Supporting Information for "Importance of Ionic Polarization Effect on the Electrophoretic Behavior of Polyelectrolyte Nanoparticles in Aqueous Electrolyte Solutions"

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Superposition Methodology

Due to the linear nature of the set of governing equations for the perturbed problem, the problem considered here can be decomposed into two hypothetical sub-problems.[R1] In the first sub-problem the particle moves with a constant scaled velocity U^* in the absence of applied electric field **E**, and in the second sub-problem **E** is applied but the particle is held fixed. To determine the electrophoretic mobility of the polyelectrolyte, both the electrical force $\mathbf{F_e}$ and hydrodynamic force $\mathbf{F_h}$ acting on it need be calculated. Let F_{ei} and F_{hi} be, respectively, the components of $\mathbf{F_e}$ and $\mathbf{F_h}$ in the direction of **E** in sub-problem i, $F_{ei}^* = F_{ei} / \varepsilon(\phi_r)^2$ and $F_{hi}^* = F_{hi} / \varepsilon(\phi_r)^2$ be the corresponding scaled quantities, and $F_i^* = F_{ei}^* + F_{hi}^*$ be the scaled magnitude of total force acting on the polyelectrolyte in the direction of $\mathbf{E}$ in sub-problem i. Then $F_1^* = C_1 U^*$ and $F_2^* = C_2 E^*$, where the proportional constants C_1 and C_2 are independent of U^* and E^*, respectively. At steady state, $F_1^* + F_2^* = 0$, yielding[R2]

$$\mu^* = \frac{U^*}{E^*} = -\frac{C_2}{C_1} \tag{S1}$$

where μ^* is the scaled electrophoretic mobility of the polyelectrolyte. F_{ei} and F_{di} can be evaluated by integrating the Maxwell stress tensor $\boldsymbol{\sigma}^{\mathbf{E}} = \varepsilon\mathbf{EE} - (1/2)\varepsilon E^2\mathbf{I}$ and the hydrodynamic stress tensor $\boldsymbol{\sigma}^{\mathbf{H}} = -\delta p\mathbf{I} + 2\eta\boldsymbol{\Delta}$, respectively, over Ω_p in sub-problem i, where $E^2 = \mathbf{E}\cdot\mathbf{E}$ with $\mathbf{I}$, $\boldsymbol{\Delta} = [\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathbf{T}}]/2$, and the superscript $\mathbf{T}$ being the unit tensor, the rate of deformation tensor, and matrix transpose, respectively, as[R2,R3]

$$F_{ei}^* = \iint_{\Omega_p^*}\left(\left[\frac{\partial\phi_e^*}{\partial n}\frac{\partial\delta\phi^*}{\partial Z} + \frac{\partial\delta\phi^*}{\partial n}\frac{\partial\phi_e^*}{\partial Z}\right] - \left[\frac{\partial\phi_e^*}{\partial n}\frac{\partial\delta\phi^*}{\partial n} + \frac{\partial\phi_e^*}{\partial t}\frac{\partial\delta\phi^*}{\partial t}\right]n_z\right)d\Omega_p^*,\ i=1,2 \tag{S2}$$

$$F_{hi}^* = \iint_{\Omega_p^*}(\boldsymbol{\sigma}^{\mathbf{H}^*}\cdot\mathbf{n})\cdot\mathbf{e}_z d\Omega_p^*,\ i=1,2 \tag{S3}$$

In these expressions, $Z = z/a$; $\Omega_p^* = \Omega_p/a^2$, $\boldsymbol{\sigma}^{\mathbf{E}^*} = \boldsymbol{\sigma}^{\mathbf{E}}/[\varepsilon(\phi_r)^2/a^2]$, and $\boldsymbol{\sigma}^{\mathbf{H}^*} = \boldsymbol{\sigma}^{\mathbf{H}}/[\varepsilon(\phi_r)^2/a^2]$ are the scaled Ω_p, the scaled Maxwell tensor, and the scaled hydrodynamic stress tensor, respectively; n_z, n, and t are the z components of the unit normal vector **n**, the magnitude of **n**, and that of the unit tangential vector **t**, respectively. Because F_{h2}^{*} always acts against the motion of the polyelectrolyte, it is usually called the scaled electroosmotic retardation force,[R2] which is dominated by an electroosmotic flow coming mainly from the motion of the counterions inside the double layer due to the application of **E**.

Note that in sub-problem one, $U^{*} \neq 0$ and $E^{*} = 0$, and in sub-problem two, $U^{*} = 0$ and $E^{*} \neq 0$. For a given E^{*}, the solution procedure includes the following steps.[R2] (i) Assume an arbitrary value of U^{*} in sub-problem one and that of E^{*} in sub-problem two, and solve eqs 2-6 in the text subject to appropriate boundary conditions. (ii) Calculate F_{ei}^{*} and F_{hi}^{*} by eqs S2 and S3, respectively, and evaluate $F_{i}^{*} = F_{ei}^{*} + F_{hi}^{*}$, i=1,2. (iii) Use $F_{1}^{*} = C_{1}U^{*}$ and $F_{2}^{*} = C_{2}E^{*}$ to calculate C_{1} and C_{2}. (iv) Apply eq S1 to evaluate μ^{*}. Note that if we initially let $U^{*} = E^{*}$, then μ^{*} can also be evaluated directly by $-(F_{2}^{*} / F_{1}^{*})$.

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