THEORY OF THE ELECTROOSMOSIS EFFECT IN ELECTROPHORESIS

T. W. NEE

Department of Physics and Optical Sciences Center, University of Arizona, Tucson, Ariz. 85721 (U.S.A.)
(Received July 5th, 1974)

SUMMARY

A general theory of the electroosmosis phenomenon in electrophoretic experiments is developed from a set of fundamental viscous fluid dynamic equations of composite fluid systems. A simple physical model is chosen for an analytic study of the detailed qualitative behavior. Neglecting all effects due to the intrinsic electric characteristics of the neutral solvent molecules, expressions for the important experimentally measurable quantities, such as electroosmotic velocity, electroosmotic pressure and electroosmotic mobility, are derived in different physical situations. Application to the real electrophoresis system is discussed.

INTRODUCTION

The so-called electroosmosis effect[1–4] is frequently observed in electrophoresis experiments. Not only the charged mobile ions but also the neutral solvent fluid moves when an electric field is applied along the tube containing the fluid whose components are to be separated. In the case of a long tube with open ends, the fluid will move in one direction[1]. The fluid circulates in a tube with closed ends[2] (Fig. 1). This electroosmosis effect is due to the existance of charge on the tube wall, which apparently induces a double layer in its neighbourhood. When an electric field is applied tangential to the wall surface, there is a net tangential electric force acting on the charged fluid in the double layer and this force causes the fluid to move. In a system with open ends, the whole fluid will be moved by these tangential forces acting in the double layer owing to the existence of shearing stress of the fluid. In a tube with closed ends, the net flow of the liquid must be zero. The flow of the liquid along the wall in the double layer is counterbalanced by a flow in the opposite direction at the center of the tube. Therefore, there must be a pressure difference between the tube ends to generate this counter flow[2,3]. Assuming a flow of Poiseuille's type, the velocity profile has been calculated[2] and the pressure difference has also been calculated by assuming known electrophoretic relations[1,3].

In this paper, we shall present a basic, detailed theory of electroosmosis. The mobile ion cloud formed from a given type of ion is considered as a component of the fluid system. Then the electrophoretic system is a system of composite fluid —the neutral solvent fluid and different ionic charged fluids. These different fluids are de-
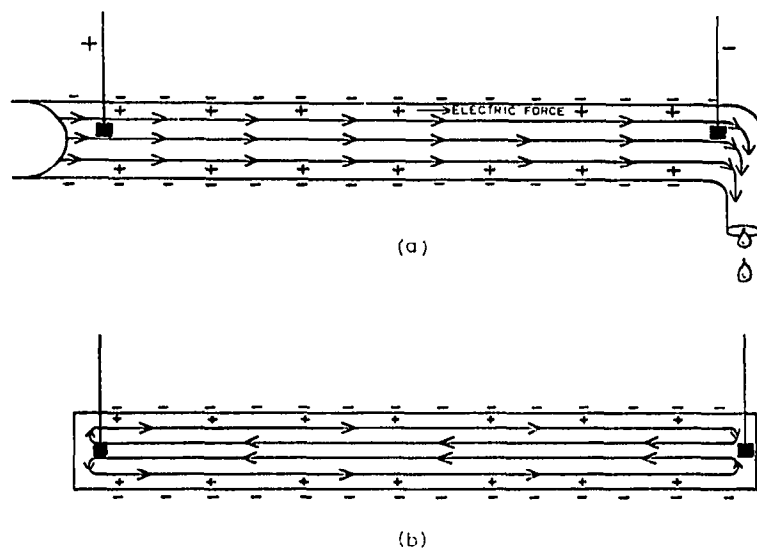
Fig. 1. The electroosmosis effect. (a) Tube with open ends. (b) Tube with closed ends.

scribed by a set of fluid dynamic equations coupled by the molecular interactions. The set of equations is derived microscopically in the Appendix. Starting from these fundamental equations, we shall study most of the characteristics of electroosmosis in a simple model system. Both open- and closed-end systems will be discussed. The important relation between the double-layer screening length (λ_s^{-1}) and the velocity profiles of different component fluids, the expressions of electroosmotic velocity and the electroosmotic pressure will be derived. We shall show that the Poiseuille type of electroosmotic flow[2,3] is a good approximation to the observations in the real electrophoresis experiments.

In the next section, we shall propose a simple model and derive the set of fundamental fluid dynamic equations. Part of these equations is solved in Section III to obtain the charge distribution (double-layer structure). In Section IV, the fluid dynamic equations are solved by neglecting the shearing stresses of the ionic fluids. The velocity profiles are calculated and the qualitative behavior is shown. The physical situation in a real electrophoresis experiment will be discussed and some conclusions will be given in the final section.

SIMPLE MODEL AND FUNDAMENTAL FORMALISM

We consider a solution system with ions A^+, B^- and solvent molecules C^0 in an electric field $\vec{E}$. There are three kinds of fluids, which are described by the density function $n_a(\vec{r},t)$ and fluid velocity $\vec{v}_a(\vec{r},t)$ $(a = +, -, 0)$ for A^+, B^- and C^0, respectively. They satisfy (see Appendix) the equation of continuity

$$\frac{\partial}{\partial t} n_a(\vec{r},t) + \nabla \cdot [n_a(\vec{r},t) \vec{v}_a(\vec{r},t)] = 0 \tag{1}$$

and the equation of motion

$$m_a n_a \left[\frac{\partial}{\partial t} + \vec{v}_a \cdot \nabla \right] \vec{v}_a (\vec{r}, t) = q_a n_a \vec{E} - \underset{\beta \neq a}{\Sigma} \xi_{a\beta} n_a n_\beta (\vec{v}_a - \vec{v}_\beta) - $$

$$- \nabla P_a + \eta_a \nabla^2 \vec{v}_a + (\nu_a + \tfrac{1}{3}\eta_a) \nabla (\nabla \cdot \vec{v}_a) \qquad (2)$$

where the terms at the right-hand side are the force densities on the fluid of type a due to different sources: $q_a n_a \vec{E}$ is the electric force density, $-\xi_{a\beta} n_a n_\beta (\vec{v}_a - \vec{v}_\beta)$ the frictional force due to fluid of type β and the latter three terms are the self-stress forces.

