CHEMISTRY 133
Spring, 2017 Homework Set 3.1 Solutions

Ch. 22: 2, 7a, 17, 19, 22, 24, 26, 28, 31, 32, 38, 42, 43

2. If you wish to extract aqueous acetic acid into hexane, is it more effective to adjust the aqueous phase to pH 3 or pH 8?
It is more effective to adjust the ***pH to 3****. The reason is because acetic acid is more organic soluble as a molecule (CH_3CO_2H) than as an ion ($CH_3CO_2^-$).*

7.a. Solute S has a partition coefficient of 4.0 between water (phase 1) and chloroform (phase 2) in Equation 23-1.
a) Calculate the concentration of S in chloroform if [S(aq)] is 0.020 M.
$K = [S(CHCl_3)]/[S(H_2O)]$
$[S(CHCl_3)] = K\cdot[S(H_2O)] = 4.0\cdot0.020M =$ ***0.080 M***

17. The partition coefficient for a solute in chromatography is $K = c_s/c_m$, where c_s is the concentration in the stationary phase and c_m is the concentration in the mobile phase. The larger the partition coefficient, the longer it takes a solute to be eluted. Explain why.
Compounds with larger K values will take longer because they spend more time in the stationary phase.

19. a) A chromatography column with a length of 10.3 cm and an inner diameter of 4.61 mm is packed with a stationary phase that occupies 61.0% of the volume. If the volume flow rate is 1.13 mL/min, find the linear flow rate in cm/min.
$u = (1.13\ mL/min)*(1\ cm^3/mL)*(1/A_{effective})$
where $A_{effective}$ *is the effective cross-sectional area* $= \pi*f*d^2/4$
and f = fraction of column made up by mobile phase (= 1 – 61.0/100)
$A_{effective} = \pi*0.390*(0.461\ cm)^2/4 = 0.0651\ cm^2$
$u = (1.13\ mL/min)*(1\ cm^3/mL)/0.0651\ cm^2 =$ ***17.4 cm/min***
b) How long does it take for solvent (which is the same as unretained solute) to pass through the column?
Time = distance/linear flow rate or time = volume/flow rate
Time = 10.3 cm/17.4 cm/min = ***0.593 min*** *or time = (10.3 cm)($A_{effective}$)/1.13 mL/min =* ***0.593 min***
c) Find the retention time for a solute with a retention factor of 10.0.
$k = (t_r - t_m)/t_m = 10.0 = (t_r - 0.593)/0.593$
$t_r = 5.93 + 0.59 =$ ***6.53 min****.*

22. Solvent passes through a column in 3.0 min but solute requires 9.0 min.
a) Calculate the retention factor, k.
k *= (9-3)/3 =* ***2.0***

b) What fraction of the time is the solute in the mobile phase in the column?
fraction of time *= 3/9 =* ***0.33***
c) The volume of the stationary phase is 1/10 of the volume of the mobile phase of the column ($V_s = 0.10V_m$). Find the partition coefficient, K, for this system.

*$K = k(V_m/V_s) = 2.0*(10) =$ **20**.*

24. Consider a chromatography column in which $V_s = V_m/5$. Find the retention factor if K = 3 and if K = 30.

*K = 3: $k = KV_s/V_m = 3*(1/5)$ **k = 0.6*** *K = 30:* ***k = 6***

26. An open tubular column has a diameter of 207 μm and the thickness of the stationary phase on the inner wall is 0.50 μm. Unretained solute passes through in 63 s and a particular solute emerges in 433 s. Find the partition coefficient for this solute and find the fraction of time spent in the stationary phase.

fraction of time spent in stationary phase = time spent in stationary phase/total time spent
fraction of time spent in stationary phase = (433 – 63 s)/433 s = ***0.854 = 85.4%***
$k = (433 - 63\ s)/63\ s = 5.873$
$K = C_s/C_m = k(V_m/V_s)$
$V_m = V_{cylinder} = \pi(d^2/4)L = \pi[(0.207\ mm)^2/4)L = 0.0337\ mm^2L$
$V_s = V_{tube} = V_{outer\ cylinder} - V_{inner\ cylinder} = \pi[(0.207\ mm)^2/4]L - \pi\{[(0.207\ mm - 2(0.0005\ mm)]^2/4\}L$
Note: for a thin tube, $V_{tube} = \pi tdL$, where t = film thickness. This same equation also can be calculated from the first equation ($V_s = V_{tube} = V_{outer\ cylinder} - V_{inner\ cylinder}$) since $V_{tube} = \pi[(0.207\ mm)^2/4]L - \pi[(0.207\ mm)^2/4]L + \pi(0.207\ mm)(0.0005\ mm)L - \pi(0.0005\ mm)^2L$. The first two terms cancel out and since 0.207 mm >> 0.0005 mm, the last term is inconsequential.
$V_s = V_{tube} = \pi(0.207\ mm)(0.0005\ mm)L = 0.000325\ mm^2L$
*$K = k(V_m/V_s) = 5.873(0.0337\ mm^2L/0.000324\ mm^2L) =$ **609** (note how L cancels out so the column length is not needed).*
*O.k. to get the same answer as the text (**603**), you must use the outer diameter not including the film (0.207 – 2*0.0005 mm) for the mobile phase volume (since the film is stationary phase, and thus not mobile phase) and the average tube diameter for the stationary phase volume (.2065 mm), or the more complete equation for tube volume (outer cylinder vol. – inner cylinder vol.). However, considering that the film thickness is only accurate to two sig. fig.s, the answer should only be given to 2 sig figs.*

