Partially Miscible Liquids
Certain pair of liquids are miscible with each other in limited range of concn and are known as partial miscible liquids. eg small amt of phenol is added to H_2O at room temp & mixture is shaken, Phenol dissolves completely in H_2O. If more phenol is added continuously, a stage is reached where the compound is no more soluble & 2 solutions are formed
(1) saturated solution of organic compound in water
(2) saturated solution of water in organic compound
These 2 solutions are in equilibrium with each other & are known as conjugate solutions. The composition of these solutions is fixed & and are independent of relative amounts of 2 solutions.
If more of organic compound is added it continues to disperse in these 2 solutions & net effect is that the amount of the solution of organic compound in H_2O is gradually decreased & amount of solution of organic compound is gradually increased. After sof Same time a stage is reached, where

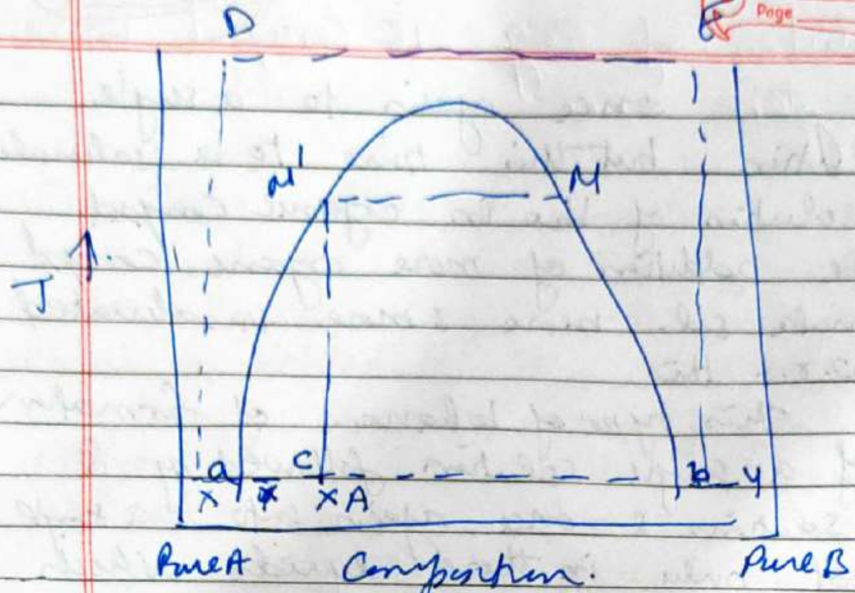
the solution of organic compd converts the system once again to a single solution but this time to a saturated solution of H_2O in organic compd.
The addition of more organic compd make sol. more & more unsaturated w.r.t H_2O

This type of behaviour of formation of a single solution followed by 2 solutions & once again into a single sol. only in those liquids which differ widely from each other & show large +ve deviations from Raoult's law

C.S.T → As temp. is raised the composition of above 2 solutions becomes closer due to increase in mutual solubilities of two components as temp. is raised.
At a certain temp. the composition of 2 solutions become identical & both solution merge into each other forming a single solution. This temp is known as Critical Solution Temp.

(1) When T > CST, two liquids are miscible in all proportions & forms a single solution. A point outside
(2) the curve represents two conjugate solution in eqn with each other
Composition of 2 conjugate solution at a given T is given by pt's on solubility curve. Like pt 'C' on horizontal line represents

compositions of two solutions. Any pt on horizontal line shows variations of A & B



Let binary solution composition is is at X this is unsaturated solution of B in A. If more B is added it continues to dissolve till pt 'a' is reached. At this pt. single solution just splits into two, a saturated solution of B in A which is present in large amt. (A) & a saturated solution A in B which has just started forming. As more 'B' is added, system continues to possess the above 2 solutions, till pt. 'b' is reached. The change is only that relative amounts of 2 solutions vary; the amt of solution of B in A decreases whereas that of A in B gradually increases.

Relative ratio can be obtained by lever rule

$\frac{ac}{bc}$ =

At pt 'b', the solution of B in A is just going to disappear & is present in a very small amount. Further addition of B gives rise to a single solution an unsaturated sol- of A in B. pt. Y.

One can go directly from X to Y without formation of 2 solution.

(1) Raise the temp. of solution shown by pt. X to a point above the C.S.T.

(2) Add more B till desired composition of A in B corresponding to pt Y is obtained

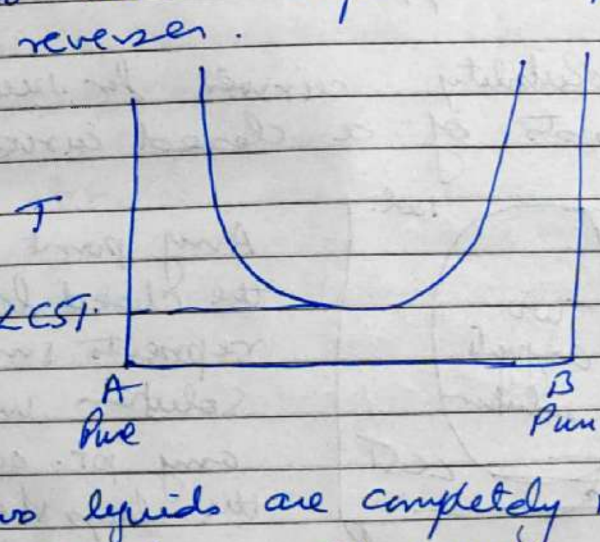
(3) Cool the resultant sol. till pt Y is reached

Effect of Temp Let a system is represented by a point C. It represents two solutions of B in A & A in B. If temp. of system is ↑ed, the state of system moved vertically the composition of solution A in B changes along bM and that of B in A along a M'.

