## Supporting Information

### SI 1. Thickness of EDL for BGE with Monovalent Cations

According to Coulomb's law, the electrical force, $F_e$, between an oxygen atom in a silanoate (SiO$^-$) group and the positive counter ion is

$$F_e = \frac{z_S z_B e^2}{4\pi\varepsilon_0\varepsilon_r x_1^2} \qquad \text{(SI-1)}$$

where $z_S$ (-1) and $z_B$ (+1) are the charge numbers of a silanoate ion and the positive counter ion respectively, and $e$ is the elementary charge ($1.602 \times 10^{-12}$ C). The work done on the system in moving a cation toward a silanoate anion a distance $dx$ from the position $\infty$ to $x_1$ is

$$dw = \left(\frac{z_S z_B e^2}{4\pi\varepsilon_0\varepsilon_r x^2}\right) dx \qquad \text{(SI-2)}$$

$$w = \int_{\infty}^{x_1}\frac{z_S z_B e^2}{4\pi\varepsilon_0\varepsilon_r x^2}dx = -\frac{z_S z_B e^2}{4\pi\varepsilon_0\varepsilon_r x_1} \qquad \text{(SI-3)}$$

This work $w$ is the electrostatic contribution to the Gibbs energy of activation, $\Delta^{\ddagger}G_{es}^{\circ}$, when two ions form an activated complex. Multiplication by the Avogadro constant $N_A$ gives the molar quantity,

$$\Delta^{\ddagger}G_{es}^{\circ} = -\frac{N_A z_S z_B e^2}{4\pi\varepsilon_0\varepsilon_r x_1} \qquad \text{(SI-4)}$$

The total molar Gibbs energy of activation, or the *standard Gibbs energy of activation*, combining with the non-electrostatic contribution, $\Delta^{\ddagger}G_{nes}^{\circ}$ is

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}G_{nes}^{\circ} - \frac{N_A z_S z_B e^2}{4\pi\varepsilon_0\varepsilon_r x_1} \qquad \text{(SI-5)}$$

According to the thermodynamic formulation of conventional transition-state theory[18], the rate constant $k$ of the reaction is

$$k = (\mathbf{k}T/h) \exp(-\Delta^{\ddagger}G^{\circ}/RT) \qquad \text{(SI-6)}$$

where $\mathbf{k}$ is Boltzmann constant ($= R/N_A$), and $h$ is Planck constant. Substitution of $\Delta^{\ddagger}G^{\circ}$ from equation SI-5 into equation SI-6 and taking natural logarithms, we then have

$$\ln k = \ln (\mathbf{k}T/h) - (\Delta^{\ddagger}G_{nes}^{\circ}/RT) + \frac{N_A z_S z_B e^2}{4\pi\varepsilon_0 \varepsilon_r x_1 RT} \cdot \qquad \text{(SI-7)}$$

Equation SI-7 can be written as

$$\ln k = \ln k_0 + \frac{N_A z_S z_B e^2}{4\pi\varepsilon_0 \varepsilon_r x_1 RT} \qquad \text{(SI-8)}$$

where $k_0 = \ln (\mathbf{k}T/h) - (\Delta^{\ddagger}G_{nes}^{\circ}/RT)$, $k_0$ is the value of $k$ in a medium of infinite dielectric constant, in which the electrostatic forces become zero.

Brønsted suggested that the rate of second order reactions 9 or 10 might be expressed as[27]

$$v = k_0 [SiO^-] [B] \frac{y_s\, y_b}{y_x} \qquad \text{(SI-9)}$$

where $k_0$ is a constant at a given temperature, B is $H^+$ or $M^+$, $y_s$ and $y_b$ are the activity coefficients of silanoate ions and the other reactants, $y_x$ is the activity coefficient of the product. Square brackets [] represent the concentrations of species in the liquid phase by convention. According to the extended Debye-Hückel law[28], the activity coefficient $y_i$ of an ion may be estimated as

$$\log_{10} y_i = -\frac{A z_i^2 I^{1/2}}{1 + B I^{1/2}} \qquad \text{(SI-10)}$$

where $z_i$ is the charge number of an ion $i$, $A = \dfrac{F^3}{4\pi N_A \ln 10}\left(\dfrac{\rho b^{\circ}}{2\epsilon^3 R^3 T^3}\right)^{1/2}$, $\rho$ is the mass density of

