Basics of Chromatography

A. Chromatography vs. Countercurrent distribution

B. Type of Chromatography

C. Chromatography Parameters: t_R, t_M, V_R, V_M, t_R', V_R', W_b, W_h.

D. Solute Retention: k, $k = t_R'/t_M$ $\quad t_R' = k\, t_M$ $\quad t_R = (k+1)\, t_M$

E. Efficiency of Chromatography and Plate Theory: N and H

$$N = (t_R/\sigma_t)^2$$

F. Measures of Solute Separation: α, R_s

G. Fundamental factors affecting resolution:

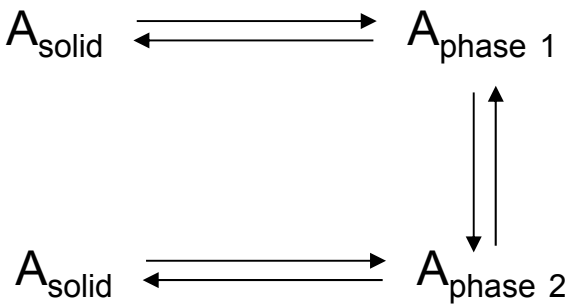
$$R_s = \frac{t_{R2} - t_{R1}}{(W_{b2}+W_{b1})/2}$$

$$R_s = [N^{1/2}/2][(k_2-k_1)/(2+k_1+k_2)$$

$$R_s = [N^{1/2}/4][(\alpha -1)/(\alpha)]*[k_2/(1+ k_2)], \quad \alpha = k_2/k_1$$

Hildebrand solubility parameters and k

$$\ln (K_D) = -\frac{\bar{V}_i}{RT} (\delta_1 - \delta_2)(\delta_1 + \delta_2 - 2\delta_A)$$



$$\ln(K) = \left(\frac{-\Delta\mu_i^0}{RT}\right) \qquad \Delta\mu_i^0 = \Delta\bar{H}_i^0 - T\Delta\bar{S}_i^0$$

$$\Delta H_i^0 = \Delta H_{i\,\beta,}^0 - \Delta H_{i,\,\alpha}^0$$

$$\Delta H_m = V_i (\bar{\delta}_i - \delta_j)^2$$

Hildebrand solubility parameter (δ).

$$\delta = (\Delta E_v/V)^{1/2}$$

Where: $\Delta E_v/V$ = energy per unit volume, required to completely vaporize a solution of pure compound

Disadvantages: not accurate because the simple model

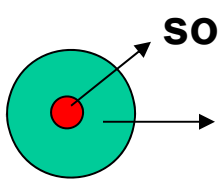
A General model for solvent-solute interactions
-- cavity model

1. The process of dissolving a solute molecule is broken down to two steps: (a) cavity formation process, and (b) solute/solvent interactions

2. Cavity formation: a cavity or hole of sufficient size to accommodate the solute molecule is constructed in the solvent. This is an endoergic process, and *the amount of the energy involved increases with the size of the solute molecule*.

3. In the second stage of the solution process, the solute is allowed to interact with solvent. (1) Dipole-dipole interactions; (2) dipole-induced dipole (Induction interactions), (3) Dispersion interaction (London forces), and (4) acid-base interactions: H-bonding (a. solvent as donor(acid) and solute as accepter(base), b. solvent as acceptor(base) and solute as donor (acid)).

$$XYZ = XYZ_0 + \text{cavity formation energy} + \sum\text{Solute-solvent interactions}$$



XYZ: Free Energy

The Essence of Chromatography: p14

Capacity factor k and intermolecular interactions

XYZ = XYZ_0 + cavity formation energy + ∑Solute-solvent interactions

***Linear Free Energy Relationship Assumption*: Free energy of solute transfer from the mobile to the stationary phase is an additive property.**

$$XYZ = XYZ_0 + m' V_x + r' R_2 + s' \pi_2^H + a' \sum \alpha_2^H + b' \sum \beta_2^H$$

$$\log k = c + mV_x + rR_2 + s\pi_2^H + a \sum \alpha_2^H + b \sum \beta_2^H \quad \text{(Liquid chromatography)}$$

$$\log k = c + rR_2 + s\pi_2^H + a \sum \alpha_2^H + b \sum \beta_2^H + l \log L^{16} \quad \text{(Gas chromatography)}$$

Separation of solute and chromatographic system contributions

$$F(x,y) = A(x)\, B(y)$$

Solute descriptors (R_2, π_2, $\sum\alpha_2$, $\sum\beta_2$, $\log L^{16}$, and V_x): depended on solute properties (Kamlet-Taft parameters)

System constants (*c, m, r, s, a, b,* and *l*): depended on chromatographic system conditions: mobile phase, stationary phase, and temperature.

