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SUPPORTING INFORMATION.

Dynamics of Ferrocene Labeled Polyethylene Glycol Chains Terminally Attached to the Outermost Monolayer of Successively Self-Assembled Monolayers of Immuno Proteins. Elastic Bounded Diffusion

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Elastic bounded diffusion: numerical solution of set (3) of differential equations

The set of equation (3) must be solved taking into account the following initial and boundary conditions:

At $\tau = 0$ and $-\mu < y < l$: $p = \exp\left(-\frac{\beta}{2}y^2\right)$, $q = 0$

At the electrode surface, $y = -\mu$: $-\left(\frac{\partial p}{\partial y}\right)_{-\mu} + \beta\mu p_{-\mu} = \left(\frac{\partial q}{\partial y}\right)_{-\mu} - \beta\mu q_{-\mu}$

At the position corresponding to full extension of the PEG chain, $y = l$:

$$\left(\frac{\partial p}{\partial y}\right)_l + \beta\mu p_l = \left(\frac{\partial q}{\partial y}\right)_l + \beta\mu q_l = 0$$

The dimensionless current ψ given by:

$\psi[erf(\lambda) + erf(\lambda_{fs})] = (\partial p/\partial y)_{-\mu} - \beta\mu p_{-\mu} = -(\partial q/\partial y)_{-\mu} + \beta\mu q_{-\mu}$

is a function of the electrode potential ξ, for given values of β, λ_{fs} and λ, the last two parameters being related respectively to l and μ since $\mu\sqrt{\beta} = \lambda/\sqrt{2}$ and $l\sqrt{\beta} = \lambda_{fs}/\sqrt{2}$.

The $-\mu$ to l interval is divided into N subintervals of length $h = (\mu + l)/N$. The space variable y is then given by $y = -\mu + ih$, with i the index of the space grid. The time interval is divided into steps of width k so that the time variable is given by $\tau = kj$, with j the index of the time grid. Then the partial derivative equations of set (3) can be converted into their finite difference equivalents:

$$p_{i-1}^{j+1}(y\beta k/2h - r) + p_i^{j+1}(2 + 2r - k\beta) - p_{i+1}^{j+1}(r + y\beta k/2h) =$$

$$p_{i-1}^{j}(r - y\beta k/2h) + p_i^{j}(2 - 2r + k\beta) + p_{i+1}^{j}(r + y\beta k/2h)$$

with $1 \le i \le N - 1$ and $r = k/h^2$,

and a similar equation is obtained for q.

The numerical equivalent of the boundary condition at the electrode surface is:[17]

$$\left(p_0^{j+1} + q_0^{j+1}\right)\left[2 + 2r - k\beta + 2h\beta\mu(r + \mu\beta k/2h)\right] - 2r\left(p_1^{j+1} + q_1^{j+1}\right) =$$

$$2r\left(p_1^{j} + q_1^{j}\right) + \left(p_0^{j} + q_0^{j}\right)\left[2 - 2r + k\beta - 2h\beta\mu(r + \mu\beta k/2h)\right]$$

Similarly, the boundary condition at the outer edge of the mesh, $y = l$, is expressed by:

$$p_N^{j+1}\left[2 + 2r - k\beta + 2h\beta l(r + l\beta k/2h)\right] - 2rp_{N-1}^{j+1} = 2rp_{N-1}^{j} + p_N^{j}\left[2 - 2r + k\beta - 2h\beta l(r + l\beta k/2h)\right]$$

Similar equations are obtained for q.

The Nernst equation gives : $p_0^{j+1} = q_0^{j+1}\exp(-\xi)$.

Combining all the above equations leads to a system of $2N + 2$ linear equations of $2N + 2$ unknowns that is solved by the Gauss elimination[17] method using an optimized algorithm taking into account that the above system is penta-diagonal. Convergence of the computation is monitored by integrating the $(p + q)$ concentration profile at each time step and making sure that the resulting integral does not differ by more than 1% from its initial value. If it does differ by more than 1%, the

computation is re-started with a higher value of N until a satisfying convergence is obtained. Practically, values of N ranging from 500 to 3000 giving values of h ranging form 0.1 to 0.01 were used. The current ψ is derived from the first three points of the p concentration profile:

$$\psi^{j+1}\left[erf(\lambda)+erf(\lambda_{fs})\right]=\left(-1.5p_0^{j+1}+2p_1^{j+1}-0.5p_2^{j+1}\right)/h-\beta\mu p_0^{j+1}$$

The accuracy on the dimensionless peak current is better than 1%.

The above simulation technique does not make use of the fact that, in the present case, $p+q=\exp\left(-\beta y^2/2\right)$ whatever y. This allows its extension to more complicated models of elastic bounded diffusion in which such an equation may not hold.

Reference

(16) Smith, G. D. *Numerical Solutions of Partial Differential Equations*, Oxford Mathematical Handbook: London, 1971, p. 23.