For a simple demonstration of the electroosmosis effect, we consider a cell system bounded by two planes at $y = \pm L$. The external electric field $\vec{E}_{\text{ext.}} = [E, 0, 0]$ is applied in the x-direction. We assume that the length $\varDelta x$ and width $\varDelta z$ of the cell are so large that we can neglect edge effects, *i.e.* we only consider the fluid behavior far from the two edges. In the steady state, the velocities are in the x-direction and have spatial y-variation only,

$$\vec{v}_a = [v_a (y), 0, 0] \qquad (a = +, -, 0) \qquad (3)$$

Then we have

$$\left[\frac{\partial}{\partial t} + \vec{v}_a \cdot \nabla \right] \vec{v}_a = 0$$

and

$$\nabla \cdot \vec{v}_a = 0$$

and the equation of motion (eqn. 2) has the equilibrium form

$$q_a n_a \vec{E} - \underset{\beta \neq a}{\Sigma} \xi_{a\beta} n_a n_\beta (\vec{v}_a - \vec{v}_\beta) - \nabla P_a + \eta_a \nabla^2 \vec{v}_a = 0 \qquad (4)$$

If an electroosmosis effect exists, it is assumed that there exist charges on the walls of the system. Owing to the electric attraction and repulsion between ions A^+, B^- and the wall, the ions are re-distributed in the neighbourhood of the wall and form a double layer there. In our model, the equilibrium densities have the form

$$n_\pm = n_\pm(y) \qquad (5)$$

and if we neglect the electric interactions between charged walls and the neutral solvent molecules (for instance, the electric dipole–quadrupole interactions, etc.), we have

$$n_0 = \text{constant} \qquad (6)$$

and the electric charge has the spatial distribution

$$\varrho_e(y) = e[n_+(y) - n_-(y)],\tag{7}$$

where we have assumed that the ions A^+, B^- have the charges $+e$ and $-e$, respectively. At the center of the tube, the system is neutral, *i.e.* the positive and negative charge densities are equal,

$$n_+(0) \approx n_-(0) \approx n_c = \text{constant}\tag{8}$$

or

$$\varrho_e(0) \approx 0\tag{9}$$

Because of the non-vanishing charge inside the double layer, there exists a screening potential $\varphi(y)$ there with the boundary values

$$\varphi(\pm L) = \varphi_L\tag{10}$$

at the wall surface. $|\varphi_L|$ is called the zeta potential of the wall. φ_L is positive (or negative) if the charge on the wall is positive (or negative). Then the total electric field inside the tube is

$$\vec{E} = [E, -\varphi'(y), 0]\tag{11}$$

The screening potential $\varphi(y)$ and screening charge ϱ_e are related by Poisson's equation

$$\varphi''(y) = -4\pi \varrho_e(y)/\varepsilon\tag{12}$$

where ε is the dielectric constant of the solvent fluid.

In practice, the ion densities are small compared with the solvent density

$$n_\pm \ll n_0\tag{13}$$

Then we consider the following two approximations:

(i) The ion–ion friction force is small and can be neglected in comparison with the ion–solvent friction force

$$\xi_{+-} n_+ n_- \ll \xi_{\pm 0} n_\pm n_0\tag{14}$$

(ii) The ionic fluid can be considered as a dilute gas and satisfies the equation of state

$$P_a = n_a(y) k_B T\tag{15}$$

In the isothermal case, *i.e.* T is constant, we have

$$\nabla P_a = k_B T [0, n'_a(y), 0]\tag{16}$$

Substituting eqns. 3, 5, 6, 11, 14 and 16 into eqn. 4, we have the x-component equations

$$\{\pm eE - \xi_\pm n_0 [v_\pm (y) - v_0 (y)]\} n_\pm (y) + \eta_\pm v_\pm'' (y) = 0 \tag{17}$$

$$\{\xi_+ n_+ [v_+ (y) - v_0 (y)] + \xi_- n_- [v_- (y) - v_0 (y)]\} n_0 + \eta_0 v_0'' (y) - P_x = 0 \tag{18}$$

and the y-component equations

$$\mp e \varphi' (y) n_\pm (y) - k_B T n_\pm' (y) = 0 \tag{19}$$

$$- \frac{\partial P_0}{\partial y} = 0 \tag{20}$$

where

$$P_x = \frac{\partial P_0}{\partial x} \tag{21}$$

is the solvent partial pressure gradient along the tube. We have chosen the simpler notation $\xi_\pm$ for $\xi_{\pm 0}$. The total pressure is the sum of three partial pressures

$$P = P_+ + P_- + P_0 \tag{22}$$

According to eqns. 15 and 22

$$P_x = \frac{\partial P_0}{\partial x} = \frac{\partial P}{\partial x} \tag{23}$$

Because the total pressure gradient $\partial P/\partial x$ is controlled by external sources (atmospheric pressure, end walls, etc.), P_x is uniform across the tube cross section and thus is a constant. Eqns. 17–19 are the fundamental equations of electroosmosis effect.

For mathematical convenience, we define the composite-fluid velocity

$$V(y) = v_0(y) + \frac{\eta_+}{\eta_0} v_+(y) + \frac{\eta_-}{\eta_0} v_-(y) \tag{24}$$

and the component relative ion-fluid velocity

$$f_\pm(y) = v_\pm(y) - v_0(y) \tag{25}$$

Then the fundamental equations of motion (eqns. 17 and 18) can be transformed to the equations of motion for V and $f_\pm$:

$$V''(y) = \frac{1}{\eta_0} \{P_x - E\varrho_e(E)\} \tag{26}$$

$$f''(y) = n_0 \left\{ \xi_\pm n_\pm \left(\frac{1}{\eta_\pm} + \frac{1}{\eta_0} \right) f_\pm(y) + \frac{\xi_\mp n_\mp}{\eta_0} f_\mp(y) \right\} \mp eE \frac{n_\pm}{\eta_\pm} \tag{27}$$

It is understood from eqn. 26 that the total electric force acting on the composite fluid is $E\varrho_c(y)$, which is identical to that on the whole system.

