

Key for Unit II Exam: Liquid-Liquid Extractions

This exam consists of three shorter problems that call for written responses and/or shorter calculations, and three longer problems that explore the modeling of a liquid-liquid extraction. Prepare your responses to each question in the form of an organized and well-written narrative that explains how you approached the problem and that clearly states your conclusions. Where derivations and coding is involved, be sure to organize and annotate your work so that I can assign partial credit where appropriate. Neatness is a plus!

You are free to use your textbook, the library, web resources, previous problem sets, your notes, and handouts from class while working on this exam. You are not free to discuss any portion of this exam with other students or with faculty members other than the instructor. This restriction applies to R as well. Please direct all questions about the exam or about the use of R to the instructor.

A *hard copy* of your answers are due in class on Friday, April 19th.

Part I: Shorter Questions

Question 1 (7 points). The amount of copper in a penny is determined by an analytical method in which zinc is an interferent. The selectivity coefficient, $K_{\text{Cu,Zn}}$, for the analytical method is 0.125. When a sample where $[\text{Cu}^{2+}]_o = 10 \times [\text{Zn}^{2+}]_o$ is carried through a separation to remove the zinc, the error in the analysis for copper is -2.42% . When a second sample where $[\text{Cu}^{2+}]_o = 0.1 \times [\text{Zn}^{2+}]_o$ is carried through the same analysis, the error is 5.88% . Knowing that the absolute error, E , is defined as

$$E = (R_{\text{Cu}} - 1) + K_{\text{Cu,Zn}} \times \frac{[\text{Zn}^{2+}]_o}{[\text{Cu}^{2+}]_o} \times R_{\text{Zn}}$$

what are the recoveries for Cu^{2+} and of Zn^{2+} ?

Answer: Substituting in the errors and the initial concentrations gives two equations

$$0.0588 = (R_{\text{Cu}} - 1) + 0.125 \times \frac{10}{1} \times R_{\text{Zn}}$$

$$-0.0242 = (R_{\text{Cu}} - 1) + 0.125 \times \frac{1}{10} \times R_{\text{Zn}}$$

with two unknowns, R_{Cu} and R_{Zn} , which we can solve for simultaneously. Subtracting the second equation from the first equation gives

$$0.083 = 1.2375 \times R_{\text{Zn}}$$

which we solve to give $R_{\text{Zn}} = 0.067$, or 6.7% . Substituting back into gives $R_{\text{Cu}} = 0.975$, or 97.5% .

Question 2 (7 points). What is the smallest distribution ratio for a solute, S , if you want to extract 99.9% of S from 50.0 mL of aqueous phase using two 25.0 -mL portions of the organic solvent?

Answer: If we extract 99.9% of the solute into the organic phase, then $q_{aq} = 0.001$; thus

$$q_{aq} = 0.001 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}} \right)^2 = \left(\frac{50}{25D + 50} \right)^2$$

