Polymer Solubility and Thermodynamics of Mixing

Polymer Solubility

Dissolution process

Stages of Dissolution:
1) _______________________________
2) _______________________________
3) _______________________________
\[ \Delta G = \Delta H - T \Delta S \]

- \( \Delta G < 0 \) : 
- In the case of gas, 
- In the case of solution,
  \[ \Delta H < 0 : \]
  \[ \Delta H > 0 : \]

How do we predict solubility?

attraction between surrounding molecules

Cohesive Energy Density (CED) =
Solubility Parameter (\( \delta \)) =

Hildebrand expression
\[ \Delta H = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \bar{V}_{mol} \]

volume fraction

How do we get the value of \( \delta \)?
Determination of $\delta$ of polymer

1. Swelling test
   (for crosslinked polymers)

2. Intrinsic viscosity, $[\eta]$
   (for linear or branch polymers)

   $[\eta] \propto \text{size of molecules}$

3. Small's method

   $$\delta = \frac{\Sigma G}{V_{\text{mol}}}$$

   \begin{tabular}{|c|c|}
   \hline
   Group & G \\
   \hline
   - CH$_3$ & 214 \\
   - CH$_2$ & 133 \\
   - CH & 28 \\
   \hline
   \end{tabular}

   Ex) Obtain $\delta$ for polyethylene.
   PE: -[CH$_2$-CH$_2$]-

See Table 2.5 in Sperling (Coursepack)
Thermodynamics of Mixing

- Statistical thermodynamics of mixture

**Boltzmann’s relation**

\[ S = k \ln \Omega \]

# of arrangement

[Lattice model]

**Assumptions**

- The components are placed in “lattice”.
- Volume is unchanged during mixing (incompressible).

[Lattice model]

\[ \Omega_1 = 1 \quad \Omega_2 = 1 \]
\[ N_1 \quad N_2 \]
\[ S_1 = 0 \quad S_2 = 0 \]

\[ \Omega_M = \frac{(N_1 + N_2)!}{N_1! N_2!} \]

\[ \Delta S_M = \]
Stirling’s approximation
\[ \ln N! = N \ln N - N \] (for large \( N \))

\[
\Delta S_m = k \left\{ \ln (N_1+N_2)! - \ln N_1! - \ln N_2! \right\}
= -k \left[ N_1 \ln N_1 - \ln (N_1+N_2) + N_2 \ln N_2 - \ln (N_1+N_2) \right]
= -k \left[ N_1 \ln \left\{ \frac{N_1}{N_1+N_2} \right\} + \ln \left\{ \frac{N_2}{N_1+N_2} \right\} \right]
\]

\[ \Delta S_m = -k \left( N_1 \ln n_1 + N_2 \ln n_2 \right) \]

small molecule/polymer (polymer solution)

\[ N_1 \times \cdot N_2 = N_1 + xN_2 \]
\[ \Omega_1 = 1 \]
\[ \Omega_2 \neq 1 \]
\[ \Omega_M \]
\[ \Delta S_M = -k \left( N_1 \ln v_1 + N_2 \ln v_2 \right) \]

where

\[
\begin{align*}
  v_1 &= \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \\
  v_2 &= \frac{N_2 V_2}{N_1 V_1 + N_2 V_2}
\end{align*}
\]

\[
\begin{align*}
  \frac{N_1}{N_1 + xN_2} &\quad \rightarrow \quad \frac{xN_2}{N_1 + xN_2} \\
  \frac{x_1N_1}{x_1N_1 + x_2N_2} &\quad \rightarrow \quad \frac{x_2N_2}{x_1N_1 + x_2N_2}
\end{align*}
\]

\[ v_1: \text{volume fraction of solvent} \]
\[ v_2: \text{volume fraction of polymer} \]
\[ V_1: \text{volume of solvent / molecule} \]
\[ V_2: \text{volume of polymer / molecule} \]
\[ N_1: \# \text{ of solvent molecules} \]
\[ N_2: \# \text{ of polymer molecules} \]
\[ x: \# \text{ of units} \]

polymer/polymer (polymer blends)

\[ \Delta S_M = -k \left( N_1 \ln v_1 + N_2 \ln v_2 \right) \]

where

\[
\begin{align*}
  v_1 &= \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \\
  v_2 &= \frac{N_2 V_2}{N_1 V_1 + N_2 V_2}
\end{align*}
\]

\[
\begin{align*}
  \frac{x_1N_1}{x_1N_1 + x_2N_2} &\quad \rightarrow \quad \frac{x_2N_2}{x_1N_1 + x_2N_2}
\end{align*}
\]

