

Chem 654, Spring 2003
Problem Set

#5, 04/03/01

#5-1

Solutions to
Problem Set 5, due 04/14/01

1. Starting from

$$\frac{\mu_1 - \mu_1^0}{RT} = \ln(1 - \phi_2) + \left(1 - \frac{1}{x_n}\right)\phi_2 + \chi_1 \phi_2^2 \quad (1)$$

for a polydisperse polymer solution where the number average degree of polymerization is represented by x_n ,

A) show that

$$\phi_{2,c} = \frac{1}{1 + \sqrt{x_n}} \quad (2)$$

$$\chi_{1,c} = \frac{(1 + \sqrt{x_n})^2}{2x_n} \quad (3)$$

$$\psi_1\left(\frac{\Theta}{T_c} - 1\right) = \frac{1}{\sqrt{x_n}} + \frac{1}{2x_n} \quad (4)$$

where

$$(\mu_1 - \mu_1^0)^E = -RT\psi_1\left(1 - \frac{\Theta}{T}\right)\phi_2^2 \quad (5)$$

B) Plot $-\frac{\mu_1 - \mu_1^0}{RT}$ vs. ϕ_2 at $x_n=1000$ for $\chi_1 = 0.50, 0.53, 0.532, 0.54$, and 0.60 , and find $\phi_{2,c}$ and $\chi_{1,c}$.

2. The following light scattering data are given for monodisperse fractions of poly(styrene) in benzene ($n_D = 1.4977$) at 20°C with a He-Ne laser as the light source. Find the molar mass M , RMS radius of gyration R_g and second virial coefficient A_2 by constructing a Zimm plot.

c/mg/mL	$(K \cdot c / R_\theta) \cdot 10^6 / \text{mol} \cdot \text{g}^{-1}$					
	$\theta = 20^\circ$	40°	60°	80°	100°	120°
1.0	3.205	3.25	3.32	3.40	3.49	3.57
2.0	4.025	4.07	4.14	4.22	4.31	4.39
3.0	4.85	4.89	4.96	5.04	5.13	5.21
4.0	5.67	5.71	5.78	5.86	5.95	6.03

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3. For polydisperse systems, prove that the molar mass and mean square radius of gyration obtained from light scattering via

$$\frac{Kc}{R_\theta} = \frac{1}{M} \left\{ 1 + \frac{16}{3} \left(\frac{\pi}{\lambda'} \right)^2 \cdot R_g^2 \cdot \sin^2(\theta/2) + \cdots \right\} + 2A_2c + \cdots \quad (6)$$

represent a weight average and z-average quantity, respectively.

4. Calculate the diffusion coefficient and sedimentation coefficient of hemoglobin, a globular protein assuming it to be spherical in shape, in the limit of infinite dilution in water at 20°C. Its $M=6.45 \cdot 10^4$ g/mol, the partial specific volume \bar{v}_2 in water is 0.75 cm³/g, and the viscosity of water at 20°C is $1.005 \cdot 10^{-2}$ g/cm³·s, i.e., 1.005 centipoise.

$$D = \frac{kT}{6\pi\eta R_s} \quad (7)$$

$$S = \frac{MD(1 - \bar{v}_2\rho)}{RT} \quad (8)$$