Taking the square root of both sides

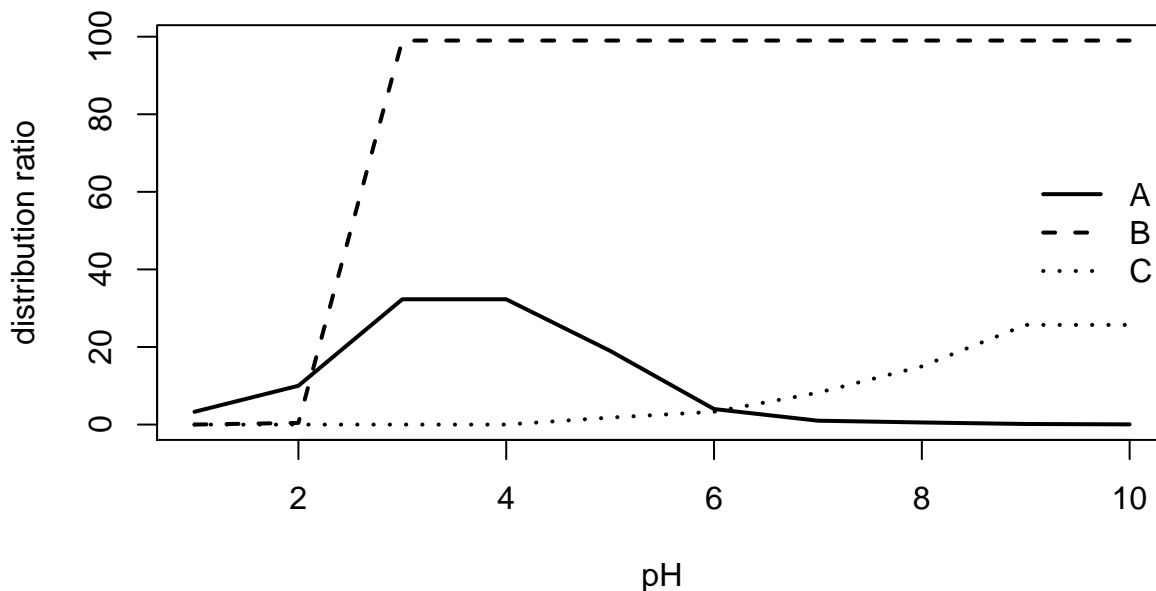
$$0.03162 = \frac{50}{25D + 50}$$

and solving for D

$$0.7906D + 1.5811 = 50$$

gives its value as 61.25 ; this is the smallest possible value for D .

Question 3 (11 points). The figure below shows the distribution ratio for the aqueous solutes A , B , and C as a function of pH. Describe how you can separate these solutes from each other and from other inert species solely by adjusting the sample's pH and extracting with a non-polar organic solvent.



Answer: The goal is to end up with each solute in a phase—organic or aqueous—that is free from all other solutes, including inert species other than A , B , and C . To accomplish this separation, we need to use a minimum of three steps. Here is one approach:

For the first step, we adjust the pH to ≈ 1 , where $D \approx 0$ for A and for C , but is ≈ 4 for B ; this allows us to extract B into the organic phase, leaving A and C in the aqueous phase. A pH of 2 also will work with a somewhat larger D for A , but with a D for B that is a touch above 0 (or, at least, that increases quickly above a pH of 2, which means any error in pH has the potential for a bad outcome).

For the second step, we adjust the pH to ≈ 3 , where $D \approx 0$ for C and ≈ 30 for A ; this allows us to extract A into the organic phase, leaving C in the aqueous phase.

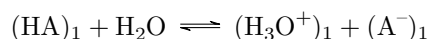
Finally, we adjust the pH to $\approx 9 - 10$, where $D \approx 25$ for C ; this allows us to extract C into the organic phase, leaving behind any inert materials in the aqueous phase.

There are other possibilities as well. For example, we can set the pH to ≈ 3 and extract A and B into the organic phase. We can then use clean aqueous phase with a pH of 9 to separate A and B by extracting A into the aqueous phase. Finally, to separate C from inert species in the original sample, we extract the original aqueous phase, which now contains only C , after adjusting its pH to $\approx 9 - 10$, a pH where C extracts into the organic phase.

Part II: Longer Questions

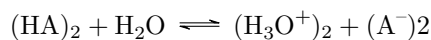
Problem 4 (25 points). Suppose you need to move a weak acid, HA , from one aqueous phase to a different aqueous phase. Because aqueous phases are completely soluble in each other, the phases are separated by a hydrophobic membrane that allows neutral molecules to pass through, but that is impermeable to ions. The following equilibrium reactions define this system, where the subscripts 1 and 2 identify the two aqueous phases:

HA 's acid dissociation reaction in aqueous phase 1



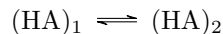
$$K_a = \frac{[\text{H}_3\text{O}^+]_1[\text{A}^-]_1}{[\text{HA}]_1}$$

HA's acid dissociation reaction in aqueous phase 2



$$K_a = \frac{[\text{H}_3\text{O}^+]_2[\text{A}^-]_2}{[\text{HA}]_2}$$

HA's partition coefficient between the two phases



$$K_D = \frac{[\text{HA}]_2}{[\text{HA}]_1}$$

Note that we are assuming that HA's K_a value is the same in both aqueous phases. Using these three equilibrium reactions, derive a mathematical expression for HA's distribution ratio, D , between the two aqueous phases. Your final equation should include the following terms only: K_D , K_a , $[\text{H}_3\text{O}^+]_1$, and $[\text{H}_3\text{O}^+]_2$. Based on your equation, if you want to move HA from aqueous phase 1 to aqueous phase 2, which of the following conditions will you use: (a) $(\text{pH})_1 \approx (\text{pH})_2 \ll 7$, (b) $(\text{pH})_1 \approx (\text{pH})_2 \gg 7$, (c) $(\text{pH})_1 \approx (\text{pH})_2 \approx 7$, (d) $(\text{pH})_1 \ll 7$ and $(\text{pH})_2 \gg 7$, (e) $(\text{pH})_1 \gg 7$ and $(\text{pH})_2 \ll 7$

Explain your choice in several sentences; although no calculations are necessary to defend your choice, you may include them if you wish. *Note: You might recognize that this is a simple model for a cell membrane that separates two physiological fluids.*

