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Theoretical Description of the Influence of External Radial Fields on the Electroosmotic Flow in Capillary Electrophoresis

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The effect of applying a radial voltage on the electroosmotic flow in capillary electrophoresis has been studied from a theoretical point of view. Based on Stern's model for the electric double layer on the surface of a fused silica capillary and on the Gouy–Chapman theory for the diffuse layer, equations describing the relation between the electroosmotic mobility and the radial electric field were derived. The thickness of the stagnant solution layer on the surface of the capillary, an important parameter in the calculations, was estimated from the electroosmotic mobility found in high-pH solutions. The theory developed predicts the experimental findings that the effect of the radial field levels off at high applied voltages and that it is smaller when the electroosmotic mobility without radial field is already high. The theoretical results were compared with experimental data taken from the literature. A good quantitative agreement was found.

The velocity of the electroosmotic flow (EOF) is a crucial parameter for separations by capillary electrophoresis (CE). It determines the range of analyte mobilities that can be handled in a single run as well as the run time. Moreover, variations in the EOF, between different capillaries and between different runs on the same capillary, are the main source of the irrepeatability and irreproducibility of the elution times so often encountered in CE.

The electroosmotic mobility is, in principle, governed by the chemical condition of the inner surface of the capillary and by the composition of the background electrolyte (BGE) used for the separation. Still, even with careful control of these parameters, large variations in the EOF are found in practice. In 1990, Lee and co-workers¹ found a way to change the EOF, and even to reverse its direction, by applying an external radial electric field. Later, external EOF control attracted the attention of a number of research groups.^{2–11} Basically, the technique of external EOF control consists of the application of a high voltage radially over the wall of the capillary, in addition to the longitudinal field for

the separation. The radial field is applied by means of a second high-voltage source between the solution inside the capillary and its outer surface. For the connection with the outer surface, conductive paint or a concentric tube filled with an electrolyte solution has been used. In later work, provisions have been made to ensure that the voltage drop over the wall of the capillary was constant over (a part of) its length, by having an appropriate current flowing through the outside conductor. A radial voltage of several kilovolts appeared to influence the EOF significantly when a BGE with low pH was used. With a high-pH BGE, when the electroosmotic mobility was already high, the radial field was generally found to have much less influence.

It may be argued that the ability to influence the EOF does not imply the ability to stabilize it; undesired variations resulting from, e.g., adsorption of sample constituents cannot be eliminated as long as a device for real-time monitoring of the EOF is not available. Still, the phenomenon is interesting in itself and worth studying, if only since radial fields may occur inadvertently in several experimental situations, possibly affecting the reliability of CE separations. Bello et al.¹¹ explained differences in the EOF observed with the same capillary with different instruments in this way.

Theories to describe and understand external EOF control were first put forward by Lee et al.² and by Hayes and Ewing.⁴ Basically, in their approach, the phenomenon was described as the effect of the radial field on the diffuse double layer in the solution close to the capillary wall, in which the driving force for the EOF resides. However, the description of these theories was not quite satisfactory for a number of reasons. First, it was expressed in old-fashioned electrostatic units, with which most younger scientists are not familiar, instead of in SI units. By using SI units, as has been done later by Bello et al.,¹¹ confusing factors such as 4π for nonspherical systems, 300 (stemming from the electrostatic system) and 1000 (from the conversion from liters to cm^3) disappear from the equations. Second, in the treatments of Lee et al. and of Hayes and Ewing, the inner surface of the capillary was modeled as an ensemble of capacitors and resistances. We believe that it is important to formulate the theory in the simplest way possible, so that cause and effect relations remain clear. In the following, we hope to show that complicated circuit diagrams are not necessary to describe EOF control. Finally, in the previous work, as theoretical basis for the description of the electrical double layer on the capillary surface, the Debye–Hückel

