STUDY OF ELECTROOSMOSIS-DRIVEN TWO-LIQUID DISPLACEMENT FLOW IN A MICROCAPILLARY

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Abstract. Multi-liquid flow, such as one liquid displacing another liquid, is frequently encountered in practice. This can be achieved by electroosmotic (EO) pumping, which has its own unique characteristics and advantages. This investigation is on EO-driven, two-liquid displacement flow in a microcapillary. A theoretical model was developed to take into consideration the axial step change of velocity flow fields at the time-dependent liquid/liquid interface, continuity requirement, and induced local pressure gradients. The electrical current

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monitoring method was employed to measure the flowrate and subsequently determine the capillary zeta potentials which are required for the model prediction. The nonlinear change of the electrical current with time under a constant applied voltage was observed during the displacement process. The theoretical and experimental results validated the hypothesis that the non-uniform zeta potential and electric field induce local pressure gradients in the two different liquids. Our experimental results indicated that the time of displacement, and thus the flow velocity, is found to be dependent on the displacing flow direction, which has hitherto not been reported in the literature. The underlying mechanisms were postulated, but demand further investigation.

**Keywords:** Electroosmosis, Multi-liquid displacement flow, Electrical current monitoring.

1. **Introduction**

In the last decade, the advances in micro-fabrication technologies, e.g. MEMS (micro-electromechanical system) fabrication technologies, have led to the development of micro-fabricated liquid handling systems or microfluidic systems. Particularly, in the field of biomedical and chemical analysis, there is a growing demand for fast, cheap and accurate analysis techniques. Due to miniaturization, microfluidic systems offer numerous advantages such as low sample consumption and reduced analysis or experiment time. They also offer the potential for massive parallelization, where a vast number of process steps can be realized within μTAS and concomitant reduction in cost per data point.

Although the majority of developments, thus far, have focused on miniaturization and integration, several crucial engineering problems and microfluidic physics for typical microfluidic processes, for instance liquid transport, mixing and separation, are still remained elucidated. This paper discusses the physics of multi-liquid manipulation flow in microchannels by utilizing an electric-based liquid transportation methods (electrokinetic effects) for liquid flow control.

1.1. Electroosmosis-Driven Liquid Transportation Mode

The electroosmosis (EO) flow induced by an applied external electric field tangentially along a charged surface is one of the basic classes of electrokinetic (EK) phenomena. It introduces a technique for manipulating liquid flow in microdevices in a controllable manner with “plug-like” flow profile. However, it is only true for an ideal EO flow in microchannels but not for multi-liquid flow operation. The deviation from the ideal EO flow behavior may occur in multi-liquid flow operations due to the absorption of ions on to the wall surface or change in the composition, pH, and ionic concentration. An in-depth understanding of the flow mechanisms is important for the control of multi-liquid EO flow. Hitherto, no comprehensive analysis of the underlying mechanisms has been conducted.

1.2. Real-time Electric Current Monitoring Method

A simple method of quantitatively studying and measuring EO flow in a microchannel is the electrical current monitoring method. In this method, an electrolyte initially filling the microchannel is electrokinetically displaced by another electrolyte or the same electrolyte but with a different concentration. As illustrated in Figure 1, a microcapillary tube is initially filled with electrolyte B and then brought into contact with another electrolyte A which has a different ionic concentration. Once an external electrical field is applied along the microcapillary, electrolyte A is gradually pumped into the capillary and displaces electrolyte B. As electrolyte A flows into the microcapillary, the system conductivity is altered, and hence the electrical current through the microcapillary is changed. When electrolyte A completely displaces electrolyte B, a constant electrical current is attained. The time for the current to reach its steady value and the length of the capillary tube are used to estimate the
average EO flow velocity, \( \bar{u}_{\text{ave}} = \frac{L_{\text{total}}}{\Delta t} \), where \( L_{\text{total}} \) is the total length of the capillary tube and \( \Delta t \) is the total time for the displacement process.

This investigation focuses on EO-driven, two-liquid displacement flow in a cylindrical microcapillary. We developed an analytical model describing an EO-driven two-liquid displacement flow in microchannels. This model takes into consideration the axial step-change of flow fields at the time dependent liquid/liquid interface, continuity requirement and induced internal pressure gradients. For experimental validation, the electrical current monitoring method is adopted for examining EO-driven two-liquid displacement flow dynamics. The dynamical response of EO displacement flow is also discussed.

