

Electroviscous effects in nanofluidic channels

Moran Wang,^{1,a)} Chi-Chang Chang,² and Ruey-Jen Yang²

¹*Computational Earth Science Group (EES-16), Earth and Environmental Sciences, Physics of Condensed Matter and Complex Systems Group (T-4), and Center for Nonlinear Study (CNLS), Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

²*Department of Engineering Science, National Cheng Kung University, Tainan, Taiwan, Republic of China*

(Received 16 October 2009; accepted 15 December 2009; published online 8 January 2010)

This paper presents a systematical study of electroviscous effects in nanofluidic channels using a triple layer model and a numerical framework. A chemical dissociation layer is introduced at solid-liquid interfaces to bridge the surface charge condition with the local properties of both solid surfaces and the ionic liquid. The electrokinetic transport in the electrical double layers is modeled by a lattice Poisson–Boltzmann method. The results indicate that there is an ionic concentration leading to the maximum electroviscosity for a given channel height, pH value, and environmental temperature. For a very high ionic concentration, a smaller channel height leads to a higher electroviscosity. When the bulk concentration reduces from $10^{-3}M$ to $10^{-6}M$, there is a critical channel height that maximizes the electroviscosity for a given ionic concentration, and the critical height increases with the decreasing ionic concentration. The electroviscosity increases with the pH of electrolyte solutions and is nearly proportional to the environmental temperature. The present study may help to improve the understanding of electrokinetic transport in nanofluidic channels.

© 2010 American Institute of Physics. [doi:10.1063/1.3290814]

I. INTRODUCTION

When an electrolyte solution contacts with a solid surface, the surface will generally be charged through an electrochemical adsorption process.^{1,2} A net countercharge distribution therefore forms in the solution near charged surfaces, which is referred as the electric double layer (EDL).^{3,4} As a result, a pressure-driven flow of an electrolyte solution in a narrow channel will cause a streaming potential opposite to the flow direction and reduce the flow rate.^{5,6} Understanding of such effect, which is often referred as the electroviscous effect,^{3,7} will help in the new designs and optimization of microfluidics and nanofluidics.

The electroviscous effects in narrow channels have been of interest for a long time. Elton⁸ might be the first one who examined the electrical resistance to the ionic liquid flow in narrow channels. Since then the electroviscous effects in homogeneously charged microchannels have been investigated analytically⁹ and numerically.^{5,10,11} Ren *et al.*^{12,13} measured the electroviscous effects of various electrolyte solutions on the flow resistance in microchannels and obtained good agreements with their numerical predictions. Furthermore Xuan presented a theoretical analysis of electroviscous effect on pressure-driven flow in heterogeneously charged microchannels.¹⁴ Recently, the electroviscous effects in nanoscale channels have been of increasing interest because of various important applications^{15,16} and have been modeled using the continuum model¹⁷ and the atomistic simulations.^{18,19} However it is still a major challenge to pre-

dict the electrokinetic transport in channels using the first principle methods for a full range of ionic concentrations.

As well known, the correct prediction and understanding of electrokinetic transport in microfluidics and nanofluidics depend on the appropriate treatment of the charge boundary conditions at interfaces.^{3,20} Most of the previous theoretical and numerical studies on electroviscous effects used a constant zeta potential^{5,9,14,15} or surface charge density^{11,19,21} at solid surfaces as the electrical boundary condition. However, the surface charge at the solid-liquid interface caused by the chemical adsorption varies actually with both the solid and the liquid properties, such as the surface chargeable site of solid and the ionic concentration and pH of liquid. Ren *et al.* measured the zeta potentials on the wall surfaces of microchannels, which changed significantly with the ionic concentration, provided the experimental data to their numerical framework, and therefore obtained satisfactory predictions.^{12,13} This scheme has seldom been extended to nanoscale since the zeta potential on surfaces of nanochannels is hardly measurable. Huang and Yang employed a chemical equilibrium model to determine the surface charge conditions and then investigated the electroviscosity varying with ionic concentration and channel height using a one-dimensional simplified model in nanochannels.¹⁷

In this contribution, we are aiming to study the electroviscous effects in nanofluidic channels systematically using a new theoretical and numerical framework. In the following sections, the mathematical formulations of a triple layer model at the solid-liquid interfaces are first introduced, based on which a numerical framework is developed. The framework is used to predict the electroviscous effects in nanochannels, varying with various environmental condi-

^{a)}Author to whom correspondence should be addressed. Telephone: 505-664-0698. Fax: 505-665-8737. Electronic mail: mwang@lanl.gov and moralwang@jhu.edu.

tions. The predictions will improve our understanding of electrokinetic transport in nanofluidic channels.