IONIC CHARGE DISTRIBUTION

In the dilute ionic-gas model, the ionic densities $n_\pm(y)$ can be solved from eqn. 19.

$$n_\pm(y) = n_c\, e^{\mp \frac{e}{k_B T}\varphi(y)} \tag{28}$$

Substituting eqn. 28 into eqn. 7, we obtain the electric charge density

$$\varrho_c(y) = 2n_c e \sinh \frac{e\varphi(y)}{k_B T} \tag{29}$$

For a demonstration of the electroosmosis effect without complicated mathematics, we consider the special case of the high-temperature limit,

$$\left| \frac{e\varphi(y)}{k_B T} \right| \leqslant \frac{e\,|\varphi_L|}{k_B T} \ll 1 \tag{30}$$

Then we have the approximate forms

$$n_\pm(y) \approx n_c \left[1 \mp \frac{e}{k_B T}\varphi(y) \right] \tag{28'}$$

and

$$\varrho_c(y) \approx \frac{2n_c e^2}{k_B T}\varphi(y) \tag{29'}$$

Using the approximate form (eqn. 29'), Poisson's equation (12) can be easily solved with the boundary condition (10),

$$\varphi(y) \approx \varphi_L \frac{\cosh \lambda_s y}{\cosh \lambda_s L} \tag{31}$$

where

$$\lambda_s = \sqrt{\frac{8\pi n_c e^2}{\varepsilon\, k_B T}} \tag{32}$$

λ_s^{-1} is the Debye screening length of the charged fluid. Substituting eqn. 31 into eqn. 29', we obtain the induced charge density

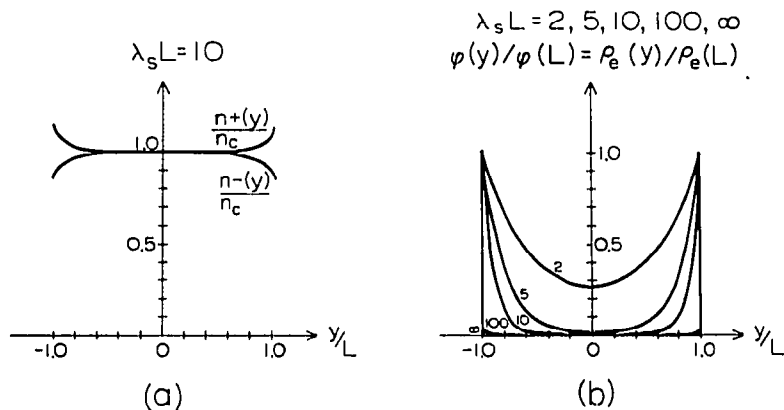$$\varrho_c(y) \approx \varrho_L \frac{\cosh \lambda_s y}{\cosh \lambda_s L} \tag{29''}$$

Fig. 2. (a) The ionic distributions. (b) The electrostatic screening potential and the screening charge distribution.

where

$$\varrho_L = \frac{2\, n_c e^2 [-\varphi_L]}{k_B T} \tag{33}$$

is the induced charge density at the wall. Note that the induced charge has opposite sign to the wall potential φ_L, i.e. the wall charge will attract charges of opposite sign. The physical situation and the charge distribution ϱ_e, electric potential $\varphi(y)$ and ionic distribution $n_{\pm}(y)$ are shown in Fig. 2. In Fig. 2, we have assumed that the wall charges are negative, such that $\varphi_L < 0$. The induced charges are positive.

ELECTROOSMOSIS EFFECT IN THE ABSENCE OF IONIC SHEARING STRESS

In practice, because the ionic density is small in comparison with the solvent density, $n_{\pm} \ll n_0$. Then the shearing stress constant of the ionic fluid is much smaller than that of the solvent

$$\eta_{\pm} \ll \eta_0 \tag{34}$$

(We shall justify this relation in a practical example later.) In the lowest approximation, we may neglect the ionic shearing stress term $\eta_{\pm} v''_{\pm}(y)$ in eqn. 17 and then we have the approximate equations

$$\{\pm eE - \xi_{\pm} n_0 [v_{\pm}(y) - v_0(y)]\}\, n_{\pm}(y) = 0 \tag{17'}$$

and

$$\{\xi_+ n_+ [v_+(y) - v_0(y)] + \xi_- n_- [v_-(y) - v_0(y)]\} n_0 + \eta_0 v''_0(y) - P_x = 0 \tag{18}$$

Then $v_0(y)$ satisfies the equation

$$v''_0(y) = \frac{1}{\eta_0}\, \{P_x - E\, \varrho_e(y)\} \tag{35}$$

Note that eqn. 35 is the lowest-order approximation of eqn. 26 for the composite fluid. From eqn. 24, $V(y) \approx v_0(y)$ in case the relation (34) is satisfied. Now, eqns. 17' and 35 can be easily solved, we obtain the solutions

$$v_0(y) = \frac{1}{\eta_0} \left(\frac{P_x}{2} y^2 - \frac{\varrho_L E}{\lambda_s^2} \frac{\cosh \lambda_s y}{\cosh \lambda_s L} \right) + C \tag{36}$$

and

$$v_\pm(y) = v_0(y) \pm \mu_\pm^{(0)} E \tag{37}$$

where

$$\mu_\pm^{(0)} = \frac{e}{\xi_\pm n_0} \tag{38}$$

are the electric mobilities of the two ions A^+ and B^-, respectively. The two constants P_x and C are to be determined from suitable boundary conditions on v_0. We shall discuss several special cases (with different boundary conditions) as follows.

