Environmental Soil Chemistry
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Lecture – 42
Pollutants - Soil Solution Interactions (Contd.,)

Welcome friends to this second lecture of module 9 of this NPTEL online course of environmental soil chemistry and in this week, we are talking about soil pollutant and soil solution interactions. So, in our first lecture we have discussed the dynamics of different pollutants in the soil solution and how they can take part in different types of reactions, exchange and adsorption reaction as well as precipitation and dissolution reactions, how they can form you know different complex formations and so on so forth.

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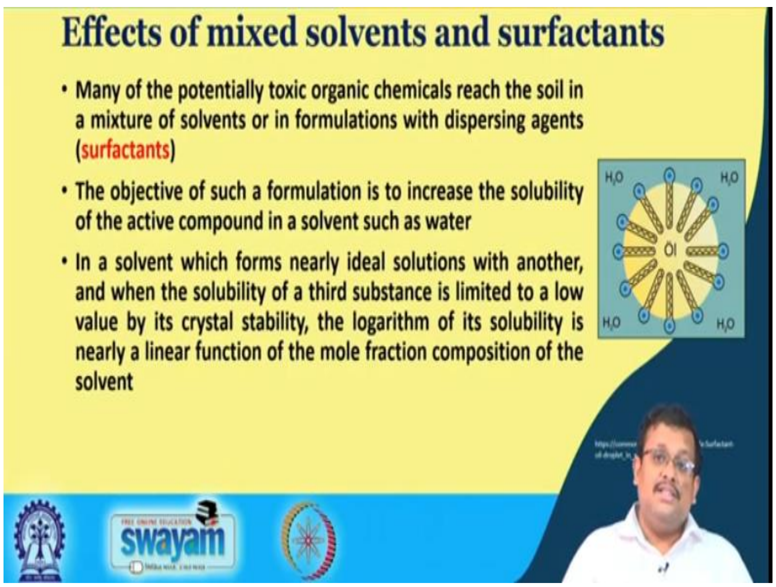

So, after that we have seen how this heavy metals can impact the soil solution and the dynamics in the soil solution and then we have discuss the acid-base equilibrium and we also discussed the precipitation and dissolution reactions. So, while discussing the precipitation dissolution reaction we talked about the relationship between the ionic activity you know, IAP or ionic activity product and the solubility product constant.

And what are the conditions to be maintained for you know, for precipitation, dissolution and saturated condition. So, we have started discussing about the effects of mixed solvents and surfactants which is one of the major important aspect of soil pollutant and soil solution interaction. Remember that a surfactant is a dispersing agent which has both hydrophobic tail and hydrophilic part.

So, this hydrophilic part is basically arranged towards the aqueous phase and the hydrophobic part is basically arranged towards the hydrophobic compound, so that is why they act as a dispersing agents. Now, many potentially toxic organic chemicals you know, reach the soil in mixture of solvents or in formulation with dispersing agents because these toxic organic chemicals can be easily bound by these dispersing agents, although they are immiscible in water due to non-polarity.

But they can be mixed with the; they can interact easily with the dispersing agents, so that is why their movement in the water you know, they can move from one place to another place. Now, the objective of such a formulation is to basically when we; when you do this kind of formulation, the objective of such formulation is to increase the solubility. Why we use a dispersing agent; to increase the solubility of the active compound in a solvent such as water.

Now, we have already discuss in our last class that when a solvent which forms a nearly identical or I am sorry, ideal solution with another and when the solubility of a third substance is limited to a low value by its crystal stability, then if we plot the logarithm of its solubility, we will get a linear function of the mole fraction composition of the solvent. So, this is one of the major you know, postulation when you talk about effects of mixed solvents and surfactants.

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Also it is important to know that in case of a pair of solvents in which the solubilities of the third substance differ greatly, so let us consider there are 2 solvents; solvent A and solvent B in which the solubility of a third substance such as C differs greatly. In one, this C is highly soluble, another is very less soluble, so you can see the solubility differs very greatly. So, these solvents due to their different solvent powers are generally much less soluble in one other and form miscible solution which are far from linear.