II. MATHEMATICS FOR THE TRIPLE LAYER MODEL

Generally the electrokinetic transport in microfluidics is described by a double layer model,³ and the surface charge condition is available from the experimental data. However in nanofluidics, the electrical boundary condition on surfaces is hardly measurable because of space limitation. In this work, we introduce a chemical dissociation layer at solid-liquid interfaces to bridge the surface charge condition with the local properties of both solid surfaces and the ionic liquid. We term the chemical dissociation layer on surfaces together with the electrical double layer in fluid as the electrical triple layer.

A. Chemical dissociation layer at interfaces

The boundary conditions are critical to modeling electrokinetic phenomena in nanofluidics. For the electrostatic boundary condition, in this work we adopt the basic Stern (BS) model developed by Behrens and Grier²² in which the solid surfaces acquire charges in contact with water by the chemical dissociation of alcohol groups on the surfaces,²³



where S represents the solid molecules. The chemical equilibrium of the dissociation leads to the zeta potential (ζ) on the interface expressed as a function of the surface charge density (σ),²²

$$\zeta(\sigma) = \frac{kT}{e} \ln \frac{-\sigma}{e\Gamma + \sigma} - (pH - pK) \frac{kT \ln 10}{e} - \frac{\sigma}{C}, \quad (2)$$

where k is the Boltzmann's constant, T the absolute temperature, e the absolute value of proton charge, Γ the surface density of chargeable sites, pK the logarithmic dissociation constant, and C the Stern layer's phenomenological capacity. Equation (2) reflects the chemical nature of the solid-water interface and its charging process; however the BS model has some limitations: (i) unsuitable for extremely acidic solutions since the protonation of doubly coordinated groups is not taken into account and (ii) unsuitable for high-salt-concentration solutions since only the solid-water interaction is considered in this simple model.

For the flat surfaces of a channel, the surface charge density is approximated using the Grahame equation,²⁴

$$\sigma(\zeta) = \sqrt{2\epsilon_r\epsilon_0 kT} \left(\sum_i n_{b,i} \left[\exp\left(-\frac{ez_i\zeta}{kT}\right) - 1 \right] \right)^{1/2}. \quad (3)$$

Especially for the monovalent electrolyte, when it flows in nanochannels with interacting double layers, Eq. (3) has a simplified form as²⁵

$$\sigma(\zeta) = \frac{\epsilon_r\epsilon_0 kT\kappa}{e} \left[2 \cosh\left(\frac{e\zeta}{kT}\right) - 2 \cosh\left(\frac{e\psi_m}{kT}\right) \right]^{1/2}, \quad (4)$$

where $\epsilon_r\epsilon_0$ denotes the permittivity of the solution, n_b denotes the bulk ionic concentration, z denotes the valence of ion, ψ_m denotes the electrical potential at the middle of the

channel, and κ^{-1} denotes the Debye screening length given by $\kappa = \sqrt{2z^2 e^2 n_b / \epsilon_r \epsilon_0 kT}$. Solving coupled Eqs. (2) and (4) yields the electrostatic boundary conditions at the solid-liquid interfaces of channels without any double layer interactions, which have been validated by comparisons with the experimental data.²⁶

B. Electrokinetics in the EDLs

Consider the electrokinetic transport process in nanofluidic channels. The mathematical models in this work are based on the following assumptions: (i) the system is in chemical and dynamic equilibrium, (ii) the transport process is in steady state, (iii) the channel height is much larger than the solvent molecular size, (iv) the ions in the Stern layer are attached on the surfaces and have no contribution to the bulk ionic current, (v) the flow in the nanochannel is very slow so that the ion convection effect is negligible, (vi) the bulk ionic concentration is not too high ($< 1M$) or not too low (the Debye length is smaller than ten times the channel width) and the channel height is larger than ten times of the solvent molecular diameter so that the Poisson-Boltzmann (PB) model is still applicable,^{27,28} and (vii) no other chemical reactions occur at surfaces except the dissociation of alcohol groups. Under these assumptions, the governing equations for the electrokinetic transport in a straight nanofluidic channel for a monovalent electrolyte solution are as follows:²

