Problem Set 4 Solutions **BE.462J/3.962J**

Issued: Day 13 **Spring 2003**

Due: Day 15

(20 pts total)

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1. Re-derive the equation for equilibrium swelling of a polyelectrolyte gel where the polymer chains contain a basic ionizable group that becomes *positively* charged with *decreasing* pH:

$$R\text{-}NH_2 \text{ -> } R\text{-}NH_3^+$$

Where R represents the polymer chain backbone. Show an example plot of the swelling ratio Q of the gel vs. pH in water for a gel that has the following parameters:

$\chi = 0.8$
$M_c = 6000$ g/mole
$M = 100{,}000$ g/mole
$v_{sp,2} = 0.8$
$\upsilon_{2,r} = 0.4$
$pK_a = 8.0$
ionic strength = 0.2 mM (1:1 electrolyte)
$M_0 = 90$ g/mole

The equilibrium of interest for the proposed cationic gel is:

$$R-NH_3^+ \rightleftharpoons R-NH_2 + H^+$$

The equilibrium constant for this reaction is:

$$K_a = \frac{[H^+][R-NH_2]}{[R-NH_3^+]}$$

The equilibrium constant can be used to define the ionization in terms of pK_a and pH (Remember $pK_a = -\log K_a$):

(1) $$i = \frac{\left[R-NH_3^+\right]}{\left[R-NH_3^+\right]+\left[R-NH_2\right]} = \frac{[H^+]}{\left[H^+\right]+K_a} = \frac{10^{-pH}}{10^{-pH}+10^{-pK_a}}$$

Now, considering the ions present inside and outside the basic gel:

Inside gel: (2) $c_+ = \gamma_+ c_s + i c_2/z_+$

(3) $c_- = \gamma_- c_s$

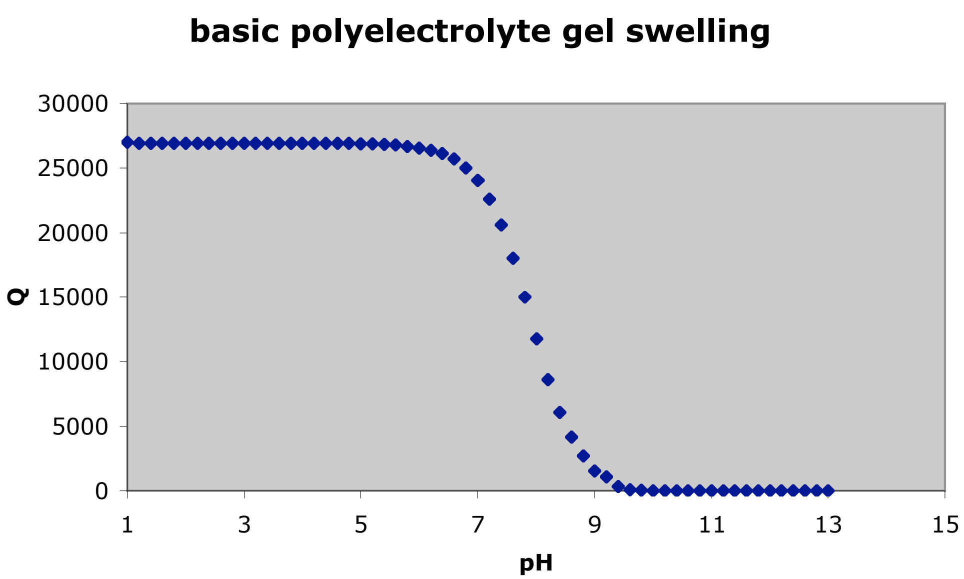
Outside gel: (4) $c_+^* = \gamma_+ c_s^*$

(5) $c_-^* = \nu_- c_s^*$

Using these expressions (1)-(5), the derivation can be performed exactly as done for anionic gels and you can see that a very similar form will result. The equilibrium condition is:

$$v_{m,1}\left(\frac{10^{-pH}}{10^{-pH}+10^{-pK_a}}\right)^2\left(\frac{\phi_{2,s}^2}{4Iv_{sp,2}^2M_0^2}\right)=\ln(1-\phi_{2,s})+\phi_{2,s}+\chi\phi_{2,s}^2+\phi_{2,r}\left(\frac{v_{m,1}}{v_{sp,2}M_c}\right)\left(1-\frac{2M_c}{M}\right)\left[\left(\frac{\phi_{2,s}}{\phi_{2,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{\phi_{2,s}}{\phi_{2,r}}\right)\right]$$

A plot of Q (= $1/\phi_{2,s}$) can be obtained by inserting the given constants and setting up an iterative nonlinear equation solution routine with a short computer program or a commercial package like Mathematica, Excel, etc:



For example, the solution can be found by plugging in an initial guess for Q at each pH and seeing how close the left and right hand sides of the equilibrium expressions are to being equal. A new guess is made either raising or lowering the test values of Q and the resulting error (absolute value of left side – right side) re-computed. If the error is decreased, keep the new solution, if the error is increased, go back to the first guess and try changing the value of Q in the other direction. This process is iterated until the solution is found. Typically, a reasonable initial guess is required to solve the equation since many local minima in the function may exist. Here, a good initial guess is obtained by knowing from the physics of the situation that the gel has to be swollen at pH < pK_a and collapsed above this pH.