Again, in the case of a pair of solvents in which the solubilities of the third substance differ greatly, these solvents due to their different solvent powers obviously are generally much less soluble in one another and form miscible solution which are far from linear. So, this is another interaction, this is another rule when we talk about the effects of mixed solvents and surfactants.

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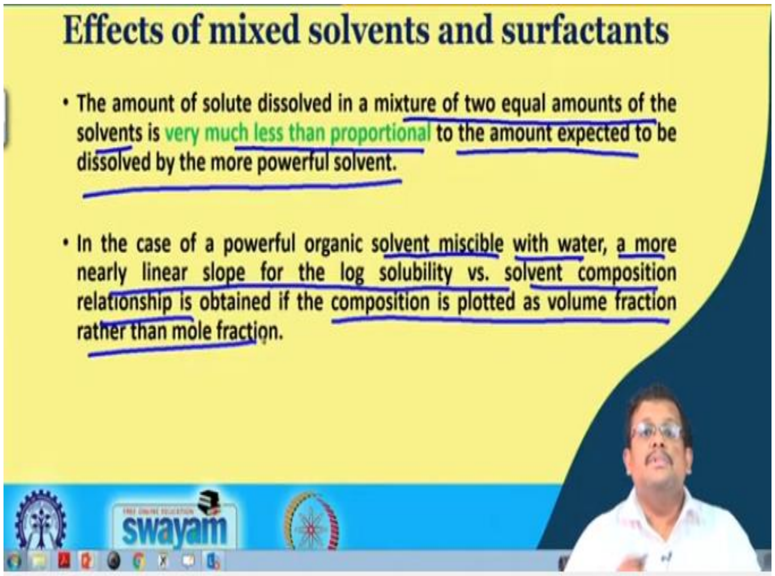

Now, remember that the amount of solute dissolved in a mixture of 2 equal amounts of solvents, let us consider there are 2 equal amounts of solvents, the amount of solute dissolved in this mixture of 2 equal amounts of solvents is very much less than proportional to the amount expected to be dissolved by the more powerful solvent. So, obviously when the third substance is expected to produce high solubility in that in a particular solvent, when we are mixing to the you know those 2, you know mixing that solvent to the that is with another solvent with an equal amount.

Then the solubility of the third substance gets you know substantially you know reduced okay, now in the case of a powerful organic solvent miscible with water, a more nearly linear slope for log solubility versus solvent composition relationship is obtained if the composition is plotted as a volume fraction rather than mole fraction. So, if you plot the composition in terms of a volume fraction as compared to the mole fraction.

We will see a more nearly linear slope for the logs solubility and solvent composition relationship and what is a precondition; the precondition is there is a powerful organic miscible solvent with water so, this is the relationship again effects of mixed solvents and surfactants.

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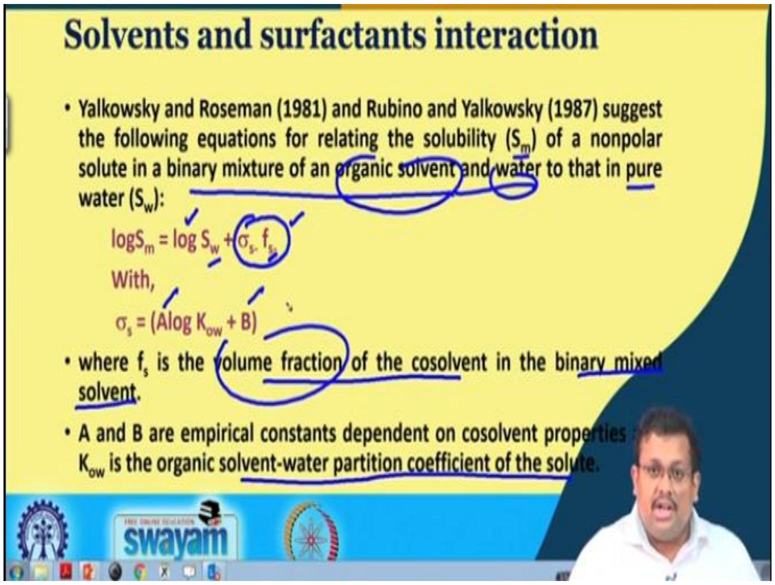