$$\nabla^2 \psi = \frac{2en_b}{\epsilon_r\epsilon_0} \sinh\left(\frac{e\psi}{kT}\right), \quad (5)$$

$$\rho_e = -2en_b \sinh\left(\frac{e\psi}{kT}\right), \quad (6)$$

$$\nabla \cdot \mathbf{u} = 0, \quad (7)$$

$$\rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u} + \rho_e \mathbf{E}, \quad (8)$$

where ψ denotes the static electric potential, $\mathbf{u}$ denotes the fluid velocity, ρ denotes the fluid density, p denotes the pressure, μ denotes the viscosity, ρ_e denotes the charge density, and $\mathbf{E}$ denotes the electric field strength. The electric field strength ($\mathbf{E}$) can be either the external electric field strength ($\mathbf{E}_{\text{ext}}$) for electro-osmotic flows or the streaming induced electric field strength ($\mathbf{E}_{\text{str}}$) for pressure-driven flows, which is often referred as the cause of the electroviscosity.^{3,29}

When the flow is driven by a pressure gradient, a streaming potential is established because of the ion transport. The streaming electric field is always opposite to the flow direction and hence diminishes the net flow in the channel. This phenomenon is commonly referred as the electroviscous effect since the liquid appears to be of higher viscosity near the surfaces.³ This induced streaming potential can be determined through the balance between the streaming current and the electrical conduction current at steady state, i.e.,

$$\mathbf{I}_s + \mathbf{I}_c = 0, \quad (9)$$

where $\mathbf{I}_s$ is the streaming current and $\mathbf{I}_c$ the conduction current. The streaming current, defined as the transport of the

net charge with the liquid flow in the double layer, can be calculated by¹²

$$\mathbf{I}_s = \int_0^h \rho_e \mathbf{u} dA, \quad (10)$$

where h is the channel height and A is the cross section area of the channel. The conduction current, defined as the transport of the excess charge driven by the electrokinetic potential in the double layer, is estimated by^{6,12}

$$\mathbf{I}_c = \mathbf{E}_{\text{str}}(A_c \lambda_0 + P_s \lambda_s), \quad (11)$$

where λ_0 is the electrical conductivity of the fluid, λ_s is the specific surface conductivity, A_c is the effective area of the channel's cross section for the bulk conduction current, which can be simplified as the cross section area (A) when the double layer thickness is comparable to the channel height in nanochannels,³⁰ and P_s is the wetting parameter of the channel, which is simplified as the perimeter of the cross section.^{6,12} Therefore the streaming induced electric field strength in nanofluidic channels with a high width-to-height aspect is calculated by

$$\mathbf{E}_{\text{str}} = - \frac{\int_0^h \rho_e \mathbf{u} dA}{(\lambda_0 + 2\lambda_s/h)A}. \quad (12)$$

C. Double layer interaction effect

However, when the Debye length is comparable to the channel height, a traditional “bulk” ionic concentration does not even exist. The local electroneutrality may be never obtained at the middle of channel for these cases. People have found the counterion enrichment when the EDL overlap occurs in the nanochannels.^{27,31} A few methods have been proposed to determine the effective bulk ionic concentration in nanochannels.^{17,32} A reasonable determination for the effective bulk ionic concentration with double layer interactions in nanochannels requires (i) to reflect the dominating ions effects on transport and (ii) to transform to the traditional bulk concentration automatically when the double layer interaction vanishes. Based on these requirements, we present a new enrichment coefficient, α , to calculate the effective bulk ionic concentration in this work, which is defined as

$$\alpha = n_{+,m}/n_{\infty}, \quad (13)$$

where $n_{+,m}$ represents the counterion concentration at the middle of the channel. The effective bulk ionic concentration is then modified as

$$n_b = \alpha n_{\infty}. \quad (14)$$

The combination of Eqs. (2), (4)–(6), (13), and (14) leads to a full description of the electrochemical boundary conditions in nanochannels. The solution process is as follows: (i) calculate the initial boundaries (ζ_0 and σ_0) using Eqs. (2) and (4) through iterations by assuming $n_b = n_{\infty}$; (ii) solve the PB equation, Eq. (5), using the initial boundary condition (ζ_0 or σ_0) to obtain the effective bulk concentration n_b based on Eqs. (13) and (14); and (iii) substitute n_b into Eqs. (2) and (4) and solve for the final boundary conditions (ζ and σ) through another iteration process. The electro-

