Determination of the Point of Zero Charge pH of Borosilicate Glass Surface Using Capillary Imbibition Method

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Abstract

The point of zero charge pH of an oxide surface is a fundamental surface chemistry property or solids or metal oxides that determine the nature of interaction at the solid-aqueous solution interface. In colloid chemistry this physical parameter controls the evolution of the electric double layer as well as adsorption and desorption processes.

In colloid chemistry a number of methods have been used for the determination of the point of zero charge pH of an oxide surface. This ranges from titrimetric to radiation chemistry approach that deals with scanning electron microscopy.

In this study, the direct effect of aqueous solution acidity on the solid-liquid interfacial free energy and the consequence of this effect on spontaneous imbibition of aqueous solution into borosilicate glass have been exploited for the determination of the point of zero charge pH of this type of glass. What is new in this method is that while the traditional titration method relies on neutralization of surface charges, the present method relies on interfacial free energy changes due to aqueous solution pH changes and the effect of this on the wettability of borosilcate glass surface. Result of point of zero charge pH obtained from the present method has been compared with those obtained using traditional methods. The comparison shows close agreements and this proves the technique used in the present work as a novel method for the determination of the point of zero charge pH of oxide surfaces.

Keywords: pint of zero charge, spontaneous imbibition, contact angle, charge density, excess adsorption

1 Introduction

1.1 Relationship of Capillary Phenomenon to Contact Angle

The point of zero charge pH of an oxide or hydroxide surface is the pH of the aqueous solution in contact with it at which the net surface charge is zero (Sposito, 1998). It is a fundamental surface chemistry property that depends among other things on the dielectric permittivity of the material, metal to oxygen bond length and Pauling bond strength per unit length (Sverjensky, 1994).

A number of approaches have been used in the chemical engineering industry for the determination of this surface parameter. Yoon *et Al.,* (1979) developed a model to calculate this parameter. In this method, Pauling's electrostatic valence principle has been applied to describe the mechanism of surface charging of oxide surfaces in equilibrium with aqueous solutions. This approach has led to the presentation of an equation that can predict point of zero charge pH of oxide surfaces from crystallographic data. Dimitr (1994) showed that by adding electrostatic solvation theory to crystal chemical and electrostatic models the point of zero charge pH of crystalline substances can be quantified. This approach sums up the contributions of Gibbs free energy associated with proton solvation, electrostatic repulsion of protons by cations underlying the surface and electrostatic attraction of protons by oxygen anions near the surface.

Noh and Scwarz, (1989); Bourikas et al., (2003); and Kosmulski (2004) determined the point of zero charge pH by titrimetry. Eggleston and Jordan (1998) used scanning electron microscopy approach to determine the point of zero charge pH of oxide surfaces.

From interface thermodynamic perspective, the interfacial free energy of the system aqueous solution-oxide surface will be affected by the surface charge density due to polar contributions   (Van Oss, Good, & Chaudhury, 1988). In view of surface charge density of oxide surfaces depending on pH, the wettability of the system oxide surface-aqueous

solution-vapor will depend on the surface charge density due to the dependence of solid-liquid interfacial tension on pH (Chatelier, Chan, Vasic, Gengenbach, & Griesser, 1995). Also, the extent of surface charging of an oxide surface at a given pH will depend on the difference between aqueous solution pH and the point of zero charge pH of the oxide surface. The objective of this paper is to use a novel approach with a completely different theoretical basis for the determination of the point of zero charge pH an oxide surface. Accordingly, this paper will exploit the oxide surface contact angle dependence on the pH of aqueous solutions for achieving this principal objective.

1.2 Motivation for This Work

1.2.1 Relationship of Capillary Phenomenon to Contact Angle

While other methods described above rely on particular principles to measure the point of zero charge pH of a solid surface, the motivation for the present work derives from the dependence sold-liquid interaction and adsorption phenomena (Barrow, Bowden, Posner, & Quirk, 1980) on the point of zero charge of the solid. Therefore, by invoking Gibbs excess adsorption theory, the effect of adoption and surface charge density on solid-liquid interfacial free energy which has a direct bearing on wettability can be explored. Lipmann (1875) recognized the contribution of externally added electrical field to the interfacial forces due to capillary. Integration of the effect of electric field/surface charge density provides a thermodynamic approach involving entropy maximization of the system vapor-liquid-solid. This approach has yielded modified equations for Laplace and Young equation   (Digilov, 2000). Thus, for Laplace equation the following modification holds (Digilov, 2000):

$$\Delta P = \gamma_{LV}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{d\gamma_{LV}}{dn} - E_{lv}\sigma_{LV} \qquad 1$$

In which ΔP is Laplace pressure (Pa), γ_{LV} is the liquid vapor interfacial tension (N/m^2), r_1 is the inner radius of curvature of the interface (m), r_2 is the outer radius of curvature (m), n is the curvature (m^{-1}), E_{LV} is the normal to the liquid-vapor interface component of the existing electrostatic field and σ_{LV} is the surface charge density at the liquid vapor interface.

In Eq. 1, the first term in the right hand side is the normal Laplace pressure in the absence of electrostatic field. The second term measures the change of liquid-vapor interfacial tension with curvature due to the electrostatic contribution to the liquid-vapor interfacial tension. The third term is the obvious contribution to Laplace pressure due to electrostatic effect, which is related to the Lipmann effect due to the presence of charges.

For Young's equation, the following modification has been presented   (Digilov, 2000):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta_q + \frac{n}{r} - E_{LV}\gamma_{SLV} \qquad 2$$

In which γ_{SV} is solid-vapor interfacial tension (N/m), γ_{SL} is solid liquid interfacial tension (N/m), γ_{LV} interfacial

tension (N/m), θ_q is charge dependent contact angle ($^\circ$) and $E_{LV}\gamma_{SLV}$ is the specific electric driving force of the

wetting line.

Equation 1 shows that in the absence of an electric field contribution, we get back to the original Laplace equation. Similarly, Eq. 2 shows that in the absence of an electric field we get back to the original Young's equation where we retain the first two terms on the right hand side of the equation. Here, the second term of the equation refers to the tension correction for Young's equation. Counting on the works of previous researchers, this paper is motivated to use the electrostatic contribution to wetting changes a step further by considering spontaneous imbibition capillary rise under varying pH conditions. This varying in aqueous solution pH is expected to cause variations in surface charge density, which is expected to cause contributions to Laplace and Young's equations similar to that dealt with by previous researchers. In this case, the variations in surface charge density and electric field will be due to ionization of surface hydroxyl functional groups (silanol) on borosilicate glass (Zhuravlev, 1987). The prime objective is to link contact angle and capillary rise to pH and to use this as the basis for determining the point of zero charge pH of Borosilicate glass surface through an appropriate mathematical model.