So, if we consider more details about the solvents and surfactants interaction, we will see that these 2 scientists; Yalkowsky and Roseman in 1981 and Rubino and Yalkowsky 1987, suggest that the following equation for relating the solubility. If we consider the solubility as Sm, then they have proposed this equation which basically relates the solubility of a nonpolar solute in a binary mixture of an organic solvent and water.

So, in this binary solvent, in this binary you know, in this mixture of solvent is basically a binary mixture of an organic solvent and water to that in pure water. So, if we consider the solubility of that particular substance in pure water is Sw. So, we get this relationship, so logarithm of solubility of a nonpolar solute in a binary mixture is basically the summation of its solubility in pure water plus this term.

Again, the solubility of a nonpolar solute in a binary mixture of organic solvent and water can be express in terms of a summation of its solubility in pure water plus this term, where this sigma s is basically, you know it is basically a log of you know it can be denoted by this A log Kow plus B, where fs is the volume fraction of the cosolvent in the binary mixed solvent. So, here this fs is basically the volume fraction of the cosolvent in the binary mixed solvent.

And the sigma s is basically this term; A log Kow + B, now here these A and B are the empirical constant depending on the cosolvent properties and Kow is the organic solvent water partition coefficient of the solute, we have discuss already the partition coefficient, okay. So, again let me repeat this thing; if a nonpolar solute, you know is dissolving in a binary mixture of an organic solvent and water.

Then its solubility in the binary solvent which is denoted by Sm can be represented by an expression which basically shows the summation of the solid solubility in pure water plus a product of the sigma s and fs, where sigma s is basically A log Kow + B, where A and B are the empirical coefficient and Kow is the organic solvent water partition coefficient of the solute and you know, fs is the volume fraction of the cosolvent in the binary mixed solvent, so this basically shows the solubility of a nonpolar solute in a binary mixture of 2 different solvents, okay.

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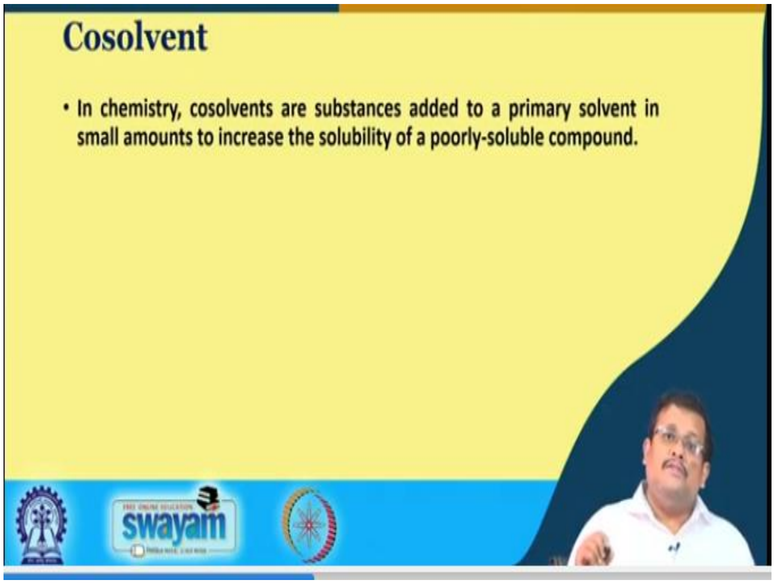

So, we have talked about a thing called cosolvent in the relationship because if you go back, you see that A and B are empirical constant depend on cosolvent properties, okay. So, what is cosolvent? Now, in chemistry, cosolvents are substances added to primary solvent in small amounts to increase the solubility of a poorly soluble compound. So, again cosolvents are substance added to the primary solvent in a small amount to increase the solubility of a poorly soluble compound.

