An Overview of the Zeta Potential - Part 1: The Concept

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Introduction   Print

The goal of this article is to provide a general overview of the basic concept of what is termed the zeta potential. A Part 2 will survey the methods and techniques available to determine it and a Part 3 will provide a glimpse at its practical, commercial significance. The reader should not assume that the content of this is complete; a deeper, more detailed understanding of the subject is beyond the scope of these short articles. However, a fairly comprehensive reference section is provided for each Part and the reader is encouraged to use it to supplement the matters raised in each text.

So, what exactly is the zeta potential (ZP) and why measure it? To address these questions, we must first briefly address the two *fundamental* parameters that control the nature and behavior of every system in which one phase is dispersed in another phase; the phases are distinguished by the terms disperse phase (for the phase forming the particles) and the dispersion medium (for the fluid in which the particles are distributed). The two fundamental parameters are the *extent* of the interface of the disperse phase and the *interfacial chemistry* of the disperse phase, respectively. The physical nature of any dispersion depends on the respective roles of the constituent phases; there are numerous examples of dispersed systems, including foams (gas-in-liquid), emulsions (liquid-in-liquid), and aerosols (solid- or liquid-in-gas), that have found application in pharmaceutics. In this overview, we shall focus on the most widely-formulated type of dispersion, *viz* suspensions (solid-in-liquid). The physicomechanical and physicochemical characteristics that constitute the two respective fundamental parameters are summarized in Table 1.
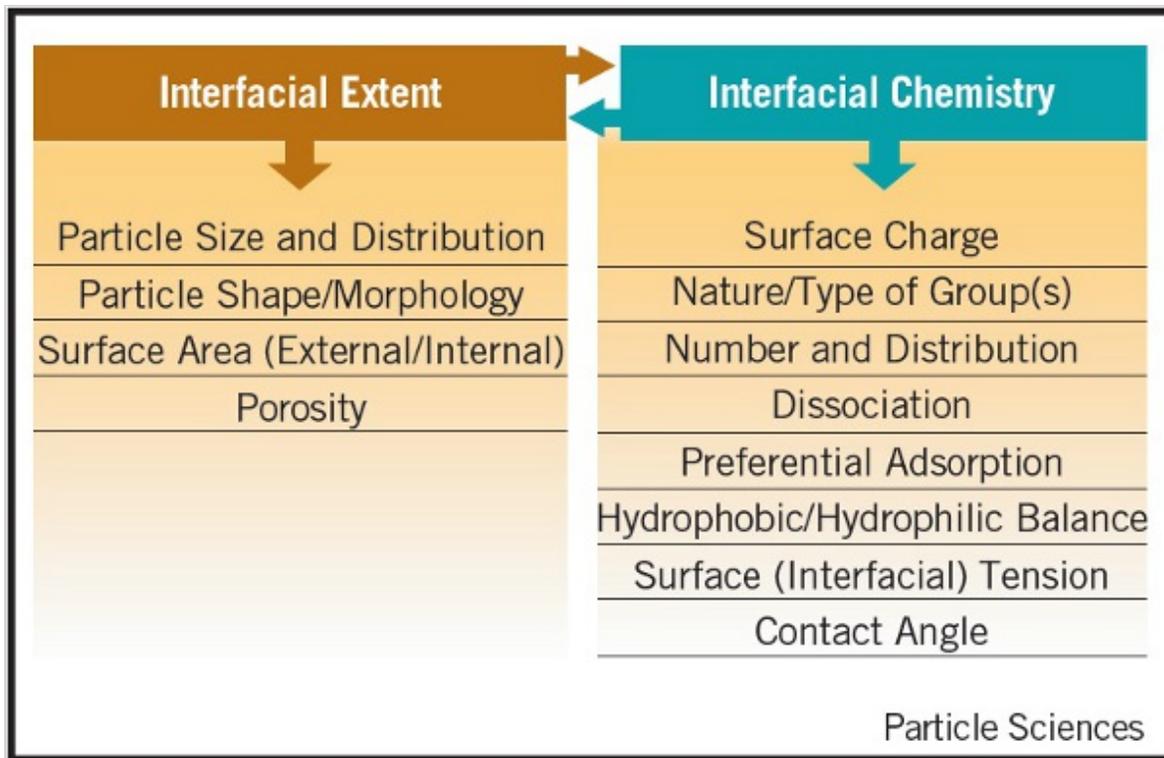
TABLE 1: Fundamental parameters that control the nature and behavior of all particulate suspensions

