



## Introducing Field Effect Electroosmosis and Three and Two Dimensional Plots of Zeta Potential for Ideal Case of Metal-Insulator-Electrolyte Structure

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The characteristics of the metal-insulator-electrolyte interface (MIE), under quasi equilibrium conditions, have been studied theoretically. Mathematical model of the MIE has been developed for ideal case. In the ideal case, a totally blocked interface has been assumed, such that the MIE behaviour is governed only by electrostatic factors. By combining MIE characteristics and the electroosmosis effect in a capillary, a novel effect called field effect electroosmosis can be postulated. Based on this effect, a new device called a metal-insulator-electrolyte-electrokinetic field effect device (MIEEK FED) can be designed. Two and three dimensional plots for zeta potential as a function of  $V_G$ , the potential between metal and electrolyte and the concentration of electrolyte are presented.

**Key Words:** Field effect, Electroosmosis, Zeta potential.

### INTRODUCTION

The electrolyte-SiO<sub>2</sub>-Si interface has been studied by several authors<sup>1-4</sup>. This structure is interesting because it is capable of sensing specific chemical species. In recent years we studied the physical and theoretical aspects of the metal-insulator-electrolyte structure for potential applications such as sensors and for a new type of electrokinetic device<sup>5-8</sup>.

In a conventional metal oxide semiconductor field effect transistor (MOSFET)<sup>9</sup>, a potential difference applied between the gate electrode (metod) and the substrate (semiconductor) causes a change in the electric field orthogonal to the silicon dioxide-silicon interface. This result in modulation of the channel conductance.

By replacing the silicon part with electrolyte, we can get the structure shown in Fig. 1. At the interface of the insulator and electrolyte, a double layer<sup>10-12</sup> is formed. The purpose for introducing this structure is to control the voltage across the double layer by applying a voltage at the outer surface of double layer can control the velocity of electrolyte flow in a capillary. This effect, which in this paper is introduced as field effect electroosmosis, is based on electrokinetic phenomena<sup>12</sup>. This phenomena, in principle, can be utilized to make a miniaturized pumping system, which has a direct application for different models of capillary electrophoresis chromatography<sup>13</sup>.

This latter electrokinetic device, depicted in Fig. 2, is based on field effect electroosmosis. It is similar to a MOSFET in

some aspects. The difference is that in an electrokinetic device the electrolyte flow may be controlled where as in a MOSFET the current flow is controlled, by the field applied perpendicular to the flows, respectively.

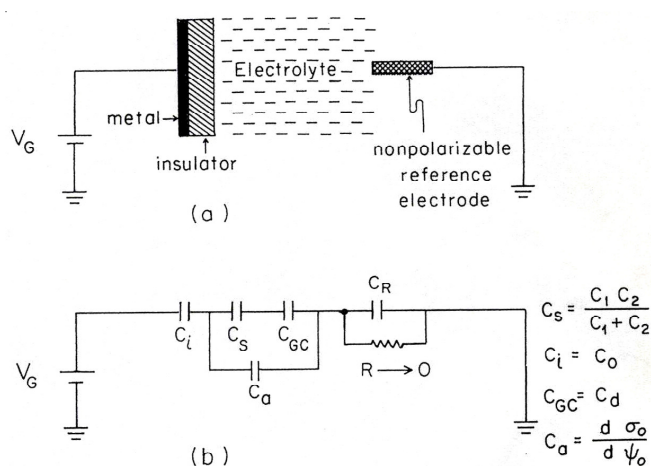


Fig. 1. (a) Metal-insulator-electrolyte and reference electrode structure (b) circuit diagram of a MIE

### Background review

**Electrolyte and electrolyte-solid interfaces:** Identical concepts are used to explain the physical properties of electron-hole density in semiconductors and H<sup>+</sup> and OH<sup>-</sup> ions