the solvent, $b^{\circ} = 1$ mol kg$^{-1}$, and $B$ is an adjustable empirical parameter. For a very low

concentration, $B = 0$, then the equation SI-10 can be simplified as

$$\log_{10} y_i = -A z_i^2 I^{1/2} \tag{SI-11}$$

The rate constant of the reaction, $k$, is

$$k = k_0 \frac{y_s\, y_b}{y_x} \tag{SI-12}$$

Taking logarithms on equation SI-12 and replacing $\log_{10} y_s$, $\log_{10} y_b$, and $\log_{10} y_x$ with equation

SI-10, we have

$$\ln k = \ln k_0 + 2(\ln 10)\, z_S\, z_B\, A I^{1/2} \tag{SI-13}$$

where $k_0$ is the rate constant extrapolated to zero ionic strength. Comparing equations SI-12 with

SI-8, since $k$ is the rate constant for the same reaction and $k_0$ has to be the same, we can solve the

thickness of the double layer $x_1$,

$$\delta = x_1 = \frac{1}{F}\sqrt{\frac{\epsilon RT}{2000 I}} \tag{SI-14}$$

## SI 2.   Thickness of EDL for BGE with Multivalent Inorganic Cations

The distance between the centers of an oxygen atom in a silanoate ion group and an inorganic

cation is $x_1$. The distance between the centers of the inorganic cation and an anion is $x_2$, and the

total distance between the centers of an oxygen atom and an anion is $x$, where $x = x_1 + x_2$. A simple

scheme is shown in Figure SI-1. It is assumed that the ions contact linearly from the capillary

wall towards the center. The portion of the surface covered by the cations alone is $\theta_M$, and the

portion of the surface covered by silanoate-cation-anion complexes is $\theta_{MA}$. Therefore, the average thickness of the electrical double layer $\delta$ is

$$\delta = \frac{\theta_M x_1 + \theta_{MA} x}{\theta_M + \theta_{MA}} = \frac{\theta_M x_1 + \theta_{MA}(x_1 + x_2)}{\theta_M + \theta_{MA}} \tag{SI-15}$$

where $\theta_M = K_M a_M^{m+}(1 - \theta_H - \theta_M - \theta_A)$, $\theta_{MA} = K_M a_M^{m+} K_A a_A^{n-}(1 - \theta_H - \theta_M - \theta_A)$, and $(\theta_H + \theta_M + \theta_A + \theta_{SiO^-}) = 1$. When only two ions interact with each other, the distance is $x_1$, derived in Section SI-1,

When three ions interact with one another, electric forces are present between an oxygen atom in a silanoate ion and a cation, the cation and an anion, and the anion and the oxygen atom. The total force $F_e$ is the sum of the three forces that are respectively shown in equation SI-16,

$$F_c = \frac{z_S z_M e^2}{4\pi \varepsilon_0 \varepsilon_r x_1^2} + \frac{z_M z_A e^2}{4\pi \varepsilon_0 \varepsilon_r x_2^2} + \frac{z_S z_A e^2}{4\pi \varepsilon_0 \varepsilon_r (x_1 + x_2)^2} \tag{SI-16}$$

where $z_S$ representing for the charge of a silanoate ion is $(-1)$, $z_M$ representing the charge of a multiply charged cation is a positive integer greater than one, and $z_A$ representing the charge of an anion is a negative integer. The work done on the system in moving the ions toward the silanoate ion a distance $dx$,

$$dw = F_e \, dx$$

$$w = \int_{\infty}^{x_1} \frac{z_S z_M e^2}{4\pi\varepsilon_0\varepsilon_r x_1^2} dx + \int_{\infty}^{x_2} \frac{z_M z_A e^2}{4\pi\varepsilon_0\varepsilon_r x_2^2} dx + \int_{\infty}^{x} \frac{z_S z_A e^2}{4\pi\varepsilon_0\varepsilon_r (x_1 + x_2)^2} dx \tag{SI-17}$$

$$w = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_r}\left(\frac{z_S z_M}{x_1} + \frac{z_M z_A}{x_2} + \frac{z_S z_A}{x_1 + x_2}\right) \tag{SI-18}$$