The two parameters are not, strictly, independent variables. The extent of the interface can be modified, for example, by particle comminution (grinding) which will not only reduce the particle size and increase available surface area but also expose new surfaces and, hence, alter the interfacial chemistry. Alternatively, a change in interfacial chemistry brought about by, say, an adjustment of solution pH can result in particle aggregation which, in turn, increases the particle size and reduces the extent of exposed surface area and can introduce porosity.

The reader may well be acquainted with the measurement of one, or more members, of the former group. However, the interfacial chemistry is often a neglected parameter (particularly in pharmaceutical applications) even though in the formulation of suspensions, it is as important as (and sometimes more so than) the interfacial extent.

The ZP is a parameter (symbol ζ), which is related to the surface charge (*vide* the interfacial chemistry), a property that all materials possess, or acquire, when suspended in a fluid. The sign and magnitude of ZP affects process control, quality control, and product specification; at the simplest level, it can help maintain a more consistent product and at a complex level, it can improve product quality and performance. At the very least its measurement answers the question: Is the electrical charge on the material particle positive or negative? Such information is often sufficient to suggest further steps in formulation or processing. The next higher level of inquiry has to do with quality control: Has the product sufficient electrostatic repulsion (because of the magnitude of the surface charge) to maintain its stability?

The Origin of Charge in Polar Media

All materials will spontaneously acquire a surface electrical charge when brought into contact with a polar medium (e.g., water) (1). Generally a material interface in deionized water is negatively charged, but there are materials that can be positively charged (2). So, how does the charge on a material arise when it is dispersed in a liquid? There are a number of charging mechanisms:

1. Affinity differences of two phases for electrons

2. Ionization of surface groups

3. Differential ion adsorption from electrolyte solution

4. Differential ion dissolution from a crystal lattice

5. Surface anisotropy

6. Isomorphous substitution

Mechanism **1** is responsible for the development of the contact potential between dissimilar metals and is important in, for example, corrosion and thermoelectric effects (3). This mechanism is a dominant process in initially determining the surface charge at the metal-solution interface. Nanoparticulate metal sols (e.g., Au and Ag) are currently being studied in wide variety of applications because they offer greatly enhanced performance. Since all metallic nanosystems are initially created as sols (i.e. colloidal dispersions) their inherent surface charge is critical to any further processing or use.

Mechanism **2** is commonly observed with all metal oxide surfaces (M-OH) as well as materials that contain carboxylic acid and amine-type functional groups. This latter category includes proteins, ionic polymers, and polyelectrolytes, many of which are widely utilized in pharmaceutical formulations. The ionization and/or dissociation of these groups (degree of charge development) and the net molecular charge (and thus sign, either positive or negative) depends strongly on the pH of the solution in which they are dispersed.

In Mechanism **3** a net surface charge arises through the process of unequal adsorption of oppositely charged ions and may result in either a net positive or net negative surface. Many *lyophobic* material suspensions (i.e., polymer latexes and APIs) fall into this category. If surfactant ions are present, their adsorption will tend to determine the net surface charge.

