

SUPPORTING INFORMATION

Metal speciation dynamics in soft colloidal ligand suspensions. Electrostatic and site distribution aspects.

Jérôme F.L. Duval

Laboratory Environment and Mineral Processing, Nancy-University, CNRS
UMR CNRS-INPL 7569, BP 40 – F-54501 Vandoeuvre-lès-Nancy Cedex, France.

1. Boltzmann statistics, a balance between diffusion and migration transports.

In the equilibrium chemical regime, the derivatives of the local M and ML concentrations with respect to time vanish so that summing eqs 13 and 14 leads to

$$a \leq r \leq a+d: \quad D_M \nabla_r^2 c_M^e(r) + \frac{z_M D_M}{z} \left\{ \frac{\partial c_M^e(r)}{\partial r} \frac{\partial y(r)}{\partial r} + c_M^e(r) \nabla_r^2 y(r) \right\} = 0, \quad (S1)$$

where the superscript ‘e’ holds for quantities at equilibrium. It is immediately seen that the above equation is also valid for radial positions $a \leq r \leq a+r_c$ (eq 15) under the condition $\partial c_M(r, t) / \partial t = 0$. Equation S1 may then be rewritten in the form

$$a \leq r \leq a+r_c: \quad \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_M^e(r)}{\partial r} \right) = - \frac{z_M}{z} \nabla \cdot \left\{ c_M^e(r) \frac{\partial y(r)}{\partial r} \right\} \quad (S2)$$

with $\nabla \cdot G(r) \equiv \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 G(r))$ the divergence operator applied to a radial function G . After straightforward simplification and integration of eq S2 between a and r , we obtain

$$a \leq r \leq a+r_c: \quad \frac{\partial c_M^e(r)}{\partial r} = - \frac{z_M}{z} c_M^e(r) \frac{\partial y(r)}{\partial r}. \quad (S3)$$

Second integration provides

$$a \leq r \leq a+r_c: \quad c_M^e(r) = c_M^e(r = a + r_c) \exp \left\{ z_M [y(r = a + r_c) - y(r)] / z \right\}, \quad (S4)$$

which is the well-known Boltzmann statistic distribution for M species across the interphase between particle and outer electrolytic medium.

2. Derivation of the effective kinetic rate constants k_a^* and k_d^* .

The integration of eq 13 for $i=ML$ over the shell volume leads to

$$\frac{\partial \rho_{ML}^s(t)}{\partial t} = -k_d \rho_{ML}^s(t) + \frac{4\pi c_L^*}{V_s} k_a \int_a^{a+d} r^2 c_M(r, t) f(r) dr, \quad (S5)$$

where we have introduced the ML concentration $\rho_{\text{ML}}^{\text{s}}$ over the shell layer volume of the particle:

$$\rho_{\text{ML}}^{\text{s}}(t) = \frac{4\pi}{V_{\text{s}}} \int_a^{a+d} r^2 c_{\text{ML}}(r, t) dr, \quad (\text{S6})$$

with $V_{\text{s}} = 4\pi \left\{ (a+d)^3 - a^3 \right\} / 3$ the volume over which the reactive binding sites L are distributed.

The condition of conservation of total binding sites throughout the soft diffuse interphase when changing α/d and/or d is ensured by eq 5. This allows us to write

$$\rho_{\text{L}}^{\text{V}} / c_{\text{L}}^* = V_{\text{s}} / V_{\text{c}}. \quad (\text{S7})$$

Substitution of eq S7 into eq S5 and multiplication of both sides of the resulting equation by $V_{\text{s}} / V_{\text{c}}$ yields

$$\frac{\partial \rho_{\text{ML}}^{\text{V}}(t)}{\partial t} = -k_{\text{d}} \rho_{\text{ML}}^{\text{V}}(t) + k_{\text{a}} \rho_{\text{L}}^{\text{V}} \rho_{\text{M}}^{\text{s}}(t), \quad (\text{S8})$$

where we have used the relationship $\rho_{\text{ML}}^{\text{V}}(t) / \rho_{\text{ML}}^{\text{s}}(t) = V_{\text{s}} / V_{\text{c}}$ (obtained from combining eq 28 for $i=\text{ML}$ with eq S6) and we have defined the concentration $\rho_{\text{M}}^{\text{s}}$ over the shell volume by

$$\rho_{\text{M}}^{\text{s}}(t) = \frac{4\pi}{V_{\text{s}}} \int_a^{a+d} r^2 c_{\text{M}}(r, t) f(r) dr. \quad (\text{S9})$$

