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Leakage current consideration of capillary electrophoresis under electroosmotic control

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ABSTRACT

The leakage current phenomenon at the capillary–solution interface was investigated with the application of *high* radial electric potential gradients across the capillary wall for the direct control of electroosmosis. The leakage current traveling through the capillary wall gave rise to a different surface potential between the controlled and uncontrolled regions, and resulted in a linear electroosmotic velocity profile from the controlled region to the ends of the capillary. The mismatch between the electroosmotic velocities was then balanced by the additional laminar flow over the entire length of the capillary. The additional dispersion induced by the laminar flow under the leakage current situation was demonstrated and compared with theoretical prediction.

INTRODUCTION

The concept of electroosmotic control in capillary electrophoresis under the influence of applied radial electric potential gradient has been intensively investigated in several laboratories [1–8]. In all the experimental devices, a radial electric potential gradient is applied over the major portion, but not the entire length of the capillary. This is to ensure the separation and isolation of applied radial electric potential gradient from the axial electric field in the capillary for electrophoresis. The potential mismatch between electroosmotic velocities in the controlled (under the influence of a radial electric potential gradient) and uncontrolled regions, and the resultant dispersion and band broadening are the subjects in our recent study [6].

It is found that there is no measurable additional dispersion and band broadening induced by the direct control of electroosmosis [6]. A d.c. short circuit phenomenon at the capillary–solution interface is proposed for averaging the surface potential over the entire length of the capillary. Thus, there is no difference in the ζ potential and the resultant electroosmosis between the controlled and uncontrolled regions. One major assumption for the "short circuiting effect", however, is that the leakage current through the capillary wall in the controlled region must be negligible. The extra current traveling through the capillary wall would give rise to a different surface potential between the controlled and uncontrolled regions. It is anticipated that the measured dispersion will increase due to this leakage current with the application of a high enough radial electric potential gradient across the capillary wall [6].

In this report, the leakage current in capillary electrophoresis with the application of a high enough radial electric potential gradient is investigated. The magnitude of applied radial electric potential gradient required for causing the leakage current and the irreversible dielectric breakdown of capillary tubing are measured. The flow profiles of bulk fluid in the capillary and the additional dispersion of solute induced

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by the leakage current phenomenon at the capillary–solution interface are presented and discussed both experimentally and theoretically.

EXPERIMENTAL

The experimental setup for measuring the leakage current across the capillary wall under the influence of applied radial electric potential gradient is shown in Fig. 1. A 25 cm long capillary (Polymicro Technologies, Phoenix, AZ, USA) with 50 μm I.D. and 150 μm O.D. was placed between two buffer reservoirs. About 85% of the external surface of capillary tubing was coated with the nickel print (GC Electronics, Rockford, IL, USA) and then connected to the ground. Platinum-wire electrodes were affixed to both reservoirs. One high-voltage power supply (Spellman High-Voltage Electronics, Plainview, NY, USA) was connected to the two reservoirs so that *a constant electric potential* was applied across the buffer solution in the capillary. Thus, a constant radial electric potential gradient across the capillary wall with respect to the external grounding (connected through the nickel print) was generated. A 10-MΩ resistor was inserted between the nickel print conductive layer and the external grounding.. This means that a 1-nA leakage current is monitored as a 10-mV potential drop across the resistor.

The experimental setup of capillary electrophoresis in a coaxial configuration for the direct control of electroosmosis has been described in details in the previous study [3]. A smaller (inner) capillary was placed inside a larger (outer) capillary. A radial electric potential gradient was employed along the annular space between the two capillaries for controlling the ζ potential and then the electroosmosis in the inner capillary.

Frontal analyses of a 0.1% dimethyl sulfoxide in phosphate buffer solution were studied with various percentages of the inner capillary under the direct control of electroosmosis. The values of total spatial variance and the changes in the bulk velocity were measured with the application of various radial electric potential gradients. The measured solute dispersion in terms of equivalent plate height was then compared with the theoretical analyses for investigating any additional dispersion induced by the leakage current phenomenon. Sodium phosphate buffer, hydrochloric acid, and dimethyl sulfoxide were purchased from Sigma (St. Louis, MO, USA). The pH of the buffer solution was adjusted with 0.1 *M* hydrochloric acid.

