less than that of the latex particles, see Table 1. This could indicate that better agreement between the laser Doppler electrophoresis and tangential streaming potential measurements could be obtained if a more highly charged positive particle is used and suggests a future study could investigate the quality of the experimental measurement using a variety of particles that span a range in charge magnitude. Overall, both sets of zeta potential data are in reasonable agreement and are certainly suitable for characterisation purposes. The membrane was also characterised using laser Doppler electrophoresis and the negatively charged latex particles, see Figure 6. In this case, the zeta potential for the membrane is now clearly negative, with the magnitude of zeta potential being -30 mV at pH 3.5, decreasing to -75 mV at pH 5.8 and stabilising at this level as pH is increased. This behaviour is in stark contrast to that obtained from the Amidine particles and tangential streaming potential measurements and clearly indicates that the latex particles are adsorbing to the surface of the membrane and modifying the surface charge from positive to negative. The fact that the latex particles are more highly charged than the Amidine particles provides an explanation for this stark deviation, which was not so pronounced for the raw PTFE membrane. The phase plot and mobility-displacement plot for this data are shown in Figure 7a and 7b respectively. As with the counter charged particle data with the unmodified PTFE membrane, the mobility-displacement plot appears to be reasonable with a surface equivalent mobility being -7.086 µmcm/Vs (-[2.11]+[-4.976]) with R^2 = 0.982. Again, when the tracer particle selected carries like charge to the membrane surface, the phase plot is very distorted. However, in this particular case, the very final set of measurements appear quite normal, see Figure 7a circled section. An explanation for this anomaly would be that the counter charge of the latex particle causes adsorption to take place and this adsorption process is fast due to the high magnitude of charge on the latex particle. If this adsorption process was indeed fast enough to conclude prior to the Zeta Sizer machine taking the last set of results, then there would in fact be a negatively charged membrane and residual negatively charged particles in solution. Hence, this would indeed constitute a normal or regular experimental run and the resulting data should indeed be of good quality.

5.0 Conclusions

The novel zeta potential measurement technique using laser Doppler electrophoresis was employed to measure the surface zeta potential of a negatively charge PTFE membrane using latex particles (also negatively charged). The results showed good correlation agreement between mobility-displacement measurements (R^2 = 0.994) and a comparison to zeta potential obtained from tangential streaming potential measurements was also in good agreement. Amidine particles were shown to have a positive zeta potential of 12.4 mV and were also used to characterize the PTFE membrane. In this case, the correlation agreement between mobility-displacement measurements was also good (R^2 = 0.984), however, the phase diagram indicated significant issues. The resultant zeta potential measurements obtained were in effect meaningless as the positive particles were adsorbing to the negative membrane surface. Thus, when using this new methodology with a surface of unknown charge, care must be taken to ensure the correct tracer particle is used and review of both the mobility-displacement and phase diagram should be made. In the ideal case, a second method for characterization such as tangential streaming potential should also be employed to provide assurance.

The PTFE membrane was then modified using APTES to generate a positive surface and this was confirmed across the pH range pH 4 to 9 via tangential streaming potential measurements. The amidine particles were identified as a successful positive tracer particle for use in the laser Doppler electrophoresis experiments allowing zeta potential measurements to be made. A comparative analysis was made between the laser Doppler electrophoresis measurements and tangential streaming potential measurements and the agreement was good, although there was a small amount of offset between the two data sets. The same membrane was then characterized using the latex particles and the data obtained demonstrated that the membrane was once again negatively charged, due to the latex particles strongly adsorbing to the initial positively charged membrane surface.

Overall, the work in this paper confirms that laser Doppler electrophoresis is a suitable method for the characterization of membrane surface charge via determination of the membrane surface zeta potential. This technique has several advantages over traditional methodologies that can be beneficial to the development scientist and industrial practitioner alike. This study now expands the methodology to cover positively charged surfaces, which allows the novel technique to span the entire measurement range required for membrane surface charge characterisation.

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Ysgoloriaethau Sgiliau Economi Gwybodaeth
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Figures and Tables

Figure 1: A representation of the electrical double layer model describing potential as a function of distance from the membrane surface.

Figure 2: The Uzgiris dip cell arrangement used in electro-osmotic flow mapping for surface zeta potential measurements.

Figure 3: Zeta potential measurements for the unmodified PTFE membrane using both tangential streaming potential (TSP) and laser Doppler electrophoresis (Zeta Sizer).

