TXQ 301 - Assignment

Zeta Potential in Textiles

Ankish Chandresh

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Faculty Mentor - Prof. B S Butola

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Abstract

In this assignment, we discuss the concept of Electrokinetic properties of surfaces, adsorbents, textile fabrics and fibres, in particular the Zeta Potential. We also interpret what the absolute and apparent value of the Zeta Potential measures and conveys information about. How Zeta potential indicates properties like hydrophobicity and other surface properties. The process of creation of such a potential is discussed - due to solid-liquid interaction upon different fabrics materials and fibres with varying properties(primarily surface) being put in contact with a suitable solution under controlled conditions and due to the interaction of the charged fabric surface with the solutes is also discussed. Various surface properties and their interpretations are also discussed along with the effect and conditions of the solute itself. The various applications of the measurement Zeta Potential and surface charge follow, after the discussion on its measurement principles and widely used method - the streaming potential method. Its usefulness, downfalls, results and interpretations are also briefly discussed for varying scope of applications as in development of surfactants, softeners, detergents under different conditions of pH, salinity etc.

The Literature survey covers Zeta Potential and other useful Electrokinetic properties like IEP and their measurement techniques, the EDL model and underestimation problem. Interface properties of the textile fabric are covered with their analysis and applications, using the streaming potential method, for Adsorption of nanoparticles, external agents, textile care and interpreting Heterogeneous material surfaces.

The various factors like the chemical properties or the compositional structure of the fabric were also studied as reported in the research articles as part of the literature review. The effect of these various factors on processes like adsorption, washing efficiency, rate of the processes is also mentioned. Subsequent studies show the role of surface functional groups attached to them, the pH levels in characterisation of the type and composition of the fabric or fibre, conclusions about the adsorption mechanism and kinetics of the surfactant and softener adsorption process in some depth. The Effects of factors like swelling are also discussed at some length.

Introduction

When a solute is dissolved in a solvent the solute may flocculate or remain stable and resist aggregation. The solutes when in the solution induce a distribution of ions creating an electrical double layer. Which results in electrostatic force of repulsion among other forces of attraction.

When electrostatic repulsion is high between the solute particles the dispersion in the solution is stable. This suggests higher the net electric charge contained within the region bounded by the slipping plane, causing a potential difference called the Zeta Potential, the more stable the dispersion. Zeta potential is a term for electrokinetic potential. This potential is a property of charged interfaces. It is widely used for measurement of surface charge. Since, when a solid surface(textile fabric) is brought into contact with an aqueous solution, surface and solid-water interfacial charge are generated spontaneously due to various properties like polar functional groups, swelling etc. and further leads to electrostatic interaction of the solid surface and the solutes, and hence similar surface charge formation is observed giving rise to many useful surface properties. Zeta Potential can be used as an indicator to measure this charge which is useful to do desired analysis as in for textile fabrics and fibres as in characterization, rate of the process, pretreatment, dyeing and fishing etc. Which helps in development of efficient detergents, effective softeners, identifying mechanisms and identifying and quantifying factors like chain length of surfactants for adsorption among others.

There are many principles for measuring zeta potential which could be apparent and not actual indicator of the properties of the charged surface, but nonetheless indicative, as in electrophoresis, sedimentation potential, electro-osmosis which varies with the size of solutes involved in the experiment, usefulness and ease. Zeta potential is often, however, measured using streaming potential which is measured using the **Helmholtz-Smoluchowski** equation improved by Fairbrother and Mastin. Which has its own issues as it relies on the EDL model and neglects factors like surface conduction.

