Quantitative Methods in Chemistry

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Lecture-35

Analytical Separations-Multistage Extractions Part 02

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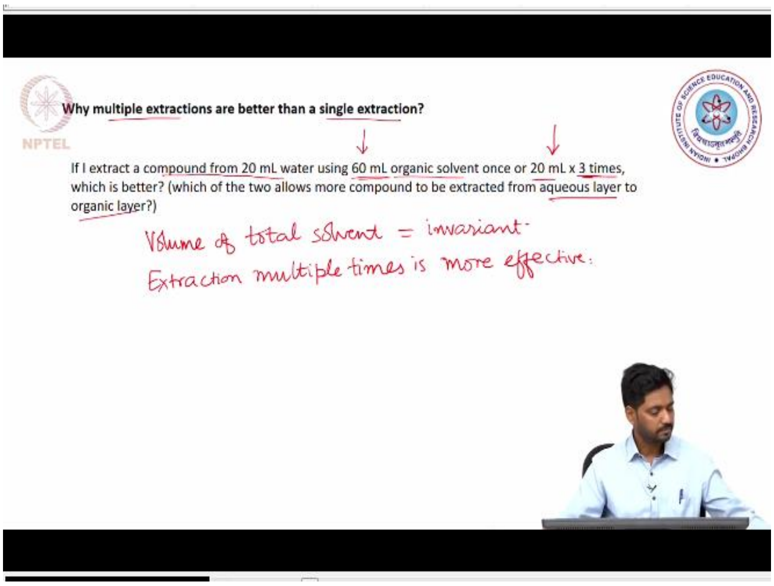

Why multiple extractions are better than a single extraction?

If I extract a compound from 20 mL water using 60 mL organic solvent once or 20 mL x 3 times, which is better? (which of the two allows more compound to be extracted from aqueous layer to organic layer?)

Volume of total solvent = invariant.

Extraction multiple times is more effective.

So, now let us move to a question as to whether multiple extractions are better than a single extraction. A simple way to rephrase this problem will be that I have a compound that is dissolved in 20 ml water and I am undertaking a solvent-solvent extraction of this compound using a particular organic solvent for example, ethyl acetate and we use 60 ml of ethyl acetate in 1 go and undertake an extraction or we can do extraction 3 times with 20 ml ethyl acetate each time.

And the question in front of us is that which of these 2 protocols is better or is more efficient in extracting the compound from aqueous layer to the organic layer. I will give you the answer to begin with and then I will try to explain you mathematically how this happens. So, what is well known is that the second condition were we are undertaking extractions multiple times is much more efficient than the first condition where the extraction is happening only once.

Even though the total volume of the solvent that we have implied is same in both the cases. So, volume of the solvent is invariant in both the conditions but extraction multiple times is considered or is more effective. Now, let us see how this happens mathematically.

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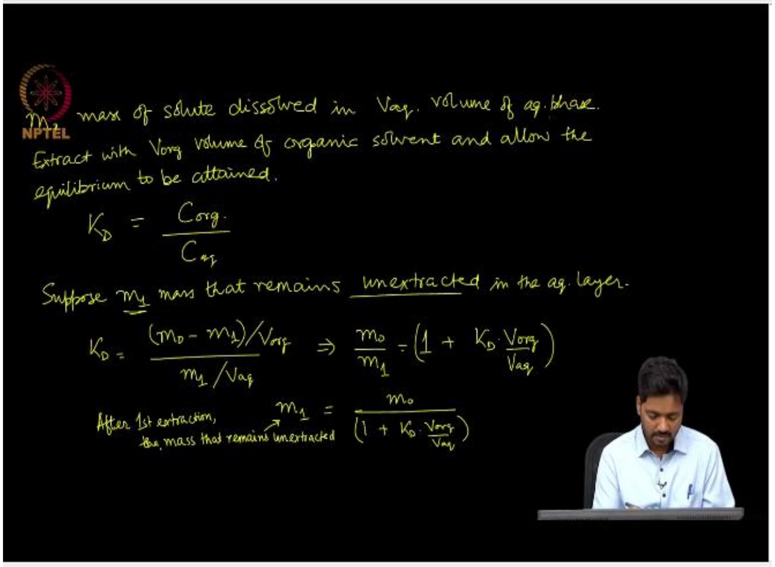

m_0 mass of solute dissolved in $V_{aq.}$ volume of aq. phase.

