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Factors Affecting Direct Control of Electroosmosis Using an External Electric Field in Capillary Electrophoresis

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The change in the direction and flow rate of electroosmosis in capillary electrophoresis with the application of an external electric field has been demonstrated and measured by the current-monitoring method. Factors such as solution condition and capillary dimension affecting the direct control of electroosmosis have been measured and analyzed in detail with the proposed capacitor model. The capacitor model predicted reasonably well the trends of experimental results at various solution pHs, electrolyte concentrations, and capillary dimensions.

INTRODUCTION

We have recently proposed and demonstrated the direct control of electroosmotic flow in capillary electrophoresis by using an additional electric field applied from outside the capillary (1). This technique vectorially couples the externally applied potential with the potential across the buffer solution inside the capillary. This electric potential gradient across the capillary wall controls the polarity and magnitude of the ζ potential on the interior surface of the capillary wall. The direction and flow rate of electroosmosis are dependent upon the polarity and magnitude of the ζ potential (2). The electroosmosis in capillary electrophoresis at the solution condition of 1 mM phosphate buffer at pH 5 was directly controlled by simply varying the external electric potential (1).

To investigate the fundamentals of the use of an external electric potential for controlling the electroosmotic flow, a capacitor model as shown in Figure 1 is proposed in this study. Under normal aqueous conditions with small binary electrolytes, the silica surface has an excess of anionic charge resulting from ionization of surface functional groups. The cationic counterions to these anions are in the diffuse layer adjacent

to the capillary walls. The potential across the diffuse layer is termed the ζ-potential (2). The capacitance of the electrostatic diffuse layer at the inner capillary/inner aqueous interface, C_{ei} in faradays (F) at 25 °C is given by

$$C_{ei} = (7.23 \times 10^{-3} \text{ F cm}^{-0.5} \text{ mol}^{-0.5})C^{1/2} \cosh\left[(19.46 \text{ V}^{-1})\zeta\right]\pi D_{i.d.} l \quad (1)$$

where C is the concentration of ions in the solution in mol/cm³, ζ is the ζ potential at the capillary interface in volts, $D_{i.d.}$ is the inner diameter of inner capillary tubing in centimeters, and l is the length of capillary tubing in centimeters (2). The capacitance of the inner capillary tubing, C_c is given by

$$C_c = \epsilon_c 2\pi l / [\ln (D_{o.d.}/D_{i.d.})] \quad (2)$$

where ϵ_c is the electrical permittivity of silica surface and $D_{o.d.}$ is the outer diameter of the inner capillary tubing (3). The capacitance of the electrostatic diffuse layer at the inner capillary/outer aqueous interface (in the annular space between the outer and inner capillaries), C_{eo} in faradays at 25 °C is given by

$$C_{eo} = (7.23 \times 10^{-3} \text{ F cm}^{-0.5} \text{ mol}^{-0.5})C^{1/2} \cosh\left[(19.46 \text{ V}^{-1})\zeta\right]\pi D_{o.d.} l \quad (3)$$

where $D_{o.d.}$ is the outer diameter of inner capillary tubing in centimeters (2). The total capacitance of three capacitors in series, C_T, is given as (3)

$$(C_T)^{-1} = (C_{eo})^{-1} + (C_c)^{-1} + (C_{ei})^{-1} \quad (4)$$

The capacitance of the capillary tubing and the electrostatic diffuse layer studied in this project are in the range of 10^{-11} F and 10^{-5}–10^{-6} F, respectively. Thus, the reciprocal of the capacitance of the capillary tubing is much greater than the reciprocal of the capacitance of the electrostatic diffuse layer. The reciprocal of the total capacitance, $(C_T)^{-1}$, and the total capacitance, C_T, can then be simplified as

