Modeling of FlowFET Characteristics

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ABSTRACT

Classical electrokinetic theory demonstrates that modulation of the ζ-potential at the shear plane can alter both the magnitude and direction of Electroosmotic Flow (EOF) induced in a microchannel at low driving field strengths. In the FlowFET, ζ-potential is modulated by applying a voltage V_G – with respect to the driving field cathode – through the insulated side walls of the device. An analytical model based on overall charge neutrality is presented which predicts the ζ-potential as a function of V_G. This is compared to values of shear plane ζ-potential extracted from EOF rate measurement data in a FlowFET. It is found that the model data and experimentally derived values for ζ-potential are within the same order of magnitude with good agreement between modeled and experimentally observed trends. Discrepancies are due to uncertainties related to experimental observation and lack of *Stern* layer modeling.

Keywords: FlowFET, Electrokinetic effects, ζ-potential, microfluidics, double layer

1. INTRODUCTION

Consider the electro-osmotic flow (EOF) of an aqueous electrolyte between two parallel, flat and electrically insulated plates. In the absence of a pressure gradient, the EOF rate in this system may be generally expressed as [1,2]:

$$Q = -AE\zeta[F(\kappa a)] \tag{1}$$

where A is constant[1], E is the driving electric field, ζ is the potential at the shear plane, κ is the *Debye-Huckel* parameter (inverse of double layer thickness), a is the plate separation distance and F is a "shape" function which expresses the influence of the double layer thickness on the flow profile. As can be seen from (1), modulation of either the driving electric field E or the ζ-potential can alter both the magnitude and direction of the induced EOF.

EOF control through ζ-potential modulation is an attractive prospect for microfluidic applications because it amplifies EOFs generated by low magnitude E-fields thus attenuating problems associated with joule heating or electrolysis. Furthermore, the EOF direction can be switched by reversing the polarity of the ζ-potential. In the FlowFET (**fig. 1**), ζ is modulated by applying a "gate" voltage – with

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[1] A full nomenclature is given at the end of this text.

respect to the driving field cathode – at electrodes on the outside surfaces of the plates [3,4,5].

A model for the relationship between the gate voltage V_G and the ζ-potential is central to understanding FlowFET behavior and is also required for finite-element calculations on microfluidic networks incorporating FlowFETs.
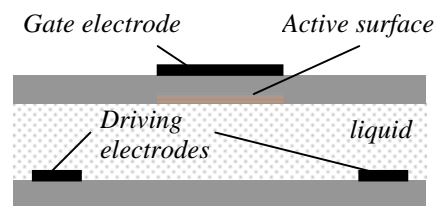

Figure 1: Schematic of FlowFET concept. ζ-potential can be modulated only on the active surface shown. The liquid must be an electrolyte.

2. MODELING

An inherent surface charge σ_0 comes into existence whenever two immiscible phases are brought into contact. The specific charging mechanism depends upon the surface chemistry of the particular system under consideration [6]. At equilibrium (i.e.: no current flow across the interface) net charge in the system must be zero. Physically, the surface charge σ_0 causes a redistribution of the ions in solution and gives rise to the formation of an electrostatic double layer (EDL), in which a surplus of counterions (ions of charge opposite in sign to σ_0) compensate the interfacial charge. **Figure 2** shows a schematic of the insulator/electrolyte interface. From the zero-net-charge electroneutrality requirement, a useful relationship between ϕ_0, ζ, pH and electrolyte concentration can be derived [7].

When a gate voltage V_G is applied, a new equilibrium will be established after a short time in which, again, the electroneutrality condition holds. Now however, in addition to the charge at the insulator surface and in the double layer, there is an additional charge stored in the insulator, which acts as a capacitor. The model presented here, is based on the application of the electroneutrality requirement with a few simplifying assumptions.

2.1 Simple electroneutrality model

As stated previously, the electroneutrality condition requires the sum of all charges stored in the insulator/electrolyte system to be zero. When a gate voltage

V_G is applied, an additional charge σ_{ins} stored in the insulator must be accounted for in addition to the charges shown in **fig. 2**, the electroneutrality condition becomes:

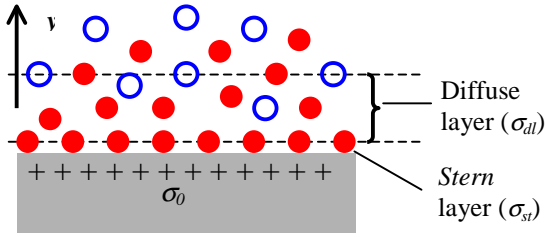$$\sigma_{ins} + \sigma_0 + \sigma_{st} + \sigma_{dl} = 0 \qquad (2)$$

Figure 2: Schematic of the physical situation at an insulator/electrolyte interface showing co-ions (open circles) and counter-ions (dots).