1.2.2 Dependence of Solid-Liquid Interfacial Tension on Aqueous Solution pH

In the system sold-liquid-vapor there are three fundamental interfacial tensions/energies. They are solid-liquid interfacial tension, liquid-vapor interfacial tension and solid-vapor interfacial tension (Liu, Yao, & Jiang, 2010): Each of

these tensions has two fundamental contributions. They are Lishfitz van der Walls forces and polar contribution, the latter sometimes called electron donor and electron acceptor contribution (van Oss *et al.*, 1988). Generally, polar contributions are pH dependent and for the solid-liquid interface the solid-liquid interfacial tension will consist of two contributions as (Chatelier, et al., 1995):

$$\gamma_{SL} = \gamma_{SL}^0 + \gamma_{SL}^{ion}$$
3a

Where:

γ_{SL}^0 = component of solid-liquid interfacial tension at the point of zero charge pH

γ_{SL}^{ion} = free energy per unit area required to form surface charges from surface ionizeable or functional groups relative

to the point of zero charge pH at the prevailing aqueous solution pH

The second term on the right hand side of Eq. 3 is pH dependent and strongly coupled to the point of zero charge and therefore, has electrostatic origin

1.2.3 Effect of Solid-liquid Interfacial Tension pH Dependence on Contact Angle

In petroleum engineering and allied disciplines, the theory of wettability quantifies this petrophysical parameter in terms of interfacial tensions between phases as (Liu, Yao, & Jiang, 2010):

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$
3b

θ = contact angle

γ_{SV} = solid vapor interfacial tension

γ_{SL} = solid liquid interfacial tension

γ_{LV} = liquid vapor interfacial tension

Hence by recognizing the pH dependence of solid-liquid interfacial tension through the second term of Eq. 3 Young's equation can be modified as:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}^0 - \Delta F_{SL}^{ion}(pH)}{\gamma_{LV}}$$
4

This equation shows the dependence of contact angle/wettability on the pH of aqueous solution. It simply means that minimum wettability or maximum contact angle will be attained when the pH dependent component of interfacial tension is a maximum, assuming other interfacial tensions remain constant.

1.3 Mathematical Model

1.3.1 Assumptions

If a capillary tube is dipped into an aqueous solution in a beaker it will rise until an equilibrium height is achieved (Martic, *et al.*, 2002). The equilibrium height will depend on the contact angle of the system which reflects wettability. This means that with varying pH of the imbibing fluid, varying surface charge density created by varying pH induced ionization of surface hydroxyl functional groups will cause varying equilibrium heights. To exploit spontaneous capillary imbibition mechanism under varying pH conditions for determining the point of zero charge pH of Borosilicate glass, the following assumptions will be made to render the solid-liquid-vapor system composing of air, a capillary tube and a pH varying imbibing fluid similar to those used by other researchers:

1. At a given capillary rise equilibrium height, there is no heat transfer between the system and the surroundings (Digilov, 2000).

2. The cylindrical model is the simplest pore shape for the mathematical formulation of capillary imbibition and will be assumed in this work.

3. There is adsorption or reaction equilibrium between the walls of the capillary and the imbibing water leading to the formation of a uniform surface charge density

4. For a given charge density there is a mechanical equilibrium in accordance with Young's equation by integrating the electrostatic contribution (Chen, Chiu, & Weng, 2006)

5. Borosilicate glass has amorphous structure (Liu, Yuan, Yan, & Zhao, 2012) at initial aqueous solution pH it will have a net negative surface charge and subsequent adsorption of protons will occur with varying pH reduction
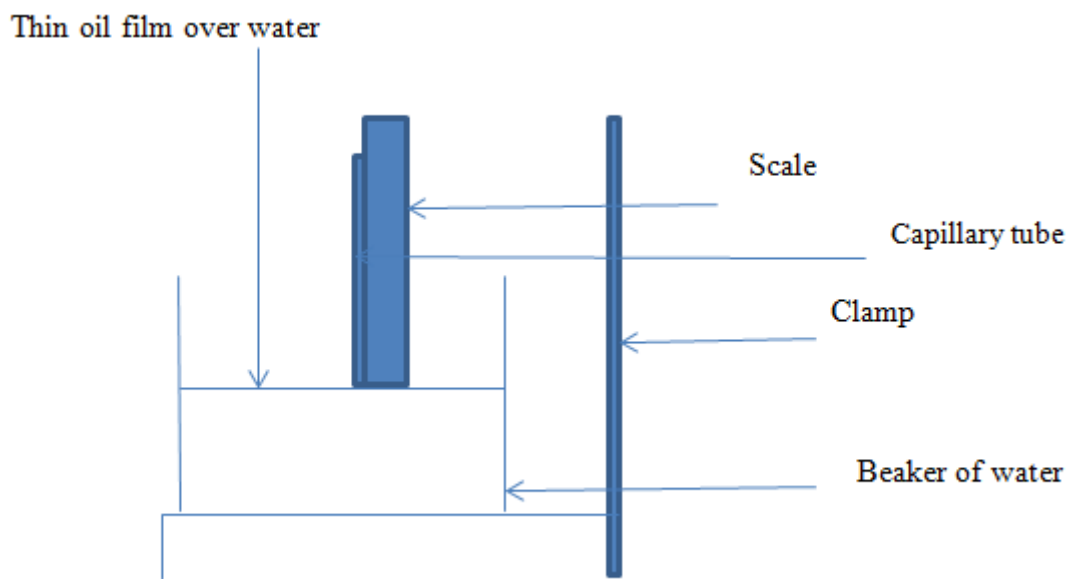

Figure 1. Schematics of capillary imbibition experiments

1.3.2 Mathematical Model Approach

Generally, the surfaces of metal oxides will have hydroxyl functional groups due to the dissociation and chemisorption of water molecules and chemisorption on the oxygen atom on the surface of the oxides (Refson, *et al.*, 1995). For silica surface this leads to the formation of silanols with specific surface densities (Zhuralev, 1987). The surface silanols of silica will undergo acidic and basic ionization reactions in accordance with the following order respectively (Peng & Barteau, 1991):

$$SOH + H_S^+ = SOH_2^+ \qquad\qquad\qquad\text{I}$$
$$SO^- + H_S^+ = SOH \qquad\qquad\qquad\text{II}$$

