

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Field-Effect Electro-osmosis – a New Dimension in Capillary Zone Electrophoresis

Kiumars Ghowsi, Hosein Ghowsi and M. Razazie

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/59114>

1. Introduction

Electrokinetic phenomena were discovered quite early in the 19th century. Investigations in the field have therefore been conducted for more than a century and a half. The discovery of electro-osmosis and electrophoresis by Reuss occurred soon after the first investigations on the electrolysis of water by Nicholson and Carlisle [1] and the electrolysis of salt solutions by Berzelius (1804) and Davy (1807). Reuss [2] carried out two experiments: the first demonstrated the effect known as electro-osmosis, and the second was the discovery of electrophoresis. Considering the simplest case of electro-osmosis in a single capillary, Helmholtz [3] obtained a formula for the linear velocity of electro-osmosis:

$$v_{eo} = -\frac{\varepsilon\xi}{4\pi\eta} E$$

where ξ is the interfacial electric potential difference, E is the electric field strength, and η is the viscosity of the liquid. Field-effect electro-osmosis is a novel interfacial phenomenon which is of particular interest. Field effect can be demonstrated by combining a metal-insulator electrolyte system (MIE) with capillary electro-osmosis. This technique uses a capillary at the outside surface, and electro-osmotic flow is controlled by applying a perpendicular electric field to the flow.

Potential applications of this effect could benefit from a flexible control of electro-osmotic flow, for example by capillary electrophoresis in separation science [4].

1.1. Theory

As a result of the elaboration of the theory, and in particular because of Saxen's experiments [5], entirely new premises appeared for experimental research. Not only did investigations of electrokinetic phenomena become possible at this stage, but studies of the double layer on the basis of these phenomena were also conducted.

The effect of the chemical nature of the surface and the ionic composition of electrolytes on the sign and magnitude of the potential (determined by the electrokinetic measurement) was determined experimentally in the early parts of this century, and furnished the grounds for solving the problem of the mechanism of the formation of the double layer of colloid particles.

Freundlich [6] called attention to a possible connection between the appearance of the double layer and an adsorption phenomenon.

It was considered that, if the adsorption coefficients of the ions were different, the strongly adsorbed ions would be present in excess on the surface, and the weakly adsorbed ions would be present in excess in the liquid part of the double layer, together giving rise to the double layer.

Another possible mechanism for the formation of the double layer is linked with the dissociation of surface ionogenic groups under the influence of a polar dispersion medium. This mechanism was first studied in regard to proteins. The ionogenic groups in proteins are of different chemical natures (acidic carboxyl, basic amino groups, etc.), and proteins are classified as amphoteric electrolytes.

In a first approximation, the amphoteric nature of monomer units of the protein molecule may be characterized by the following model:



At low pH, the protein carries a + charge. As pH is increased, the isoelectric point is first reached, and then there is a change in the sign of the charge on the protein.

Chemical groups on the insulator surface, at an interface between a liquid and an insulating solid, dissociate similarly to the above mechanism. Due to this surface ionization and specific adsorption, the interface is charged and ions of opposite polarity to the interfacial charge (counter-ions) are attracted to it, while ions of the same polarity are repelled.

2. Theoretical modelling of the Metal-Insulator Electrolyte (MIE) and postulation of a novel electrokinetic effect called field-effect electroosmosis

The zeta potential, which is the potential across the surface of the insulator and electrolyte, has been shown in the past to be manipulated by pH (surface ionization) and ionic concentration

(specific adsorption). A novel phenomenon is postulated by us in which the zeta potential in a capillary can be controlled by an external field. If a thin-wall capillary is coated with a metallic conductor on the external surface and a voltage V_G is applied between the metal electrode and the electrolyte (Fig.1), electro-osmotic flow can be controlled. By changing V_G , the voltage drop across the double layer changes, and this change includes the change in zeta potential, ξ , which in turn causes a modification in the electro-osmotic flow. We name this phenomenon “external field-effect electro-osmosis,” or simply “field-effect electro-osmosis”. Therefore, zeta potential, ξ (pH, C, V_G), is a function of three variables: pH, C (the ionic concentration in the electrolyte), and V_G . To understand this approach, there is a need to model the metal-insulator-electrolyte system in more detail. This is addressed in the following sections.