**Generalized expression**

\[ \Delta S_M = -k \sum N_i \ln v_i \]
small molecule/polymer (polymer solution)

\[
\begin{array}{c}
\frac{1}{2} \quad \text{solvent} \\
\frac{1}{2} \quad \text{polymer}
\end{array}
\]

\[
\begin{array}{c}
\text{Energies associated with the respective pair contacts} \\
\begin{cases}
\omega_{11} \text{ for solvent/solvent} \\
\omega_{22} \text{ for solvent/polymer} \\
\omega_{12} \text{ for polymer/polymer}
\end{cases}
\end{array}
\]

\[\Delta \omega = \omega_{12} - \frac{1}{2}(\omega_{11} - \omega_{22})\]

\[\Delta H_M = p_{12} \Delta \omega\]

\[\text{# of 1-2 pairs} \quad \quad \rightarrow \quad z \text{ neighbors} \quad \quad (z: \text{coordination number})\]

\[P_{12} = x \ N_2 \ z \ \nu_1\]

\[\Delta H_M = p_{12} \Delta \omega\]

\[=\]

\[=\]
Introduce
\[ \chi_1 \equiv z \Delta \omega / kT : \text{Interaction parameter} \]
(interaction per unit thermal energy)

\[ \therefore \Delta H_M = N_1 v_2 \chi_1 kT \]

\[ \Delta G_M = \Delta H_M - T \Delta S_M \]

\[ \therefore \Delta H_M = N_1 v_2 \chi_1 kT \]

\[ \Delta S_M = -k (N_1 \ln v_1 + N_2 \ln v_2) \]

\[ \Delta G_M = kT (N_1 \ln v_1 + N_2 \ln v_2 + N_1 v_2 \chi_1) \]

Flory-Huggins Theory
Key Concepts

- Combination of the Hildebrand expression and Enthalpy term in Flory-Huggins Theory shows how $\chi_1$ can be calculated through the solubility parameter:

$$\chi_1 = \frac{V_r(\delta_1 - \delta_2)^2}{RT}$$

Where $V_r$ is the molar volume of the solvent (or mer in polymer blend system), $V_r = \text{(solvent or mer molecular weight)}/\text{density}$

- This predicts that $\chi_1$ is always ____________________________ and LCST behavior is not predicted

- In practice, $\chi_1$ is often found by assuming a form such as

$$\chi_1 = \alpha T^{-1} + \beta$$

where $\alpha$ and $\beta$ are ____________________________ and may depend on volume fraction, degree of polymerization, temperature, and molecular architecture.

If $\alpha$ is positive, decreasing $T$, increases $\chi_1$, and an upper critical solution temperature (UCST) results. If $\alpha$ is negative and $\beta$ is positive, then a _____________________ may result.

- Flory-Huggins can alternately be written on a per segment basis as (from Bates’ Paper):

$$\frac{\Delta G_M}{kT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{(1-\phi_A)}{N_B} \ln(1-\phi_A) + \phi_A(1-\phi_A) \chi$$

- Increasing molecular weight ___________________ entropy of mixing

- Methods of causing phase separation
(a) ___________________
(b) ___________________
(c) ___________________
(d) ___________________ (RIPS – Reaction induced phase separation)
Example (Phase Separation)

You want to create a polystyrene/poly(methyl methacrylate) miscible blend at a 50/50 volume at 175°C. What is the maximum molecular weight of the two polymers before phase separation? (Assume cell (mer) volume of PMMA is equal to styrene and degree of polymerization is the same for PS and PMMA):

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybutadiene</td>
<td>8.4$^a$</td>
<td>1.01</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>7.9</td>
<td>0.85 (amorphous)</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>9.45</td>
<td>1.188</td>
</tr>
<tr>
<td>Polytetrafluorethylene</td>
<td>6.2</td>
<td>2.00 (amorphous, estimated)</td>
</tr>
<tr>
<td>Polyisobutene</td>
<td>7.85</td>
<td>0.917</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>9.10</td>
<td>1.06</td>
</tr>
<tr>
<td>Cellulose triacetate</td>
<td>13.60</td>
<td>1.28$^b$</td>
</tr>
<tr>
<td>Cellulose tributyrate</td>
<td>—</td>
<td>1.16$^b$</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>13.6</td>
<td>1.24</td>
</tr>
<tr>
<td>Poly(ethylene oxide)</td>
<td>9.9</td>
<td>1.20</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>9.6</td>
<td>1.39</td>
</tr>
</tbody>
</table>

$^a$ Note: 1(cal/cm$^3$)$^{1/2}$ = 2.046 $\times$ 10$^{21}$ (J/m$^3$)$^{1/2}$.