Extract with V_{org} volume of organic solvent and allow the equilibrium to be attained.

$$K_D = \frac{C_{org.}}{C_{aq}}$$

Suppose $\underline{m_1}$ mass that remains $\underline{\text{unextracted}}$ in the aq. layer.

$$K_D = \frac{(m_0 - m_1)/V_{org}}{m_1/V_{aq}} \Rightarrow \frac{m_0}{m_1} = \left(1 + K_D \cdot \frac{V_{org}}{V_{aq}}\right)$$

After 1st extraction, the mass that remains unextracted

$$m_1 = \frac{m_0}{\left(1 + K_D \cdot \frac{V_{org}}{V_{aq}}\right)}$$

So, let us go to the board and let us start with a presumption that we have initially M 0 mass of solute which is dissolved in V aqueous volume of aqueous phase. Now, we extract it with V organic volume of organic solvent and allow the equilibrium to be attained. Now, when we do that, we will define the K D as equal to the concentration of the analyte in organic solvent divided by it is concentration in the aqueous V.

Now m 1 is the mass that remains and extracted. So, please note that m 1 is the mass that we consider to be remaining unexpected. So, we can define K D as equal to m 0 minus m 1, this is the amount that is getting transferred into the organic layer. This will be divided by the V organic because we are extracting it with this volume of the organic solvent and this will be divided by m 1 which is the mass that remains un extracted in the aqueous layer divided by v aqueous which was the volume of the aqueous layer.

And when we rearrange this, we get m 0 by m 1 is equal to 1 plus K D into V org by v aqueous and finally, rearranging it gives us the un extracted mass as equal to the initial mass of the solute divided by 1 plus K D V organization by V aqueous. So, this is the mass that remains unextracted after first extraction, that is given by m 1 and that is equal to m 0 by 1 plus K D into V org by V aqueous.

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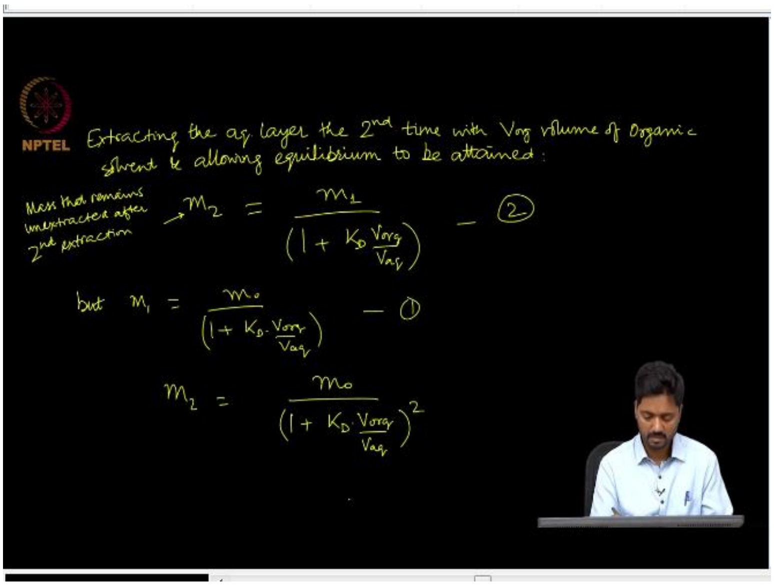

Extracting the aq. layer the 2nd time with Vorg volume of organic solvent & allowing equilibrium to be attained:

Mass that remains unextracted after 2nd extraction → $m_2 = \dfrac{m_1}{\left(1 + K_D \dfrac{V_{org}}{V_{aq}}\right)}$ — ②

but $m_1 = \dfrac{m_0}{\left(1 + K_D \cdot \dfrac{V_{org}}{V_{aq}}\right)}$ — ①

$$m_2 = \frac{m_0}{\left(1 + K_D \cdot \frac{V_{org}}{V_{aq}}\right)^2}$$

Now, suppose we undertake the same extraction the second time what we get is so extracting the aqueous layer second time with V org volume of organic solvent and allowing equilibrium to be attained. This gives us the m 2 now is equal to m 1 divided by 1 plus K D V organization by V aqueous. So, please note here that in the second extraction, we will be initially dealing with the m 1 mass of the analyte present unextracted after the first extraction.

