Critical Solution Temperature

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Introduction

Some liquid pairs do not give homogeneous Solutions at all compositions. Such liquid pairs are said to be partially miscible liquids. phenol-water, ether-water, aniline-water Etc. Two solutions of partially miscible liquids, which are in equilibrium are called conjugated Solutions at a particular temperature. The two layers of a conjugated solutions become completely miscible at a certain temperature whose value depends upon the nature of the two liquids.

"The temperature at which two partially miscible liquids become completely miscible at all proportions is called the Critical Solution Temperature (CST) or **consulate temperature of the system"**.

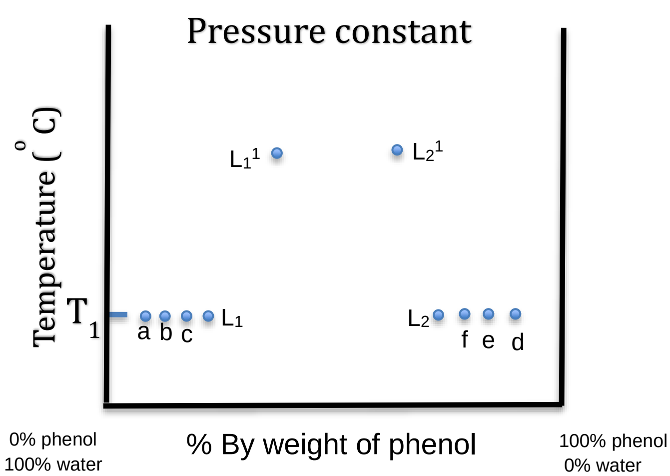
When the critical solution temperature is lower than the room temperature, it is known as **Lower Critical Solution Temperature** which may be achieved by lowering the temperature of the system. On the other hand, when the critical solution temperature is higher than the room temperature, it is known as **Upper Critical Solution Temperature** which may be achieved by raising the temperature of the system.

Depending upon the Critical Solution Temperature, partially miscible systems are categorized into three classes.

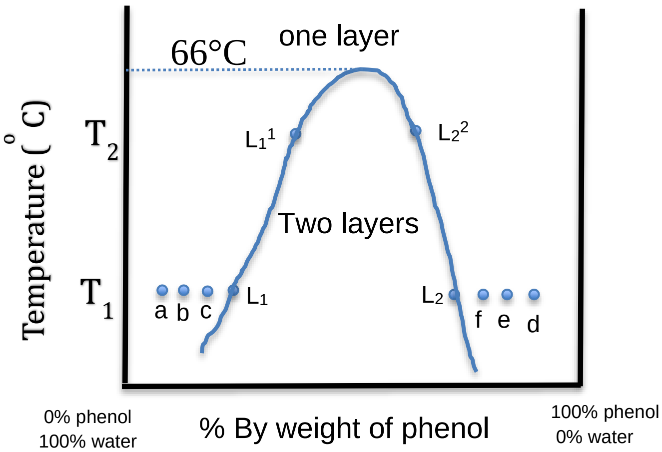
1. Type I: Partially miscible systems with Upper critical solution temperature (UCST), e.g.: phenol- water system
2. Type II: Partially miscible systems with Lower critical solution temperature (LCST), e.g.: triethylamine-water system
3. Type III: Partially miscible systems with Upper CST and Lower CST, e.g.: nicotine-water system

Type I: Systems with Upper CST: (e.g.: phenol- water system)

