

# THE IMPORTANCE OF WALL CHEMISTRY IN NANOFUIDICS

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## ABSTRACT AND INTRODUCTION

It is common knowledge that the surface charge in micro- and nanofluidic systems and hence the intensity of electrokinetic phenomena is a function of pH, ionic strength and type of solute. It is not often realized however that transient changes in surface charge will be accompanied by changes in the concentration of the surface-binding ions. Since the latter effect increases with increasing surface-to-volume ratio, it is especially relevant in nanofluidic systems. Ionic binding also limits the efficiency of voltage gating in so-called ionic transistors, causing changes in ionic concentration rather than changes in surface potential. In this contribution we present a conceptual model that accounts for ion binding and apply it to proton equilibria in several nanofluidic devices as well as to the flowFET and the ISFET pH sensor.

**KEYWORDS:** Nanofluidics, surface charge density, surface potential, voltage gating, ionic transistor, ISFET, flowFET

## THEORETICAL MODEL

The surface charge on fluidic channel walls results from specific ion binding to surface groups. Glass walls for example possess silanol (SiOH) groups which either bind protons ( $pK_a \approx -1.9$ ) or deprotonate ( $pK_a \approx 6.7$ ). As a result a glass surface is uncharged (point of zero charge, PZC) at  $pH \approx 2.4$  and increasingly negatively charged in solutions of higher pH. The surface charge density and surface potential can be calculated using models for the proton dissociation and the electrical double layer [1].

This paper presents a conceptual model describing protonation equilibria in fluidic channels. The model employs capacities on which protons are stored as function of the local proton energy. In equilibrium the proton energy is the same in the entire system, i.e. for the wall-bound protons, the protons in solution directly at the surface at the surface potential  $\psi_s$  and the protons in the electroneutral bulk ( $\psi_b = 0$ ). We employ electrical units for the proton energy (Joule/Coulomb = Volt) and represent the different proton capacities per unit area. Scaled units are derived as  $pH^* = 2.3RTpH/F$  and  $c^* = hcF/2$ , where  $c$  is the proton concentration ( $\text{mol}/\text{m}^3$ ),  $R$  ( $8.31 \text{ J}/(\text{mol K})$ ) the gas constant,  $T$  (K) the absolute temperature,  $F$  Faraday's constant ( $96485 \text{ C}/\text{mol}$ ) and  $h/2$  half the nanochannel height (m), used to convert concentration units per  $\text{m}^3$  into units per  $\text{m}^2$  for rectangular channels with width  $\gg$  height.

### Proton energy

Limiting the model to the protons in free solution directly at the surface (subscript  $s$ ) and the protons in the electro-neutral bulk (subscript  $b$ ), in equilibrium the proton energy in Volts at both locations is given by the equality

$$\psi_s - pH_s^* = \psi_b - pH_b^* \quad (1)$$

When the system is disturbed, for example by a change of surface potential or bulk pH, protons will redistribute until the proton energy again is identical throughout the system. Redistribution entails changes of local pH and potential which can be derived using an electrical equivalent circuit.

### Circuit elements and circuits

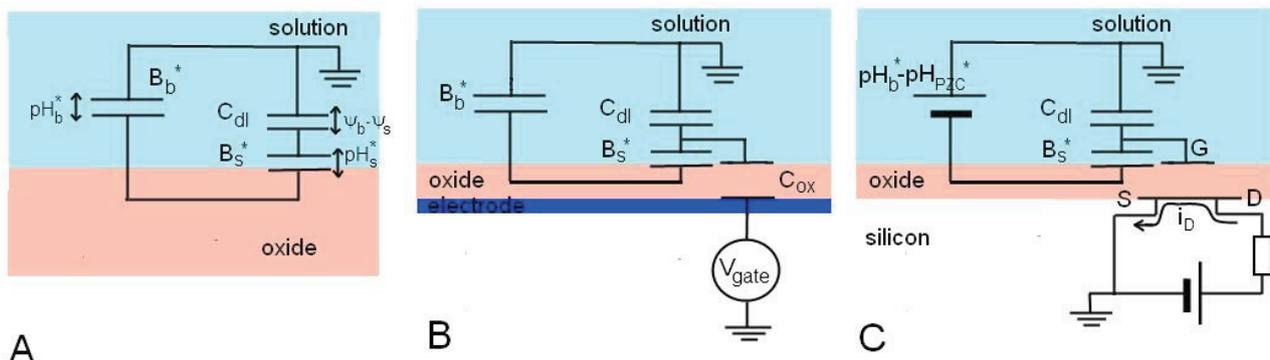


Figure 1: Equivalent electrical circuits describing A) a channel wall in contact with solution; B) a gated fluidic system such as a nanofluidic transistor; C) an ISFET. These circuits can be used to derive the surface charge and surface potential, as well as the bulk pH and surface pH.