In which SOH is a surface hydroxyl species, SO^- is a surface deprotonated species, SOH_2^+ is a surface protonated species, H_s^+ is proton near the surface of the solid (silica) and S is a metal attached to a crystal lattice sometimes written as $S \equiv O$

The proton near the surface H_s^+ can be linked to bulk solution hydrogen ion concentration by the work done in transferring a proton from bulk solution to the surface of the solid under the electric field potential due to the surface charge density (Sverjensky, 1994)

Reaction I is typical of acidic conditions while reaction II is typical of basic conditions. Therefore, for a given solution pH, a definite surface charge density exists on the surface of borosilicate glass due to the ionizations reactions. The

objective of the following section is to link this surface charge density to aqueous solution pH and contact angle and to further exploit it as the basis for achieving the principal objective of this paper.

Following Carré, *et al.* (2003), the mechanical equilibrium for the system carbon dioxide, brine and aquifer rock surface can be written as before in accordance with the following equation:

$$\gamma_{VL} Cos\,\theta = \gamma_{SV} - \gamma_{SW} \qquad 5$$

In which γ_{LV} is liquid-vapor interfacial tension [N/m], γ_{SV} is solid-vapor interfacial tension [N/m] γ_{SW} is

solid-water interfacial tension [N/m] and θ is the contact angle of the system

Normally, when hydroxyl functional groups such as silanols are in contact with water they will either adsorb protons or ionize depending on the ambient pH. When an acidic solution is added (such as carbon dioxide dissolution and carbonic acid formation) to change the pH, the interfacial tension between water and vapor phase can be considered constant, but the contact angle will change. This is because the contact angle is a function of three interfacial tensions namely the vapor-liquid interfacial tension, the vapor solid interfacial tension and the solid liquid interfacial tension. Literally, the addition of the acid causes pH changes that upset the surface charges of the solid and this impact the solid-liquid interfacial tension in accordance with Eq.4. However, liquid-vapor interfacial tension changes will be negligible if pH control is achieved by using minute drops of acid solution. This is in accordance with the work of Randles and Schiffrin (1966), Figure 4.

Consequently, Eq.5 can be differentiated as:

$$\gamma_{VL} dCos\,\theta = -d\gamma_{SW} \qquad 6$$

Using Gibbs excess adsorption equation, the change in solid-water interfacial tension reads (*Carre et al.*, 2003)

$$d\gamma_{SW} = -\Gamma_{H^+} RTd \ln\left|H^+\right| = 2.303\Gamma_{H^+} RTd\left(pH\right) \qquad 7$$

$$\Gamma_{H^+}, R, T$$

In which Γ is the surface excess adsorption of protons [mol/ m^2], R universal gas constant [J /^{o}K] and T is absolute.

The surface charge density is the result of surface ionization or protonation reactions. For protonation or adsorption reaction Gibbs equation can be written as (Carré, *et al.* 2003):

$$\sigma = \Gamma_{H^+} F \qquad 8$$

In which σ is the surface charge density of water-rock interface [C/m^2] and F is Faradays constant [Cmol^{-1}]

This formulation is in accordance with the single site model approach (Lu & Smith, 1996) which assumes the presence of only one type of surface hydroxyl group acting as a surface site where dissociation can take place amphoterically leading to protonation or deprotonation.

Putting together Eqs. 6 through 8 yield the following equation:

$$\frac{dCos\,\theta}{dpH} = -\frac{2.303RT\sigma}{F\gamma_{LV}} \qquad 9$$

This equation predicts a turning point at the point of zero charge on silica surface in the context of aqueous solution pH variation. With decreases in wettability following pH decreases as established in a previous research work (Kim, Wan, Kneafsey, & Tokunaga, 2012) the wettability of silica surface will be a minimum at the point of zero charge pH of silica surface.

From Eq. 9 the following can be written:

$$dCos\,\theta = -\frac{2.303RT\sigma}{F\gamma_{LV}} dp\left(H\right) \qquad 10$$

The relationship between surface charge density and surface charge potential reads (Atkinson, Posner, & Quirk, 1967)

$$\frac{e\psi}{k_B T} = \sigma\sqrt{\frac{2\pi}{\varepsilon n k_B T}}$$ 11

In which ψ is the surface potential of minerals surface [V] and n is the ion density [mol /m^3]

In the following section this equation will be exploited for deriving the pH wettability relationship.

1.4 Applications of Mathematical Model to Spontaneous Imbibition Dynamics

1.4.1 Capillary Rise pH Relationship
In this model, an aqueous solution with varying pH is assumed. The relationship between charge density, potential, dielectric constant of the electrolyte, temperature and solution concentration is written as (Atkinson et al., 1967).

$$\frac{e\psi}{k_B T} = \sigma\sqrt{\frac{2\pi}{\varepsilon n k_B T}}$$ 12

The Nernst equation gives (Bowden, Posner, & Quirk, 1977):

$$\psi = -2.303\frac{k_B T}{e}\Delta pH = -2.303\frac{k_B T}{e}\left(pH - pH_{pzc}\right) = \frac{2.303 k_B T}{e}\left(pH_{pzc} - pH\right)$$ 13

Wettability or cosine of the contact angle change gives:

$$dCos\theta = -\frac{2.303 RT\sigma}{F\gamma_{LV}}dpH$$ 14

The relationship between capillary rise and contact angle gives:

$$h_w = \frac{2\gamma_{LV}Cos\theta_c}{\rho g r}$$ 15

In which h_w is the spontaneous imbibition rise in a capillary [m], θ_c is the contact angles [deg.], r is the radius of capillary tube [m], ρ is the density of liquid [kg/m^3] and g is the gravitational constant [m/s^2]. All other symbols have already been explained

Equation 23 shows a direct relationship between capillary rise and contact angle, which is a measure of wettability. This shows that capillary imbibition, which is a direct measure of the extent of capillary rise will be greater the greater the water wettability of the capillary glass surface.