And that is extracted with V org volume of organic solvent. So, the mass that remains unextracted after second extract is given as m 2 and we have already seen that m 1 is nothing but m 0 by 1 plus K D V org by V aqueous. So, when we insert this value of m 1 into the equation 2 we get m 2 is equal to m 0 by 1 plus K D V org by V aqueous square.

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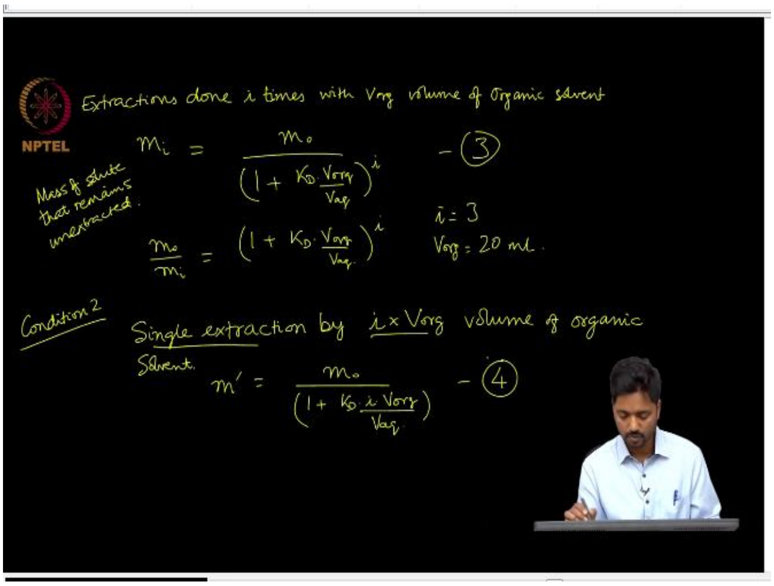

Extractions done i times with Vorg volume of organic solvent

Mass of solute that remains unextracted.

$m_i = \dfrac{m_0}{\left(1 + K_D \cdot \dfrac{V_{org}}{V_{aq}}\right)^i}$ — ③

$\dfrac{m_0}{m_i} = \left(1 + K_D \cdot \dfrac{V_{org}}{V_{aq}}\right)^i$

$i = 3$

$V_{org} = 20$ ml.

Condition 2

Single extraction by $i \times V_{org}$ volume of organic solvent.

$m' = \dfrac{m_0}{\left(1 + K_D \cdot \dfrac{i\,V_{org}}{V_{aq}}\right)}$ — ④

Now, if we keep doing this extraction for i times with V organic volume of organic solvent then what we have is that the mass that remains unextracted after these i repetitions of extractions is given by m i is equal to m 0 divided by 1 plus K D into V org by V aqueous to the power of r. So, this becomes the mass of solute that remains unextracted. Now, we can rewrite this as m 0 by m i equal to 1 plus K D V organization by V aqueous to the power of i.

Similarly, if we are doing in condition 2 we are doing a single extraction by i into V org volume of organic solvent. So the example that we were discussing this i into V org will be equal to 60 ml of the organic solvent, while in the condition 1, we were extracting 3 times with the V org of 20 ml. So, the total volume that is being implied for the organic solvent remains constant in condition 1 and condition 2.

Now, when we do this single extraction by i into V org volume of organic solvent, we will consider the mass that remains unextracted as m dash is equal to m 0 by 1 plus K D into i into V organization, that is the total volume of organic solvent that has been used now, divided by V aqueous.