$$(C_T)^{-1} = (C_c)^{-1} \quad (5a)$$

$$C_T = C_c \quad (5b)$$

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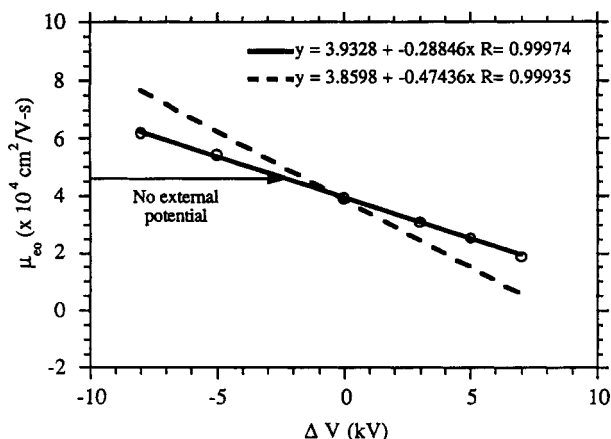[1] Hewlett-Packard Laboratories, 1501 Page Mill Rd, Palo Alto, CA 94304.

Figure 1. Proposed capacitor model for predicting the change in ζ potential due to the application of an external electric field.

The change in the ζ potential at the inner capillary/inner aqueous interface, $\Delta\zeta$, due to the applied potential gradient across the inner capillary wall, ΔV, is then given by

$$\Delta\zeta = \Delta V/[(C_{ei})/(C_T)] = \Delta V/[(C_{ei})/(C_c)] \qquad (6)$$

As shown in eq 6, the effectiveness of the applied potential gradient for controlling the ζ potential is dependent upon the ratio of the capacitance of the electrostatic diffuse layer at the inner capillary/inner aqueous interface to the capacitance of the inner capillary tubing. The capacitance of the electrostatic diffusion layer is controlled by the electrolyte concentration and the ζ potential as shown in eq 1. The ζ potential itself is a function of the electrolyte concentration and the solution pH (2). The capacitance of the electrostatic diffusion layer is therefore affected by both the electrolyte concentration and the solution pH. The solution conditions such as pH and electrolyte concentration are important factors for affecting the direct control of electroosmosis in capillary electrophoresis by using an external electric field.

In the current practice of capillary electrophoresis, it is also desirable to demonstrate the practicality and effectiveness of the external electric field for controlling the ζ potential and the electroosmotic flow at the high electrolyte concentration. If the sample concentration is high, the electrical conductivity of the sample can locally perturb the potential field gradient within the capillary. This can produce a severely distorted peak and degrade the separation efficiency in capillary electrophoresis (4). In practice, peak distortion due to such field perturbations can be controlled by ensuring that the conductivity of the sample does not exceed about 0.5% of the conductivity of the supporting electrolyte. Thus, the most common electrolyte concentration for capillary electrophoresis is between 10–50 mM, which is within the concentration range of this study.

As shown in eq 1, the capacitance of the electrostatic diffusion layer decreases with the decrease in the inner diameter of capillary tubing. The effectiveness of the application of an external electric potential for controlling the ζ potential can therefore be enhanced by using the capillary tubing with the smaller inner diameter (see eq 6). For capillary tubing with a fixed inner diameter, the capacitance of the capillary tubing increases with the decrease in the outer diameter (see eq 2). As shown in eqs 5 and 6, the total capacitance and the effectiveness of the applied potential gradient for controlling the ζ potential can therefore increase with the use of thinner capillary tubing. Thus, the inner and outer diameters of the capillary tubing are other important factors affecting the direct control of electroosmosis in capillary electrophoresis with the use of an external electric field.