Let introduce the colloidal complex stability constant K^* defined by

$$K^* = k_{\text{a}}^* / k_{\text{d}}^*. \quad (\text{S10})$$

Then, eliminating the time-derivative terms between eqs 27 and S8 and using eq S10, one obtains the searched general relationship (eq 30 in the main text) between k_{a}^* and k_{a} :

$$\frac{k_{\text{a}}^*(t)}{k_{\text{a}}} = \frac{\rho_{\text{M}}^{\text{s}}(t) \rho_{\text{L}}^{\text{V}} - \rho_{\text{ML}}^{\text{V}}(t) K^{-1}}{\rho_{\text{M}}^{\text{V}}(t) \rho_{\text{L}}^{\text{V}} - \rho_{\text{ML}}^{\text{V}}(t) K^{*-1}}, \quad (\text{S11})$$

where the time-dependences of $\rho_{\text{M}}^{\text{s}}$, $\rho_{\text{M}}^{\text{V}}$, $\rho_{\text{ML}}^{\text{V}}$ and k_{a}^* have been written explicitly. The remaining issue is the derivation of the expression for the stability constant K^* , which is presented below.

Under chemical equilibrium conditions reached at $t \rightarrow \infty$ where $\partial \rho_{\text{ML}}^{\text{V}}(t) / \partial t = 0$, eq S8 shows that

$$\frac{k_{\text{a}}}{k_{\text{d}}} = \frac{\rho_{\text{ML}}^{\text{V,e}}}{\rho_{\text{L}}^{\text{V}} \rho_{\text{M}}^{\text{s,e}}}, \quad (\text{S12})$$

where the superscript ‘e’ refers to quantities defined at chemical equilibrium. Similarly, eq 27 provides at $t \rightarrow \infty$

$$\frac{k_a^*}{k_d^*} = \frac{\rho_{ML}^{V,e}}{\rho_L^V \rho_M^{V,e}}. \quad (S13)$$

Recalling that the intrinsic (chemical) stability constant of ML complex is given by $K = k_a / k_d$, the combination of eqs S10, S12 and S13 gives

$$K^* = K \frac{\rho_M^{s,e}}{\rho_M^{V,e}} \quad (S14)$$

Equations 13-15 may be straightforwardly integrated under chemical equilibrium conditions ($\partial \rho_{i=M,ML}^V(t) / \partial t = 0$), and the results reads as the well-known Boltzmann formulation, *i.e.* eq S4.

As shown above, eq S4 basically results from the balance between free metal migration and diffusion fluxes. For cases where $\kappa r_c \gg 1$, *i.e.* in the absence of EDL overlap between adjacent particles, eq S4 reduces to

$$c_M^e(r) = c_M^e(r = a + r_c) \exp(-z_M y(r) / z). \quad (S15)$$

Combining eqs S9, S14 and S15, we finally obtain

$$\frac{K^*}{K} = \frac{V_c}{V_s} \frac{\int_a^{a+d} r^2 f(r) \exp(-z_M y(r) / z) dr}{\int_a^{a+r_c} r^2 \exp(-z_M y(r) / z) dr}, \quad (S16)$$

which is eq 32 in the main text.

3. Numerical analysis for evaluating the M and ML concentration profiles.

In this section, the numerical analysis of eqs 13-22 is detailed for the case where there is no significant overlap between electric double layers (EDL) around adjacent particles (*i.e.* $\kappa r_c \gg 1$). From a numerical point of view, this situation is the most complex since the associated partial differential equations (eqs 13-15) are stiff with EDL extensions ($\kappa^{-1} \sim O(1\text{nm} - 30\text{nm})$ for $c^\infty = 0.1\text{mM} - 100\text{mM}$) that are several orders of magnitude shorter than the free metal diffusion length scale at steady-state ($O(\mu\text{m})$).