Electroosmosis in an open-ends tube with rough wall

Because the two ends are open, the pressures at the two ends are equal to the external atmospheric pressure. We assume that the tube is horizontal and the gravitational force can be neglected. Then there is no pressure difference along the tube, *i.e.* the pressure gradient P_x vanishes,

$$P_x = 0 \tag{39}$$

From the rough-wall boundary condition

$$v_0(\pm L) = 0 \tag{40}$$

the constant C is determined and we obtain the solutions

$$v_0(y) = \frac{1}{\eta_0} \frac{\varrho_L E}{\lambda_s^2} \left(1 - \frac{\cosh \lambda_s y}{\cosh \lambda_s L} \right) \tag{41}$$

The neutral solvent is moving inside the tube with velocity $v_0(y)$ in the presence of an applied electric field ($E \neq 0$) and owing to the existence of the wall charges ($\varphi_L \neq 0$, and thus $\varrho_L \neq 0$). This is the so-called electroosmosis effect (Fig. 1a). Because of the solvent motion, the ions are moving with the apparent velocities

$$v_\pm(y) = \pm \mu_\pm^{(0)} E + v_0(y) \tag{37}$$

which are different from the values $\pm \mu_{(0)}^\pm E$ in the absence of electroosmosis effect. The behaviors for different values of $\lambda_s L$ are shown in Fig. 3. Because $v_0(y)$ is proportional to E, we can define the apparent ionic electric mobilities by

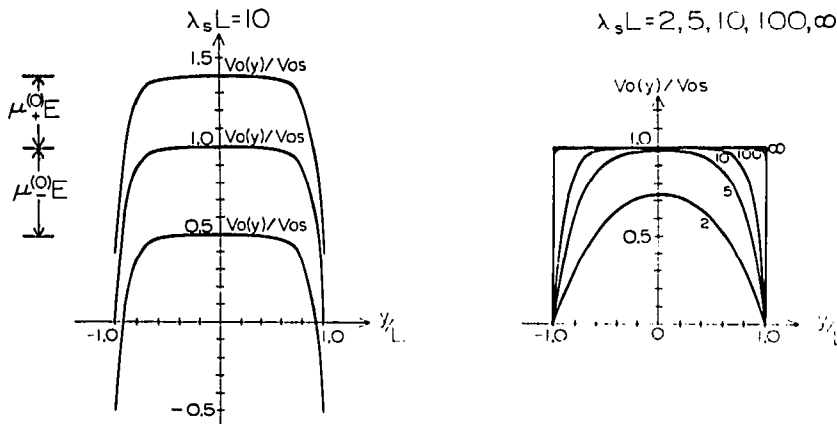$$\mu_\pm(y) = \pm \frac{v_\pm(y)}{E} \tag{42}$$

Fig. 3. Electroosmosis effect in an open-end tube with rough wall. (a) The velocity profiles of component fluids. Positive, negative ion flows and the neutral solvent flow. The screening parameter $\lambda_s L = 10$ is chosen. (b) The velocity profiles of neutral solvent fluid for different values of the screening parameter $\lambda_s L = 2$, 5, 10, 100 and ∞.

and we obtain the expression

$$\mu_{\pm}(y) = \mu_{\pm}^{(0)} \pm \frac{\varrho_L}{\eta_0 \lambda_s^2} \left(1 - \frac{\cosh \lambda_s y}{\cosh \lambda_s L} \right) \tag{43}$$

In a practical situation, $L \approx 1$ cm, $\lambda_s \approx 10^{+6}$ cm^{-1} (see eqn. 65 of Section V), then

$$\lambda_s L \approx 10^6 \gg 1$$

Except very close to the tube wall, the solvent will move at a constant velocity $v_{os.}$, i.e.

$$v_0(y) = v_{os.} = \frac{1}{\eta_0} \frac{\varrho_L E}{\lambda_s^2} \qquad (L - |y| \gg \lambda_s^{-1}) \tag{44}$$

$v_{os.}$ is called the electroosmotic velocity[1,2]. For mathematical convenience, we may define the electroosmotic mobility,

$$\mu_{os.} = \frac{v_{os.}}{E} = \frac{\varrho_L}{\eta_0 \lambda_s^2} \tag{45}$$

and from eqns. 32 and 33, it has the form

$$\mu_{os.} = \frac{\varepsilon[-\varphi_L]}{4\pi\eta_0} \tag{46}$$

This is the well-known Helmholz–Smoluchowski result[1,4]. Then the apparent ionic mobilities will be

$$\mu_{\pm} = \mu_{\pm}^{(0)} \pm \mu_{os.} \tag{47}$$

Electroosmosis in a closed-end tube

In a closed-end tube (we also assume that the tube is very long, then we can neglect the end effect when we are considering the fluid far from the ends), the solvent fluid pulled by the electric field E near the wall cannot keep its forward motion everywhere across the tube cross section. The fluid will be pushed back by the end walls and a counter flow is formed at the center (Fig. 1b). Owing to the mass conservation of solvent at any tube cross section, instead of eqn. 39, we have the boundary condition

$$\int_{-L}^{L} \mathrm{d}y \; v_0(y) = 0 \tag{48}$$

Another boundary condition is due to the tube-wall condition. For mathematical convenience we shall consider two limiting cases: rough wall and smooth wall.

The rough-wall cell. The rough-wall condition is

$$v_0(\pm L) = 0 \tag{49}$$

Then we may calculate the pressure gradient

$$P_x = \frac{3\varrho_L E}{(\lambda_s L)^2} \left(1 - \frac{\tanh \lambda_s L}{\lambda_s L}\right) \tag{50}$$

and another constant C in eqn. 36 to obtain the solution

$$v_0(y) = \frac{\varrho_L E}{\eta_0 \lambda_s^2} \left\{ \frac{1}{2} \left[3\left(\frac{y}{L}\right)^2 - 1 \right] - \frac{\cosh \lambda_s y}{\cosh \lambda_s L} - \frac{3\tanh \lambda_s L}{2\lambda_s L} \left(\frac{y^2}{L^2} - 1\right) \right\} \tag{51}$$

The characteristic behaviors are shown in Fig. 4. In most practical situations, $\lambda_s L \gg 1$. At where not very close to the tube wall, the solvent will move with a parabolic velocity profile[2]:

$$v_0(y) = \frac{v_{os.}}{2} \left(3\left(\frac{y}{L}\right)^2 - 1\right) \qquad (\lambda_s L \gg 1) \tag{52}$$

where

$$v_{os.} = \frac{\varrho_L E}{\eta_0 \lambda_s^2} \tag{53}$$

is called the electroosmotic velocity[2], and the constant pressure gradient P_x is given by

$$P_x = \frac{3 \varrho_L E}{(\lambda_s L)^2} \qquad (\lambda_s L \gg 1) \tag{54}$$

