

## Chapter 4

# Polymer Solutions

### 4.1 Introduction

There are many reasons for studying polymer solutions. One obvious reason is to understand the nature of those solutions. A practical reason is that polymer solutions are often used when measuring molecular weight. Some common molecular weight determination methods are osmotic pressure measurements, solution viscosity, solution light scattering, and gel-phase chromatography. Each of these methods uses a polymer solution. Before discussing these or other polymer characterization techniques, we therefore will spend some time discussing the thermodynamics of polymer solutions.

### 4.2 Solution Thermodynamics

Solutions are often characterized in terms of Gibbs free energy —  $G$ .  $G$  can be viewed as a multivariable function that depends on temperature ( $T$ ), pressure ( $P$ ), and the number of moles of each component ( $n_i$  for  $i = 1$  to number of components). By multivariable math analysis, the differential in free energy following a change in any or all of the key variables is:

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j \neq n_i} dn_i \quad (4.1)$$

The subscripts on the partial derivatives mean that those variables are held constant while taking the derivative. We will be using lower case  $n$  to mean moles of some component and upper case  $N$  to mean molecules. The number of molecules  $N$  is always equal to  $nL$  where  $L$  is Avagadro's number.

We know some of the terms in the  $dG$  expression from conventional thermodynamics. Consider a solution with constant composition (*i.e.*,  $dn_i = 0$  for all  $i$ ). The total free energy is

$$G = H - TS \quad (4.2)$$

The differential in free energy follows the well known relation

$$dG = VdP - SdT \quad (4.3)$$

Comparing this expression to the solution results above gives

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_i} = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_{P,n_i} = -S \quad (4.4)$$

We do not have a similar result for  $\partial G/\partial n_i$ . Instead  $\partial G/\partial n_i$  is given a name; it is called the chemical potential and denoted by  $\mu_i$  or  $G_i$ . Specifically:

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} = \mu_i = G_i \quad (4.5)$$

Using these new results, the differential in  $G$  for a solution becomes

$$dG = VdP - SdT + \sum_i \mu_i dn_i \quad (4.6)$$

Next we consider the change in free energy upon mixing two components ( $A$  and  $B$ ) at constant temperature and pressure ( $dP = dT = 0$ ). Only the chemical potential terms cause a change in  $G$ . The differential form reduces to

$$dG = \mu_A dn_A + \mu_B dn_B \quad (4.7)$$

Integrating  $dG$  from 0 to  $n_A$  and from 0 to  $n_B$  which corresponds to the mixing process gives

$$G = \mu_A n_A + \mu_B n_B \quad (4.8)$$

If instead of mixing  $A$  and  $B$  we consider pure components  $A$  and  $B$ , the expression for  $G$  will be the same except that the chemical potentials will be different. If we denote the chemical potential of pure components with a superscript “ $\circ$ ”, the free energy of the separated pure components is

$$G^\circ = \mu_A^\circ n_A + \mu_B^\circ n_B \quad (4.9)$$

Comparing the solution  $G$  and the pure component  $G^\circ$ , we find the change in free energy on mixing or  $\Delta G_{mix}$  to be:

$$\Delta G_{mix} = n_A (\mu_A - \mu_A^\circ) + n_B (\mu_B - \mu_B^\circ) = n_A (G_A - G_A^\circ) + n_B (G_B - G_B^\circ) \quad (4.10)$$

To understand solutions we need to evaluate terms like  $(\mu_A - \mu_A^\circ)$ . As expressed, chemical potential is somewhat awkward for practical use. We thus redefine it in terms of activity. Activity at first appears no better than chemical potential, but we will soon show that it has useful interpretations under important special cases. We thus write chemical potential as

$$\mu_A = \mu_A^\bullet + RT \ln a_A \quad (4.11)$$

where  $a_A$  is the relative activity of component  $A$  and  $\mu_A^\bullet$  is the chemical potential in an arbitrarily chosen reference state. In terms of chemical potential, the activity is

$$a_A = \exp\left(\frac{\mu_A - \mu_A^\bullet}{RT}\right) \quad (4.12)$$

We next apply the definition of activity to the analysis of a solution in equilibrium with its vapor. At equilibrium the chemical potential of component  $A$  in the vapor is equal to its chemical potential in the solution. We assume the vapor is an ideal gas and use the above result that  $\partial G/\partial P = V$  to get