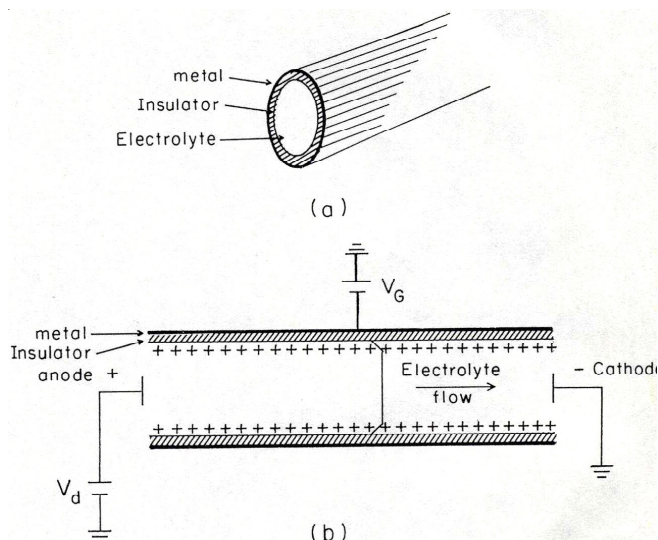


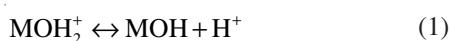
Fig. 2. (a) A capillary covered with metallic coating (b) cross section of metal-insulator-electrolyte field effect device (MIEEKFD)

densities in electrolytes<sup>11</sup>. For example, the law of mass action for the equilibrium state of an electrolyte is  $[H^+][OH^-] = K_w \approx 10^{-14} (\text{mole/liter})^2 = 3.6 \times 10^{-27} (\text{Ions.cm}^{-3})^2$ .

The addition of acids or bases to pure water alters the balance between  $H^+$  and  $OH^-$  ions. This is very similar to the equilibrium which occurs when either donors or acceptors are added to a semiconductor. However, ions in solution (especially cations) are generally hydrated, *i.e.*, they have a sheath of associated water molecules and their movement in the electrolyte is subject to a variety of interactions such as ion-ion, hydrogen bonding and hydrodynamic drag effects.

When a solid and an electrolyte are brought together, depending on what the insulator is or what types of ions are present, one or more of the following processes can occur.

**Surface ionization:** Surface ionization may occur at the interface of ionic solids, especially the oxide/electrolyte interface, based on the site binding model of Yates *et al.*<sup>14</sup>.



The insulator surface becomes negatively charged, positively charged, or neutral depending on the pH of the electrolyte. The pH at which the surface has zero charge is called the point of zero charge ( $pH_{pzc}$ ). Since both  $H^+$  and  $OH^-$  ions are responsible for the state of the charge on the surface, they are called potential-determining ions. Other ions present could participate in ionization. For a typical univalent counter ion, for example, if potassium and chloride ions are present in solution, we have these two equilibria.



**Electroosmosis:** Electroosmosis is the flow of liquid, in contact with a solid surface, under the influence of a tangentially applied electric field. Detailed descriptions of the phenomenon may be found in many standard texts<sup>12,15-17</sup>. Electroosmosis essentially has been attributed to the formation of an electric double layer at the solid/liquid interface, the latter as

described in previous section. Under the influence of a tangential electric field, a portion of the diffuse layer moves because of the electric forces acting on the excess ionic charge in it and a shear plane is set up at some distance from the solid surface. A constant flow-rate is reached when the force exerted on the counter ions (and thus on the liquid as a whole) is balanced by the frictional forces arising from the viscosity of the liquid. The potential at the shear plane, is called the zeta potential ( $\zeta$ ). The position of the slipping plane, or shear plane, is not yet clear. But it is concluded that, although the exact position of slipping plan is not known, it remains a reasonable assumption to set the zeta potential equal to the potential at the outer Helmholtz layer ( $\Psi_d$ ) (Fig. 3). Therefore, we have the justification for the ample attention given to double layer theory in the preceding section and the need for quantitation of its structure.

