NAME ____

1. (35 pts total) Polyvinyl chloride (PVC) and methyl ethyl ketone (MEK) are combined at 25 °C, where the Flory-Huggins interaction parameter χ is equal to 0.40.

0.11 g of PVC of molecular weight ~~50~~ 45,000 g/mol are combined with 0.90 cm^3 of MEK. The densities of PVC and MEK are 1.39 g/cm^3 and 0.805 g/cm^3, respectively. The molecular weight of MEK is 72.1 g/mol; the monomer molecular weight of PVC is 62.5 g/mole.

a) (8 pts) Assume the lattice site size is equal to the volume occupied by a molecule of MEK. How many lattice sites does each PVC molecule occupy?

Vol. occupied by an MEK molecule $= V_{MEK} = \dfrac{M}{\rho N_{AV}} = \dfrac{72.1 \frac{g}{mol}}{\left(0.805 \frac{g}{cm^3}\right)\left(6.02\times10^{23} \frac{molecules}{mol}\right)} = 1.49\times10^{-22} \frac{cm^3}{molecule}$

$$V_{PVC} = \frac{M}{\rho N_{AV}} = \frac{45{,}000 \frac{g}{mol}}{\left(1.39 \frac{g}{cm^3}\right)\left(6.02\times10^{23} \frac{molecules}{mol}\right)} = 5.38\times10^{-20} \frac{cm^3}{mol.}$$

$$N_{PVC} = \frac{V_{PVC}}{V_{MEK}} = \frac{5.38\times10^{-20}}{1.49\times10^{-22}} = 361$$

← Each PVC molecule occupies 361 sites

b) (8 pts) What is the total number of lattice sites for this system?

Total # of lattice sites is $m = N_{AV}\left(n_{MEK} + n_{PVC} N_{PVC}\right)$

moles

$$n_{MEK} = n_1 = \frac{\rho_{MEK}(0.90\ cm^3)}{M_{MEK}} = \frac{(0.805\ g/cm^3)(0.90\ cm^3)}{72.1\ g/mole} = 1.005\times10^{-2}\ moles$$

$$n_{PVC} = n_2 = \frac{0.11\ g}{M_{PVC}} = \frac{0.11\ g}{45{,}000\ g/mole} = 2.44\times10^{-6}\ moles$$

$$m = \left(6.02\times10^{23} \frac{molecules}{mole}\right)\left(1.005\times10^{-2} + (2.44\times10^{-6})(361)\ moles\right)$$

$$\underline{m = 6.581\times10^{21}\ sites}$$

NAME ____

c) (8 pts) Show by means of an appropriate calculation whether or not the PVC will dissolve in MEK to form a solution at this temperature.

PVC will dissolve in MEK if $\Delta G_m < 0$

use Flory-Huggins theory:

For system:

$$\Delta G_m = RT\left[n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_1 \phi_2 \chi \right]$$

or

$$\Delta G_m = mkT\left[\phi_1 \ln\phi_1 + \frac{\phi_2}{N} \ln\phi_2 + \phi_1\phi_2\chi \right]$$

Volume of MEK $= 0.90\ cm^3$

Volume of PVC $= \dfrac{0.11\ g}{1.39\ g/cm^3} = 7.91 \times 10^{-2}$

$$\phi_1 = \phi_{MEK} = \frac{0.90\ cm^3}{0.90 + 7.91\times 10^{-2}\ cm^3} = \frac{0.90}{0.9791} = 0.919$$

$$\phi_2 = \phi_{PVC} = 0.081$$

$$\Delta G_m = \left(8.314\ \tfrac{J}{K\cdot mol}\right)(298\ K)\Big[\underbrace{(1.005\times10^{-2}\ mol)\ln(0.919)}_{-8.489\times10^{-4}} + \underbrace{(2.44\times10^{-6}\ mol)\ln(0.081)}_{-6.132\times10^{-6}}$$
$$+ \underbrace{(1.005\times10^{-2}\ mol)(0.081)(0.40)}_{3.256\times10^{-4}}\Big]$$

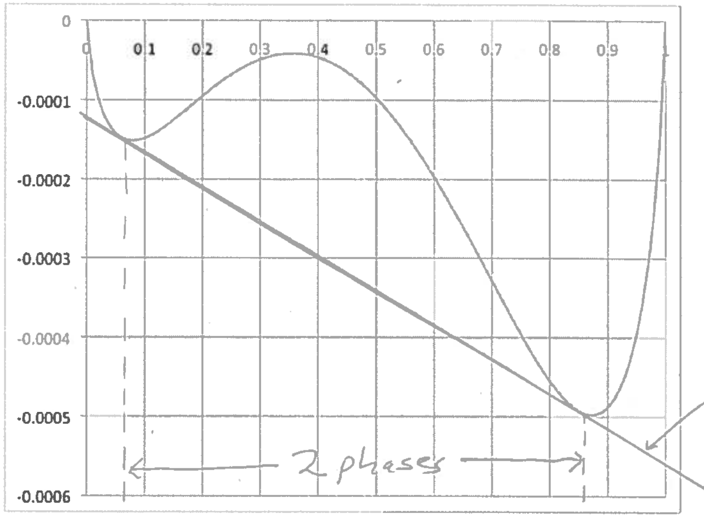
$= \underline{-1.312\ J}$ $\Rightarrow$ Mixing!

