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# Field effect electroosmosis

KIUMARS GHOWSI*
*Department of Chemistry and Biochemistry, Texas Tech University, Box 4260, Lubbock, TX 79409-1061 (USA)*
and
ROBERT J. GALE
*Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-6100 (USA)*

## ABSTRACT

A novel effect, called field effect electroosmosis has been postulated. By coating the outside of a silica capillary with a conductive layer and applying a perpendicular voltage, $V_G$, across its wall, the zeta potential, can be changed by varying $V_G$. Through flexible control of the zeta potential, the electroosmotic flow can be controlled. This adds a new dimension to capillary electrophoresis (both capillary zone electrophoresis and micellar electrokinetic capillary chromatography). Some of the advantages, including tuneability, are discussed. Based on this effect, the design of the first electrokinetic transistor, called a metal–insulator–electrolyte–electrokinetic field-effect device (MIEEKFED), was proposed. This device could be used for separation-based sensors. It also has great potential for miniaturization, especially because of the advances that have occurred in the micromachining technology of silicon. Recently, an experimental study of the use of an additional electric field outside a capillary to control the zeta potential has been reported. This work provides confirmation of our theoretical predictions.

## INTRODUCTION

Capillary electrophoresis (CE), as an instrumental technique, started with the work of Hjertén [1] and continued slowly through the works of Virtanen [2] and Mikkers *et al.* [3]. The first revolution in the field was that of Jorgenson and Lukacs [4]. In their study, plate heights of less than 1 mm were predicted and values of a few micrometers were experimentally obtained by their timely advance to smaller diameter capillaries. This work, which demonstrated the potential of CE as a very powerful instrumental technique for separation, was termed capillary zone electrophoresis (CZE). The second revolution in the field was the work of Terabe and co-workers [5,6]. Before their work, CE was limited to the analysis of charged species. They demonstrated that by adding micelles to the liquid the separation of neutral solutes is also possible. This technique was termed micellar electrokinetic capillary chromatography (MECC). Recently, we proposed the novel technique of field effect electroosmosis [7–9], which has the potential to be a further revolution in the field.

Capillary electrophoresis places a buffer-filled capillary between two buffer reservoirs and a potential field is applied across the capillary. The electric field creates an electroosmotic flow of buffer solution toward the cathode. The electric field also causes electrophoretic flow of ionic solutes in CZE or micelles in MECC. Separation takes place due to different ion mobilities of the solutes or micelles. The electroosmotic flow and solutes travel toward the cathode, where the latter can be detected.

Electroosmosis, the major component of CE, is flow of a liquid (generally a polar liquid) in contact with a porous solid under the influence of an applied electric field. Electroosmotic flow in a capillary has been attributed to the formation of an electric charged layer at the solid/liquid interface. Under the influence of an electric field parallel to that interface, a portion of the liquid's diffuse layer moves. This migration of cations causes a concomitant migration of fluid through the capillary. The electric potential across the diffuse layer is called $\zeta$, the zeta potential.

## THEORY

The linear velocity, $\upsilon$, of the liquid under the influence of an applied electric field $E$ is approximately

$$\upsilon = \left(\frac{\varepsilon}{4\pi\eta}\right)\zeta E \tag{1}$$

where $\varepsilon$ is the dielectric constant of the liquid and $\eta$ is its viscosity. Thus $\upsilon$ is proportional to the zeta potential. The magnitude of the zeta potential depends on, among other things, the nature of the solid surface, the concentration of ions and the pH of the electrolyte.

One method to control the rate of electroosmosis is to change the voltage applied across the length of the capillary, but such a change also affects the electrophoretic flow of solute and will not affect the overall degree of electrophoretic separation. Other methods of controlling the rate of electroosmosis are to change the concentrations of species in solution or suspension, to change the pH or to change the nature of material forming the inner layer of the capillary. None of these methods is flexible or capable of rapid change and each has disadvantages [4,10].

Field effect electroosmosis is a novel means of controlling the rate of electroosmosis due to a first electric potential across a capillary. In this method, a second electric potential is applied between the electrically insulating walls of a capillary and the liquid. This field changes the charge on the wall of the capillary and thus allows manipulation of the zeta potential within the capillary. Manipulation of the zeta potential in this manner permits flexible and rapid control of the rate of electroosmosis independent of the rate of electrophoresis.

Based on this principle of field effect electroosmosis, we proposed the first field effect electrokinetic transistor called a metal–insulator–electrolyte–electrokinetic field-effect device (MIEEKFED) [7–9]. This device could be considered analogous in some ways to the conventional metal oxide field-effect transistor (MOSFET) in electronics. In a MIEEKFED the electrolyte flow may be controlled, whereas in a MOSFET the electric current flow may be controlled, in either case by means of an electric field applied perpendicular to the respective flow.