Then P_x and $v_{os.}$ are related by Poiseuille's law[3]
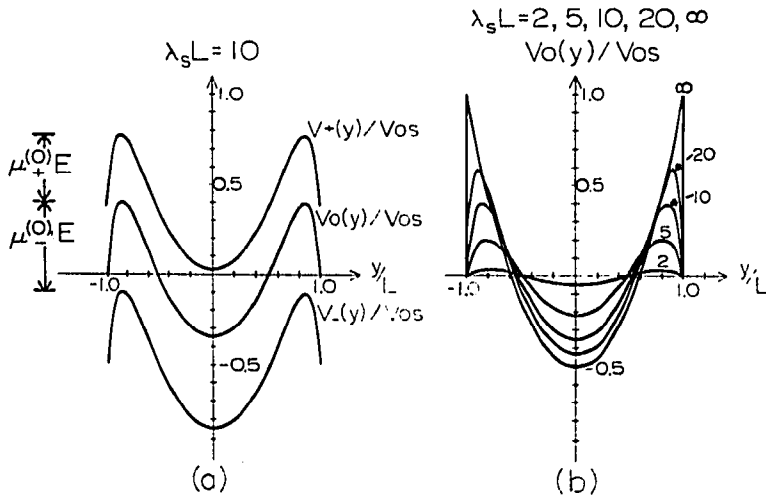
$$P_x = \frac{3\eta_0 v_{os.}}{L^2} \tag{55}$$

Fig. 4. Electroosmosis effect in a closed-end tube with rough wall. (a) The velocity profiles of component fluids. The ionic mobilities $\mu^{(0)}_{\pm}$ are chosen the same as in Fig. 3a, $\lambda_s L = 10$. (b) The velocity profiles of neutral solvent fluid for $\bar{\lambda}_s L = 2, 5, 10, 20$ and ∞.

and the velocity profile can be re-written in the Poisseuille form[2]

$$v_0(y) = v_{os.} + \frac{P_x}{2\eta_0}(y^2 - L^2) \tag{56}$$

The smooth-wall cell. If the wall surface is smooth, the stress of solvent at the wall will vanish, and we have

$$v_0'(\pm L) = 0 \tag{57}$$

Together with the boundary condition (48), we obtain the results:

$$P_x = \frac{\varrho_L E}{\lambda_s L} \tanh \lambda_s L \tag{58}$$

and

$$v_0(y) = \frac{\varrho_L E}{\eta_0 \lambda_s^2} \left\{ \frac{\lambda_s L}{3} \tanh \lambda_s L \left[\frac{3\left(\frac{y}{L}\right)^2 - 1}{2} \right] + \frac{\tanh \lambda_s L}{\lambda_s L} - \frac{\cosh \lambda_s y}{\cosh \lambda_s L} \right\} \tag{59}$$

The characteristic behavior of $v_0(y)$ for different values of $\lambda_s L$ is shown in Fig. 5. In practical cases, $\lambda_s L \gg 1$. At where not very near the tube walls,

$$v_0(y) \approx \frac{v_{os.}}{2} \left(3\left(\frac{y}{L}\right)^2 - 1 \right) \qquad (\lambda_s L \gg 1) \tag{60}$$
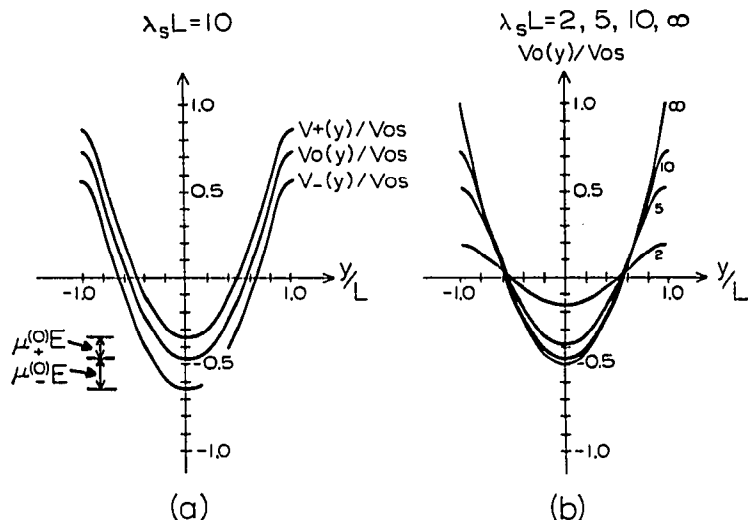
Fig. 5. Electroosmosis effect in a closed-end tube with smooth wall. (a) The velocity profiles of component fluids. The ionic mobilities $\mu_{\pm}^{(0)}$ are chosen the same as in Figs. 3a and 4a, $\lambda_s L = 10$. (b) The velocity profiles of neutral solvent fluid for $\lambda_s L = 2$, 5, 10 and ∞.

has the same form as the rough-wall case (eqn. 52). But the electroosmotic pressure

$$P_x = \frac{3\varrho_L E}{\lambda_s L} \qquad (\lambda_s L \gg 1) \tag{61}$$

and electroosmotic velocity

$$v_{os.} = \frac{\varrho_L E}{\eta_0 \lambda_s^2} \frac{\lambda_s L}{3} \tag{62}$$

are different from the values of rough-wall cases, eqns. 55 and 53, respectively. Since the electroosmotic velocity $v_{os.}$ is experimentally measurable, it is possible to determine the wall boundary condition (rough or smooth) from the experimental data. The bigger values of $v_{os.}$ and P_x in the smooth-wall case are physically expected because in the rough-wall case there exists the additional frictional force between wall and the fluid, which can slow down the fluid motion and reduce the electroosmotic velocity. The reversed pressure force (P_x) to cause the counter-flow will be proportionally smaller.