chemical boundary conditions are solved out in the MATLAB software.³³

III. RESULTS AND DISCUSSION

After the electrochemical boundary conditions are calculated, the governing Eqs. (1)–(4) are solved numerically by a lattice PB framework^{34–36} in a two-dimensional long straight nanochannel. The lattice PB method can be regarded as a highly efficient solver for the strongly nonlinear equations governing the multiphysical electrokinetic transport.³⁴ Unlike conventional computational methods for differential equations, the lattice evolution method solves the governing equations by tracking the distribution functions of particle packets on lattices.³⁷ The lattice PB framework includes an electric potential evolution method on discrete lattices to solve the nonlinear PB equation and a density evolution method on the same set of discrete lattices to solve the Navier–Stokes equations and has been validated with analytical solutions and experimental data for micro- and nano-scale electrokinetic flows.^{34,35,38} This framework is very easy to extend to three dimensional and parallel computations.

In the present work, we consider a special case of a KCl solution flow in a long silica nanofluidic channel. For such a case, we use the nonslip model at the silica surfaces as the hydrodynamic boundary condition. Although the slip boundaries have been adopted by some recent researchers³⁹ and have shown significant effects on ion transport in nanochannels, a careful molecular study showed that the hydrodynamic boundary condition, slip or not, depended on the molecular interactions between fluid and solid and the channel size.⁴⁰ For the dilute solution in silica nanochannels considered in this work ($h \geq 3$ nm), the nonslip boundary condition is still valid very well.^{21,41}

A 200×200 lattice system is used for most cases, and the lattices are refined when necessary, ensuring the lattice size smaller than one third of the Debye length (κ^{-1}) for acceptable numerical accuracy. When the Debye length is smaller than 3% of the channel width, it satisfies the “thin layer” hypothesis, and the electrokinetic transport is simply calculated based on the Helmholtz–Smoluchowski model.²

The fluid properties, if not specified, are $\rho = 999.9$ kg/m³, $\epsilon_r \epsilon_0 = 6.95 \times 10^{-10}$ C²/J m, $\mu = 0.889$ mPa s, $D_{K^+} = 1.96 \times 10^{-9}$ m²/s, and $D_{Cl^-} = 2.03 \times 10^{-9}$ m²/s.^{36,42} The electrochemical properties of silica surfaces are $\Gamma = 8$ nm⁻², $pK = 7.9$ and $C = 2.9$ F/m² from Ref. 22. Although the fluid electrical conductivity (λ_0) depends on the ionic concentration and mobility and the temperature as well,^{12,43} and the surface conductivity (λ_s) may vary with the surface charge density,⁴⁴ we use the constants λ_0 and λ_s for simplification in this work: $\lambda_0 = 1.42 \times 10^{-3}$ Ω^{-1} m⁻¹ and $\lambda_s = 1.64 \times 10^{-9}$ Ω^{-1} .^{34,45}

A. Ionic concentration effects

The ionic concentration effects on the electroviscosity in nanochannels have been studied much using either constant zeta potential or constant boundary conditions. As stated above, the ionic concentration influences not only the zeta potential and surface charge density on solid surfaces but

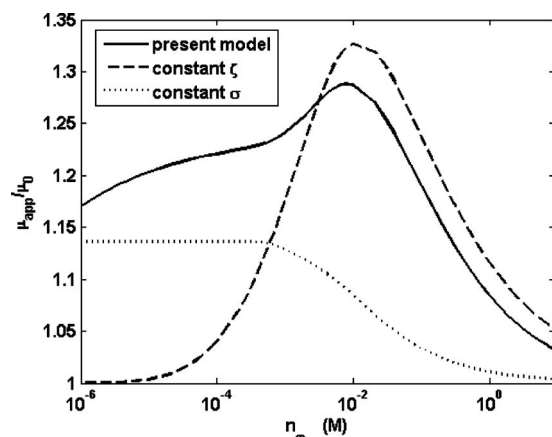


FIG. 1. Electroviscous effect varying with ionic concentration in a channel at $h=50$ nm for different boundary conditions. μ_{app} denotes the apparent viscosity of the electrolyte flow in nanochannels and μ_0 the fluid viscosity with no ions.