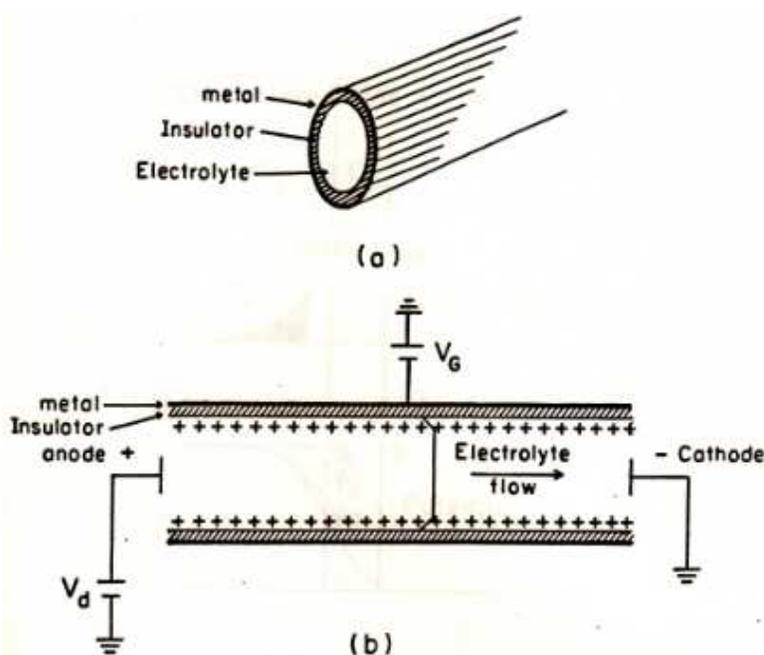


Figure 1. a) A Capillary covered with metallic coating; b) Cross-section of metal-insulator electrolyte, field-effect electro-osmosis

3. Ideal metal-insulator electrolyte structures

The ideal metal-insulator electrolyte (MIE) system is similar to what Siu et al. [7] have defined as the totally blocked interface of an insulator/electrolyte. In an ideal MIE, there is a complete absence of interfacial reactions between the electrolyte and oxide; in other words, there is neither specific adsorption nor surface ionization. Since the interfacial electrochemical processes are absent, the charge and potential distribution in this MIE system are dictated solely by electrostatic considerations. As shown in Fig. 2, the metal electrode is chosen to be ground and the applied voltage, V_G , is applied to the reference electrode. The reference electrode is chosen as nonpolarizable, where the voltage drop across it is negligible, so it can

be assumed that 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-Boltzmann equation [8]. From Gauss's law and the solution to this equation, we find that for an electrolyte the charge per unit area in the Gouy-Chapman space-charge region is given by:

$$\sigma_d = (8\varepsilon_e k T n_0)^{1/2} \sinh[q(V_G - \varphi_d) / 2kT] \quad (1)$$

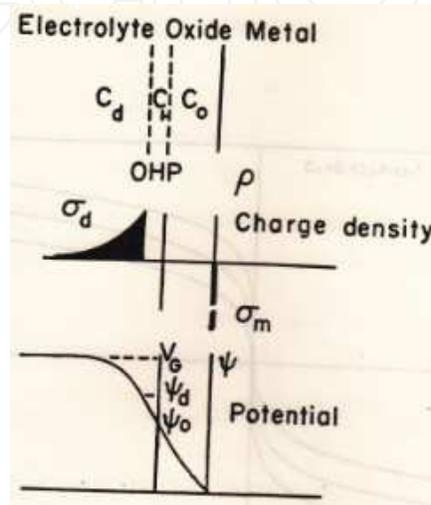


Figure 2. The charge and potential profile in a totally block metal-insulator electrolyte (MIE)

