Gibbs Energies; Liquid Mixtures; Immiscibility

For a given binary liquid mixture (at defined T and p) characterised by a plot of excess Gibbs energy $G_m^E$ against mole fraction, $G_m^E$ can be positive. Indeed if $[G_m^E / R \cdot T]$ strongly exceeds 0.5, the mixture is partially miscible. That is to say the liquid comprises two liquid phases having different mole fraction compositions.

A fascinating variety of patterns emerge in the context of partial miscibilities.

(a) Some binary liquid mixtures are completely miscible but become partially miscible with increase in temperature. The corresponding miscibility curve has a minimum at a Lower Critical Solution Temperature, LCST. For example in the case of 2-butoxyethanol + water, the LCST is at 322.2 K where $x(H_2O) = 0.942$ [1]. In fact all commonly quoted examples of this class of systems have water as one component.

A fascinating example concerns propionitrile+ polystyrene mixtures. The miscibility curves indicate that the LCST occurs at negative pressures; in effect when the mixture is ‘stretched’ [2].

(b) Many binary liquid mixtures (e.g/ phenol + water has (at ambient pressure).are partially miscible, becoming completely miscible on raising the temperature. The miscibility curve has a maximum at an Upper Critical Solution Temperature, UCST. At ambient pressure a small number of liquid mixtures exhibit both UCST and LCST. In other words the miscibility plot forms a closed loop.

Partial miscibility plots also show deuterium isotope effects. In the case of CH$_3$CN+H$_2$O (component 2 = CH$_3$CN) the UCST is 272.10 K at $x_2 = 0.38$ [2].

Footnotes