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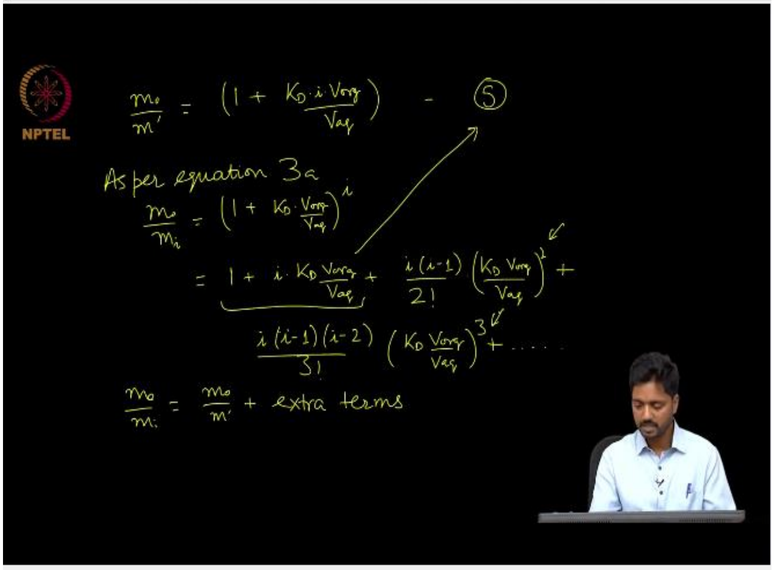

$$\frac{m_0}{m'} = \left(1 + \frac{K_D \cdot i \cdot V_{org}}{V_{aq}}\right) \quad - \quad ⑤$$

As per equation 3a

$$\frac{m_0}{m_i} = \left(1 + K_D \cdot \frac{V_{org}}{V_{aq}}\right)^i$$

$$= \underbrace{1 + i \cdot K_D \frac{V_{org}}{V_{aq}}} + \frac{i(i-1)}{2!}\left(\frac{K_D V_{org}}{V_{aq}}\right)^2 + \frac{i(i-1)(i-2)}{3!}\left(K_D \frac{V_{org}}{V_{aq}}\right)^3 + \ldots$$

$$\frac{m_0}{m_i} = \frac{m_0}{m'} + \text{extra terms}$$

Now, this equation 4 can be written as m 0 by M dash is equal to 1 plus K D into i into V org by V aqueous and this will consider as equation 5. So, what we see here is that as per equation 3a is what we define this equation as, as per equation 3a m 0 by m i is equal to 1 plus K D V org by V aqueous to the power of i. And if this is expanded, this becomes as 1 plus i into K D V org by V aqueous plus i into i minus 1, 2 factorial into K D V org by V aqueous squared.

And the other term here would be i into i minus 1 and i minus 2 by 3 factorial multiplied by K D V org by V aqueous to the power of 3, so on and so forth. So, if we see the first 2 terms of this expansion, this is nothing but m 0 by m dash as shown in equation 5. So, in other words, m 0 by m i is equal to m 0 by m dash, which was the mass fraction that was remaining unextracted after the single extraction plus extra terms, which are given as the square and the cube terms.

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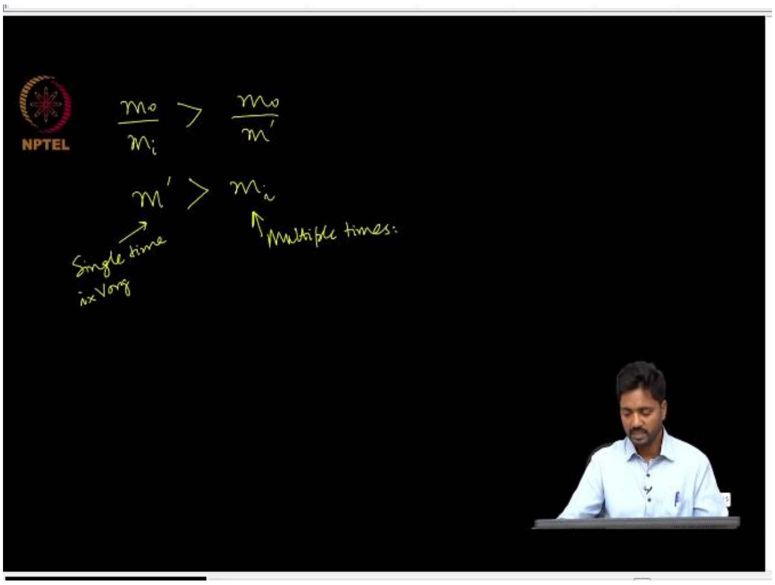

$$\frac{m_0}{m_i} > \frac{m_0}{m'}$$

$$m' > m_i$$

So, what we see here is that m 0 by m i will turn out to be greater than m 0 by m dash or in other words when we rearrange this m dash will turn out to be greater than m i. So, the extraction single time with i into V org volume of the organic solvent results in more amount of solute that remains unextracted in the organic layer compared to this same volume of organic solvent used multiple times. Now, let us look at this from a real examples perspective.