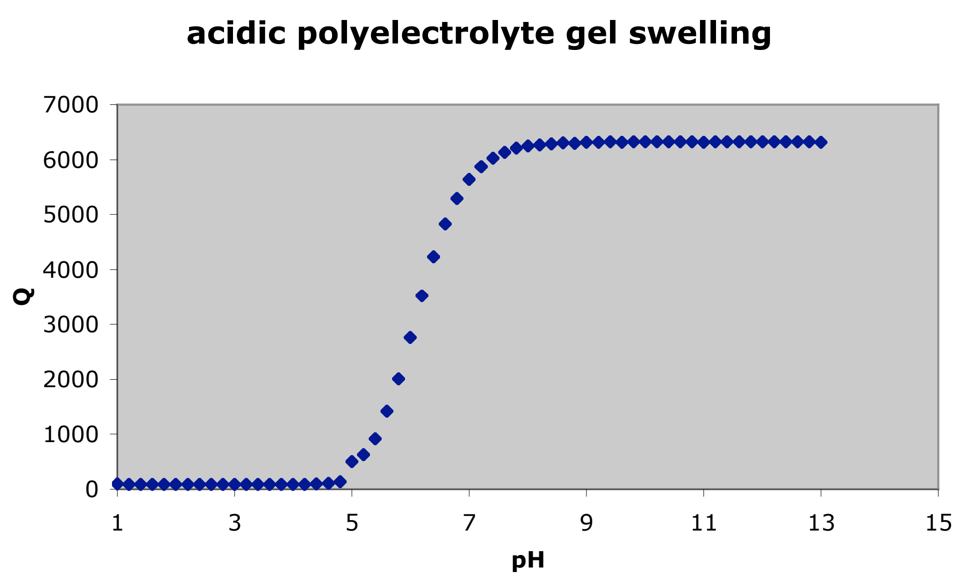
2. An anionic polyelectrolyte gel is synthesized with the physical parameters given below, and swollen in a solution with ionic strength = 0.5 mM and pH 7.4. What physical parameters of the gel you could alter to obtain the same swelling ratio at pH 7.4 if the gel is to be used in an ionic strength of 0.1 mM, assuming you must use the same polymer repeat units and you can't add organic solvents to the system? For one of the possible changes to the gel parameters, calculate what new value the parameter would take to obtain the desired swelling ratio to show that it is physically achievable.

   χ = 0.8
   M_c = 12,000 g/mole
   M = 75,000 g/mole
   $v_{sp,2}$ = 0.8
   $\upsilon_{2,r}$ = 0.5
   pK_a = 6.0
   (1:1 electrolyte)
   M_0 = 90 g/mole

The equilibrium expression for swelling of a mono-protic anionic hydrogel as we derived in class is:

$$v_{m,1}\left(\frac{10^{-pK_a}}{10^{-pH}+10^{-pK_a}}\right)^2\left(\frac{\upsilon_{2,s}^2}{4Iv_{sp,2}^2M_0^2}\right)=\ln(1-\upsilon_{2,s})+\upsilon_{2,s}+\chi\upsilon_{2,s}^2+\upsilon_{2,r}\left(\frac{v_{m,1}}{v_{sp,2}M_c}\right)\left(1-\frac{2M_c}{M}\right)\left[\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)\right]$$

The swelling curve for the gel parameters given above would be as shown below, if one numerically solves the above equation.



The parameters that can be altered can be divided into two categories:

Polymer dependent: pKa, Mo, $v_{sp,2}$, Mc, M
Solvent dependent: $V_{m,1}$

The interaction parameter χ is dependent on the polymer-solvent combination. Since, the solvent and repeat units need to be the same in each case, the only factors that can be changed are M_c and M. M_c is the molecular weight between crosslinks and M is the molecular weight of the polymer chain. Normally, M is large or 1/M is small and therefore, any alteration in M does not affect swelling significantly. Therefore, the only suitable parameter that can be altered is M_c.

From the above plot, we obtain the maximum swelling ratio of this gel as ~6100. Using this value of swelling ratio and I = 0.1 mM, we obtain M_c as ~3200 g/mole.

While solving this (and the previous) problem, following are important considerations that must be kept in mind:

1. *Consistency of units: Molarity is moles/l whereas specific and molar volumes are in cc/g and cc/mole respectively. Units must be corrected before plugging the parameter values in the equation.*
2. *$\upsilon_{2,s}$ is always smaller than $\upsilon_{2,r}$.*
3. *For small values of $\upsilon_{2,s}$, one can use the approximation that $ln(1- \upsilon_{2,s}) = -\upsilon_{2,s}$ and remove all the terms with small coefficients to get an algebraic equation that can be solved directly to get the value of $\upsilon_{2,s}$ at a specified condition.*