

Quantitative Theory of Electroosmotic Flow in Fused-Silica Capillaries Using an Extended Site-Dissociation–Site-Binding Model

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To optimize separations in capillary electrophoresis, it is important to control the electroosmotic mobility of the running buffer and the factors that affect it. Through the application of a site-dissociation–site-binding model, we demonstrated that the electroosmotic mobility could be controlled qualitatively and quantitatively by the parameters related to the physical and chemical properties of the running buffer: pH, cation valence, ionic strength, viscosity, activity, and dissociation constant. Our study illustrated that the logarithm of the number of apparent silanol sites on a fused-silica surface has a linear relationship with the pH of a buffer solution. The extension of the chemical kinetics approach allowed us to obtain the thickness of the electrical double layer when multivalent inorganic cations are present with monovalent cations in a buffer solution, and we found that the thickness of the electrical double layer does not depend on the charge of anions. The general equation to predict the electroosmotic mobility suggested here also indicates the increase of electroosmotic mobility with temperature. The general equation was experimentally verified by three buffer scenarios: (i) buffers containing only monovalent cations; (ii) buffers containing multivalent inorganic cations; and (iii) buffers containing cations and neutral additives. The general equation can explain the experimental observations of (i) a maximum electroosmotic mobility for the first scenario as the pH was varied at constant ionic strength and (ii) the inversion and maximum value of the electroosmotic mobility for the second scenario when the concentration of divalent cations was varied at constant pH. A good agreement between theory and experiment was obtained for each scenario.

Capillary electrophoresis (CE) is a liquid-phase separation technique and has been applied in many fields. Throughout many years since its emergence, researchers have understood that the driving force for conventional capillary zone electrophoresis is the bulk electroosmotic flow (EOF) under the presence of the electric field. However, the drawback of this separation technique is its poorer precision compared with the more mature and popular

separation technique, high-performance liquid chromatography, partly due to an imprecise control of EOF. This has significantly limited the acceptance and application of CE by industry, despite its low operating cost. Therefore, the purpose of this paper is to provide practical means for predicting EOF not only qualitatively but also quantitatively, through an established site-dissociation–site-binding model¹ from both a chemical equilibrium and a chemical kinetic point of view. With this insight, we may be able to understand and control EOF better.

The origin of EOF is directly related to the material made of the capillary. The most common material made of the capillary for CE is fused silica. Silica itself is silicon dioxide (SiO_2). There are many types of silica with varieties of different physical properties. The soluble form of silica is the monomeric acid, or $\text{Si}(\text{OH})_4$. All other forms of silica are the polymers of SiO_2 containing certain numbers of silanol (SiOH) groups; fused silica, a type of massive dense amorphous silica glass, is one of them. The catalyst of this process is the hydroxyl ion, OH^- . Therefore, the hydrolysis process is largely dependent upon the solution pH. As claimed in most publications,^{2–4} the pK_a for the equilibrium between $\text{Si}(\text{OH})_4$ and $(\text{OH})_3\text{SiO}^-$ is in the range of 9–10. Above pH 11, the hydroxyl ions convert $\text{Si}(\text{OH})_4$ to silicate ions and silicate ions leave the solid surface so that the silica continues to dissolve into the solution. Below pH 11, OH^- ion is only the catalyst that controls the rate at which silica dissolves until the solution reaches saturation.⁵ Smit et al.⁶ demonstrated that the characteristics of vitreous silica (or fused silica), after soaking in NaCl solution at pH 10 for up to 28 h, were changed. Its surface charge after the treatment was much lower than it was before. Therefore, the maximum pH of this study was up to pH 9 so that the characteristics of the fused silica were unchanged. We focus on establishing a mathematical formula that predicts the EOF inside the fused-silica capillary with consideration of varying pH, ionic strength, and valence charge of ions.

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THEORY

Electroosmosis. When a fused-silica capillary is filled with the buffer, the surface silanol (SiOH) groups are ionized to negatively charged silanoate (SiO⁻) groups catalyzed by the OH⁻ ions in the solution. The positive counterions in liquid phase will compensate the negative charge of the wall so that an electrical double layer (EDL) is created at the interface between the solid wall and the liquid phase. An electric potential difference across the double layer is created and called the zeta potential. Under the external applied voltage along the capillary, the positive counterions attracted to the negative capillary wall will move toward the cathode and form the electroosmotic flow. The velocity of the electroosmotic flow, v_{eo} , is given by the Smoluchowski equation⁷

$$v_{eo} = \epsilon \xi E / \eta \quad (1)$$

where ϵ is the permittivity of the buffer (and is commonly expressed as $\epsilon_0 \epsilon_r$, ϵ_0 is the permittivity of a vacuum, ϵ_r is the relative permittivity), ξ is zeta potential or the potential of EDL, E is the applied voltage per unit length (in V/m), and η is the viscosity of the buffer (in N m⁻² s (or Pa s)). Since $v_{eo} = \mu_{eo} E$, therefore,

$$\mu_{eo} = \epsilon \xi / \eta \quad (2)$$

where μ_{eo} is the electroosmotic mobility. Equation 2 is known as Helmholtz–Smoluchowski equation, and it is a qualitative expression of electroosmotic mobility. No assumptions are made in its derivation from the Poisson equation as to the actual structure of the EDL except that both η and ϵ retain their normal bulk values. To obtain the μ_{eo} quantitatively, we need to explore more about the zeta potential.

The variation of potential with distance from a charged surface of arbitrary shape is described by the Poisson equation,

$$\nabla^2 \psi = -\rho^* / \epsilon \quad (3)$$

where ∇^2 is the Laplacian operator, ψ is the potential at the given position within the EDL, and ρ^* is the charge density in three dimensions (i.e., C m⁻³).⁸ ψ is the same as ξ , which is just a different notation for the potential. For the subsequent text, we replace ψ with ξ . Considering the potential from the capillary wall perpendicular toward the center of the capillary, we define this dimension as the r -coordinate. Then the potential at the given position x within the EDL is described by the Poisson–Boltzmann equation,⁸

$$\frac{d^2 \xi}{dr^2} = -\frac{e}{\epsilon} \sum_i z_i n_{i0} \exp\left(\frac{-z_i e \xi}{kT}\right) \quad (4)$$

where e is elementary charge, z_i is the valence number, n_{i0} is the bulk concentration, k is the Boltzmann constant, and T is the temperature. Using the Debye–Hückel approximation that the

potential of EDL is less than 25 mV at 25 °C, the Poisson–Boltzmann equation can be simplified to