RESULTS AND DISCUSSION

The leakage current across the capillary wall was only measurable when the applied radial electric potential gradient was at or greater than −10 kV. In the experimental setup, an electric potential equal to or greater than +10 kV was employed at both buffer reservoirs containing 10

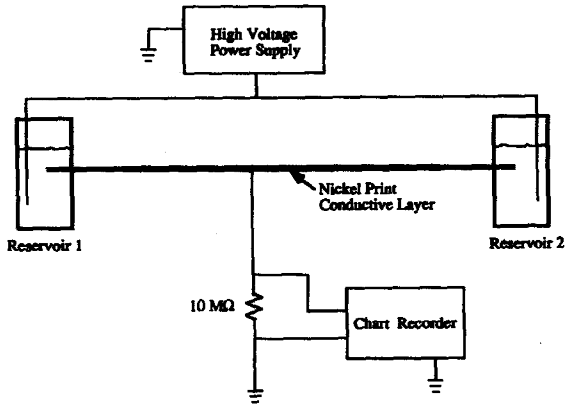

Fig. 1. Test setup for measuring the leakage current across the capillary wall.

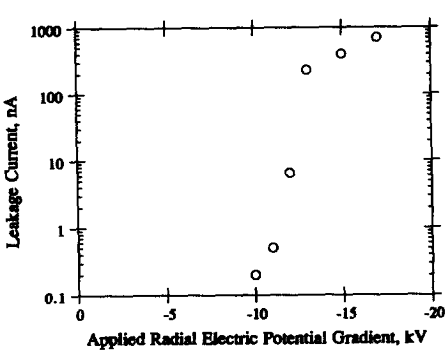

Fig. 2. Plot of leakage current *vs.* applied radial electric potential gradient across a fused-silica capillary with 50 μm I.D. and 150 μm O.D.

mM phosphate at pH 3. As shown in Fig. 2, a significant increase in the leakage current was observed with the application of a −13-kV or higher potential gradient. There was no hysteresis effect in the leakage current measurement. The experimental error for measuring the leakage current was about 10–15% for over 5 repeated runs. The capillary tubing was broken by applying any potential gradients which were greater than −17 kV. The irreversible dielectric breakdown of fused-silica capillary with 50 μm I.D. and 150 μm O.D. was thus occurred at a field strength around 17 kV/50 $\mu m = 3.4 \cdot 10^8$ V/m in our study. This measured dielectric strength was about one order of magnitude greater than those reported by Polymicro Technologies (Phoenix, AZ, USA) in the range of $2.5 \cdot 10^7$–$4 \cdot 10^7$ V/m.

In our previous study [6], the d.c. short circuit phenomenon at the inner capillary–solution interface is proposed for averaging the surface potential over the entire length of the capillary. Thus, there is no difference in the ζ potential and the resultant electroosmosis between the controlled and uncontrolled regions. Furthermore, there is no additional laminar flow and dispersion induced by the use of a radial electric potential gradient for the electronic adjustment of electroosmosis. The averaged electroosmotic flow which is constant over the entire length of the capillary is equal to

$$V_{\mathrm{eo,avg}} = xV_{\mathrm{eo,100\%}} + (1-x)V_{\mathrm{eo,0\%}} \qquad (1)$$

where x is a fraction of the total length of the capillary under the influence of a radial electric potential gradient and $V_{\mathrm{eo,0\%}}$ is the measured electroosmotic velocity in the absence of a radial electric potential gradient. Based on eqn. 1, $V_{\mathrm{eo,100\%}}$ is estimated by

$$V_{\mathrm{eo,100\%}} = (V_{\mathrm{eo,85\%}} - 0.15V_{\mathrm{eo,0\%}})/0.85 \qquad (2)$$

where $V_{\mathrm{eo,85\%}}$ is the measured electroosmotic velocity with 85% of the inner capillary under the influence of a radial electric potential gradient.