The relative amount of 2 solutions also vary, the amounts of B in A is gradually ↑ed while A in B is gradually decreased. The

continues to have 2 solutions, till the point M' is reached where the solution of A in B is present in vanishing amount.
System of 2 solutions becomes a single saturated sol. of B in A. The temperature at which this happens is known as mutual solubility temp. (MST)
When temp is further increased an unsaturated sol. of B in A. CST is maximum of all mutual solubility temperatures

Lower C.S.T. There are some binary liquids mixture which show increase in mutual solubilities as temp is decreased - so their Temps vs Composition graph is reverse.



Two liquids are completely miscible with each other in all respects so long as temp is below LCST eg hydroxy & amine compound or hydroxy - keto or ether gp. Two components partially associate through H-bonding

$-O-H---N\equiv$ or $O-H---O=C\langle$

hydroxy gp, Amine gp, hydroxy gp, Keto gp

The extent of such association depends upon temp of system & ↓ it as temp is raised

That is why mutual solubilities ↓ as temp is ↑ed

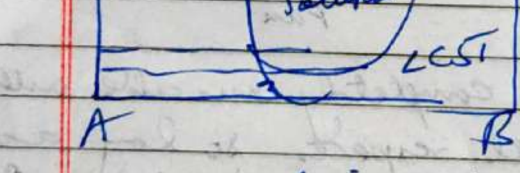
eg triethylamine - H_2O 18.5°C

γ-Collidine - H_2O 6

Glycerol - m-toluidine 6.7

It is found that mutual solubilities don't continue to ↓ as temp is increased. After a certain temp, the solutions behave in normal manner & solubilities again start increasing with rise in temp. Such solutions also show upper critical solution temp.

Solubility curves for such system consists of a closed curve



Any point within the closed loop represents single solution while any pt. outside the loop shows single solution

eg Nicotine - H_2O

UCST = 208°C

LCST = 60.8°C

They are completely miscible in each other at Temp > 208°C & T < 60.8°C

The UCST temp for most liquids pairs are very high & is obtained only at very high pressures. In many cases UCST is not attainable experimentally as it lies above ~~their~~ their respective C.S.T. of liquids, so the system volatalizes much before CST is reached

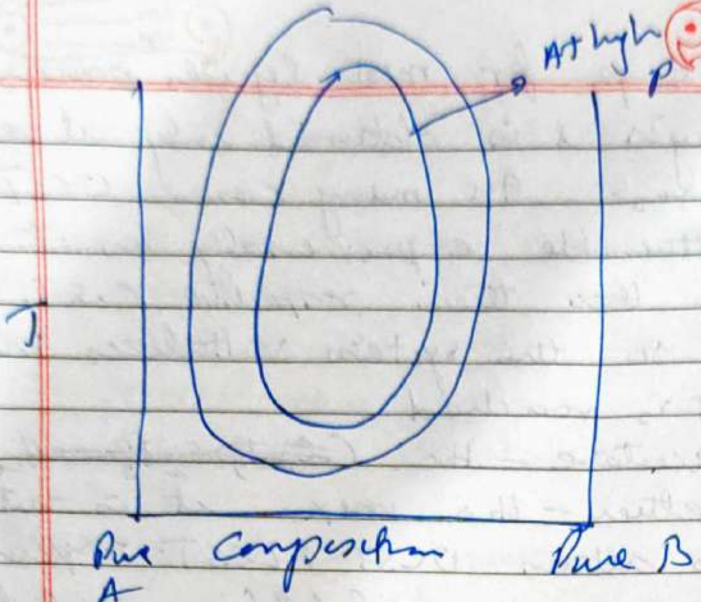
Ethylacetate — H_2O (~~$C_2H_5OC_2H_5$ — H_2O~~)
~~CH_3OCH_3~~ ether — H_2O mix it is not possible to attain UCST & LCST experimentally

In both cases, the solubilites, ethylalcohol ether in H_2O ↓ with ↑ temp. but their C.S.T. for both systems lie below freezing pt of H_2O i.e. H_2O freezes completely before these temp are attained

UCST for $CHCl_3$ — H_2O is not reached experimentally UCST lies above Critical temp of $CHCl_3$.

∴ It is concluded that one could not observe experimentally ~~U~~CST when
(1) upper CST lies above the critical temp of either of 2 liquids
(2) Lower CST lies below the freezing pt of ~~the~~ two liquids

Effect of P on CST → Every liquid mixture has a CST at a particular value of external pressure. If external is changed CST also varies. Since the mutual solubility of two components ↑ with ↑ of external P. UCST will ↓ while LCST will ↑ as external P is increased



The area of loop becomes smaller & smaller with ↑ in P until ultimately a stage is reached where area is reduced to a point. At this point 2 liquids become miscible with each other in all proportions & forms a single liquid solution

Effect of Impurities on CST

Impurities have a marked effect on CST. Nature of the effect depends whether the added substance is soluble in one liquid or in both liquids

(1) If the substance is soluble in only one liquid, it will affect the solubility of other liquid in this liquid. Solubility is ↓, ie mutual solubility of 2 liquids are decreases, CST is raised

eg 0.1 mol of KCl is added to phenol H_2O system raises CST by 8K

while 0.1 mole of  of Phenol - H_2O
raises nearly by 20 K

(2) If the added substance is soluble in both the liquids its increases the mutual solubilities of two liquids & CST is lowered given by graph line II this happens because the added substance will distribute itself between two conjugate liquid mixtures in a definite manner & is being continuously exchanged between them. A stage of dynamic equilibrium exists.

This to & fro movement of molecules of added substance as a cementing force between the two conjugate liquid mixtures & brings about more solubility of 2 liquids

eg succinic acid is added to phenol — H_2O system