So, in a binary mixture, if let us consider that a you know, here we are talking about nonpolar solute, so nonpolar solute will be less soluble in water. So, to increase their solubility, if we add some organic solvent in the water and creating a binary mixture, then these organic solvent will be called as a cosolvent, okay. So, I think that the concept of cosolvent is now clear.

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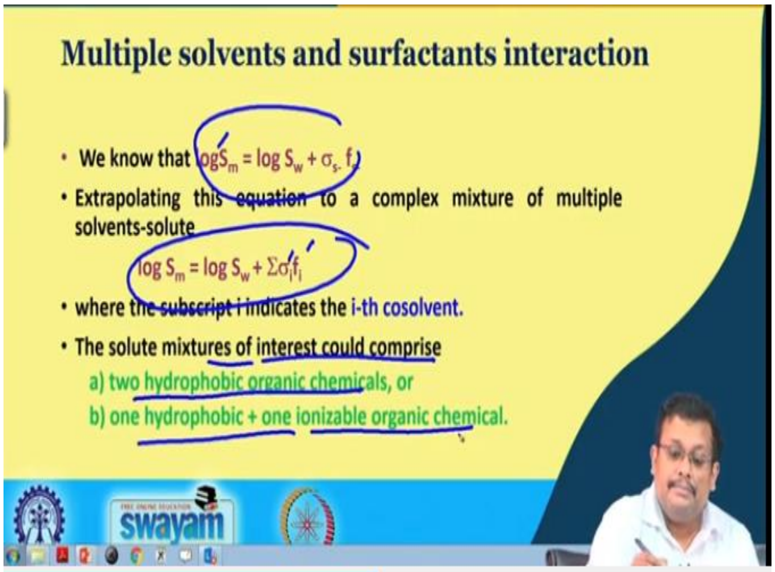

Now, let us see the multiple solvents and surfactant interaction again, we know already from the previous relationship that logarithmic of; logarithm of Sm equal to log of Sw plus sigma s into fs. Now, if we extrapolate this equation to a complex mixture of multiple solvent solute, here we are considering the equation and we are extrapolating these equation to a complex mixture of multiple solvent, solute.

Then we will get this relationship that log Sm equal to log Sw plus summation of sigma I fi, where the subscript i indicates the ith cosolvent. Now, remember that the solute mixture of interest could be comprise of 2 hydrophobic organic chemicals in this case and 1 hydrophobic plus 1 ionisable organic chemical. So, in this condition when we are considering this equation here, we are considering complex mixture of multiple solvents and solutes.

So, solvents are already you know, multiple, solutes are also multiple, so when the solutes are multiple, we can assume that these comprise 2 hydrophobic organic chemicals or 1 hydrophobic plus 1 ionisable organic chemical, okay.

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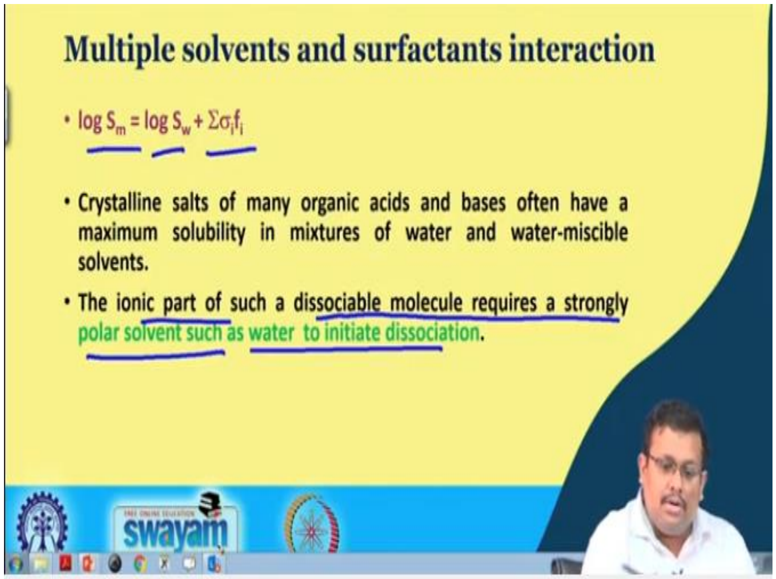