To satisfy the proposed "short circuit effect" at the capillary–solution interface, the leakage current across the capillary wall must be negligible [6]. In combination with the surface conductivity, the extra current traveling through the capillary wall would give rise to a difference in the surface potentials between the controlled and uncontrolled regions. By assuming a linear change in the ζ potential from the controlled region to the ends of the capillary, the electroosmotic velocity is thus varied linearly from $V_{\mathrm{eo,100\%}}$ in the controlled region to $V_{\mathrm{eo,0\%}}$ at the ends of the capillary. Under the leakage current situation, the mismatch between the electroosmotic velocities will have to be balanced by the additional laminar flow. The averaged bulk velocity of fluid over the entire length of the capillary is thus equal to

$$V_{\mathrm{avg}} = xV_{\mathrm{eo,100\%}} + (1-x)\bar{V} \qquad (3)$$

where $\bar{V}$ is the average of $V_{\mathrm{eo,100\%}}$ and $V_{\mathrm{eo,0\%}}$. Based on the theory of field-amplified capillary electrophoresis, the laminar flow caused by the mismatch between the electroosmotic velocities will then result in extra dispersion and band broadening for solutes inside the capillary [9].

Thus, the flow profiles and solute dispersion in the capillary are dependent on the "short circuit effect" or the "leakage current phenomenon" at the capillary–solution interface. To demonstrate such difference in the flow profiles and solute dispersion between these two surface phenomena, the percentage of the inner capillary under the direct control of electroosmosis was varied from 85, 60, 40, to 20%. The inner capillary was filled with 10 mM phosphate buffer at pH 3. A constant inner electric field strength equal to 5.5 kV/25 cm = 220 V/cm was applied during the experiment.

As shown in Fig. 3, the measured velocities of bulk fluid in the capillary with various percentages of tubing under the influence of a −5-kV potential gradient were in good agreement with those predicted by eqn. 1 as the "short circuit effect" at the capillary–solution interface. In contrast, the measured bulk velocities as shown in Fig. 4 with various percentages of tubing under the influence of a −10-kV potential gradient were more close to the prediction based on eqn. 3 as the "leakage current phenomenon" at the capillary–solution interface. The difference

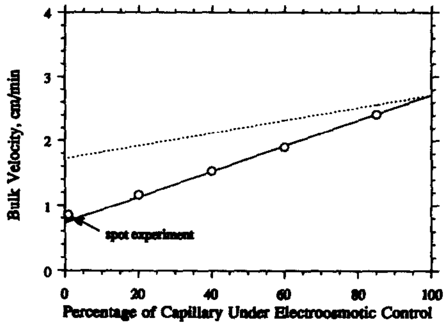

Fig. 3. Plot of bulk velocity *vs.* various percentages of capillary under the influence of a – 5-kV potential gradient. The experimental data are shown as open circles. The prediction obtained from eqn. 1 and eqn. 3 are represented as the solid and dashed lines, respectively.

in the prediction obtained from eqn. 1 (the solid line) and eqn. 3 (the dashed line) was more pronounced with the lower percentage of capillary under the direct control of electroosmosis. It was interesting to notice that the predicted bulk velocity at 0% of the capillary under the influence of a radial electric potential gradient was $V_{eo,0\%}$ from eqn. 1, but became $\bar{V}$ (as the average of $V_{eo,100\%}$ and $V_{eo,0\%}$) from eqn. 3.

To further reduce the percentage of the capillary under the direct control of electroosmosis, we simply applied a spot of nickel print on the external surface of capillary tubing. An electrical connection was then made between the spot of nickel print and a (external) high-voltage power supply. By assuming a linear potential drop across the buffer solution in the capillary, various radial electric potential gradients were applied at the spot of nickel print through the (external) high-voltage power supply. As shown in Fig. 3, there was almost no change for the measured velocity in the absence or presence of a −5-kV potential gradient through the spot of nickel print. In contrast, the measured velocity shown in Fig. 4 was increased to a value close to $\bar{V}$ (as the average of $V_{eo,100\%}$ and $V_{eo,0\%}$) in the presence of a −10-kV potential gradient. The experimental error in the measurement of bulk velocity was about 0–4% for over 5 repeated runs.