also the double layer interactions in the channel and therefore changes the electrokinetic transport properties. Figure 1 shows the normalized electroviscosity as a function of ionic concentration resulted from different models for a 50 nm high channel. We use $pH=8$ and $T=293$ K for the present model, $\sigma=-10$ mC/m² for the constant σ model, and $\zeta=-100$ mV for the constant ζ model in the simulations. The results indicate that the constant ζ model over-rates the electroviscous effect a little at very high ionic concentrations ($n_{\infty} > 10^{-2}M$) but under-rates significantly the effect at low concentrations ($n_{\infty} < 10^{-3}M$). The reason lies in the enriched ionic concentration by the interacting double layers at low concentrations. Different from the results of the constant σ model, which decrease with the ionic concentration monotonically, nearly constant at the low concentration region ($n_{\infty} < 10^{-4}M$) and decreasing slowly at the high concentration region ($n_{\infty} > 10^{-3}M$), the present model has a concentration at around $n_{\infty}=10^{-2}M$, leading to the maximum electroviscosity for this case. If we vary the channel height, we find that the maximum electroviscosity increases, but the critical ionic concentration value decreases with the channel height, as shown in Fig. 2. When the channel height $h=5$ nm, the maximum effective viscosity is 60% higher than normal,

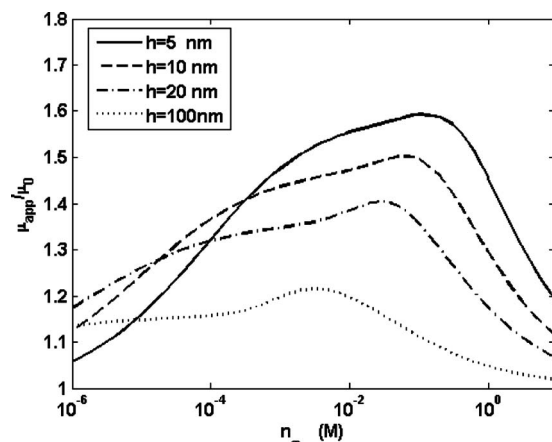


FIG. 2. Electroviscous effect varying with ionic concentration for four different channel heights.

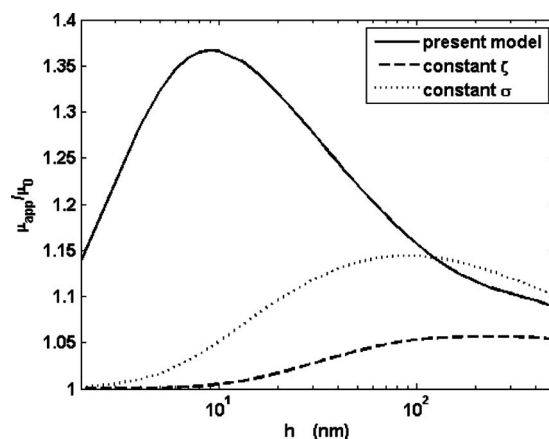


FIG. 3. Electroviscous effect varying with channel height for different models at $n_{\infty}=10^{-4}M$. The other parameters are the same as those in Fig. 1.

caused by the electroviscous effect. For a very high ionic concentration ($n_{\infty} > 1M$), a smaller channel height leads to a higher electroviscosity, while for a very low concentration ($n_{\infty} < 10^{-4}M$), there is a critical channel height that results in the highest electroviscosity.

B. Channel height effect

Figure 3 compares the electroviscous effects as a function of channel height (3 ~ 500 nm) from different models at a given ionic concentration of $n_{\infty}=10^{-4}M$, where the other parameters are the same as those in Fig. 1. When the channel height is comparable to or even smaller than the double layer thickness, the interaction of double layers will enrich the bulk ionic concentration, which is considered only in the present model. Therefore both the constant σ and constant ζ models under-rate the electroviscous effect significantly for very small channel size ($h < 50$ nm). Each model predicts one channel height that maximizes the electroviscosity for the given ionic concentration. For the currently given concentration at $n_{\infty}=10^{-4}M$, the critical channel height predicted by the present model is about 10 nm, while those by the constant ζ and σ models are one order of magnitude higher. Figure 4 thus shows the electroviscous effect varying with the channel height for four different concentrations. The re-