Answer: The distribution ratio must account for the concentrations of HA and of A^- in both phases; thus

$$D = \frac{[\text{HA}]_2 + [\text{A}^-]_2}{[\text{HA}]_1 + [\text{A}^-]_1}$$

To account for the secondary equilibrium in each phase, we note that the concentration of A^- in each phase is related to the concentration of HA and the concentration of H_3O^+ through the K_a expression

$$[\text{A}^-]_i = \frac{K_a[\text{HA}]_i}{[\text{H}_3\text{O}^+]_i}$$

where i is the phase. Substituting into the equation for D

$$D = \frac{[\text{HA}]_2 + \frac{K_a[\text{HA}]_2}{[\text{H}_3\text{O}^+]_2}}{[\text{HA}]_1 + \frac{K_a[\text{HA}]_1}{[\text{H}_3\text{O}^+]_1}}$$

and factoring out HA in both the numerator and the denominator gives

$$D = \frac{[\text{HA}]_2}{[\text{HA}]_1} \times \left(\frac{1 + \frac{K_a}{[\text{H}_3\text{O}^+]_2}}{1 + \frac{K_a}{[\text{H}_3\text{O}^+]_1}} \right)$$

Finally, we note that the ratio $[\text{HA}]_2/[\text{HA}]_1$ is equivalent to K_D and neaten up the remainder of the equation to avoid having fractions in the numerator and the denominator, leaving us with a final equation of

$$D = K_D \frac{([\text{H}_3\text{O}^+]_2 + K_a)[\text{H}_3\text{O}^+]_1}{([\text{H}_3\text{O}^+]_1 + K_a)[\text{H}_3\text{O}^+]_2}$$

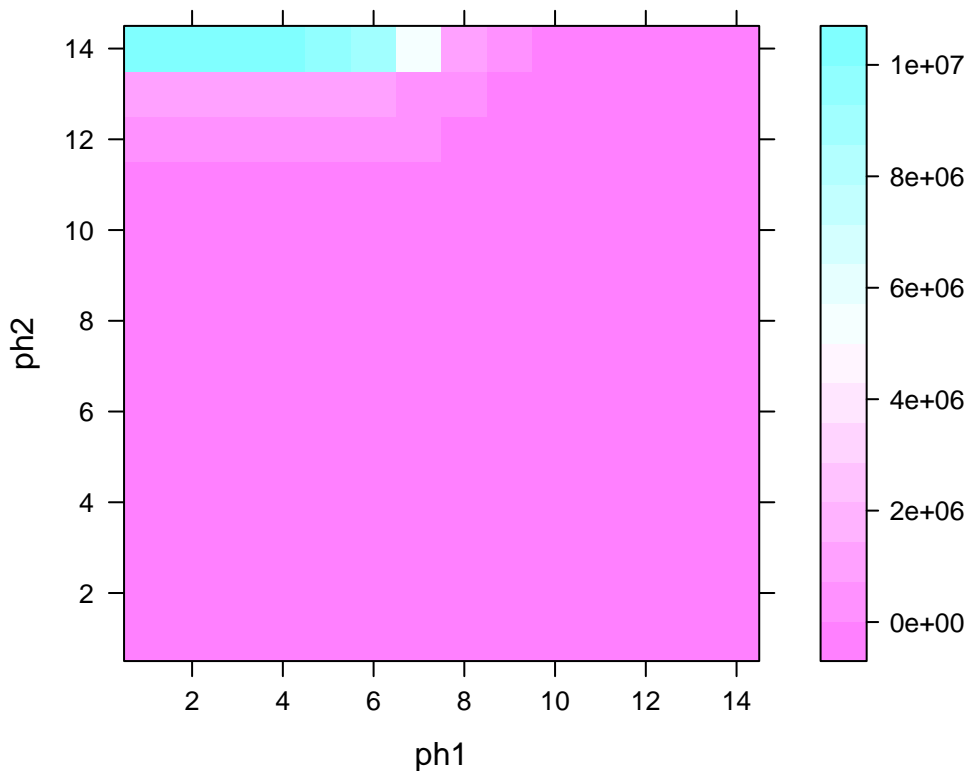
To evaluate the best set of pH values, you can reason using Le Châtelier's Principle. If we want to move HA from phase 1 into phase 2, then we want the pH in phase 1 to favor its conjugate weak acid form, HA, and we