$$\frac{\partial \mu_A^{vap}}{\partial P} = \frac{\partial G_A^{vap}}{\partial P} = \frac{\partial}{\partial P} \frac{\partial G^{vap}}{\partial n_A} = \frac{\partial}{\partial n_A} \frac{\partial G^{vap}}{\partial P} = \frac{\partial V}{\partial n_A} = V_A \quad (4.13)$$

where  $V_A$  is the partial molar volume of component  $A$ . In an ideal vapor of  $A$ ,  $V = n_A RT/P_A$  where  $P_A$  is the partial pressure due to component  $A$ . Differentiating with respect to  $n_A$  to get  $V_A$  gives

$$\frac{\partial \mu_A^{vap}}{\partial P_A} = \frac{RT}{P_A} \quad \text{or} \quad d\mu_A^{vap} = RT \frac{dP_A}{P_A} \quad (4.14)$$

Integrating we get

$$\mu_A^{vap} = RT \ln P_A + \text{const} \quad (4.15)$$

The integration constant is found by using the reference state where  $\mu_A = \mu_A^\bullet$ . Finding the constant results in

$$\mu_A^{vap} = \mu_A^\bullet + RT \ln \frac{P_A}{P_A^\bullet} \quad (4.16)$$

where  $P_A^\bullet$  is the partial pressure of component  $A$  in the reference state.

We turn next to the chemical potential in the liquid. Because the liquid is in equilibrium with the vapor, the chemical potential of component  $A$  in the liquid must be equal to its chemical potential in the vapor. Thus

$$\mu_A^l = \mu_A^{vap} = \mu_A^\bullet + RT \ln \frac{P_A}{P_A^\bullet} \quad (4.17)$$

A good reference state for liquids is the chemical potential of the pure liquid. Defining  $\mu_A^\circ$  as the chemical potential of the pure liquid we have

$$\mu_A^\circ = \mu_A^\bullet + RT \ln \frac{P_A^\circ}{P_A^\bullet} \quad (4.18)$$

Solving for  $\mu_A^\bullet$  and substituting into the expression for  $\mu_A^l$  gives

$$\mu_A^l = \mu_A^{vap} = \mu_A^\circ + RT \ln \frac{P_A}{P_A^\circ} \quad (4.19)$$

In general,  $P_A < P_A^\circ$  which implies  $\mu_A^l < \mu_A^\circ$ . Physically, this observation means that compounds are less *active* in solution than they are in pure form. In the above analysis we have assumed the vapor is an ideal vapor. In effect, we have proposed a physical model for the liquid/vapor

equilibrium. In this model, the activity is no longer an abstract property; it is defined in terms of physical quantities. The activity of any component is the ratio of its partial pressure to the partial pressure that exists over a pure liquid of that component. Thus, the activity of component  $A$  is  $P_A/P_A^\circ$ .

We can extend our model by introducing an assumption about the solution properties. Let's say that the solution (as well as the vapor) is ideal in that it obeys Raoult's law which states that  $P_A = X_A P_A^\circ$  where  $X_A$  is the mole fraction of component  $A$  in the solution. With this new assumption, the activity coefficient of component  $A$  is  $X_A$  and its chemical potential is

$$\mu_A = \mu_A^\circ + RT \ln X_A \quad (4.20)$$

In examining the free energy of mixing, we noted that we need terms like  $(\mu_A - \mu_A^\circ)$ . For an ideal solution and an ideal vapor

$$\mu_A - \mu_A^\circ = RT \ln X_A \quad (4.21)$$

Our previous result for free energy of mixing becomes

$$\Delta G_{mix} = RT (n_A \ln X_A + n_B \ln X_B) \quad (4.22)$$

This free energy of mixing can be split up into an entropy part and an enthalpy part with

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \quad (4.23)$$

We begin with entropy of mixing. A fundamental relation of thermodynamics is  $\partial G / \partial T = -S$ . Applying this relation to chemical potentials by taking the temperature derivative of  $\mu_A$  gives

$$S_A = -\frac{\partial \mu_A}{\partial T} = S_A^\circ - R \ln X_A \quad (4.24)$$

Following the free energy of mixing analysis, the entropy of mixing is

$$\Delta S_{mix} = n_A(S_A - S_A^\circ) + n_B(S_B - S_B^\circ) = -R(n_A \ln X_A + n_B \ln X_B) \quad (4.25)$$

Finally, the enthalpy of mixing is

$$\Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} = 0 \quad (4.26)$$

$\Delta H_{mix}$  for an ideal solution is zero.  $\Delta H_{mix}$  is zero because the assumption of an ideal solution implies no interactions between the components of the solution.