Figure 4: Information derived from the laser Doppler electrophoretic measurements for the unmodified PTFE membrane using latex particles (negatively charged), a) the phase plot and b) mobility-displacement plot.

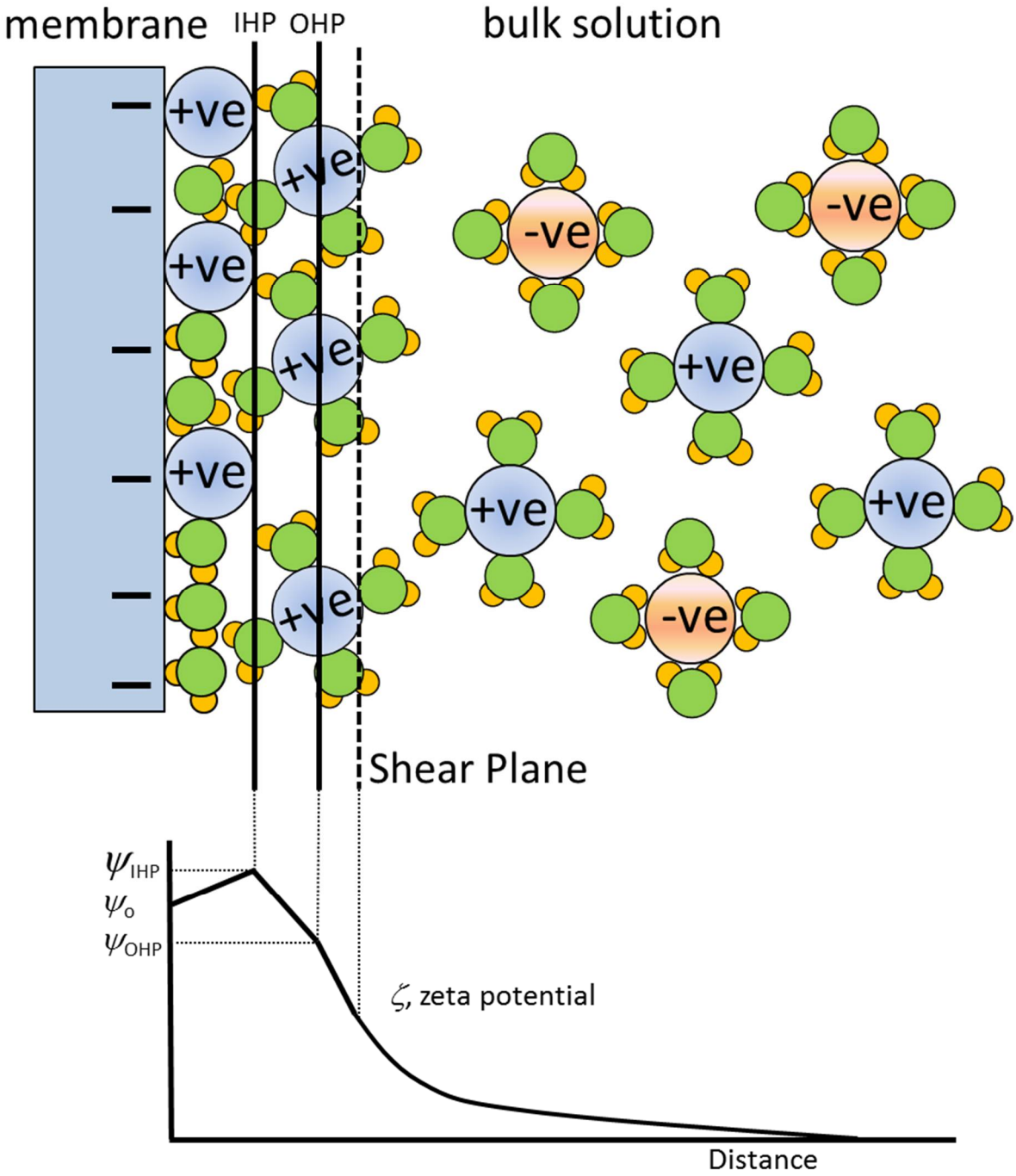
Figure 5: Information derived from the laser Doppler electrophoretic measurements for the unmodified PTFE membrane using Amidine particles (positively charged), a) the phase plot and b) mobility-displacement plot.