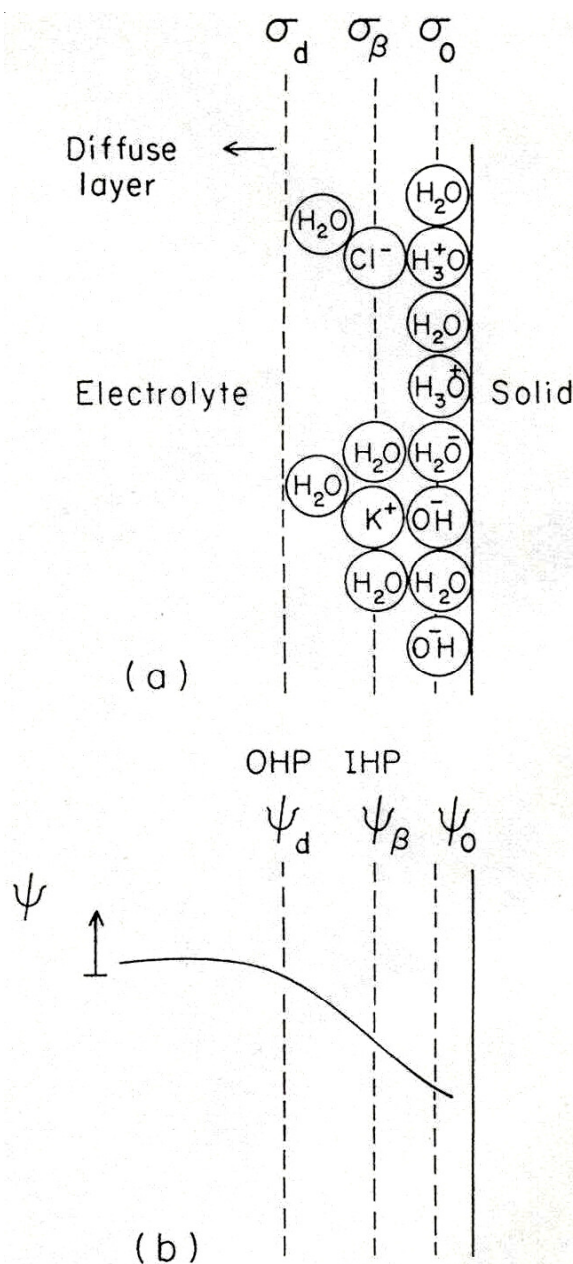


Fig. 3. Schematic diagram showing (a) the charge distribution and (b) potential profile at the insulator-electrolyte interface

The linear velocity,  $v$  of the liquid under influence of an applied electric field,  $E$ , is given by

$$v = \left( \frac{\epsilon}{\eta} \right) E \delta \quad (5)$$

where  $\epsilon$  and  $\eta$  are the dielectric constant and viscosity of the liquid, respectively. Equation (5) is strictly valid only if surface conduction is negligible and if the channels, through which the fluid flows, are considerably larger than the thickness of the double layer,  $\delta$ . The term  $\delta$  is defined as the distance from the immobile layer to a point at which the potential is equal to 0.37 times the potential at the interface between the immobile and diffuse layers.

The zeta potential, as mentioned before, depends on the nature of the solid surface and the ionic state of the liquid. Polar solvents, *e.g.*, water, give rise to zeta potentials of as much as 100 mV in contact with either polar, *e.g.*, glass, or non-polar, *e.g.*, graphite, surfaces.

Electroosmotic flow differs from laminar flow is another important respect. As shown schematically in Fig. 4, laminar flow causes a parabolic velocity profile. In electroosmotic flow, the flow profile is much flatter and resistance due to mass transfer occurs only in the region of laminar flow, *i.e.*, in the regions  $\delta$ . The numerical value of  $\delta$  depends essentially on the conductance of the liquid and it may be as low as several micrometers in reasonably conducting solvent. More details concerning the mathematical treatment of electroosmosis are provided in references<sup>12,15-17</sup>.

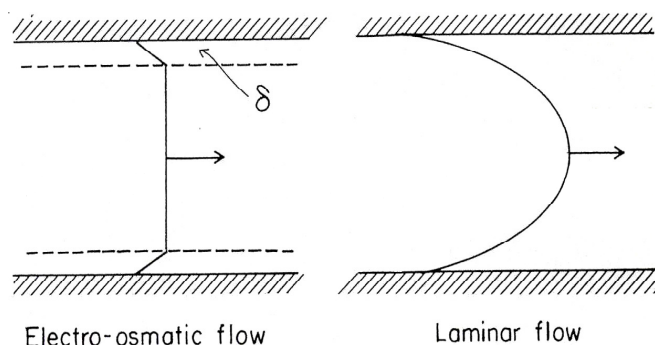


Fig. 4. Flow profile under two types of flow

**Field effect electroosmosis:** Field effect electroosmosis<sup>5-8</sup> can be defined as a novel phenomena which combines the metal-insulator-electrolyte system with capillary electroosmosis. Through field effect electroosmosis, we should like to control the electroosmosis flow in a capillary by an applied perpendicular electric field called  $V_G$ . By changing  $V_G$  the voltage drop across the double layer changes. This change includes the change in zeta potential,  $\delta$ , which in turn causes a modification in the electroosmotic flow. Until the discovery of field effect electroosmosis the only ways to change the zeta potential are to vary the pH of electrolyte or to modify the surface by using different coating. But by field effect electroosmosis, it should be possible to change the zeta potential easily by applying the appropriate external voltage. To understand this approach, there is a need to model the metal-insulator electrolyte system in more detail, which has been addressed as follows.