The inherent surface charge σ_0 is a function of the pH (where at pH_{PZC}, the point of zero charge, $\sigma_0 = 0$) and is evaluated by comparing H^+ ion concentration at the interface with H^+ concentration in the bulk of the solution. Hence the "equivalent" electrical circuit represented schematically in **fig. 3** is proposed where it is assumed that interaction between the interfacial charge σ_0 and the potential ϕ_0 can be modeled as a capacitor. Applying the electroneutrality condition to this circuit yields:

$$C_{ins}(V_G - \phi_0) + C_2 \phi_0 = 0 \qquad (3)$$

where,

$$C_2 = \left(\frac{1}{C_{st}} + \frac{1}{C_{dl}} \right)^{-1} + C_0 \qquad (4)$$

as the *Stern* layer capacitance is known to be very large (20 $\mu F/cm^2$) compared to the diffuse layer capacitance [7,8], equation (4) can be simplified and substituted into (3), thus

$$\sigma_{ins} + \sigma_0 + \sigma_{dl} = 0 \qquad (5)$$

Note that in this model ϕ_0 and the ζ - potential become interchangeable and σ_{st} has been ignored resulting in numerical errors which will be further discussed. Substituting the appropriate expressions for the charge variables in (5) yields the following expression for V_G:

$$V_G = \zeta - \frac{d}{\varepsilon_{ins}} \left[eN_s \left(\frac{A+1-\left(1+\frac{8}{AK}\right)^{\frac{1}{2}}}{A+2} \right) - \sqrt{8n_0 \varepsilon_s k_b T} \sinh\left\{ \frac{ze\zeta}{2k_b T} \right\} \right] \qquad (6)$$

where,

$$A = \frac{2}{\sqrt{K}} \exp\left\{ 2.303[pH_{PZC} - pH] - \frac{ze\zeta}{k_b T} \right\} \qquad (7)$$

Equation (6) is obtained under the assumption that K, which is inversely proportional to the "reactivity" of the interface, is very large compared to 1. As (6) is deterministic, the desired function $\zeta = f(V_G)$ is simply the inverse of (6).
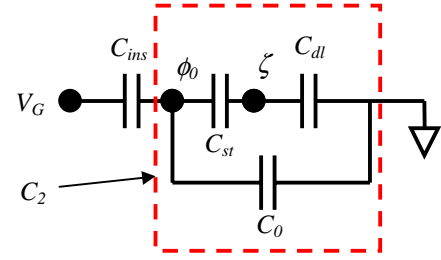

Figure 3: Proposed equivalent circuit.

2.2 Model results

Applying equation (6) to a system where the FlowFET wall material is SiO_2 of thickness $d = 350$ nm, the electrolyte is a dissolved symmetric salt of valence 1 at a concentration of 2 mM and plotting the inverse yields a family of curves as shown in **fig. 4**. As expected, the values for ζ - potential are within a reasonable range (between 0 and 100 mV), in addition, the model correctly predicts $\zeta > 0$ for pH < pH_{PZC} and vice versa.

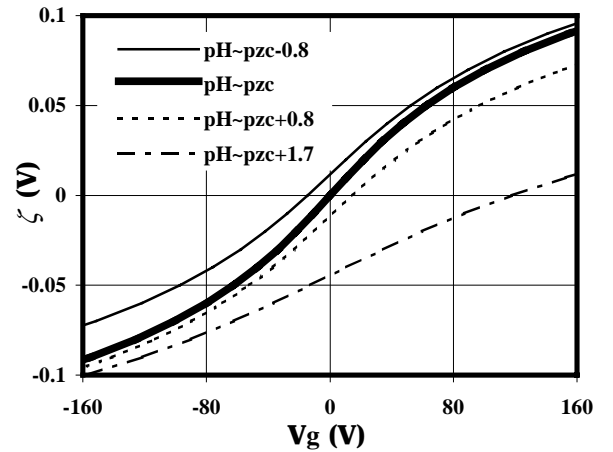**Figure 4:** Modeled V_G - ζ characteristic curves at different solution pH values, $pH_{PZC} \sim 2.8$ for SiO_2.