Capillary rise is, therefore, a function of wettability at isothermal conditions. Under isothermal conditions therefore the derivative of capillary rise with regard to wettability or cosine of the contact angle is given by:

$$\frac{dh_w}{dCos(\theta)} = -\frac{2\gamma_{LV}}{\rho g r}$$ 16

Thus:

$$dCos(\theta) = -\frac{\rho g r}{2\gamma_{LV}}dh_w$$ 17

Substitution of Eq. 17 into Eq. 14 for change in cosine of contract angle gives:

$$\frac{\rho g r}{2\gamma_{LV}}dh_w = \frac{2.303RT\sigma}{F\gamma_{LV}}dpH \qquad\qquad 18$$

Thus:

$$dh_w = \frac{2.303RT\sigma}{F\rho rg}dpH \qquad\qquad 19$$

This implies capillary rise is also a function of pH

In Eq. 13 substitution of the surface potential from Eq. 12 gives:

$$\frac{e}{k_BT}\left[\frac{2.303k_BT}{e}\left(pH_{pzc}-pH\right)\right]=\sigma\sqrt{\frac{2\pi}{\varepsilon nk_BT}} \qquad\qquad 20$$

This gives surface charge density as:

$$\sigma = 2.303\left(pH_{pzc}-pH\right)\left(\frac{2\pi}{\varepsilon nk_BT}\right)^{-0.5} \qquad\qquad 21a$$

Substitution of this into Eq. 19 gives:

$$dh_w = 2.303\left(pH_{pzc}-pH\right)\left(\frac{2\pi}{\varepsilon nk_BT}\right)^{-0.5}\frac{2.303^2RT}{F\rho rg}dpH \qquad\qquad 21b$$

Hence:

$$dh_w = \left(\frac{2\pi}{\varepsilon nk_BT}\right)^{-0.5}\frac{2.303^2RT}{F\rho rg}\left(pH_{pzc}-pH\right)dp(H) \qquad\qquad 22$$

This can be integrated as:

$$\int_{h_0}^{h}dh_w = \int_{pH_0}^{pH}\left(\frac{2\pi}{\varepsilon nk_BT}\right)^{-0.5}\frac{2.303^2RT}{F\rho rg}\left(pH_{pzc}-pH\right)dpH \qquad\qquad 23$$

In which h_o is the capillary rise at initial pH of aqueous solution [m], h is the capillary rise at a given pH of aqueous solution [m], pH_o is the initial pH of aqueous solution [-] and pH is the final pH of aqueous solution. All other symbols have already been explained.

This gives the following equation:

$$h = -0.5 \varsigma pH^2 - \varsigma pH_{pzc} pH + \varsigma \left(0.5 pH_0^2 - pH_{pzc} pH_0 \right) - h_0 \qquad \text{24a}$$

Thus, for initial height equal to zero, Eq. 24a becomes:

$$h = -0.5 \varsigma pH^2 - \varsigma pH_{pzc} pH + \varsigma \left(0.5 pH_0^2 - pH_{pzc} pH_0 \right) \qquad \text{24b}$$

$$\varsigma = \frac{2.303^2 RT}{F \rho r g} \left(\frac{2\pi}{\varepsilon n k_B T} \right)^{-0.5} \qquad \text{25}$$

This equation shows a parabolic relationship between capillary imbibition height and pH of the aqueous solution. Equation 24 provides a direct experimental advantage because by varying the pH of the aqueous solution the corresponding capillary imbibition height can be measured. By theory, a plot of capillary imbibition height versus solution pH must give a parabolic graph.

1.4.2 Wettability pH Relationship

In order to derive pH cosine of contact angle or wettability relationship the basic equations used before will be recalled as (Atkinson *et al*., 1967):

$$\frac{e\psi}{k_B T} = \sigma \sqrt{\frac{2\pi}{\varepsilon n k_B T}} \qquad :$$

In which all symbols have already been explained. Thus:

$$\sigma = 2.303 \left(pH_{pzc} - pH \right) \left(\frac{2\pi}{\varepsilon n k_B T} \right)^{-0.5} \qquad \text{26}$$

$$\psi = -2.303 \frac{k_B T}{e} \Delta pH = -2.303 \frac{k_B T}{e} \left(pH - pH_{pzc} \right) = \frac{2.303 k_B T}{e} \left(pH_{pzc} - pH \right)$$

The derivative of wettability or cosine of the contact angle gives:

$$dCos\theta = -\frac{2.303 RT \sigma}{F \gamma_{LV}} dpH$$

Substitution for surface charge density from Eq.36 into equation 38 gives:

$$dCos\theta = -\frac{2.303 R^2 T}{F \gamma_{LV}} \left(\frac{2\pi}{\varepsilon n k_B T} \right)^{-0.5} \left(pH_{pzc} - pH \right) dpH \qquad \text{27}$$

Under normal conditions there is pH reduction from near neutral pH to a lower value closer to the point of zero charge

pH of silica surface. The integration limits are the initial pH of formation water to the pH of interest and the wettability (cosine of contact angle) at initial pH (pH$_o$) to the wettability at a given pH of interest. Application of these limits leads to:

$$\int_{\cos(\theta)_o}^{\cos(\theta)} dCos\,\theta = -\int_{pH_o}^{pH} \frac{2.303^2\,RT}{F\gamma_{LV}} \left(\frac{2\pi}{\varepsilon n k_B T}\right)^{-0.5} \left(pH_{pzc} - pH\right)dp(H) \qquad 28$$

In which $\cos\theta_o$ is the cosine of the contact angle at point of zero charge pH [-] and $\cos\theta$ is the cosine of the final contact angle [-]

The final integration gives:

$$\cos(\theta) = \cos(\theta)_o - \frac{2.303^2\,RT}{F\gamma_{LV}} \left(\frac{2\pi}{\varepsilon n k_B T}\right)^{-0.5} \left[pH_{PZC}\,pH - \frac{pH^2}{2} \right]_{pH_o}^{pH} \qquad 29$$

Expanding the term in the square bracket on the right hand side of the equation gives:

$$\cos(\theta) = \cos(\theta)_o$$

$$+ \frac{2.303^2\,RT}{F\gamma_{LV}} \left(\frac{2\pi}{\varepsilon n k_B T}\right)^{-0.5} \left[0.5\,pH^2 - pH_{PZC}\,pH + \left(pH_{pzc}\,pH_o - 0.5\,pH_o^2\right) \right] \qquad 30$$