(or

$$= (6.581\times10^{21})(1.381\times10^{-23}\ \tfrac{J}{K})(298\ K)\left[(0.919)\ln(0.919) + \frac{0.081}{361}\ln(0.081) + (0.919)(0.081)(0.40)\right]$$

$= \underline{-1.311\ J}$ ✓

d) (4 pts) A sketch of $\Delta G_m/kT$ (on vertical axis) vs ϕ_2 (horizontal axis) for a slightly different system is shown below. On the sketch, show by means of an appropriate construction, the region or regions, if any, where two phases can coexist. *Label the region clearly.*

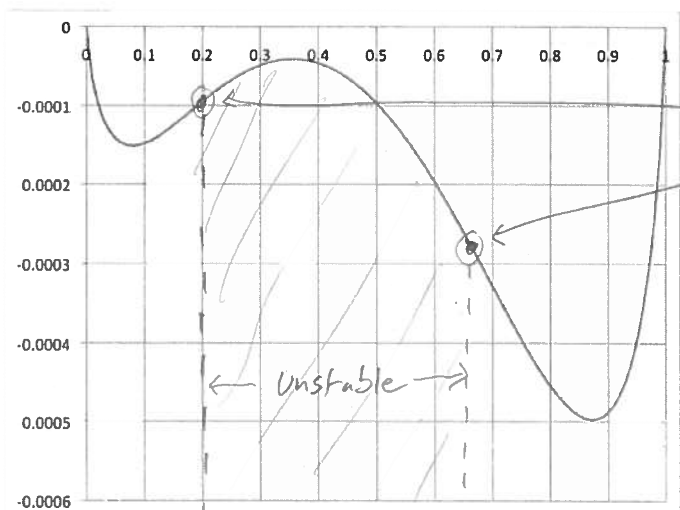


Common tangent

ϕ_{2b}' ϕ_{2b}''

binodal compositions

e) (7 pts) On the sketch below (reproduced from part d), show the region(s) of the diagram, if any, where the mixture will spontaneously phase separate. Indicate the region(s) clearly by shading them.



inflection points

ϕ_{2s}' & ϕ_{2s}'' are spinodal compositions

ϕ_{2s}' ϕ_{2s}''

f) Calculate the second virial coefficient for this system at 25 °C. *Include units!*

$$B = \left(\tfrac{1}{2} - \chi\right) \bar{V}_1 \frac{N^2}{M^2}$$ from Flory-Huggins Theory

$$\bar{V}_1 = \frac{72.1\ g/mol}{0.805\ g/cm^3} = 89.57\ \frac{cm^3}{mol} \Rightarrow B = \left(\tfrac{1}{2} - 0.40\right)\left(89.57\ \frac{cm^3}{mol}\right)\frac{(361)^2}{\left(45{,}000\ \frac{g}{mol}\right)^2}$$

$B = 5.764 \times 10^{-4}\ mol \cdot cm^3 \ldots$

g) If χ has the following dependence on temperature, at what temperature will you have a system in which no phase separation can occur? (In other words, at what temperature will the system be one phase for all compositions?) Your answer may contain the constants α and β.

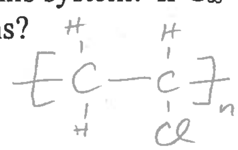
$$\chi = \frac{\alpha}{T} + \beta$$

Since the entropic contributions to ΔG_m are always negative, no phase separation will occur as long as

$\chi = 0 \rightarrow \frac{\alpha}{T} + \beta = 0 \Rightarrow \boxed{T = -\frac{\alpha}{\beta}}$

h) At T= 35 °C, χ = 0.50 for this system. If C_∞ = 6.9, what is the radius of gyration of the polymer under these conditions?

polyvinyl chloride



Now N = degree of polymeriz $= \frac{M}{M_0} = \frac{45000 \text{ g/mol}}{62.5 \text{ g/mol}} = \underline{720}$

n = # of bonds $= 2N = 1440$

$l = 0.154$ nm

$\langle h^2 \rangle_0 = C_\infty n l^2 = (6.9)(1440)(0.154 \text{ nm})^2 = 235.6 \text{ nm}^2$

$R_g = \left(\frac{\langle h^2 \rangle_0}{6}\right)^{1/2} = \left(\frac{235.6 \text{ nm}^2}{6}\right)^{1/2} = \underline{6.27 \text{ nm}}$

i) At the initial conditions given in part a (that is, T=25 °C), would you expect the polymer coil to be larger or smaller than your value in part h? Briefly explain.

At $T = 25°C$, $\chi < \frac{1}{2}$, so it is a good (or at least better than theta) solvent, so the coil would be expanded or larger than the value in h.

