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CBE 521

2 December 2015

Homework 2

1. Let the electrophoretic mobility be given by

$$\mu_{ep} = \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta}f_1(\kappa R)$$

The correction function $f_1(\kappa a)$ is given by (Henry)

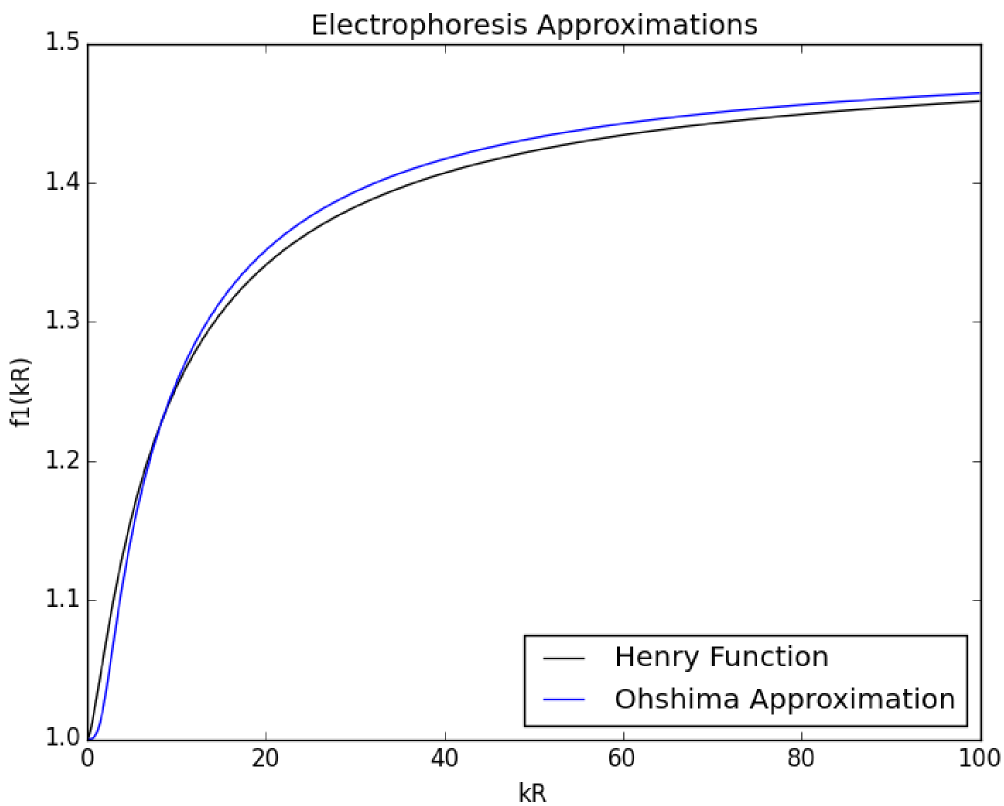
$$f_1(\kappa R) = 1 + \frac{(\kappa R)^2}{16} - \frac{5(\kappa R)^3}{48} - \frac{(\kappa R)^4}{96} + \frac{(\kappa R)^5}{96} - \left[\frac{(\kappa R)^4}{8} - \frac{(\kappa R)^6}{96}\right]\exp(\kappa R)\int_{\infty}^{\kappa R}\frac{\exp(-t)}{t}dt$$

Or by the Ohshima approximation

$$f_1(\kappa R) = 1 + \frac{1}{2\left\{1 + \left[\frac{5}{2\kappa R}\left(1 + 2e^{-\kappa R}\right)\right]\right\}^3}$$

Using software of your choice, plot both Henry and Ohshima's expressions and comment on the agreement/disagreement between them. Is the Ohshima approximation reasonable to use?

To calculate the electrophoretic mobility of the intermediate case (when $\kappa R \sim 1$) the Henry electrophoretic equation may be used. Furthermore, for $\kappa R < 100$, the Henry correction function is applied. This case may also be approximated with the Ohshima equation. To check the validity of the Ohshima approximation, the functions are plotted in terms of $\kappa R$ and compared.




As can be seen from the plot, the approximation agrees quite closely with the function. Over the domain, $0 < \kappa R < 100$, assigned by assumptions, the Ohshima approximation incurs less than 1% of error. That small amount of error is within reason and so the Ohshima approximation is a reasonable approximation to use considering the added complexity of the Henry correction function.

2. The electrostatic potential in a slit-shaped channel is

$$\widetilde{\Psi} = \widetilde{\Psi}_0 \frac{\cosh\left[\kappa\left(\frac{h}{2} - x\right)\right]}{\cosh\left[\kappa\frac{h}{2}\right]} \approx \tilde{\zeta}\frac{\cosh\left[\kappa\left(\frac{h}{2} - x\right)\right]}{\cosh\left[\kappa\frac{h}{2}\right]}$$

Calculate the average migration conductivity for $\kappa h = 1$ and $\tilde{\zeta} = 1$.