A schematic diagram of a MIEEKFED is shown in Fig. 1. This device should

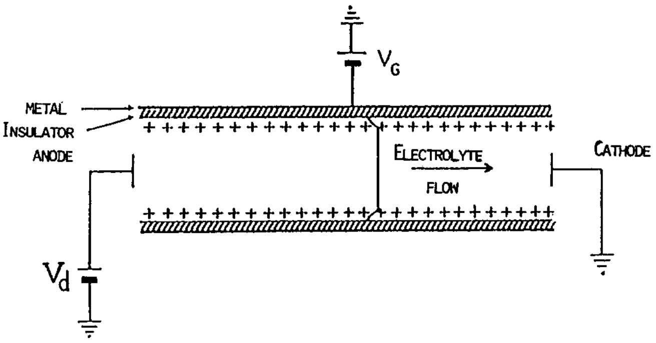

Fig. 1. Cross-section of a MIEEKFED. $V_d$ is the voltage applied between cathode and anode and $V_G$ is the voltage between metal layer and cathode.

allow the control of the flow of an electrolyte by two voltages, $V_d$, the applied voltage across the capillary, and $V_G$, the gate voltage. First, it is necessary to show how the zeta potential is a function of $V_G$. When pyrogenic silica is in contact with an aqueous solution, its surface hydrolyzes to form silanol surface groups. These groups may be positively charged, negatively charged or neutral, depending on the electrolyte pH. For silica, the surface group density is of the order of $5 \cdot 10^{14}$ cm$^{-2}$ and can be described by the following equations:

$$\mathrm{SiOH} \rightleftharpoons \mathrm{SiO^-} + \mathrm{H_s^+} \qquad K_a = \frac{[\mathrm{SiO^-}][\mathrm{H^+}]_s}{[\mathrm{SiOH}]} \tag{2}$$

$$\mathrm{SiOH} + \mathrm{H_s^+} \rightleftharpoons \mathrm{SiOH_2^+} \qquad K_b = \frac{[\mathrm{SiOH_2^+}]}{[\mathrm{SiOH}][\mathrm{H^+}]_s} \tag{3}$$

where $[\mathrm{H^+}]_s$ is the concentration of hydrogen ions at the surface and $[\mathrm{SiO^-}]$, $[\mathrm{SiOH}]$ and $[\mathrm{SiOH_2^+}]$ are the surface sites at the oxide.

In addition to the amphoteric dissociation mentioned previously, the supporting electrolyte can also form ion pairs with the charged surface sites. This is illustrated below using potassium chloride as a typical, univalent, supporting electrolyte:

$$\mathrm{SiOH_2^+} + \mathrm{Cl_s^-} \rightleftharpoons \mathrm{SiOH_2Cl} \qquad K' = \frac{[\mathrm{SiOH_2^+}][\mathrm{Cl^-}]_s}{[\mathrm{SiOH_2Cl}]} \tag{4}$$

$$\mathrm{SiO^-} + \mathrm{K^+} \rightleftharpoons \mathrm{SiOK} \qquad K'' = \frac{[\mathrm{SiO^-}][\mathrm{K^+}]_s}{[\mathrm{SiOK}]} \tag{5}$$

where $[\mathrm{SiOH_2Cl}]$ and $[\mathrm{SiOK}]$ are the surface sites at the oxide. The total number of sites per unit area is given by

$$N_s = [\mathrm{SiOH}] + [\mathrm{SiOH_2^+}] + [\mathrm{SiO^-}] + [\mathrm{SiOH_2Cl}] + [\mathrm{SiOK}] \tag{6}$$

The concentrations of $[Cl^-]_s$, $[K^+]_s$ and $[H^+]_s$ at the surface could be related to the bulk electrolyte by the Boltzmann distribution, given by the following equations [8,9,11]:

$$[H^+]_s = [H^+] \exp(-q\psi_a/kT) \tag{7}$$

where $\psi_a = \psi_0 - V_G$, $\psi_0$ is the potential at the insulator electrolyte interface, $q$ is electronic charge magnitude, $k$ is the Boltzmann constant and $T$ is temperature.

