POLYMER SOLUTION

Upper and lower Critical Solution Temperatures

Cloud-point or precipitation curves for different polymer-solvent systems have different shapes (Figures 6 & 7). The maxima and minima on these curves indicate the upper critical solution temperature (UCST) and lower critical solution temperature (LCST), respectively. As indicated in Figs 6 and 7 the phase diagram of a polymer solution has two regions of limited miscibility: (i) below UCST associated with the theta temperature and (ii) above LCST.

Different polymer-solvent systems may have completely different phase diagrams. For some systems, such as polystyrene-cyclohexane, UCST < LCST [Figs 7 (a)] but for others, e.g, highly polar systems like polyoxyethylene-water, UCST > LCST and closed solubility loop found [Figs 7 (b)].
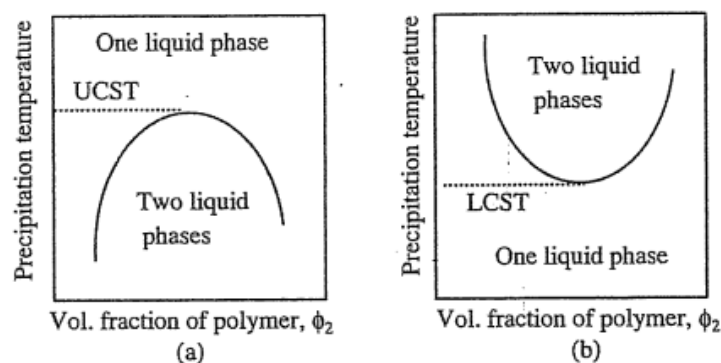

Figure 6. Schematic phase diagrams for polymer-solvent systems showing (a) UCST and (b) LCST.
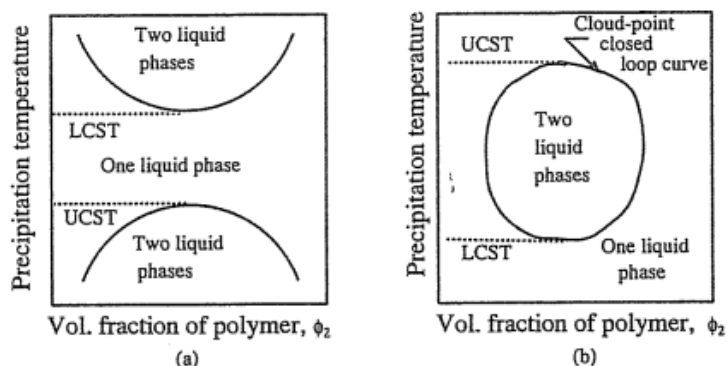

Figure 7. Schematic phase diagrams for polymer-solvent systems where (a) UCST < LCST and (b) UCST > LCST.

The solubility of a polymer in a solvent therefore depends on the temperature. If a single (homogeneously mixed) phase only exists above a certain temperature, this is referred to as an *upper critical solution temperature* (UCST). Here the separation below the UCST is an enthalpy-driven process—at lower temperatures the contribution of the enthalpy of mixing to the free enthalpy of mixing is greater than the effect of entropy (eq. 14).

However, if a solution is only thermodynamically stable below a certain temperature, the separation that occurs at this temperature must, by analogy, be driven by entropy. When a thermodynamically stable phase of the polymer–solvent-mixture occurs below a critical temperature, this is referred to as the LCST (*lower critical solution temperature*). This temperature denotes the maximum temperature at which the polymer still dissolves.

Formally, this behavior can be explained by interpreting the Gibbs–Helmholtz equation and considering the signs of the enthalpy and entropy terms. Assuming a negative enthalpy of mixing and a normal, positive entropy of mixing, the solution is completely miscible at all temperatures. An LCST occurs when the entropy and enthalpy of mixing take on negative values. As previously stated, because the entropy of mixing is usually positive, this case is rare and is only observed for a few polymers. If the signs of both the entropy and enthalpy of mixing are positive, the system has a UCST. This is often the case in reality. If the enthalpy of mixing is positive and the entropy of mixing negative, the system is not miscible at any temperature.

For real mixtures the situation is not so trivial, as both enthalpy and entropy of mixing are not monotonically dependent on the temperature. A detailed investigation shows that all polymer–solvent mixtures should display a UCST as well as an LCST. However, these are not always observable by experiment. This can often be explained by the UCST and LCST occurring at temperatures above or below the melting or the boiling point of the solvent.

PHASE EQUILIBRIA

Whether or not a polymer and solvent are mutually soluble, or *miscible*, is governed by the sign of the Gibbs free energy of mixing, ΔG_m, which is related to the enthalpy and entropy of mixing by eq. (14). Three different dependencies of ΔG_m on solution composition (i.e., volume fraction of polymer) at constant temperature are illustrated in **Figure 8**. If ΔG_m is positive over the entire composition range, as illustrated by curve I, the polymer and solvent are totally immiscible over the complete composition range and will coexist at equilibrium as

two distinct phases. Two other possibilities are those of partial and total miscibility, as illustrated by curves II and III, respectively. For total miscibility, it is *necessary* that

$$\Delta G_m < 0 \qquad \qquad 21$$

and that the second derivative of ΔG_m with respect to the volume fraction of solvent (component 1) or polymer (component 2) be greater than zero over the entire composition range as formally expressed by

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2} \right)_{p,T} > 0$$

$$22$$

Both conditions for miscibility are satisfied by curve III but not curve II, which exhibits two minima in ΔG_m, and therefore the derivative criterion expressed by eq. (22) is not satisfied at all points along the . ΔG_m–composition curve. A solution that exhibits such minima will phase-separate at equilibrium into two phases containing different compositions of both components. The compositions of the two phases are given by the points of common tangent as illustrated in **Figure 8**, where the composition of the solvent-rich phase is identified as ϕ_2^A and that of the polymer-rich phase as ϕ_2^B.