DISCUSSION AND CONCLUSION

In a typical electrophoresis system, the orders of magnitude of different quantities are listed below:
Mass of ion or solvent molecule

$$m_{\pm}, m_0 \approx 10^{-23} \text{ g}$$

Solvent molecular density

$n_0 \approx 10^{22} \text{ cm}^{-3}$

Ionic densities

$n_{\pm} \approx n_c \approx 10^{19} \text{ cm}^{-3}$

Ionic charge

$e \approx 4.8 \cdot 10^{-10} \text{ e.s.u.}$

Ionic mobilities

$\mu_{\pm}^{(0)} \approx 10^{-4} \text{ cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1} \approx 10^{-2} \text{ cm}^3 \cdot \text{sec}^{-1} \cdot \text{e.s.u.}^{-1}$

Room temperature

$T \approx 300 \text{ °K}$

Solvent shearing viscosity

$\eta_0 \approx 10^{-1} \text{ P}$

Solvent dielectric constant

$\varepsilon \approx 10^2$

Tube cross-sectional radius

$L \approx 1 \text{ cm}$

Applied electric field

$E \approx 10^3 \text{ V/cm}$

Then from eqn. 38, the ion–solvent frictional constant is

$$\xi_{\pm} = \frac{e}{\eta_0 \mu_{\pm}^{(0)}} \approx 10^{-30} \text{ c.g.s. unit} \tag{63}$$

From eqn. A18 of Appendix and the kinetic theory[5], the ionic shearing viscosity can be calculated and has the order of magnitude

$$\eta_{\pm} \approx \frac{n_{\pm} k_B T m_{\pm}}{n_0 \xi_{\pm}} \approx 10^{-10} \text{ P}$$

Then we have

$$\frac{\eta_{\pm}}{\eta_0} \approx 10^{-9} \tag{64}$$

and the relation (34) is justified. It is a good approximation to neglect the ionic shearing stress in the calculation.

From eqn. A18 of Appendix,

$$\xi_{\pm 0} \approx \xi_{+-}$$

if the sizes of the ions and solvent molecules are of the same order. Then the magnitude of the frictional force between ions will be small compared with that between ions and solvent molecules,

$$\left| \frac{\xi_{+-} n_+ n_- (v_+ - v_-)}{\xi_{+0} n_+ n_0 (v_+ - v_0)} \right| \approx \frac{n_-}{n_0} \ll 1$$

because the relative velocities $v_\alpha - v_\beta$ are of the same order. Then it is also a good approximation to neglect the ion–ion frictional force in the calculation.

The ionic screening constant λ_s can be estimated from eqn. 32, we have

$$\lambda_s \approx 10^6 \, cm^{-1} \tag{65}$$

$$\lambda_s L \approx 10^6 \tag{66}$$

then eqns. 44–47, 52–56 and 60–62 are excellent approximations, *i.e.*

Open-end cell with rough wall:

$$v_0(y) \approx v_{os.} = \frac{1}{\eta_0} \frac{\varrho_L E}{\lambda_s^2} = \frac{\varepsilon[-\varphi_L]}{4\pi\eta_0} \tag{67}$$

$$P_x = 0 \tag{68}$$

Closed-end cell:

$$v_0(y) \approx v_{os.} + \frac{P_x}{2\eta_0} (y^2 - L^2) \tag{69}$$

where

$$v_{os.} = \frac{\varepsilon[-\varphi_L]}{4\pi\eta_0} E \cdot \begin{cases} 1 & \text{rough tube wall} \\ \dfrac{\lambda_s L}{3} & \text{smooth tube wall} \end{cases} \tag{70}$$

and

$$P_x = \frac{3 \varrho_L E}{(\lambda_s L)^2} \cdot \begin{cases} 1 & \text{rough tube wall} \\ \dfrac{\lambda_s L}{3} & \text{smooth tube wall} \end{cases} \tag{71}$$

Then the apparent ionic mobility has the form

$$\mu_{\pm}(y) = \mu_{\pm}^{(0)} \pm \frac{\mu_{os.}}{2} \left[3\left(\frac{y}{L}\right)^2 - 1 \right] \tag{72}$$

where

$$\mu_{os.} = \frac{\varepsilon[-\varphi_L]}{4\pi\eta_0} \cdot \begin{cases} 1 & \text{rough tube wall} \\ \dfrac{\lambda_s L}{3} & \text{smooth tube wall} \end{cases} \tag{73}$$

The quantity $\mu_{os.}$ can be determined by measuring $\mu_{\pm}(y)$ experimentally (eqn. 72). Then we can determine the zeta potential $|\varphi_L|$ from eqn. 73. For example, from the result in Abramson's experiment[2,6],

$$\mu_{os.} = 1.8 \cdot 10^{-4} \, \text{cm}^2 \cdot \text{sec}^{-1} \cdot \text{V}^{-1}.$$

We may determine the order of magnitude of $|\varphi_L|$, P_x and $e|\varphi_L|/k_B T$ and the values obtained are listed in Table I.

TABLE I

VALUES OF $|\varphi_L|$, P_x AND $\dfrac{e|\varphi_L|}{k_B T}$ FOR ROUGH-WALL AND SMOOTH-WALL CELLS

	Rough wall	Smooth wall
Zeta potential of tube wall $|\varphi_L|$ (V)	10^{-2}	10^4
Pressure gradient P_x (dyne·cm^{-3})	10^{-2}	10^{-2}
$\dfrac{e|\varphi_L|}{k_B T}$	$\lesssim 1$	10^6

We find from Table I that the wall zeta potential value $|\varphi_L|$ is too big for the case of the smooth wall. The value for the rough wall is reasonable. Then we conclude that the rough-tube-wall boundary condition is close to the practical situation.

At room temperature, we find that the parameter $e|\varphi_L|/k_B T$ is not much smaller than unity; especially in the smooth-wall case, it is a big number. This means that the linear approximations (eqns. 28′, 29′) in our calculations are not satisfactory for a real fitting, especially in case of smooth wall, where $e|\varphi_L|/k_B T \gg 1$ and thus there is great amount of screening charge in the neighbourhood of the wall (eqn. 29). Then the exact numerical calculation in a computer is necessary. However, considering only the high-temperature limit, we have clearly seen the physical mechanism and characteristic behavior of the electroosmosis effect in this paper.