![Experimental setup for measuring EO flow by the electrical current monitoring method. The polarity of the power supply is chosen in such a way that the EO flow is always from reservoir 1 to reservoir 2 through the microcapillary.](image)

**2. Mathematical Formulation**

The analytical solution, describing an EO-driven flow of one liquid displacing another liquid in a cylindrical microcapillary, is presented in the following sections. In the mathematical modeling, the continuity, the momentum and the Poisson-Boltzmann equations will be solved with the assumption of a Newtonian liquid in steady and low Reynolds number flow. Another major assumption is the sharp and flat liquid/liquid interface based on the claim of Ren et al.\(^5\).

A cylindrical microcapillary with a cylindrical coordinate system was employed. When an external electric field is applied along the microcapillary, different EO flow velocities are induced along the microcapillary due to the different zeta potentials, \( \zeta_1 \) and \( \zeta_2 \), at upstream and downstream respectively.

**2.1. Velocity Field with Pressure Gradient for EO-Driven Single Uniform Liquid Flow in a Cylindrical Microcapillary**

In the presence of an applied electric field, the momentum equations for a fully developed flow in a cylindrical microcapillary can be expressed as

\[
\mu \nabla^2 \bar{u} + \rho_s \mathbf{E} = \nabla p
\]

where, \( \mu \) and \( \bar{u} \) are the viscosity and the velocity vector of the liquid, \( p \) is the pressure, \( \rho_s \) is the volumetric net charge density and \( \mathbf{E} \) is the applied electric field strength. The viscosity is constant for a Newtonian fluid.

According to the theory of electrostatics, \( \rho_s \) can be related to the local potential, \( \psi \), in the diffuse EDL by the Poisson equation, which is expressed as

\[
\nabla^2 \psi = -\frac{\rho_s}{\varepsilon_0}
\]
where $\varepsilon_0$ is the permittivity of the vacuum, $\varepsilon_r$ is the dielectric constant and $\psi$ represents the electric potential of EDL.

The dielectric, $\varepsilon = \varepsilon_r \varepsilon_0$, of the liquid is taken to be constant, and thus the polarization and electrostriction effect are neglected. Both $\psi$ and $u$ are subject to the boundary conditions:

$$\psi(a) = \psi_0; \quad \frac{d\psi(0)}{dr} = 0 \quad \& \quad u(a) = 0; \quad \frac{du(0)}{dr} = 0$$  \hspace{1cm} (3)

To solve for the EO velocity field, an expression for the electric potential distribution, $\psi(r)$ is required. Using the Boltzmann equation for a symmetric electrolyte and the Deby-Huckel approximation, the analytical solution to the electric potential distribution is obtained as

$$\psi(r) = \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)}$$  \hspace{1cm} (4)

In Eq.(4), $l_0$ is the zero-order modified Bessel function of the first kind, and $a$ is the radius of the cylindrical microcapillary. The parameter $\lambda_D$ is the Debye length of the electrolyte.

The flow is present only along the axial (longitudinal) direction, $x$, of the cylindrical microcapillary. Other velocity components, namely $u_r$ and $u_\theta$, along the radial, $r$, and angular, $\theta$, directions respectively, are taken to be zero. Hence, by substituting Eq.(2) & (4) into Eq.(1), and integrating with the boundary condition given in Eq.(3), the EO velocity distribution with pressure gradient in a cylindrical microcapillary can be expressed as

$$u(r) = -\frac{\varepsilon_r \varepsilon_0 E_0 \zeta}{\mu} \left[ 1 - \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \frac{dp}{dx} \frac{a^2}{4\mu} \left[ 1 - \frac{r^2}{a^2} \right]$$  \hspace{1cm} (5)

2.2. Velocity Field for EO-Driven Two-Liquid Displacement Flow in an Open-ended Cylindrical Microcapillary

For a two-liquid displacement system, a step-change in liquid concentration (caused by the difference in concentration at the interface of the two liquids) under a constant applied electric field leads to a step change in electric field at the interface of the two liquids and hence in EO velocity flow field. Due to the mass continuity requirement, this step-change in the EO velocity at the interface must be compensated by inducing an internal pressure locally (at the upstream and downstream of the interface of the two liquids). However, the overall system pressure is taken as zero because both ends of the capillary are exposed to the atmospheric pressure.