2\. a) at $T = 30\,°C$,

$$\frac{\Pi}{RTc} \times 10^5 = 0.7000\,(c \times 100) + 1.53846$$

$$\frac{\Pi}{RTc} = 0.7000\,c\left(\frac{100}{10^5}\right) + 1.53846 \times 10^{-5}$$

$$\frac{\Pi}{RTc} = (0.700 \times 10^{-3})\,c + 1.53846 \times 10^{-5} = Bc + \frac{1}{M_n}$$

$$\Rightarrow \boxed{B = 7.00 \times 10^{-4}\ \frac{mol \cdot cm^3}{g^2}}$$

b) M_n can be obtained from $\frac{1}{\text{intercept}}$

take average of 3 intercepts for best value

$$\text{Avg of intercepts} = \frac{1.53846 + 1.56250 + 1.55039}{3} \times 10^{-5}$$

$$= 1.55045 \times 10^{-5}$$

$$\Rightarrow \boxed{M_n = 64{,}497\ \frac{g}{mole}}$$ number-average molecular weight

c) Sample B at 30 °C

Assuming (as in Flory-Huggins theory) that B is independent of molecular weight, we know $B = 7.00 \times 10^{-4}\ \frac{mol \cdot cm^3}{g^2}$ from above.

Also assuming higher order terms in virial expansion are negligible;

So

$$\frac{\Pi}{RTc} = \frac{1}{M_n} + Bc$$

$c = 0.008 \frac{g}{cm^3}$ $\Pi = 0.003254$ atm $T = 30 + 273 = 303$ K

substituting:

$$\frac{0.003254 \text{ atm}}{\left(82.1 \frac{cm^3 \text{ atm}}{K \cdot mol}\right)(303 K)\left(0.008 \frac{g}{cm^3}\right)} = \frac{1}{M_n} + \left(7.00 \times 10^{-4} \frac{mol \cdot cm^3}{g^2}\right)\left(0.008 \frac{g}{cm^3}\right)$$

$$1.6351 \times 10^{-5} \frac{mol}{g} = \frac{1}{M_n} + 5.60 \times 10^{-6} \frac{mol}{g}$$

$$\boxed{M_n = 93{,}020 \frac{g}{mol}}$$

d) (check M_w:

Intercept $= 10.75 \times 10^{-6}$

$M_w = 93{,}020$ g/mole (sample is monodisperse!))

since $M_w/M_n = 1.00 \Rightarrow$ Living (anionic) Polymeriz.

e) Radius of gyration is obtained from Zimm plot extrapolation to $c \to 0$

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w}\left(1 + \frac{q^2}{3} R_g^2 + \ldots\right) + 2B\overset{0}{c}$$

$$= \frac{1}{M_w}\left(1 + \frac{1}{3}\frac{16\pi^2 n^2}{\lambda_0^2} R_g^2 \sin^2\left(\frac{\theta}{2}\right)\right)$$

$$= \frac{1}{M_w} + \underbrace{\frac{1}{3}\frac{16\pi^2 n^2}{\lambda_0^2}\frac{1}{M_w} R_g^2}_{\text{slope}} \sin^2\left(\frac{\theta}{2}\right)$$

$$\frac{1}{3}\frac{16\pi^2 n^2}{\lambda_0^2}\frac{1}{M_w} R_g^2 = 0.6075 \times 10^{-6}$$

$R_g^2 = 126.8$ nm^2 $\underline{R_g = 11.26 \text{ nm}}$

f) yes! at $T = 20\ ^\circ C$, LS data shows slope of $\theta \to 0$ line is identically zero. $\Rightarrow B' = 0$, $\chi = \frac{1}{2}$ so $T = 20\ ^\circ C$ is the theta temperature for PEO in this solvent.

g) Since we are at the theta temperature, the coils will have unperturbed dimensions.

Therefore

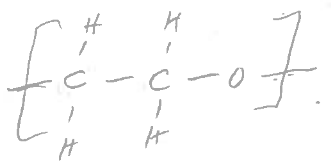
$$\langle h^2 \rangle_0 = C_\infty n l^2 = N b^2$$

$$\text{\&} \quad R_g = \left(\frac{\langle h^2 \rangle_0}{6} \right)^{1/2}$$

$$6 R_g^2 = C_\infty n l^2$$

$$C_\infty = \frac{6 R_g^2}{n l^2}$$

For PEO:



$$l_{eff} = \frac{2(\text{C-O bonds}) + 1(\text{C-C bond})}{3} = \frac{2(0.143\ \text{nm}) + 1(0.154\ \text{nm})}{3}$$

$$l_{eff} = 0.1467\ \text{nm}$$

$$n = 3N = \frac{3M}{M_0} = \frac{3(93{,}020\ \text{g/mole})}{44.05\ \text{g/mole}} = 6335$$

$$C_\infty = \frac{6(11.26\ \text{nm})^2}{(6335)(0.1467\ \text{nm})^2} = \boxed{5.58}$$