For the sake of mathematical and numerical convenience, we introduce the dimensionless variables

$$\tilde{t} = t D_M / \left[p(a+d)^2 \right], \quad (S17)$$

$$k_{an} = k_a p(a+d)^2 c_L^* / D_M, \quad (S18)$$

$$k_{\text{dn}} = k_{\text{d}} p (a + d)^2 / D_{\text{M}}, \quad (\text{S19})$$

$$x = (r - a) / (a + d), \quad (\text{S20})$$

$$\text{and} \quad \tilde{c}_{\text{M,ML}}(r, t) = c_{\text{M,ML}}(r, t) / c_{\text{M}}^*. \quad (\text{S21})$$

One of the difficulties in the original formulation of the problem as given in [17] is the existence of a sharp discontinuity at the radial position $r = a + d$ that marks the transition between the reactive particle phase and the electrolyte medium. This difficulty is here circumvented by the introduction of the continuous function f given by eqs 4-5. The continuity of f is verified for any position $r \in [a, a + r_{\text{c}}]$ and any values of α / d . The set of eqs 13-15 may then be reduced to

$$a \leq r \leq a + r_{\text{c}} : \begin{cases} \frac{\partial \tilde{c}_{\text{ML}}(x, \tilde{t})}{\partial t} = -\{k_{\text{dn}} \tilde{c}_{\text{ML}}(x, \tilde{t}) - k_{\text{an}} c_{\text{M}}(x, \tilde{t}) f(x)\} \\ \frac{\partial \tilde{c}_{\text{M}}(x, \tilde{t})}{\partial t} = p \nabla_x^2 \tilde{c}_{\text{M}}(x, \tilde{t}) + \{k_{\text{dn}} c_{\text{ML}}(x, \tilde{t}) - k_{\text{an}} c_{\text{M}}(x, \tilde{t}) f(x)\} \\ + p \frac{z_{\text{M}}}{z} \left\{ \frac{\partial c_{\text{M}}(x, \tilde{t})}{\partial x} \frac{\partial y(x)}{\partial x} + c_{\text{M}}(x, \tilde{t}) \nabla_x^2 y(x) \right\} \end{cases} \quad (\text{S22, S23})$$

with $\nabla_x^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{2}{x + a / (a + d)} \frac{\partial}{\partial x}$. The dimensionless time \tilde{t} is discretized according to

$$k = 1, \dots, N : \quad \tilde{t}_k = (k - 1) \Delta t, \quad (\text{S24})$$

with N an integer and $\Delta t = 1 / (N - 1)$ the time discretization step. Replacing the time derivatives in eqs S22, S23 by their implicit backward Euler finite element differences equivalent, we obtain

$$a \leq r \leq a + r_{\text{c}} :$$

$$\begin{cases} \tilde{c}_{\text{ML}}^{k+1}(x) = -\{k_{\text{dn}} \tilde{c}_{\text{ML}}^{k+1}(x) - k_{\text{an}} \tilde{c}_{\text{M}}^{k+1}(x) f(x)\} \Delta t + \tilde{c}_{\text{ML}}^k(x) \\ \tilde{c}_{\text{M}}^{k+1}(x) = p \Delta t \nabla_x^2 \tilde{c}_{\text{M}}^{k+1}(x) + \{k_{\text{dn}} \tilde{c}_{\text{ML}}^{k+1}(x) - k_{\text{an}} \tilde{c}_{\text{M}}^{k+1}(x) f(x)\} \Delta t \\ + p \Delta t \frac{z_{\text{M}}}{z} \left\{ \frac{\partial \tilde{c}_{\text{M}}^{k+1}(x)}{\partial x} \frac{\partial y(x)}{\partial x} + \tilde{c}_{\text{M}}^{k+1}(x) \nabla_x^2 y(x) \right\} + \tilde{c}_{\text{M}}^k(x) \end{cases} \quad (\text{S25, S26})$$

, where we define $\tilde{c}_{\text{M,ML}}^k(x) = \tilde{c}_{\text{M,ML}}(x, \tilde{t}_k)$. Let us now pose $Y_1^{k+1}(x) = \tilde{c}_{\text{M}}^{k+1}(x)$ and $Y_2^{k+1}(x) = \partial \tilde{c}_{\text{M}}^{k+1}(x) / \partial x$. Combining eqs S25-S26, one shows that eq S26 may be rearranged in a set of two ordinary differential equations of the first order as follows

$a \leq r \leq a + r_c :$

$$\begin{cases} \frac{dY_1^{k+1}(x)}{dx} = Y_2^{k+1}(x) \\ \frac{dY_2^{k+1}(x)}{dx} = -Y_2^{k+1}(x) \left\{ \frac{2}{x+a/(a+d)} + \frac{z_M}{z} \frac{\partial y(x)}{\partial x} \right\} + Y_1^{k+1}(x) \left[\frac{1}{p\Delta t} + \frac{k_{an}}{p} f(x) - \right. \\ \left. \frac{z_M}{z} \nabla_x^2 y(x) - \frac{1}{p} \frac{k_{dn} k_{an} \Delta t f(x)}{1 + k_{dn} \Delta t} \right] - \Omega^k(x) \end{cases} \quad (S27, S28)$$