Eq.(5) can now be evoked to solve for this EO driven liquid/liquid displacement flow associated with non-uniform liquid properties together with the following constraints:

Flow Continuity: $\dot{Q}_{\text{upstream}} = \dot{Q}_{\text{downstream}}$ & Null system pressure:

$$\frac{dp_{\text{upstream}}}{dx} (X(t)) + \frac{dp_{\text{downstream}}}{dx} (L - X(t)) = 0$$  \hspace{1cm} (6)

In Eq.(6), $\dot{Q}$ is the average flowrate, $X(t)$ is the length of the upstream bulk liquid column (namely, the interface location) and $L$ is the length of the microcapillary.

Hence, the analytical solutions for the velocity flow field at upstream and downstream of the interface of the two liquids can be expressed as

$$u_i = -\frac{\varepsilon_1 \varepsilon_2 \zeta_1}{\mu_1} \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \left[ \frac{2}{1 - \frac{r^2}{a^2}} \right] (L - X(t)) \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right]$$

$$u_i = -\frac{\varepsilon_1 \varepsilon_2 \zeta_1}{\mu_1} \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \left[ \frac{2}{1 - \frac{r^2}{a^2}} \right] X(t) \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right] \left[ \frac{l_0(\phi/\lambda_D)}{l_0(\lambda_D/a)} \right]$$  \hspace{1cm} (7)
\[ u_2 = \frac{\varepsilon_2 \varepsilon_0}{\mu_2} \left[ \frac{l_0(a_f^2/A_d^2)}{1 - \frac{l_0(a_f^2/A_d^2)}{l_0(a_f^2/A_d^2)}} \right] + \frac{2X(t)}{L} \left[ \frac{l_0(a_f^2/A_d^2) - \frac{2\lambda_2}{\mu_2} I_1(a_f^2/A_d^2)}{\mu_2 l_0(a_f^2/A_d^2)} - \frac{2\lambda_1}{\mu_1} I_1(a_f^2/A_d^2) \right] \]

(8)

**Note:** Subscripts 1 and 2 in Eqs.(7) and (8) represent upstream and downstream, respectively.

2.3. **Relationship of Time versus Liquid/Liquid Interface Movement**

Figure 2 clearly shows that the time-dependent electric current flow is a function of the movement of the interface of the two liquids. The two column bulk liquids at upstream and downstream can be treated analogously as two variable resistors connected in series under a constant applied electric field. As a result, the relationship of time versus interface movement can link the mathematical model presented in this study with the experimental results obtained from the electrical current monitoring method.

![Figure 2. Equivalent electrical circuit for EO-driven two-liquid displacement flow.](image)

In this study, the change of each column liquid can be treated as the displacement of the interface under the assumption of a flat and sharp interface. This is acceptable as long as the interface region is relatively small compared to the overall length of the microcapillary. The displacement of the interface, \( X(t) \) associated with the average velocity of EO flow can be expressed as,

\[ X(t) = \frac{t}{l_0} u_{ave} dt \quad \Rightarrow \quad \frac{dX(t)}{dt} = u_{ave} dt \]

(9)

Therefore, with reference to the upstream column liquid velocity flow field, the analytical solution for process time in term of the displacement of the interface can be written as Eq. (10) (refer to last page).

2.4. **Relationship of Electric Current versus Displacement Time**

The equivalent variable resistances can be written as

\[ R_1(t) = \frac{X(t)}{\lambda_1 A_{cross}}; \quad R_2(t) = \frac{L - X(t)}{\lambda_2 A_{cross}} \]

(11)

where, \( R(t) \) is the resistance, \( \lambda_i \) is the bulk liquid conductivity and \( A_{cross} \) is the cross-sectional area of the column bulk liquid.

By applying Ohm’s law, the electrical current can be expressed as...
\[ I_{\text{system}}(t) = \frac{V_{\text{supply}}}{R_{\text{system}}(t)} = \frac{A_{\text{cross}} V_{\text{supply}} \lambda_1 \lambda_2}{\left( \lambda_2 - \lambda_1 \right) X(t) + L \lambda_1} \tag{12} \]

Hence, using Eq.(10) with Eq.(12), one can correlate the analytical solution to the experimental data.