Ionic solids, such as calcite ($CaCO_3$), hydroxyapatite [$Ca_5(PO4)_3(OH)$] and barite ($BaSO_4$) can acquire a surface charge via Mechanism **4** by virtue of unequal dissolution of the oppositely charged ions of which they are composed. Addition of small concentrations (ca $10^{-3}M$) of Ca^{2+} ions (by using, for example, $CaCl_2$) can be used to adjust the net charge of a suspension of $CaCO_3$. Thus, the hardness of water becomes a factor that must be considered when formulating aqueous suspensions.

Mechanism **5** arises from the simple fact that most crystal lattices are anisotropic. Charge development occurs because of *n* and *p* defects in the crystal structure. For mineral oxides, this results in amphoteric hydroxyl groups (-OH) that can undergo reaction with either H^+ or OH^-. One pharmaceutically useful material in this group is the silicas (4); the surface charge is negative because the silanol, -SiOH, groups are weakly acidic.

The oxides of most di- and trivalent metals (e.g., MgO and Al_2O_3, respectively) are amphoteric; any dissolution tends to be in the form of the hydroxide. Swings in solution pH must be avoided because it can cause re-precipitation back onto the oxide surface in a different chemical form, thus altering the surface chemistry and, hence, the magnitude of the surface charge that develops.

Mechanism **6**, isomorphous substitution, is a more extreme case of Mechanism **5**. It occurs in clay materials (e.g., montmorillonite and vermiculite), where a large negative charge arises because of the difference in valence between the Al^{3+} and the Si^{4+} ions in the alumino-silicate crystal structure (5); varying proportions of minor elements leads to a

dizzying variety and complexity of minerals (6). The net surface charge of any clay depends on the clays' prehistory; it may not be possible to substitute, or replace, one clay from a given manufacture with another from a different manufacturer or supplier. It is critically important that the ZP versus pH profile be determined for suspensions of any clay material.

Electrical Properties in Non-aqueous Media

In solvents with moderate dielectric constants (>10 compared with ≈ 80 for water) some degree of ionization is possible; charging mechanisms parallel to those in water can occur. Examples include LMW alcohols, amines, aldehydes and ketones; ionic surfactants (e.g. Aerosol OT) and some simple ionic salts (e.g. LiCl) can dissociate to some extent in such media.

Although electrolytes cannot ionize in fully nonpolar media (solvents of very low dielectric, ≈ 2, such as alkanes) particles dispersed in such a medium can acquire charge and electrostatic forces *are* important and do play a key rôle in stabilizing non-aqueous suspensions (7, 8) but the charging mechanism is *not* the same as in aqueous dispersions. It arises because of acid-base (or electron donor-acceptor) interactions between the particle surface and the dispersing agent (9, 10). This is why acidic (e.g. PVC) or basic (e.g. PMMA) polymers are very effective suspendants of particles in non-aqueous media.

The nature of electrical charges and surface charging in non-aqueous media is an extremely complex subject but very important technologically; it has been extensively reviewed (11, 12); in pharmaceutics it impacts, for example, the stabilization of API's in propellant for drug delivery.

Traces of polar impurities, especially water play a key role not only in the magnitude but also the sign of ζ (13-15). Hence, in any non-aqueous application is it critically important to determine the water content of **all** components.

The Electric Double-Layer

A particle dispersed in a liquid is solvated and the extent of the solvated layer is influenced by the solution conditions such as composition (i.e., pH, ionic strength), temperature and pressure (16). The boundary between the edge of this solvated layer and bulk liquid is termed the *shear plane*.