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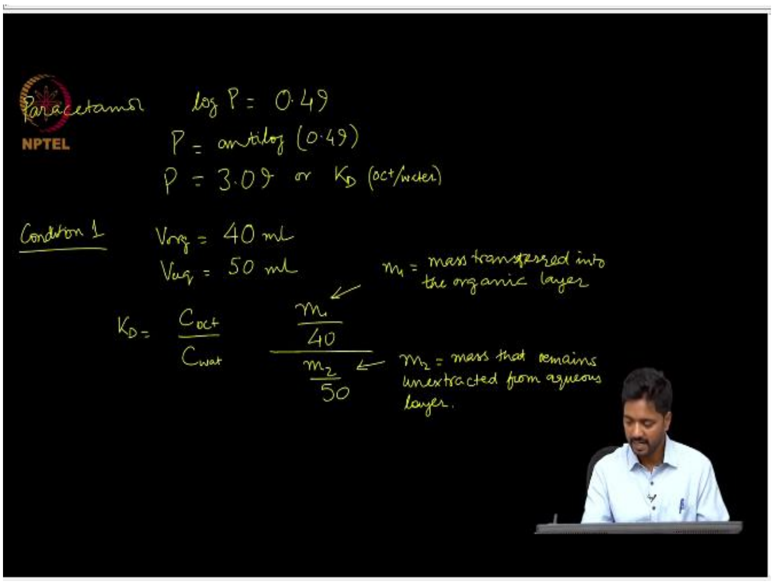

Paracetamol $\log P = 0.49$

$P = \text{antilog}\,(0.49)$

$P = 3.09$ or K_D (oct/water)

Condition 1

$V_{org} = 40$ ml

$V_{aq} = 50$ ml

$$K_D = \frac{C_{oct}}{C_{wat}} \qquad \frac{\frac{m_1}{40}}{\frac{m_2}{50}}$$

m_1 = mass transferred into the organic layer

m_2 = mass that remains unextracted from aqueous layer.

So, for that I have taken the example of paracetamol and this is of course a very commonly employed drug and I am sure all of us would have taken paracetamol at some point of time in our lives and paracetamol is known to have a log P value of 0.49, this is literature value. And what we need to consider is the question that is given in the example here.

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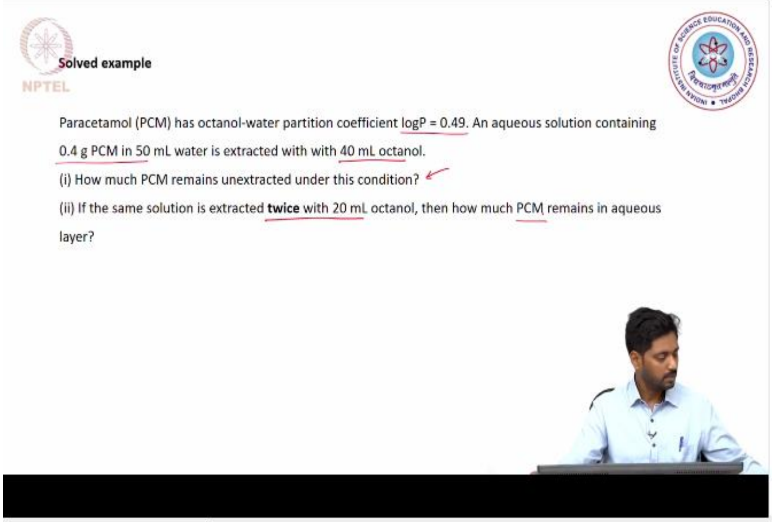

Solved example

Paracetamol (PCM) has octanol-water partition coefficient logP = 0.49. An aqueous solution containing 0.4 g PCM in 50 mL water is extracted with with 40 mL octanol.