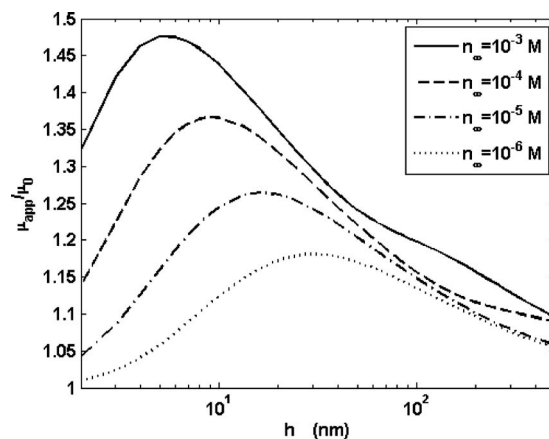


FIG. 4. Electroviscous effect as a function of channel height for four different ionic concentrations.

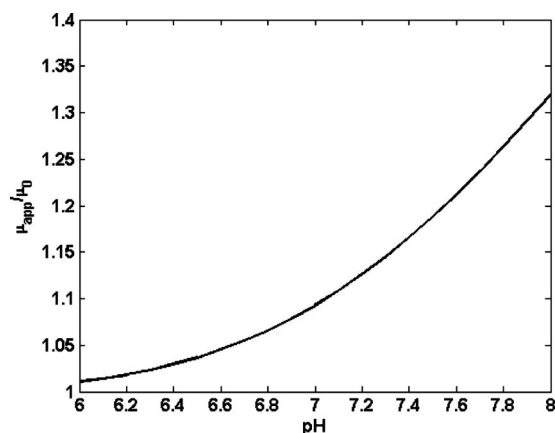


FIG. 5. Electroviscous effect variation with the pH of solution at $n_{\infty} = 10^{-4}M$, $h=20$ nm, and $T=293$ K.

sults indicate that the critical channel height that maximizes the electroviscosity increases as the ionic concentration decreases from $10^{-3}M$ to $10^{-6}M$. When the electrolyte is very dilute ($n_{\infty}=10^{-6}M$), the maximum apparent viscosity (μ_{app}) is about 18% higher than the reference viscosity (μ_0) at a channel height of $h \approx 30$ nm.

C. pH value effect

The pH value effects on the electroviscosity in nanochannels have seldom been reported in previous studies. Since the pH of electrolyte solutions influences the surface charge status, it will therefore affect the electroviscous effect. Figure 5 shows the variation in normalized electroviscosity with the pH value at $n_{\infty}=10^{-4}M$, $h=20$ nm, and $T=293$ K. The results indicate that the electroviscosity increases slowly when $pH < 7$ and sharply otherwise with the pH value. For the current given parameters, the apparent viscosity at $pH=8$ is 30% higher than that at $pH=6$.

D. Temperature effect

The environmental temperature effect is also studied in this work. Figure 6 shows the normalized electroviscosity changing with the temperature at $n_{\infty}=10^{-4}M$, $h=20$ nm, and $pH=8$ when the temperature varies from 280 to 320 K. We

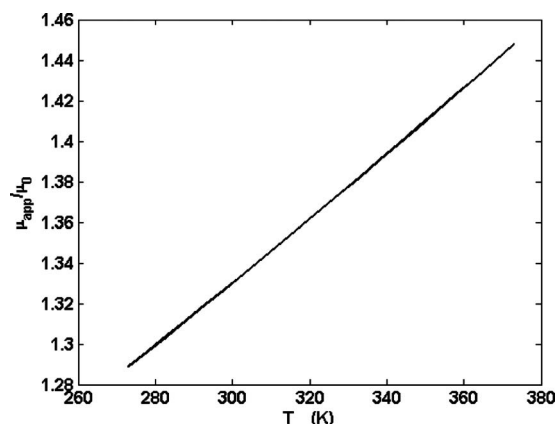


FIG. 6. Electroviscous effect variation with the temperature at $n_{\infty}=10^{-4}M$, $h=20$ nm, and $pH=8$.

use constant fluid properties in this simulation. The results indicate that the electroviscous effect is nearly proportional to the temperature. If the variable properties of fluid and ions were used, the electroviscous effect might be weakened because the fluid viscosity decreases with the temperature.