So, based on these equation that is log of Sm equal to log of Sw plus summation of sigma i fi, which in see that crystalline salts of many organic acids and bases often have a maximum solubility in mixtures of water and water miscible solvents. So, again crystalline salts of many organic acids and bases often have a maximum solubility in mixture of water and water miscible solvents.

So, the ionic part of such a dissociable molecule requires a strongly polar solvent such as water to initiate the dissociation. So, here you can see it is a crystalline salts of many organic acids, so basically that contained some ionic part and dissolution of this ionic part requires a strongly polar solvent like water. So, water is a polar solvent you know, most of the organic solvents are nonpolar. So, for dissolution of these crystalline salts which are ionic in nature, we need a strongly polar solvents like water to initiate the dissolution or dissociation, okay, alright.

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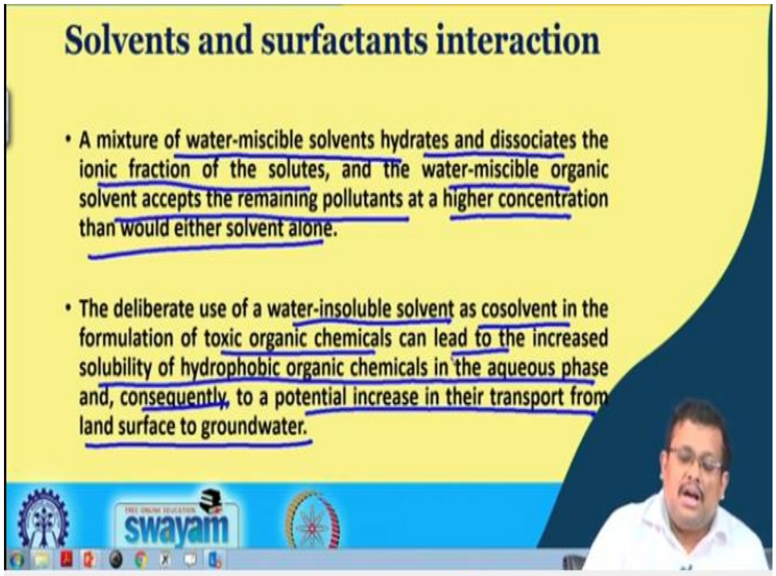

So, the mixture of water miscible solvents hydrates and dissociates the ionic fraction of the solutes, so again a mixture of water miscible solvents hydrates and dissociates the ionic fraction of the solutes, as we have talked in the last slide and the water miscible organic solvent accept the remaining pollutant at a higher concentration than would either solvent alone. So, if there is a mixture of water miscible solvents, they hydrates and dissociates the ionic fraction of the solutes and the water miscible organic solvents accept the remaining pollutants at higher concentration that would either solvent you know alone.

Now, the deliberate use of water insoluble solvent as cosolvent in the formulation of toxic organic chemicals can lead to the increase solubility of hydrophobic organic chemicals in the aqueous phase and consequently, to a potential increase in the transport from land surface to ground water. So, this is very, very important as far as their movement of this toxic chemical are concern.

So, if we deliberately use the water insoluble solvent as a cosolvent in the formulation of a toxic organic chemical that can lead to the increase solubility of hydrophobic organic chemicals in the aqueous phase and as a result, they can move from one place to another place increasing their transport, so that is very, very; you know, very, very problematic as far as the environmental fates are concerned.