Phase equilibrium is strongly affected by solution temperature. In fact, any of three types of phase behavior illustrated in **Figure 8** may result from a change in the temperature (or pressure) of the system. Our usual experience with solutions of low-molecular-weight compounds is that solubility increases with an increase in temperature, as illustrated by the phase diagram shown in **Figure 9**. In this example, the solution is homogeneous (i.e., the two components are totally miscible) at temperatures above the point identified as UCST, which stands for the *upper critical solution temperature* as described below. At lower temperatures (i.e., below the UCST), phase separation may occur depending upon the overall composition of the mixture. At a given temperature below the UCST (e.g., T_1), compositions lying *outside* the curves are those constituting a homogeneous phase, while those lying inside the curves are thermodynamically unstable and, therefore, the solution will phase-separate at equilibrium. The compositions of the two phases, identified as phases A and B, are given by points lying along the curve called the *binodal*. The binodal is the locus of points that satisfy the conditions for thermodynamic equilibrium of a binary mixture given as

$$\mu_1^A = \mu_1^B \qquad \qquad 23$$

$$\mu_2{}^A = \mu_2{}^B \qquad\qquad 24$$

As the chemical potential is given by the derivative of the Gibbs free energy with respect to composition (eq. 25),

$$\Delta\mu_1 = \mu_1 - \mu_1^\circ = \overline{\Delta G_m} = \left(\frac{\partial \Delta G_m}{\partial n_1}\right)_{T,p} \qquad\qquad 25$$

the chemical potentials are obtained graphically from the intercepts of the common tangent drawn to curve II with the free energy axes as illustrated in **Figure 3-9**.
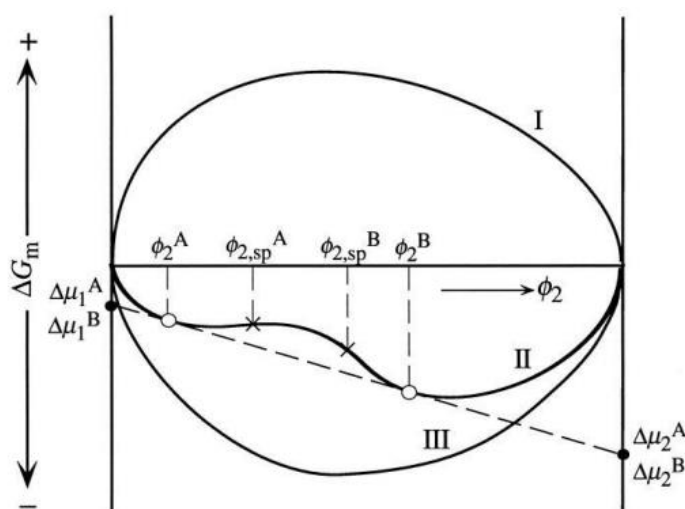

Figure 8. Dependence of the Gibbs free energy of mixing, ΔG_m, of a binary mixture on volume fraction of polymer, φ₂, at constant pressure and temperature. I. Total immiscibility. II. Partial miscibility. III. Total miscibility. In the case of partial miscibility (curve II), the mixture will separate into two phases whose compositions (○) are marked by the volume-fraction coordinates, φ₂^A and φ₂^B, corresponding to points of common tangent to the freeenergy curve. Spinodal points, compositions φ₂,sp^A and φ₂,sp^B, occur at the points of inflection (x).

Between the binodal and the unstable region lies the *metastable* region, which is bounded by the *spinodal*. In the metastable region, the system can resist small concentration fluctuations but will eventually equilibrate to the stable two-phase state given by the binodal. Points lying along the spinodal correspond to the points of inflection identified in curve II of the free energy diagram (**Figure 3-9**) and satisfy the relationship

$$\left(\frac{\partial^2 \Delta G_m}{\partial \phi_2^2}\right)_{p,T} = 0 \qquad\qquad 26$$

The binodal and spinodal coincide at the *critical point*, which satisfies the following equality for the third derivative of the Gibbs free energy with respect to composition:

$$\left(\frac{\partial^3 \Delta G_{\mathrm{m}}}{\partial \phi_2^3} \right)_{p,T} = 0$$

27

In the case of the upper critical solution temperature (UCST), the critical point lies at the top of the phase diagram as shown in **Figure 3-10**.
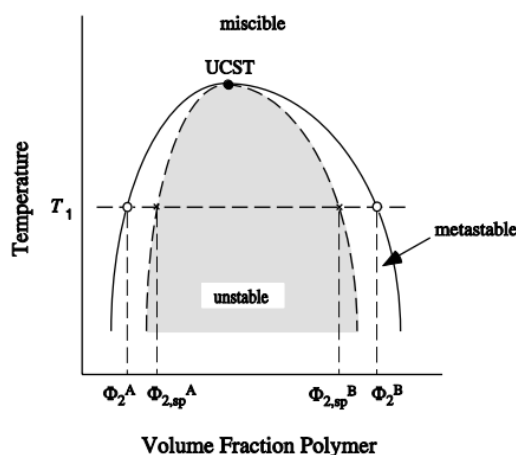

Figure 9. Representative phase diagrams for a polymer solution showing an upper critical solution temperature (UCST) (○), spinodal curve (– – – –), and binodal curve (_____).

Although the UCST behavior of dilute polymer solutions had been observed for many years, it was not until 1961 that phase separation of polymer solutions was first reported to occur with an *increase* in temperature. In this case, the bimodal and spinodal curves coincide at a temperature and composition called the *lower critical solution temperature* or LCST. One serious limitation of the Flory–Huggins theory is that it fails to predict LCST behavior.

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