The control of electroosmotic flow by electronic means for capillary zone electrophoresis is presented. This is accomplished by the application of a radial voltage field with a rugged and flexible conductive polymer sheath. Fundamental theory for effect of the applied radial voltage on electroosmotic flow is developed. In addition, the effects of surface pretreatments are examined and compared to trends predicted by the theory.

The emergence of capillary electrophoresis (CE) has brought about many changes in the field of separation science. This emergence of CE as a powerful technique is due to its extremely high efficiency and compatibility with a large range of materials. One of the most important features in allowing a large range of analytes is the electroosmotic flow (EOF). This flow often causes migration of cations, anions, and neutrals in one direction, allowing them to be detected at one end of the capillary. The EOF is a function of the separation potential and the potential drop across the interface between the capillary wall and the bulk buffer. The understanding and control of this capillary–buffer interface has implications in defining resolution, solute adsorption, and efficiency.

The potential drop across the interface is defined by the properties of the surface and the buffer. It may be altered by surface-active species, buffer pH, buffer composition, temperature, or chemical derivatization of the surface. In addition to this, a potential field superimposed across this interface may alter its properties. In this paper, the theory of EOF control using a potential field superimposed across the capillary wall is addressed. In addition, experimental data is presented which is consistent with theory developed for EOF control with an applied radial voltage.

Theory has been developed by approximating the behavior of the quartz tube as a cylindrical capacitor and resistor in parallel. Several experiments concerning the effects of tube pretreatment on radial voltage control of EOF are also discussed. These experiments include the effects of rinsing the capillary with potassium hydroxide, the effects of deactivating the capillary surface with methyl- and phenyl-trichlorosilanes) the capillary tubing, and the effects of grounding of the conducting sheath.

**THEORY**

**Electroosmotic Flow.** The theoretical considerations presented here are for fused silica capillaries. The interface between the fused silica tube wall and the bulk buffer inside the capillary has been discussed extensively. The structure of this interface may be divided into three parts: (1) the silica surface (which is negatively charged when in contact with solutions of pH greater than approximately 2), (2) the immobile layer (also called the Stern layer or inner Helmholtz plane), and (3) the diffuse layer.

The immobile layer is modeled as tightly bound countercations and the diffuse layer as solvated, loosely held countercations. Due to the Coulombic forces this charge separation at the interface forms a potential. This potential field has been shown to be related to electroosmotic flow (\( \nu_{eo} \)) by the following relation:

\[
\nu_{eo} = \frac{\xi}{(D_e/\eta)} E_{app}^{\text{app}}
\]

where \( \xi \) is the potential drop across the diffuse layer, \( D_e \) is the permittivity, \( \eta \) is the viscosity, and \( E_{app}^{\text{app}} \) is the applied separation field. The electroosmotic flow velocity is proportional to the potential drop across the diffuse layer, \( \xi \). Since this potential drop is formed by the countercations attracted to the charged silica surface, the charge density at the surface defines the number and density of countercations. Some of these countercations which are entrained in the diffuse layer generate flow. Therefore surface charge density ultimately is directly related to flow.

The capillary inner surface charge is described by the dissociation constant of the free hydroxyl groups of the silica surface. In the absence of other factors the charge density at the surface due to pH may be calculated according to the following reaction:

\[
[\text{SiOH}_2^-] + [\text{H}^+] \rightarrow [\text{SiO}_2^-] + [\text{H}_2\text{O}]
\]

where the SiOH and SiO transitions are surface functional groups given as functional groups per unit area. The charge density (\( \sigma_{si} \)) is calculated as function of pH (appendix I):

\[
\sigma_{si} = \frac{\gamma}{(1 + ([\text{H}^+] / K))}
\]

where \( \gamma \) is the number density of surface SiOH groups, \( K \) is the dissociation constant for surface hydroxyl groups on fused silica, and \( [\text{H}^+] \) is the bulk buffer hydrogen ion concentration. The \( \sigma_{si} \) may be the only source of surface charge density in many cases. However, the total surface charge density, \( \sigma_t \), regardless of its source, must be considered when developing the following relationships.