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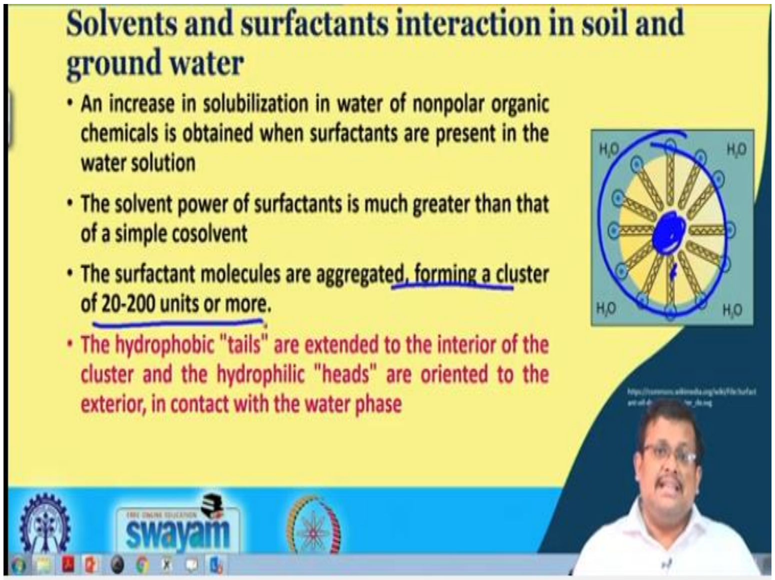

So, an increase in solubilisation in water of nonpolar organic chemicals is obtained when the surfactants are present in the water solution obviously, an increase in solubilisation of water of nonpolar organic chemicals is obtained when the surfactants are present because that is their function, they are acting as a dispersant obviously, how? Because they have this hydrophobic tail, this hydrophobic tail basically, attach to this nonpolar organic chemical.

Here some are nonpolar organic chemical and here, basically this is the hydrophilic part which is extent towards the water, so their solubility as a whole increase due to the presence of this dispersant. Now, the solvent power of the surfactants is much greater than that of a simple cosolvent obviously, because of their structure and their: you know, of their solubility mechanism.

Now, the surfactant molecules are aggregated forming a cluster of 20 to 200 units or more, so if you see the surfactant molecules, this surfactant molecules are aggregated they can form a cluster of 20 to 200 units or more. Remember that this hydrophobic tails are extended to the interior of the cluster and hydrophobic heads; hydrophilic heads are oriented to the exterior in contact with the water phase.

So, this is how this surfactant as a dispersing agent increase the movement or solubility of this toxic organic chemicals in the water and helps in their movement from one part to another part of the environment.

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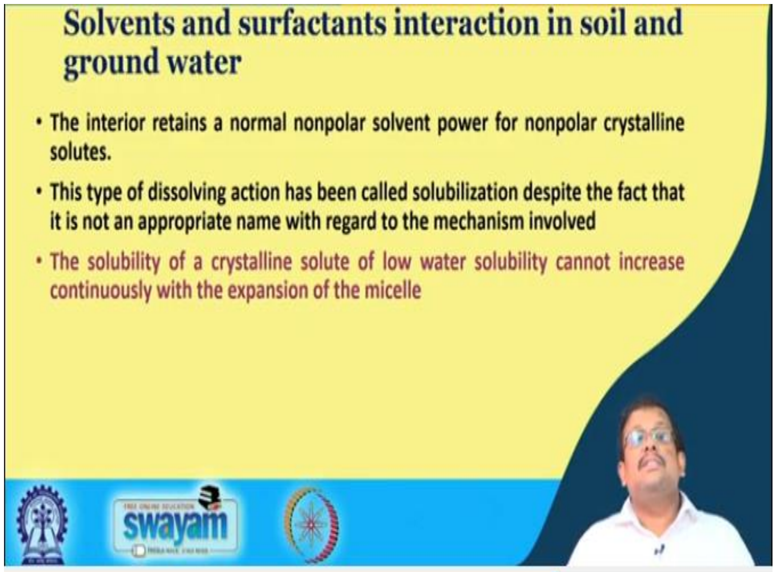

So, we know that the interior remains in the surfactant, you know this surfactant, the interior retains a normal nonpolar solvent you know, for nonpolar crystalline you know, solvent part for nonpolar crystalline solutes and this type of dissociation action has been called solubilisation despite the fact that it is not an appropriate name with regard to the mechanism involved. Now, remember that the solubility of a crystalline solute of low water solubility cannot increase continuously with the expansion of the micelle or the particle, okay.