Figure 6: Zeta potential measurements for the APTES modified PTFE membrane using both tangential streaming potential (TSP) and laser Doppler electrophoresis (Zeta Sizer).

Figure 7: Information derived from the laser Doppler electrophoretic measurements for the APTES-modified PTFE membrane using latex particles (negatively charged), a) the phase plot and b) mobility-displacement plot.

Table 1: Characterisation data for the tracer particles.

522 Figure 1:



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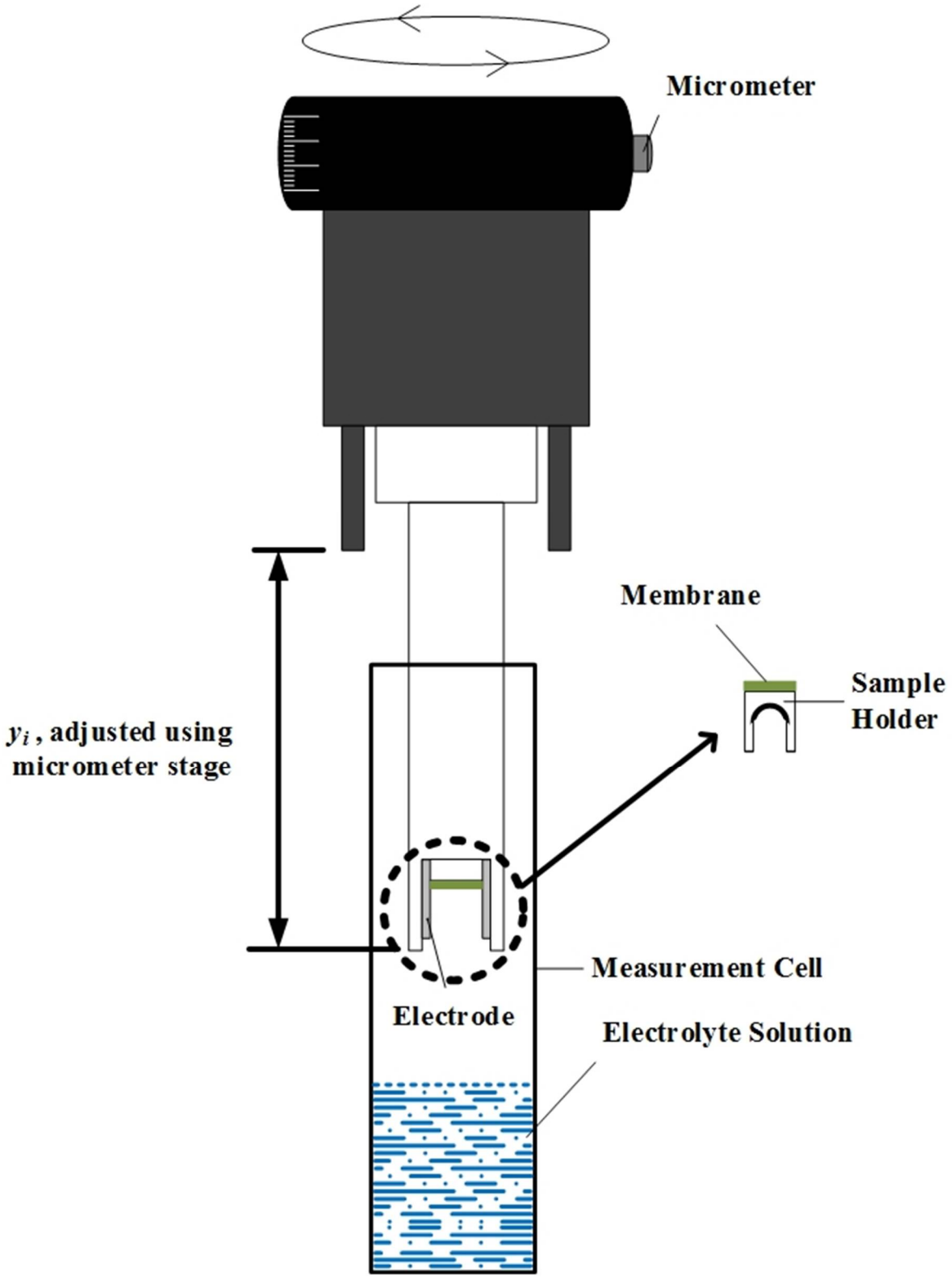
526 Figure 2:



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531 Figure 3:
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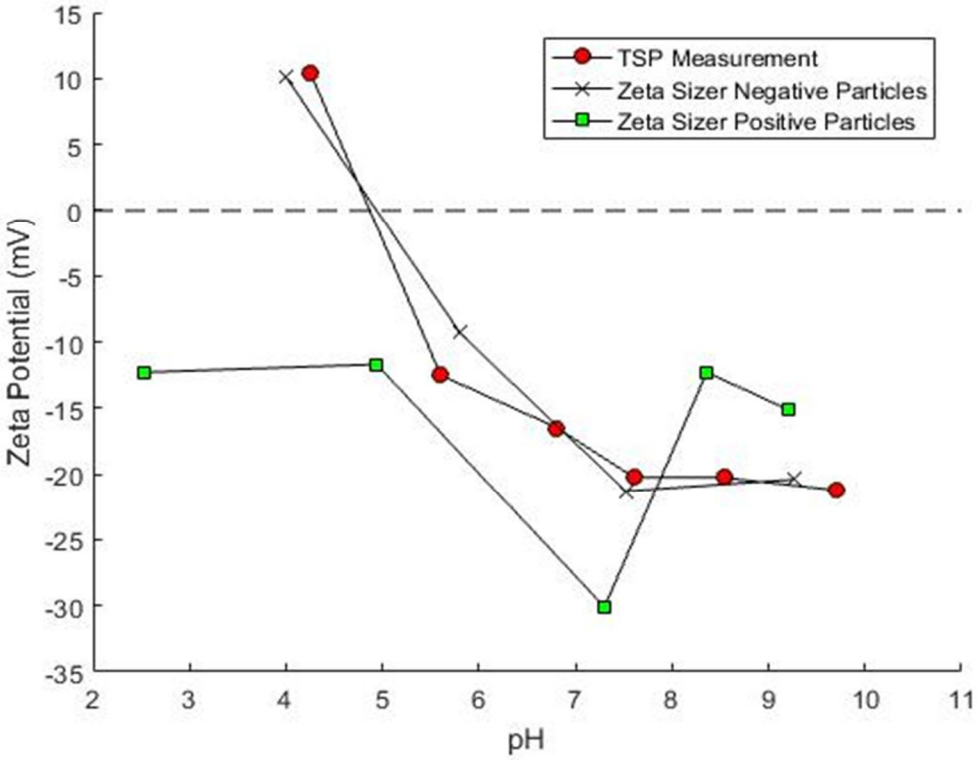