Regardless of how charge separation is generated, the distribution of electrical charges at the interface is different from that in the bulk liquid phase. A "structure", called the *electric double-layer* (EDL*)* will be developed such that the particle surface charge is neutralized by an adjacent layer in solution containing an excess of ions of opposite charge to that of the surface, i.e. *counterions;* ions of the same charge as the surface are termed *coions*. The theory of the electric double-layer, (EDL) is extremely complex (17) and beyond the scope of this overview.
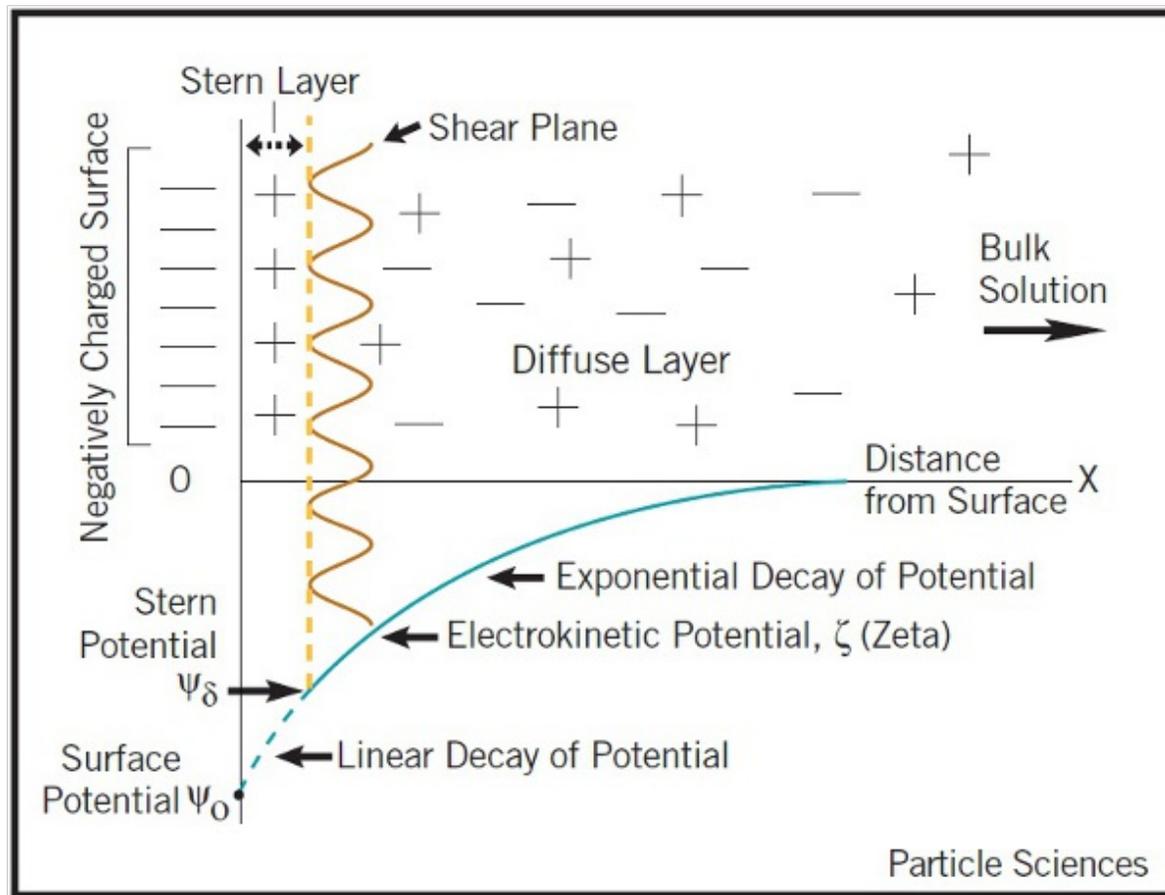
The simplest model for the EDL is shown in Figure 1.

FIGURE 1: Simplified model of the electric double-layer at a charged interface in aqueous solution

The EDL can be regarded as consisting of two regions or layers (hence the term electric double-layer): a region closest to the surface (the Stern layer) that is considered immobile (and it may include adsorbed ions) and an outer region (the *diffuse* layer) that allows diffusion of ions that are distributed according to the influence of electrical forces and random thermal motion (18).

