

Hello and welcome students. To begin with let's start with

Programme : S. Y. B. Sc. and Subject : Chemistry

Semester : III and Paper Code : CHC-103

Paper Title : Physical Chemistry and Organic Chemistry

My Unit name : Solutions

Module Name and number : Partial miscibility of liquids :Critical solution temperature (07)

Myself. Mrs Pooja Gadekar from Dnyanprassarak Mandal's College and Research Centre, Assagao, Mapusa-Goa

Moving on to the outline.

The first topic would be miscibility of liquids in liquids.

Second effect of temperature on miscibility.

Third introduction to Phase Diagrams with examples

Fourth concept of critical solution temperature

Once the topic is completed, the students will be able to explain

Types of Miscibility

Effect of temperature on Miscibility

Critical Solution Temperature and Phase Diagrams

Effect of added substances on Critical Solution Temperature

Coming to the main topic now, Miscibility of liquids in liquids. There are three different cases with respect to liquids.

First one showing complete miscibility. An example would be water and ethyl alcohol.

In the second case we have the liquids which show complete immiscibility. An example in this case would be water in Mercury or another example would be water and benzene.

Next is the liquids that show partial miscibility . An example with respect to this system is water & phenol

(Please note - In this case one will have a definite miscibility in other).

Moving further to the main topic, i.e. In cases of partial miscibility

The degree of miscibility may be dependent on the temperature i.e.

In first case miscibility increases with increase in temperature (water-phenol)

It decreases with increase in temperature (water-triethylamine)

In the third case it increases with increase & decrease in temperature (water-nicotine)

In the last case miscibility shows that it is not affected by temperature

Please note in case of three component systems the third liquid may influence the degree of miscibility of the 2 liquid systems.

The effect of temperature variation on the degree of miscibility in these systems is described by means of phase diagrams.

A Phase diagram is a graph of temperature (T) versus composition at constant pressure (P)

Now let us understand each case in more depth i.e the first case - Systems showing an increase in miscibility with rise in temperature. The example that we have already come across in previous slide

Phenol Water System

From the plot of temperature versus composition(percent by weight) we have Phase A: as water rich phase and Phase B: as phenol rich phase

moving from point M to point N, the phase B continually increases and phase A decreases.

The line *MN* is called the tie line that contains the two phases.

This line is always parallel to the baseline in two component systems.

The points M and N will give the composition of the two components in the mixture at the noted temperature.

The point K in the graph is very important and is known as Critical / consolute solution temperature. It is divided into two types i.e. upper consolute temperature and lower consolute temperature

It is defined as the maximum temperature at which the two phase region exists and above or below this temperature the components are completely miscible and yield one-phase liquid systems.

The Phenol-water shows the upper consolute temperature at 66.8°C.

The other examples, in case of upper critical solution temperature include Methanol-Cyclohexane and Hexane-Aniline

Moving on further to the second case of miscibility with respect to temperature i.e. Systems showing a decrease in miscibility with rise in temperature (Triethylamine –Water system):

From the plot it is clear that the miscibility of liquid pairs decreases with increase in temperature.

A lower consolute temperature of 18.5°C is obtained in this example that we have considered.

Below this temperature a single phase is obtained while above the temperature two separate layers are present. The composition of the two components can be determined from the graph through the points X and Y respectively.

Other examples with respect to this particular system would include Diethylamine-Water & 1-Methylpiperidine-Water

Coming to the third case i.e. system shows both upper as well as lower critical solution temperatures. The most common example known is the Nicotine-water system. From the figure it is clearly seen that the given system contains both upper as well as lower critical solution temperature. Usually at normal temperatures nicotine is completely miscible in water, which gives us a single layer. But as we increase the temperature what happens is it separates out into two layers and further increase will again give me a single layer. Therefore the nicotine water system shows an upper consolute temperature of 208 degrees Celsius while lower consolute temperature of 61 degrees Celsius.

Thus from the figure it can be observed that inside the curve we have two different layers while outside the curve we are having one single layer.

The points A and B will give the corresponding content of Nicotine and Water respectively.

Other examples include Glycerine – *m*-Toluidine & Water – β -Picoline

The last case which includes systems with no critical solution temperature. The typical example would be Ethyl ether - water. Such systems neither show an upper nor a lower consolute temperature.

Once we know what is miscibility and what is critical solution temperature, we should know what is the effect of added substances or impurities on the critical solution temperature. Now if we talk about critical solution, this temperature is very very sensitive to add impurities or substances and based upon or depending upon the solubility of added material the critical solution temperature may decrease or increase. The condition wherein it decreases will occur if the added material is soluble in any one of the components or maybe soluble for certain extent in both the components. In this particular situation, the critical solution temperature decreases, whereas if the add substance is soluble to the same extent in both the components, then the critical solution temperature increases. Such a process is referred to as blending or salting out process.

Students please note in other words, what I'm trying to say is that the addition of substances leads to an upper CST to be lowered and a lower CST to be raised.

These are my few references.

Thank you.