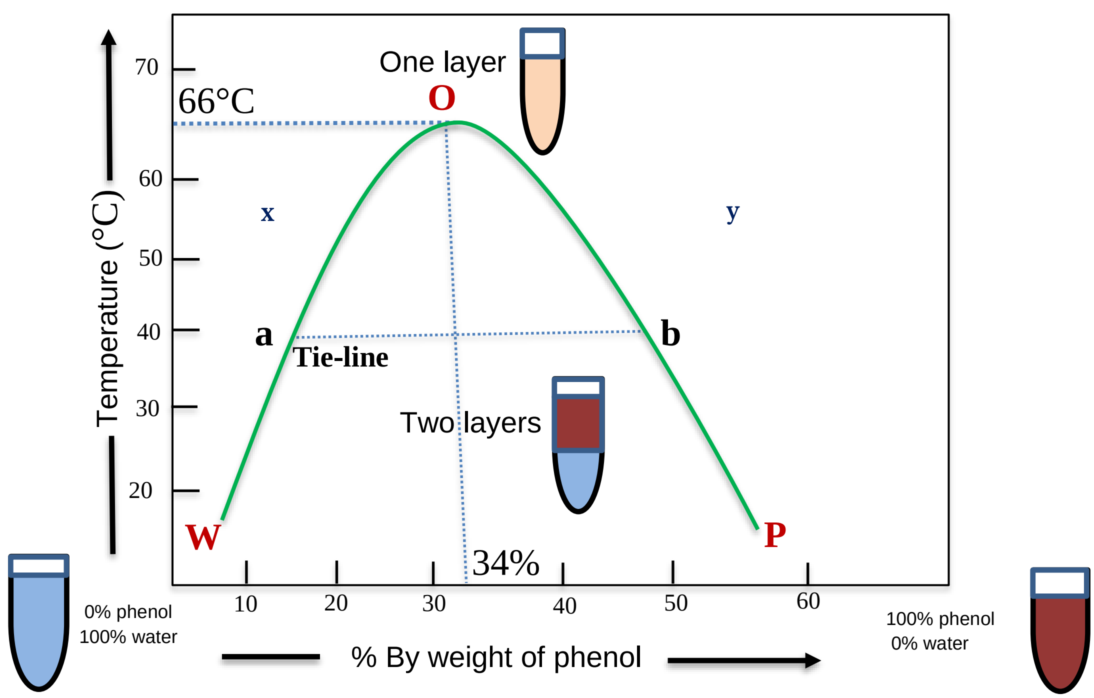
- When roughly equal amounts of phenol and water are mixed two layers are produced. Viz. a solution of phenol in water and a solution of water in phenol.
- The composition of each of these layers is fixed at any given temperature and can be determined by the analytical methods.
- At temperature T_1, small amount of phenol added to water dissolves completely.
- The points a, b, c represents the composition of liquid mixture after addition of different amounts of phenol to water.
- If the addition of phenol is continued, solubility limit L_1 is reached.
- If more phenol is added, it won't dissolve in water and a second liquid layer is formed.



- Region to the right of L_1 is two phase region.
- Region to the left of L_2 is two phase region.
- region between L_1 and L_2 there exist two liquid layers, a conjugate solution. Hence it is a two-phase region.
- With increase of temperature, the solubility of water in phenol and phenol in water increases.
- At a higher temperature (above T_1), solubility limit will increase from L_1 to L_1^1 and L_2 to L_2^1.
- Joining the solubility curves: dome -shaped area (curves passing through L_1 & L_1^1 and L_2 & L_2^1).



- If the system is warmed the amount of phenol in water layer as well as the amount of water in phenol layer increase, eventually at a certain temperature the two layers becomes one layer i.e. solution becomes homogeneous.
- This temperature (critical solution temperature) for phenol-water system is found to be 66°C and the composition at 66°C is found to be 34% phenol by weight.
- Above this temperature the two liquids become miscible with each other in all proportions.
- When Mutual solubility of water and phenol is Plotted against temperature a parabolic curve is observed.



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The graph leads to the following significant conclusions:

1. Whatever may be the composition phenol and water, At and above 66°C both are completely miscible with each other.
2. At any temperature below 66°C, if the composition of the system lies within the range of the parabolic Curve WOP there are two layers in the equilibrium. The composition of one layer corresponds to the point **a** and that of other to the point **b** The line **ab** is called **tie line**.
3. At any temperature below 66°C if the composition lies outside the curve, we get only one solution.
   For example, if the composition lies on the left of the curve **WO** as represented by the point line **x**, the mixture will then consist only of unsaturated solution of phenol in water.
   On the other hand, if the composition lies on the right of the curve **OP**, as represented by the point **y**, the mixture will then consist only of unsaturated solution of water in phenol.