, with
$$\Omega^k(x) = \frac{1}{p\Delta t} Y_1^k(x) + \frac{1}{p} \frac{k_{dn}}{1 + k_{dn} \Delta t} \tilde{c}_{ML}^k(x) \quad (S29)$$

Let \mathfrak{S} be a numerical solver which enables the calculation of the searched $Y_1^{k+1}(x)$ and $Y_2^{k+1}(x)$ at any k for a given function Ω^k , *i.e.*

$$k = 1, \dots, N-1: \quad Y_{1,2}^{k+1}(x) = \mathfrak{S}(\Omega^k(x)). \quad (S30)$$

The function Ω^1 corresponds to the situation at $\tilde{t} = 0$ with $Y_1^1(x) (= \tilde{c}_M^1(x))$ and $\tilde{c}_{ML}^1(x)$ provided by eqs 16-18. Iterating k from 1 to $N-1$, eq S30 leads to the evaluation of $Y_1^{k+1}(x)$ and $Y_2^{k+1}(x)$, recalling that the local concentrations $\tilde{c}_{ML}^{k+1}(x)$ and $\tilde{c}_{ML}^k(x)$ are interrelated *via* the recursive relationship S25 which reads as

$$a \leq r \leq a + r_c: \quad \tilde{c}_{ML}^{k+1}(x) = (1 + k_{dn} \Delta t)^{-1} \left\{ k_{an} \Delta t Y_1^{k+1}(x) f(x) + \tilde{c}_{ML}^k(x) \right\}. \quad (S31)$$

Equations S27-S31 thus provide the M and ML concentrations profiles at any time \tilde{t}_k . Let us now describe the numerical procedure subsumed in the solver \mathfrak{S} .

The set of differential equations (S27-S28) may be written for a given \tilde{t}_k in the concise form

$$i = 1, 2: \quad \frac{dY_i^{k+1}(x)}{dx} = \Gamma_i(x, Y_1^{k+1}, Y_2^{k+1}), \quad (S32)$$

with $(\Gamma_i)_{i=1,2}$ the operators that define the right hand sides of eqs S27 ($i=1$) and S28 ($i=2$). At

$x = x_1 = 0$, Y_2^{k+1} satisfies eq 19 rewritten as

$$Y_2^{k+1}(x_1) = 0. \quad (S33)$$

At the position x_1 , we set

$$Y_1^{k+1}(x_1) = \zeta_I^{k+1}, \quad (S34)$$

where ζ_1^{k+1} is a time-dependent parameter to be subsequently determined. At the edge of the unit cell, *i.e.* at the position $x = x_2 = r_c / (a + d)$, eq 20 provides

$$Y_2^{k+1}(x_2) = 0, \quad (\text{S35})$$

and we define $Y_1^{k+1}(x_2)$ as

$$Y_1^{k+1}(x_2) = \zeta_2^{k+1}, \quad (\text{S36})$$

with ζ_2^{k+1} a second time-dependent variable to be evaluated. The two boundary problem (S32)-(S36) is solved by numerical shooting from the position x_1 to x_f (forward shooting, denoted as FS) and from the position x_2 to x_f (backward shooting, denoted as BS) with $x_1 < x_f < x_2$ and

$$Y_1^{k+1}(x_f)_{\text{BS}} = Y_1^{k+1}(x_f)_{\text{FS}}, \quad (\text{S37})$$

$$Y_2^{k+1}(x_f)_{\text{BS}} = Y_2^{k+1}(x_f)_{\text{FS}}. \quad (\text{S38})$$

For that purpose, ζ_1^{k+1} and ζ_2^{k+1} are iteratively updated with a globally convergent Newton-Raphson¹ scheme till the continuity equations S37 and S38 are satisfied. This method called ‘shooting to a fitting point’ (located at $x = x_f$) is based on the use of an adaptive stepsize Runge-Kutta method of the fifth-order implemented with the aforementioned Newton-Raphson scheme.¹ Within this procedure, many small steps tiptoe through treacherous spatial regions (especially at the edge of the shell layer *i.e.* at $x = d / (a + d)$) where strong variations of the function to be determined are encountered, while larger step sizes are automatically defined in ‘uninteresting spatial zones’ where smooth function gradients are computed (*i.e.* far from the shell layer). Doing so, fast convergence is met for $x_f \sim d / (a + d)$.