The Meaning of System Constants and Solute Descriptors

$$\log k = c + mV_x + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H \quad \text{(Liquid chromatography)}$$

$$\log k = c + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l\log L^{16} \quad \text{(Gas chromatography)}$$

Solute descriptors (V_x, R_2, π_2^H, $\sum\alpha_2^H$, $\sum\beta_2^H$ and $\log L^{16}$): depended on solute properties

V_x: molar volume calculated via Mcgowan's method (sum of atomic volumes, then subtract 6.56 for each bond of any type, number of bond= N-1+R, unit: $cm^3 \cdot mol^{-1}$). Where, N is the total number of atoms and R is number of rings. This method is suitable for estimating molar volume for all the kinds of compounds. The unit for V_x is $cm^3 \cdot mol^{-1}/100$.

Example, atomic volume: C = 16.35, H = 8.71, O = 12.42, calculate the value of V_x for phenol. Phenol = 6*C + 6*H + O – 6.56*(13-1+1) = 77.5 $cm^3 \cdot mol^{-1}$
V_x = 0.775 $cm^3 \cdot mol^{-1/}100$ (Page 16)

R_2: <u>The interactions between phases and solute though n and π electron pairs</u>.

$$R_2 = 10 * V_x[(n^2-1)/(n^2+2)] - 2.832\,V_x + 0.526$$

(n: refractive index of solute, 20°C for sodium d-line)

π_2^H: dipole-dipole, induction interactions

$\sum\alpha_2^H$:hydrogen bond acidity (H donor)

$\sum\beta_2^H$: hydrogen bond basicity (H acceptor)

$\log L^{16}$: the solute gas-liquid distribution in hexadecane. *Cavity effect and dispersion interactions (London force) in gas chromatography.*

$$\log k = c + mV_x + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H \quad \text{(Liquid chromatography)}$$

$$\log k = c + rR_2 + s\pi_2 + a\sum\alpha_2 + b\sum\beta_2 + l\log L \quad \text{(Gas chromatography)}$$

The meaning of system constants (*c, m, r, s, a, b,* and *l*) is corresponding to that of solute descriptors.

We can evaluate the properties of chromatographic systems!

It is very important in material characterization, retention prediction, and method development in chromatography

Evaluation of the properties of chromatographic systems

Example: page 19 in *The Essence of Chromatography*

Calculate the value of log k for phenol, benzyl alcohol, aniline, toluene, chlorobenzene, and predict the order retention of these molecules in a reversed-phased chromatographic system.

Solute	Descriptors				
	V_X	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$
Phenol	0.775	0.805	0.89	0.60	0.31
Benzyl Alcohol	0.916	0.803	0.87	0.33	0.56
Aniline	0.816	0.955	0.96	0.26	0.50
Toluene	0.857	0.601	0.52	0	0.14
Ethylbenzene	0.998	0.613	0.51	0	0.15
Naphthalene	1.085	1.340	0.92	0	0.20
Benzaldehyde	0.873	0.820	1.00	0	0.39
Nitrobenzene	0.890	0.871	1.11	0	0.28
Chlorobenzene	0.838	0.718	0.65	0	0.07
Acetophenone	1.014	0.818	1.00	0	0.49

System constants

c = -1.82,
m = 2.99,
r = 0.46,
s = -0.44,
a = 0.30,
b = -1.88

$$\log k = c + mV_x + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H$$

$\log k_{(phenol)} = -1.82 + 2.99*0.775 + 0.46*0.805 - 0.44*0.89 + 0.3*0.60 - 1.88*0.31$
$= -.273$

Solute	Descriptors					log k	
	V_X	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^0$	Experimental	Predicted
Phenol	0.775	0.805	0.89	0.60	0.31	-0.306	-0.273
Benzyl Alcohol	0.916	0.803	0.87	0.33	0.56	-0.268	-0.252
Aniline	0.816	0.955	0.96	0.26	0.50	-0.386	-0.380
Toluene	0.857	0.601	0.52	0	0.14	0.553	0.524
Ethylbenzene	0.998	0.613	0.51	0	0.15	0.997	0.937
Naphthalene	1.085	1.340	0.92	0	0.20	1.185	1.256
Benzaldehyde	0.873	0.820	1.00	0	0.39	-0.017	-0.011
Nitrobenzene	0.890	0.871	1.11	0	0.28	0.143	0.225
Chlorobenzene	0.838	0.718	0.65	0	0.07	0.618	0.597
Acetophenone	1.014	0.818	1.00	0	0.49	0.275	0.236