Similar to the previous section for the monovalent model, this work $w$ is the electrostatic contribution to the Gibbs energy of activation, $\Delta^{\ddagger}G_{es}^{\circ}$, when three ions form an activated

complex, multiplied by the Avogadro constant $N_A$ to give the molar quantity. The total molar Gibbs energy of activation, or the *standard Gibbs free energy of activation*, combining with the non-electrostatic contribution, $\Delta^{\ddagger}G_{nes}{}^{\circ}$ is

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}G_{nes}{}^{\circ} - \frac{N_A e^2}{4\pi\varepsilon_0\varepsilon_r RT}\left(\frac{z_S z_M}{x_1} + \frac{z_M z_A}{x_2} + \frac{z_S z_A}{x_1 + x_2}\right) \tag{SI-19}$$

Following the same process at that in section SI-1, we have

$$\ln k = \ln k_0 + \frac{N_A e^2}{4\pi\varepsilon_0\varepsilon_r RT}\left(\frac{z_S z_M}{x_1} + \frac{z_M z_A}{x_2} + \frac{z_S z_A}{x_1 + x_2}\right) \tag{SI-20}$$

For a third order reaction involving three ions, the equation SI-12 can be extended to[18]

$$\log_{10} k = \log_{10} k_0 + 2\left(z_S z_M + z_M z_A + z_S z_A\right) A I^{1/2} \tag{SI-21}$$

Similar to the previous section, since $z_S = -1$, we can resolve $x_2$,

$$x_2 = x_1 \sqrt{\frac{z_M}{z_M - 1}} \tag{SI-22}$$

Replacing $x_1$ and $x_2$ in equation SI-15 with equations SI-14 and SI-22, the average thickness of the electrical double layer $\delta$ is

$$\delta = \frac{1}{F}\sqrt{\frac{\varepsilon RT}{2000 I}} \times \frac{1 + K_A a_{A^{n-}}\left(1 + \sqrt{\frac{z_M}{z_M - 1}}\right)}{1 + K_A a_{A^{n-}}} \tag{SI-23}$$

## SI 3. Symbols

### Roman Alphabet

$a_X$    activity of the subscripted specie X in mol L$^{-1}$.

$B$:     Debye- Hückel empirical constant

$e$:     elementary charge,

$E$:     applied electric field per unit length in V/m

$F$:     Faraday constant

$F_e$:     electrical force

$h$:     Planck constant

$I$:     ionic strength

$\mathbf{k}$:     Boltzmann constant

$k_0$:     value of the rate constant in a medium of infinite dielectric constant, in which the electrostatic forces become zero.

$K_A$:     equilibrium constants and $K_A = \dfrac{[SiO^- M^{m+} A^{n-}]}{[SiO^- M^{m+}]a_{A^{n-}}}$

$K_H$:     equilibrium constants and $K_H = \dfrac{[SiOH]}{a_{H^+}[SiO^-]}$

$K_M$:     equilibrium constants and $K_M{}^+ = \dfrac{[SiOM]}{a_{M^+}[SiO^-]}$

$K_M{}^{m+}$:     equilibrium constants and $K_M{}^{m+} = \dfrac{[SiO^- M^{m+}]}{a_{M^{m+}}[SiO^-]}$

$K_N$:     equilibrium constants and $K_N = \dfrac{[SiO^- N]}{[SiO^-][N]}$

$l_d$:     effective length (from injection end to the detection window)

$l_t$:     total length (from injection end to the detection window)

$N_A$:     Avogadro constant

$Q_{0,a}$:      number of apparent silanol groups in all forms per unit area at the capillary surface (in mol dm$^{-2}$)

$R$:      universal gas constant

$t_0$:      retention time of unretented peak

$t_{buf}$:      retention time of eof marker when buffer was used as the background electrolyte

$t_d$:      electronic delay time

$t_i$:      retention time of peak i

$t_{inj}$:      time consumed per injection of sample

$t_{rmp}$:      voltage ramp time

$t_v$:      time used for voltage application

$t_{water}$:      retention time of eof marker when water was used as the background electrolyte

$T$:      temperature

$w$      work done on the system in moving a cation toward a silanoate anion

$V$:      applied voltage

$x$:      total distance between the centers of an oxygen atom and an anion is, where $x = x_1 + x_2$. It is assumed that the ions contact linearly from the capillary wall towards the center.