$$d^2 \xi / dr^2 = \kappa^2 \xi \quad (5)$$

and the solution of eq 5 is the Debye–Hückel equation,^{9,10}

$$\xi = \sigma \kappa^{-1} / \epsilon \quad (6)$$

where σ is the surface charge density at the place where the zeta potential is located and κ^{-1} is known as the Debye length, which is loosely the distance away from a charged species at which electrostatic interactions with other charged species become negligible.¹⁰ κ^{-1} is also referred as the thickness of the electrical double layer.⁹ Although the zeta potential of the electrical double layer is clearly defined theoretically, its precise quantitative meaning cannot be defined, because it is not clear at what location within the double layer the potential is measured.⁸ Researchers have suggested more detailed descriptions for the electrical double layer such as dividing the double layer into more sections (i.e., absorbed layer, compact layer, and diffuse layer¹¹). On the other hand, for our purpose of study, it is not critical to know the exact value of the potential at the specific position within the double layer. What we are interested in is the bulk effect of zeta potential of the electrical double layer on the electroosmotic mobility inside a fused capillary. We replace ξ in eq 2 with eq 6. Then the electroosmotic mobility can be expressed as

$$\mu_{eo} = \sigma \kappa^{-1} / \eta \quad (7)$$

The importance for eqs 6 and 7 is that they express the critical relationships of zeta potential and μ_{eo} with the surface charge density and thickness of the double layer. Although eqs 6 and 7 are obtained under the Debye–Hückel approximation and they are only theoretically valid when the surface potential is low (<25 mV), considering the ambiguity of the measurement of the potential and the dynamic charge of the capillary surface itself, it does not prohibit us from generalizing the concept explored by eq 7 empirically. Replacing the thickness of EDL κ^{-1} with symbol δ , we can qualitatively express μ_{eo} as

$$\mu_{eo} = \sigma \delta / \eta \quad (8)$$

In the following sections, we derive the quantitative relationships of surface charge density and thickness of EDL with pH, ionic strength, and species in the solutions through the application of a site-dissociation–site-binding model from chemical equilibrium and chemical kinetics point of views, respectively. The resulting empirical equations derived from eq 8 are not subject to the Debye–Hückel approximation.

Surface Charge Density. The term site-dissociation–site-binding model was suggested by Hunter.¹ The application of a

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chemical dissociation process in solution and surface to the electrical double layer was developed by Huang et al.¹² and others.^{11,13–16} These studies provided further understanding of the chemical process between the solution phase and the solid surface, yet the ideas were not incorporated into the evaluation of electroosmotic mobility. Tavares and McGuffin provided an empirical equation that was obtained through computer simulation of experimental data for the calculation of zeta potential.¹⁷ Mammen et al.¹⁰ took one step further by applying the dissociation model to the prediction of the electroosmotic mobility in a background electrolyte (BGE) when either monovalent or multivalent inorganic cations are present and suggesting an empirical equation to calculate μ_{eo} ; yet they did not consider the impact of pH variation on the electroosmotic mobility, which is explored extensively in this study. Furthermore, we also covered the scenarios when the monovalent cations coexist with multivalent inorganic cations in a buffer solution, a neutral additive is present in a buffer solution, or both. The derivation is based upon the assumptions that there is no interaction between the adsorbed cations, the silica surface is smooth and uniform, and the interaction between cations and silanolate ions is in a state of kinetic equilibrium. The positive counterions in the solution phase are considered as two groups: H^+ and other inorganic cations (M^+ or M^{m+}). The two types of cations as well as the neutral additives if present compete for the interaction with silanolate (SiO^-) groups on the wall as shown in Figure 1.

(1) BGE with Monovalent Cations. For the scenario when only monovalent cations are present in a BGE, at the capillary surface,



where the equilibrium constants $K_M^+ = [SiO^-M^+]/a_{M^+}[SiO^-]$ and $K_H = [SiOH]/a_{H^+}[SiO^-]$ and a is the activity of the subscripted species. The surface charge is contributed from SiO^- ions. Therefore, the charge density σ (in $C\ dm^{-2}$) is $F\ \{[SiO^-]\}$ and F is Faraday constant ($9.6485 \times 10^4\ C\ mol^{-1}$). $\{\}$ represents the surface concentration. Since Si-associated species are in the solid phase, the activity coefficients of these species are equal to 1. The number of apparent silanol groups $Q_{0,a}$ in all forms per unit area at the capillary surface can be expressed as $(\{[SiO^-]\} + \{[SiO^-M^+]\} + \{[SiOH]\})$. Then, we can derive the surface charge density as

$$\sigma = \frac{FQ_{0,a}}{1 + K_M a_{M^+} + K_H a_{H^+}} \quad (11)$$

(2) BGE with Multivalent Inorganic Cations. For the scenario when the buffer consists of an $M_n^{m+}A_m^{n-}$ type of inorganic

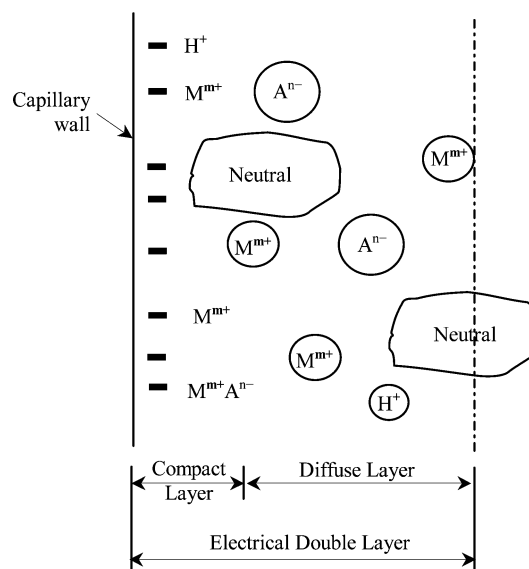


Figure 1. Simple scheme of the electrical double layer with neutral additives present in buffer. A " M^{m+} " or " H^+ " represents a nonsolvated cation. A " H^+ ", " M^{m+} ", and " A^{n-} " in circle represent a solvated ion. m here can be either 1 or more than 1. M^+ and M^{m+} can both be present in a buffer.

compound, m is a positive integer greater than 1 and n is a positive integer greater than 0, the following reactions 12 and 13 may occur on the capillary column wall in addition to reaction 9.



where $K_M^{m+} = [SiO^-M^{m+}]/a_{M^{m+}}[SiO^-]$ and $K_A = [SiO^-M^{m+}A^{n-}]/[SiO^-M^{m+}]a_{A^{n-}}$. The surface charge comes from SiO^- , SiO^-M^{m+} , and $SiO^-M^{m+}A^{n-}$. Therefore, the charge density σ is $F\ (\{[SiO^-]\} - (m-1)\{[SiO^-M^{m+}]\} + (n-m+1)\{[SiO^-M^{m+}A^{n-}]\})$. The activities of the species on the solid surface are equal to their surface concentrations. The total apparent silanol groups $Q_{0,a}$ in all forms are $(\{[SiO^-]\} + \{[SiOH]\} + \{[SiO^-M^{m+}]\} + \{[SiO^-M^{m+}A^{n-}]\})$. In other words, the excess positive charge on a silanolate–cation complex (SiO^-M^{m+}) attracts an anion so that a three-member complex, $SiO^-M^{m+}A^{n-}$, is formed. Additionally, since the silanolate is attached to the capillary wall, the three-member complex is immobile, and it is present at the kinetic equilibrium with the surroundings. Further attachment or exchange of molecules is possible between the interface of solid surface and the solution phase, but the formation of four- or more-member complexes on the solid surface of the capillary wall is less likely because the electric force toward the solid surface is much weaker when the distance gets further, and the repulsive force from the M^{m+} inorganic ions also resists to the formation of the complex with the additional layer of cations. In addition, we simplified the model by considering that one M^{m+} interacts with one SiO^- (1:1) as indicated in reaction 12. As we can see later, the bulk effect of multivalent inorganic cations on μ_{eo} is reflected through the empirical equilibrium constant K_M^{m+} . The surface charge density σ can be expressed as