- (1) Lee, C. S.; Blanchard, W. C.; Wu, C.-T. *Anal. Chem.* **1990**, *63*, 1550.
- (2) Lee, C. S.; McManigill, D.; Wu, C.-T.; Patel, B. *Anal. Chem.* **1991**, *63*, 1519.
- (3) Lee, C. S.; Wu, C.-T.; Lopes, T.; Patel, B. *J. Chromatogr.* **1991**, *559*, 133.
- (4) Hayes M. A.; Ewing, A. G. *Anal. Chem.* **1992**, *64*, 512.
- (5) Wu, C.-T.; Lopes, T.; Patel B.; Lee, C. S. *Anal. Chem.* **1992**, *64*, 886.
- (6) Wu C.-T.; Lee, C. S. *Anal. Chem.* **1992**, *64*, 2310.
- (7) Wu, C.-T.; Huang T.-L.; Lee, C. S. *J. Chromatogr. A* **1993**, *652*, 277.
- (8) Keely, C. A.; Holloway, R. R.; van de Goor, T. A. A. M.; McManigill, D. J. *Chromatogr. A* **1993**, *652*, 283.
- (9) Wu, C.-T.; Huang, T.-L.; Lee, C. S.; Miller, C. J. *Anal. Chem.* **1993**, *65*, 568.
- (10) Huang, T. L.; Tsai, P.; Wu C.-T.; Lee, C. S. *Anal. Chem.* **1993**, *65*, 2887.
- (11) Bello, M. S.; Capelli L.; Righetti, P. G. *J. Chromatogr. A* **1994**, *684*, 311.

approximation of the Gouy and Chapman model¹² was used. In this paper it will be shown that this approximation is often not justified.

In the theoretical treatment presented in this paper, we use the Stern model for the electrical double layer and apply Gauss's law of electrostatics to describe the influence of the radial field on it. Furthermore, the Gouy–Chapman theory is used to describe the diffuse double layer, with the Debye–Hückel approximation as a special case. With this, the influence of the external radial field on the electroosmotic mobility is modeled. The results of the theoretical treatment are compared with experimental data taken from the literature.

THEORY

Electroosmotic Mobilities and ζ Potentials. In the theoretical treatment of electroosmotic flow (EOF), it is generally assumed that there is a stagnant layer of solution with a finite thickness δ on the wall of the capillary. The electrostatic force of the axial electric field on the excess charge in the solution outside this stagnant layer causes the EOF. It can easily be shown that the electroosmotic mobility μ_{eo} is related to the solution potential at the outside of the stagnant layer $\phi(\delta)$, also called the ζ potential, by

$$\mu_{eo} = -\frac{\epsilon_{aq}\epsilon_0}{\eta}\phi(\delta) \quad (1)$$

where ϵ_{aq} is the dielectric constant of the (aqueous) solution, ϵ_0 the permittivity of free space, and η the viscosity of the solution. The osmotic mobility is independent of the potential path in the mobile solution. Therefore, in the discussion of EOF control by an external, radial electric field over the wall of the capillary, only the influence of this field on the ζ potential need be regarded. Unfortunately, there is no way to measure directly the ζ potential or the thickness of the stagnant layer. The existence of a stagnant layer of (aqueous) solution on a charged surface is usually explained as the result of strong dipole interactions between water molecules in the high electric fields close to the surface, causing a locally increased viscosity of the solution. However, electrokinetic phenomena on silica, the standard capillary material in CE, have been found to be unusually small in comparison to those occurring on other solids with a similar surface charge density.¹³ As a possible explanation for this, the presence of a gel-like structure on top of the silica surface has been proposed, extending the thickness of the stagnant layer.^{14,15} Other models developed to reconcile the high surface charge of silica with its low ζ potential account for the complexation of “indifferent” cations with the anionic groups on the surface.^{16,17} Whatever explanation is the most correct one, clearly a proper modeling of the potential gradients in the stagnant layer is crucial to describe the influence of the surface charge density and of radial fields on the electroosmotic mobility.

Figure 1. Model of the electrostatic double layer on the silica surface.

Influence of the Radial Field on the Diffuse Double Layer.

We use the Stern model for the electric double layer on the capillary wall. The double layer in this model is divided in two parts: an inner, compact layer and an outer, diffuse layer. The compact layer comprises the specifically adsorbed ions and the first layer of nonspecifically adsorbed ions. It has been shown that the capacity of the inner layer is relatively constant,¹⁸ which means that the surface charge density in the compact layer is an approximately constant fraction of the charge density on the solid surface. Since in the compact layer strong, short-range forces play a major role, it may be reasonable to assume that the influence of an external radial field on the surface charge density in this layer is negligible.