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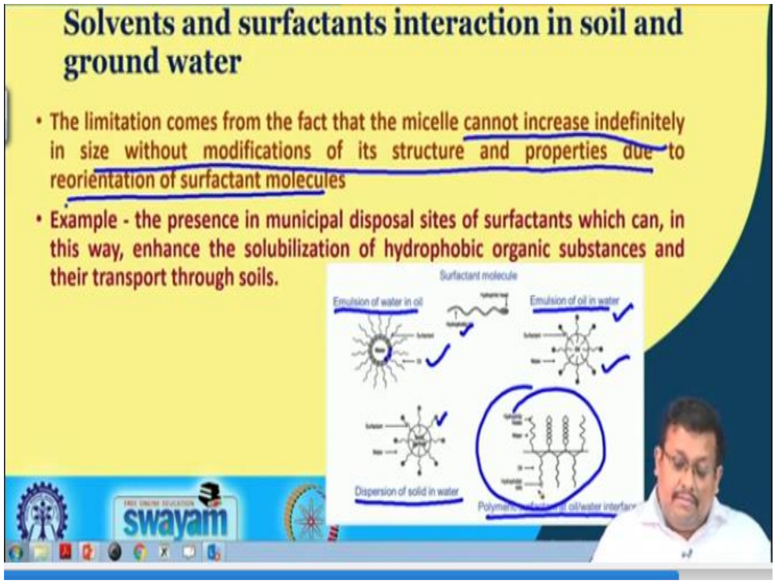

So, if we see the interaction; the limitation, so the limitation basically comes from the fact that the micelle cannot increase infinitely in size without modification of its structure and properties due to the reorientation of the surfactant molecule. So, you can see here you know, this is water which is in aqueous phase and if this is in surfactant, this surfactant has these hydrophilic ends which are surrounding the aqueous phase or water.

And they have hydrophobic tails also which are in the vicinity of the oil, so ultimately it is producing emulsion of water in oil. So, when we consider dispersion of solid in water, you can see the solid particles and they are basically, again the surfactant molecule, the solid particles are basically are covered by this hydrophobic tail and the hydrophilic part is extended towards the aqueous phase and ultimately this forming the dispersion of solid in water.

And you can also see surfactant molecule as a hydrophilic head you know and hydrophobic tail we have discussed it and you know, when we talk about the emulsion of this is basically, emulsion of water in oil and this is basically, emulsion of oil in water, so we have already seen that in our previous slide, okay and this basically polymeric surfactant at oil and water interface. So, if this is a water and this is the oil, so basically it has a hydrophobic tail and hydrophobic head.

So, basically when they polymerise, they produce polymeric surfactant at you know, oil water interfaces, you can see in this picture. Now, example for you know, the presence of municipal disposal sites of surfactants which can in this way, enhance the solubilisation of hydrophobic organic substances and their transportation through the soils. We have already discussed that how these; you can see here, this disperse solid in water can be mediated through the surfactants, emulsion of oil in water can be maintained by the surfactants.

Emulsion of oil in water can be maintained by the surfactants and also you know, so basically to this reaction, the presence of these surfactants you know, enhances the solubilisation of hydrophobic organic substances, sometimes they are toxic in nature and their transporting through the soil. So, as far as the movement of different hydrophobic toxic organic chemicals are concern in the environment, the impact of surfactants are very, very you know important and we cannot neglect that.