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$$\sigma = FQ_{0,a} \times \frac{1 - (m-1)K_M a_{M^{m+}} + (n-m+1)K_M a_{M^{m+}} K_A a_{A^{n-}}}{1 + K_H a_{H^+} + K_M a_{M^{m+}} + K_M a_{M^{m+}} K_A a_{A^{n-}}} \quad (14)$$

(3) BGE with Neutral Additives. Most of the neutral species in the capillary electrophoresis applications are dipolar molecules or molecules with dipolar functional groups. When the neutral additives, N, are added to the buffer consisting of an $M_n^{m+}A_m^{n-}$ type of compound, due to the electrostatic interactions between the silanolate ions and the dipoles of the neutral species, the neutral species compete with the cations and a certain amount of silanolate sites are covered by the neutral molecules, which is expressed in eq 15. Although the net charge of the SiO^-N complexes is negative, the negative charge from SiO^- ion is localized on the solid surface so that the outer layer of these sites is noncharged and therefore is considered as being neutral and shown in Figure 1.



where $K_N = [SiO^-N]/[SiO^-][N]$ and K_N is the equilibrium constant of eq 15. The unit of concentration of a neutral compound, [N], is in weight/volume. The net charge on the second layer is not changed since the neutral species carry no charge. Therefore, the expression of apparent silanol sites $Q_{0,a}$ is $(\{[SiO^-]\} + \{[SiOH]\} + \{[SiO^-M^{m+}]\} + \{[SiO^-M^{m+}A^{n-}]\} + \{[SiO^-N]\})$. Similar to eqs 11 and 14, the expression of charge density σ for the buffer system containing both multivalent inorganic cations and neutral species are revised due to the addition of term $K_N[N]$ at the denominator.

$$\sigma = \frac{1 - (m-1)K_M a_{M^{m+}} + (n-m+1)K_M a_{M^{m+}} K_A a_{A^{n-}}}{1 + K_H a_{H^+} + K_M a_{M^{m+}} + K_M a_{M^{m+}} K_A a_{A^{n-}} + K_N[N]} FQ_{0,a} \quad (16)$$

When $m = 1$, $K_A \approx 0$, eq 16 can be simplified to eq 17 for a buffer containing monovalent cations and neutral species,

$$\sigma = \frac{1}{1 + K_H a_{H^+} + K_M a_{M^+} + K_N a_N} \times FQ_{0,a} \quad (17)$$

Thickness of Electrical Double Layer. The silanol groups in the inner capillary wall are ionizable and form a negatively charged layer. The same chemical process is evaluated from the perspective of kinetics. The positive counterions are attracted to the negatively charged surface under the electrostatic forces. This simple treatment is similar to that of the “double-sphere” model for a reaction between two ions.¹⁸ We assume that the buffer solution in the capillary is continuous, that is, the dielectric constant is the same throughout. For a diluted buffer solution, a monovalent cation approaches a silanolate ion (SiO^-) and forms an activated complex in which the center of the ions is separated

by a distance x_1 and is equal to the thickness of the electrical double layer, δ . (See the solution in the Supporting Information for more detail.)

$$\delta = x_1 = \frac{1}{F} \sqrt{\frac{\epsilon RT}{2000I}} \quad (18)$$

where 1000 is the unit conversion factor, R is the universal gas constant, and I is the ionic strength. The expression of x_1 is the same as that of Debye length (κ^{-1}).^{1,19,20}

When a multiply charged cation is present in the solution, an anion in the solution may be attracted to it by the electric force. For the same chemical process in a diluted solution described in reactions 12 and 13, the average thickness of the electrical double layer δ is resolved as (See the solution in the Supporting Information for more detail.)

$$\delta = \frac{1}{F} \sqrt{\frac{\epsilon RT}{2000I}} \frac{1 + K_A a_{A^{n-}} \left(1 + \sqrt{\frac{z_M}{z_M - 1}}\right)}{1 + K_A a_{A^{n-}}} \quad (19)$$

This is the application of the chemical kinetics when both monovalent cations and multivalent inorganic cations are present. Interestingly, the thickness of the electrical double layer was found to depend on the charge of the cations, not upon the charge of the anions. For the buffers containing neutral additives, the thickness of the electrical double layer due to the addition of neutral additives is not affected since the neutral species carry no charge. The thickness of EDL obtained from eqs 18 or 19 is the result of the bulk effect of a given buffer solution.

Quantitative Description of Electroosmotic Mobility. In general, if p types of monovalent cations $M_{i,1}$ and q types of neutral species N_j coexist with one type of multivalent inorganic cation M_X of a positive charge of m in a buffer solution, since it is very rare to have more than one type of multivalent inorganic cation in a buffer solution, and there is one type of dominant anion A with a negative charge of n , the surface charge density σ , the thickness of electrical double layer δ , and the electroosmotic mobility μ_{eo} can be summarized as

$$\sigma = FQ_{0,a} \times \frac{1 - (m-1)K_{M_X} a_{M_X^{m+}} + (n-m+1)K_{M_X} a_{M_X^{m+}} K_A a_{A^{n-}}}{1 + K_H a_{H^+} + \sum_{i=1}^p K_{M_{i,1}} a_{M_{i,1}^+} + \sum_{j=1}^q K_{N_j} [N]_j + K_{M_X} a_{M_X^{m+}} (1 + K_A a_{A^{n-}})} \quad (20)$$

$$\delta = \frac{1}{F} \sqrt{\frac{\epsilon RT}{2000I}} \times \frac{\sum_{i=1}^p K_{M_{i,1}} a_{M_{i,1}^+} + K_{M_X} a_{M_X^{m+}} \left(1 + K_A a_{A^{n-}} \left(1 + \sqrt{\frac{m}{m-1}}\right)\right)}{\sum_{i=1}^p K_{M_{i,1}} a_{M_{i,1}^+} + K_{M_X} a_{M_X^{m+}} (1 + K_A a_{A^{n-}})} \quad (21)$$

