

Chem 41010/6010 Problem Set #2  
 Patonay - Chromatography Information/Questions

1. During an isothermal GC run, K is determined by the enthalpy of vaporization:

$$\log K = \frac{\Delta H}{2.3 RT} + \text{constant}$$

where  $\Delta H$  can be estimated using Trouton's rule ( $\Delta H = 21T_B$ ) for the members of a homologous series.

Using these relationships and other basic chromatographic equations, explain why temperature program results in shorter retention times for the members of a homologous series?

2. Given the following retention times for n-alkanes on a GC column at 150 °C, calculate the retention time of heptadecane under the same conditions: CH<sub>4</sub>, t<sub>R</sub> = 25 sec, C<sub>13</sub>H<sub>28</sub>, t<sub>R</sub> = 1.20 min, C<sub>15</sub>H<sub>32</sub>, t<sub>R</sub> = 6.35 min.
3. What solvent or solvent mixture will have approximately the same solvent strength as 14% methanol and 2% water in hexane?

Solvent Characteristics of Mixed Solvents

Solvent	Selectivity Group	Solvent Strength Weighting Factor (S <sub>1</sub> )	
		Reversed-Phase <sup>a</sup>	Normal Phase
Methanol	II	2.6	5.1
Acetonitrile	VI	3.2	5.8
Tetrahydrofuran	III	4.5	4.0
Water	—	0	10.2
Chloroform	VIII		4.1
Methylene Chloride	V		3.1
Methyl t-butyl ether	I		ca. 2.5
Ethyl ether	I		2.8
Hexane	—		0

<sup>a</sup>Approximate values for some other common solvents are acetone (3.4), dioxane (3.5), ethanol (3.6) and isopropanol (4.2).

4. The normal retention time of trace amounts of  $\text{Na}^+$  on a certain ion-exchange chromatographic column is 2.4 hr. A molecule of mobile phase (which is unretained by the resin) passes through the column in 23 min. It has been determined experimentally that a mobile-phase  $\text{Na}^+$  concentration of 0.080 M is sufficient to keep all the exchange sites in the  $\text{Na}^+$  form. While the column ion is being washed with a 0.080 M  $\text{Na}^+$  solution, a trace of radioactive sodium ion is added to the eluent at the column inlet. When does the radioactive sodium ion first appear in the eluate? Explain your answer.
5. A molecular-exclusion chromatographic column is made from an old 50-mL buret. Having no other information, what statement can you immediately make about elution volumes for this column?
6. Imagine that you can make a porous material with any range of pore sizes that you wish. In order to obtain maximum resolution of a particular pair of compounds, do you create a material with a wide range of pore sizes or a very narrow range of pores sizes? Why?
7. Assume that the solvent strength for an HPLC separation is about optimum in the methanol-water (60:40) mixture. We wish to change solvent selectivity to adjust resolution. Determine one binary and one ternary solvent system you would use to vary selectivity. Use the table below and the selectivity triangle below.

Solvent	Selectivity Group	Solvent Strength Weighting Factor
Methanol	II	2.6
Acetonitrile	VI	3.2
Tetrahydrofuran	III	4.5
Water	-	0

