Modeling Multi-Component Surface-Volume Reactions

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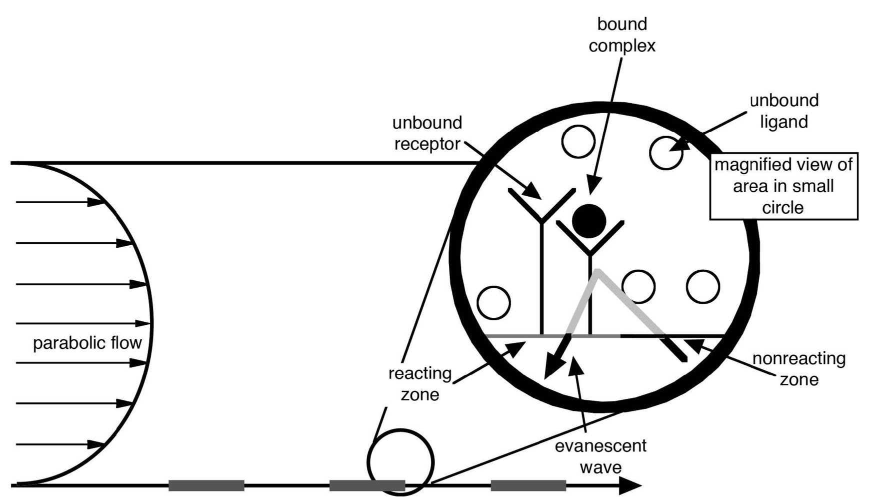
Introduction

- In a surface-volume reaction, one reactant (the unbound ligand) is convected in a fluid over a surface to which another reactant (the receptor) is confined.
- These reactions are quite common and occur in antigen-antibody interactions, drug absorption, and blood clotting, among others [1,2,3].
- Mathematical models exist for single component reactions, but there is little quantitative information regarding multi-component reactions. Here we analyze a mathematical model multi-component surface volume reactions.
- Below is a schematic for ligand flow through a channel [4].



Mathematical Model

- It is the reactions occuring at the boundary that are of primary interest:

$$E \underset{{}_1k_d}{\overset{{}_1k_a}{\rightleftharpoons}} B_1 \underset{{}^1_2k_d}{\overset{{}^1_2k_a}{\rightleftharpoons}} B_{12} \underset{{}^2_1k_a}{\overset{{}^2_1k_d}{\rightleftharpoons}} B_2$$

$$E \underset{{}_2k_d}{\overset{{}_2k_a}{\rightleftharpoons}} B_2$$

- By the mass-action principle the governing equations for B_1, B_{12}, B_2 are:

$$\frac{\partial B_1}{\partial t} = (1 - B_\Sigma)C_1 + {}^1_2K_d B_{12} - {}_1K_d B_1 - {}^1_2K_a B_1 C_2 \tag{1}$$

$$\frac{\partial B_{12}}{\partial t} = {}^1_2K_a B_1 C_2 + {}^2_1K_a B_2 C_1 - {}^1_2K_d B_{12} - {}^2_1K_d B_{12} \tag{2}$$

$$\frac{\partial B_2}{\partial t} = {}_2K_a(1 - B_\Sigma)C_2 + {}^2_1K_d B_{12} - {}^2_1K_a B_2 C_1 - {}_2K_d B_2 \tag{3}$$

- Here $C_i(x, \eta, t)$ denotes the unbound ligand concentration. It can be shown that at the boundary $C_i(x, 0, t)$ is given by the formula:

$$C_1(x,0,t) = 1 - \frac{\mathrm{Da}}{3^{\frac{1}{3}} D_r^{2/3} \Gamma(\frac{2}{3})} \int_0^x \left\{ \frac{\partial B_1}{\partial t} + \frac{\partial B_{12}}{\partial t} \right\} (x-v)^{-\frac{2}{3}} \, \mathrm{d}v \tag{4}$$

$$C_2(x,0,t) = 1 - \frac{\mathrm{Da}}{3^{\frac{1}{3}} \Gamma(\frac{2}{3})} \int_0^x \left\{ \frac{\partial B_{12}}{\partial t} + \frac{\partial B_2}{\partial t} \right\} (x-v)^{-\frac{2}{3}} \, \mathrm{d}v \tag{5}$$

- Here $B_\Sigma := B_1 + B_{12} + B_2$, Da - Damköhler number, *key perturbation parameter and is very small*. Represents the *ratio of reaction to diffusion*. Also $D_r = \frac{\tilde{D}_1}{\tilde{D}_2}$, the ratio of the diffusivities of the two ligands.
- The integral terms in (4), (5) represent upstream ligand depletion.