We next examine the sign of  $\Delta G_{mix}$ . Both  $n_A$  and  $n_B$ , the numbers of moles, must be positive. Both  $X_A$  and  $X_B$ , the mole fractions, must be between 0 and 1, which means that both  $\ln X_A$  and  $\ln X_B$  must be negative. These facts mean that  $\Delta G_{mix}$  is always negative and  $\Delta S_{mix}$  is always positive. In other words all two component ideal solutions are miscible in all proportions. The driving force for this miscibility is the increase in entropy of mixed components *vs.* pure separated

A	A	B	A	B	B	A	A
A	B	A	A	A	A	B	A
B	A	A	B	B	A	A	A
A	B	B	A	A	B	A	B
A	A	A	B	B	A	B	A
A	B	B	A	A	A	B	A
A	B	A	A	A	B	A	A

Figure 4.1: A simple lattice model for a solution of  $A$  and  $B$ .

components. The fact that not all materials are soluble in all other materials means that many solutions deviate from ideality. Deviations from ideality often mean that enthalpy is important and not zero. To make two components immiscible,  $\Delta G_{mix}$  must be positive which implies that  $\Delta H_{mix} \neq 0$  and further that  $\Delta H_{mix}$  is sufficiently positive that it overwhelms the entropy or that  $\Delta H_{mix} > T\Delta S_{mix}$ .

### 4.3 Physical Origins of Entropy of Mixing

The physical origins of the entropy of mixing can be modeled using a simple lattice model for the structure of a solution. Say the simple lattice model in Fig. 4.1 represents a solution of  $A$  and  $B$ . By statistical thermodynamics, entropy  $S$  is

$$S = k \ln W \quad (4.27)$$

where  $W$  is the number of possible configurations of  $A$  and  $B$  solution. In the simple lattice, it is easy to count the number of ways of putting  $N_A$   $A$  units and  $N_B$   $B$  units into  $N_A + N_B$  lattice sites. The result from combinatorial analysis is

$$W = \binom{N_A + N_B}{N_A} = \frac{(N_A + N_B)!}{N_A! N_B!} \quad (4.28)$$

(Note we now use upper case  $N$ 's because they refer to individual molecules of component  $A$  and  $B$ ).

For large  $N_A$  and  $N_B$  (*i.e.*, for many molecules) we can apply Stirling's approximation for factorials ( $\ln n! \approx n \ln n$ ) to get

$$W = N_A [\ln(N_A + N_B) - \ln N_A] + N_B [\ln(N_A + N_B) - \ln N_B] \quad (4.29)$$

A	A	B	A	A	A	A	A
A	A	B	A	A	A	A	A
A	A	B	B	B	A	B	A
A	A	A	A	B	A	B	A
A	B	B	B	B	A	B	A
A	B	A	A	A	A	B	A
A	B	B	B	B	B	B	A

Figure 4.2: Polymer molecule  $B$  in a lattice model for a solution in solvent  $A$ .

We can even replace the  $\approx$  by a straight equal sign because  $N_A$  and  $N_B$  will be so large that Stirling's approximation is effectively exact. By definition of mole fraction  $X_A = N_A/(N_A + N_B)$  and  $X_B = N_B/(N_A + N_B)$ . Introducing Avagadro's number,  $L$ , and realizing that  $R = Lk$ ,  $N_A = Ln_A$ , and  $N_B = Ln_B$ , we quickly derive

$$\Delta S_{mix} = -R(n_A \ln X_A + n_B \ln X_B) \quad (4.30)$$

This result agrees exactly with the activity analysis for entropy of mixing. Thus the lattice model recovers all details of the thermodynamics analysis. A lattice can be viewed as a good physical picture of an ideal solution.

We find some interesting results when we apply the lattice model to a polymer solution. The *physics* of mixing is unchanged, but now we must consider the case where one molecule is much larger than the other molecule. Figure 4.2 shows a lattice model for one polymer (component  $B$ ) in solvent  $A$ . It is clear that the number of ways of introducing the polymer molecule into solvent  $A$  will be much less than the number of ways of introducing the same amount of monomer molecules  $B$  into the same solvent. To count the polymer lattice configurations we could go back to the lattice model for a solution of  $A$  and  $B$  and examine all of the  $W$  configurations. For that large set of configurations we must now reject all configurations that do not have connected  $B$  molecules. The remaining configurations, which will be much less than  $W$ , will be the number of configurations of polymer  $B$  in solvent  $A$ . The conclusion is that the entropy of polymer solutions is much less than the corresponding entropy for monomer solutions of the same weight fractions  $A$  and  $B$ .