#### Values of $R$

| $8.314472$ J · K$^{-1}$ · mol$^{-1}$ |
| $0.08205746$ L · atm · K$^{-1}$ · mol$^{-1}$ |
| $8.2057459 \times 10^{-5}$ m$^3$ · atm · K$^{-1}$ · mol$^{-1}$ |
| $8.314472$ L · kPa · K$^{-1}$ · mol$^{-1}$ |
| $62.3637$ L · mmHg · K$^{-1}$ · mol$^{-1}$ |
| $62.3637$ L · Torr · K$^{-1}$ · mol$^{-1}$ |
| $83.14472$ L · mbar · K$^{-1}$ · mol$^{-1}$ |
| $1.987$ cal · K$^{-1}$ · mol$^{-1}$ |
| $10.7316$ ft$^3$ · psi · °R$^{-1}$ · lbmol$^{-1}$ |

$k_B = \frac{R}{N_A}$

$N_A= 6.0221415 \times 10^{23}$ units/mole
Example Small’s Method

Table 2.5  Group molar attraction constants at 25°C according to Small

<table>
<thead>
<tr>
<th>Group</th>
<th>( G^a )</th>
<th>Group</th>
<th>( G^a )</th>
<th>Group</th>
<th>( G^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{CH}_3)</td>
<td>214</td>
<td>\text{Ring}</td>
<td>5-membered</td>
<td>105–115</td>
<td>Br</td>
</tr>
<tr>
<td>(-\text{CH}_2)</td>
<td>133</td>
<td>\text{Ring}</td>
<td>6-membered</td>
<td>95–105</td>
<td>I</td>
</tr>
<tr>
<td>(-\text{CH}&lt;)</td>
<td>28</td>
<td>\text{Conjugation}</td>
<td>20–30</td>
<td>\text{CF}_2</td>
<td>( a )-fluorocarbons only</td>
</tr>
<tr>
<td>(&gt;\text{C}&lt;)</td>
<td>(-93)</td>
<td>\text{H}</td>
<td>Variable</td>
<td>80–100</td>
<td>\text{CF}_3</td>
</tr>
<tr>
<td>(\text{CH}:=)</td>
<td>190</td>
<td>\text{O}</td>
<td>Ethers</td>
<td>70</td>
<td>S</td>
</tr>
<tr>
<td>(-\text{CH=})</td>
<td>111</td>
<td>\text{CO}</td>
<td>Ketones</td>
<td>275</td>
<td>\text{SH}</td>
</tr>
<tr>
<td>(&gt;\text{C}=\text{C}&lt;)</td>
<td>285</td>
<td>\text{CN}</td>
<td>Esters</td>
<td>310</td>
<td>\text{ONO}</td>
</tr>
<tr>
<td>(&gt;\text{C}:=\text{C}&lt;)</td>
<td>222</td>
<td>\text{Cl}</td>
<td>Mean</td>
<td>410</td>
<td>\text{NO}_2</td>
</tr>
<tr>
<td>\text{Phenyl}</td>
<td>735</td>
<td>\text{Cl}</td>
<td>Single</td>
<td>260</td>
<td>\text{PO}_4</td>
</tr>
<tr>
<td>\text{Phenylene} ( o,p,p )</td>
<td>658</td>
<td>\text{Cl}</td>
<td>Twinned as in ( &gt;\text{C}:=\text{C}&lt; )</td>
<td>260</td>
<td>Si</td>
</tr>
<tr>
<td>\text{Naphthyl}</td>
<td>1146</td>
<td>\text{Cl}</td>
<td>Triple as in ( &gt;\text{C}:=\text{C}&lt; )</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

\* \( G \) has units of cal^{1/2}·cm^{3/2}/mol

Estimate the Solubility of PMMA using Small’s Method

\[
\begin{align*}
\text{CH}_3 \\
(CH_2-C)n \\
O=C-O-CH_3
\end{align*}
\]

\[
\delta = \frac{\rho \sum G}{M}
\]
Equation-of-state theories

One of the basic assumptions of the Flory-Huggins Theory is the absence of a change in volume on mixing. However, this assumption is generally not valid. Because of time constraints, equation-of-state theories will not be covered in detail. These theories do a better job at predicting LCST behavior than Flory-Huggins, but are generally more phenomenological in nature.