(i) How much PCM remains unextracted under this condition?

(ii) If the same solution is extracted **twice** with 20 mL octanol, then how much PCM remains in aqueous layer?

That paracetamol has the log P value of 0.49 and an aqueous solution containing 0.4 gram of paracetamol in 50 ml is extracted with 40 ml octanol. So, the question for us is if we use this 40 ml octanol in 1 go, how much is the paracetamol that remains extract unextracted and the other condition that we will employ is where we use 2 extractions with 20 ml extract each. So, the total volume still remains 40 ml of extract that is used.

In this condition, how much of the paracetamol remains in that aqueous layer. So, let us try to solve this question by going to the board. So, we are given log P value as 0.49 and from there, we can calculate the P value is the antilog of 0.49 and this turns out to be 3.09 as the P value or in our parlance this will be the K D value as per the discussion that we are having. KD value specifically for the partitioning between octanol and water.

So, here condition 1 tells us that we have the V org as equal to 40 ml and the V aqueous is equal to 50 ml. Now, K D is defined as the concentration of PCM in octane all by the concentration of the drug in aqueous medium or water and this will depend upon the mass that gets transferred into the octanol versus the mass that remains in the organic layer. So, suppose m 1 is the mass that gets transferred into the octanol the volume of octanol in this case is 40 ml.

And the amount that remains unextracted into the aqueous layer is m 2 that is dissolved in 50 ml of the aqueous layer or the water. So, just to repeat m 1 is equal to the mass transferred into the organic layer and m 2 is equal to mass that remains unextracted from aqueous layer.

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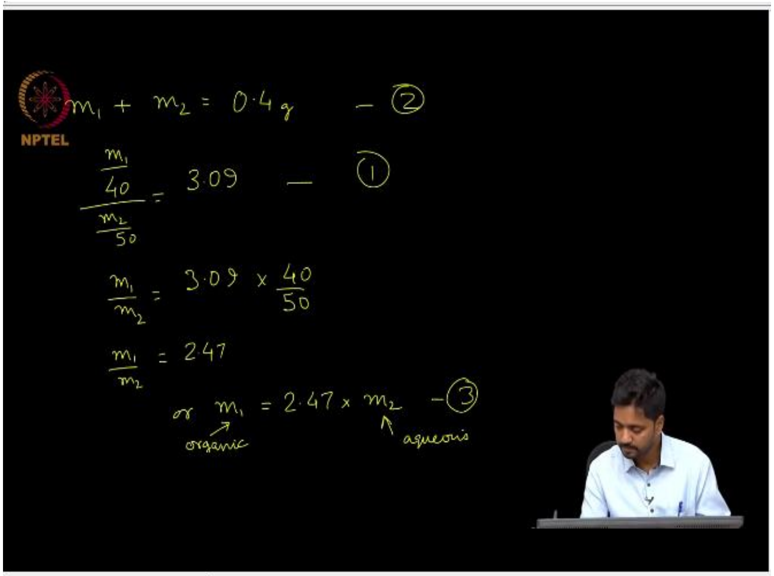

$$m_1 + m_2 = 0.4\,g \quad — ②$$

$$\frac{\frac{m_1}{40}}{\frac{m_2}{50}} = 3.09 \quad — ①$$

$$\frac{m_1}{m_2} = 3.09 \times \frac{40}{50}$$

$$\frac{m_1}{m_2} = 2.47$$

$$\text{or } \underset{\substack{\nearrow \\ \text{organic}}}{m_1} = 2.47 \times \underset{\substack{\uparrow \\ \text{aqueous}}}{m_2} \quad — ③$$

Now, what is also clear from this equation from the mass balancing equation is that m 1 plus m 2 is equal to 0.4, which is the grams of drug which was originally present in the medium. So, we will solve these 2 equations, we see that m 1 by 40 divided by m 2 by 50 is equal to the K D value, which is nothing but 3.09. Now, when we solve this out, we get m 1 by m 2 is equal to 3.09 into 40 by 50.