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Replacing the charge density σ and the thickness δ in eq 8 with

eqs 20 and 21, we have

$$\mu_{eo} = \sqrt{\frac{\epsilon RT}{2000I}} \times \frac{Q_{0,a}}{\eta} \times \frac{1 - (m-1)K_{M_X}a_{M_X^{m+}} + (n-m+1)K_{M_X}a_{M_X^{m+}}K_Aa_{A^{n-}}}{1 + K_Ha_{H^+} + \sum_{i=1}^p K_{M_{Li}}a_{M_{Li}^+} + \sum_{j=1}^q K_{N_j}[N]_j + K_{M_X}a_{M_X^{m+}}(1 + K_Aa_{A^{n-}})} \times \frac{\sum_{i=1}^p K_{M_{Li}}a_{M_{Li}^+} + K_{M_X}a_{M_X^{m+}} \left(1 + K_Aa_{A^{n-}} \left(1 + \sqrt{\frac{m}{m-1}}\right)\right)}{\sum_{i=1}^p K_{M_{Li}}a_{M_{Li}^+} + K_{M_X}a_{M_X^{m+}}(1 + K_Aa_{A^{n-}})} \quad (22)$$

When only monovalent cations are present in BGE,

$$\mu_{eo} = \sqrt{\frac{\epsilon RT}{2000I}} \frac{Q_{0,a}}{\eta} \frac{1}{(1 + K_Ma_{M^+} + K_Ha_{H^+})} \quad (23)$$

When a neutral additive is present in a BGE with monovalent cations,

$$\mu_{eo} = \sqrt{\frac{\epsilon RT}{2000I}} \frac{Q_{0,a}}{\eta} \frac{1}{1 + K_Ha_{H^+} + K_Ma_{M^+} + K_N[N]} \quad (24)$$

The effects of a neutral additive on μ_{eo} are through an increase in viscosity, a decrease in permittivity, and an increase in the denominator of the last term in eq 24 due to the addition of $K_N[N]$. All of the three factors result a decrease in μ_{eo} . This is supported by eq 24 and the experimental results in Table 5.

EXPERIMENTS

Instrument and Apparatus. All experiments were performed on an Agilent Hewlett-Packard ³DCE instrument, model G1600AX, equipped with a UV diode array detector. Chemstation software Rev. A.06.03 was used for data acquisition (20 Hz). Fused-silica capillaries from the same batch (Polymicro Technologies, Phoenix, AZ) with 50- μ m inner diameter, 365- μ m outer diameter, 24.5-cm effective length, and 33-cm total length were used. The cassette holding the capillary column was controlled at 25 °C. The data were collected at three wavelengths, 200, 214, and 234 nm. The data collected at 200 nm were used for quantitation. The pH of all solutions was measured by Orion pH meter, model 420A. Fresh capillaries were pretreated by flushing with 1.0 N NaOH for 10 min, 0.1 N NaOH for 10 min, water for 10 min, and the running buffer for 40 min. This procedure was also used at the beginning of each sequence of runs. The 40 min of flushing buffers was applied between different buffer solutions and 2 min of flushing the buffer before injection of samples. Triplicate injections of the samples were made to measure the electroosmotic mobility and viscosity of each buffer solution. The capillary was flushed with water for 10 min at the end of each sequence.

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Chemicals and Solutions. Purified DI water was from a Barnstead E-pure filtration system with a resistance of at least 18 M Ω . Methanol and phosphoric acid (reagent grade, 85%) were purchased from Fisher Scientific. Sodium hydroxide pellets and barium acetate were purchased from J. T. Baker (Philipsburg, NJ). Propiophenone and hydroxyethylcellulose (HEC, M_r , ~250 000) were purchased from Aldrich (Milwaukee, WI). Standard pH buffers at 4.0, 7.0, and 10.0 were purchased from VWR (West Chester, PA). Glacial acetic acid was purchased from Corco Chemical Corp. (Fairless Hills, PA). Four different concentrations of monovalent cationic buffers, sodium ions at 10, 15, 20, and 25 mM, were prepared by transferring controlled volumes of 0.1 N NaOH in certain amounts of water and adjusting pH to 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0 with 1 N H₃PO₄ and then diluted H₃PO₄. Concentrations of multivalent cationic buffers, barium acetate at 5, 10, 20, 30, 40, 50, and 100 mM, were prepared by weighing the controlled amount of barium acetate salt and adjusting pH to 4.5, 5.0, and 5.6 by adding 0.1 or 1.0 M acetic acid. Monovalent cationic buffers with HEC containing 0.05, 0.1, 0.15, and 0.20% (w/v %) HEC were prepared in 5 mM sodium phosphate buffer solution at pH 4.0 and pH 5.7. The samples were prepared by weighing ~5 mg of propiophenone and dissolving it in 0.25 mL of methanol first. Then, the solutions were diluted in 5 mL of the lowest concentration of buffer at the lowest pH for each category of buffer solutions.

Measurement of Electroosmotic Mobility. Sample solutions were used for measurement of electroosmotic mobility for each background electrolyte. The electroosmotic mobility of a monovalent cationic buffer solution was measured and calculated by $L_d L_t / (t_0 - 0.5t_{rmp})V$ or the product of L_d and L_t (represent the effective and total capillary lengths, respectively) divided by the product of the adjusted time ($t_0 - 0.5t_{rmp}$, where t_0 is the migration time of the neutral marker that was propiophenone and t_{rmp} is the voltage ramp time) and applied voltage V .

For buffers containing multivalent inorganic cations or neutral additives in which the electroosmotic mobility was quite low, the electroosmotic mobility was measured by Williams and Vigh's method²¹ and was determined by the time differences between the sample signals from the electropherograms as shown in eq 25,

$$\mu_{eo} = \frac{(t_3 + t_1 - 2t_2) L_d L_t}{\left(t_3 + \frac{t_{inj}}{2} - t_d\right) V t_v} \quad (25)$$

where t_1 , t_2 , and t_3 are the retention times of the sample signals, t_{inj} is the time consumed per injection of the sample, t_v is the time used for voltage application, t_d is the electronic delay time, which was 0.1 s, L_d is the effective length to the detection window, L_t is the total length of the capillary column, and V is the applied voltage. The voltage ramping up and down times were zero, so they are not shown in eq 25.

Measurement of Viscosity. Except as stated otherwise, the viscosity of a buffer solution with the neutral additive (HEC) was measured by using the capillary electrophoresis instrument. A sample plug was introduced into the capillary by hydrodynamic