The quantities describing the proton energy as defined in equation 1 can be recognized in Figure 1A as voltages over electrical capacities. The electrical equivalent circuit applicable to protonation equilibria in simple nanofluidic channels

(Figure 1A) consists of three capacities in series. Protons binding to the surface change the surface charge density  $\sigma_0$  ( $C/m^2$ ) resulting in a change of surface potential described by the double layer capacity,  $C_{dl} = d\sigma_0/d\psi_s$  ( $F/m^2$ ). The change of bound proton density (the surface charge) with the change of surface pH is given by the intrinsic surface buffer capacity,  $B_s^* = d\sigma_0/dpH_s^*$  ( $F/m^2$ ). The change of (bound or unbound) proton concentration in the bulk solution  $c^*$  ( $C/m^2$ ) for a change of solution pH is given by the bulk buffer capacity,  $B_b^* = dc^*/dpH_b^*$  ( $F/m^2$ ).

Figure 1B shows the circuit that applies to gated fluidic systems such as ionic transistors and flowFETs. It contains in addition the oxide capacity via which the surface potential is modulated,  $C_{ox}$  ( $F/m^2$ ) using an external electrode. The circuit applicable to ion-sensitive field effect transistors (ISFETs) (Figure 1C) is a variant of the latter circuit, where the surface potential capacitively changes the electron density in the silicon, modifying the source/drain current. Furthermore here an infinite bulk is assumed, so that the solution buffer capacity is replaced by a battery of  $pH_b^*-pH_{PZC}^*$ .

Simple electrical network theory can be used to calculate the change in electrical potential over the capacities described if the system is subjected to some parameter change. The surface potential equals the voltage drop over  $C_{dl}$ , the scaled surface pH the voltage drop over  $B_s^*$  and the scaled bulk pH the voltage drop over  $B_b^*$ . The charge on  $B_s^*$  furthermore equals the surface charge. It should be noted that all capacities mentioned are not constant but a function of ionic strength and pH. If small changes are considered however they can be assumed constant.

## MODEL APPLICATION AND DISCUSSION

### Surface wetting

Before a bulk solution wets the walls of a nanostructure, it initially possesses protons of energy  $pH_{init}^*-pH_{PZC}^*$  Volt that form the charge on a capacitor with a capacitance of  $B_b^* F/m^2$ . The structure walls have surface-bound protons with an initial energy of  $pH_{PZC}^*$  Volt and the initial surface potential is 0. When the surface is wetted the bulk capacity contacts the other two capacities and protons redistribute until the proton energy is everywhere the same. Using the equivalent circuit of Figure 1A we can calculate the charge left on the bulk capacity, the charge created on the surface buffer capacity and the charge on the double layer from the relative magnitude of all capacities. We can furthermore derive the final surface potential, surface pH and bulk pH. In the scaled units defined above we find

$$pH_{final}^* = pH_{PZC}^* + pH_{init}^* - pH_{PZC}^* \cdot \frac{1}{\frac{1}{B_b^*} \cdot \frac{B_s^* \cdot C_{dl}}{B_s^* + C_{dl}} + 1} \quad (2)$$

When both the surface buffer capacity  $B_s^*$  and the double layer capacity  $C_{dl}$  are much larger than the bulk capacity  $B_b^*$ , equation 2 gives  $pH_{final}^* = pH_{PZC}^*$ , in other words, the bulk solution is protonated until the point of zero charge of the wall material is reached. On the other hand when  $C_{dl}, B_b^* \ll B_s^*$ , or when  $B_s^*, B_b^* \gg C_{dl}$ ,  $pH_{final}^* = pH_{init}^*$ . It should be remarked that this simple model does not account for convective proton transport, and hence should be extended to describe capillary nanochannel filling. Filling experiments have been performed in 50nm nanochannels using fluorescein as pH indicator and solution acidification was indeed observed [2]. Experiments at different values of the pH, bulk buffer capacity and ionic strength combined with modeling allowed extraction of the Stern capacity and the oxide  $pK_a$ .

### FlowFET and ionic transistor operation

In the flowFET (Figure 1B) the electroosmotic flow in microchannels is modulated by applying a gate potential between an exterior electrode and the bulk solution to modulate the surface potential [3]. In ionic transistors the same procedure is used to modulate the permselectivity of a nanochannel. From the equivalent circuit of Figure 1B and assuming that  $C_{ox} \ll C_{dl}, B_s^*$  it can be deduced that an applied voltage  $V_{gate}$  changes the surface potential as

$$\Delta\psi_s = \frac{C_{ox}}{C_{dl} + \frac{B_s^* B_b^*}{B_s^* + B_b^*}} V_{gate} \quad (3)$$