3. Results and Discussion

Figure 3 shows comparison between the model predictions and the experimental results of Herr et al.\(^6\). Although the operating conditions of Herr et al.\(^6\) are slightly different from our model, in that the interface of mismatch of zeta potentials of Herr et al.\(^6\) is fixed and not moving with the flow of the liquids, there is sufficient similarity to warrant a qualitative comparison. Our model predicts a discontinuity of upstream and downstream velocity fields at the interface, which is not physically realizable. This implies that the sharp interface assumption is inadequate to model the local velocity flow field at the interface. At region away from the interface, the flow front profiles agree reasonably well qualitatively. As such, refinement of the model is required to reveal the details of the underlying mechanisms at the interfacial region. From the comparison, we can conclude that the theoretical and experimental results validate the hypothesis that the non-uniform zeta potential and electric field induce local pressure gradients in the two different liquids. This results in the deviation of the velocity flow profile from the ideal plug-like flow profile expected for EO flow.

Figure 3 (a). Experimental image obtained from coupled capillary system where 66% of the total system length was EOD-suppressing (adapted from Herr et al.\(^6\)). (b) Theoretical velocity flow field for water (left figure) displacing NaCl 10\(^{-2}\) M (right figure) at fluid/fluid interface located at 66% of capillary length. For both cases, the capillary diameter (ID) = 75 \(\mu\)m, electrical field strength = 84 V/cm, capillary length = 30 cm.

In Figure 4, the nonlinear change of the electrical current with time under a constant applied voltage is observed during a displacement process. This is mainly caused by the time-dependent non-uniform zeta potential distribution in the microcapillary. It can also be predicted by using the theoretical results presented in this paper. The model predictions agreed well with the experimental data when a low concentration liquid displaces a high concentration liquid, but not vice versa. The time of displacement, and thus the flow velocity, is found to be dependent on the displacing flow direction. A detailed discussion can be found in our previous work (Gan et al.\(^7\)).
Figure 4. Comparison between model predictions and real-time electrical current response measurements of electroosmotic flow in a fused-silica microchannel for NaCl $10^{-2}$ M & $5 \times 10^{-4}$ M displacement flow in a mirocapillary of 75μm in diameter (ID) and $E_x = 100$ V/cm.

4. Conclusion

Model predictions with an assumption of a sharp interface between the two-electrolyte solutions agreed qualitatively with the empirical results obtained by Herr et. al. The prediction of a velocity discontinuity at the interface is not physically realizable, indicating that the assumption of a sharp interface has to be relaxed to reveal the detailed flow field at the vicinity of the interface. There were discrepancies between the predictions and the experimental observations i.e. the total process time for liquid A displacing liquid B was different to the time for liquid B displacing liquid A. Such difference cannot be predicted using the assumption of a flat and sharp interface. This phenomenon may be caused by the instability of the time-dependent electrical double layer (EDL) forming at the interface region, implying that the interface could not be flat and sharp.

Nevertheless, the theoretical model and the experimental results confirm that the induced internal pressure at the liquid/liquid interface is caused by the mismatch of upstream and downstream fluid velocities. As a result, the flow induced in the microchannel by the external applied voltage is a hybrid flow type of EO and pressure-driven flows, and the flow profile has a “parabolic-like” shape. Our model requires further refinement in order to obtain a rigorous analytical solution to describe the flow field at the interface. Mixing zone between the two bulk liquids should be introduced to rectify the theoretical model, which will be considered in our future studies.
\[ I = \frac{X(\beta_k - 1)}{\mu_2} \]

\[
= \frac{\varepsilon_1 \varepsilon_2 \mu_1 \mu_2}{\mu_1 \mu_2} \left[ \frac{I_0(\alpha/\Delta_D) - 2\lambda\Delta_D I_1(\alpha/\Delta_D)}{\mu_2} \right] - \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] \]

\[
= \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] - \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] \]

\[
\ln \left( \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] - \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] \right) \]

\[
= -\ln \left( \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] - \frac{\varepsilon_2 \varepsilon_2 \mu_1 \mu_2}{\mu_2} \left[ \frac{I_0(\alpha/\Delta_D^2) - 2\lambda\Delta_D I_1(\alpha/\Delta_D^2)}{\mu_2} \right] \right) \]

\[(10)\]

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