Electronic Supplementary Information for "Importance of Temperature on the Gel Electrophoresis of a Charge-regulated, Zwitterionic Sphere"

Jyh-Ping Hsu,[1,*] Chih-Hua Huang,[1] Shiojenn Tseng[2,*]

[1]Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, Tel: 886-2-23637448, Fax: 886-2-23623040

[2]Department of Mathematics, Tamkang University, Tamsui, Taipei, Taiwan 25137

Scaled governing equations

In scaled forms, the equations governing the present problem can be summarized as following:

$$\nabla^{*2}\phi_e^* = -\frac{(\kappa a)^2}{1+\alpha}\left[\exp(-\phi_e^*) - \exp(\alpha\phi_e^*)\right] \tag{S1}$$

$$\nabla^{*2}\delta\phi^* = \frac{(\kappa a)^2}{1+\alpha}\left[(\delta\phi^* + g_1^*)\exp(-\phi_e^*) + \alpha(\delta\phi^* + g_2^*)\exp(\alpha\phi_e^*)\right] \tag{S2}$$

$$\nabla^{*2}g_1^* - \nabla^*\phi_e^* \cdot \nabla^*g_1^* = Pe_1\mathbf{u}^* \cdot \nabla^*\phi_e^* \tag{S3}$$

$$\nabla^{*2}g_2^* + \alpha\nabla^*\phi_e^* \cdot \nabla^*g_2^* = Pe_2\mathbf{u}^* \cdot \nabla^*\phi_e^* \tag{S4}$$

$$\nabla^* \cdot \mathbf{u}^* = 0 \tag{S5}$$

$$-\nabla^*\delta p^* + \nabla^{*2}\mathbf{u}^* + \left(\nabla^{*2}\phi_e^*\nabla^*\delta\phi^* + \nabla^{*2}\delta\phi^*\nabla^*\phi_e^*\right) - (\lambda a)^2\mathbf{u}^* = \mathbf{0} \tag{S6}$$

$$n_1^* = \exp(-\phi_e^*)\left[1 - (\delta\phi^* + g_1^*)\right] \tag{S7}$$

$$n_2^* = \exp(\alpha\phi_e^*)\left[1 + \alpha(\delta\phi^* + g_2^*)\right] \tag{S8}$$

In these expressions, $\nabla^* = a\nabla$, $\nabla^{*2} = a^2\nabla^2$, $\kappa = [\sum_{j=1}^{2} n_{j0}(ez_j)^2/\varepsilon k_B T]^{1/2}$, $n_j^* = n_j/n_{j0}$,

$\lambda = \sqrt{\gamma/\eta}$, $\phi_e^* = \phi_e/\zeta_R$, $\delta\phi^* = \delta\phi/\zeta_R$, $g_j^* = g_j/\zeta_R$, $\zeta_R = k_B T/z_1 e$,

$Pe_j = \varepsilon(k_B T/z_1 e)^2/\mu D_j$, $\mathbf{u}^* = \mathbf{u}/U_{ref}$, $\delta p^* = \delta p/p_{ref}$, $U_{ref} = \varepsilon(k_B T/z_1 e)^2/a\mu$, and

$p_{\text{ref}} = \varepsilon \zeta_R^2 / a^2$. κ and Pe_j are the reciprocal Debye screening length and the electric

Peclet number of ionic species j, $j=1,2$, respectively.

Solution procedure

Instead solving the original problem directly, it is decomposed into two sub-problems.

In the first sub-problem, the particle moves with a constant velocity $\mathbf{U}$ in the absence of $\mathbf{E}$,

and in the second sub-problem, $\mathbf{E}$ is applied but the particle remains fixed in the space.

Solving these two sub-problems separately, and the results used to evaluate the forces

acting on the particle, including the electrical force $\mathbf{F}_E$ and the hydrodynamic force $\mathbf{F}_H$.

The pseudo steady state condition assumed suggests that the sum of these forces vanishes,

which can be applied to calculate the mobility of the particle. Let $\mathbf{F}_i$ be the total force

acting on the particle in the z direction in sub-problem i and F_i be its magnitude,

$i=1,2$. Then $F_1 = \chi U$ and $F_2 = \beta E$, where U is the particle velocity, and χ, and β

are and proportional constant. At pseudo steady state, $F_1 + F_2 = 0$, yielding $U = -\beta E / \chi$.

Therefore, the mobility of the particle, $\mu_E = U/E$, is

$$\mu_E = -\frac{\beta}{\chi} = -\frac{F_2 U}{F_1 E} \tag{S9}$$

Let F_{Ei} and F_{Hi} be the z components of $\mathbf{F}_E$ and $\mathbf{F}_H$ in sub-problem i,

respectively, $i=1,2$, and $F_{Ei}^* = F_{Ei} / \varepsilon \zeta_R^2$ and $F_{Hi}^* = F_{Hi} / \varepsilon \zeta_R^2$ be the corresponding

scaled values. Then F_{Ei}^* and F_{Hi}^* can be evaluated by[S1]

$$F_{\mathrm{E}i}^{*} = \int_{\Omega_{\mathrm{p}}^{*}} \left(\frac{\partial \phi_{\mathrm{e}}^{*}}{\partial n} \frac{\partial \delta \phi^{*}}{\partial z} - \left(\frac{\partial \phi_{\mathrm{e}}^{*}}{\partial t} \frac{\partial \delta \phi^{*}}{\partial t} \right) n_{z} \right) d\Omega_{\mathrm{p}}^{*} \qquad (S10)$$

$$F_{\mathrm{H}i}^{*} = \int_{\Omega_{\mathrm{p}}^{*}} \left(\boldsymbol{\sigma}^{\mathbf{H}^{*}} \cdot \mathbf{n} \right) \cdot \mathbf{e}_{z} d\Omega_{\mathrm{p}}^{*} \qquad (S11)$$