Order retention of these molecules in this reversed-phased chromatographic system

$$T_R = T_m*(1+k)$$

System parameter

Solute parameter

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D. Solute Retention: k, $k = t_R'/t_M$ $\quad t_R' = k\, t_M$ $\quad t_R = (k+1)\, t_M$

E. Efficiency of Chromatography and Plate Theory: N and H

$$N = (t_R/\sigma_t)^2$$

F. Measures of Solute Separation: α, R_s

G. Fundamental factors affecting resolution:

$$R_s = \frac{t_{R2} - t_{R1}}{(W_{b2}+W_{b1})/2}$$

K. Evaluation of capacity factor k and chromatographic systems

$$\log k = c + mV_x + rR_2 + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H$$

System constants Solute descriptors

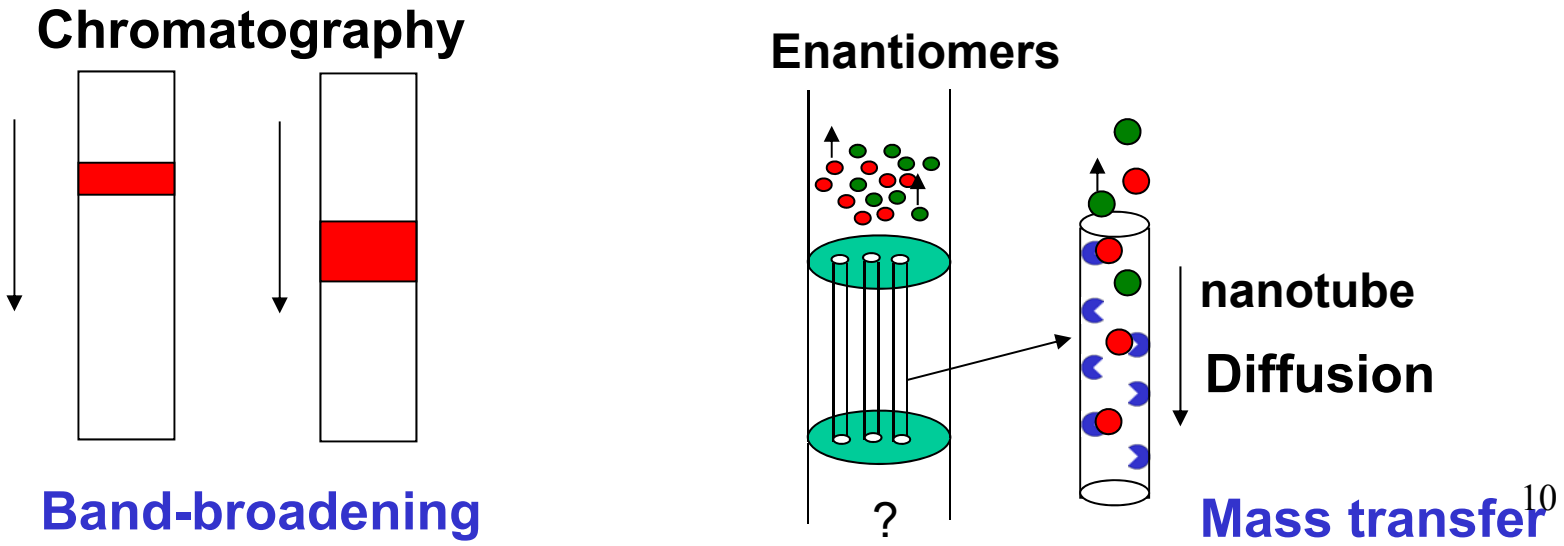
Diffusion and Fluid Flow

1. **Diffusion: Diffusion refers to the transport of substance against a concentration gradient.** $\Delta S>0$

   Mass transfer: movement of mass from one place to another

   Diffusion: movement of mass from region of high concentration to low concentration. $J = -D\frac{dN}{dz}$ **(Flux of mass, D: diffusion coefficient)**

2. **Diffusion is an important process in chromatography in determining the mass transfer and band-broadening**



Next Class:

What determines the diffusion coefficient?

What determines fluid flow?

Problem solving

Basic method for problem solving:

1. **Understanding the question.**
2. **Lay out the parameters regarding this question.**
3. **Try to use concepts and formulas to find the connections.**
4. **Solving the question.**

3. A chromatogram with ideal Gaussian bands, t_R = 9.0 and W_h = 2.0 min.

(a) How many theoretical plates are present?

(b) Find the plate height if the column is 10 cm long.

8. Two components, each with plate height H = 0.0025 cm, are observed to migrate to positions X = 10.1 cm and X =9.9 cm, respectively, along a uniform column. How long must the column to be achieve baseline resolution? (Hint: migration rate is constant for both components)