want the pH in phase 2 to favor its conjugate weak base form, A^- . To accomplish this, we use condition (d) where $(\text{pH})_1 \ll 7$ and where $(\text{pH})_2 \gg 7$. Under this condition, the HA in phase 2 is converted to A^- , which decreases the concentration of HA, causing more HA to move from phase 1 to phase 2. Note that we arrive at the same conclusion by considering just the relative values of $[\text{H}_3\text{O}^+]_1$, $[\text{H}_3\text{O}^+]_2$, and K_a ; thus, if $(\text{pH})_1 \ll 7$ and $(\text{pH})_2 \gg 7$, then, for any reasonable value of K_a we have $[\text{H}_3\text{O}^+]_1 \gg K_a$ and $[\text{H}_3\text{O}^+]_2 \ll K_a$, which allows us to simplify the equation for the distribution ratio to

$$D \approx K_D \frac{K_a [\text{H}_3\text{O}^+]_1}{[\text{H}_3\text{O}^+]_1 [\text{H}_3\text{O}^+]_2} \approx \frac{K_a}{[\text{H}_3\text{O}^+]_2} \gg 1$$

Another approach is a brute force calculation of D for a variety of pH values with $K_D = 1$ and $K_a = 1 \times 10^{-7}$; here is one such calculation and plot of the data, which leads to the same conclusion. The code includes a function called `model` that calculates D for any two pH values and the R function `outer` that calculates D for all possible combinations of pH levels. The function `levelplot` from the `lattice` package shows how D varies with changes in pH.

```
ph1 = seq(1,14,1)
ph2 = seq(1,14,1)
h3o1 = 10^-ph1
h3o2 = 10^-ph2
kd = 1
ka = 1e-7
model = function(h3o1,h3o2){kd * (h3o1 * (h3o2 + ka))/(h3o2 * (h3o1 + ka))}
d = outer(h3o1, h3o2, model)
library(lattice)
levelplot(d, xlab = "ph1", ylab = "ph2", zlab = "D", row.values = ph2,column.values = ph1)
```



Problem 5 (25 points). The ligand 8-hydroxyquinoline, $\text{C}_9\text{H}_6\text{ON}$, also known as oxine, is both a weak acid and a weak base. If we represent its neutral form as BH , then its fully protonated form is BH_2^+ and its fully deprotonated form is B^- . Oxine's two $\text{p}K_a$ values are 4.81 and 9.81, and its K_D between water and chloroform is 720. The distribution ratio, D , for oxine depends on the pH of the aqueous phase and is defined

as

$$D = K_D \times \frac{K_{a1}[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]^2 + K_{a1}[\text{H}_3\text{O}^+] + K_{a1}K_{a2}}$$

Using this information, create a plot that shows the fraction of oxine extracted into chloroform as a function of pH assuming a single extraction using equal volumes of water and chloroform. You may choose to use R or Excel to create your plot. If you use R, you may begin with the script `acidbaseLLE.R` that we examined in class, modifying it to meet your needs. In addition to your plot, be sure to submit your script file if you use R, or your spreadsheet file if you use Excel.

Answer: Before creating the plot, it helps to begin by considering what we expect to see. Given the information about oxine, its neutral form is the predominate form in the pH range 4.81 to 9.81; thus, we expect that the fraction extracting into CHCl_3 will be at its greatest for moderate pH values and will decrease toward zero when the pH becomes sufficiently acidic or basic. Here is the code and plot, both modified from the code in the file `acidbaseLLE.R`:

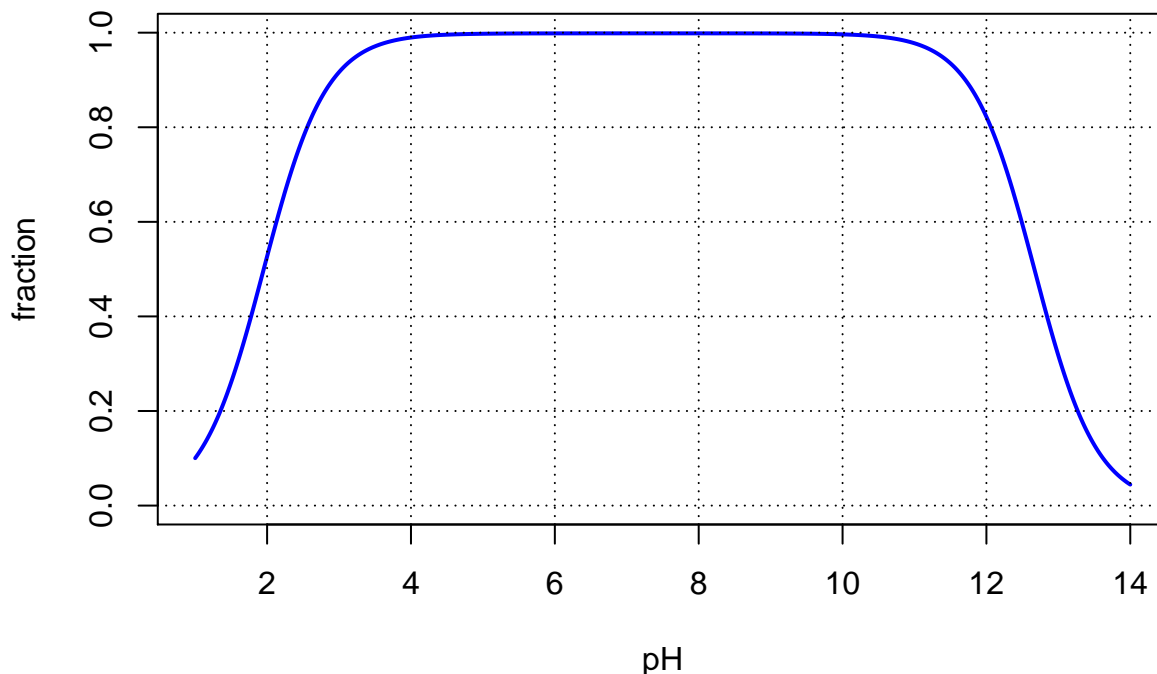
```
#' Enter the pKa values and the Kd value
pka1 = 4.81
pka2 = 9.81
kd = 720

#' Set up range of pH values
ph = seq(1, 14, 0.01)
h = 10^-ph

#' Calculate distribution ratio
ka1 = 10^-pka1
ka2 = 10^-pka2
d = kd * (ka1 * h)/(h^2 + ka1 * h + ka1 * ka2)

#' Calculate the fraction of oxine in the organic layer
qaq = 1/(d + 1)
qorg = 1 - qaq

#' Examine results as a function of pH
plot(ph, qorg, type = "l", lwd = 2, lty = 1, col = "blue",
      xlab = "pH", ylim = c(0, 1), ylab = "fraction")
grid(col = "black")
```



Problem 6 (25 points). The script `cce_exam.R` contains two functions for exploring the countercurrent extractions of a mixture of three diprotic acids, each of which take the forms H_2X^+ , HX , and X^- , in which, as is the case for oxine (see previous problem), the fully protonated species is a cation and the fully deprotonated species is an anion. The function `ccextract`

```
ccextract(pH)
```

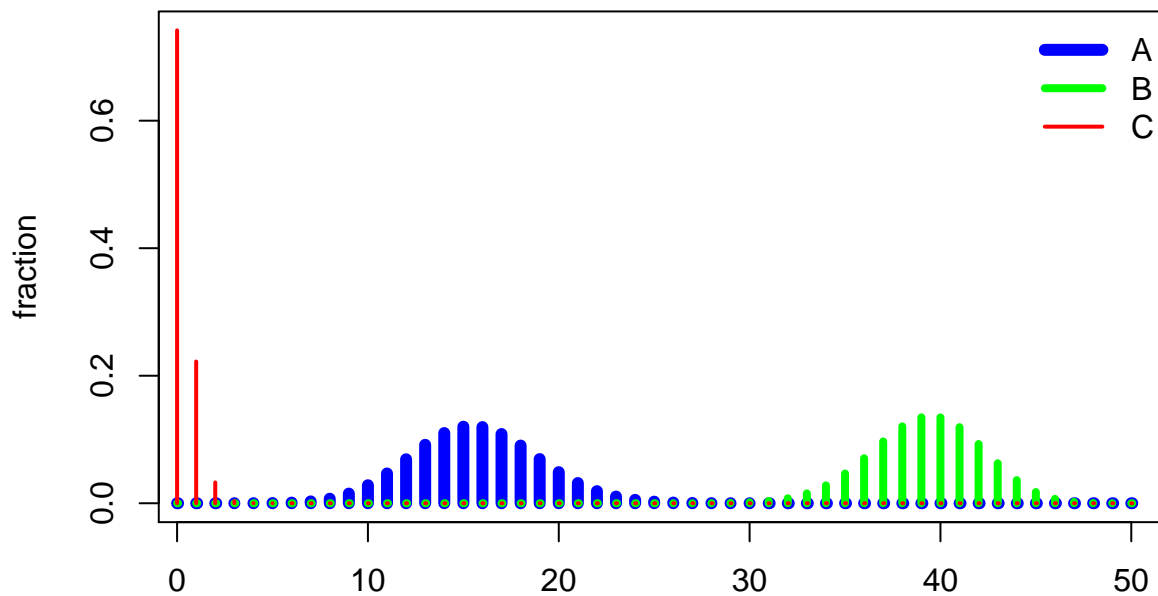
models the extraction over 50 cycles, or steps, using the pH passed to the function. The three weak acids have K_D values of 5, 4, and 6 for, respectively, HA, HB, and HC, but differ significantly in their $\text{p}K_a$ values, which are 5 and 9 for H_2A^+ , 3 and 7 for H_2B^+ , and 7 and 11 for H_2C^+ . The function `cce.plot` displays the distribution of the three compounds at the end of the 50 cycles

```
cce.plot(x)
```

