Chem 654, Spring 2003
Problem Set
Solutions to
Problem Set 4. due 03/31/03

1. Show that for a monodisperse system of polymer solution

$$\Delta\mu_1 = \mu_1 - \mu_1^o = RT[\ln(1-\phi_2) + (1-\frac{1}{r})\phi_2 + \chi_1\phi_2^2] \quad (1)$$

from $$\Delta G^M = RT(n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1\phi_2\chi_1) \quad (2)$$

Note: $$\left(\frac{\partial \Delta G^M}{\partial n_1}\right)_{T,P,n_2} = \mu_1 - \mu_1^o \quad (3),$$

since $$\Delta G^M \equiv \sum_i n_i(\mu_i - \mu_i^o) \quad (4)$$

and $$\phi_1 = \frac{n_1}{n_1 + rn_2} \quad \text{and} \quad \phi_2 = \frac{rn_2}{n_1 + rn_2} \quad (5)$$

with r being the degree of polymerization of solute.

2. In the dilute solution limit where $\phi_2 << 1$, show that

$$\Delta\mu_1 = -RT[\frac{\phi_2}{r} + (\frac{1}{2} - \chi_1)\phi_2^2 + \cdots] \quad (6),$$

where $r \equiv \overline{V}_2^o / \overline{V}_1^o$ and $\rho = M/\overline{V}_2^o$ such that

$$\frac{\Pi}{c} = RT\{\frac{1}{M} + [(\frac{1}{2} - \chi_1)\frac{1}{\overline{V}_1^o \rho^2}]c \cdots\} \quad (7)$$

where the definition of osmotic pressure is

$$\Pi \equiv -\frac{\Delta\mu_1}{\overline{V}_1^o} = -\frac{RT\ln a_1}{\overline{V}_1^o} \quad (8)$$

and M, ρ, and c are the molar mass, density and solution mass concentration of the monodisperse polymer solute, and $\overline{V}_1^o$ and $\overline{V}_2^o$ are the molar volumes of solvent and solute in pure state, respectively.

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Comments:
It should also be noted that Equation (7) is frequently expressed as

$$\frac{\Pi}{c} = RT\{\frac{1}{M} + A_2c + A_3c^2 \cdots\} = \frac{RT}{M}\{1 + \Gamma_2 c + \Gamma_3 c^2 \cdots\} \qquad (9)$$

where A_2 and A_3 are called the second virial and third virial coefficient, respectively, and M, ρ, and c are the molecular weight, density and solution mass concentration of solute, and $\overline{V}_1^0$ is the molar volume of solvent in pure state. Also, it can be shown theoretically and empirically that $\Gamma_3 = (\Gamma_2/2)^2$ such that

$$(\frac{\Pi}{c})^{1/2} = (\frac{RT}{M})^{1/2} \cdot [1 + \frac{\Gamma_2}{2}c] \qquad (10).$$

which is often very useful when the osmotic pressure data are available for a finite concentration range such that the quadratic term in c needs to be included in either Equation (9) or (10).

3. a) Prove that the intercept of a plot of Π/c vs. c yields the number average molecular weight M_n for a polydisperse system.
b) Determine M_n and A_2 of 3 samples of poly(*p*-methylstyrene) in toluene at 30°C. The following data are given for the three samples.

sample						
1	**c(mg/mL)**	3.44	5.78	8.98	11.29	11.85
	Π(cm of sol'n)	0.156	0.416	1.049	1.761	1.990
2	**c(mg/mL)**	3.49	7.13	7.82	9.15	11.36
	Π(cm of sol'n)	0.284	0.935	1.064	1.453	2.247
3	**c(mg/mL)**	4.18	5.61	8.43	10.75	12.42
	Π(cm of sol'n)	0.741	1.105	2.042	3.107	3.898

Note that Π expressed in the column height of toluene solution h, can be converted to pressure by Π=ρgh where the solution density ρ can be equated to that of pure toluene, ρ(toluene) = 0.8563 g/mL since the solutions are all dilute enough , and g=9.8 m/s^2. Use Equation (10) instead of (9), for Π/c vs. c will be substantially curved for the range of concentration given so that it will not yield reliable intercepts.

1. $$\Delta\mu_1 = \left(\frac{\partial \Delta G_m}{\partial n_1}\right)_{T,P,n_2} = RT\left[\frac{\partial}{\partial n_1}\left(n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1\phi_2\chi_1\right)\right]_{T,P,n_2}$$

$$\frac{\partial}{\partial n_1}(n_1\ln\phi_1) = \ln\phi_1 + \frac{n_1}{\phi_1}\frac{\partial\phi_1}{\partial n_1} = \ln\phi_1 + \frac{n_1}{\phi_1}\frac{\partial}{\partial n_1}\left(\frac{n_1}{n_1+xn_2}\right)$$

$$= \ln\phi_1 + \frac{n_1}{\phi_1}\left[\frac{(n_1+xn_2)-n_1}{(n_1+xn_2)^2}\right]$$

$$= \ln\phi_1 + \frac{n_1}{\phi_1}\left(\frac{xn_2}{n_1+xn_2}\cdot\frac{1}{n_1+xn_2}\right)$$

$$= \ln\phi_1 + \frac{n_1}{\phi_1}\cdot\phi_2\cdot\frac{\phi_1}{n_1} = \ln\phi_1 + \phi_2$$

$$\frac{\partial}{\partial n_1}(n\ln\phi_2) = \frac{n_2}{\phi_2}\frac{\partial\phi_2}{\partial n_1} = n_2\cdot\left(\frac{n_1+xn_2}{xn_2}\right)\cdot\frac{-xn_2}{(n_1+xn_2)^2}$$

$$= -\frac{n_2}{n_1+xn_2} = -\frac{\phi_2}{x}$$

$$\frac{\partial}{\partial n_1}(n_1\phi_2\chi_1) = \chi_1\left(\phi_2 + n_1\frac{\partial\phi_2}{\partial n_1}\right) = \chi_1\left[\phi_2 + n_1\frac{-xn_2}{(n_1+xn_2)^2}\right]$$

$$= \chi_1(\phi_2 - \phi_1\phi_2) = \chi_1\phi_2(1-\phi_1) = \chi_1\phi_2^2$$

$$\therefore \Delta\mu_1 = RT\left[\ln\phi_1 + \phi_2 - \frac{\phi_2}{x} + \chi_1\phi_2^2\right]$$

$$= RT\Big[\underbrace{\ln(1-\phi_2) + \left(1-\tfrac{1}{x}\right)\phi_2}_{\text{comes from } \Delta S_m} + \underbrace{\chi_1\phi_2^2}_{\text{from } \Delta H_m}\Big]$$

$$\approx RT\left(\ln(1-\phi_2) + \phi_2 + \chi_1\phi_2^2\right)$$

↑ if $x >> 1$