The total surface charge density (\( \sigma_t \)) and solution properties define the potential (\( \psi \)) across the interface. According to Davies and Rideal this relationship is

\[
\psi = (2kT / \epsilon) \sinh^{-1} \left( 500 \pi \nu_{app} / D_e R T \right)^{1/2}
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \epsilon \) is the elementary charge, \( R \) is the gas constant, and \( C \) is the concentration. If ionized surface hydroxyl groups are the sole source of surface charge, then \( \sigma_{si} = \sigma_t \) and the electroosmotic flow is a function of pH (and other established variables). Of course buffer ions and surface-active species will affect the surface charge density in real experimental conditions, but eq 3 still holds no matter the source of the charges.

The value calculated in eq 3 for surface potential, \( \psi \), is not directly responsible for the flow in CE. The \( \psi \) is the total potential drop across the double layer and \( \xi \) is the potential drop across the diffuse layer only. Although, the relationship between \( \xi \) and \( \psi \) is not clear, within certain limits it may be estimated. If it is assumed that the dielectric and viscous properties of the double layer are constant, the relationship would simply obey the Debye–Huckel theory and would be:

\[
\xi = \psi e^{x^2}
\]

where

\[
x = (2 \eta_a Z_e^2 / D_e k T)
\]
Debye–Hückel inverse length—considered the width of the double layer at potentials less than 50 mV.  

Development of the relationship given in eqs 4 and 5 assumes that the dielectric and viscous properties are constant across the double layer. This is not entirely valid. The dielectric and viscous properties are dependent on \( \Psi \). Regardless of the uncertainty of this relationship it is clear \( \zeta \) is of the same sign and order of magnitude as \( \Psi \). At surface potentials higher than 50 mV the actual \( \zeta \) is smaller, although exactly how much is not established.  

Another approach which shows \( \zeta \) to be less than predicted by Debye–Hückel is to not define a particular layer which is immobile, but a general relationship between \( \Psi \) and \( \nu_{\text{eo}} \), which is as follows:  

\[

\nu_{\text{eo}} = \frac{E_{\text{app}}}{4\pi} \int_{0}^{\Psi} \frac{D}{\eta} d\Psi 
\]

In this equation, \( D \) and \( \eta \) are the permittivity and viscosity, respectively, but are functions of the potential gradient, \( \Psi \), of the double layer. It has been shown that \( D \) decreases and \( \eta \) increases in the double layer relative to bulk solution. This again leads to the conclusion that \( \zeta \) is less than calculated by the Debye–Hückel theory.  

Even with these limitations, important relationships may be developed using the Debye–Hückel approximation. Combining the equations relating \( \nu_{\text{eo}} \) to \( \zeta \) (eq 1), \( \zeta \) to \( \Psi \) (eq 4), and \( \Psi \) to \( \sigma_{\text{f}} \) (eq 3) the following relationship between flow, \( \nu_{\text{eo}} \), and surface charge density, \( \sigma_{\text{f}} \), can be formulated:

\[

\nu_{\text{eo}} = \frac{E_{\text{app}}(D_{o}/\eta_o)(e^{-\kappa})(2kT/\epsilon)}{\sinh^{-1}[(500\pi\sigma_{\text{f}}/D_oRTc)^{1/2}]} \times \frac{1}{\ln\left(\frac{r_o}{r_i}\right)}
\]  

The important parameter in this equation is the surface charge density, \( \sigma_{\text{f}} \). According to eq 2, the charge density is affected by surface pH. However, at a given pH, the surface charge density may also be altered by a radial voltage applied across the radius of the capillary.  

**Effect of Applied Potential Field across the Capillary Wall**

To examine the effect of a radially applied potential \( (V) \), the fused silica tubing has been modeled as a capacitor and resistor in parallel with conductors on either side of the wall (Figure 1). Upon application of a radial voltage the capillary charges rapidly. As the fused silica of the capillary has a finite resistance \( (R) \) associated with it, current leaks across the fused silica wall. The typical values of resistance and capacitance for the fused silica used in common CE systems are \( 10^{10} \Omega \) and \( 10^{11} \text{ F} \), respectively. These values are calculated according to the following equations for capacitance \( (C) \) and resistance \( (R) \):

\[

C = 2\pi\epsilon_{\text{f}}(1/\ln\left(\frac{r_o}{r_i}\right)) 
\]

\[

R = (\rho_l/2\pi) \ln\left(\frac{r_o}{r_i}\right)
\]

where \( l \) is the length of the capillary, \( r_o \) is the outer radius,

\( R_t \) is the inner radius, \( \rho_l \) is the resistivity of quartz (approximately the same value as fused silica), and \( \epsilon_{\text{f}} \) is the permittivity for quartz. The charge \( (q) \) acquired on the inner surface of the capillary when a voltage is applied across the capillary wall (outside to inside) is

\[

q = C_{\text{f}}V_{\text{r}}
\]