From Fig. 2, a charge neutrality equation can be written as follows:

$$\sigma_d + \sigma_m = 0 \quad (2)$$

Also, $C'_o = \frac{C_H C_o}{C_H + C_o}$ since $C_H \gg C_o$ and

$$C'_o \cong C_o \quad (3)$$

since $C_d \gg C_o$ then $\varphi_d - \varphi_o \ll \varphi_o$, or

$$\varphi_d \approx \varphi_o \quad (4)$$

and

$$\varphi_o C_o \approx -\sigma_m \quad (5)$$

$$-\sigma_m = \sigma_d \approx C_o \varphi_d \quad (6)$$

Thus, from eqs. (1) to (6) we find that:

$$C_o \varphi_d = -(8\varepsilon_e k T n_o)^{1/2} \sinh[q(\varphi_d - V_G) / 2kT] \quad (7)$$

Rearranging eq. (7), we obtain:

$$V_G = \frac{2kT}{q} \sinh^{-1} \left(\frac{\varphi_d C_o}{(8\varepsilon_e k T n_o)^{1/2}} \right) + \varphi_d \quad (8)$$

$$\xi \approx \frac{2kT}{q} \sinh^{-1} \left(\frac{\varphi_d C_o}{(8\varepsilon_e k T n_o)^{1/2}} \right) + \varphi_d \quad (9)$$

Since the difference between V_G and φ_d is very small (in the range of millivolts), whereas the difference between V_G and φ_d is several volts, by substituting φ_d into the parenthesis of eq. (9) V_G , the calculations are simplified. Thus, the following equation is found for the zeta potential:

$$\xi \approx \frac{2kT}{q} \sinh^{-1} \left(\frac{\varphi_d C_o}{(8\varepsilon_e k T n_o)^{1/2}} \right) \quad (10)$$

4. Contributions

It is interesting that much of the basic science involved in electrokinetic phenomena was discovered more than a century and a half ago¹. After the discovery of dissociation of water by electricity and the scientific curiosity that ensued, electrokinetic phenomena were discovered in parallel with electrolysis of water. If a V-shaped test tube is filled with soil and with electrolyte, and a direct current voltage is applied across the soil, electrolyte is pumped from one side to the other side. This electrokinetic phenomenon is called electro-osmosis. Electro-osmosis can occur at a capillary as well. The charge at the interface of the wall of the capillary is forced by the electric field applied across the capillary. We propose field-effect electro-osmosis, a novel phenomena where the zeta potential, ξ , is proportional to the charge at the interface of oxide and electrolyte, and V_G is the voltage perpendicular to the interface.

Fig. 3 shows two-dimensional zeta potential as a function of V_G at different concentrations of electrolytes. The basic science was electrokinetic.

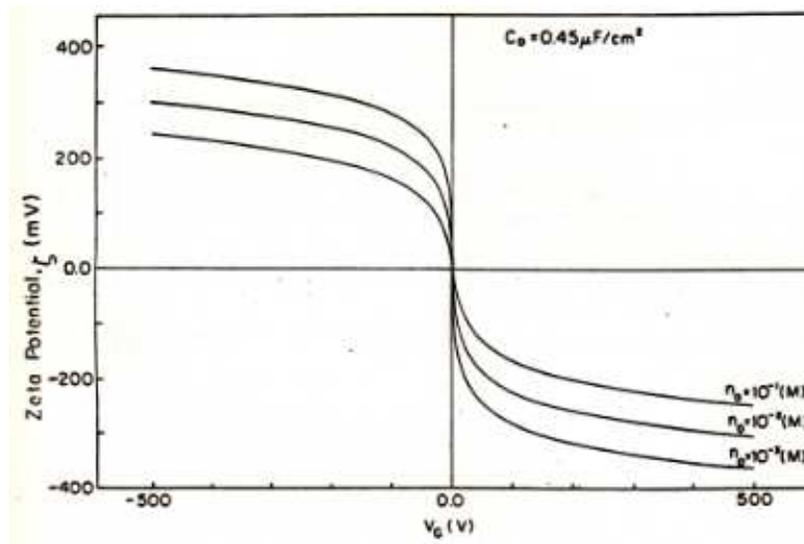


Figure 3. Change in zeta potential ξ as a function of V_G for various ionic concentrations for ideal case

Gradually during the past 30 years, CZE (capillary zone electrophoresis) [9] and micellar electrokinetic capillary chromatography (MECC) [10] have become applied sciences in their own right, through several publications [11]. Fig. 4 shows field-effect electro-osmosis at work in separation. The electro-osmosis in Fig.4 uses $V_d - V_G$ to make the voltage at the interface uniform. With field-effect electro-osmosis one can make the zeta potential zero or positive or negative.