In microchannels where mostly  $B_b^* \gg B_s^*$ , a surface buffer capacity  $B_s^*$  which is much higher than the double layer capacity is thus detrimental for operation. The oxide surface is then mainly charged, instead of the electrical double layer (see Figure 2A). However when  $B_s^* \approx 0$ , a maximal surface potential change is obtained (Figure 2B). For  $SiO_2$  at  $pH = pH_{PZC}$ ,  $B_s^* \approx 0$  and the surface potential change is maximal while at  $pH = 7$  where  $C_{dl} \approx 0.8 F/m^2$  and  $B_s \approx 1.7 F/m^2$ , the same applied gate potential produces a three times smaller surface potential change. The field effect will therefore only operate well when both  $B_b^*$  and  $B_s^* > C_{dl}$ . It was indeed experimentally observed with the flowFET that the zeta potential could only successfully be modified below  $pH = 4$  [3]. Also for ionic transistors both Eijkel and Jiang recently argued that operation would be less efficient when  $B_s^* > C_{dl}$  [4-5]. Both authors however overlooked the fact that transient operation will again be possible when  $C_{dl} > B_b^*$ , as can easily be the case in nanochannels. In this case protons released from the surface acidify the channel solution, suppressing further deprotonation and enabling successful gating (Figure 2C). In time the magnitude of the gating based on this mechanism will however decrease since protons will be exchanged by proton interdiffusion with electroneutral reservoirs. Figure 2 depicts these three different regimes of operation.

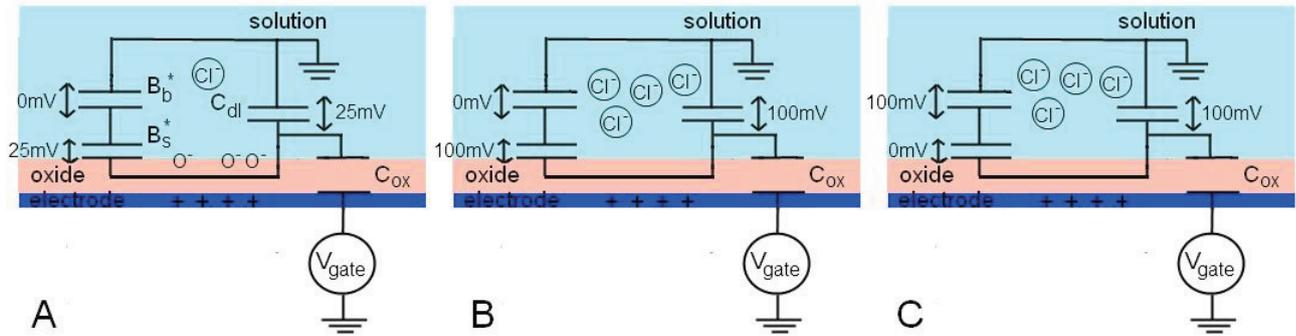


Figure 2: Three possible regimes of operation of a field-effect device, for  $\Delta\psi_s(\max)=100\text{mV}$ . A) Operation when the surface buffer capacity is three times larger than the double layer capacity but much smaller than the bulk buffer capacity ( $B_b^* \gg B_s^* = 3C_{dl}$ ). Only one in four negative charges resides in the double layer. B) Operation when both the double layer capacity and the bulk solution buffer capacity are much larger than the surface buffer capacity ( $B_b^*, C_{dl} \gg B_s^*$ ). The surface potential is maximally modulated by the field effect. C) Operation when the surface buffer capacity is much larger than the double layer capacity is much larger than the bulk buffer capacity (often in nanochannels) ( $B_s^* \gg C_{dl} \gg B_b^*$ ). Also in this case the surface potential is maximally modulated by the field effect.

### Proton actuator

The surface protons released (or taken up) from a field-effect device change the pH in the bulk solution of the fluidic structure. This pH change can be derived from Figure 1B as

$$\Delta\text{pH}_b^* = \frac{C_{ox}}{\frac{C_{dl}(B_s^* + B_b^*)}{B_s^*} + B_b^*} V_{gate} \quad (4)$$

The pH can therefore successfully be changed when  $B_s^* > B_b^*$  and  $B_b^* < C_{dl}$ . On the basis of this phenomenon Veenhuis et al. constructed a field-effect proton actuator using a silicon nitride insulator surface and demonstrated successful proton titrations of attomole amounts in a 7 picoliter volume [6].

### ISFET response

The pH sensitivity of an Ion-Sensitive Field Effect Transistor (ISFET) can be derived from the circuit of Figure 1C as

$$\frac{d\psi_s}{d\text{pH}_b^*} = -\frac{B_s^*}{B_s^* + C_{dl}} \quad (5)$$

A Nernstian response ( $-2.3RT/F = -59 \text{ mV}$  per decade of pH) is therefore obtained when  $B_s^* \gg C_{dl}$  [1]. It can also easily be understood that the ISFET response depends on the ionic strength since the double-layer capacity depends on the ionic strength. When the ionic strength is changed in a step-wise manner it therefore causes a step-wise change in surface potential. In a system with constant bulk pH, protons will then redistribute over the surface buffer capacity and double layer capacity. The step change and redistribution cause a transient change of the surface potential which can be measured by the ISFET and can form the basis of a surface-potential sensor [7].

### CONCLUSION

The mode of operation of various micro- and nanofluidic phenomena and devices can be described using equivalent electrical circuits as simple conceptual models.

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