28. Chromatograms of compounds A and B were obtained at the same flow rate with two columns of equal length. (Refer to plot in text)
a) Which column has more theoretical plates?
***Column 1** because peaks eluting at the same time are narrower.*
b) Which column has a larger plate height?
***Column 2** because H = L/N and L is the same.*
c) Which column gives higher resolution?
***Column 1** because peaks have retention times that are the same but peak widths for column 1 are narrower.*
d) Which column gives a greater relative retention?
*They are **the same** since the retention times are the same.*
e) Which column has a higher retention factor?
***Compound B** (it elutes later).*
f) Which compound has a greater partition coefficient?

Compound B *(partition coefficient is proportional to capacity factor)*
g) What is the numerical value of the separation factor?
γ = 10/8 = ***1.25***

31. Why is longitudinal diffusion a more serious problem in gas chromatography than in liquid chromatography?
Diffusion is faster in the gas phase than in the liquid phase.

32. In chromatography, why is the optimal flow rate greater if the stationary phase particle size is smaller?
A smaller stationary particle size generally will decrease the mass transport (or C term) in the van Deemter equation. Since the C term increases with an increase in flow rate, a smaller C term will result a shift in the minimum to greater linear velocities or greater flow rates.

38. A chromatogram with ideal Gaussian bands has t_r = 9.0 min and $w_{1/2}$ = 2.0 min.
a) How many theoretical plates are present?
$N = 5.55(9.0\ \text{min}/2.0\ \text{min})^2 =$ **112**
b) Find the plate height if the column is 10 cm long.
H = 100 mm/112 = **0.89 mm**

42. A band from a column eluted at 0.66 mL/min has a width at half-height, $w_{1/2}$, of 39.6 s. The sample was applied as a sharp plug with a volume of 0.40 mL, and the detector volume is 0.25 mL. Find the variances introduced by injection and detection. What would $w_{1/2}$ be if the only broadening occurred on the column?
To solve this problem, we need to convert to the same width units. I will use σ in s as in the example in Sect. 22-5.
The equation for the observed dispersion ($\sigma_{(meas)}$) is given as:
$\sigma_{(meas)}^2 = \sigma_{(col)}^2 + \sigma_{(inj)}^2 + \sigma_{(det)}^2$
where: $\sigma_{inj}^2 = \Delta t_{inj}^2/12 = [(0.40\ \text{mL})(1/0.66\ \text{mL/min})(60\text{s/min})]^2/12 = (36.36\ \text{s})^2/12 = 110.2\ \text{s}^2$
$\sigma_{(det)}^2 = \Delta t_{det}^2/12 = [(0.25\ \text{mL})(1/0.66\ \text{mL/min})(60\text{s/min})]^2/12 = (36.36\ \text{s})^2/12 = 43.0\ \text{s}^2$
$w_{1/2} = 2.35\sigma$ or $\sigma_{(meas)} = w_{1/2}/2.35 = (39.6\ \text{s})/2.35 = 16.85$ s
$\sigma_{(meas)}^2 = 284.0\ \text{s}^2$
Solving for $\sigma_{(col)}^2$: $\sigma_{(col)}^2 = \sigma_{(meas)}^2 - (\sigma_{(inj)}^2 + \sigma_{(det)}^2)$
$\sigma_{(col)}^2 = 284.0\ \text{s}^2 - (110.2\ \text{s}^2 + 43.0\ \text{s}^2) = 130.8\ \text{s}^2$
Or on a % basis, 39% of the variance comes from injection and 15% from detection
$\sigma_{(col)}$ = 11.43 s, so $w_{1/2(col)} = 2.35\sigma_{(col}$ = **26.9 s**

43. Two compounds with partition coefficients of 15 and 18 are to be separated on a column with V_m/V_s = 3.0 and t_m = 1.0 min. Calculate the number of theoretical plates needed to produce a resolution of 1.5.