The model can be most usefully compared to a previously published data set [5] obtained from velocity measurements in a FlowFET at pH ~ pH_{PZC}. By balancing electrostatic and shear forces over carefully selected control volumes, an expression can be found which relates the measured velocity to the ζ - potential at the active surfaces at pH_{PZC}.

$$\zeta_a = -\frac{\mu U}{\varepsilon_s E_x} \left(1 + \frac{k_{top} - 1}{(2a_r + 1)} \right) \qquad (8)$$

where k_{top} is the ratio between top wall shear plane velocity and the average velocity in the active zone of the FlowFET and a_r is the aspect ratio (depth/width) of the active region. To obtain expression (8), pressure forces were neglected and double layer thickness was assumed very small compared to channel dimensions.

In the case of EOF between parallel flat plates of infinite width, both of which have a non-zero and equal ζ - potential the term in brackets in eq. (8) reduces to 1, yielding the classical *Smochulowski* equation. Thus (8) is simply *Smochulowski's* equation with a correction factor. If only one of the plates has a non-zero ζ - potential then it can be shown that the correction factor has a value of 2 which corresponds to a linear flow profile similar to *Couette* flow. Consequently, for the physical situation of interest, the correction factor should lie somewhere between 1 and 2 hence we can write, $1 \leq k_{top} \leq 2a_r + 2$. Intuitively a low value for k_{top} should be expected. Selecting $k_{top} = 2$ provides inferred values for ζ - potential which are compared to model predictions in **fig. 5**.
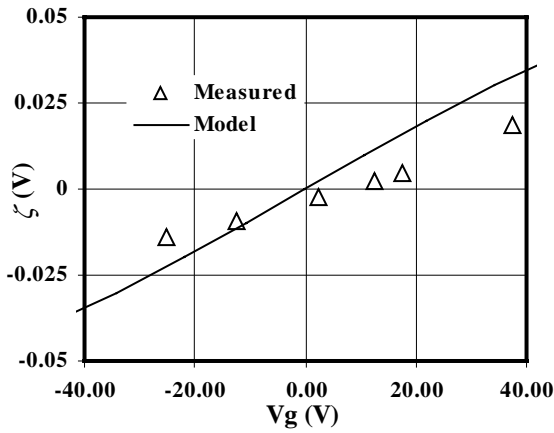

Figure 5: Comparison between model predictions and values extracted from measurement values for ζ-potential as a function of V_G.

In **fig. 5** the response curve computed using (6) assumes that pH = pH$_{PZC}$. The agreement appears to be quite reasonable with respect to trends although the numerical predictions appear to overestimate ζ - potential by a factor of about 2. The offset at $V_G = 0$ demonstrates that the data was not taken at the exact point of zero charge.

On a more qualitative level, it was observed during experiment that the ζ - V_G response displayed the saturation behavior predicted by the model. In addition it was observed that at high values of pH (pH ~ 4.5), although the rate of EOF could be modulated, it was unfortunately not possible to reverse the flow direction. **Fig. 4** shows that at pH ~ 4.5, the gate voltage required to switch flow is approximately 80V which is beyond the voltage at which dielectric breakdown occurs for the SiO$_2$ insulating layer used.

3. DISCUSSION

As the model seems to agree reasonably well, both qualitatively and quantitatively with experimental observations, equation (6) can be used to predict the effect of design changes on FlowFET behavior with some degree of confidence. Of the physical parameters which can be controlled in (6) for a given electrolyte. Wall thickness d can be modified and the parameters ε_{ins} and K can be modified through a judicious choice of FlowFET materials.

For greatest sensitivity one seeks to minimize (6) and an obvious way to do that is to minimize d/ε_{ins}. For the curves shown in **fig. 4**, the insulating material was assumed to be SiO$_2$, used in the current FlowFET fabrication process; unfortunately it has a low dielectric constant of approximately 4.5. Various oxides, which display similar properties to SiO$_2$ when exposed to inorganic electrolytes have higher dielectric constants and would thus increase FlowFET sensitivity. These include Alumina (D = 9), Tantalum pentoxide (D = 34) and Titanium oxide (D = 86). Assuming *Knoop* hardness to be an indication of material strength [9], all of the alternatives listed above are suitable candidates in the sense that allowable wall thickness d can be reduced if stronger materials are used. Alumina for instance is approximately 1.5 times as hard as SiO$_2$ [10].