Ω_{p}^{*} is the dimensionless surface area of the particle scaled by a^{2}; $\partial/\partial n$ and $\partial/\partial t$ are

the rate of change with distance along the unit normal $\mathbf{n}$ and the unit tangential $\mathbf{t}$,

respectively; n_{z} is the z component of $\mathbf{n}$; $\boldsymbol{\sigma}^{\mathbf{H}^{*}} = \boldsymbol{\sigma}^{\mathbf{H}}/\left(\varepsilon \zeta_{\mathrm{R}}^{2}/a^{2} \right)$ is the scaled shear stress

tensor with $\boldsymbol{\sigma}^{\mathbf{H}}$ being the corresponding shear stress tensor.

Code verification

The applicability of the solution procedure and the software adopted is verified by

solving the electrophoresis of an SiO_2 particle in an infinite aqueous solution for the case

where a=20 nm, pK_A=7, pK_B=2, C_{NaCl}=10^{-3} M, and N_{total}=5$\times$10^{-6} mol/m^2, solved

previously by Hsu and Tai.[S2] To simulate their conditions, a small value of 0.01 % is

assumed for w. Fig. S1 shows the variation of the particle mobility with pH at three

representative levels of T; both their result and the present result are presented. This

figure reveals that the performance of the present approach is satisfactory. Note that the

magnitude of the present mobility is slightly smaller than that Hsu and Tai,[S2] which is

reasonable because although the value of w assumed is small, the hydrodynamic drag

acting on the particle in a gel medium is still slightly greater than that in an aqueous
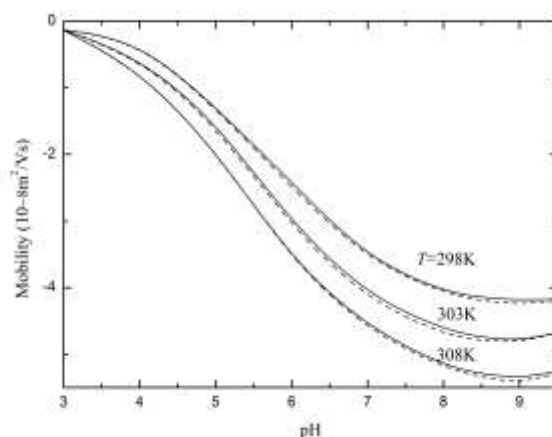
medium.

Fig. S1 Variation of mobility with pH at various levels of T for the case where a=20 nm, pK_A=7, pK_B=2, C_{NaCl}=10^{-3} M, and N_{total}=5×10^{-6} mol/m^2. Solid curve: present result at w=0.01 %; dashed curve: result of Hsu and Tai (w=0 %).[S2]

Temperature dependence of physical properties

In our case, we assume that the temperature dependence of the relative permittivity ε_r can be expressed as[S3]

$$\varepsilon_r(T) = \exp[4.47615 - 4.60128 \times 10^{-3}(T-237) + 2.6952 \times 10^{-7}(T-237)^2] \qquad (S12)$$

As T varies from 283 K to 323 K, ε_r decreases from 83.945 to 69.879.

The expression below is assumed for the dependence of the liquid viscosity η on T:[S4]

$$\eta(T) = 883.08[(\Delta T) + 2.28 \times 10^{-3}(\Delta T)^2 - 1.14 \times 10^{-5}(\Delta T)^3 + 1.55 \times 10^{-8}(\Delta T)^4], \qquad (S13)$$

where $\Delta T = T - 225.334$. As T increases from 283 K to 323 K, η decreases from 1.314 to 0.549 $(m \cdot Pa \cdot s)$.

The Nernst-Haskell equation below is used for the temperature dependence of the ionic diffusivity D_j:[S5]

$$D_j = \frac{RT}{F^2} \left(\frac{1/|z_j|}{1/\lambda_j^0} \right), \tag{S14}$$

where R and λ_j^0 are gas constant and the limiting conductance of ionic species j,

respectively. If T is raised from 283 K to 323 K, the diffusivity of K^+ increases from

1.90 to 2.17 (m^2/s), and Cl^- from 1.90 to 2.17 (m^2/s).

The temperature dependence of the equilibrium constant K_A can be expressed as

$$\ln K_A = -\frac{\Delta_r G}{k_B T}, \tag{S15}$$

where $\Delta_r G$ is the change in the standard Gibbs energy for the reaction expressed in eqn

(1). The $\Delta_r G$ for the dissociation of H^+ on the particle surface is ca. 13.4 kcal/mol,[S6]

implying that K_A increases from 3.01×10^{-8} to 5.76×10^{-7} (M) as T is raised from

283 K to 323 K.

The temperature dependence of the dissociation constant of water, K_W, can be

expressed as[S7]

$$K_W = 8.754 \times 10^{-10} \exp\left(\frac{-1.01 \times 10^6}{T^2} \right), \tag{S16}$$

where T is in K. K_W varies from 2.92×10^{-15} to 5.47×10^{-14} as T changes from 283 to

323 K.

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