$$[Cl^-]_s = n_0 \exp\left(\frac{q\psi_b}{kT}\right) \tag{8}$$

$$[K^+]_s = n_0 \exp\left(\frac{-q\psi_b}{kT}\right) \tag{9}$$

where $\psi_b = \psi_\beta - V_G$, $\psi_\beta$ is the inner Helmholtz layer potential [8,9] and $n_0$ is the concentration of bulk electrolyte. By solving the above equations, a complex analytical function can be found which relates $V_G$ to $\zeta$ [7]:

$$V_G = f(\zeta) \text{ and } \zeta = f^{-1}(V_G); \qquad V_d = 0 \tag{10}$$

Figs. 2 and 3 depict the zeta potential as a function of $V_G$ for different pH values and different concentrations of potassium chloride solution. For these figures, an

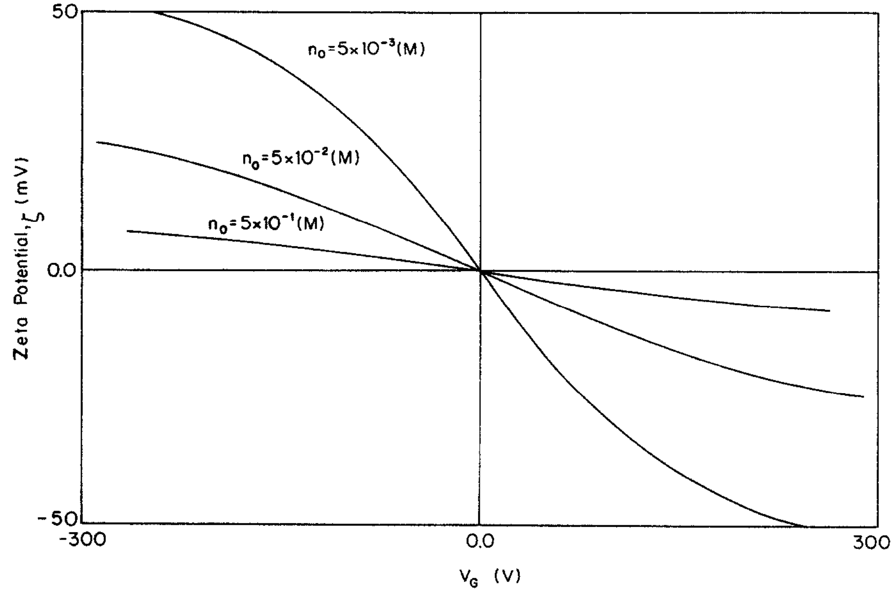

Fig. 2. Change in zeta potential as a function of $V_G$ for potassium chloride solutions of different concentrations, $n_0$, and a constant pH of 3.0. $C_0 = 35 \cdot 10^{-10}$ F/cm$^2$; $x_{ox}$ (insulator or capillary wall thickness) $= 1$ $\mu$m.

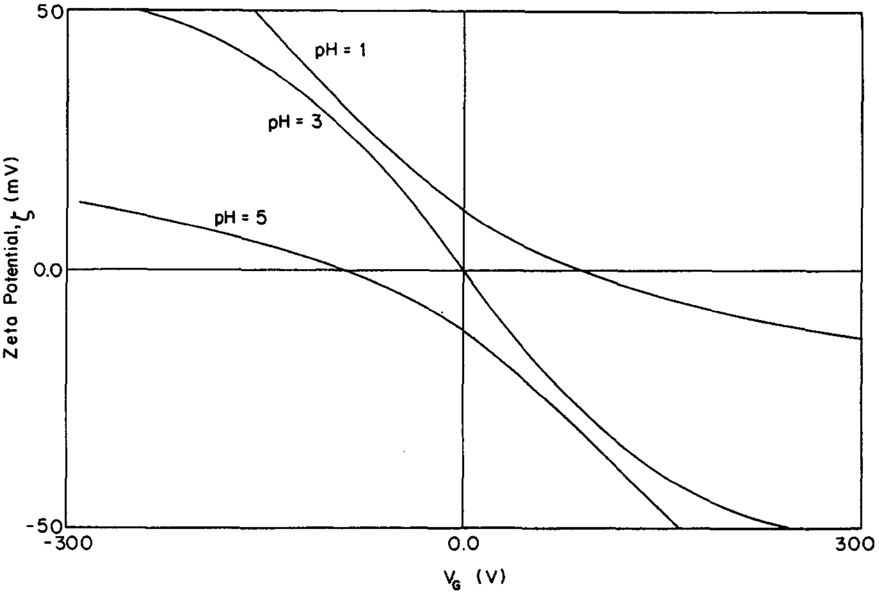

Fig. 3. Change in zeta potential as a function of $V_G$ for potassium chloride solutions of different pH values and a constant concentration of $5 \cdot 10^{-3}$ *M*. $C_0 = 35 \cdot 10^{-10}$ F/cm$^2$; $x_{ox} = 1$ μm.