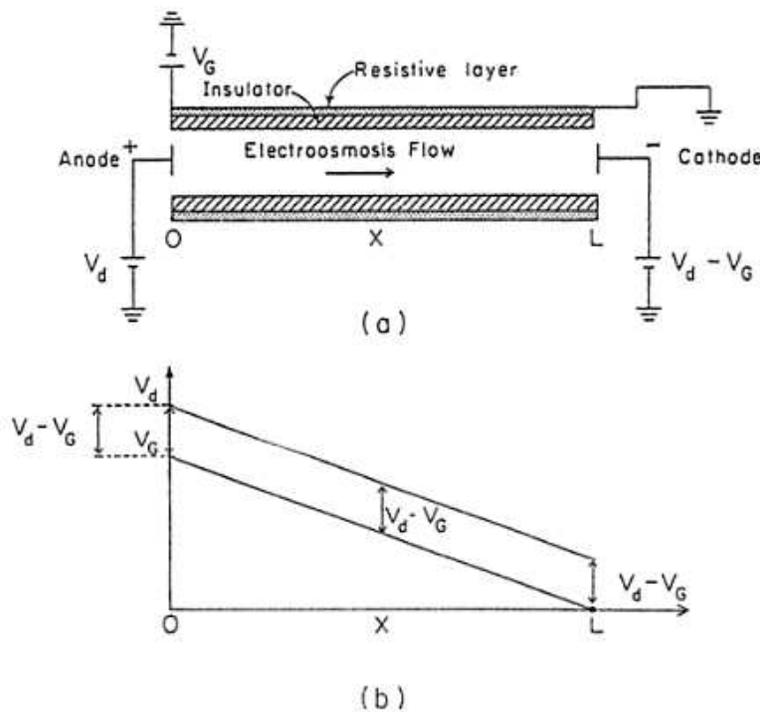


Figure 4. a) The schematic of field-effect electro-osmosis with the constant zeta potential across the capillary; b) The voltage perpendicular to the wall of the capillary versus X

This can achieve the separation of protein with less tailing or shift the movement of electro-osmosis to the left or right [12] (Fig. 5).

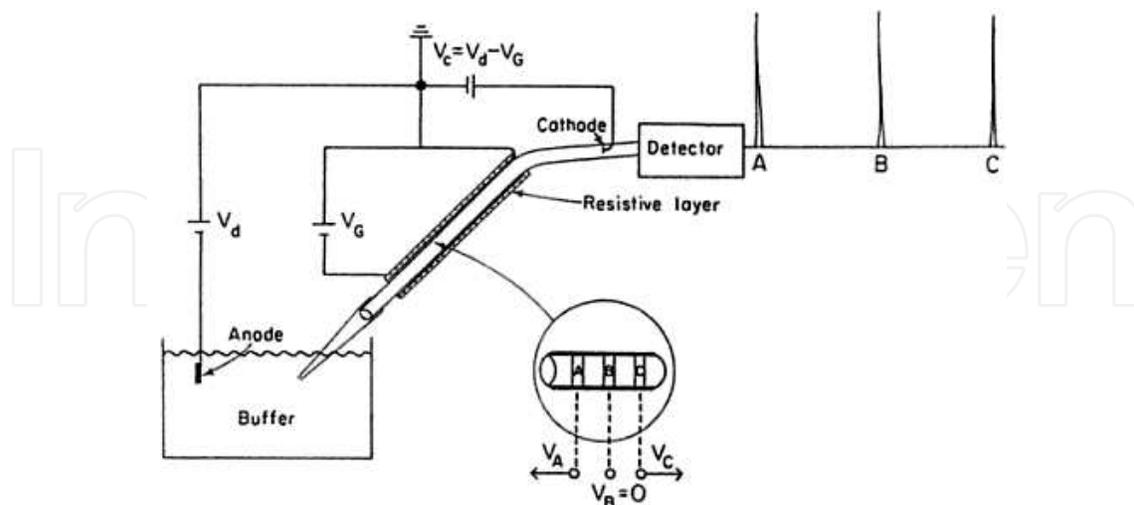


Figure 5. Field-effect electro-osmosis used in separation (source: Biosensor)