In this paper, because we neglect the ionic-fluid shearing stress in the calculation, the ionic flow velocity will always have the form

$$v_{\pm}(y) = v_0(y) \pm \mu_{\pm}^{(0)} E \tag{37}$$

There is no special boundary condition necessary for the calculation of $v_{\pm}(y)$. For example, in the closed-end tube case, $v_{\pm}(y)$ never satisfied the mass-conservation boundary condition, *i.e.*,

$$\int_{-L}^{L} dy \, v_{\pm}(y) \neq 0$$

Furthermore, in the rough-wall case,

$$v_{\pm}(\pm L) \neq 0.$$

Then it is obvious that the solutions obtained here by neglecting the ionic shearing stress are not exact. It is only expected to be approximate. But how good is it? Under what conditions is this approximation valid? This is an interesting problem currently under investigation and results will be published[7].

We have seen in this paper that the electroosmosis effect is essentially due to the existence of charges on the cell walls [then $\varphi_L \neq 0$]. It has been shown experimentally that the electroosmosis effect exists in a system with solvent fluid made of polar molecules (like water)[8,9]. Then the charges on the walls are physically expected to be the induced charges due to the permanent electric dipoles of the solvent molecules near the walls. Furthermore, the electrostatic screening effect of the electric dipole and quadrupole moments of the solvent molecules will also contribute to the electroosmosis effect. This has been neglected here. Then the electric characteristics of the solvent molecules play very important roles for the electroosmosis effect. These are very interesting for further investigations.

In this paper, we have re-derived the very important and useful fluid dynamic eqn. 2 of multiple component system. It provides the fundamental fluid dynamic equation for electrophoresis with an electroosmosis effect. For mathematical simplicity, we have considered a cell bounded by two planes at $y = \pm L$ and made calculations only at the high-temperature limit. The characteristic behavior of electroosmosis have been studied and discussed in detail. For a real system in a circular tube, cylindrical coordinates must be used. However, qualitative changes are not expected.

APPENDIX

Simple derivation of the modified Navier–Stokes equation for multiple component viscous fluid

We consider a fluid system with several types of molecules. The molecules of the same type α ($\alpha = 1, 2, \ldots, r$) have the same mass m_α and charge q_α and form a component fluid system with density

$$n_\alpha(\vec{r}, t) = \left\langle \sum_{j=1}^{N\alpha} \delta[\vec{r} - \vec{r}_j^{(\alpha)}(t)] \right\rangle \tag{A1}$$

and current density

$$\vec{J}_\alpha(\vec{r}, t) = \left\langle \sum_{j=1}^{N\alpha} \delta[\vec{r} - \vec{r}_j^{(\alpha)}(t)] \frac{\vec{p}_j^{(\alpha)}(t)}{m_\alpha} \right\rangle \tag{A2}$$

where N_α is the total number of molecules of type α. $\vec{r}_j^{(\alpha)}(t)$ $[\vec{p}_j^{(\alpha)}(t)]$ is the position [momentum] of the jth molecule of type a at time t. $\langle\ \rangle$ is the equilibrium ensemble average.

Following the same derivation as in ref. 10, we can obtain the particle conservation equation

$$\frac{\partial}{\partial t}\, n_\alpha(\vec{r},t) + \nabla\cdot\vec{J}_\alpha(\vec{r},t) = 0 \tag{A3}$$

and the momentum conservation equation

$$m_\alpha n_\alpha \left[\frac{\partial}{\partial t} + \vec{v}_\alpha\cdot\nabla\right]\vec{v}_\alpha(\vec{r},t) = \vec{F}_\alpha^{\mathrm{B}}(\vec{r},t) + \nabla\cdot\overleftrightarrow{T}_\alpha(\vec{r},t) \tag{A4}$$

for each component with molecules of type a, where ∇ is the gradient operator, and

$$\vec{v}_\alpha(\vec{r},t) = \vec{J}_\alpha(\vec{r},t)/n_\alpha(\vec{r},t) \tag{A5}$$

is the fluid velocity of component α.

$$\vec{F}_\alpha^{\mathrm{B}}(\vec{r},t) = \left\langle \sum_{j=1}^{N_\alpha}\delta[\vec{r}-\vec{r}_j^{(\alpha)}(t)]\,\vec{F}_j^{(\alpha)}(t)\right\rangle \tag{A6}$$

is the bulk force density and

$$\overleftrightarrow{T}_\alpha(\vec{r},t) = -m_\alpha\left\langle \sum_{j=1}^{N_\alpha}\delta[\vec{r}-\vec{r}_j^{(\alpha)}(t)]\left(\frac{\vec{p}_j^{(\alpha)}(t)}{m_\alpha}-\vec{v}_\alpha\right)\left(\frac{\vec{p}_j^{(\alpha)}(t)}{m_\alpha}-\vec{v}_\alpha\right)\right\rangle \tag{A7}$$

the stress force tensor on the component fluid of type a. $F_j^{(\alpha)}(t)$ is the total force acting on the jth molecule of type α at time t, and can be written as a sum of forces due to different sources:

$$\vec{F}_j^{(\alpha)}(t) = q_\alpha\,\vec{E}\,[\vec{r}_j^{(\alpha}(t),\,t] - \vec{F}_{tj}^{(\alpha)}(t) + \vec{F}_j^{\mathrm{ext.}}(t) \tag{A8}$$

where $\vec{E}[\vec{r}_j^{(\alpha)}(t),\,t]$ is the electric field at the location of the molecule, $\vec{F}_j^{\mathrm{ext.}}(t)$ is the force due to non-electric external source. $\vec{F}_{tj}^{(\alpha)}(t)$ is the frictional force due to the fluid (of all types) surrounding the jth molecule of type a. It can be written as[10,11]

$$\vec{F}_{tj}^{(\alpha)}(t) = -\sum_\beta \zeta_{\alpha\beta}\left\{\dot{\vec{r}}_j^{(\alpha)}(t) - \vec{v}_\beta\,[\vec{r}_j^{(\alpha)}(t),\,t]\right\} \tag{A9}$$