IV. CONCLUSIONS

The electroviscous effects in nanofluidic channels have been systematically studied using a triple layer model and a numerical framework. A chemical dissociation layer is introduced at solid-liquid interfaces to bridge the surface charge condition with the local properties of both solid surfaces and the ionic liquid. The electrokinetic transport is solved in the electrical double layers by the lattice PB framework. The electroviscous effects in nanofluidic channels are therefore calculated for various cases. The results indicate that there is an ionic concentration leading to the maximum electroviscosity for given channel height, pH value, and environmental temperature. For a very high ionic concentration ($n_{\infty} > 1M$), a smaller channel height leads to a higher electroviscosity. When the bulk ionic concentration is low, such as from $10^{-6}M$ to $10^{-3}M$, there is a critical channel height that results in the highest electroviscosity for a given ionic concentration. The highest electroviscosity will increase, but the critical height will decrease with the ionic concentration. The electroviscosity increases with the pH value of electrolyte solutions slowly when $pH < 7$ and sharply otherwise. The electroviscous effect is nearly proportional to the environmental temperature. The present investigations may help to improve the understanding of the electrokinetic transport mechanism in nanochannels and to develop new designs and optimize nanofluidic devices.

ACKNOWLEDGMENTS

This work was supported by LANL's LDRD Project under Grant No. 20080727PRD2 through the J. R. Oppenheimer Fellowship awarded to M.W. The authors would like to thank Professor D. Q. Li, Professor J. Santiago, and Professor X. C. Xuan for helpful discussions.

- ¹H. J. Butt, K. Graf, and M. Kappl, *Physics and Chemistry of Interfaces*, 2nd ed. (Wiley-VCH, Weinheim, 2006).
- ²R. B. Schoch, J. Y. Han, and P. Renaud, *Rev. Mod. Phys.* **80**, 839 (2008).
- ³D. Q. Li, *Electrokinetics in Microfluidics* (Academic, Oxford, 2004).
- ⁴T. M. Squires and S. R. Quake, *Rev. Mod. Phys.* **77**, 977 (2005).
- ⁵W. R. Bowen and F. Jenner, *J. Colloid Interface Sci.* **173**, 388 (1995).
- ⁶D. Q. Li, *Colloids Surf., A* **195**, 35 (2001).
- ⁷R. J. Hunter, *Zeta Potential in Colloid Science* (Academic, London, 1981); J. A. Menjivar and C. Rha, *J. Chem. Phys.* **79**, 953 (1983).
- ⁸G. A. H. Elton, *Proc. R. Soc. London Ser., A* **194**, 259 (1948); **194**, 275 (1948).
- ⁹C. L. Rice and R. Whitehead, *J. Phys. Chem.* **69**, 4017 (1965); S. Levine, J. R. Marriott, G. Neale, and N. Epstein, *J. Colloid Interface Sci.* **52**, 136 (1975).
- ¹⁰G. M. Mala, D. Q. Li, C. Werner, H. J. JacObasch, and Y. B. Ning, *Int. J. Heat Fluid Flow* **18**, 489 (1997); M. R. Davidson and D. J. E. Harvie, *Chem. Eng. Sci.* **62**, 4229 (2007).
- ¹¹R. P. Bharti, D. J. E. Harvie, and M. R. Davidson, *Chem. Eng. Sci.* **63**, 3593 (2008).
- ¹²L. Q. Ren, D. Q. Li, and W. L. Qu, *J. Colloid Interface Sci.* **233**, 12 (2001).
- ¹³L. Q. Ren, W. L. Qu, and D. Q. Li, *Int. J. Heat Mass Transfer* **44**, 3125 (2001).