$x_1$:      distance between the centers of an oxygen atom in a silanoate ion group and a cation.

$x_2$:      distance between the centers of a cation that is attached to an oxygen on the silanoate and the center of an anion in buffer solution

$y_i$:      activity coefficient of an ion

$z_A$:      charge of an anion

$z_B$      charge number of a positive ion (+1)

$z_i$:      charge of an ion $i$

$z_M$:      charge of a multivalent cation, a positive integer greater than one,

$z_S$     charge number of a silanoate ion (-1)

**Greek Alphabet**

$\Delta^{\ddagger}G^{\circ}$:     standard Gibbs energy of activation

$\Delta^{\ddagger}G_{es}^{\circ}$:     electrostatic contribution to the Gibbs energy of activation

$\Delta^{\ddagger}G_{nes}^{\circ}$:non-electrostatic contribution

$\delta$:     thickness of the electrical double layer in m

$\varepsilon$ :     permittivity of the buffer and commonly expressed as $\varepsilon_0\varepsilon_r$

$\varepsilon_0$:     permittivity of a vacuum

$\varepsilon_r$:     relative permittivity

$\eta$:     viscosity of the buffer in $Nm^{-2}s$ (or Pa·s)

$\kappa^{-1}$:     Debye length

$\mu_{ep}$:     electrophoretic mobility

$\mu_{eo}$:     electroosmotic mobility

$v_{eo}$:     velocity of the electroosmotic flow

$\theta_A$:     fraction of surface covered by $A^{n-}$ and $\theta_A = \dfrac{K_A a_{A^{n-}}}{1 + K_{M^{m+}} a_{M^{m+}} + K_H a_{H^+} + K_A a_{A^{n-}}}$

$\theta_H$:     fraction of surface covered by $H^+$ and $\theta_H = \dfrac{K_H a_{H^+}}{1 + K_{M^{m+}} a_{M^{m+}} + K_H a_{H^+} + K_A a_{A^{n-}}}$

$\theta_M$:     fraction of surface covered by $M^{m+}$ and $\theta_M = \dfrac{K_{M^{m+}} a_{M^{m+}}}{1 + K_{M^{m+}} a_{M^{m+}} + K_H a_{H^+} + K_A a_{A^{n-}}}$

$\theta_{MA}$:    fraction of the surface covered by silanoate-cation-anion complexes when the charge of

M greater than 1. $\theta_{MA} = K_M \, a_M{}^{m+} \, K_A \, a_A{}^{n-} \, (1 - \theta_H - \theta_M - \theta_A)$,

$\sigma$:    charge per unit surface area or charge density.

$\sigma_v$:    surface charge density due to the applied radial voltage

$\sigma_{Si}$:    surface charge density due to the ionization of the silanol groups
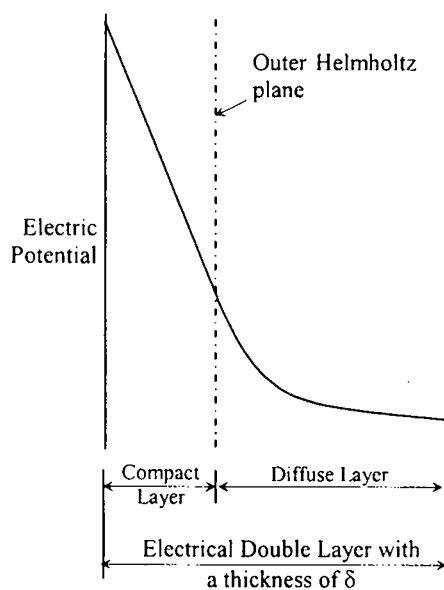
$\xi$:    zeta potential

Figure SI-1. A simple electrical double layer model, Gouy-Chapman-Stern model.

In the case that monovalent cations are present, $\delta = x_1$. In the case that multivalent inorganic cations are present, $\delta = x$. $x_1 \neq x$.

x