The electric potential decreases linearly from ψ_0 (the actual *thermodynamic* surface potential) to the Stern potential, ψ_d and then it decays exponentially to zero in the diffuse layer; described, in the most simple mathematical model, by:

$$\psi = \psi_d \exp[-\kappa x]$$

where, x is the *distance* from the material surface and κ, called the Debye-Hückel parameter, is defined as:

$$\kappa = [2e^2 N_A c z^2 / \varepsilon \varepsilon_0 k_b T]^{1/2}$$

where, e is the protonic charge, N_A is Avogadro's constant, c is the concentration of electrolyte of valence z, ε is the dielectric constant, ε_0 is the permittivity of free space and k_b is the Boltzmann constant.

Hence, it can be seen that the electric potential *depends* (through κ) *on the ionic composition of the medium.* If κ is increased (the electric double layer is "compressed") then the potential must decrease.

Unfortunately, the fundamental interfacial property, ψ_0, is fundamentally inaccessible (19). What can be derived (and ultimately measured) is an *electrokinetic* potential – termed the zeta potential, ζ. This quantity, defined as the potential at the *shear plane,* has become a very useful *experimental* parameter to monitor electrokinetic behavior of suspensions, especially changes in such behavior (2).

The Relation between Zeta Potential and Surface Charge

Although ζ is not the actual thermodynamic (or surface) potential, in theoretical calculations ζ is frequently taken to be identical with the Stern potential, ψ_d.