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534 Figure 4:
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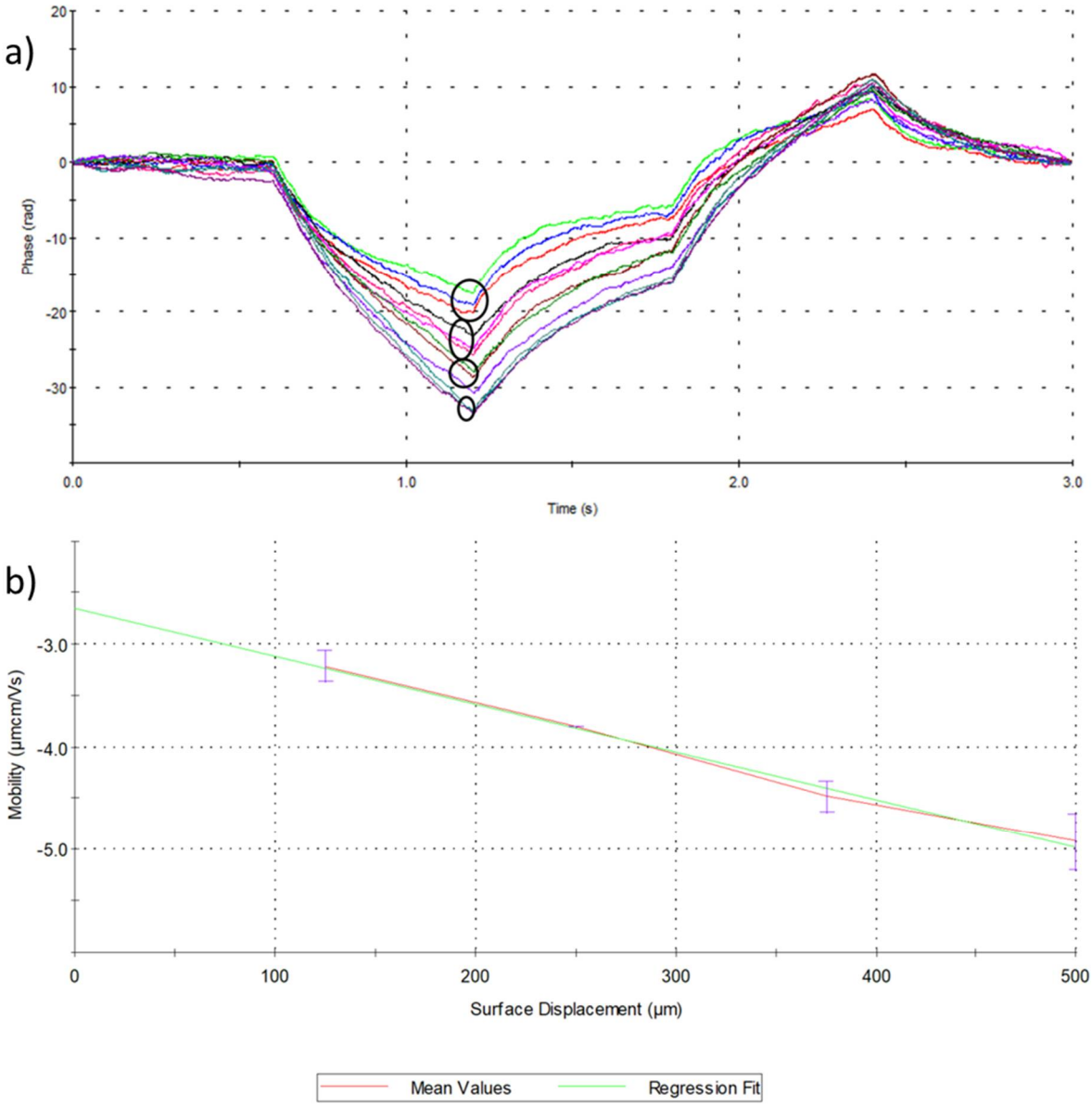

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542 Figure 5:
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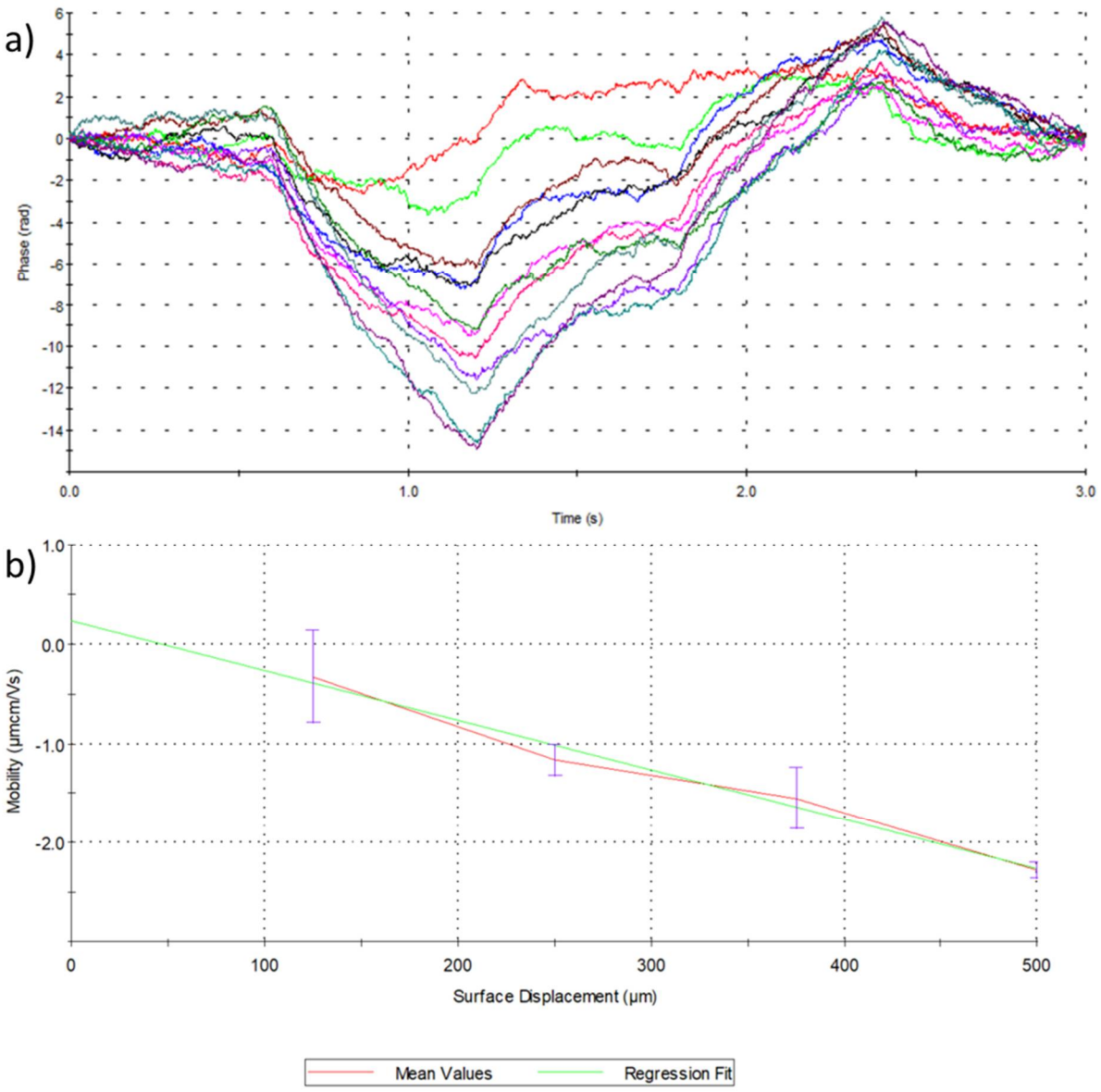