This equation can be written as:

$$\cos(\theta) = \cos(\theta)_o + \varsigma \left[0.5\,pH^2 - pH_{PZC}\,pH + \left(pH_{pzc}\,pH_o - 0.5\,pH_o^2\right) \right] \qquad 31$$

Where:

$$\varsigma = \frac{2.303^2\,RT}{F\gamma_{LV}} \left(\frac{2\pi}{\varepsilon n k_B T}\right)^{-0.5} \qquad 32$$

1.4.3 Theoretical Derivation of the Point of Zero Charge pH

It is interesting to note that in Eq. 24b, capillary rise can be linked to a given pH of aqueous solution. At the same pH of aqueous solution there is a definite wettability. The implication for Eq. 24b is that if contact angle can be calculated using capillary rise data for a given pH, then this contact angle can be plotted against solution pH in accordance with Eq. 31. Since Eq. 31 shows a parabolic relationship between contact angle and pH, the pH derivative of this equation when equated to zero and solved for pH will give the point of zero charge pH of the solid surface. Accordingly, the relationship between capillary rise and contact angle is given as (Jones, n.d.):

$$\cos\theta = \frac{rgh}{\gamma_{LV}} \qquad 33$$

Thus:

$$\theta = \cos^{-1}\left[\frac{rgh}{\gamma_{LV}}\right]$$

34

In which θ is the contact angle r is capillary radius, h is capillary imbibition rise and γ_{LV} is liquid-air interfacial tension.

Equation 31 permits a plot of wettability, hereby defined as the cosine of the contact angle (Bhattacharya, Datta, Berg, & Gangopadhyay, 2005) and contact angle respectively versus pH of aqueous solution. Fitting the resulting plots with quadratics models permits determination of the point of zero charge pH of solid surface using maxima and minima principles of differential calculus. This approach will be used in this paper for the determination of the point of zero charge pH of borosilicate glass.

1.5 Experimantal Determination of the Point of Zero Charge pH of an Oxide Surface

1.5.1 pH Measurement

pH was measured using the pH probe pH TESTR 30 (double junction). This is capable of measuring pH to two decimal places with an error of 0.01 pH. pH adjustment of aqueous solution was achieved by using nitric acid.

1.5.2 Brine Preparation and Core Sample Characterization

For synthetic brine experiments involving spontaneous imbibition brine was prepared by using laboratory grade sodium chloride and calcium chloride manufacture by Sigma Aldrich. These bought from Ottawa in Canada were used without further purification.

1.5.3 Density Measurement

Precise density measurement was achieved by first weighing an empty graduated cylinder. The cylinder was then weighed with a known volume of brine sample. The weight difference was divided by the volume of brine to obtain density at ambient conditions. Weights were measured using the Entris weight measuring instrument manufactured by the Sartorium Laboratory Instrument GmbH of Gottingen in Germany. It measures weights to three decimal places.

1.5.4 pH Control

pH control was achieved by preparing 0.25 M of dilute nitric acid solution. Laboratory grade acid was purchased from Sigma Aldrich in Ottawa, Canada. To change the pH of the experimental brine the tip of a 2 mm glass rod was dipped into the acid solution and the experimental brine was stirred using the rod to obtain a uniform solution. This procedure was used to obtain a measurable pH change.

1.5.5 Capillary Tube

Capillary tubes for the experiments were produced by the Chemistry Department of Dalhousie University. Each capillary tube has a diameter of 0.6 mm.

1.6 Experimental Procedures under Ambient Conditions

1.6.1 Capillary Imbition Experimental Procedures

All spontaneous imbibition experiments involving capillary tube were performed at room temperature. The capillary tube was glued to the side of scale to make it easier to read height rise of the meniscus. The experimental set up is seen in Fig. 2. To avoid evaporation of water from the surface of water in the beaker a thin film of minerals oil was poured on the water. To begin the experiment, the capillary tube with scale is dipped into the beaker with part of the system below water level. The equilibrium height was then read with the surface of water as the zero level. This procedure was used for different pH of the aqueous solution.
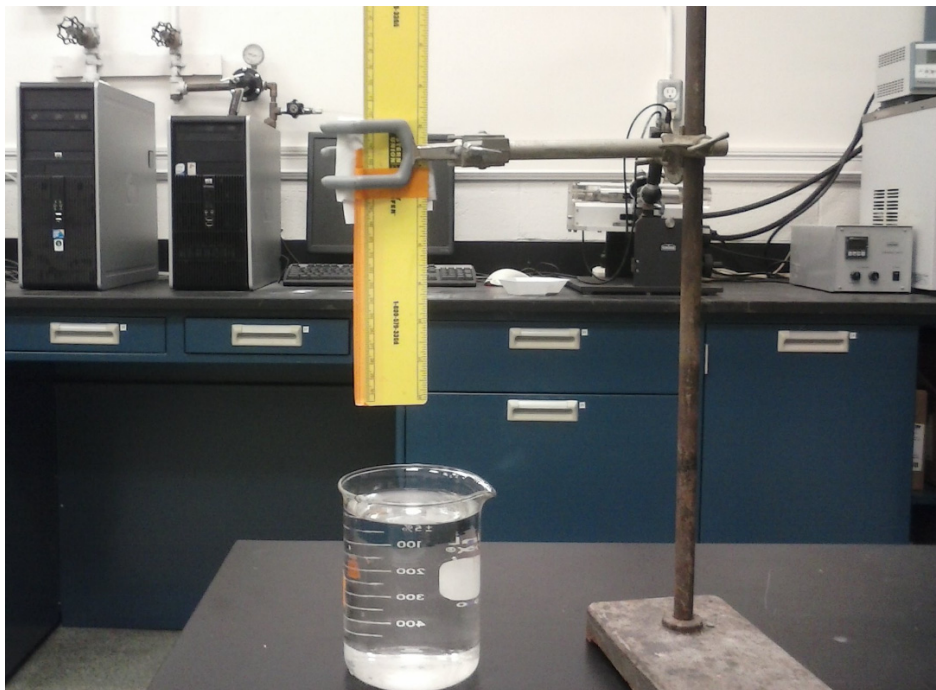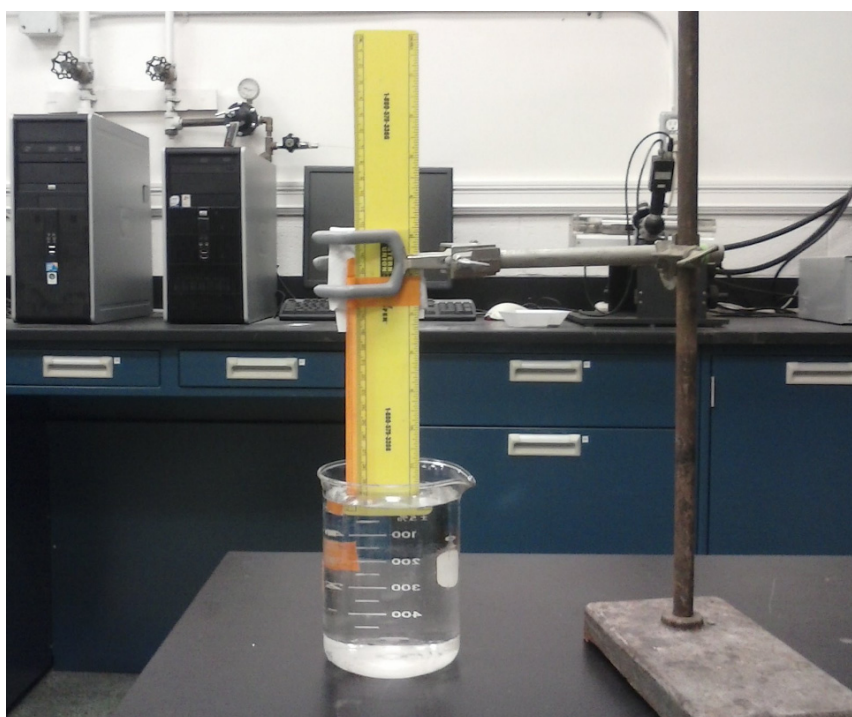
Figure 2. Set up for capillary rise experiment