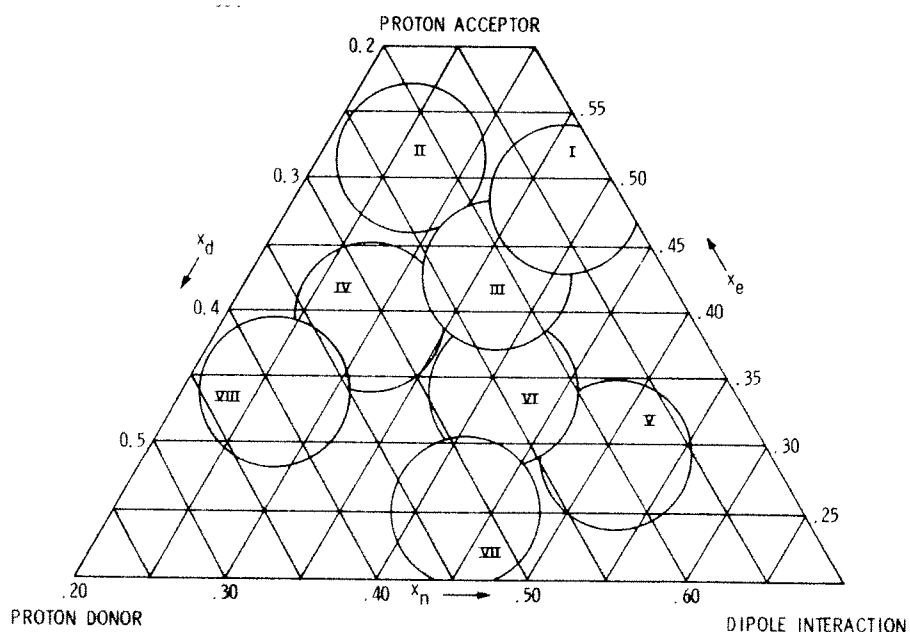


Figure 4.14 Selectivity triangle for solvents.

8. Are the following statements true or false?

Using cyclodextrin solution as mobile phase and polyamide as stationary phase:

- A. Increasing formation constant of cyclodextrin-solute complex increases the retardation factor.  
(True or False)
- B. Increasing hydrophobicity of mobile phase increases the retardation factor.  
(True or False)

Using cyclodextrin bonded phase as stationary phase:

- C. Increasing formation constant of cyclodextrin-solute complex increases the retardation factor.  
(True or False)
- D. Increasing hydrophobicity of mobile phase increases the retardation factor.  
(True or False)

9. Compound A migrates 7.5 cm from its point of application on a thin-layer chromatographic plate, whereas in the same time the solvent front migrates 16.2 cm beyond the point of sample application.

- A. Calculate  $R_f$  for compound A.
- B. On an identical plate, the solvent front has moved 14.3 cm beyond the point of sample application; where should compound A be located on this plate?

10. Silica sample A has an  $R_f$  for quinazoline of 0.50 with a one-to-three benzene-methanol solvent. With the same sample and solvent system, silica sample B has an  $R_f$  of 0.40. Which silica is more active?

11. If you want to product maximum activity in a particular silica sample, how do you treat it?

12. Diatomite is a form of  $\text{SiO}_2$  with a surface area per unit mass of less than  $50 \text{ m}^2/\text{gm}$ . Should it be more or less active than silica gel?

13. Calculate the resolution between two spots observed on a high performance thin layer chromatography plate. The solvent front traveled 9.5 cm and the two spots traveled 5.2 cm and 6.1 cm, respectively. The diameter of both spots is 4 mm. Determine the HEPT values of this plate. How does the resolution change with longer development time? Will the HEPT value be affected?
14. A mixture of a benzoic acid, a naphthoic acid and two pyrene carboxylic acids ( $K_1 > K_2$ ) is separated on a polyamide plate using 0.07 M  $\alpha$ -,  $\beta$ - and  $\gamma$ - cyclodextrin solutions as mobile phase. Where do you expect the components on the TLC plate after development with the three different cyclodextrin mobile phase? Make a simple sketch of the TLC plates and give explanation of the expected results. ( $K_1$  and  $K_2$  refers to the formation constants of pyrene carboxylic acids with  $\gamma$ -cyclodextrin.)
15. What mobile phase pH and what type of ion exchanger would you choose in order to attempt the ion-exchange chromatographic fractionation of a mixture of carboxylic acids?
16. Which acid would be eluted first, one with a  $pK_a$  of 4 or one with a  $pK_a$  of 5? Explain your answer.
17. Which acid would be eluted first, propanoic or octadecanoic? Explain your answer. (These acids have approximately equal  $pK_a$  values).