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Table 1. Calculation of Charge Density, Thickness of EDL, and Electroosmotic Mobility of Buffers Containing Monovalent Cations

pH	[Na] (M)	γ_{Na^+}	ionic strength ($\times 10^{-2}$ M)	viscosity ^e η (10^{-4} Pa s)	charge density ^a (C/dm ²)	thickness of EDL ^b (10^{-9} m)	μ_{eo} (10^{-8} m ² /V·s)		error of μ_{eo} ^d (%)
							calcd ^c	exptl	
4.0	0.01	0.902	1.00	8.94	1.01×10^{-4}	3.04	3.44	3.64	-5.5
4.0	0.015	0.882	1.50	8.95	1.02×10^{-4}	2.48	2.83	2.76	2.5
4.0	0.02	0.871	2.00	8.97	1.01×10^{-4}	2.15	2.42	2.52	-3.9
3.9	0.025	0.861	2.50	8.99	9.98×10^{-5}	1.92	2.14	1.87	14.2
5.0	0.01	0.902	1.01	8.94	1.40×10^{-4}	3.03	4.74	4.52	4.9
5.0	0.015	0.882	1.51	8.95	1.40×10^{-4}	2.48	3.86	3.76	2.7
5.0	0.02	0.871	2.01	8.97	1.40×10^{-4}	2.14	3.34	3.54	-5.7
5.0	0.025	0.861	2.52	8.99	1.40×10^{-4}	1.92	2.98	2.64	12.9
6.0	0.01	0.902	1.06	8.93	1.91×10^{-4}	2.96	6.33	6.45	-1.8
6.0	0.015	0.882	1.58	8.95	1.91×10^{-4}	2.42	5.16	6.16	-16.2
6.0	0.02	0.871	2.11	8.96	1.91×10^{-4}	2.09	4.46	5.52	-19.1
6.0	0.025	0.861	2.65	8.97	1.92×10^{-4}	1.87	4.01	5.20	-22.9
7.0	0.01	0.902	1.28	8.91	2.60×10^{-4}	2.69	7.85	7.45	5.4
7.0	0.015	0.882	1.92	8.92	2.60×10^{-4}	2.20	6.41	6.03	6.2
7.0	0.02	0.871	2.56	8.93	2.60×10^{-4}	1.90	5.54	5.87	-5.6
7.0	0.025	0.861	3.17	8.94	2.60×10^{-4}	1.71	4.97	5.30	-6.1
8.0	0.01	0.902	1.46	8.92	3.39×10^{-4}	2.52	9.57	8.23	16.3
8.0	0.015	0.882	2.20	8.93	3.39×10^{-4}	2.05	7.78	7.39	5.2
8.0	0.02	0.871	2.93	8.94	3.39×10^{-4}	1.78	6.73	6.72	0.2
8.0	0.025	0.861	3.66	8.95	3.39×10^{-4}	1.59	6.02	6.07	-0.9
9.0	0.01	0.902	1.50	8.92	3.10×10^{-4}	2.48	8.63	7.25	19.0
9.0	0.015	0.882	2.24	8.94	3.10×10^{-4}	2.03	7.05	7.12	-1.0
9.0	0.02	0.871	2.99	8.95	3.10×10^{-4}	1.76	6.09	6.98	-12.7
9.0	0.025	0.861	3.74	8.96	3.10×10^{-4}	1.57	5.44	6.55	-16.9

^a Calculated by using eqs 11 and 27. ^b Calculated by using eq 18. ^c Calculated by using eqs 23 and 27. ^d Error of μ_{eo} (%) = [(experimental value - calculated value)/experimental value] $\times 100$. ^e Data were extrapolated from the viscosity of sodium phosphate salts by using the weight fraction of monobasic, dibasic, and tribasic forms at the same temperature.²⁶

Table 2. Experimentally Determined Parameters

parameter	value	parameter	value
K_{Na}	0	α_{Na}	0.864
K_{H}	1.72×10^9	β_{Na}	0.517
K_{Ba}	18.3	α_{Ba}	0.964
K_{Acetate}	7.5	β_{Ba}	0.570
K_{HEC}	4.32×10^4	α_{HEC}	1.01
		β_{HEC}	2.54

injection. Then, a constant pressure was applied to push the sample out of the capillary column with the tested solution such as water and each buffer solution. The migration times of the sample plugs were recorded, and those obtained from the buffer solutions were compared with that of water. Since the temperature was maintained the same, the viscosity of the solution was proportional to the retention time of the sample signal. The viscosity of the buffer solution was the viscosity of the water multiplied by the ratio of t_{buf} and t_{water} (the migration times of the sample plugs in the buffer solution and water, respectively).

RESULTS AND DISCUSSION

Electroosmotic Mobility of the Buffers Consisting of Monovalent Cations. The activities of cations or sodium ions were calculated based upon the known concentrations of the ions. The activity coefficient, γ , of the ions at 25 °C were taken from Table 8-1 in ref 22 and interpolated between different concentrations. K_{Na} is the equilibrium constant and defined in the same

Table 3. Number of Apparent Silanol Sites $Q_{0,\text{A}}$ Related to pH

pH	[Na ⁺] (M)	$Q_{0,\text{a}}$ (mol/dm ²) ^a	$-\log Q_{0,\text{a}}$
4.0	0.010	1.93×10^{-4}	3.72
4.0	0.015	1.81×10^{-4}	3.74
4.0	0.020	1.93×10^{-4}	3.72
3.9	0.025	2.09×10^{-4}	3.68
5.0	0.010	2.48×10^{-5}	4.60
5.0	0.015	2.48×10^{-5}	4.60
5.0	0.020	2.48×10^{-5}	4.60
5.0	0.025	2.48×10^{-5}	4.60
6.0	0.010	3.40×10^{-6}	5.47
6.0	0.015	3.40×10^{-6}	5.47
6.0	0.020	3.40×10^{-6}	5.47
6.0	0.025	3.27×10^{-6}	5.49
7.0	0.010	4.66×10^{-7}	6.33
7.0	0.015	4.66×10^{-7}	6.33
7.0	0.020	4.66×10^{-7}	6.33
7.0	0.025	4.66×10^{-7}	6.33
8.0	0.010	6.25×10^{-8}	7.20
8.0	0.015	6.37×10^{-8}	7.20
8.0	0.020	6.37×10^{-8}	7.20
8.0	0.025	6.37×10^{-8}	7.20
9.0	0.010	8.72×10^{-9}	8.06
9.0	0.015	8.72×10^{-9}	8.06
9.0	0.020	8.72×10^{-9}	8.06
9.0	0.025	8.72×10^{-9}	8.06

^a Calculated from eq 27.

way as K_{M} for eq 10. The value of K_{Na} was obtained by fitting the experimentally determined μ_{eo} with eq 23. K_{Na} was found to be zero, which indicates that the dissociation of SiO^-Na^+ was so large that, at a given moment, the presence of SiO^-Na^+ was negligible.

(22) Harris, D. C. *Quantitative Chemical Analysis*, 5 ed.; W. H. Freeman and Co.: New York, 1999.