Figure 3. Capillary rise experiments in progress

1.7 Capillary Imbibition Experimental Results and Discussion

Figures 4, 6 and 8 give plots of wettability versus pH with regression coefficients of 0.97, 0.79 and 0.91 respectively while figures 5, 7 and 9 give plots of contact angle versus pH of aqueous solution with regression coefficients of 0.81, 9.99 and 0.91 respectively. These regression coefficients are quite satisfactory.
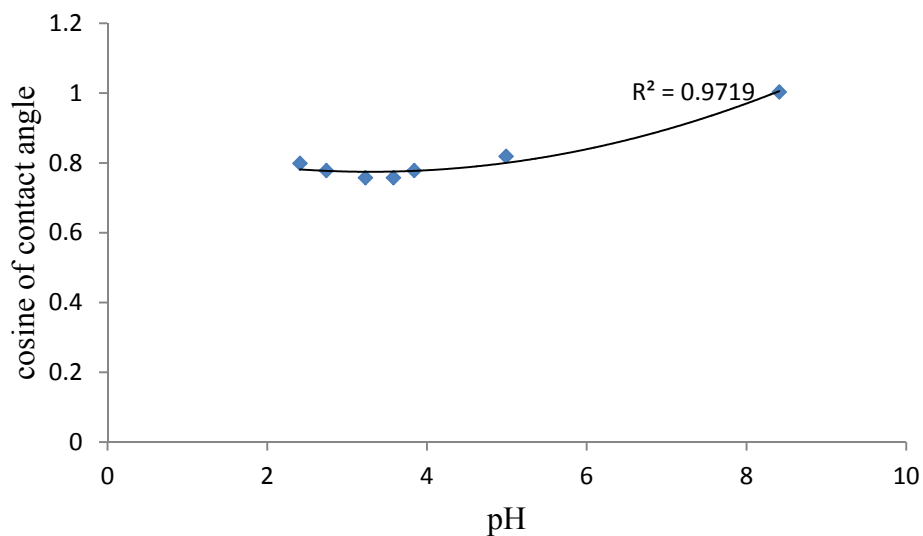
Figure 4. A plot of wettability versus pH of brine for experiment 1 under ambient conditions
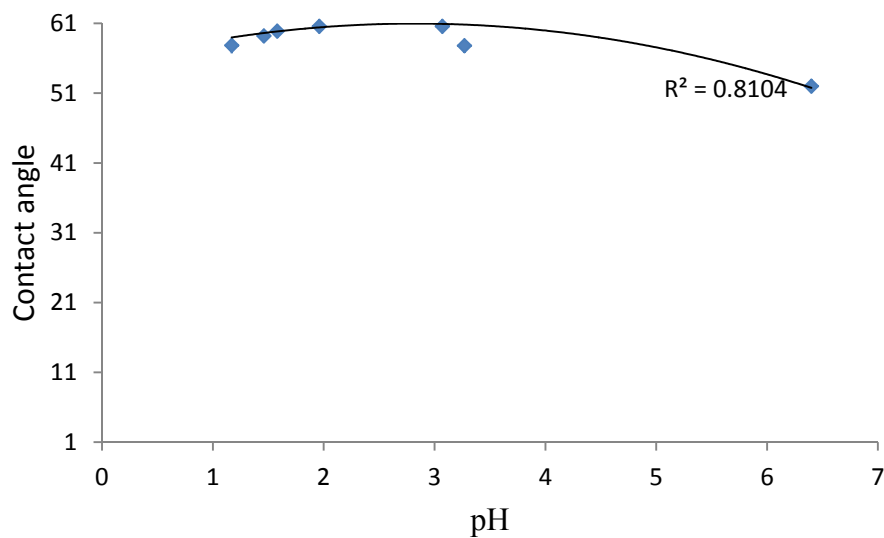
Figure 5. A plot of contact angle versus pH of brine for experiment 1 under ambient conditions
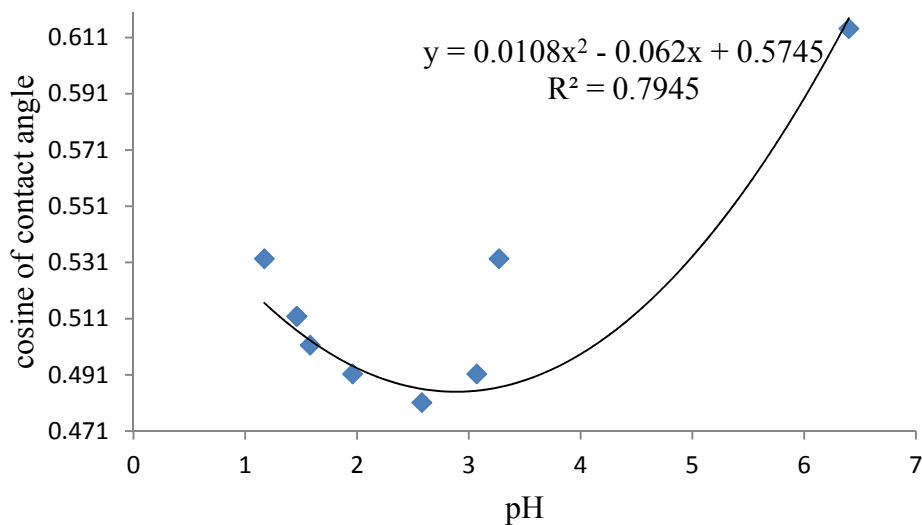
Figure 6. A plot of wettability versus pH of brine for experiment 2 under ambient conditions
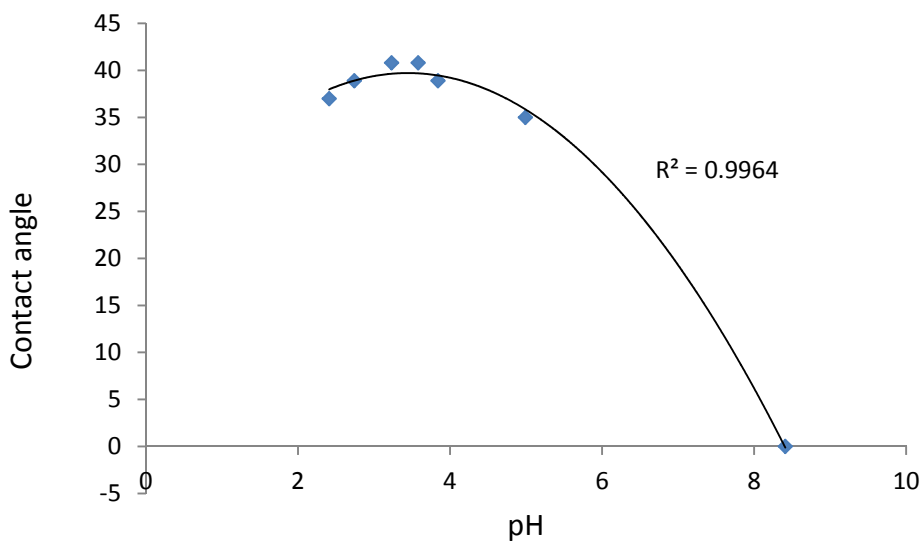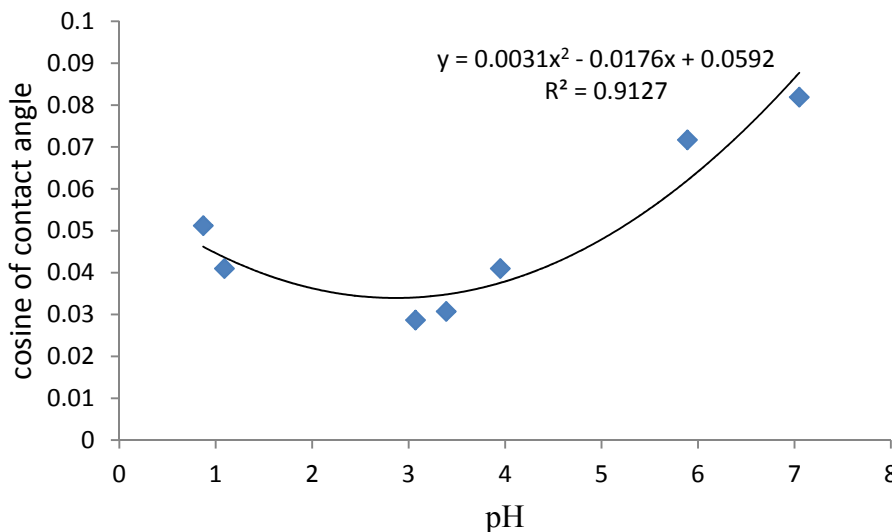