And this turns out to be 2.47 or m 1 is 2.47 times m 2. Now, what is important in this equation, which we can call as equation 3 is, so, this is our equation 2 and this is our equation 1. So, from equation 3 it is very clear that more amount of the drug gets partitioned into the organic layer and much less remains in the aqueous layer which is given by m 2.

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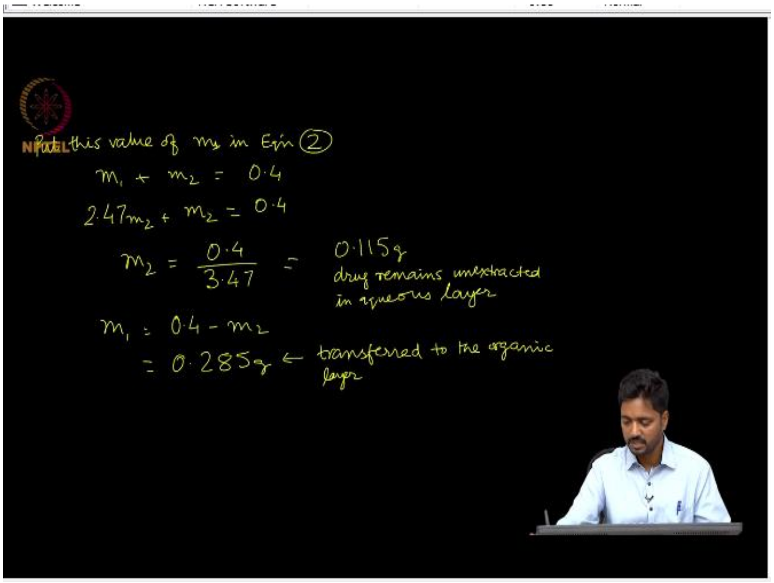

Put this value of m_1 in Eqn ②

$$m_1 + m_2 = 0.4$$

$$2.47 m_2 + m_2 = 0.4$$

$$m_2 = \frac{0.4}{3.47} = 0.115\,g$$

drug remains unextracted in aqueous layer

$$m_1 = 0.4 - m_2$$

$$= 0.285\,g \leftarrow$$

transferred to the organic layer

So, when we plug in this value of m 1 into equation 2, which was seeing that m 1 plus m two we get 2.47 m 2 plus m 2 is equal to 0.4. And this solves m 2 as 0.4 divided by 3.47. And that turns out to be equal to 0.115 grams. So, this much drug remains unextracted in aqueous layer. Now, how much drug gets transferred. That is simple that is m 1 is nothing but 0.49 minus m 2, and that turns out to be equal to 0.285 grams.

So, we clearly see that a major chunk of the drug has been transferred to the organic layer by a single extraction with 40 ml of the organic solvent in this case 1 octanol. Now, the other condition 2 was that we extracted it multiple times.

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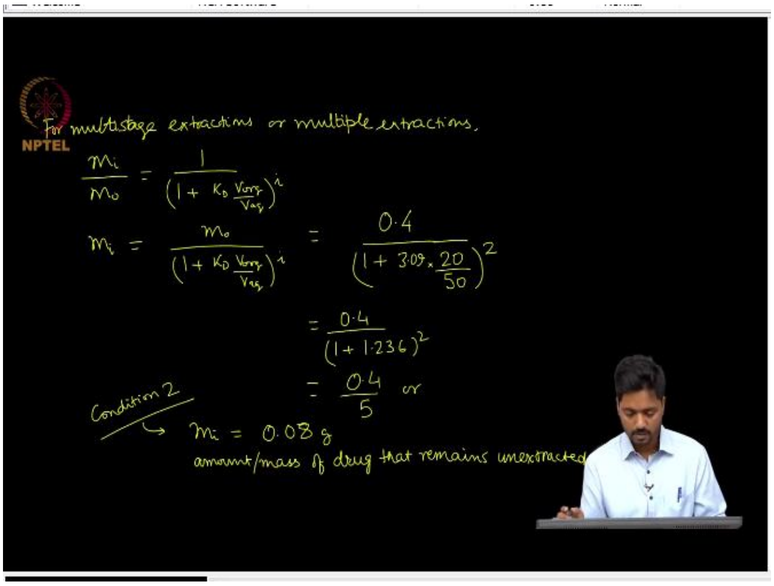