The basis for our treatment is Gauss's law of electrostatics, which states that the net charge inside an imaginary surface A is given by the integral of the electric field E over the surface:

$$q = \int \epsilon_i E \, dA \quad (2)$$

where ϵ_i is the dielectric constant of the medium at the surface. We draw two adjacent Gaussian surfaces over a part of the capillary wall of unit area (see Figure 1). One plane of the first surface (I) is located inside the wall material (the fused silica), not too far from the surface; the opposite plane is located in the solution on the interface between the compact layer and the diffuse layer. For this enveloping surface, Gauss's law holds:

$$\sigma_w = \epsilon_{si}\epsilon_0 E_{ext} - \epsilon_{aq}\epsilon_0 \left(\frac{d\phi}{dx}\right)_0 \quad (3)$$

where σ_w is the surface charge density of the wall including the compact layer, ϵ_{si} and ϵ_{aq} are the dielectric constants of the silica wall material and the solution, respectively, and E_{ext} is the field strength of the radial field over the fused silica close to the surface. The x coordinate is taken perpendicular to the surface, with its zero point at the interface between the compact and the diffuse layers.

The other Gaussian surface (II) has one plane coincident with the first; the second plane is located in the bulk of the solution, where the solution potential has dropped to zero. For this surface,

(12) Bard A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; J. Wiley & Sons: New York, 1980; Chapter 12.

(13) Hunter, R. J. *Foundations of Colloid Science*; Clarendon Press: Oxford, 1987; Chapter 6.

(14) Van Lier, J. A.; de Bruyn P. L.; Overbeek, J. Th. G. *J. Phys. Chem.* **1960**, *64*, 1675.

(15) Lyklema, J. *J. Electroanal. Chem.* **1968**, *18*, 341.

(16) Yates, D. E.; Levine S.; Healy, T. W. *Trans. Faraday Soc.* **1974**, *70*, 1807.

(17) Davis, J. A.; James, R. O.; Leckie, J. O. *J. Colloid Interface Sci.* **1978**, *69*, 480.

(18) Fried, I. *The Chemistry of Electrode Processes*; Academic Press: London, 1973; Chapter 4.

Gauss's law is

$$\sigma_d = \epsilon_{aq} \epsilon_0 \left(\frac{d\phi}{dx} \right)_0 \quad (4)$$

where σ_d is the surface charge density of the diffuse layer in the solution. Combination of eqs 3 and 4 gives

$$\sigma_d = -\sigma_w + \epsilon_{si} \epsilon_0 E_{ext} \quad (5)$$

In the reasoning above, the wall surface has been regarded as a flat plane. This is only allowed when the value at the inner surface of the capillary is taken for the external field strength. In the cylindrical geometry of the capillary, E_{ext} can be calculated from the applied radial voltage V_{ext} as

$$E_{ext} = \frac{V_{ext}}{R_{in} \ln(R_{out}/R_{in})} \quad (6)$$

where R_{in} and R_{out} are the inner and outer radii of the capillary, respectively.

The charge density in the diffuse layer in our model is composed of two independent contributions: one related to the chemical processes on the wall material (ionization and adsorption phenomena), and one representing the charge separation caused by the external radial field. The finding that the excess charge caused by the external field is found only in the diffuse layer is the consequence of our assumption that the compact layer charge is not affected. Hayes and Ewing⁴ have brought up the importance of the silanol group ionization for the surface charge density. It may be argued that the changes in the potential brought about by the applied radial field may influence the ionization degree of the silica, thereby changing the surface charge of the compact layer. As will be shown later, changes of the double layer potential on the order of 50 mV are easily obtained with external EOF control. When these potential changes would reside mainly in the compact layer, they could change the pK_a value of the silanol groups by 0.5–1 unit. (A potential change of 59 mV corresponds to a change of pK_a by 1 unit.) However, it has been generally observed that the dependency of the EOF on pH does not resemble a simple titration curve with a single pK_a value. Rather, in the pH range from 2 to 9, a gradual increase of the EOF, and therefore of the surface ionization, is seen. This may indicate that there is a strong heterogeneity in the acidity of silanol groups. Whatever the right explanation may be, when pH changes of 1 unit have a minor effect on surface ionization, the same can be expected for potential changes on the order of 50 mV. Also, with the excess charge caused by the radial field mainly in the compact layer, one would predict a much smaller efficacy of external EOF control than is found in practice. The assumption that the excess charge brought about by the radial field (mainly) resides in the diffuse layer is, therefore, more consistent with the experimental findings.

Relation between the Surface Charge and the ζ Potential.