Combining eqs 10 and 8 and dividing by the inner radius surface area \( (2\pi R_t) \) yields a surface charge density \( (\sigma_{\text{f}}) \) that is the result of capacitive effects:

\[

\sigma_{\text{f}} = (\epsilon_{\text{f}}V_{\text{r}}/R_t)(1/\ln\left(\frac{r_o}{r_i}\right))
\]

The immobile layer and diffuse layer also have capacitances and resistances associated with them. Both of these are a function of potential, and in our model they are considered to be in parallel with each other (and in series with the quartz RC). Hence a more complete model would be represented by Figure 2. Resistance of the electrical double layer is quite low compared to quartz, and capacitance values can be estimated at 5–25 \( \mu\text{F} \): much larger than that of quartz.  

In this model the silica wall and the surface–solution double layer are in series. The smallest capacitor and the largest resistor should dominate the circuit. Hence, the electrical properties of the applied radial voltage system are dominated by the capacitance and resistance of the fused silica capillary. The charging of the inner surface may be described by the charging of the quartz capillary wall modeled as a capacitor. Also, due to the finite resistance of the quartz, current leaks across the \( 10^{10} \Omega \) resistance (applied radial voltages in the kV range result in picocammere leakage current). Under some special experimental conditions this low-level current might be detected.  

Assuming that the low level current is negligible and surface charge is due to pH and capacitance only, the following equation holds:

\[

\sigma_{\text{f}} = \sigma_{\text{ef}} + \sigma_{\text{si}} \quad (12)
\]

This, of course, assumes that the electrostatic charges and the ionization of surface hydroxyl groups charges are additive and have no interaction between one another. With these assumptions, the overall effect of the applied radial voltage on electroosmotic flow is found by combining eqs 12 and 7 which yields

\[

\nu_{\text{eo}} = \frac{E_{\text{app}}(D_{o}/\eta_o)(e^{-\kappa})(2kT/\epsilon)}{\sinh^{-1}[(500\pi\sigma_{\text{f}}/D_oRTc)^{1/2}]} \times \frac{1}{\ln\left(\frac{r_o}{r_i}\right)}
\]

This equation describes the relationship between EOF, temperature \( (T) \), buffer concentration \( (C) \), pH (though \( \epsilon_{\text{f}} \) and eq 2) and radial voltage (through \( \sigma_{\text{f}} \) and eq 12). The applied radial voltage can be positive or negative and, hence, the surface charge density may be enhanced or depleted. Thus...
the EOF may be directly increased or decreased.

Two plots of predicted EOF versus applied radial voltage under separate experimental conditions are shown in Figure 3. Theoretical predictions developed from eq 13 for EOF appear to be consistent with experimental results for the effect of applied radial voltage, pH, 9 temperature, and buffer concentration. \(^\text{15}\) Comparison of the theoretical predictions shown here to the experimentally observed results when a voltage is applied across the capillary wall is discussed later in this paper.

EXPERIMENTAL SECTION

Apparatus. The experimental apparatus is shown in Figure 4. This consisted of two Plexiglas interlock boxes. One box contained the separation power supply and electrode and the other contained the sheath electrodes and power supplies. The conducting sheath was applied by painting a 5\% solution of Nafion (Scientific Specialities, Mendenhall, PA) onto the polyimide between electrical contacts made with carbowax/graphite paste. After drying, a Nafion ionomer film was left on the capillary. The resistance of the dried Nafion was measured by applying a potential field and measuring the current. By applying Ohm's law and making geometric assumptions (40-cm length, 10-\mu m-thick film with an inner radius equal to the outer radius of the capillary) the resistivity was determined to be ca. 10\(^{11}\) \(\Omega\)-cm.

An ultraviolet detector (Linear 200, Reno NE) was installed on-line. Approximately 6 cm from one end of the capillary a 1-cm section of the polyimide coating was removed by heat as a UV detection window. Data was collected at a wavelength of 214 nm.