List of symbols

C_1 Inner Helmholtz layer capacitance

C_2 Outer Helmholtz layer capacitance

C_a Capacitance due to variation of surface charge σ_0 on the insulator with surface potential φ_0

C' Total capacitance of C_H and C_o in series for ideal case

C_o Oxide capacitance

C_d Diffusion layer capacitance

C_T Total capacitance for MIE

C_H Helmholtz capacitance for MIE

E Electric field

E_{bd} Break-down electric field

K Boltzmann constant

n_0 Concentration of electrolyte

Q Electron charge

T Temperature

V_{eo} Electro-osmotic velocity

V_G Voltage between metal and electrolyte

V_d Voltage between cathode and anode

V_{ss} Saturated surface potential

V_{pzz} Voltage V_G at which zeta potential is zero

V_{zs} Zero surface-charge potential

X_{ox} Oxide thickness

Z_{ie} Total impedance of double layer in parallel with Ca and the Warburg impedance Z_w

Greek alphabet

ϵ_e Dielectric constant of electrolyte

ϵ_0 Absolute dielectric constant of vacuum

ϵ_r Relative dielectric constant

ξ Zeta potential

η Viscosity of the liquid

ρ Charge density

σ_m Charge at the metal-insulator interface

σ_o Surface charge at the insulator electrolyte due to specific adsorption

σ_B Charge at inner Helmholtz layer

σ_d Charge in the diffuse layer

φ_o Potential at the insulator-electrolyte interface

φ_B Potential at the inner Helmholtz layer

φ_d Potential at the outer Helmholtz layer

6. Conclusion

A novel effect has been postulated by the name of field-effect electro-osmosis. The effect can change the electro-osmosis flow from left to right or from right to left, or it can make electro-osmosis zero.

Electro-osmosis is an electrokinetic phenomenon.

Author details

Kiumars Ghowsi^{1*}, Hosein Ghowsi² and M. Razazie³

*Address all correspondence to: k_ghowsi@yahoo.com

1 Department of Chemistry, Majlesi Branch, Islamic Azad University, Isfahan, Iran

2 Department of Mathematics, Payame Noor University, Tehran, Iran

3 Department of Material, Majlesi Branch, Islamic Azad University, Isfahan, Iran

References

- [1] Nicholson and Carlisle, I. Nat. Philos., 4, 179 (1800); cited by H.A. Abramson, Electrokinetic Phenomena and Their Application to Biology and Medicine, Chemical Catalog Company, New York 1934.
- [2] F.F. Reuss, Memoires de la Society Imperiale des Naturalites de Moscou, 2, 327 (1809).
- [3] H. Helmholtz, Wied. Ann., 97, 337 (1879).
- [4] K. Ghowsi, R.J. Gale, J. Chromatogr., 559, 95 (1991).
- [5] V. Saxen, Wied. Ann., 47, 46 (1892).
- [6] H. Freundlich, Kapillrchemie, Akademische Verlags Gesellschaft, Leipzig (1909).
- [7] W.J. Siu, R.S.C. Cobbold, IEEE Trans. Electron Devices. Vol. Ed. -26, 1805-1851 (1979).
- [8] J.O.M. Bockris and A.K.N. Keddy, Modern Electrochemistry, Vols. 1 and 2, New York, Plenum Press (1970).
- [9] J. Jorgenson and K.D. Lukacs, Anal. Chem., 53, 1298 (1981).
- [10] S. Terabe and T. Ando, Anal. Chem., 57, 834 (1985).
- [11] K. Ghowsi Electrophoresis, Intech 1012 Chapter [online] Available at: www.intechopen.com
- [12] K. Ghowsi, R.J. Gale, Biosensor Technology, Buck et al. (eds.) (1990).