To find the relation between the ζ potential $\phi(\delta)$ and σ_d , the usual treatment, based on the electrostatic Poisson equation, can be followed, as found in many textbooks on electrochemistry (e.g., ref 12). For a simple $z:z$ electrolyte, the potential at the surface

Figure 2. Course of the potential in the diffuse layer as a function of the surface charge density. $I = 0.05 \text{ mol L}^{-1}$. $\sigma_d = 0.05$ (a), 0.2 (b), and 0.8 (c) C m^{-2} .

of the diffuse layer φ_0 is given by

$$\sinh\left(\frac{ze\phi_0}{2kT}\right) = -\frac{\sigma_d}{(8kT\epsilon_{aq}\epsilon_0 n^0)^{1/2}} \quad (7)$$

where n^0 is the number concentration of the electrolyte ions and the other symbols have their usual meanings. The solution potential at a distance x in the diffuse layer is described by

$$\frac{\tanh(ze\phi(x)/4kT)}{\tanh(ze\phi_0/4kT)} = \exp(-\kappa x) \quad (8)$$

The inverse diffuse layer thickness κ in this equation is given by

$$\kappa = \left(\frac{2n^0 z^2 e^2}{\epsilon_{aq}\epsilon_0 kT} \right)^{1/2} \quad (9)$$

Equations 7–9 can be evaluated to give the direct relation between $\varphi(x)$ and σ_d :

$$\phi(x) =$$

$$\frac{2kT}{ze} \ln \frac{[S + (S^2 + 1)^{1/2} + 1][1 + \exp(-\kappa x)] - 2 \exp(-\kappa x)}{[S + (S^2 + 1)^{1/2} + 1][1 - \exp(-\kappa x)] + 2 \exp(-\kappa x)} \quad (10)$$

where, for convenience, a parameter S has been introduced, which is given by

$$S = \frac{\sigma_d}{(8kT\epsilon_{aq}\epsilon_0 n^0)^{1/2}} \quad (11)$$

In Figure 2 the dependency of φ on x is shown for different values of σ_d , as calculated from eq 10 for a 0.05 mol L^{-1} solution of a 1:1 electrolyte ($1/\kappa = 1.36 \text{ nm}$). The potential drops relatively more rapidly with the distance from the wall for high values of σ_d . In Figure 3, the influence of σ_d on the potential at the edge of the compact layer (ϕ_0) and at some distance (0.8 nm) in the diffuse layer ($\phi(x)$) is shown. At a small distance in the diffuse layer, the potential reaches a plateau value when ϕ_0 still increases with σ_d .

Figure 3. Dependency of the solution potential on the charge density of the diffuse layer. $I = 0.05 \text{ mol L}^{-1}$. $x = 0$ (a) and 0.8 (b) nm. (c) As (b), calculated with the Debye–Hückel approximation.

Table 1. Calculated Values of the Maximum Electroosmotic Mobility as a Function of the Ionic Strength, Using Different Values for the Stagnant Layer Thickness δ ($T = 25^\circ \text{C}$)

$I \text{ (mol L}^{-1}\text{)}$	$\mu_{eo}^0 \text{ (} 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}\text{)}$		
	$\delta = 0.6 \text{ nm}$	$\delta = 0.8 \text{ nm}$	$\delta = 1.0 \text{ nm}$
0.002	12.3	11.2	10.4
0.005	10.5	9.4	8.5
0.01	9.1	8.0	7.1
0.02	7.7	6.6	5.8
0.05	5.9	4.8	4.1
0.1	4.6	3.6	2.8

For the electroosmotic mobility, the solution potential at the surface of the stagnant layer $\phi(\delta)$, the ζ potential, is of importance. The value of δ , the thickness of the stagnant layer of solution on the capillary wall, is still uncertain. Using eqs 1 and 10 with different assumed values of δ , we have calculated the electroosmotic mobility for various ionic strengths (at 25°C) to be obtained when the silica surface is completely ionized, having a surface charge density of 0.8 C m^{-2} . The results of the calculations are given in Table 1. These values of the electroosmotic mobility are to be expected for solutions of high pH. In previous experimental work^{19,20} we used various concentrations of hydroxide solutions as BGE. An estimation of δ can be obtained by comparing experimental values of μ_{eo} after correction for the change of the solvent viscosity with the temperature with the calculated values given in Table 1. The best fit was obtained for a value of 0.8 nm for δ .

