Chemistry 243 Winter Quarter 2017.
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Problem Set #4

A. Electrochemical Kinetics

Please read the paper by Chris Chidsey on potential step measurements of electroactive alkanethiol monolayers:

http://unicorn.ps.uci.edu/243/papers/chidseypaper.pdf

1) Chidsey uses potential step measurements in Figure 3, in which he predicts the observed current will be a single exponential decay with a time constant $(k_f + k_b)$. Use LaPlace tranforms with the appropriate initial conditions using the first order kinetic rate equation:

$$\frac{d\Gamma_o}{dt} = -k_f \Gamma_O + k_b \Gamma_R$$

to get $\Gamma_O(t)$ and the current $i(t) = nFA\, d\Gamma_O(t)/dt$. Hint: the total surface coverage Γ^* is equal to $\Gamma_O + \Gamma_R$.

2) Use the Butler-Volmer equation (Eq 3) to predict the potential dependence of $(k_f + k_b)$ as in Figure 4 for the charge transfer coefficient alpha $= 0.3, 0.5$, and 0.7.

3) Chidsey analyzes his rate constant measurements in terms of Marcus Theory. It can also be described with a phenomenological alpha that varies linearly with potential. Try to fit Chidsey's data with this approach.

B. Langmuir Adsorption Kinetics

The vast majority of surface bioaffinity measurements utilize the specific adsorption of target biomolecules (T) from solution onto a surface that has been chemically modified with probe biomolecules (P). If the target and probe interact in a simple 1:1 ratio, then in the absence of bulk transport the surface reaction can be represented in the form:

$$T + P \underset{k_d}{\overset{k_a}{\rightleftharpoons}} TP \tag{1}$$

where TP is the surface bound target-probe complex. Both P and TP are surface species, and in the Langmuir approximation their surface concentrations Γ_P and Γ_{TP} are linked to the total concentration of surface sites Γ_{tot} by eq 2:

$$\Gamma_P + \Gamma_{TP} = \Gamma_{tot} \tag{2}$$

4) If we define θ as the fraction of occupied surface sites, $\theta = \Gamma_{TP} / \Gamma_{tot}$, write down the differential equation for the time evolution of θ ($d\theta/dt = \ldots$) using k_a and k_d. and the bulk concentration [T].

5) Find the steady state equilibrium surface coverage θ_{eq}, which is obtained in the steady state approximation ($d\theta/dt = 0$). This equation defines the Langmuir adsorption coefficient $K_{ads} = k_a/k_d$. What is θ_{eq} at a bulk concentration equal to $1/K_{ads}$?

6) Using Laplace transform methods, convert the differential equation in question #4 into an algebraic equation in Laplace space, and then find the inverse transform to determine the time dependence of the fractional surface coverage, $\theta(t)$. Find this time dependence for two cases: (i) where $\theta = 0$ at $t = 0$ and the bulk concentration [T] = T_0, and (ii) where $\theta = 1$ at $t = 0$ and the bulk concentration [T] = 0.

7) The coupling of diffusion to a surface and Langmuir adsorption kinetics has been handled in the steady state by many researchers, including J. M. Saveant:

http://unicorn.ps.uci.edu/243/papers/Saveant.pdf

Eq 1 and 2 come from a steady state approximation of one of Fick's Laws. Can you identify the approximation?

a) Using Igor Pro, redo Figure 2 which plots θ^* vs tau for values of log(lambda) and log(kappa) ranging from -3 to 3, which can be set by two variable boxes.

b) (A bit more difficult) Using either Igor Pro, Matlab or Mathematica, redo the plot in Figure 1 to make it 3D using Eq. 4. Keep the same X and Y axes, but use $\log(\tau)$ as the Z variable, where τ is the reduced time. The normalized surface coverage θ^* becomes a variable that changes the plot (θ^* varies from 0 to 1).