Figure 2. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 1 mM/2 mM phosphate buffer solution (pH 5) with the use of 75 μm i.d. and 375 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

EXPERIMENTAL SECTION

The experimental setup and the experimental procedures using the current-monitoring method (5) for measuring the change in the direction and flow rate of electroosmotic flow have been described in detail in the previous study (1). The high-voltage power supply (Spellman High-Voltage Electronics, Plainview, NY) is capable of delivering up to ±30 kV. Uncoated fused-silica capillary tubings with dimensions of 25 μm i.d./150 μm o.d., 50 μm i.d./150 μm o.d., 50 μm i.d./192 μm o.d., and 75 μm i.d./375 μm o.d. were obtained from Polymicro Technologies, Inc., Phoenix, AZ. The sodium phosphate buffer and KCl were purchased from Sigma (St. Louis, MO).

RESULTS AND DISCUSSION

The experimental results as presented in the previous study (1) for the control of electroosmosis inside a 75 μm i.d. and 375 μm o.d. capillary tubing at 1 mM/2 mM phosphate buffer of pH 5 were used to compare with the predictions obtained from the proposed capacitor model. The ζ potential in the presence of a 0 potential gradient, –18 mV, was used to calculate the capacitance of the electrostatic diffuse layer in eq 1. Due to the nature of the current-monitoring method employed in the experiment for measuring the change in the electroosmotic flow, the phosphate buffer concentration inside the inner capillary was varied between 1 and 2 mM during the experiment. Thus, 1.5 mM was used as the electrolyte concentration for the calculation of the capacitance of the electrostatic diffuse layer in eq 1. The change in the ζ potential due to the applied electric potential gradient, $\Delta\zeta$, was calculated by using eq 6. A 20 cm long capillary tubing with 75 μm i.d. and 375 μm o.d. was used as the inner capillary and placed inside a 17 cm long capillary with 530 μm i.d. and 660 μm o.d. The external electric field was applied to the 17 cm long annular space between the two capillaries filled with the buffer solution. Thus, only 17 cm of the 20 cm long inner capillary tubing was affected by the external electric field for controlling the electroosmotic flow inside the inner capillary. The change in the ζ potential based on the proposed capacitor theory, $\Delta\zeta$, was therefore multiplied by a factor of 17 cm/20 cm = 0.85. The controlled ζ potential, ζ_{theory}, was then obtained by adding –18 mV to $0.85\Delta\zeta$.

The controlled electroosmotic mobility, $\mu_{eo(theory)}$, is given as

$$\mu_{eo(theory)} = (\epsilon/\eta)\zeta_{theory} \qquad (7)$$

where ϵ is the permittivity of the solution, η is the viscosity, and ζ_{theory} is the controlled ζ potential (2). As shown in Figure
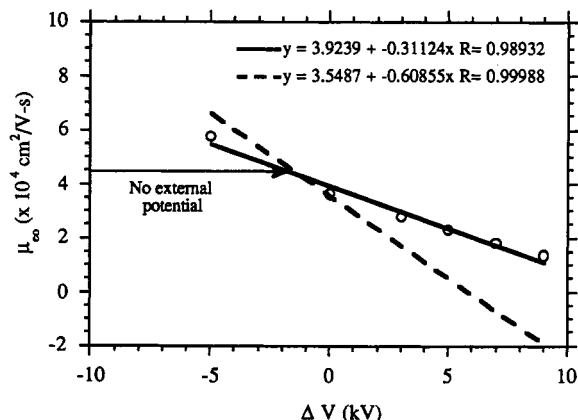
Figure 3. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 1 mM/2 mM phosphate buffer solution (pH 6) with the use of 50 μm I.d. and 192 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

Figure 4. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 1 mM/2 mM phosphate buffer solution (pH 6) with the use of 50 μm I.d. and 150 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

2, the capacitor model predicted reasonably well the observed change in the electroosmotic mobility with the application of various potential gradients across the capillary. The experimental error in measuring the change in the electroosmotic flow was about 5–10% for various potential gradients for over six runs (1).