When specific adsorption of charged moieties takes place at a surface, *counterion* adsorption usually predominates over *coion* adsorption; examples would be Ca^{2+} adsorbed on a negatively charged silica surface or PO_4^{3-} on a positively charged alumina surface. With polyvalent and, certainly, surface-active *counterions* it is even possible for a reversal of charge to take place within the Stern player – i.e. for ψ_0 and ψ_d (and, hence ζ) to have opposite signs (Figure 2a and 2b). The adsorption of nonionic (e.g. polyoxyethylene-based) surfactants would result in a ζ being close to zero (Figure 2c). As the MWt of any macromolecular species increases it results in the shear plane being located at a larger distance from the Stern plane and, in consequence, of ζ being significantly smaller than ψ_d (Figure 2d). All these types of "charge modifying agents" are used extensively in formulations of suspensions.
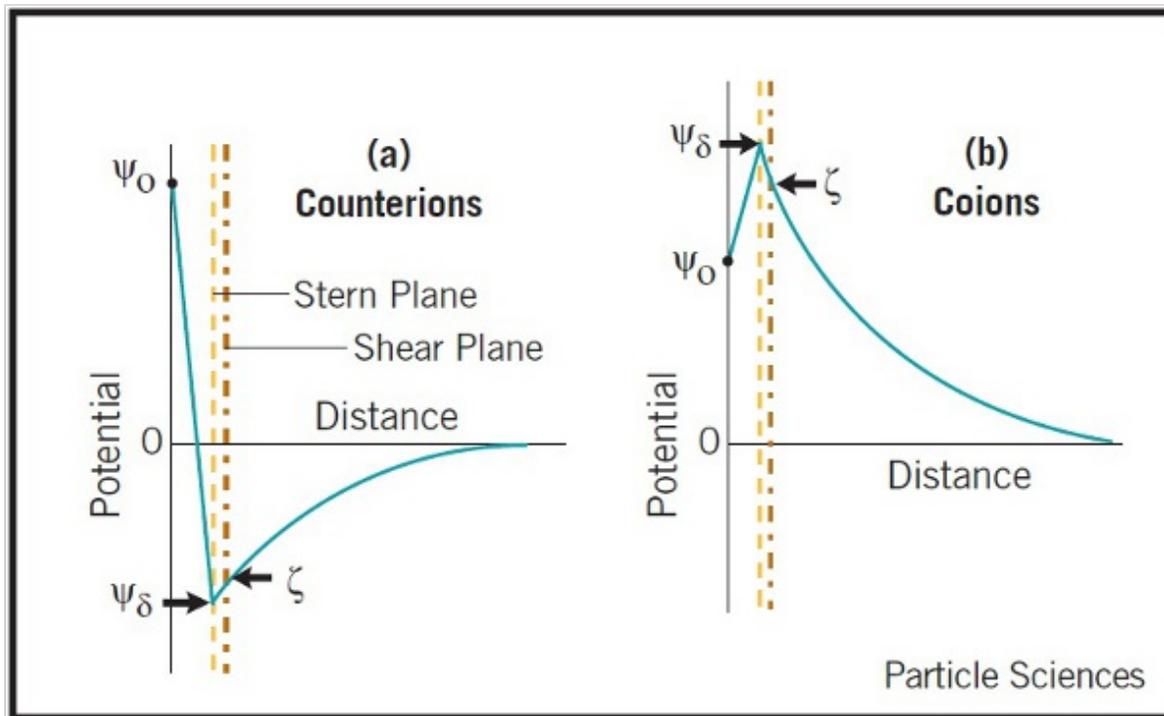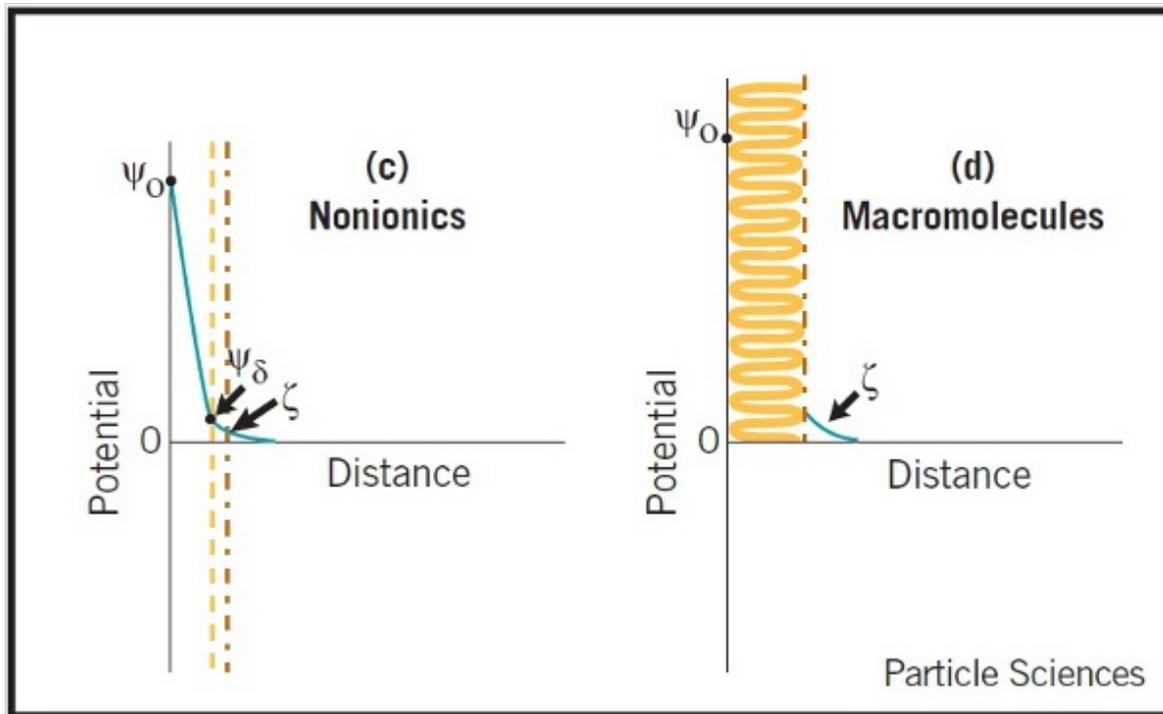
FIGURE 2: The effect of specific adsorption on zeta potential

Thus, it is entirely possible that a surface can have an inherent (thermodynamic) charge but have no measurable ZP and *vice-versa* (20). This does not mean to imply that the ZP measurement is not useful. On the contrary, ζ is, in the practical sense, the *effectiveness* of the particle surface charge in solution. While ζ may derive, initially, from the fundamental number of surface sites, (how many, what type, etc.), more importantly, from a *practical* application, are the solution conditions themselves because they control the resulting final sign and magnitude of ζ. The consequence of this to the process of dispersing particles is critical. And importantly, it is useless to quote a measured ζ value without specifying the suspension conditions under which the measurement was made.

