Available online at www.sciencedirect.com
ScienceDirect
Journal of Colloid and Interface Science 304 (2006) 505–511
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

Estimation of the zeta potential and the dielectric constant using velocity measurements in the electroosmotic flows

H.M. Park *, S.M. Hong

Department of Chemical and Biomolecular Engineering, Sogang University, Seoul, South Korea

Received 14 July 2006; accepted 8 September 2006
Available online 16 October 2006

Abstract

In this paper we develop a method for the determination of the zeta potential ζ and the dielectric constant ε by exploiting velocity measurements of the electroosmotic flow in microchannels. The inverse problem is solved through the minimization of a performance function utilizing the conjugate gradient method. The present method is found to estimate ζ and ε with reasonable accuracy even with noisy velocity measurements.

Keywords: Electroosmotic flow; Estimation of zeta potential and dielectric constant; Inverse problem

1. Introduction

Aqueous solutions are conductive due to the presence of dissolved ions. A dilute solution in contact to a surface with trapped surface charge experiences redistribution of its ions, resulting in formation of an electric double layer. The resulting electrical double layer (EDL) screens the surface charge over a characteristic Debye length λ. The diffuse part of the double layer is established when diffusive transport tending to smooth ion gradients balances electrostatic transport, driving counterions toward the interface [1]. Electroosmotic flow is generated when an electric field is imposed through an ionic solution parallel to the charged surfaces of capillary [2,3]. The recent advent of microfluidics fabrication technologies allows widespread application of the lab-on-a-chip concept. Microfluidic devices and systems find applications in inkjet printing, blood analysis, biochemical detection, chemical synthesis, drug screening and delivery, protein analysis, DNA sequencing, and so on. In these devices and systems the target chemical species are delivered by activating electroosmotic flow.

However, electroosmotic flows are not very robust, as they depend sensitively on the physicochemical properties of the solution and channel walls. Electroosmotic flows depend on the zeta potential, which varies with solution pH, ionic strength, dielectric constant, and solute molecules adsorbed onto the walls [4]. Strictly speaking, the surface electric potential ψ_0 is slightly different from the zeta potential ζ. But in most practical situations we may take the same values for ζ and ψ_0 [2,3]. Electrochemical reactions must occur at electrodes in order to impose an electric field in solution, which incurs metallic ion injection, water electrolysis, and the variation of pH. These adverse effects may influence the zeta potential and the dielectric constant. Since the zeta potential ζ and the dielectric constant ε are the two crucial factors influencing the electroosmotic flow under a given external electric field, it is imperative to determine values of ζ and ε accurately before guaranteeing a secure operation of the system.

In the present investigation, we consider a method of estimating zeta potential ζ and dielectric constant ε by exploiting velocity measurements in the microchannel. The velocity distribution in the microchannel may be measured using a microparticle image velocimetry (μPIV) technique [4–6] or a caged dye fluorescence technique [7]. Recent advances in micro-PIV allows measurements of velocity in microfluidic devices for a time resolution of 500 μs and a spatial resolution of 2 μm [5]. However, a set of simulated measurements is employed in the present investigation, which is constructed by adding random errors to the computed exact velocity.

* Corresponding author.
E-mail address: hmpark@sogang.ac.kr (H.M. Park).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2006.09.012

The problem under consideration is an inverse problems and can be regarded as discovering the cause from a known result. The solution of inverse problems is not straightforward, due to their ill-posedness in the sense of Hadamard: small perturbations in the observed functions may result in large changes in the corresponding solution [8]. One powerful method of solving inverse problems, which alleviates these difficulties associated with the ill-posed nature of the inverse problems, is to convert them into the minimization problems of a performance function using the conjugate gradient method [9]. The performance function is usually posed by the sum of squared residuals between calculated and observed velocity at measurement locations.

Considering the importance of the accuracy of the zeta potential ζ and dielectric constant ε for the reliable prediction of electroosmotic flows and the probable variation of these values due to the electrode reaction, the present technique may be employed regularly to detect changes of these parameters in a given microchannel.

2. Formulation of problem

Under the continuum hypothesis, the electroosmotic flow can be modeled by the Navier–Stokes equation, including the electroosmotic body force, which is generated by the interaction between the excess ions of the electric double layer and the external electric field [10–12]. The distribution of electric potential is described by the Poisson–Boltzmann equation.

2.1. Governing equation for the electric potential

We consider simple electrolytes that dissociate into two equally charged ions of valence z and $-z$. The electroosmotic flow is created by applying an external electric field $-\nabla\phi$ in the streamwise direction. Then the total electric field that interacts with the ions in the electrical double layer, thus creating an electrokinetic body force, is $-\nabla\psi - \nabla\phi$, where ψ is the internal electric potential created by ions.