Perturbation Analysis

- Experimentalists are interested an approximation to the average of $\vec{B}$:

$$\vec{\overline{B}}(t) = \frac{1}{x_{\max} - x_{\min}} \int_{x_{\min}}^{x_{\max}} \vec{B}(x,t) \mathrm{d}x$$

- A regular expansion of the form

$$\vec{B} = \vec{B}_0 + \mathrm{Da}\vec{B}_1 + \mathcal{O}(\mathrm{Da}^2)$$

has a secular term.

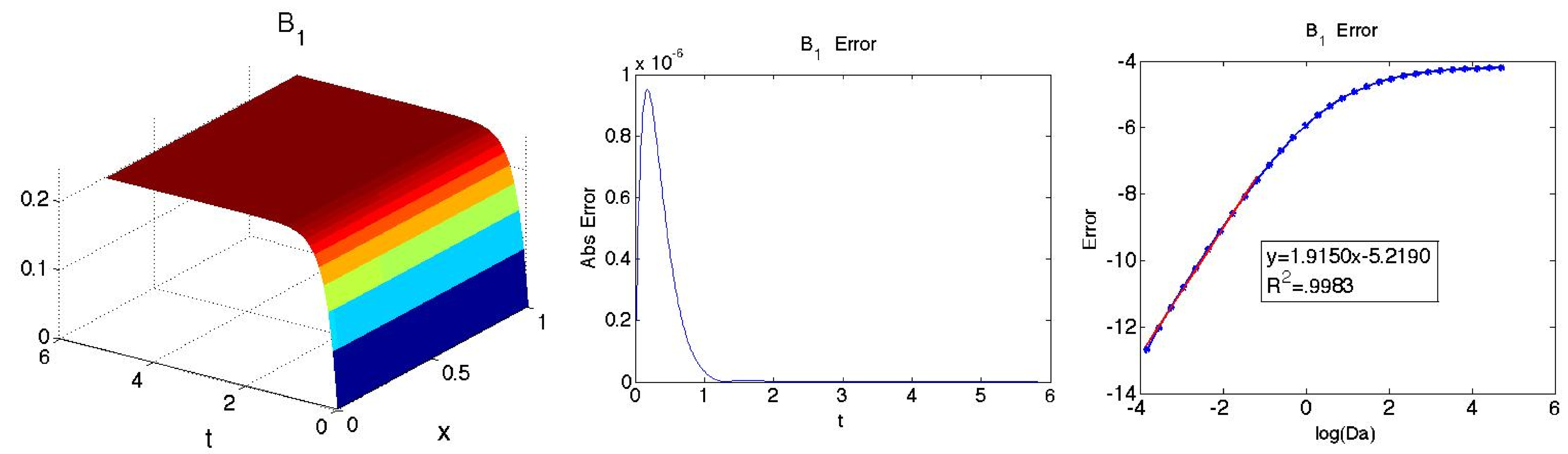
- By manipulating the average of equations (1)-(3), together with (4) and (5), we obtain a simple set of ODE's:

$$\frac{\mathrm{d}\vec{\overline{B}}}{\mathrm{d}t} = M^{-1}(t)(A\vec{\overline{B}} + \vec{f}) + \mathcal{O}(\mathrm{Da}^2) \tag{6}$$

- We have eliminated the secularity without the aid of a multiple scale expansion. Also we don't have to manipulate the data to obtain the average.

Numerical Verification

- In order to test the accuracy of our approximation (6) we developed a semi-implicit finite difference scheme. The results are depicted for B_1 below. Similar results for B_{12}, B_2 hold.



Left: B_1, Middle: Error in (6) for $\mathrm{Da} = .01$, Right: Error in (6) for different Da

- Our approximation (6) does quite well, giving five digits of accuracy for $\mathrm{Da} = .01$.
- Motivated by previous results [5] and (6) we asked: how well does our approximation - that is only formally valid for $\mathrm{Da} << 1$ - do for moderate and large Da?
- Error remains small, and reaches an asymptote corresponding to about a one percent error.

References

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Acknowledgments

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