REFERENCES

1. Lyklema J, *Fundamentals of Interface and Colloid Science*. Amsterdam, The Netherlands: Elsevier Publishing Company; 1991

2. Hunter RJ, *Zeta Potential in Colloid Science*. London, England: Academic Press: 1981

3. Fisher LH and Varney RN, Contact potentials between metals – history, concepts and

persistent misconceptions. *Am. J. Physics*. 1976; 44(5): 464-475.

4. Iler RK, *Chemistry of Silica.* Weinheim, Germany: Wiley-VCH Verlag; 1979

5. van Olphen H, *Introduction to Clay Colloid Chemistry*. London, England: Interscience Publishers; 1963

6. Carmichael RS, *Physical Properties of Rocks and Minerals*. Boca Raton, FL, USA: CRC Press Inc.; 1989

7. Van der Minne JL, Hermanie, Electrophoresis measurements in benzene – correlation with stability. Part 2, results of electrophoresis, stability and adsorption. *J. Colloid Sci*., 1953; 8: 38-52

8. Pugh RJ *et al,* The dispersibility and stability of carbon black in media of low

dielectric constant. Part 1, electrostatic and steric contributions to colloid stability.

 Colloids and Surfaces, 1983; 7: 183-287

9. Labib ME, Williams R, The use of zeta potential measurements in organic solvents

to determine the donor-acceptor properties of solid surfaces. *J.Colloid and Interface Sci.,* 1984; 97: 356-366

10. Fowkes FM, *et al*. Mechanism of Electric Charging of Particles in *Nonaqueous*

Liquids. ACS Symposium Series. 1982; No. 200. Chapter 15:307-324.

11. Hair M, Croucher MD, (eds). *Colloids and Surfaces in Reprographic Technology.*

Washington, DC, USA: American Chemical Society Publications; 1982.

12. Morrison ID. Electrical charges in nonaqueous media. *Colloids and Surfaces A*.

1993; 71: 1-37.

13. McGown DN, *et al*. Stability of nonaqueous dispersions. Part 1, the relationship

between surface potential and stability in hydrocarbon media. *J. Colloid Interface*

Sci. 1965; 20: 650-664.

14. Kosmulski M, Matijevic E. Microelectrophoresis of silica in mixed solvents of

low dielectric constant. *Langmuir.* 1991; 7: 2066-2071.

15. Mysko DD, Berg JC. Mechanisms influencing the stability of a nonaqueous

phosphor dispersion. *Ind Eng Chem Res*. 1993; 32: 854-858.

16. Hunter RJ, *Foundations of Colloid Science*. 2nd Edition. Oxford, England: Oxford University Press; 2001

17. Parsons R, Parsons R. The Electric Double Layer at Solid/Liquid Interfaces.

J. Electroanalytical and Interfacial Electrochemistry. 1981; 118(2): 3-18.

18. Kruyt HR (ed), *Colloid Science.* Volume 1, Amsterdam, The Netherlands: Elsevier Publishing Company; 1949

19. Guggenheim EA. The conceptions of electrical potential difference between two

phases and the individual activities of ions. *J. Phys. Chem*. 1929; 33: 842-849.

20. Miller NP, Berg JC. A comparison of electroacoustic and microelectrophoretic

zeta potential data for titania in the absence and presence of a poly(vinyl alcohol)

adlayer. *Colloids and Surfaces*. 1991; 59: 119-128.