where `x` is the name of an object created using `ccextract`. Examine the effect of pH on the separation of the three compounds and explain your results in terms of the properties of the compounds. Your analysis should be in the form of 1–3 well-written paragraphs supplemented with figures that support your analysis. Give attention to how pH affects the order in which the compounds move through the system and pH values that favor a separation of all three compounds.

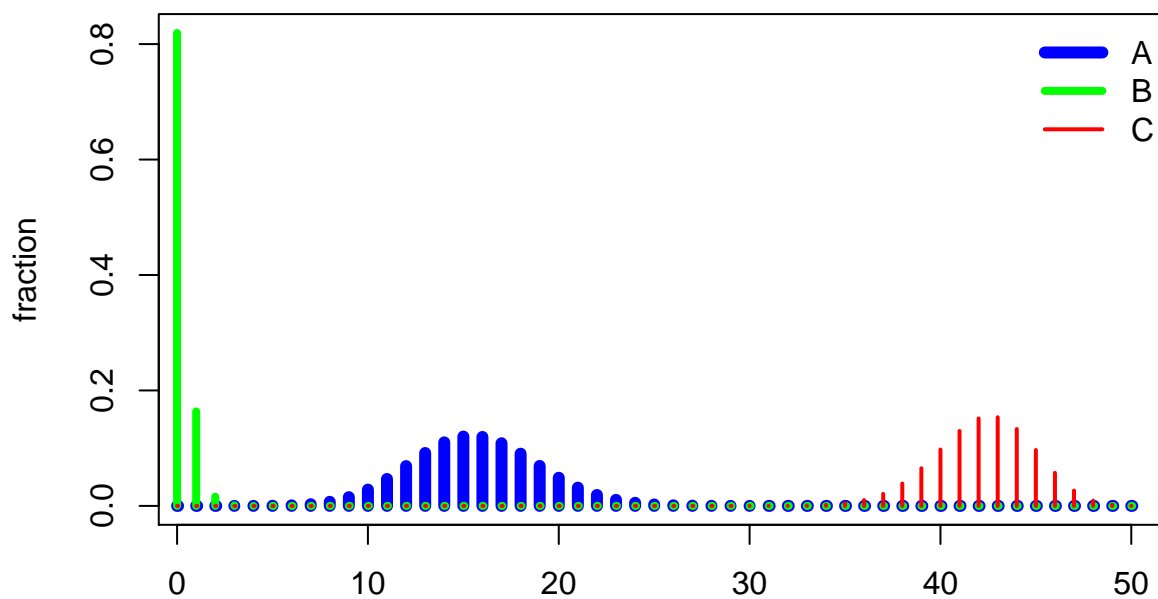
Answer: Although we can methodically explore the effect of pH on this separation by running scenarios over a wide range of pH values, it is best to consider what we might expect given the properties of the three compounds. Given the nature of the compounds, each will move through the system when in its neutral form (the simulation assumes that the mobile phase is organic and the stationary phase is aqueous); thus, given their respective $\text{p}K_a$ values, we expect that lower pHs will favor the movement of HB and that higher pHs will favor the movement of HC, as shown in the following two plots at pH levels of 4 and of 10