Compared to the monomer solution problem (Fig. 4.1), it is a much harder task to count the number of configurations in which all  $B$  units are connected into chains of length  $x$  with excluded volume on a lattice with solvent  $A$ . An approximate calculation gives the following result for the

entropy of mixing:

$$\Delta S_{mix} = -R(n_A \ln v_A + n_B \ln v_B) \quad (4.31)$$

where  $v_A$  and  $v_B$  are volume fractions of solvent (component  $A$ ) and polymer (component  $B$ ):

$$v_A = \frac{N_A}{N_A + xN_B} \quad \text{and} \quad v_B = \frac{xN_B}{N_A + xN_B} \quad (4.32)$$

Consider two solutions of equal weight fractions of component  $A$  and  $B$  — monomer  $B$  molecules in solvent  $A$  and a polymer of connected  $B$  monomers in solvent  $A$ . The mole fractions of  $A$  and  $B$  in the monomer solution are identical to the volume fractions of  $A$  and  $B$  in the polymer solution. Likewise,  $n_A$  will be the same for both solution. The  $\Delta S_{mix}$  expression differs only in the value for  $n_B$ . Because the polymer solution connects many  $B$  monomers into a single polymer,  $n_B$  in the polymer solution will be hundreds or thousands of times lower than  $n_B$  in the monomer solution. Furthermore, in dilute solutions, the  $n_B \ln X_B$  and  $n_B \ln v_B$  terms are the dominant entropy terms. We thus conclude that the entropy of mixing for polymer solutions will be hundreds or thousands of times lower than the entropy of mixing for monomer solutions.

One thing that monomer solutions and polymer solutions have in common is that they both obey conventional thermodynamics. We do not need to derive new methods for understanding polymer solutions. A major difference, however, is that polymer solutions are much more likely to deviate from ideal behavior at comparable concentrations (in weight fraction solute). The deviations from ideality are direct consequence of the size of polymer molecules. The large size reduces the entropy of mixing which reduces the term  $T\Delta S_{mix}$ . When the entropy of mixing term is small, it is much easier for the  $\Delta H_{mix}$  term to assume a greater role. It also easy for  $\Delta H_{mix}$  to be greater than  $T\Delta S_{mix}$  and therefore for polymers to be insoluble in many solvents.

## 4.4 Flory-Huggins Theory

We introduce a simple model for dealing with polymer solutions called the Flory-Huggins theory. In brief, the theory attempts to estimate  $\Delta H_{mix}$  using the lattice theory for solutions. We consider nearest neighbor interaction between  $A$  and  $B$  molecules. Then

$$\Delta H_{mix} = kT\chi N_A v_B = RT\chi n_A v_B \quad (4.33)$$

where  $N_A$  is the number of molecules of component  $A$ ,  $n_A$  is the number of moles of component  $A$ ,  $v_B$  is the volume fraction of polymer, and  $\chi$  is the Flory interaction parameter. The interaction parameter describes the level of interaction between pairs of  $A$  and  $B$ . A high positive  $\chi$  indicates a repulsive interaction and causes a positive  $\Delta H_{mix}$  which tends to inhibit the solution process. A negative  $\chi$  indicates an attractive interaction and causes a negative  $\Delta H_{mix}$  which guarantees dissolution.

The free energy of mixing in the Flory-Huggins theory is

$$\Delta G_{mix} = RT (n_A \ln v_A + n_B \ln v_B + \chi n_A v_B) \quad (4.34)$$

Unfortunately, the Flory-Huggins theory is not very good. In practice solution property data cannot be predicted by using a single value of the interaction parameter. The theory is particularly bad for dilute solutions. Reasons for these problems will be discussed later. Despite its shortcomings, the Flory-Huggins theory has some applications for physical understanding of solution properties. We will make qualitative use of this theory when discussing osmotic pressure experiments.

## Problems

- 4-1. Compare the entropy of mixing for two solutions. The first is a solution 1% by weight of monomer B in solvent A (assume the molecular weights of A and B are the same). The second is a polymer of monomer B in a 1% by weight solution in solvent A where the polymer has a degree of polymerization of 100,000.
- 4-2. Explain the physical origin of each term in the Flory-Huggins expression for free-energy of mixing in polymer solutions.
- 4-3.
  - a. Explain why two components that form an ideal solution are miscible in all proportions.
  - b. When two components form a nonideal solution, it is common to observe that the solute will precipitate out at low temperature and only be soluble in the solvent at elevated temperatures. Explain why increasing the temperature often makes it more likely for one component to dissolve in another component even when the resulting solution is nonideal.