Figure 7. A plot of contact angle versus pH of brine for experiment 2 under ambient conditions

Figure 8. A plot of wettability versus pH of brine for experiment 3 under ambient conditions
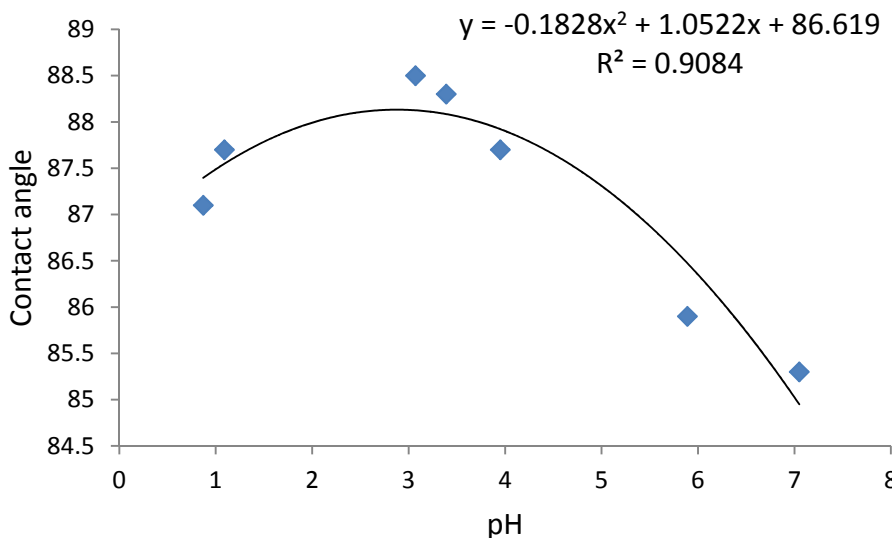

Figure 9. A plot of contact angle versus pH of brine for experiment 3 under ambient conditions

Theoretically at the point of zero charge pH of the solid surface the gradient of the plot of wettability versus pH must be zero because this is the minimum wettability. In order to obtain this pH for the solid surface the quadratic fits equations are differentiated and equated to zero. The pH when the resulting equation is solved is equal to the point of zero charge pH. Using this approach, the following are the point of zero charge pH of borosilicate glass surface for the three experiments