pH = 4



tube number

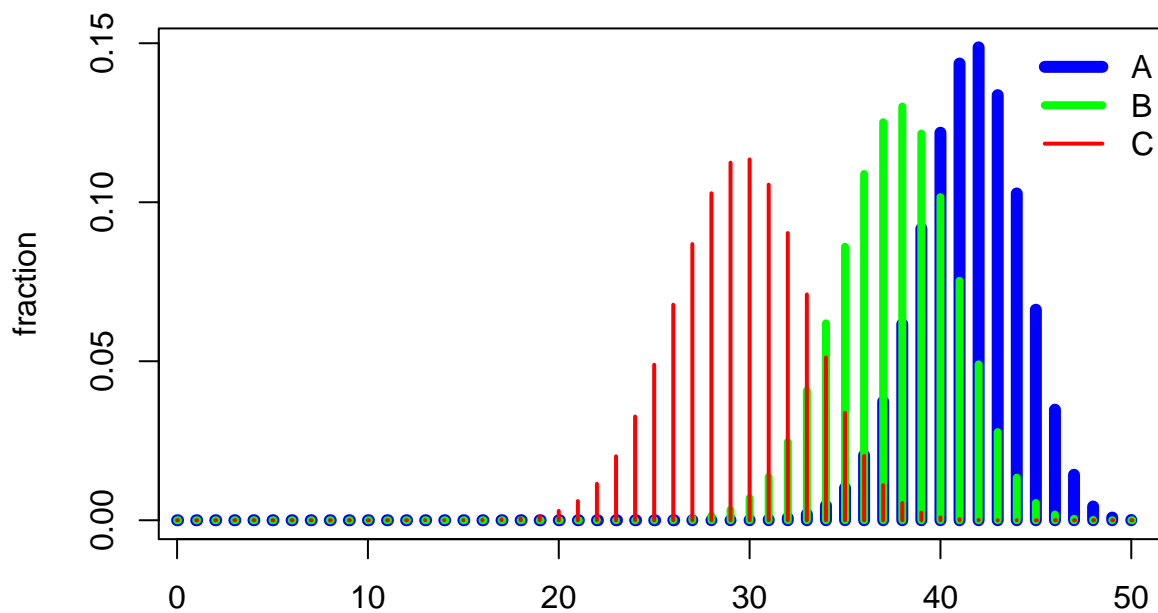
pH = 10



tube number

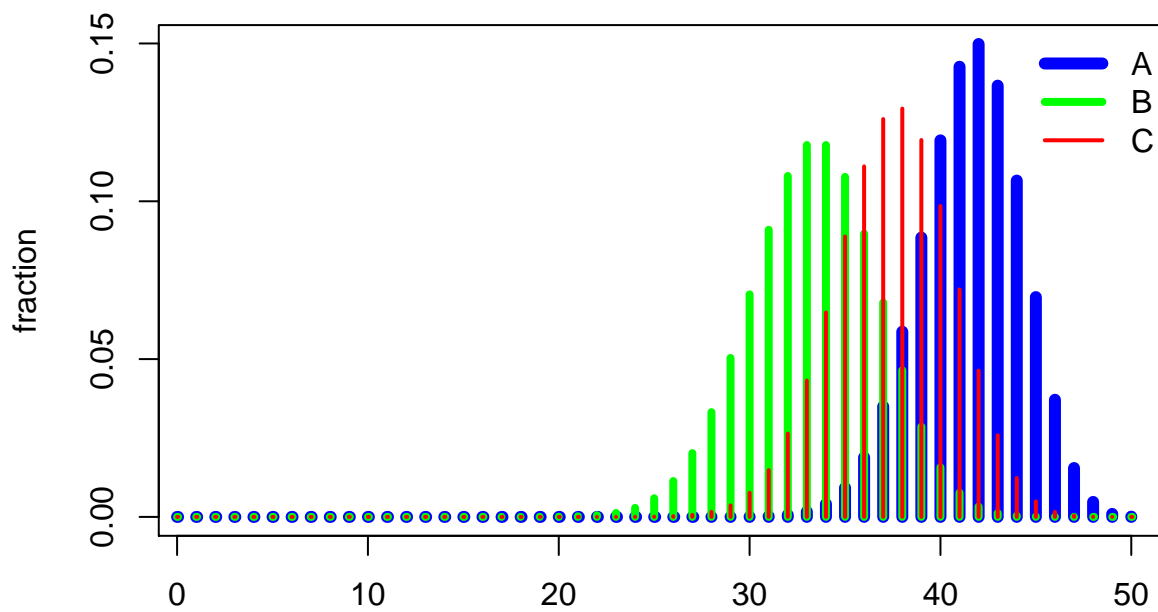
Given their relative pK_a values, we should not be surprised to see that all three species migrate at more neutral pH values, as shown here for pH values of 6.5, 7, and 7.5, which prevents a clean separation of the three compounds.