- In this type of system, the mutual solubility increases with rise in temperature.
- Some other liquid pairs with an upper critical solution temperature along with corresponding composition are given in the below table.

System	Upper CST	% by weight of the first component
Aniline-water	168°C	40%
Aniline-Hexane	60°C	52%
Methanol-CS_2	49.1°C	29%
Methanol-Cyclohexanone	40.5°C	20%

Type II: Systems with Lower CST: (eg: triethylamine- water system)

- In this system the mutual solubility of two liquids increases with decreasing temperature.
- Thus, cooling of the system to an 18°C temperature causes the two components(liquids) to become completely miscible with each other.
- This temperature is called Lower critical solution temperature (LCST) or lower Consulate temperature.

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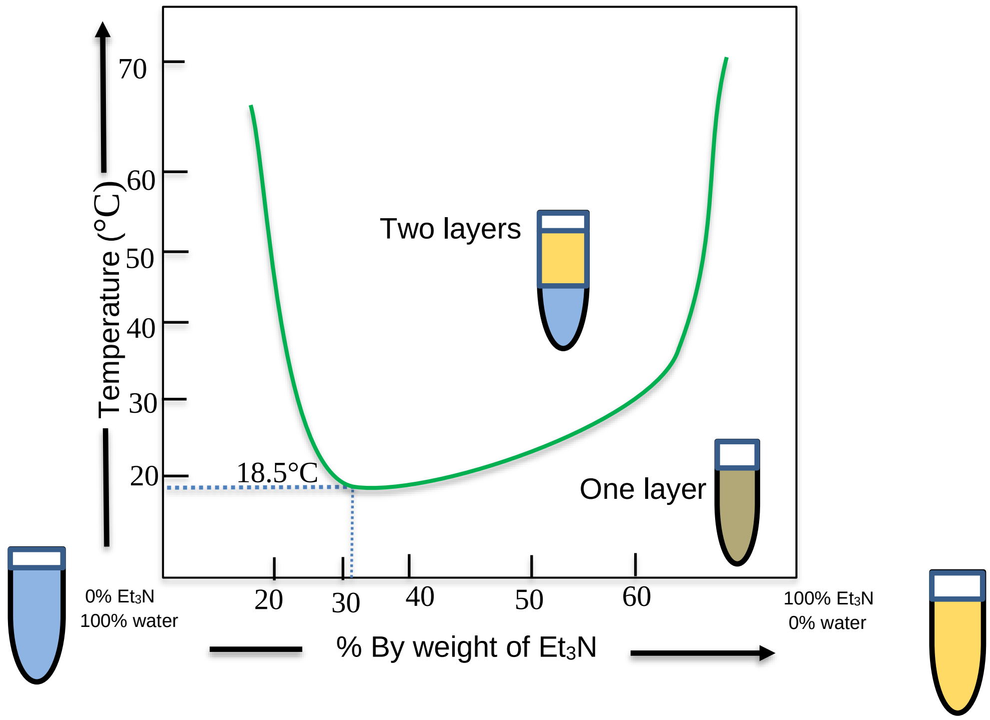


The above graph leads to the following important conclusions.

1. At and Below 18°C the two liquids are completely miscible in all compositions. That is the system is homogeneous and exists in one layer.
2. Above 18°C two cases are possible.