Initially the current monitoring method\(^\text{16}\) was utilized. However, a standard deviation of 10-15\% in the data collected prevented reliable comparisons of trends for EOF versus \(V_r\) plots. Similarly, high standard deviations were observed in previous current monitoring work where the effect of applied radial voltage on EOF has been discussed.\(^\text{10,11}\)

For the experiments reported here, phenol was used as a neutral marker to monitor EOF.\(^\text{18}\) Five data points were taken for each radial voltage setting (-14 to +6 kV), and a standard deviation of 0.9\% resulted.

Three power supplies were used in the apparatus. The separation potential was provided at 0-30 kV, and the sheath voltages were 0-10 and 0-30 kV (Spellman, Plainview, NY). All power supplies were reversible to negative polarity, and all high-voltage surfaces were contained in Plexiglas interlock boxes for operator safety.

Fused silica capillary tubing (Polymicro, Phoenix, AZ) of 25- and 75-\mu m i.d. and 49-cm length was used as received, except where noted otherwise. Commercially available deactivated capillaries (P/N 160-2655, J&W Scientific, Folsom, CA) were utilized also.

The external potential field was manipulated to maintain a constant radial voltage along the sheathed portion of the capillary. The potential drop across the length of the sheath was made to mirror that of the calculated interior potential. The exterior potential field was offset from the interior field by the experimental value indicated (see Figure 4).

Chemicals. Solutions were made from \(\text{NaH}_2\text{PO}_4\) (Sigma, St. Louis, MO) and the pH adjusted to 6.32 with \(\text{NaOH}\). Twice-distilled (Megapure-Corning, Corning, NY) water was used for all buffers and solutions. Phenol solutions were made from "phenol liquified" (Fisher, Fairlawn, NJ). All chemicals were used as received with no further purification.

RESULTS

Control of Electroosmotic Flow with an Applied Radial Voltage. Lee et al. have previously shown that EOF in silica capillaries can be increased, decreased, and even reversed by application of a separate potential field across the wall of the capillary.\(^\text{10,11}\) Their system used a sheath capillary surrounding the CE capillary, filled with a separate buffer, to apply the potential field gradient along the CE capillary. We describe here results obtained when this linear potential field is applied via a dry Nafion ionomer on the outside of the capillary. For this system we have examined the relationship between EOF and applied radial voltage (\(V_r\)). The \(V_r\) is calculated assuming a linear voltage drop in the bulk buffer inside the capillary from one end to the other. A linear potential field gradient is applied along the outer sheath to provide a constant radial voltage over the length of the sheath. Since the ends of the capillary are unsheathed, these regions of no applied radial voltage have been included to calculate the average radial voltage over the total capillary length.

Data has been collected using three procedures. These include (1) increasing the applied radial voltage stepwise, (2) decreasing the radial voltage stepwise, and (3) alternating the radial voltage from the test value to zero then to the next test value. All of these methods yield similar results. Experimental data for the dependence of EOF on applied radial voltage are shown in Figure 5.

Effects of Chemically Treating the Capillary Inner Wall. Effects of KOH Rinse. Electroosmotic flow in individual capillaries has been observed to drift from day to day. Assuming this drift is due to adsorption of materials at the inner surface of the capillary (affecting the zeta potential), a basic (KOH) rinse appears warranted. KOH solubilizes the first few layers of the fused silica surface, removing contaminants with the silica.\(^\text{19}\) This procedure, however, has been observed to dramatically increase EOF. Typical flow in a
This allows for more varied geometric effects from long-term capacitive charging effects or varied dramatically. A conductive ionomer (Nafion) coating painted on the outside of the capillary would be established along the outside of the capillary coating is conductive enough to allow a linear potential field (V/cm potential field), whereas following a KOH rinse the capillary with the polyimide intact and a thin flexible methyl, phenyl, and alkyl functionalities to prevent polar effects to the application of radial voltage.

Application of Deactivated Tubing. Another attempt has been made to minimize long-term drift by employing commercially available deactivated fused silica tubing. Deactivation procedures derivatize the surface hydroxyl groups with phenol. The standard deviation of each point is approximately 2.5 cm/min (142 V/cm potential field), whereas following a KOH rinse this flow increases to approximately 10–11 cm/min. New capillaries were used to plot eq 13 and generate the solid line (see text). Each data point represents the average of three separate injections of the neutral marker phenol. The standard deviation of each data point is 0.02 cm/min.