Literature Review(And Independent Interpretations)

The EDL Model, Zeta Potential and The Streaming Potential:

We often use the EDL model for the distribution of charge over a surface when a solid is made to come in contact with an aqueous solution. Which is that the electrical state of a charged surface is determined by the spatial distribution of ions around it and such a distribution of charges has been called an electrical double layer (EDL). It is a physical model in which one layer of the EDL is seen as a fixed charge with the surface charge, firmly bound to the particle or solid surface, while the other layer is distributed diffusely within the solution in contact with the surface(slip plane)[5]. The potential difference between this solution surface and bulk of the solution is called the zeta potential. The nature of the surface, its charge, the electrolyte or adsorbate concentration in the solution, the nature of the electrolyte and of the solvent and their mutual interaction under constant pH and temperature determine the Zeta potential(ζ)[5]. There are however many issues in estimating zeta potential reliably. One being, Surface Conduction, where the excess electric conduction that takes place in dispersed systems owing to the presence of the electric double layers may contribute to the excess conductivity leading to lower Zeta potential estimates than the actual measure as in [3]. The most commonly used method is however the Streaming Potential Method which allows in determining in situ measurements. Streaming potential occurs when liquid flows through a capillary or a membrane under a pressure difference applied between the both ends of the capillary. Accumulation of counter-charges due to the movement in the direction of the liquid flow leads to the formation of an electric potential called the Streaming Potential[1].

In the **Helmholtz–Smoluchowski theory** this streaming potential **Ustr** is related to the pressure difference **p** linearly. Streaming potential measurements are a function of various parameters such as pH, salinity, nanoparticles adsorption, composition, chemical structure and temperature etc. considering various applications explored in this survey.

For a reliable streaming potential analysis, the EDL model requires the surface to be flat with an infinite extension, non-porous and non-conductive. This is certainly not the case for textile fabrics [1]. However, with the improved **Helmholtz and Smoluchowski** theory by Fairbrother and Mastin for evaluation of the zeta potential from streaming potential measurement of fibrous samples, Zeta Potential and Streaming Potential measurements proved to be useful and indicative as in [1 - 8]. There have been further extensions and improvements recently[1].

Applications of Zeta Potential and Interpretations:

Zeta potential has found immense utility for fabrics and fibres, be it natural, synthetic, cellulose based, heterogeneous composite or functionalized [1- 8]. As in zeta potential analysis can be useful in monitoring the electrostatic interaction of solutes, ranging from molecules to nanoparticles, with the charged fabric surfaces, such as in dyeing or finishing, surface modification and treatment [1, 2]. Well understanding of the textile electrokinetic behaviour, surface charges and surface properties is an important step for the development of functionalized textiles [4]. It is also used in characterization, analysis and adsorption properties of agents of Heterogeneous Materials of varying composition[1, 3]. Zeta potential is not a constant value for textiles and could be very different under different experimental conditions and the sample under consideration, it varies across the surface, with time and other dynamic factors like pH, salinity etc. However, it can be used for characterisation of certain fabrics and fibres and give information about the nature of functional groups, chemical structure, surface chemistry[6], heterogeneous composition[3], hydrophilicity or hydrophobicity of the fibre surface, its effect on the solute or adsorbate concentration present, swelling capacity and adsorption mechanisms among other surface properties and supramolecular structure information like molecular orientation[2]. This information finds application in textiles among many as in the detection of the adsorption of surfactants (e.g., fabric softeners, laundry detergents), polyelectrolytes, and nanoparticles and as an indicator for solute-on-surface adsorption processes[2].

Applications of a reliable Zeta Potential measurement could also reveal the rates of processes such as adsorption and desorption. It is used to analyse the effect of washing of protein and pigment stained raw cotton fabrics in and analyse the washing efficiency[6] and durability with multiple wash cycles after modification with nano-particles. In another study analysis of the Zeta Potential could be used to identify suitable processes for synthetic and natural fibres as the zeta potential indicates their hydration capacity for adsorption of agents, hence varying care and finishing processes.[2] All of which results in development of efficient pretreatment process and agents like detergents that are specific to contaminant, washing, characterization as in functional groups, quantification of important parameters like rate of adsorption, controlled adsorption.