The electrostatic potential is first calculated at the wall and the middle of the slit,

$$at\ x = 0 \rightarrow \widetilde{\Psi} = \tilde{\zeta}\frac{\cosh\left[\kappa\left(\frac{h}{2} - 0\right)\right]}{\cosh\left[\kappa\frac{h}{2}\right]} = \tilde{\zeta}\frac{\cosh\left[\kappa\frac{h}{2}\right]}{\cosh\left[\kappa\frac{h}{2}\right]} = \tilde{\zeta}$$

$$at\ x = \frac{h}{2} \rightarrow \widetilde{\Psi}_m = \tilde{\zeta}\frac{\cosh\left[\kappa\left(\frac{h}{2} - \frac{h}{2}\right)\right]}{\cosh\left[\kappa\frac{h}{2}\right]} = \frac{\tilde{\zeta}}{\cosh\left[\kappa\frac{h}{2}\right]}$$

The migration conductivity is a component of the total current in a single double layer and is calculated by the following,

$$K_{mig}(x) = \frac{e^2}{K_B T}\sum_i z_i^2 \mathcal{D}_i n_i^o e^{-\frac{ze\Psi(x)}{K_B T}}$$

In a slit-shaped channel, the single double layers on both sides overlap which results in an average migration conductivity which is calculated as the following and integrated,

$$\overline{K}_{mig} = 1 + \frac{4}{\kappa h}\int_{\tilde{\zeta}}^{\widetilde{\Psi}_m} \frac{\sinh\widetilde{\Psi}\, d\widetilde{\Psi}}{\sqrt{2\left[\cosh\tilde{\zeta} - \cosh\widetilde{\Psi}_m\right]}}$$

$$\overline{K}_{mig} = 1 + \frac{4}{\kappa h}\left(\frac{\cosh\widetilde{\Psi}}{\sqrt{2\left[\cosh\tilde{\zeta} - \cosh\widetilde{\Psi}_m\right]}}\right|_{\tilde{\zeta}}^{\widetilde{\Psi}_m}$$

$$\overline{K}_{mig} = 1 + \frac{4}{\kappa h}\left(\frac{\cosh\widetilde{\Psi}_m}{\sqrt{2\left[\cosh\tilde{\zeta} - \cosh\widetilde{\Psi}_m\right]}} - \frac{\cosh\tilde{\zeta}}{\sqrt{2\left[\cosh\tilde{\zeta} - \cosh\widetilde{\Psi}_m\right]}}\right)$$

$$\overline{K}_{mig} = 1 + \frac{4}{\kappa h}\left(\frac{1}{\sqrt{2\left[\cosh\tilde{\zeta} - \cosh\widetilde{\Psi}_m\right]}}\left(\cosh\widetilde{\Psi}_m - \cosh\tilde{\zeta}\right)\right)$$

The electrostatic potential is then plugged into the average migration conductivity as well as the following known terms,

$$\tilde{\Psi}_m = \frac{\tilde{\zeta}}{\cosh\left[\kappa \frac{h}{2}\right]} \quad \kappa h = 1 \quad \tilde{\zeta} = 1$$

$$\overline{K}_{mig} = 1 + \frac{4}{\kappa h}\left(\frac{1}{\sqrt{2\left[\cosh\tilde{\zeta} - \cosh\left(\frac{\tilde{\zeta}}{\cosh\left[\kappa\frac{h}{2}\right]}\right)\right]}}\left(\cosh\left(\frac{\tilde{\zeta}}{\cosh\left[\kappa\frac{h}{2}\right]}\right) - \cosh\tilde{\zeta}\right)\right)$$

$$\overline{K}_{mig} = 1 + \frac{4}{1}\left(\frac{1}{\sqrt{2\left[\cosh 1 - \cosh\left(\frac{1}{\cosh\left[\frac{1}{2}\right]}\right)\right]}}\left(\cosh\left(\frac{1}{\cosh\left[\frac{1}{2}\right]}\right) - \cosh 1\right)\right)$$

$$\overline{K}_{mig} = 1 + 4\left(\frac{1}{\sqrt{2\left[\cosh 1 - \cosh\left(\frac{1}{\cosh\left[\frac{1}{2}\right]}\right)\right]}}\left(\cosh\left(\frac{1}{\cosh\left[\frac{1}{2}\right]}\right) - \cosh 1\right)\right)$$

The average migration conductivity is then,

$$\overline{K}_{mig} = 6.417 \times 10^{-3}\ \frac{C^2}{N \cdot s}$$

3. The measured values of electrophoresis mobilities for two different samples are $\tilde{\mu}_{ep} = 3$ and $\tilde{\mu}_{ep} = 5$. The electrolyte is $1{:}1$ type and in both cases $\kappa R = 1$. Since double layer polarization is likely, use the expression

$$\tilde{\mu}_{ep} = \frac{3\tilde{\zeta}}{2} - \frac{6\left[\frac{\tilde{\zeta}}{2} - \frac{\ln 2}{z}\left(1 - \exp\left(-z\tilde{\zeta}\right)\right)\right]}{2 + \frac{\kappa R}{M}\exp\left(-\frac{z\tilde{\zeta}}{2}\right)}$$

To obtain the zeta potential for both samples.

First, using the provided knowledge, the $z$ and $M$ terms must be identified. Since the electrolyte is $1{:}1$ type, $z$ must be equal to 1. Next the $M$ term is determined assuming double layer polarization for $KCl$,

$$M = 1 + \frac{3m}{z^2} = 1 + \frac{3(0.184)}{1^2} = 1.552$$

Plugging in

$$\kappa^{-1} = \frac{0.304}{\sqrt{M}} = \frac{0.304}{\sqrt{1.552}} = 0.244$$

$$R = \frac{1}{\kappa} = 0.244$$