"Contaminated" system is approximately 2.5 cm/min (142 V/cm potential field), whereas following a KOH rinse this flow increases to approximately 10–11 cm/min. New capillaries generate flow of 9–10 cm/min. Interestingly, the flow in the capillaries rinsed with KOH no longer have a measurable response to the application of radial voltage.

Effect of Grounding of the Capillary Sheath. One operating system has been altered such that the outer sheath is a grounded conductor. This has been accomplished by covering the capillary with silver paint and attaching this directly to ground. An ungrounded and unpainted capillary that yields EOF of 5.35 cm/min (142 V/cm) has an increase in EOF to 9.91 cm/min upon application of a grounded sheath, as described.

DISCUSSION

A simple and rugged dynamic method to control EOF by electronic means has been presented here. Previous systems described for the control of EOF by an applied radial voltage have used buffer-filled sheath fused silica capillaries with the polyimide removed. The system presented in this paper utilizes a capillary with the polyimide intact and a thin flexible conductive ionomer (Nafion) coating painted on the outside. This allows for more casual handling of the capillary in various geometries. Also, the high resistivity of the ionomer (10$^{11}$ $\Omega$-cm) allows the passage of minimal current. Thus, the coating is conductive enough to allow a linear potential field gradient to be established along the outside of the capillary but is resistive enough to limit the current flow and thereby minimize heating of the system.

The data in Figure 5 clearly shows that the EOF can be varied dramatically as a function of applied radial voltage in this system. Three different protocols have been used to rule out effects from long-term capacitive charging effects or temperature variations. Also shown in Figure 5 is a plot of EOF versus applied radial voltage predicted from eq 13 using the same parameters in which the experimental data was collected. The values predicted have been adjusted by a factor of 0.5 to match the magnitude of the flow in the experimental data set. Since eq 10 is developed for monovalent buffers and is based on Debye–Hückel approximations, it obviously does not account for all the complexities of the surface-buffer interface. This equation also does not account for effects due to surface roughness on the inside of the capillary. However, eq 13 predicts general experimental trends for changes in EOF due to the effects of applied radial voltage, pH, temperature, and buffer concentration. According to eq 13, a flow reversal is not predicted to occur within the experimental applied radial voltage range of pH of 6.32 (25-µm i.d./250-µm o.d.) (also see eq 11). Earlier work (Lee et al.10) demonstrated a reversal of EOF at ca. +3–5 kV and pH 6.0 (75-µm i.d./350-µm o.d.). This is consistent with the theory presented for the effect of pH and radius on the surface charge and it's interaction with the radial voltage. The theoretical plots in Figure 3 predict the effect of applied radial voltage on EOF for the two sets of experimental conditions described above for the work shown here (Figure 3a) and that of Lee et al.10 (Figure 3b).

Obviously, EOF may be controlled by many different methods. In this study the surface charge density has been altered electronically. To understand this system the details must be examined in considerable depth. At a given separation field strength and buffer system, the electroosmotic flow is controlled solely by the surface charge or more specifically by the structure of the surface charge density. For a native silica surface this value is generated by the dissociation of silanol groups. Unfortunately, the value of the dissociation constant for reaction is not clear; with reports for the pK$_a$ ranging from 1.5 to 10 and the most likely value to be 5–7.14 These values are determined for HPLC packing materials which contain a number of impurities relative to fused silica. Fused silica might be expected to approach the pK$_a$ of the pure silicic acid of 10.14,20 Certainly the pK$_a$ of fused silica may be determined experimentally, but to our knowledge it has not been reported in the literature.

The actual effect of the surface charge on EOF is dependent on the interplay between the surface and the immobile and diffuse layers. The simplistic approach assumes that, as charge builds up at the surface, the potential drop across the diffuse layer will increase and, hence, EOF will increase. However, deviation from linearity for the flow versus surface charge relationship is indicated in eq 3. This is derived from the Boltzmann distribution and indicates a flattening at extreme potentials, both high and low. This is explained in previous models, in that the double layer thickness decreases dramatically with surface potential field strength.7 This shrinkage causes most of the potential drop to occur across the immobile layer. Hence, the diffuse layer contains a smaller fraction of the counterions, and increases in EOF are proportionally less.