The pH in the 1 mM/2 mM phosphate buffer solution was increased from 5 to 6. The negative value of the ζ potential in the presence of a 0 potential gradient measured in the experiment was then increased from 18 to 50 mV accordingly (2). On the basis of eq 1, the capacitance of the electrostatic diffuse layer increased with the increase in the ζ potential. However, the use of an inner capillary tubing with smaller inner diameter, 50 μm i.d. (192 μm o.d.) in comparison with 75 μm i.d. (375 μm o.d.), would decrease the capacitance of the electrostatic diffuse layer. The effect of the smaller inner diameter was greater than the effect of the stronger surface potential on the capacitance of the electrostatic diffuse layer. Thus, the capacitance of the electrostatic diffuse layer was smaller at pH 6 with the use of a 50 μm i.d./192 μm o.d. capillary tubing than at pH 5 with the use of a 75 μm i.d./375 μm o.d. capillary tubing in the same phosphate buffer concentration. In addition, the ratio of the outer diameter to the inner diameter in eq 2 for calculating the capacitance of the silica tubing was smaller with the use of a 50 μm i.d./192 μm o.d. capillary tubing than with the use of a 75 μm i.d./375 μm o.d. capillary tubing. Thus, the capacitance of the silica tubing increased with the use of a 50 μm i.d./192 μm o.d. capillary tubing. The larger capacitance of the silica tubing in combination with the smaller capacitance of the electrostatic diffuse layer would therefore result in better direct control of the ζ potential (see eq 6) with the solution condition of 1 mM/2 mM phosphate buffer at pH 6 and with the use of a 50 μm i.d. and 192 μm o.d. capillary tubing. As shown in Figure 3, the slope of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV, measured from the experiment in the absolute value was 0.29, greater than 0.28 in Figure 2. The capacitor model seemed to be able to predict the trend of experimental results at different solution conditions and capillary dimensions. However, the direct control of the electroosmotic flow observed in the experiment was not as efficient as predicted in the capacitor model. The slope in the absolute value obtained from the capacitor model was 0.47, much greater than 0.29 observed in the experiment. The experimental error in measuring the change in the electroosmotic flow was about 5–15% for various potential gradients for over five runs.

For a capillary tubing with a fixed inner diameter (50 μm i.d.), the capacitance of the silica tubing increased with the decrease in the outer diameter (see eq 2). The total capacitance and the effectiveness of the applied potential gradient for controlling the ζ potential would therefore all increase with the use of a 50 μm i.d. and 150 μm o.d. capillary tubing in the same solution condition. As shown in Figure 4, the slope of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV, measured from the experiment in the absolute value was 0.31, greater than 0.29 in Figure 3. The capacitor model again predicted the trend of experimental results at different capillary dimensions but overestimated the effectiveness of the applied potential gradient for controlling the ζ potential. The slope in the absolute value obtained from the capacitor model was 0.61, much greater than the 0.31 as observed in the experiment. The experimental error in measuring the change in the electroosmotic flow was about 5–15% for various potential gradients for over five runs.

As shown in eq 2, the capacitance of the silica tubing increased with the decrease in the ratio of the outer diameter to the inner diameter of the capillary tubing. The capacitance of a 25 μm i.d. and 150 μm o.d. capillary tubing was therefore smaller than the capacitance of a 50 μm i.d. and 150 μm o.d. capillary tubing in the same 1 mM/2 mM phosphate buffer solution at pH 6. However, the capacitance of the electrostatic diffuse layer as shown in eq 1 decreased with a greater degree by using the smaller inner diameter capillary tubing. The use of a 25 μm i.d./150 μm o.d. capillary tubing would therefore result in better direct control of the ζ potential with the application of external electric field. As shown in Figure 5, the slope of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV, measured from the experiment in the absolute value was 0.44, greater than 0.31 in Figure 4. However, the slope in the absolute value obtained from the capacitor model was 0.73, greater than the 0.44 as observed in the experiment. The experimental error in measuring the change in the electroosmotic flow was about 0–10% for various potential gradients for over five runs.