Table 4. Calculation of Charge Density, Thickness of EDL, and Electroosmotic Mobility of Buffers Containing Multivalent Inorganic Cations

(CH ₃ COO) ₂ Ba concn (M)	pH	initial concn of acetic acid (M)	ionic strength (M)	viscosity η ($\times 10^{-4}$ Pa·s) ^e	charge density ^a (C/dm ²)	thickness of EDL ^b (m)	μ_{eo} (m ² /V·s)		error of μ_{eo} ^d (%)
							calcd ^c	exptl	
0.005	4.5	0.01	8.19×10^{-3}	8.94	4.67×10^{-5}	3.41×10^{-9}	1.76×10^{-8}	1.53×10^{-8}	-15.3
0.020	4.5	0.035	2.88×10^{-2}	9.07	4.10×10^{-5}	1.86×10^{-9}	8.97×10^{-9}	1.04×10^{-8}	13.6
0.030	4.5	0.06	4.61×10^{-2}	9.16	3.62×10^{-5}	1.50×10^{-9}	6.56×10^{-9}	7.58×10^{-9}	9.0
0.050	4.5	0.10	8.24×10^{-2}	9.33	2.61×10^{-5}	1.16×10^{-9}	3.74×10^{-9}	3.24×10^{-9}	-15.6
0.100	4.5	0.18	1.45×10^{-1}	9.72	8.76×10^{-6}	9.26×10^{-10}	7.15×10^{-10}	7.44×10^{-10}	4.0
0.005	5.0	0.0035	8.28×10^{-3}	8.94	4.76×10^{-5}	3.32×10^{-9}	1.78×10^{-8}	1.67×10^{-8}	-7.0
0.010	5.0	0.0056	1.42×10^{-2}	8.99	4.61×10^{-5}	2.61×10^{-9}	1.38×10^{-8}	1.53×10^{-8}	9.3
0.020	5.0	0.0124	3.15×10^{-2}	9.07	4.12×10^{-5}	1.79×10^{-9}	8.87×10^{-9}	1.05×10^{-8}	15.6
0.040	5.0	0.020	5.33×10^{-2}	9.25	3.50×10^{-5}	1.40×10^{-9}	6.08×10^{-9}	6.38×10^{-9}	4.7
0.050	5.0	0.025	6.98×10^{-2}	9.33	3.04×10^{-5}	1.25×10^{-9}	4.73×10^{-9}	4.81×10^{-9}	1.5
0.005	5.6	0.001	9.27×10^{-3}	8.94	4.87×10^{-5}	3.21×10^{-9}	1.81×10^{-8}	1.76×10^{-8}	-2.7
0.010	5.6	0.002	1.86×10^{-2}	8.99	4.60×10^{-5}	2.29×10^{-9}	1.26×10^{-8}	1.40×10^{-8}	10.0
0.030	5.6	0.005	4.74×10^{-2}	9.16	3.76×10^{-5}	1.48×10^{-9}	7.03×10^{-9}	7.32×10^{-9}	4.0
0.040	5.7	0.006	7.52×10^{-2}	9.25	3.02×10^{-5}	1.22×10^{-9}	4.77×10^{-9}	4.49×10^{-9}	-3.2
0.050	5.6	0.008	7.98×10^{-2}	9.33	2.82×10^{-5}	1.18×10^{-9}	4.26×10^{-9}	3.81×10^{-9}	-12.0
0.100	5.6	0.014	1.39×10^{-1}	9.72	1.01×10^{-5}	9.34×10^{-10}	9.11×10^{-10}	8.98×10^{-10}	-1.4

^a Calculated by using eqs 16 and 27. ^b Calculated by using eq 19. ^c Calculated by using eqs 22 and 27. ^d Error of μ_{eo} (%) = [(experimental value - calculated value)/experimental value] $\times 100$. ^e Data were extrapolated from the viscosity of sodium acetate at the same temperature.²⁶

Table 5. Calculation of Charge Density, Thickness of EDL, and Electroosmotic Mobility of the Buffers Containing Neutral Additives

pH	[Na] (M)	HEC (%, w/v)	ionic strength ($\times 10^{-3}$ M)	viscosity η (Pa·s)	charge density ^a ($\times 10^{-4}$ C/dm ²)	thickness of EDL ^b ($\times 10^{-9}$ m)	μ_{eo} ($\times 10^{-8}$ m ² /V·s)		error of μ_{eo} ^d (%)
							calcd ^c	exptl ^e	
4.00	0.005	0	5.00	8.36×10^{-4}	1.13	4.33	6.74	6.71	-0.5
4.65	0.005	0.05	5.00	9.66×10^{-4}	1.33	4.33	5.45	5.75	5.3
4.83	0.005	0.1	5.00	1.19×10^{-3}	1.40	4.33	3.99	3.66	-9.0
4.96	0.005	0.15	5.00	1.38×10^{-3}	1.44	4.33	2.97	3.20	7.3
5.11	0.005	0.2	5.00	1.80×10^{-3}	1.50	4.33	1.86	1.83	-1.4

^a Calculated by using eq 17. ^b Calculated by using eq 18. ^c Calculated by using eq 24. ^d Error of μ_{eo} (%) = [(experimental value - calculated value)/experimental value] $\times 100$. ^e Calculated by using eq 25.

The value of K_H was determined to be 1.72×10^9 , or the value of dissociation constant K_{SiOH} ($1/K_H$) is 5.83×10^{-10} .

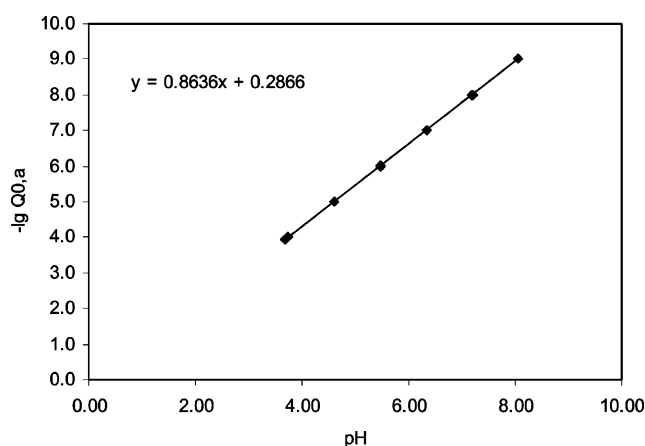
It was found that the values of $Q_{0,a}$ among different pH were much different. Additionally, it was noticed that there was a linear relationship between the negative logarithm of the numbers of the apparent silanol sites per unit area, $Q_{0,a}$, and the corresponding pH, shown in eq 26, Table 3 and Figure 2.

$$-\log Q_{0,a} = 0.864 \text{ pH} + 0.287 \quad (26)$$

The correlation coefficient of eq 26 (R^2) was not statistically different from unity. After rearranging the eq 26, we obtained

$$Q_{0,a} = \beta \{a_{H^+}\}^\alpha \quad (27)$$

where α is the slope of the line in eq 26 (0.864 in this case) and β is $10^{-\text{intercept}}$ (or 0.517 in this case). Both α and β are experimentally determined constants, and they are unitless. The values of both α and β were found to be in the range between 0 and 2 and 0 and 10, respectively. (Note: The unknown parameters K_H , K_{Na} , α_{Na} , and β_{Na} were obtained through Microsoft Excel-Solver by a simultaneous fit of the data into eqs 23 and 27 listed

**Figure 2.** Negative natural logarithm of the number of apparent silanol sites $Q_{0,a}$ vs pH.

in Table 2.) α and β reveal the capillary surface condition, and their values depend on how the capillary column is treated and used. Equation 27 illustrates that the apparent silanol sites are strongly dependent upon the pH of buffer. Both eq 18 and the calculated data demonstrated that the thickness of EDL decreases with an increase of ionic strength. The agreement of the fitted