Functional Groups, Swelling, pH and Zeta Potential:

Since, interfacial interaction, surface charge and properties are heavily governed by the chemical structure and presence of functional groups hence indicating Zeta Potential could be used for measuring their effect. As in discussed in [2, 4] the zeta potential of the higher hydrophobic fibre is larger than that of higher hydrophilic fibres due to hydration capacity. Cotton and viscose fabrics have hydroxy and carboxy groups and have the lowest zeta potential. The wool fibre has a high zeta potential due to the presence of numerous carboxylate groups giving rise to an anionic character at pH 10 and other chargeable groups, including nitrogen-containing groups giving rise to positive charge at lower pH values. Similar reasoning and results are presented for polyamide(amide), elastane(Urea), bamboo fibres and Acrylic in [2, 4]. As discussed earlier, pH of the solution also plays a role in the adsorption, surface charge and other electrokinetic properties. The effects of pH of the solution on surface charge and electrokinetic potential are complex[7]. It affects swelling properties which changes the effective accessible surface(based on the ionic species used for the experiment) area and dissociation of functional groups like Carboxylic acid [7].

Adsorption and Rate of Adsorption:

Zeta Potential or Streaming Potential as discussed above is very useful for interpreting surface properties and charge. One, such a use case is controlled and principled adsorption. Monitoring the change of the streaming potential can also give insights to the rate of adsorption and kinetics which further give insights of affinities of adsorbents for the present adsorbates[3, 8]. Adsorption depends on the properties of adsorbate and involves processes like electrostatic interaction between adsorbate and adsorbent like cationic particles[8], hydrocarbon surfactants, softeners[3] among other factors like the long hydrocarbon chain of surfactants, the effect of alkyl chain length, chain structure, concentration and the pH of the solution, on the adsorption process for surfactants[8]. Adsorption and its rate also depends on the adsorbent properties such as the nature of structural groups, the composition as studied in [3] as well as the aqueous solution. All of which can be interpreted using Zeta Potential and Streaming Potential which in the following example from study in [3, 8] depends on the softener concentration under the error of Surface Conduction. The rate of adsorption for the composition of the knitted fabrics with the fabric with higher cotton content(as compared to modacrylic yarn) exhibits a lower rate due the higher surface area of the cotton fibre and the stronger affinity of the fatty acid chain of the cationic surfactant to the hydrophobic modacrylic fibre.

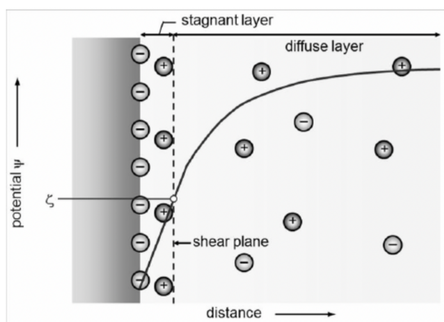
As also observed in [8] apart from the primary adsorption there could be a second process with a lower rate of kinetics of kinetics between the adsorbate(softener) and adsorbent(knitted fabric) leading to non-linear kinetics violating the assumption of linear kinetics initially.

Finally it allows analysis and quantifications of properties of the adsorbates like the molar cohesive free energy per mol of CH2-group in the alkaline chain of the surfactant as in[8].

Desiderata

Above discussion reviews a lot of important facts, findings, goals, trends and results of the articles surveyed. It also connects the information across all of these articles using some of the independent interpretations. Following discussion builds up on it and gives some more insights.

Based on the EDL theory as discussed, Zeta potential is an electrokinetic property, as shown in the figure below, among many like IEP and Point of Zero Charge(PZC). It can be used as an indicator to measure many useful quantities that then can be used to do desired analysis and also in the case of textiles, where we do Zeta Potential Analysis for various applications, characterization, rate of the process etc.