The electrolyte concentration in the 25 μm i.d. and 150 μm o.d. capillary tubing was increased from 1 mM/2 mM phosphate buffer at pH 6 to 10 mM/20 mM KCl at pH 7, and then to 45 mM/55 mM KCl at pH 7. As shown in eq 1, the capacitance of the electrostatic diffuse layer increased with the increase in the electrolyte concentration. This clearly explained why the slope of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV, measured from the experiment in the absolute value was 0.44 in Figure 5,
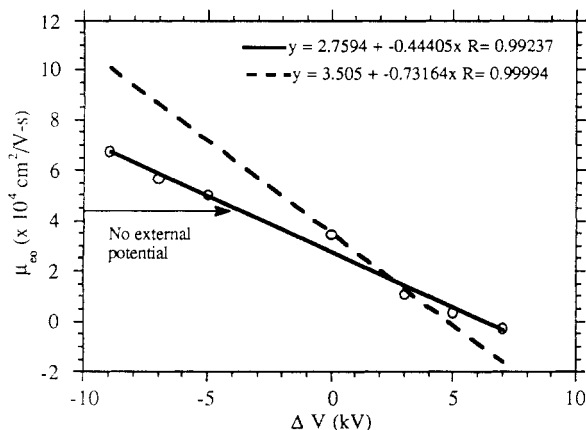
Figure 5. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 1 mM/2 mM phosphate buffer solution (pH 6) with the use of 25 μm i.d. and 150 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.
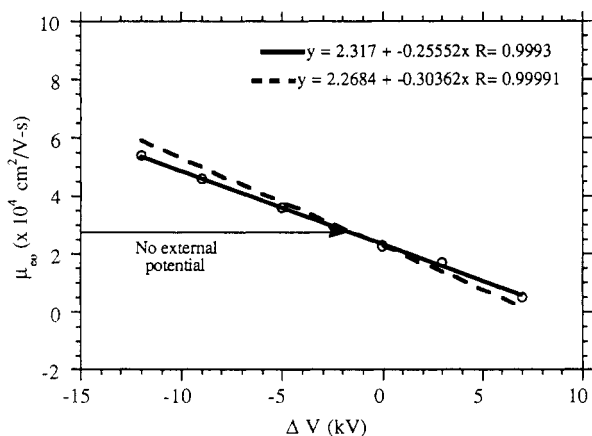

Figure 7. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 45 mM/55 mM KCl solution (pH 7) with the use of 25 μm i.d. and 150 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

Figure 6. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 10 mM/20 mM KCl solution (pH 7) with the use of 25 μm i.d. and 150 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

Figure 8. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 45 mM/55 mM KCl solution (pH 7) with the use of 50 μm i.d. and 192 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

greater than 0.26 in Figure 6 and 0.10 in Figure 7. The capacitor model not only predicted the trend of experimental results at different electrolyte concentrations but also estimated reasonably well the effectiveness of the applied potential gradient for controlling the ζ potential in 10 mM/20 mM KCl at pH 7 (see Figure 6). The experimental error in measuring the change in the electroosmotic flow was about 5–15% for various potential gradients for over five runs at every solution condition.