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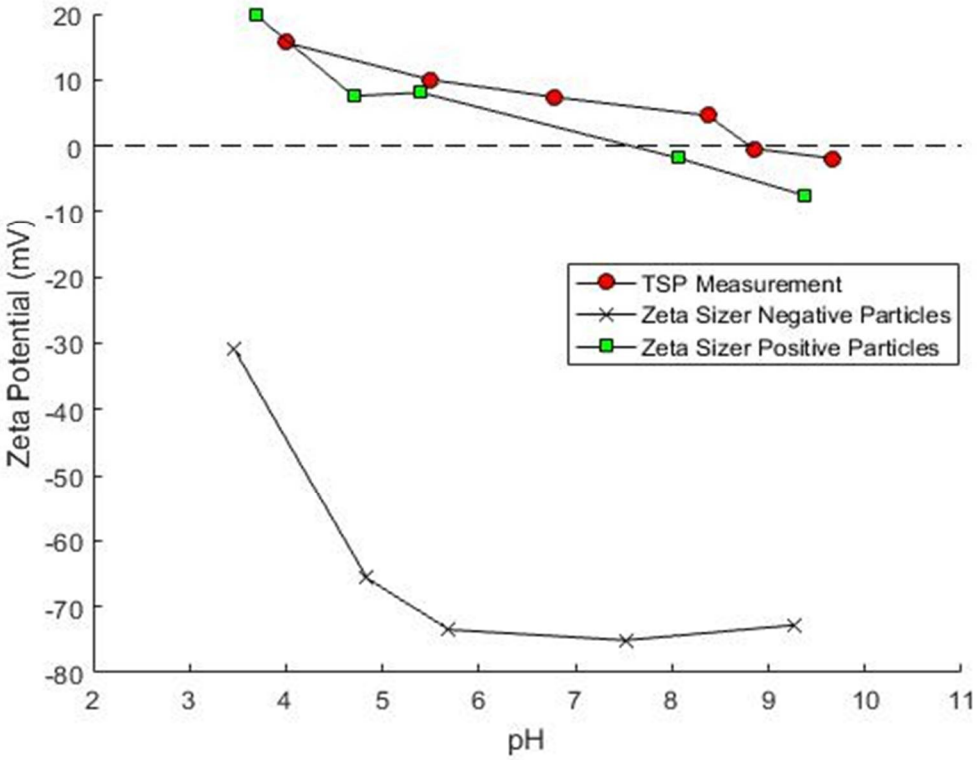

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554 Figure 7:

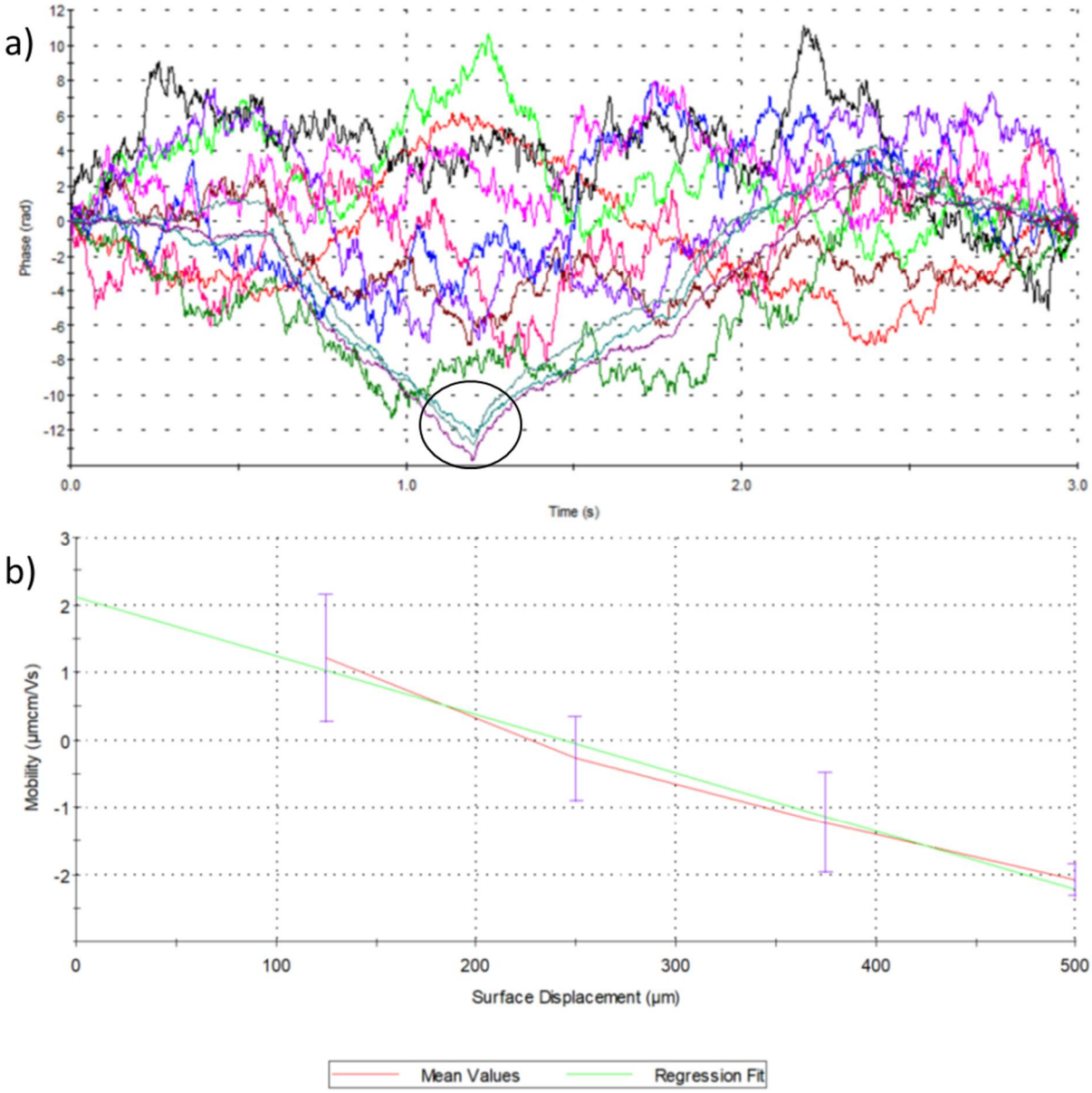

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Table 1:

Parameter/Particle	*Latex*	*Amidine*
Zeta Potential (mV)	-52.8	12.4
Standard Deviation	8.56	2.83
Mobility (µmcm/Vs)	-4.119	0.784
Conductivity (mS/cm)	0.192	0.104

Highlights

- Laser Doppler Electrophoresis was successfully applied to positively charged membranes
- Laser Doppler Electrophoresis was successful for membrane charge characterization
- Results were compared to Streaming Potentials and found to correlate well
- The novel technique now spans the entire membrane range

Graphical abstract