So, obviously that is why the surfactants are consider as one of the major environmental pollutant because of this, of the dispersing characteristics, okay they can enhance the solubility of the harmful toxic organic chemicals which are nonpolar in nature because since they are nonpolar, they cannot mix in this polar water. So, for their mixture in the polar water and to form their emulsion in the water, they require the help of the surfactants and in this way, surfactant is not beneficial for the environmental point of view.

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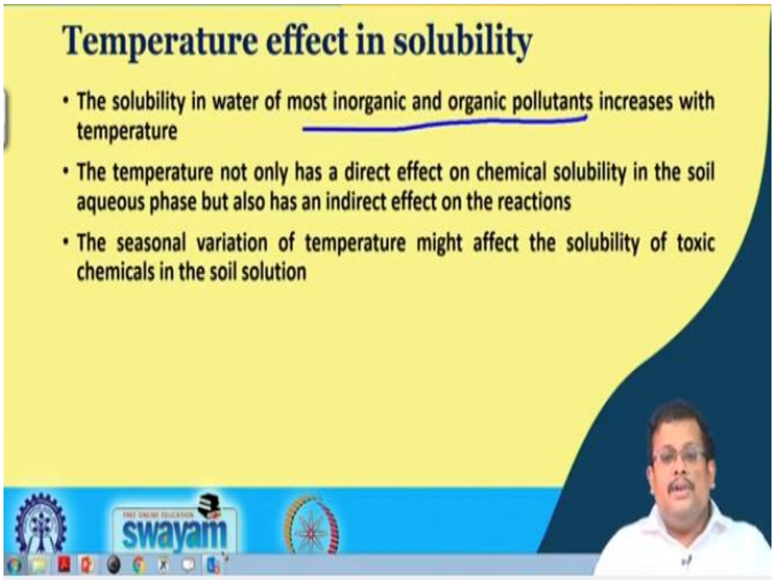

So, what are the importance of temperatures in the solubility of a solute? So, the solubility in water of most inorganic and organic pollutants increases with temperature, now the temperature not only has a direct effect on chemical solubility in the soil aqueous phase but also has an indirect effect on the reactions. So, we know, what we know; we know that the solubility of both inorganic and organic pollutants increases with the temperature.

So, irrespective of inorganic nature of organic nature, the solubility of the pollutants increases with the temperature and the temperature not only has a direct effect on chemical stability; chemical solubility in the soil aqueous phase but also has an indirect effect on its reactions and third is a seasonal variation of temperature; seasonal variation of temperature might affect the solubility of toxic chemicals in the soil solution.

So, these are the 3 important points and the last point again shows, you know when they obviously the change of season produces the change of temperature which also affects the solubility of toxic chemicals in the soil solution, when there is an increase in temperature or surrounding temperature, there is the increase in solubility of the toxic chemical. So, in this lecture we have discussed a very important aspect.

We have discussed the interaction between the surfactant and the pollutants and we have seen that due to their typical structure, this surfactants can access a dispersing agent for toxic organic chemicals and most of the organic chemicals are nonpolar in nature, some of; so for solubility for nonpolar organic chemicals, the surfactant plays a very important role and that is why the surfactants are considered as environmentally you know, environmental pollutant.

And also, we have seen the definition of cosolvent and how the mixture of different solvents impact the solubility of a third product, either it is you know organic or inorganic nature. So, these solubility dynamics impact greatly the movement and of different environmental pollutants and as far as the; you know, and these dynamics are very, very important when you consider the pesticide movement and other organic pollutants which are present in our natural environment.

So, we have covered this important aspect and also at the last, we have talked about the temperature effects in the solubility, so let us wrap of our lecture here. In the next lecture, we will be talking more about you know, acid rain and the other you know, important environmental consequences like saline alkali soils and how they impact the gypsum solubility and so many other things. So, let us wrap our lecture here and let us meet in our next lecture to discuss this interaction between soil pollutants and soil solution in more details, thank you very much.