**Ideal metal-insulator-electrolyte structures:** In this section, the ideal metal-insulator-electrolyte system is analyzed, for the totally blocked interface. The non-ideal case is studied in the following section. This approach of ideal and non ideal structure is similar to metal-oxide-semiconductor (MOS) analysis<sup>9</sup>. The ideal MIE system is similar to Siu *et al.*<sup>1</sup> has defined as the totally blocked interface of an insulator/electrolyte part of a semiconductor-insulator-electrolyte structure. In ideal MIE, there is a complete absence of interfacial reactions between the electrolyte and the oxide or, in other words, there is no surface ionization. Since the interfacial electrochemical processes are absent, the charge and potential distribution in this MIE system is dictated solely by electrostatic considerations.

Furthermore, because the oxide exhibits no specificity to ionic species in the electrolyte the response is determined by the total ionic strength, *i.e.*, the combined effects of all the ions in the electrolyte. As shown in Fig. 5, the metal electrode is chosen to be ground and the applied voltage,  $V_G$ , is applied to the reference electrode. We choose the reference electrode as a non-polarizable one, where the voltage drop across it is negligible, so it can be assumed that the  $V_G$  is applied to the electrolyte. The charge per unit area and the potential in the electrolyte space-charge region are related by the Poisson-Boltzman equation<sup>11</sup>. From Gauss's law and the solution to this equation, we find that for an electrolyte the charge per unit area in Gouy-Chapman space-charge region is given by

$$\sigma_d = (8\epsilon_e kTn^0)^{1/2} \sinh[q(V_G - \Psi_d)/2kT] \quad (6)$$

From Fig. 5, we can write a charge neutrality equation

$$\sigma_d + \sigma_m = 0 \quad (7)$$

$$\text{and } c'_o = \frac{c_H c_o}{c_H + c_o}, \text{ since } c_H \gg c_o \text{ and } c'_o \cong c_o \quad (8)$$

$$\text{since } c_d \gg c_o \text{ then } \Psi_d - \Psi_o \ll \Psi_o, \text{ or } \Psi_d = \Psi_o \quad (9)$$

$$\text{and } \Psi_o C_o = -\sigma_m \quad (10)$$

$$-\sigma_m = \sigma_d \approx C_o \Psi_d \quad (11)$$

Thus, from (6) to (11), we find

$$C_o \Psi_d = -(8\epsilon_e kTn^0)^{1/2} \sinh[q(\Psi_d - V_G)/2kT] \quad (12)$$

Rearranging equation (12), we obtain

$$V_G = \frac{2kT}{q} \sinh^{-1} \left( \frac{\Psi_d C_o}{(8\epsilon_e kTn^0)^{1/2}} \right) + \Psi_d \quad (13)$$

$$\delta \approx \Psi_d - V_G = -\frac{2kT}{q} \sinh^{-1} \left( \frac{\Psi_d C_o}{(8\epsilon_e kTn^0)^{1/2}} \right) \quad (14)$$

Since the difference between  $V_G$  and  $\Psi_d$  is very small (in the range of millivolts), where as  $V_G$  and  $\Psi_d$  are several volts, by substituting  $\Psi_d$  in the parenthesis of equation (14) with  $V_G$ , the calculations are simplified. Thus we have

$$\delta \cong \frac{2kT}{q} \sinh^{-1} \left( \frac{V_G C_o}{(8\epsilon_e kTn^0)^{1/2}} \right) \quad (15)$$