pH = 6.5



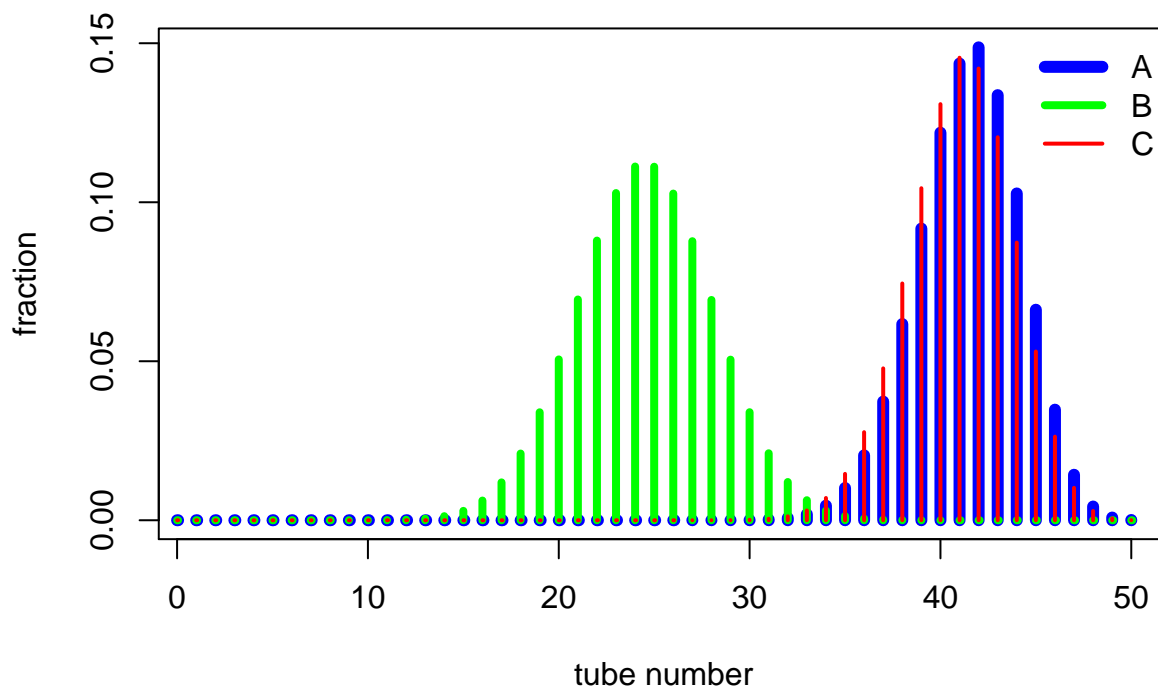
tube number

pH = 7



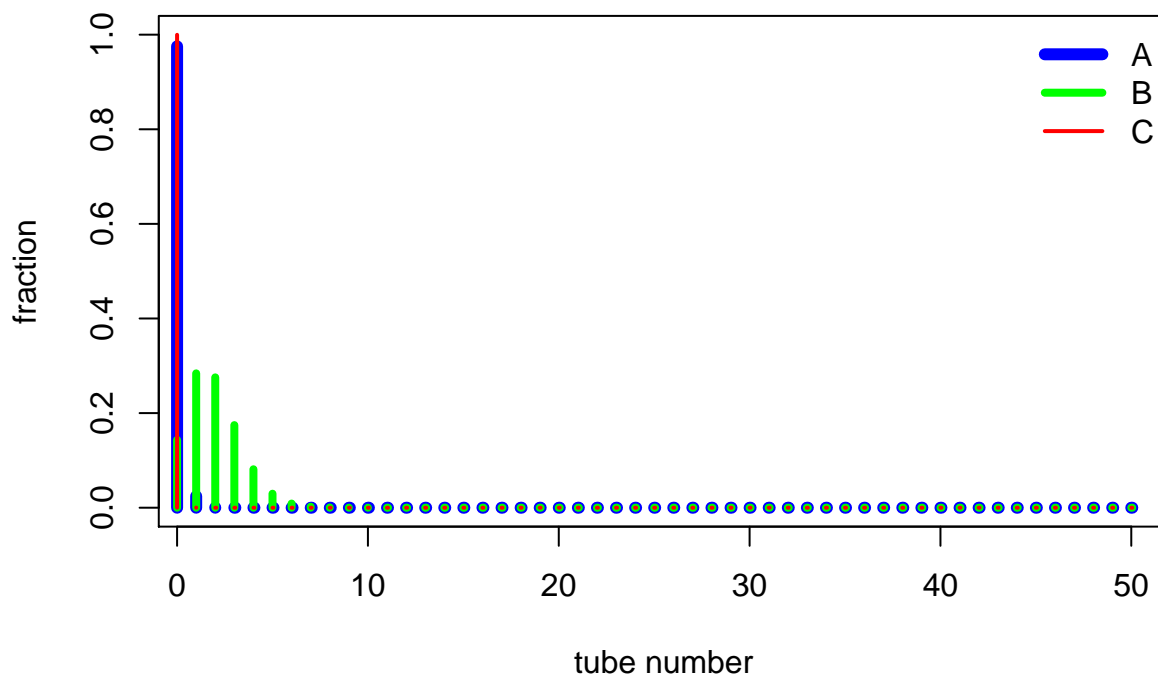
tube number

pH = 7.5



Finally, we should not be surprised to see that there is little movement of any compound for more extreme pH values, such as a pH of 1 and a pH of 14.

pH = 1



pH = 14