Electrophoresis, sedimentation, potential, electro-osmosis streaming current/potential, potential of colloidal vibration and electrokinetic sound amplitude are some principles to measure the zeta potential. The methods of streaming current/ potential or electro-osmosis are used more often for fibres and materials with large size in dispersion, under the errors and limitations of the EDL and the **Helmholtz–Smoluchowski** theory. The streaming current/potential method is indicative and useful for most of the applications which doesn't require precise measurements of Zeta potential and is mostly used for indicative measurement of the same. The results and measurements are reproducible and interpretable under varying spectrum of conditions. Under the realm of precise measurements, however, its value may differ under different methods for the same conditions.

As a result of an applied pressure across the ends of a capillary causes the liquid phase to move tangentially to the solid phase, inducing a charge displacement in the electrical double layer causing the phenomena of streaming current and streaming potential. This streaming potential can be measured between two electrodes, upstream and downstream in the liquid flow, connected via a high-input impedance voltmeter as discussed in [5]. The ratio between the streaming potential(Ustr) and the pressure drop(Δp) is the zeta potential upto a scaling factor, given by:

$$\frac{U_{\mathrm{str}}}{\Delta p} = \frac{\varepsilon_{\mathrm{rs}} \varepsilon_0 \zeta}{\eta} \frac{1}{K_{\mathrm{L}}}.$$

Above is valid when surface conduction is neglected, thus the estimate is lower than the actual potential difference created. The two more underlying assumptions as discussed in [7] are that the electrical double layers are thin relative to the dimensions of the passages through the porous material; and the solid materials and the surface of those materials are non-conductive under the conditions of testing.

This apparent potential is observed for varying pH levels, and as a function of time for different fabrics and for different processes including adsorption. The approach commonly used in the studies surveyed and referenced for observing and performing the pH dependence of the surface charge is done by adding dilute acid or base with a concentration of 0.05-0.1 mol/l to the measuring solution as in [1]. The pH dependence of the zeta potential reveals material specific properties and helps in their characterisation.

We thus described the subject matter: Zeta Potential in Textiles, by first covering definition, origins and interpretation of the Zeta Potential and the theory behind its quantification and its various measurement techniques also using the EKA apparatus. And later formation of surface charge in textile fabrics and fibres governed by various mechanisms and material specific properties, we also covered different applications and processes, all of which are seen through the lens of surface properties and Zeta Potential as result of properties of the solute, solvent and the surface of fabric under different physical conditions. For instance, for the application of functionalization of textile fabric, attachment of nanoparticles or microcapsules to the fabric surface is performed and the streaming potential is used as an indicator to interpret the kinetics of adsorption of positively charged nanoparticles on cotton and polyamide fabrics.

Discussion and Independent Interpretation

Since, analysis of various textile fabrics and fibres with their growing use with a suitable solvent is much needed and to expand the scope of the research in this area we need precise methods for exact quantification, analysis and interpretation of different properties of the surface of these fabrics or fibres when put in contact with solvents of different pH, conductivity and viscosity that are either implicit like the number of functional groups present that govern the interaction with solute, adsorbate or the aqueous solution, and hydration etc. or explicit as in functionalized textile. Factors like hydration capacity, hydrophilicity, swelling are also intrinsic, all of which are encoded in the distribution of the induced charge on the textile fabric surface due its interaction with the solvent and the solute and adsorbates present. Which creates the potential difference relative to the bulk of the solvent. This interaction is electrostatic(coulombic) as well as due to affinity of the solutes for the surface(chemical) and spontaneously leads to action of the solute on the material surface which may be surfactants, softeners or other agents the process may be adsorption or desorption, surface modification or treatment all of which further alters the surface charge and their distribution. This process eventually reaches an equilibrium. If we measure that the surface charge does not change for some time we can conclude that the process has reached equilibrium, thus the change in this surface charge and properties can give information about the rate of the process(generally adsorption). We can also notice for structurally different fabrics such as Cotton, Wool, Polyamide the equilibrium surface charge varies differently(including their sign) for different pH ranges, indicating their difference of chemical and physical properties like swelling, hydrophilicity etc. suggesting a natural way to characterise these different fabric and fibres. Sometimes a deviation from surface charge can also be observed as in the case of cotton, bamboo and polyamide without softener as in [4] due to the water adsorption on the surface, which causes a shift of the slip plane of the electrical double layer into the solvent. Under controlled conditions, the information about kinetics can even reveal about the specific mechanism involved in the adsorption process as is the case with the use of electrokinetics for the adsorption mechanism of surfactants. For pH dependence of the streaming potential coefficient for cotton/modacrylic knitted fabrics with different compositions we observe a more negative zeta potential for the higher content of modacrylic yarn. We observe this since different mechanisms of surface charge formation give rise to this potential for the two components. For cotton, the de-protonation of acidic surface functional groups (C–OH and O–C–OH) introduces negative charge, while for modacrylic yarn hydroxide ion (OH–) adsorption dominates the interfacial charge formation.