Following the above numerical strategy, the author verified that two modes of computations are equivalent. In the first mode, the resolution of the time dependent M and ML concentration profiles is carried out according to eq S30 with initial guesses for ζ_1^{k+1} and ζ_2^{k+1} obtained from the solutions at \tilde{t}_k . In the second mode, the computation is performed according to

$$Y_{1,2}^{k+1}(x) = \Im(\Omega^1(x)), \quad (\text{S39})$$

where the time \tilde{t}_k (eq S24) is now iterated upon changing N on the premise that $\Delta t = 1 / (N - 1)$ remains well below 1.

The accuracy and stability of the numerical solution was systematically verified by controlling the independence of the results on the quantities x_f , p , Δt , the initial guesses for ζ_1^{k+1} and ζ_2^{k+1} as

well as the convergence criterion that defines how well the continuity conditions S37-S38 for $Y_{1,2}^{k+1}$ at $x = x_f$ are satisfied. Typical values for N around 300 or above lead to numerical results with accuracy up to three digits.

Once the spatial and temporal dependences of $c_{M,ML}$ are known and therewith the EDL potential distribution throughout the soft interphase (see point 4 below), the calculation of the quantities K^* , $\rho_M^S(t)$, $\rho_M^V(t)$ and $\rho_{ML}^V(t)$ may be easily carried out *via* the numerical evaluations (using Simpson's rule¹) of the various integrals involved in eqs 28, S9 and 32. Following this, eq 30 straightforwardly leads to the searched ratio $k_a^*(t)/k_a$.

The evaluation of the time- and space-dependent M and ML concentration profiles as previously described requires knowledge of the scaled equilibrium potential y . Derivation of the latter is presented below.

4. Numerical analysis for evaluating the equilibrium potential profile.

The spatial variable r is now rewritten in dimensionless form as follows

$$\tilde{x} = (r - a) / R_o, \quad (S40)$$

and is discretised according to

$$i = 1, \dots, M : \quad \tilde{x}_i = (i - 1) \Delta \tilde{x}, \quad (S41)$$

with $\Delta \tilde{x} = 1 / (M - 1)$ the space discretization step and R_o the position where $dy/d\tilde{x}|_{\tilde{x}=1} < \varepsilon$ with ε a prescribed scalar satisfying $\varepsilon \ll 1$, typically of the order of 10^{-4} or lower. It is recalled that $R_o \ll r_c$ for $\kappa r_c \gg 1$. Given eqs S40-S41, the finite element differences formulation of eqs 7, 23-26 is given by

$$i = 2, \dots, M - 1 : \quad y_{i+1} - 2y_i \left[1 - \frac{\Delta \tilde{x}}{\tilde{x}_i + a / R_o} \right] + y_{i-1} \left[1 - \frac{2\Delta \tilde{x}}{\tilde{x}_i + a / R_o} \right] - (\kappa R_o \Delta \tilde{x})^2 \left\{ \sinh(y_i) - \frac{z_L c_L^*}{2zc^\infty} f(\tilde{x}_i) \right\} = 0 \quad (S42)$$

$$y_2 - y_1 = 0 \quad (S43)$$

$$y_M - y_{M-1} = 0 \quad (S44)$$

, with $y_i = y(\tilde{x}_i)$. The non-linear tridiagonal system that consists of the M equations (S42-S44) with the $(y_i)_{i=1, \dots, M}$ as unknown variables, was solved using a globally convergent Newton-Raphson method already invoked above. R_o was iteratively updated till the far field condition (S44)-