Another interesting interaction between surface charge and flow occurs after rinsing the capillary with KOH (0.10 M). Rinsing with KOH increases the flow dramatically. This may be explained by speculating an increased surface area from the roughening of the silica.19 This roughening has the net effect of increasing the surface charge as projected from the surface to the diffuse layer. More than one charge on the surface may be induced by a given volume in the diffuse layer. Large amounts of charge may be built up in the nooks and crannies which leads to an induced charge in the double layer and therefore increased flow.

Rinsing of the capillary with KOH also prevents an applied radial voltage from having any measurable effect on EOF.
This overwhelming effect appears to result from the additive nature of charges induced from the applied radial voltage and the ionized functional groups. Since the charges from ionized functional groups are proportional to surface area (eq 2 and Appendix I) and the electrostatic charges are independent of surface area (eq 10), the ionized surface groups at the etched surface will far exceed the charge induced by the radial voltage.

In contrast, at low surface charge density the applied radial voltage has a much more dramatic effect. This occurs at low pH's and deactivated or polymer-covered inner surfaces. This increased effect is, again, a result of the additive nature of the ionized hydroxyl group charge and the electrostatic charge. If the functional group charges are quite low then the electrostatic charges induced by the applied radial voltage have a much greater relative effect on EOF.

The internal environment of the CE capillary is definitely influenced by the exterior through the applied radial voltage induced capacitive effect. Noting this, the column was passively grounded: it was painted with silver paint and attached to ground. This, in essence, has the effect of forming a radial voltage which varies over the length of the capillary according to the internal potential versus earth ground. This would cause a variation of $\gamma$ over the length of the capillary and might lead to laminar flow and band broadening. Although this is a crude experiment it demonstrates three important points. First, EOF may be increased over the native-surface-charge-induced flow without extra power supplies. Second, electrical alteration of EOF may be accomplished inexpensively and with simple technology. Finally, and perhaps most important, the external environment of the capillary directly affects the operation of the CE system. Holders, supports, nuts, bolts, etc., all may have an effect on the EOF if they are near the capillary.

CONCLUSIONS

Electroosmotic flow may be increased or decreased by application of an applied voltage across the capillary wall, but only within certain limits. General trends in EOF have been defined theoretically by an inverse hyperbolic sine function. The theory presented is expected to fit more closely to trends in EOF in capillaries filled with buffers at lower pH's. Electroosmotic flow can be controlled in this manner with a rugged, but flexible coating of ionomer film (Nafion). Finally, passive conductors near the capillary may affect the electroosmotic flow through this capacitive effect.

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APPENDIX I

Calculation of Surface Charge Density Due to Buffer pH. The first assumption is that the only significant reaction causing surface charge on the fused silica surface is the following:

$$[\text{SiOH}_3^+] \xrightarrow{K} [\text{SiO}_3^2^-] + [\text{H}^+]$$

and

$$[\text{SiO}_3^2^-][\text{H}^+] / [\text{SiOH}_3^+] = 4.2 \times 10^{-10} \text{ (a1)}$$

The equilibrium constant, $K$, is assumed to approach the logical limit of silic acid, $\text{SiO}_2\text{H}_4^-$, and is $4.2 \times 10^{-50}$. Since the constant and $pK_a$ are known, the ratio of $[\text{SiO}_3^2^-]$ and $[\text{SiOH}_3^+]$ may be calculated as follows:

$$[\text{SiO}_3^2^-] / [\text{SiOH}_3^+] = K / [\text{H}^+] \text{ (a2)}$$

Also, the concentration of hydroxyl groups per unit surface area, $\gamma$, on the inner surface of the capillary is known. This may be written as

$$[\text{SiO}_3^2^-] + [\text{SiOH}_3^+] = \gamma \text{ (a3)}$$

Combining equations a1 and a3 and solving for $[\text{SiO}_3^2^-]$ gives the number of surface charges per unit area, $q_{\text{Si}}$, as a function of $[\text{H}^+]$. This relationship is

$$[\text{SiO}_3^2^-] = \gamma / (1 + [(\text{H}^+)^2 / K]) = q_{\text{Si}} \text{ (a4)}$$

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