With this assumed stagnant layer thickness, Figure 4 was constructed, where the influence of an external radial field on μ_{eo} is shown for different values of μ_{eo}^0 , the electroosmotic mobility in the absence of a radial field. The different starting values of the electroosmotic mobility (μ_{eo}^0) were obtained by choosing an appropriate value for σ_d ; the lines were then calculated from eqs 1, 5, 10, and 11. In fact, the curves in this figure all represent a part of the curve for $\phi(x)$ in Figure 3, with different starting points for σ_d . The figure clearly illustrates that the theoretical Stern model for the electrical double layer on the capillary wall, explains two empirical findings in EOF control: (1) with high external fields, the influence of the external field on μ_{eo} decreases and (2) when the osmotic mobility without external field is already high,

Figure 4. Influence of the external radial field on the electroosmotic mobility. $I = 0.01 \text{ mol L}^{-1}$. $\mu_{eo}^0 = 0$ (a), 3 (b), and 6×10^{-8} (c) $\text{m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

the influence of an external field is smaller than with low μ_{eo}^0 . A similar “sigmoid” relation between the electroosmotic mobility and the surface charge density of the diffuse layer was also proposed by Hayes et al.²¹ A difference between their treatment and ours is that they did not take into account the dependency of the potential profile in the diffuse layer on the value of $\phi(0)$. This may partly explain the large (quantitative) difference in the theoretical and experimental data obtained by them.

Linear Approximation at Low μ_{eo} . For small values of σ_d ($S < 0.5$ and $\phi(0) < 25 \text{ mV}$), eq 10 can be simplified to

$$\phi(x) = \frac{\sigma_d}{\epsilon_{aq}\epsilon_0\kappa} \exp(-\kappa x) \quad (12)$$

This is equivalent to the Debye–Hückel treatment of the double layer theory, as has been used by Hayes and Ewing⁴ and by Bello et al.¹¹ Using for the ζ potential the potential at distance δ in the diffuse layer, eqs 1 and 12 give the electroosmotic mobility in the presence of a radial external field:

$$\mu_{eo} = \mu_{eo}^0 + \frac{\epsilon_{si}\epsilon_0 E_{ext}}{\eta\kappa} \exp(-\kappa\delta) \quad (13)$$

This equation predicts, for small values of μ_{eo} , a change of μ_{eo} proportional to the applied radial field. The linear simplification is, therefore, only valid for low “starting” values of the electroosmotic mobility with moderate external fields, as well as for higher values of μ_{eo}^0 with an external field largely opposing the chemical surface charge on the capillary wall.

A linear relation between the applied radial voltage and the change of the electroosmotic mobility was also derived by Lee et al.² They considered as model a series circuit of capacitors, which essentially consisted of the capacitance of the diffuse double layer on the one hand and that of the capillary tubing on the other. The change of the ζ potential was found to be linearly dependent on the ratio of these two capacitances. A careful comparison of the results of Lee et al. with ours shows that (for small ζ potentials) their results are exactly equivalent to our approximate eq 13. With high values of σ_d , the linearity is lost for two reasons: (1) the relation between $\phi(0)$ and σ_d levels off at high values of σ_d (in treatises on electrochemistry, this is called the increase of the

(19) Xu, X.; Kok, W. Th.; Poppe, H. *J. Chromatogr. A* **1995**, 716, 231.

(20) Huang, X.; Kok, W. Th. *J. Chromatogr. A* **1995**, 707, 335.

(21) Hayes, M. A.; Kheterpal I.; Ewing, A. G. *Anal. Chem.* **1993**, 65, 27.

Figure 5. Comparison of calculated (solid line) and experimental (marks) values of μ_{eo} . Experimental values taken from Lee et al.,² Figure 3. $d_{in} = 50 \mu\text{m}$; $d_{out} = 192 \mu\text{m}$; $I = 0.002 \text{ mol L}^{-1}$; 85% coverage. The dotted line gives the theoretical relation described in the original publication.

Figure 6. Comparison of calculated (solid line) and experimental (marks) values of μ_{eo} . Experimental values taken from Lee et al.,² Figure 10. $d_{in} = 50 \mu\text{m}$; $d_{out} = 192 \mu\text{m}$; $I = 0.05 \text{ mol L}^{-1}$; 85% coverage. The dotted line gives the theoretical relation described in the original publication.

differential capacity of the diffuse double layer at potentials removed from the "potential of zero charge", and (2) with increasing $\phi(0)$, the drop of the potential in the diffuse layer becomes steeper, resulting in an even slower rise of the ζ potential with σ_d .