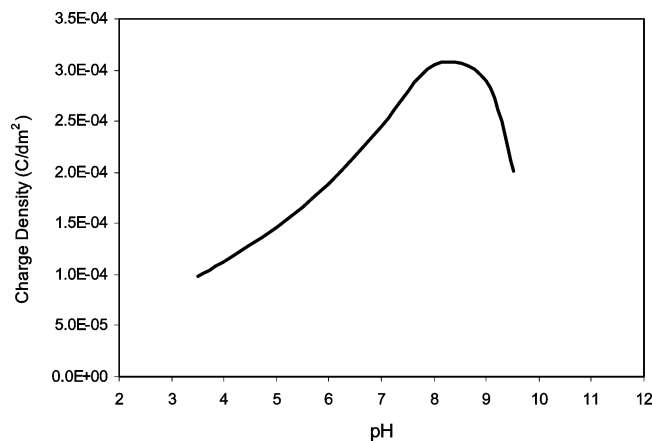


Figure 3. Dependence of charge density on pH at a sodium concentration of 10.0 mM. The charge density was calculated by using eqs 11 and 27. The maximum pH of the experimental study was up to pH 9.

μ_{eo} with the experimentally obtained μ_{eo} was demonstrated by the errors of μ_{eo} (%) shown in Table 1. It was found that the theoretical model did not fit well for the experimental data of EOF and zeta potential at pH 10. This is quite possibly due to the solvation of SiOH at pH above its pK_a value (9.23).

Dependence of Charge Density and μ_{eo} on the pH of Solution. The data in Table 1 indicated that there is a maximum charge density and maximum μ_{eo} at about pH 8 when the ion concentration was held constant. A maximum charge density and μ_{eo} at the sodium concentration of 0.01 M is also demonstrated in Figures 3 and 4. When the buffer solution concentration is held constant, the changes of the ionic strength and the buffer viscosity due to the change of pH are considered negligible. Taking the derivative eqs 20 and 22 over the derivative of proton activity a_{H^+} , at the maximum, there must be $d\sigma/da_{H^+} = 0$ and $d\mu_{eo}/da_{H^+} = 0$. After resolving the derivative equations, we can obtain that the maximum charge density or μ_{eo} is reached when

$$pH = \log \left(\frac{K_H}{P} \frac{1 - \alpha}{\alpha} \right) \quad (28)$$

where

$$P = 1 + \sum_{i=1}^p K_{M_{Li}} a_{M_{Li}^+} + \sum_{j=1}^q K_{N_j} a_{N_j} + K_{M_X} a_{M_X^{m+}} (1 + K_A a_{A^{n-}})$$

When $\alpha = 1$, there is no maximum in the charge density or maximum μ_{eo} and eq 28 does not apply. In this experiment in which only sodium ions were present in the buffers, $P = 1 + K_{Na} a_{Na}$, and a maximum charge density σ_{max} at the maximum electroosmotic mobility $\mu_{eo,max}$ existed when the pH was at ~ 8.5 calculated by eq 28. Therefore, the suggested model agrees with the experimental data quite well, and this is shown in Figure 4. The observation of the maximum μ_{eo} was also reported elsewhere in a study on μ_{eo} versus pH at a constant concentration of ionic solution.²³

(23) Sonnefeld, J.; Lobbus, M.; Vogelsberger, W. *Colloids Surf., A: Physicochem. Eng. Aspects* **2001**, *195*, 215–225.

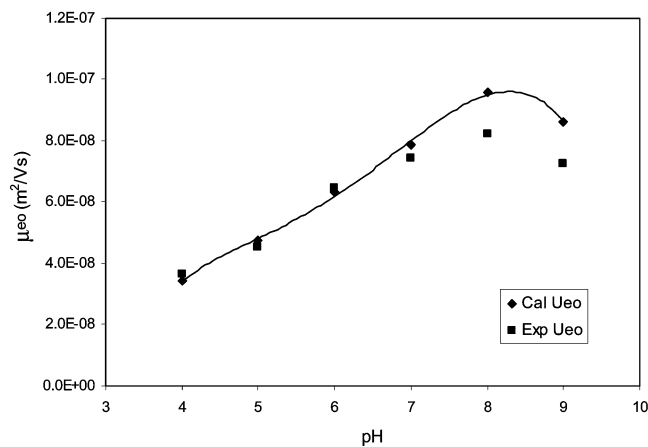


Figure 4. pH dependence of predicted and experimentally observed μ_{eo} at a sodium concentration of 10.0 mM. The predicted μ_{eo} was calculated by using eqs 23 and 27. The line is drawn through the calculated μ_{eo} data to guide the eyes. Cal Ueo = calculated μ_{eo} . Exp Ueo = experimentally observed μ_{eo} .

Electroosmotic Mobility of Buffers Consisting of Multivalent Inorganic Cations. The activities of barium cations and acetate ions in the solutions were calculated based upon the pH, the initial concentration of acetic acid, and its pK_a . It was found that the accuracy of pH measurement was very critical in order to calculate the electroosmotic mobility of the solution. For the given reagents, the equilibrium constants K_{Ba} and $K_{Acetate}$ were defined similar to those for reactions 12 and 13. Similar to the method used for solving the unknown parameters in the scenario of the presence of monovalent cations, the unknown parameters K_{Ba} , $K_{Acetate}$, α_{Ba} , and β_{Ba} were obtained through Microsoft Excel-Solver simultaneously by fitting the data into the model, eq 22, and are shown in Table 2. The difference of α_{Ba} and β_{Ba} (0.964 and 0.570) from the values of the monovalent ions could be due to the difference of usage of the capillary columns. The values of K_{Ba} and $K_{Acetate}$ (18.3 and 7.5) were fairly large, which indicated that the binding of these ions to the silanoate group was quite favorable.

Noticeably, the values of charge density from the solutions containing barium ions, shown in Table 4, are almost a magnitude lower than those of sodium-containing buffers at similar ionic strength and pH. Therefore, the charge density dramatically decreases with the increase of the charge of cations in a buffer solution. When the multiply charged inorganic cations interact with the silanoate ions, the excessive positive charges from SiO^-M^{m+} ions sometimes result in an electroosmotic flow toward the anode.^{24,25} The calculated μ_{eo} of barium acetate solutions using eq 22 demonstrated a good agreement with the experimentally obtained μ_{eo} through the low errors of μ_{eo} (%) listed in Table 4.

Electroosmotic Mobility of Buffers Consisting of Neutral Additive. To evaluate the effect of a neutral additive on μ_{eo} , the

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(25) Zhou, M. X.; Foley, J. P. *Electrophoresis* **2004**, *25* (4–5), 653–664.

(26) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 56 ed.; CRC Press: Cleveland, OH, 1975.

(27) Bronsted, J. N. *Z. Phys. Chem.* **1922**, *102*, 169–207.

(28) Atkins, P. *Physical Chemistry*, 6 ed.; W. H. Freeman and Co.: New York, 1998.