insulator thickness of 1 μm was chosen. For silica as an insulator, the capacitance, $C_0$, per cm$^2$ and with a 1-μm thickness would be $35 \cdot 10^{-10}$ F/cm$^2$. The applied voltage, $V_G$, in Figs. 2 and 3 ranges from −500 to +500 V and these voltages can create a maximum electric field of $5 \cdot 10^6$ V/cm, which is below the dielectric strength of silica of $1 \cdot 10^7$ V/cm. In order to manipulate the voltage distribution in the double layer, one needs to apply an electric field within the same order of magnitude as the electric field in the double layer. That is why an insulator with high dielectric breakdown such as silica is required. For higher oxide thicknesses, $V_G$ must be increased in order to generate a high enough electric field for the manipulation of the zeta potential. A suitable electric field would be ±500 V/μm. For instance, for 10 and 100 μm the proper ranges of $V_G$ would be ±5 kV and 50 kV, respectively.

Physical modeling of the first field-effect electrokinetic transistor for electroosmosis has been proposed by us [7].

In a MIEEKFED, a second voltage $V_d$ is applied across the length of a capillary of length $L$, then the voltage perpendicular to the capillary wall is not constant or equal to $V_G$. The new voltage at any point across the capillary, at a distance $X$ from the cathode, is

$$V_G - \left(V_d \cdot \frac{X}{L}\right) \tag{11}$$

where $L$ is the length of the capillary. Now the zeta potential as a function of $X$ is

$$\zeta(x) = \mathrm{f}^{-1}\left[V_G - \left(V_d \cdot \frac{X}{L}\right)\right] \tag{12}$$

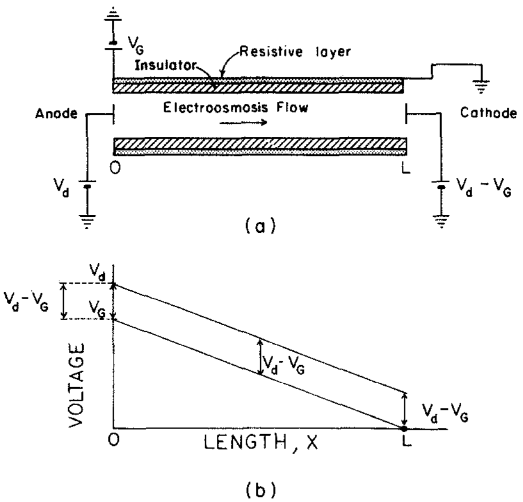

Fig. 4. (a) Schematic diagram of a MIEEKFED with constant zeta potential across the capillary. (b) Voltage perpendicular to the wall of the capillary *versus* length, $X$.

The design shown in Fig. 4a is proposed for constant zeta potential across the capillary. As illustrated in Fig. 4b, this circuit topology creates a constant voltage $(V_d - V_G)$ between the resistive layer and the electrolyte. The zeta potential across the capillary is

$$\zeta = f^{-1}(V_d - V_G) \tag{13}$$

Substituting eqn. 12 into eqn. 11 gives the field-effect electroosmosis velocity:

$$\zeta = f^{-1}(V_d - V_G) \tag{14}$$

and the electroosmosis mobility, $\mu_{EO}$, is proportional to the zeta potential:

$$\mu_{EO} = \left(\frac{\varepsilon}{4\pi\eta}\right)\zeta \tag{15}$$

## POTENTIAL APPLICATIONS

The major advantage of a MIEEKFED is its tuneability. If the rate of electroosmosis is adjusted to be equal and opposite to the electrophoretic mobility of a certain component of the analyte, that component will become essentially immobile within the capillary, *i.e.*, it is trapped. Maintaining this trapping position for a while causes the separation of that particular component. In the next step, the electroosmotic mobility could be increased such that the component is drifted toward the cathode and it is detected there. This application of MIEEKFED could be categorized as the use of a separation-based sensor.

Using MIEEKFED in a capillary electrophoresis apparatus results in a number of advantages. The zeta potential, and therefore the rate of electroosmosis, may be flexibly controlled without unwanted restrictions on pH, electrolyte concentration or the inner layer of the capillary. The MIEEKFED could also be used to reduce the degree of "tailing" commonly observed in the capillary electrophoresis of macromolecules. The tailing can be reduced by creating a low zeta potential and a low charged layer at the solid electrolyte interface.

The MIEEKFED has great potential for miniaturization, particularly in the light of recent advances in the technology of micromachining silicon [12]. Thus, in conclusion, although our work and predictions [7–9] have been based on theory and model computer simulations, Lee *et al.* [13] have recently demonstrated field-effect electroosmosis experimentally. These experimental data unequivocably support our first prediction of this effect.

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