Experiments 1 = 3.30

Experiments 2 = 2.87

Experiment 3 = 2.84

The average is 3.00

2. Comparison with Literature Values

Kyriakos Bourikas *et al.*, (2003) used different techniques to obtain the point of zero charge pH of quartz. The following were their values for five different methods:3.1, 3.3, 3.0, 2.9, 3.2, Ave = 3.14

Information from the capillary glass tube manufacturer indicates it is borosilicate or fused glass. This type of glass is preferred in the laboratory because of its very low thermal expansivity and high boiling point. Zeta potential of borosilicate glass versus pH for borosilicate glass has been made (Barz, Vogel, & Steen, 2009), Appendix C in the

present work. Normalizing the zeta potential with the negative logarithm of the ionic strength results in a collapse of data onto a single curve. The result could be fitted with a curve and the extrapolation of this curve to zero zeta potential that corresponds to the isoelectric point also known as the point of zero charge pH for static conditions gave a range of pH values between 1.7 and 2. In addition to this, Kirby & Hasselbrink, (2004) reported values of the isoelectric point of borosilicate glass to be between 2.6 and 2.8. The average for these literature values gives 2.4. The difference between this and that obtained using spontaneous imbibition is 0.6.

3. Conclusion

Results of the experimental work show that the quadratic relationship between wettability and or contact angle derived in this study is theoretically appreciable. Another point of interest is that the quadratic fits give average values of the point of zero charge pH of borosilicate glass from which the capillary tubes are made to be 3 on the average. Appendix A and appendix B show values for silica with close agreement. This is quite within the range of values reported for silica glass, which come from quartz with the same value of point of zero charge pH. The value also agrees with the average value obtained by Kryiakos Bourikas, 2003[5]. The following sums up the principal conclusion of this experiment:

1. Trends in wettability variation with aqueous solution pH agree with the mathematical model.
2. The relationship between wettability and aqueous solution pH using capillary imbibition can be used to obtain information about the point of zero charge pH of glass.

Acknowledgements

Appendices

Add appendix A: Point of zero charge of oxides (Kosmulski, 2002)

Material	Description	Salt	T	Method	pH_0
SiO_2	Aerosil OX 50 Degussa	10^{-3}–0.1 mol dm^{-3} NaCl	25	pH iep	<4 if any 2.4
SiO_2	Polysciences	10^{-4}–0.1 mol dm^{-3} KNO$_3$		iep	<3 if any
SiO_2	Aerosil 380	10^{-2} mol dm^{-3} NaCl, NaNO$_3$	25	iep Acusto	2–4 (if any)
SiO_2	Quartz	10^{-2} mol dm^{-3} NaCl, NaNO$_3$	25	iep Acusto	2–4 (if any)
SiO_2	Duke	10^{-3}–10^{-2} mol dm^{-3} NaCl		iep	2.5–4.5
SiO_2	Quartz, Alfa Aesar	KOH + HNO$_3$		Acusto	2.3
SiO_2	Stöber	10^{-3} mol dm^{-3} KBr		iep	2
SiO_2	Aerosil 380	10^{-3}–0.1 mol dm^{-3} NaClO$_4$	25	iep pH	$\zeta = 0$ at pH <5 <3 if any
SiO_2	Geltech	10^{-3} mol dm^{-3} NaCl, KCl, LiCl, CsCl		Acusto	$\zeta = 0$ at pH 2
SiO_2	Quartz, Sigma	0.1 mol dm^{-3} NaCl, KCl, LiCl, CsCl		Acusto	<2 if any
SnO_2	Cassiterite, natural	None		iep	<3 if any

Appendix B: Point of zero charge pH of some oxides (Parks and De Bruyn, 1962)

Solid	Z.p.c.	pH Min. solubility	I.e.p. (calcd.)	Comment	Ref.
			1		35
WO$_3$	0.43	0.43		a,e	36
SiO$_2$	<2			b,e,f	37, 38, 16
SnO$_2$	4.5			a,e	16
	(5.5–7.3)			b,e	16
TiO$_2$	6.7			b,f	39
	6			a,e	16
	(4.7)			b.c.e	16
ZrO$_2$	~4			b,g	38
Al$_2$O$_3$	6.94 ± 0.37			a,e	40
	(8.4)			b,e	16
	(9.45)			b,f	41
		7.7			42

Appendix C: Zeta potential of borosilicate glass versus pH (Barz *et al*, 2009)

$$\zeta(pH) = (1.015\,pH^2 - 14.95\,pH + 25.48)\,mV$$
$$\frac{}{-\log(I)}$$
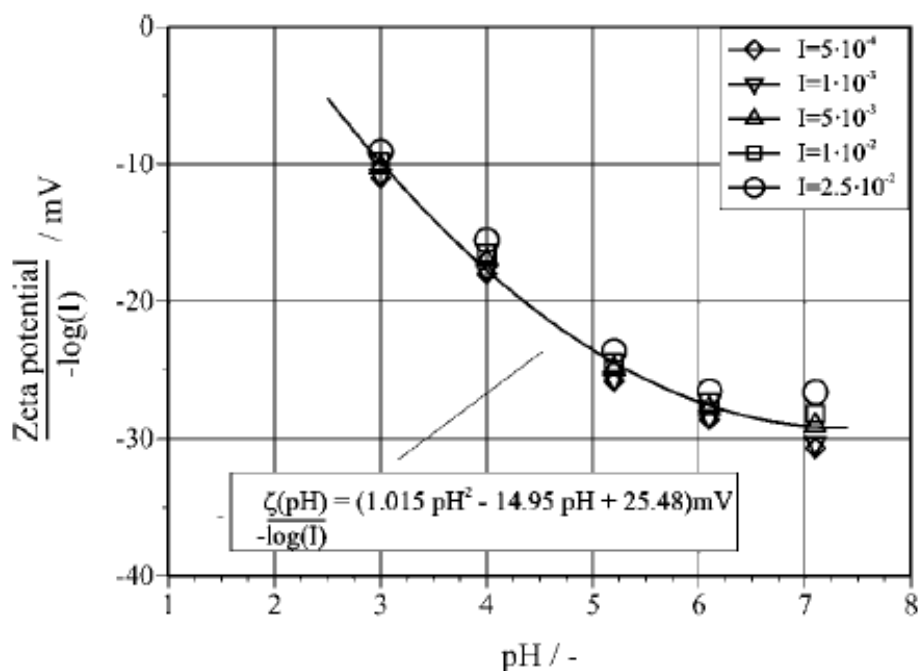
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