- ¹⁴X. C. Xuan, *Microfluid. Nanofluid.* **4**, 457 (2008).
- ¹⁵N. A. Mortensen and A. Kristensen, *Appl. Phys. Lett.* **92**, 063110 (2008).
- ¹⁶H. Sakuma, K. Otsuki, and K. Kurihara, *Phys. Rev. Lett.* **96**, 046104 (2006); T. Das, S. Das, and S. Chakraborty, *J. Chem. Phys.* **130**, 244904 (2009); J. C. T. Eijkel and A. van den Berg, *Microfluid. Nanofluid.* **1**, 249 (2005).
- ¹⁷K. D. Huang and R. J. Yang, *Nanotechnology* **18**, 115701 (2007).
- ¹⁸R. Qiao and N. R. Aluru, *J. Chem. Phys.* **118**, 4692 (2003).
- ¹⁹R. Qiao and N. R. Aluru, *Langmuir* **21**, 8972 (2005).
- ²⁰F. H. J. van der Heyden, D. Stein, and C. Dekker, *Phys. Rev. Lett.* **95**, 116104 (2005).
- ²¹R. Qiao and N. R. Aluru, *Appl. Phys. Lett.* **86**, 143105 (2005).
- ²²S. H. Behrens and D. G. Grier, *J. Chem. Phys.* **115**, 6716 (2001).
- ²³J. Westall and H. Hohl, *Adv. Colloid Interface Sci.* **12**, 265 (1980).
- ²⁴F. Baldessari and J. G. Santiago, *J. Colloid Interface Sci.* **331**, 549 (2009).
- ²⁵J. Gonçalves, P. Rousseau-Gueutin, and A. Revil, *J. Colloid Interface Sci.* **316**, 92 (2007).
- ²⁶M. Wang and Q. J. Kang, "Electrochemomechanical energy conversion efficiency in silica nanochannels," *Microfluid. Nanofluid.* (in press).
- ²⁷M. Wang, J. Liu, and S. Chen, *Mol. Simul.* **33**, 1273 (2007).
- ²⁸M. Wang and S. Y. Chen, *Comm. Comp. Phys.* **3**, 1087 (2008).
- ²⁹V. G. Levich, *Physico-Chemical Hydrodynamics* (Prentice-Hall, New York, 1962).
- ³⁰R. B. Schoch and P. Renaud, *Appl. Phys. Lett.* **86**, 253111 (2005).
- ³¹Q. S. Pu, J. S. Yun, H. Temkin, and S. R. Liu, *Nano Lett.* **4**, 1099 (2004); L. J. Cheng and L. J. Guo, *ibid.* **7**, 3165 (2007).
- ³²R. Qiao and N. R. Aluru, *Int. J. Multiscale Comp. Eng.* **2**, 173 (2004).
- ³³M. Wang, *Scientific Computation with MATLAB*, 2nd ed. (Publishing House of Electronics Industry, Beijing, 2003).
- ³⁴J. K. Wang, M. Wang, and Z. X. Li, *J. Colloid Interface Sci.* **296**, 729 (2006).
- ³⁵M. Wang and S. Chen, *J. Colloid Interface Sci.* **314**, 264 (2007).
- ³⁶M. Wang and Q. Kang, *Anal. Chem.* **81**, 2953 (2009).
- ³⁷S. Chen and G. D. Doolen, *Annu. Rev. Fluid Mech.* **30**, 329 (1998).
- ³⁸M. R. Wang, J. K. Wang, and S. Y. Chen, *J. Comput. Phys.* **226**, 836 (2007).
- ³⁹C. Davidson and X. C. Xuan, *J. Power Sources* **179**, 297 (2008); Y. Q. Ren and D. Stein, *Nanotechnology* **19**, 195707 (2008); S. Pennathur, J. C. T. Eijkel, and A. van den Berg, *Lab Chip* **7**, 1234 (2007).
- ⁴⁰J. F. Dufreche, V. Marry, N. Malikova, and P. Turq, *J. Mol. Liq.* **118**, 145 (2005); L. Joly, C. Ybert, E. Trizac, and L. Bocquet, *Phys. Rev. Lett.* **93**, 257805 (2004).
- ⁴¹M. Wang, J. Liu, and S. Chen, *Mol. Simul.* **33**, 239 (2007); C. D. Lorenz, P. S. Crozier, J. A. Anderson, and A. Travesset, *J. Phys. Chem. C* **112**, 10222 (2008).
- ⁴²H. Daiguji, P. D. Yang, and A. Majumdar, *Nano Lett.* **4**, 137 (2004).
- ⁴³D. Stein, M. Kruithof, and C. Dekker, *Phys. Rev. Lett.* **93**, 035901 (2004).
- ⁴⁴J. Lyklema, *J. Phys.: Condens. Matter* **13**, 5027 (2001).
- ⁴⁵B. Li and D. Y. Kwok, *J. Chem. Phys.* **120**, 947 (2004).