As shown in eq 2, the capacitance of the silica tubing was larger with the use of a 50 μm i.d. and 192 μm o.d. capillary tubing than with the use of a 25 μm i.d. and 150 μm o.d. capillary tubing. However, the capacitance of the electrostatic diffusion layer as shown in eq 1 increased with a greater degree by using the larger inner diameter capillary tubing. The effectiveness of the applied potential gradient for controlling the ζ potential with the use of a 50 μm/192 μm capillary tubing would therefore be weaker than with the use of a 25 μm/150 μm capillary tubing in the same 45 mM/55 mM KCl solution at pH 7. As shown in Figure 8, the slope of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV, measured from the experiment in the absolute value was 0.041, smaller than 0.10 in Figure 7. The experimental error in measuring the change in the electroosmotic flow was about
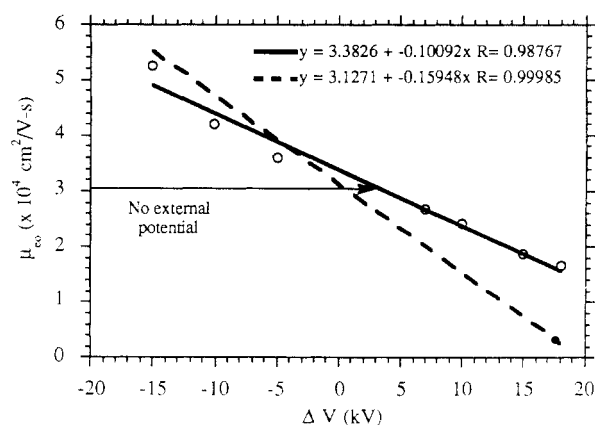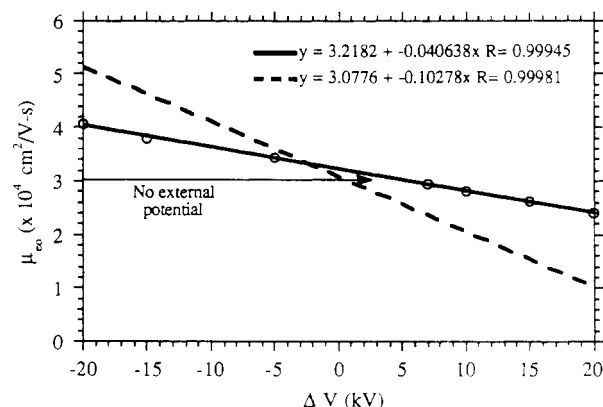
0–5% for various potential gradients for over five runs.

The ζ potential at the silica/aqueous interface decreased with the decrease in the solution pH (2). This explained why the negative value of the ζ potential in the absence of an external electric field decreased from 40 mV in 45 mM/55 mM KCl at pH 7 to 33 mV in the 45 mM/55 mM phosphate buffer at pH 6, and to 17 mV in the 45 mM/55 mM phosphate buffer at pH 5. As shown in eq 1, the capacitance of the electrostatic diffuse layer decreased with the decrease in the ζ potential. This clearly explained why the slope of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV, measured from the experiment in the absolute value was 0.067 in the 45 mM/55 mM phosphate buffer at pH 5 (see Figure 9), greater than 0.045 in the 45 mM/55 mM phosphate buffer at pH 6 (see Figure 10) and 0.041 in 45 mM/55 mM KCl at pH 7 (see Figure 8). The experimental error in measuring the change in the electroosmotic flow was about 0–10% for various potential gradients for over five runs at every solution condition.

In conclusion, we have proposed and demonstrated the direct control of the ζ potential and the electroosmotic flow with an applied external potential gradient by using the current-monitoring method. We have also analyzed the effectiveness of the direct control of the electroosmotic flow at various operating conditions including different solution pHs, electrolyte concentrations, and capillary dimensions. The

Table I. Effect of External Electric Field on Electroosmosis

dimension of capillary tubing (i.d./o.d.), μm	electrolyte concn, mM	solution pH	slope of μ_{eo} vs ΔV,[a] $\times 10^7$cm^2/(V s)	slope of μ_{eo} vs ΔV,[b] $\times 10^7$cm^2/(V s)	% of the diff[c]
75/375	1/2	5	−0.37	−0.28	24
50/192	1/2	6	−0.47	−0.29	38
50/150	1/2	6	−0.61	−0.31	49
25/150	1/2	6	−0.73	−0.44	40
25/150	10/20	7	−0.30	−0.26	13
25/150	45/55	7	−0.16	−0.10	38
50/192	45/55	7	−0.10	−0.041	59
50/192	45/55	6	−0.11	−0.045	59
50/192	45/55	5	−0.13	−0.067	48