For dispersion studies, the inner capillary was filled with 1 m*M* phosphate buffer at pH 3. A constant electric field strength equal to 7.5 kV/25 cm = 300 V/cm was applied in the inner capillary. 85% of the inner capillary was under the influence of various radial electric potential gradients from 0 to −8 kV. As shown in Fig. 5, the experimental results (the open circles) were in good agreement with the theoretical plate height based on only molecular diffusion (the solid line). A diffusion coefficient equal to $1 \cdot 10^{-5}$ cm^2/s was used for dimethyl sulfoxide in the calculation of molecular diffusion. With the application of low pH and ionic strength buffer, the electroosmotic flow was enhanced easily with

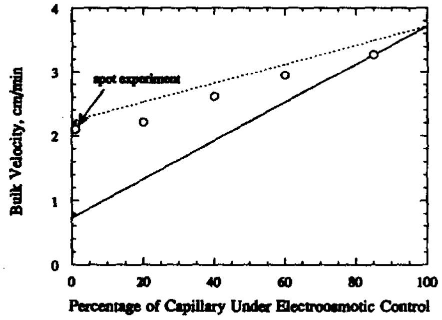

Fig. 4. Plot of bulk velocity *vs.* various percentages of capillary under the influence of a – 10-kV potential gradient. The experimental data are shown as open circles. The prediction obtained from eqn. 1 and eqn. 3 are represented as the solid and dashed lines, respectively.

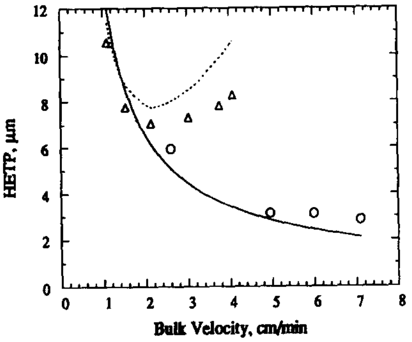

Fig. 5. The comparison of the prediction and the measured values of plate height at various operation conditions. The experimental data are shown as open circles for 85% and open triangles for 40% of the inner capillary under the direct control of electroosmosis. The solid line is the prediction based on only molecular diffusion. The solute dispersion contributed by molecular diffusion and laminar flow is represented by a dashed line. HETP = Height equivalent to a theoretical plate.

85% of the inner capillary under the direct control of electroosmosis.

The ionic strength of buffer solution in the inner capillary was increased to 10 m*M* phosphate at the same pH. The percentage of the inner capillary under the influence of a radial electric potential gradient was reduced from 85% to 40%. Various radial electric potential gradients ranged from 0 to −14 kV were thus required to obtain the bulk velocities similar to those discussed previously. The measured solute dispersion (the open triangles) shown in Fig. 5 started to deviate from the theoretical plate height based on only molecular diffusion (the solid line) when the bulk velocity was around 2.1 cm/min with the application of a −8-kV potential gradient. In fact, the measured solute dispersion was increased with the enhancement of bulk velocity from 2.1 cm/min to 4.1 cm/min under the influence of a radial electric potential gradient from −8 to −14 kV.

Under the leakage current situation at high radial electric potential gradients, the mismatch between the electroosmotic velocities over the entire length of the capillary would induce the additional laminar flow and result in extra dispersion and band broadening for sample inside the capillary. As discussed in our previous study [6], a model based on Chien and Helmer's [9] theory in field-amplified capillary electrophoresis was developed for calculating the additional dispersion and band broadening induced by the laminar flow. As shown in Fig. 5, the measured solute dispersion under the influence of high radial electric potential gradients (from −8 to −14 kV) was quite close to the theoretical plate height contributed by molecular diffusion and laminar flow. The experimental error in the measurement of solute dispersion was about 10–15% for over 5 repeated runs.

Depending on the "short circuit effect" or the "leakage current phenomenon" at the capillary–solution interface, the flow profiles and band broadening of solute in the capillary under the direct control of electroosmosis could be significantly different. The difference in the flow profiles and solute dispersion between the "short circuit effect" and the "leakage current phenomenon" was increased with the decrease in the percentage of the capillary under the direct control of electroosmosis. The required potential gradient across the capillary wall for inducing the leakage current was determined as 10 kV/50 μm = $2 \cdot 10^8$ V/m for a 25-cm long capillary with 50 μm I.D. and 150 μm O.D. used in this study.

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