The following dimensionless variables and dimensionless groups are introduced:

$$\mathbf{x}^* = \frac{\mathbf{x}}{L}, \quad \psi^* = \frac{\psi}{\zeta}, \quad \mathbf{v}^* = \frac{\mathbf{v}}{U},$$
$$\tilde{P}^* = \frac{P}{\rho U^2}, \quad t^* = \frac{t}{L/U}, \quad \phi^* = \frac{\phi}{\zeta},$$
$$w = \frac{1}{\kappa} = \sqrt{\frac{8\pi n_0 e^2 z^2}{\varepsilon_0 \varepsilon k_B T}}, \quad \alpha = \frac{ez\zeta}{k_B T},$$
$$\beta = \frac{(wL)^2}{\alpha} = \frac{L^2 8\pi n_0 ez}{\varepsilon_0 \varepsilon \zeta},$$
$$\delta = \frac{zen_0\zeta}{\rho_f U^2}, \quad \mathrm{Re} = \frac{\rho LU}{\mu}. \tag{1}$$

Here, L is the width of channel, ζ is the zeta potential, U is the characteristic velocity, ρ_f is the fluid density, μ is viscosity, ε_0 is the permittivity of vacuum, ε is the dielectric constant, and κ is the Debye length. Then the governing equations of the electroosmotic flows may be rewritten using these dimensionless variables:

$$\frac{\partial \mathbf{v}^*}{\partial t^*} + \mathbf{v}^* \cdot \nabla^* \mathbf{v}^* = -\nabla^* \tilde{P}^* + \frac{1}{\mathrm{Re}} \nabla^{*2} \mathbf{v}^* + 2\delta \sinh(\alpha\psi^*) \nabla^* \psi^* + 2\delta \sinh(\alpha\psi^*) \nabla^* \phi^*, \tag{2}$$

$$\nabla^* \cdot \mathbf{v}^* = 0, \tag{3}$$

$$\nabla^{*2} \psi^* = \beta \sinh(\alpha\psi^*). \tag{4}$$

The third term on the right hand side of Eq. (2) may be combined with the pressure gradient term for convenience in numerical calculation. If we define a modified dimensionless pressure as

$$P^* = \tilde{P}^* - \frac{2\delta}{\alpha} \cosh(\alpha\psi^*), \tag{5}$$

Equation (2) is simplified as follows [13,14]:

$$\frac{\partial \mathbf{v}^*}{\partial t^*} + \mathbf{v}^* \cdot \nabla^* v^* = -\nabla^* P^* + \frac{1}{\mathrm{Re}} \nabla^{*2} \mathbf{v}^* + 2\delta \sinh(\alpha\psi^*) \nabla^* \phi^*. \tag{6}$$

To demonstrate the feasibility of the estimation of surface electric potential ζ and dielectric constant ε from the velocity measurement, we employ the two-dimensional and three-dimensional microchannels depicted in Fig. 1, where typical flow fields are also depicted. These channels are made of two different materials. The first material has zero zeta potential and is used at the inlet and the outlet portions of the channel. The second material exhibits strong zeta potential and is used for the middle part of the channel. These materials can be prepared

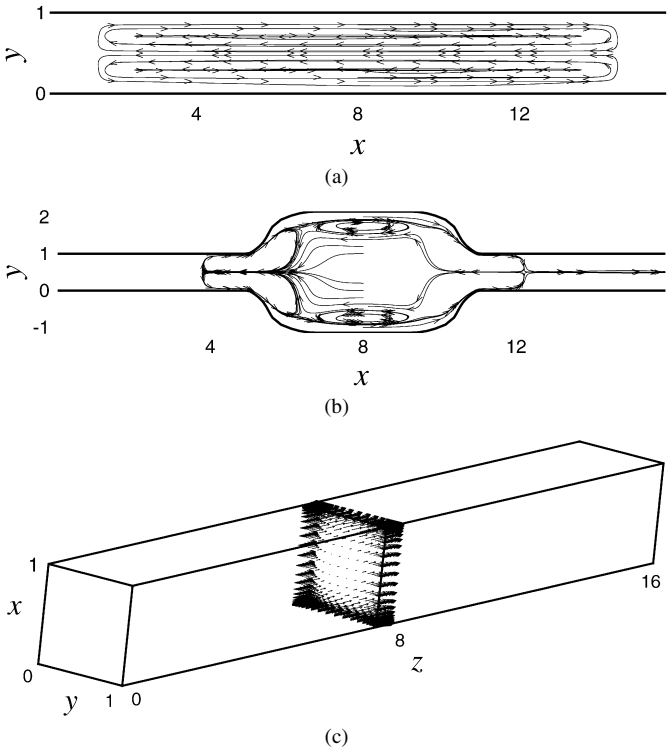

Fig. 1. Microchannels employed in the present work: (a) two-dimensional straight channel, (b) two-dimensional irregular channel, and (c) three-dimensional straight channel.