For multistage extractions or multiple extractions.

$$\frac{m_i}{m_0} = \frac{1}{\left(1 + K_D \frac{V_{org}}{V_{aq}}\right)^i}$$

$$m_i = \frac{m_0}{\left(1 + K_D \frac{V_{org}}{V_{aq}}\right)^i} = \frac{0.4}{\left(1 + 3.09 \times \frac{20}{50}\right)^2}$$

$$= \frac{0.4}{(1 + 1.236)^2}$$

$$= \frac{0.4}{5} \text{ or}$$

Condition 2 $\hookrightarrow$ $m_i = 0.08\,g$

amount/mass of drug that remains unextracted

And we have already seen in this lecture that under these conditions for multistage extractions or multiple extractions. The amount that remains an extracted is given by this equation or in other words, the amount that remains unextracted is given by m 0 divided by 1 plus K D V org by V aqueous to the power of i. Now, here we have all these numbers, m 0 is the initial mass of the drug that was present in the medium which is 0.4 grams.

And K D value is 3.09 V org in this case is 20 ml and we aqueous is 50 ml. Finally, we are extracting this twice, so, i is 2 here and when we solve this out, this becomes as 0.4 divided by 1 plus 1.236 whole squared. And this ultimately becomes as 0.4 divided by 5 or finally, m i is equal to 0.08 grams. So, in condition 2 the amount that remains amount or mass of drug that remains unextracted is 0.08 grams. And if we look back the amount that was remaining unextracted in condition 1 was 0.115 grams.

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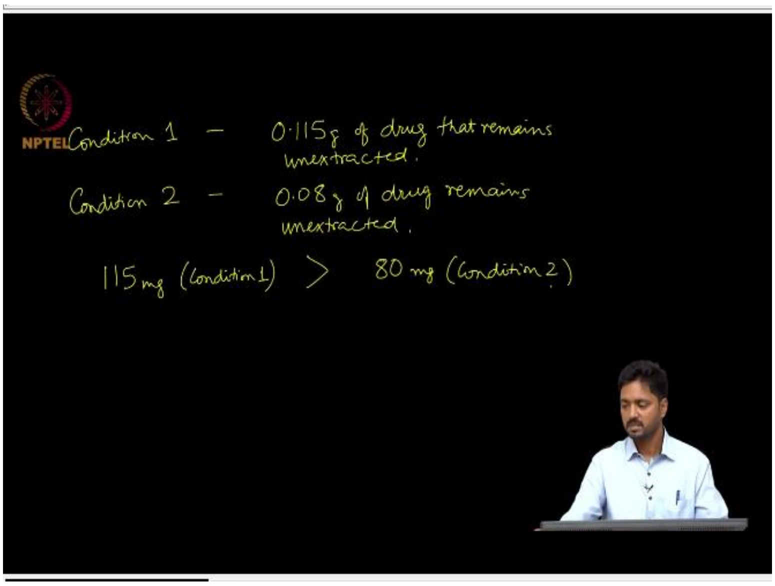

Condition 1 – 0.115g of drug that remains unextracted.

Condition 2 – 0.08g of drug remains unextracted.

115 mg (Condition 1) > 80 mg (Condition 2)

So, condition 1 of single extraction had 0.115 grams of drug that remains and unextracted on the contrary, during the multi stage or multiple extractions in condition 2 only 0.08 grams of drug remains unextracted. So, if you write it in terms of milligrams 115 milligram is unexpected in condition 1 while only 80 milligrams is remaining unextracted in condition 2. So, obviously, we see that condition 2 of multiple extractions results in much less amount of the drug remaining unextracted compared to single extraction.

So, I hope this concept is clear to you now, that a multistage extraction is indeed, a more effective method of extracting organic compounds into the organic layer from the aqueous layer. And this efficiency will depend upon the equilibrium constant or the partition coefficient that we have already discussed. Plus, it will also depend upon ensuring that the equilibrium is attained by undertaking the extractions for relevant period of times.

So, if we are patient during the extractions the extractions will be more efficient and by doing the extractions multiple times, we can very effectively increase the efficiency of extractions. Now, in the next class, we will be studying about variables chromatographic techniques. So we will come back in the next class. Thank you.