Lee found a good agreement between the theory and experimental practice only when the electroosmotic mobility in the absence of a radial field was low ($< 2 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$). The theoretical treatment discussed above shows the reason for this behaviour. For higher electroosmotic mobilities, the ζ potential exceeds 25 mV, and the Debye–Hückel approximation is no longer valid. This is shown by line c in Figure 3, which represents the Debye–Hückel approximation for the potential at a distance of 0.8 nm in the diffuse layer. For ζ potentials $> 25 \text{ mV}$ the discrepancy with the exact solution is considerable.

COMPARISON WITH EXPERIMENTAL DATA

We have compared our theoretical results with experimental data given in the literature. From the original literature, the data on the capillary diameters, the applied radial voltages, and the percentage of the length of the capillary over which the radial field was applied were taken. The ionic strength of the solution had to be estimated in some cases when the composition of the buffer had not been exactly indicated. Then, the appropriate charge density of the silica surface including the compact layer

Figure 7. Comparison of calculated (solid line) and experimental (marks) values of μ_{eo} . Experimental values taken from Lee et al.,³ Figure 3. $d_{in} = 50 \mu\text{m}$; $d_{out} = 150 \mu\text{m}$; $I = 0.002 \text{ mol L}^{-1}$; 87% coverage. The dotted line gives the theoretical relation described in the original publication.

Figure 8. Comparison of calculated (solid line) and experimental (marks) values of μ_{eo} . Experimental values taken from Lee et al.,³ Figure 6. $d_{in} = 25 \mu\text{m}$; $d_{out} = 150 \mu\text{m}$; $I = 0.01 \text{ mol L}^{-1}$; 87% coverage. The dotted line gives the theoretical relation described in the original publication.

Figure 9. Comparison of calculated (solid line) and experimental (marks) values of μ_{eo} . Experimental values taken from Keely et al.,⁸ Figure 2. $d_{in} = 50 \mu\text{m}$; $d_{out} = 180 \mu\text{m}$; $I = 0.0078 \text{ mol L}^{-1}$; 70% coverage.

(σ_d) was estimated by fitting the calculated result for the electroosmotic mobility in the absence of a radial field (μ_{eo}^0) with the experimental value. Using a spreadsheet program, the electroosmotic mobility was calculated for a range of applied voltages for the part of the capillary length over which the field was applied. Next, the average electroosmotic mobility over the shielded and unshielded parts of the capillary was calculated. These values have been plotted in Figure 5–10. Experimentally determined values of the electroosmotic mobility, estimated from figures in

Figure 10. Comparison of calculated (solid line) and experimental (marks) values of μ_{eo} . Experimental values taken from Hayes et al.,²¹ Figure 4. $d_{in} = 10 \mu\text{m}$; $d_{out} = 144 \mu\text{m}$; $I = 0.002 \text{ mol L}^{-1}$; 60% coverage. The dotted line gives the theoretical relation described in the original publication.

the original literature, are included in Figures 5–10. The figures show the influences of the ionic strength (Figure 5 vs Figure 6) and of the value of μ_{eo}^0 (Figure 7 vs Figure 8) on the extent to which the EOF can be manipulated. The agreement of experimental values with the theory is, in most cases, remarkably good, and often better than with theoretical models used by the authors themselves (e.g., Figures 5, 7, and 10). The dotted lines in Figures 5–8 give the theoretical predictions with the linearized model of Lee et al.^{2,3} In Figure 10 are shown the theoretical values calculated by Hayes et al.,²¹ without the fitting factor of 3.9 that the authors used to match the calculation results with the experimental data.

While the Debye–Hückel approximation usually gives an overestimation of the influence of the radial field, with our theory this influence is sometimes slightly underestimated. An explana-

tion for this could be that the assumed thickness of the stagnant layer (0.8 nm) is too large.

CONCLUSIONS

From the agreement of the theoretically predicted and the experimentally observed influence of radial fields on μ_{eo} , it follows that the models used (the Stern model of the double layer and the Gouy–Chapman description of the diffuse layer) are adequate to describe the electrostatic phenomena on a fused silica surface. The only “unknown” parameter we had to use in the theoretical model is the thickness of the stagnant layer δ . However, a good estimate of δ could be derived from independent experiments.

Our theory does not use implicit assumptions on the chemical processes (ionization and adsorption of ions) at the fused silica surface; the surface charge density of the wall including the compact layer is estimated from the electroosmotic mobility without radial field. However, since our theory clearly distinguishes between the processes in the compact layer and those in the diffuse layer, the equations derived can be used to study the chemistry of the silica surface. By combining titration data with data on μ_{eo}^0 in different electrolytes, it could be possible, for instance, to study the specific adsorption of buffer cations in the compact layer.

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