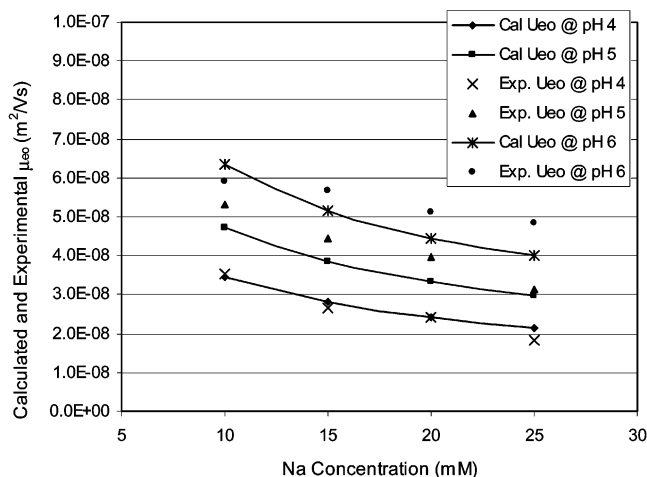


Figure 5. Effect of sodium concentration and buffer pH on electroosmotic mobility. The data are taken from Table 1. Cal Ueo = calculated μ_{eo} . Exp Ueo = experimentally obtained μ_{eo} . The lines are drawn to guide the eyes.

buffer (sodium phosphate) concentration was held constant, while different amounts of HEC were added to the sodium phosphate buffer solution. On the capillary column wall, the adsorption of HEC occurred as indicated in eq 15, and the equilibrium constant K_{HEC} was defined similar to K_N . The apparent pH of the solution increased with increasing concentration of HEC, as did the viscosity of the buffer solutions (Table 5).

Since HEC is electrically neutral, the value of HEC activity was assumed to be the same as its concentration. The unknown parameters K_{HEC} , α , and β were obtained through Microsoft Excel-Solver simultaneously by fitting the data into the model, eq 24. The values of α_{HEC} and β_{HEC} were found to be 1.01 and 2.54, respectively. In this case, the value of β_{HEC} is much larger than those of β_{Na} and β_{Ba} in the first two scenarios. The equilibrium constant K_{HEC} was obtained through fitting the experimental data of μ_{eo} through eq 24. The value of K_{HEC} was determined to be 4.32×10^4 , which indicates that the activity of silanoate–neutral complexes was much higher than the product of the activities of silanoate ions and the neutral compound, HEC.

Comparing the calculated charge density and thickness of EDL with those in Table 1, the addition of the HEC did not change much on the charge density and thickness of EDL. The decrease of μ_{eo} is more due to the increase of viscosity with the increase of HEC in solution and strong association of HEC with SiO^- . The obvious agreement of the calculated μ_{eo} with the experimental μ_{eo} is demonstrated by the low errors of μ_{eo} (%) shown in Table 5.

Impact of Charge Status of Cations and pH on Electroosmotic Mobility. The data in Tables 1 and 4 indicate that pH of the buffer solutions has a greater effect on the μ_{eo} for a solution containing monovalent cations compared with a solution containing divalent cations. For a monovalent cationic buffer system, both the sodium concentration and the pH affected the μ_{eo} , which is shown in Figure 5. The impact of barium concentration on the μ_{eo} was dominant as demonstrated in Figure 6, while the difference of pH between 4.5 and 5.6 at the same magnitude and the pH at a region similar to those in Figure 5 did not have much of an influence on the μ_{eo} . This observation agreed with the suggested models for the monovalent and multivalent inorganic cations. For

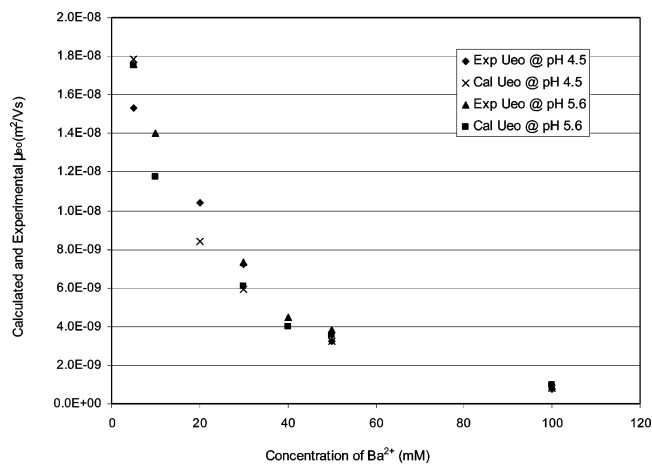


Figure 6. Effect of barium concentration and buffer pH on electroosmotic mobility. The data are taken from Table 4. Cal Ueo = calculated μ_{eo} . Exp Ueo = experimentally obtained μ_{eo} .

the situation when multivalent inorganic cations were present, the negative charge on the wall was overcome by the positive charge on the multivalent inorganic cations, so that the charge density was decreased dramatically. When the charge or the concentration of the multivalent inorganic cations is increased, the charge density is reduced to a certain extent that the sign of the net surface charge can even be changed, which is demonstrated in eq 14. The calculated electroosmotic mobility using the suggested models was also consistent with the experimentally obtained data.

CONCLUSIONS

Through the incorporation of the site-dissociation–site-binding model into the electrical double layer, by evaluating the chemical process, we established a general empirical equation (eq 22) for the prediction of μ_{eo} . Through our study, we found that the logarithm of the number of apparent silanol sites on a fused-silica surface has a linear relationship with the pH of a buffer solution, and the number of apparent silanol sites is determined by two empirical parameters α and β . Both α and β are directly related to the fused-silica surface condition, which indicates that the uncertainty of μ_{eo} from run to run and day to day is due to the surface modification caused by the running buffer. The chemical kinetics approach allows us to obtain the thickness of electrical double layer when multivalent inorganic cations coexist with monovalent cations in a buffer solution. Because the solutions we used in this study were not very concentrated, we applied the Debye–Hückel limiting law (see SI-11 in the Supporting Information). If moderate concentrated solutions are used, the extended Debye–Hückel law should be applied and a coefficient of $(1 + BI^{1/2})$ should be added to eq 22. Furthermore, eq 22 also demonstrates the temperature effect on μ_{eo} . When the temperature is increased, the viscosity of the buffer is decreased and the relative permittivity of the buffer is increased. As the result, μ_{eo} is increased with temperature. Due to the change of the chemical process on the surface of fused silica when the pH of a buffer solution exceeds 10, eq 22 is only applicable to the pH of a buffer solution up to 9. Additionally, the general equation is limited to the buffer solutions containing one type of multivalent inorganic cation coexisting with other monovalent cations, neutral additives, or both, although practically, it is very unusual to prepare a buffer

solution with more than one type of multivalent inorganic cations. Equation 22 suggested in our study that one can both qualitatively and quantitatively predict the effect on μ_{eo} from a given buffer solution through its characteristic parameters such as pH, valence charge, ionic strength, viscosity, activity, and dissociation constant. The general equation and the method used here can also be used to obtain the equilibrium constant of a species with silanol groups.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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