For calculation of the inverse hyperbolic sine, it is convenient to use the following identity,

$$\sinh^{-1} x = \ln[x + (x^2 + 1)^{1/2}] \quad (16)$$

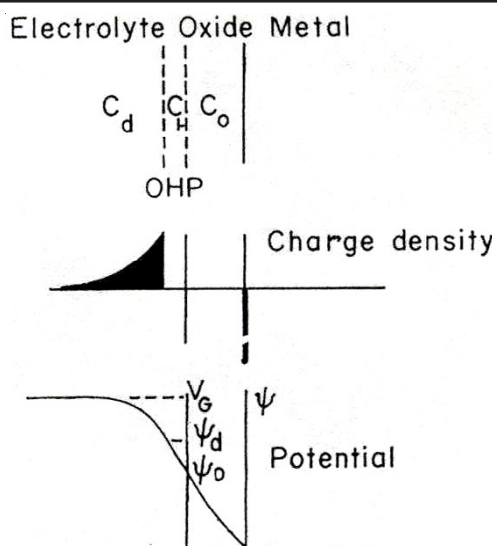


Fig. 5. The charge and potential profile in a totally blocked MIE system

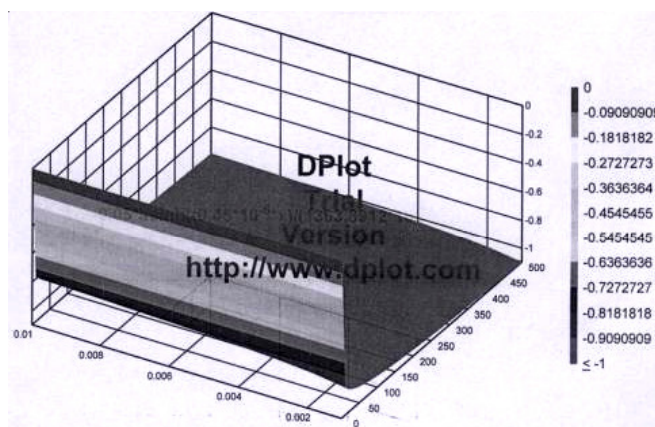


Fig. 6. Three dimensional plot of zeta potential as a function of  $V_G$  and electrolyte concentration

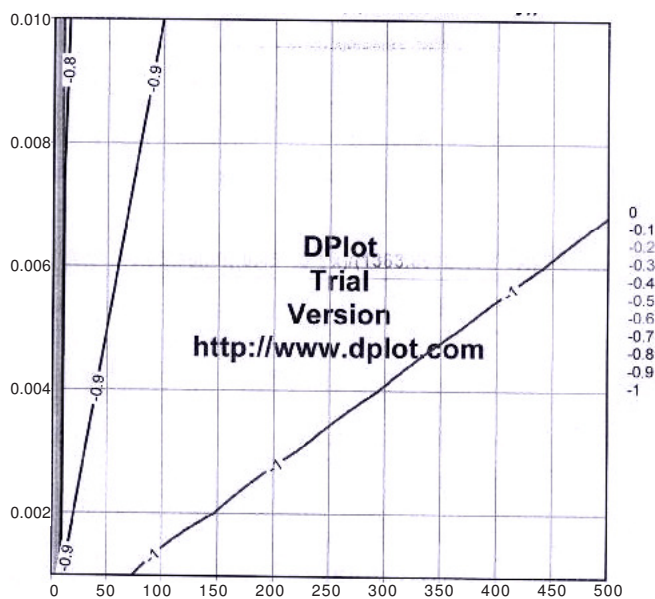


Fig. 7. Two dimensional surface plot of zeta potential as a function of  $V_G$  and electrolyte concentration

Using equation (15) and equation (16), the zeta potential is plotted versus  $V_G$  the potential between the metal and electrolyte and  $n^0$  the concentration of electrolyte. This three dimensional plot is done by the software of Dplot for the first time in this work in Fig. 6. Fig. 7 is the surface plot the projection of the three dimensional plot of Fig. 6 on the surface of  $\delta = 0$ .

Fig. 6 shows the zeta potential varies between 0 to 1 volt for  $V_G$  changes between zero to 500 volts.

### Conclusion

The metal-insulator-electrolyte structure has been modeled mathematically. It is shown that the zeta potential, defined as the voltage drop across the diffusion layer, can be changed by varying the voltage applied across the MIE. By combining the MIE system with electroosmosis, a new effect can be postulated, which has been termed filed effect electroosmosis.

We also proposed a new device based on this effect, which was called metal-insulator-electrolyte-electrokinetic field device or MIEKFED.

The MIE system and MIEKFED have many similarities with counterparts in solid state electronic, metal oxide semiconductor, Mos system and metal oxide semiconductor field effect transistor, MOSFET. This work could be a new beginning in direct application for the development of modified types of capillary electrophoresis chromatography<sup>13</sup>.

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