where $\dot{\vec{r}}_j^{(\alpha)}(t) - \vec{v}_\beta[\vec{r}_j^{(\alpha)}(t),\,t]$ is the relative velocity of the molecule of type α with respect to its surrounding fluid of type β. $\zeta_{\alpha\beta}$ is the frictional constant between a

molecule of type α and the fluid of type β. Substituting eqns. A8 and A9 into eqn. A6, following the same calculations as in ref. 10, we obtain the bulk force density

$$\vec{F}_\alpha^B(\vec{r},t) = q_\alpha n_\alpha(\vec{r},t)\,\vec{E}(\vec{r},t) - \sum_{\beta \neq \alpha} \zeta_{\alpha\beta}\bar{n}_\alpha(\vec{r},t)[\vec{v}_\alpha(\vec{r},t) - \vec{v}_\beta(\vec{r},t)] + \vec{F}_B^{ext\cdot}(\vec{r},t) \quad (A10)$$

where $\vec{F}_B^{ext\cdot}(\vec{r},t)$ is the bulk force density due to non-electric external source.

It is obvious from eqn. A10 that the term

$$\zeta_{\alpha\beta}\,n_\alpha(\vec{r},t)\,[\vec{v}_\alpha(\vec{r},t) - \vec{v}_\beta(\vec{r},t)] \qquad\qquad (A11)$$

· is the frictional force density acting on fluid of type α due to the fluid of type β. Conversely,

$$\zeta_{\beta\alpha}\,n_\beta(\vec{r},t)\,[\vec{v}_\beta(\vec{r},t) - \vec{v}_\alpha(\vec{r},t)] \qquad\qquad (A12)$$

is the frictional force density acting on fluid of type β due to the fluid of type α. By Newton's third law, we know that the two forces in eqns. A11 and A12 are action and reaction with each other, we have

$$\zeta_{\alpha\beta}\,n_\alpha(\vec{v}_\alpha - \vec{v}_\beta) = -\zeta_{\beta\alpha}\,n_\beta(\vec{v}_\beta - \vec{v}_\alpha)$$

Then we have

$$\zeta_{\alpha\beta} = \xi_{\alpha\beta}\,n_\beta \qquad\qquad (A13a)$$

and

$$\zeta_{\beta\alpha} = \xi_{\beta\alpha}\,n_\alpha \qquad\qquad (A13b)$$

with

$$\xi_{\alpha\beta} = \xi_{\beta\alpha} \qquad\qquad (A14)$$

is a constant characteristic of the molecular collisions between the two types of molecules α and β.

Substituting eqns. A13a and A13b into eqn. A10, the bulk force density can be written as

$$\vec{F}_\alpha^B(\vec{r},t) = q_\alpha n_\alpha(\vec{r},t)\,\vec{E}(\vec{r},t) - \sum_{\beta \neq \alpha} \xi_{\alpha\beta}n_\alpha(\vec{r},t)n_\beta(\vec{r},t)[\vec{v}_\alpha(\vec{r},t) - \vec{v}_\beta(\vec{r},t)] + \vec{F}_B^{ext\cdot}(\vec{r},t)$$

$$(A15)$$

The stress tensor $\overleftrightarrow{T}_\alpha$ is also due to the molecules collisions. It can be written in a standard form[11,12]

$$\overleftrightarrow{T}_\alpha(\vec{r},t) = -P_\alpha\overleftrightarrow{I} + \overleftrightarrow{\sigma}_\alpha(\vec{r},t) \qquad\qquad (A16)$$

where P_a is the partial pressure, $\overleftrightarrow{\sigma_a}$ the stress tensor of the component fluid of type a, and

$$\nabla \cdot \overleftrightarrow{\sigma_a} = \eta_a \nabla^2 \vec{v}_a + \left(\nu_a + \frac{\eta_a}{3}\right) \nabla(\nabla \cdot \vec{v}_a) \tag{A17}$$

η_a and ν_a are the viscosity coefficients of component fluid a.

In case of mixture of dilute gases, the frictional coefficients in eqns. A13a and A13b can be calculated from Boltzmann's kinetic theory[12,13]. By assuming hard sphere collision with total cross section $\sigma_{a\beta}$ between molecules of types a and β, the constant $\xi_{a\beta}$ can be calcultaed and has the form[13]

$$\xi_{a\beta} = \frac{5}{3\pi} \sigma_{a\beta} \sqrt{2\pi k_B T \frac{m_a m_\beta}{m_a + m_\beta}} \tag{A18}$$

where T is the absolute temperature and k_B the Boltzmann constant.

ACKNOWLEDGEMENTS

REFERENCES

1 H. A. Abramson, L. S. Moyer and M. H. Gorin, *Electrophoresis of Proteins and the Chemistry of Cell Surfaces*, Hafner, New York, 1964, Ch. 1 and 5.
2 C. C. Brinton, Jr. and M. A. Lauffer, in M. Bier (Editor), *Electrophoresis, Theory, Methods and Application*, Vol. 1, Academic Press, New York, 1959, Ch. 10.
3 E. Heftmann, *Chromatography*, Reinhold, New York, 1967, Ch. 10.
4 C. Fan, *Convection Phenomena in Electrophoresis Separation*, LMSC-HREC TR D306300 Lockheed Missiles and Space Company, Huntsville, Ala., December, 1972.
5 K. Huang, *Statistical Mechanics*, Wiley, New York, 1963, Ch. 5.
6 H. A. Abramson, L. S. Moyer and A. Voet, *J. Amer. Chem. Soc.*, 58 (1936) 2362.
7 T. W. Nee, in preparation and to be published.
8 R. W. Phillips and S. V. R. Mastrangelo, *J. Appl. Phys.*, 43 (1972) 3840.
9 F. Fairbrother and M. Balkin, *J. Chem. Soc. (London)*, 134 (1931) 1564.
10 T. W. Nee, *J. Chromatogr.*, 93 (1974) 7.
11 L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Addison and Wesley, Reading, Mass., 1959.
12 J. M. Burgers, *Flow Equations for Composite Gases*, Academic Press, New York, 1969.
13 T. W. Nee, unpublished results.