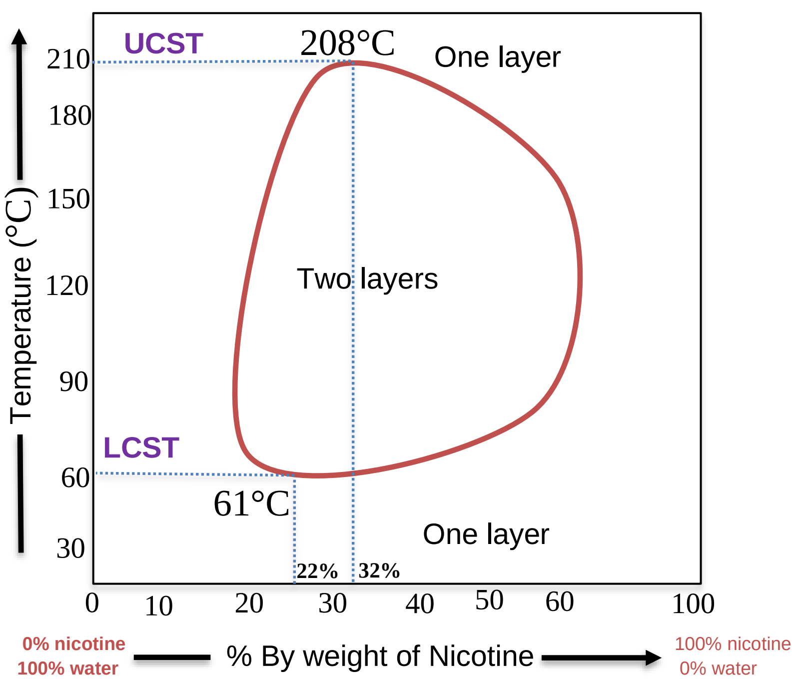
<u>Case-i:</u> When composition of the system lies within the curve, the two liquids are not completely miscible. The system is heterogeneous and thus two layers exist.
<u>Case-ii:</u> When composition of the system lies outside the curve, only one layer exists. If the point representing the composition lies left of the curve, the one layer consists of solution of triethylamine in water. While if the point is present right to the curve the only layer consists of the solution of water in triethylamine.

Other examples of LCST are

1. Diethylamine - water: 13% diethylamine- 43°C
2. 1-methyl piperidine – water: 48°C - 5% methyl piperidine.

Type III: Systems with an Upper and Lower CST: (eg: nicotine- water system)

- In this type of system, the mutual solubility of two liquids increases with both increase of temperature as well as with decrease of temperature.
- In other words, these liquids are completely miscible at certain higher temperature UCST as well as at certain lower temperature LCST.
- Between these two limiting temperatures, they are partially miscible.
- Nicotine-water system has two critical solution temperatures Viz. 208°C at which the system contains 32% of nicotine and 61°C at which mixture contains 22 %nicotine.



- Within the closed curve at any point, there are two layers. Whereas outside of the curve there is only one layer.

Effect of pressure: The systems with upper and lower CST are affected by pressure. With increase of pressure the LCST is raised while the UCST is lowered gradually until they become one. In other words, as the pressure increases the closed area becomes smaller and smaller until it becomes a point. Therefore, at higher pressures the liquids are completely miscible at all temperatures and in all compositions.

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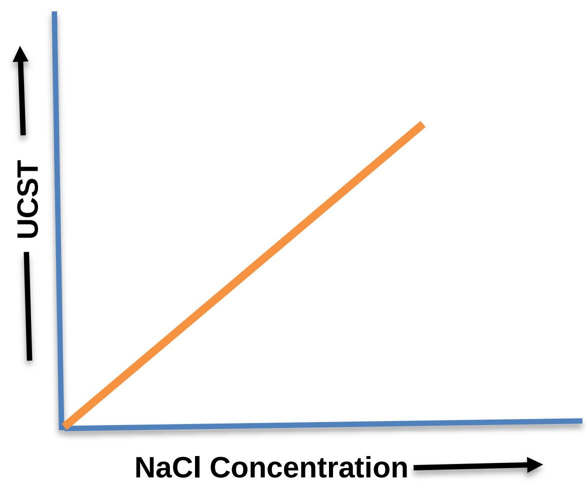
Effect of impurities on CST

- The addition of an impurity which is soluble in partially miscible systems, increase its miscibility.
- This process is known as blending or 'salting-out' in pharmaceuticals and is used to select the best solvent for the drugs.
- In this process, a salt is added to separate the aqueous phase from the organic phase.
- If the added salt (impurity) dissolves in one of the liquids only, it results in an increase in the Upper CST (e.g. addition of NaCl raises the CST of water-phenol system), and a decrease in the Lower CST.



- Further, if the added salt (impurity) is soluble in both the phases, then the Upper CST is lowered (e.g. addition of succinic acid to water-phenol system) and the Lower CST is raised, thus increasing the miscibility of the system.
- This increase or decrease in the CST depends on the nature and the amount of the added substance and the composition of the system.

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