The time dependence of the surface properties/charge can give information about the order of the kinetics, as in adsorption of softener example we are able to conclude existence of a slower secondary process of interaction between the softener and the knitted fabric since the plot of streaming potential over time becomes non-linear which is linear initially, hence describale using first-order kinetics equations.

And as argued in previous sections, Zeta Potential and Streaming Potential can well indicate these surface properties and quantity the surface charges, thus their reliable measurement under varying physical conditions is crucial, which unfortunately is not always the case due to lacking theory and faults in the EDL model as in Surface Conduction. Hence, for most use cases that concern us precise estimation of the Zeta Potentials is not needed since, it is very sensitive to the conditions and we only need to detect the change in the electrical state of the surface. The apparatus commonly used is the electrokinetic analyser(EKA) as is used in a majority of the studies as mentioned in the surveyed articles. The material sample is inserted between a pair of perforated Ag/AgCl disc electrodes. A pressure difference is applied across the inlet and outlet of the capillary system and an electrolyte solution is forced through this capillary system in which the textile(solid phase) is held stationary and the liquid phase moves over the solid phase tangentially. Due to this motion of ions and the creation of Zeta Potential - Streaming potential (Up) and streaming current (Ip) can be observed, as are the quantities of interest for most applications under consideration and can be estimated using the Helmholtz–Smoluchowski equations. The concepts can be extended for natural as well as synthetic fibres and fabrics. Thus the scope of textile research expands significantly, covering all kinds of fibres and fabrics(cotton, wool etc.) including functionalized textiles. And as discussed, the scope is also wide in terms of the agents used in processes like adsorption, whose properties and effect can also be estimated and quantified based on process mechanisms observed using the Zeta/Streaming potential method as discussed in [8].(e.g. Chain lengths of surfactants and washing of stained cotton fabric)

Conclusion

We discussed the important and useful electrokinetic properties of the surfaces of various textile fibres and fabrics, focusing on Zeta Potential and the relevant theory and models behind it. We explored causes of surface charge and the created potential difference giving rise to the Zeta Potential at different pH levels and solute or adsorbate concentration and for different fabrics and fibres with factors like functional groups that affect the extent of the same. In order to expand the scope in a principled way various recent research articles suggest the use of the streaming potential measurement of the Zeta Potential. Since, Zeta potential is an indicator of surface charge and surface properties, keeping conditions constant its variation with pH, ionic strength, across different adsorbates and for fabrics and fibres of varying composition and chemical structure and with time gives information for concluding various processes. It allows for quantification of the process parameters like molar cohesive free energy per mol of the used surfactant. Measurement of the change of the streaming potential also gives information about the mechanism of adsorption, and their rate of adsorption among many others discussed.

Which allows us to conclude that development of new ways of dyeing, surface modification, efficient wet processing, washing, durability and effect with washing steps of different kinds of stains(protein and pigment), contaminant selective and efficient surfactants, detergents and softeners is possible by reliable estimates of the Zeta potential despite of the failures such as limitation of the EDL theory and Surface Conduction for textile fabrics and research.

Thus, this discussion enables all the applications as above, as we detail the measurement problem and apparatus used and reiteration of the facts explored in the literature survey in some detail and possibly connect some dots that are spread across the research articles.

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