equivalent to setting $y(\tilde{x}=1)=0$ under the condition $\kappa r_c \gg 1$ - was satisfied within the predefined convergence criterion $dy/d\tilde{x}|_{\tilde{x}=1} < \varepsilon$. Initial guesses for R_0 and $(y_i)_{i=1,\dots,M}$ were obtained from the analytical solution of the linearized Poisson-Boltzmann equation (Debye-Hückel approximation) given by eq 34. It was systematically verified that the computed potential distributions were independent of the electrostatic cut-off condition $dy/d\tilde{x}|_{\tilde{x}=1} < \varepsilon$ and on the grid size ($M \sim 400$ or larger). Once the electric potential distribution is known on the uniform grid $(\tilde{x}_i)_{i=1,\dots,M}$, it is cubic-spline interpolated in the r -space region $[a, a+r_c]$ (with $y(r > a+R_0)=0$ and $dy(r)/dr|_{r>a+R_0}=0$) or equivalently in the x -space region $[0, r_c/(a+d)]$ as defined by eq S20. Subsequently, the Laplacian term $\nabla_x^2 y$ appearing in eq S28 may be evaluated for any position x according to the expression

$$\nabla_x^2 y(x) = [\kappa(a+d)]^2 \left\{ \sinh[y(x)] - \frac{z_L c_L^*}{2zc^\infty} f(x) \right\}, \quad (\text{S45})$$

which directly follows from eqs 7, 12, 23 and 24. The electric field $dy(x)/dx$ involved in eq S28 may be straightforwardly estimated *via*

$$\frac{dy(x)}{dx} = \frac{a+d}{R_0} \frac{dy(\tilde{x})}{d\tilde{x}}, \quad (\text{S46})$$

where $dy(\tilde{x})/d\tilde{x}$ is the function cubic-spline interpolated from the field values $(y_{i+1} - y_i)_{i=1,\dots,M-1} / \Delta\tilde{x}$ evaluated on the uniform grid $(\tilde{x}_i)_{i=1,\dots,M}$. The author experienced that this way of determining the double layer electric field, while very accurate for $\kappa d \gg 1$, suffers at $\kappa d = O(1)$ from instability at spatial positions located in the vicinity of $r = a + d$, *i.e.* in the EDL region where the potential distribution is the steepest. This instability is reflected in subtle but significant (a few percent) variations of $dy(\tilde{x})/d\tilde{x}|_{\tilde{x} \sim d/R_0}$ upon variation of R_0 and/or M even for $\Delta\tilde{x}$ values as low as $< 10^{-3}$. This feature ultimately leads to very inaccurate evaluation of k_a^*/k_a at low κd , thereby recalling that the coupled electric field and M/ML concentration gradients exhibit abrupt developments in the vicinity of $r = a + d$. To solve for this issue, the electric field was determined as follows. Posing $Y^{(1)}(x) = dy/dx$ (with x defined by eq S20), one may show on the basis of the non-linear PB equation (eqs 23-24) that the electric field $Y^{(1)}$ is governed by

$$\frac{dY^{(1)}(x)}{dx} = -\frac{2}{x + a/(a+d)}Y^{(1)}(x) + \nabla_x^2 y(x) \quad (\text{S47})$$

where $\nabla_x^2 y(x)$ is yielded by eq S45. Equation S47 is solved following a numerical procedure of the type ‘shooting to a fitting point’ similar to that employed for solving eqs S32-S36. For that purpose, the boundaries verified by $Y^{(1)}$ at $x = x_1 = 0$ and $x = x_2 = r_c/(a+d)$ (eqs 25-26 in the main text) are written in the form

$$Y^{(1)}(x_1) = \nu_1 \quad (\text{S48})$$

and
$$Y^{(1)}(x_2) = 0, \quad (\text{S49})$$

with ν_1 a scalar to be determined. The advantage of this method over that which consists in evaluating the electric field on the basis of a uniform grid, is the use of an adaptive step size-mesh with, in particular, detailed computation in the vicinity of $x = d/(a+d)$ ($\sim x_f$). The value of ν_1 is updated by means of a globally convergent Newton Raphson method till continuity of the electric field is met at $x = x_f$. Comparison of eqs S48 with eq 25 reveals that ν_1 must be zero, in agreement with the numerical outcome (typical values obtained for ν_1 are well below 10^{-4}). The consistency of the above method for evaluating the field distribution was verified by changing the starting guess value chosen for ν_1 as well as the convergence criterion that defines how well the continuity condition for the electric field at $x = x_f$ is met. Finally, the electric field was cubic-spline interpolated over the whole x -space region $[0, r_c/(a+d)]$ on the basis of the field values obtained on the non-uniform mesh grid. The resulting function, which allows the evaluation of the electric field for any position x , was then employed within the numerical scheme adopted for solving the M and ML concentration profiles.

References.

[1] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. in *Numerical recipes in Fortran, The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: New-York, 1986.