[a] The slope was obtained from the proposed capacitor theory. [b] The slope was obtained from the experimental results. [c] The % of the difference = (the slope predicted by the capacitor theory − the slope obtained from the experimental results)/(the slope predicted by the capacitor theory).
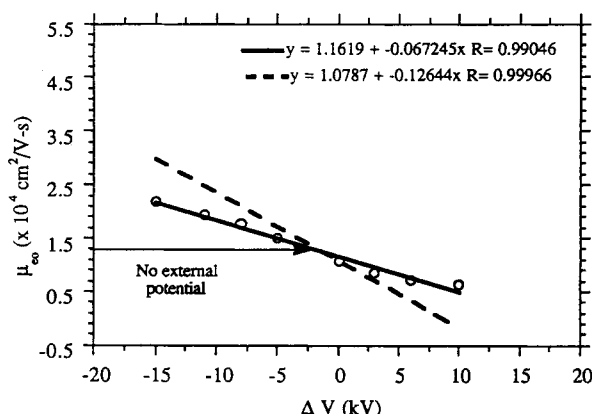
Figure 9. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 45 mM/55 mM phosphate buffer solution (pH 5) with the use of 50 μm i.d. and 192 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

Figure 10. Plot of the electroosmotic mobility, μ_{eo}, against the applied potential gradient, ΔV. The experimental data at 45 mM/55 mM phosphate buffer solution (pH 6) with the use of 50 μm i.d. and 192 μm o.d. tubing as the inner capillary tubing in the current monitoring method were shown as O and the solid line. The predictions obtained from the capacitor theory were shown as the dashed line.

proposed capacitor theory in comparison with the experimental results was summarized in Table I. The capacitor theory predicted well the trend of experimental results at various solution conditions and capillary dimensions. In the two out of the total nine experimental conditions, the quantitative predictions obtained from the capacitor theory were in a relatively good agreement with the experimental data. In the rest of experimental conditions, the differences between the capacitor theory and experimental results as defined in Table I ranged between 38% and 59%. The i.d. and o.d. tolerances for the various capillary tubings examined in this study were 3 and 6 μm, respectively (Polymicro Technologies, Inc.; Phoenix, AZ). The effect of errors in the i.d. and o.d. of the capillary on the predictions obtained from the capacitor theory could only contribute to 5–15% of the difference between the capacitor theory and the experimental results. The efforts for improving the capacitor theory as a quantitative model for predicting the effectiveness of the applied external electric field for controlling the electroosmotic flow is currently under study. One thought is to add the capacitance of the Stern layer (2) to the capacitor theory. The Stern layer is the first layer of ions that are constrained to lie next to the capillary surface with a thickness defined by the spherical size of the ions. However, the addition of the Stern layer with the
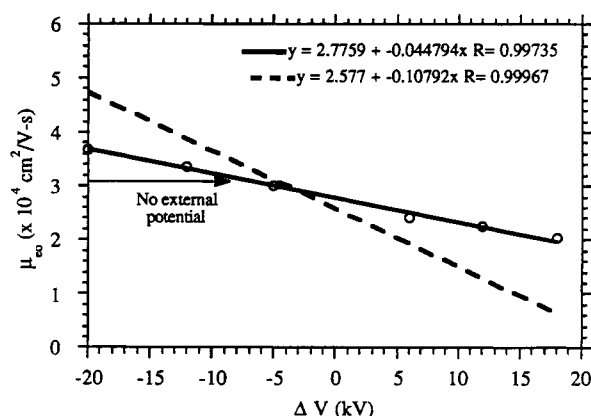
capacitor theory will decrease the capacitance of the electrostatic layer at the capillary/aqueous interface (2). This addition of the Stern layer will then increase the effectiveness of the applied potential gradient for controlling the ζ potential (see eq 6) and further enlarge the differences between the predictions based on the capacitor theory and the experimental results.

ACKNOWLEDGMENT

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