Parameter K ($\log_{10} K$ is sometimes referred to as ΔpK in the literature) expresses the sensitivity of the surface to pH. For high values of K the surface becomes essentially insensitive to the presence of H$^+$ ions, the second term in (6) tends to a constant value. The behavior of ζ as a function of V_G then becomes dominated by the last term of the equation. For switching mode operation of the FlowFET, a highly un-reactive coating (i.e. one with a high value of K) offers the prospect of flow direction control at relatively low voltages.

As a final note, electrolyte composition can also be varied for given applications, for instance in the case of drug delivery or chemical synthesis microsystems. If this is the case, buffers with a low ionic concentration and a low dielectric constant could be used for increased modulation sensitivity.

4. CONCLUSIONS

A simple model for the sensitivity of ζ - potential to FlowFET gate voltage has been presented which is good enough to provide an estimate of the ζ - potential under various physical constraints and is useful for the development of the FlowFET concept. However, the model presented here also has a glaring weakness, namely the consistent overestimation of ζ - potential for given values of V_G. This is probably due in part to the neglect of the *Stern* layer. However, since the *Stern* layer charge was not investigated within the framework of this project, it is not possible to estimate the magnitude of the *Stern* layer "effect". It is possible that the ISFET literature would be a good source for information on these phenomena.

Another possible source of error in this model is the inherent assumption that all of the potential energy introduced into the FlowFET system by electrifying the insulator is converted into electrical energy. It is entirely possible that for some oxides, electrification of the insulator leads to a change in the dissociation characteristics at the insulator/electrolyte surface. For SiO$_2$ it has been suggested that this effect is very slight [7].

A simple method for deriving ζ - potential from EOF measurements in microchannels has also been proposed

which, within limits can be applied to channels of almost any shape as long as three conditions are fulfilled:

- ❖ The double layer thickness is negligible with respect to the hydraulic diameter of the channel.
- ❖ At the length scale of the double layer, the surface can be locally assumed to have a negligible radius of curvature
- ❖ Shear losses can be expressed as kU/δ where δ is a characteristic length scale corresponding to the double layer thickness in regions where ζ - potential is non-zero at the surface and hydraulic diameter otherwise.

More generally, this work leads to the conclusion that surface phenomena can be very advantageously used to provide new microfluidic functionalities.

5. ACKNOWLEDGMENTS

6. NOMENCLATURE

5.1 Physical constants

k_b *Boltzmann* constant, 1.381 x 10^{-23} [J/K]
e Charge of one electron, 1.603 x 10^{-19} [C]

5.2 Geometrical parameters

a Active region, channel height [m]
b Active region, channel width [m]
w inlet/exit region channel width [m]
a_r Aspect ratio (a/b) [none]
d Active region, wall thickness [m]
δ Characteristic length scale [m]

5.3 Liquid solution physical properties

ε_s Solution permittivity [F.m^{-1}]
μ Dynamic viscosity of bulk liquid [Kg.m^{-1}.s^{-1}]
n_0 Ionic strength [ions.m^{-3}]

5.4 Surface / material physical properties

ε_{ins} Insulator permittivity [F.m^{-1}]
ζ Potential at flow shear plane with respect to bulk [V]
N_s Number of surface sites [none]
ϕ_0 Surface potential with respect to bulk [V]
k_+ Chemical equilibrium constant for positive amphoteric dissociation
k_- Chemical equilibrium constant for negative amphoteric dissociation
K Inverse reactivity defined as $(k_+ k_-)^{-1}$

5.5 Independent system parameters

V_G Gate voltage with respect to bulk [V]
E_x EOF driving field strength [V.m^{-1}]
T Absolute temperature [K]
x Spatial coordinate in flow direction [m]

5.6 Dependent system parameters

pH_{PZC} pH for which surface charge is zero if $V_G = 0$
σ_0 Surface charge [C.m^{-2}]
α_0 Dimensionless surface charge = σ_0/eN_s
σ_{st} Charge stored in *Stern* layer [C.m^{-2}]
σ_{dl} Charge stored in diffuse layer [C.m^{-2}]
σ_{ins} Charge stored in insulator [C.m^{-2}]
u local liquid speed [m.s^{-1}]
U Average liquid velocity [m.s^{-1}]

7. REFERENCES

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