

**Interfacial Engineering**  
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**Lecture-19**  
**HLB guidelines; Debye plot**

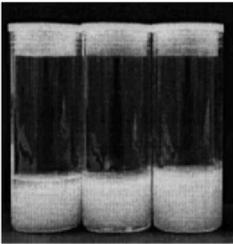
**HLB; Debye plot; light scattering; non-ionic surfactants**

Welcome back.

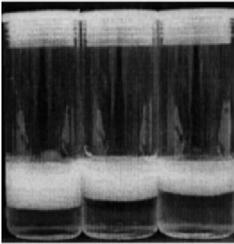
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**Hydrophile-Lipophile Balance (HLB)**

**W/O Emulsion**



**O/W Emulsion**



**Emulsions can be divided into two:**

- (1) W/O - Water is dispersed phase
- (2) O/W - Oil is dispersed phase

- Some surfactants stabilize W/O and some stabilize O/W.
- Most stable emulsion is formed when the surfactant has higher solubility in the continuous phase.

➤ Griffin (1949) developed a hydrophile-lipophile balance (HLB) method.

➤ Griffin made a HLB scale between 0-20.

Bancroft rule says that water-soluble surfactant should stabilize O/W emulsion and oil-soluble surfactant should stabilize W/O emulsion.

0 – 10 → *Lipophilic*                      10 – 20 → *Hydrophilic*



**The solubility of surfactant varies depending on HLB value**

In today's video lecture, we will explore the hydrophile-lipophile balance (HLB) guideline and the Debye plot. Following our discussion on these topics, we will proceed to the tutorial section, where we will solve problems related to the aggregation number and the critical packing factor. Based on the critical packing factor obtained from the problem, we can provide insightful comments. Let's begin.

Today, we will examine the hydrophile-lipophile balance, commonly referred to as the HLB number. This guideline is particularly useful when you want to stabilize oil-in-water emulsions or, conversely, water-in-oil emulsions. What determines the type of emulsion—whether it is oil-in-water or water-in-oil? As you know, surfactants are amphiphilic compounds consisting of both hydrophilic and hydrophobic groups.

Sometimes, the hydrophobic groups may be more dominant than the hydrophilic groups. In such cases, the given surfactant will stabilize water-in-oil emulsions. In these situations, the surfactants tend to maximize their exposure to the oil.

Because they would like to maximize their contact with the oil phase, in such cases, you can expect that they will stabilize water-in-oil emulsions. Alternatively, sometimes you might deal with surfactants that are more hydrophilic in nature. In these cases, you can expect that they will stabilize oil-in-water emulsions. The continuous phase will be the one in which the emulsifier is most soluble.

For instance, if it is a water-in-oil emulsion, you can say that the emulsifier is most soluble in the oil phase. This concept comes from the Bancroft rule, which states that the continuous phase will be the one in which the emulsifier is most soluble. Alternatively, you can also say that more water-soluble surfactants should stabilize oil-in-water emulsions, and those that are most oil-soluble will stabilize water-in-oil emulsions.

Now, the question is, what is the use of the HLB guideline? Griffin developed this HLB guideline, which is similar to the pH scale. The pH scale ranges from 1 to 14, and you know how pH behaves when it is less than 7 and when it is greater than 7. Similarly, Griffin developed the HLB scale between 0 and 20.

This means that when the HLB is very close to 0, it indicates that the surfactant is completely lipophilic or hydrophobic. When it is 20, it indicates that the surfactant is completely hydrophilic. In between these values, the surfactants will exhibit a mix or combination of both hydrophobic and hydrophilic properties.

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## Hydrophile-Lipophile Balance (HLB)



For non-ionic surfactants

$$HLB = 20 \times \left( \frac{M_h}{M} \right)$$

$M_h$  = Molecular weight of hydrophilic groups

$M$  = Molecular weight of the whole molecule

➤ Hydrophilic groups are usually polyhydric alcohol or ethylene oxide

Water soluble, when  $HLB > 10$

Oil soluble, when  $HLB < 10$

Mono oleic acid ester

Non-ionic surfactant

$$M_h = x \{9EO; (OCH_2CH_2)_9\}$$

$$M = 671$$

$$HLB = 20 \times \left( \frac{?}{671} \right) = ?$$

$$HLB = 20 \times \left( \frac{?}{671} \right) = 11.8$$

Application	HLB range
W/O emulsifier	4-6
O/W emulsifier	8-18
Wetting agents	7-9
Detergents	13-15
Solubilizing agents	15-18

Griffin, W. C. (1949). Classification of surface-active agents by "HLB". J. Soc. Cosmet. Chem., 1, 311-326.

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What Griffin has done is tabulate a range of HLB values for different applications. For example, if the HLB range of a given surfactant is between 4 and 6, you can say that this particular surfactant will most likely stabilize water-in-oil emulsions. On the other hand, surfactants with HLB values between 8 and 18 will stabilize oil-in-water emulsions. Wetting agents typically fall between 7 and 9, while detergents are usually between 13 and 15. Solubilizing agents are generally between 15 and 18.

Depending on this range, one can predict the type of emulsion or dispersion that a surfactant can stabilize. To calculate the HLB, Griffin's scale is used, which is primarily applicable to non-ionic surfactants. The formula involves the molecular weight of the hydrophilic group (denoted as  $M_h$ ) and the molecular weight of the whole molecule (denoted as  $M$ ). A multiplication factor of 20 is used to ensure that the calculated HLB is an integer between 0 and 20.

The rule is simple: if the HLB is greater than 10, the surfactant is more hydrophilic; if it is less than 10, it is more hydrophobic. I have provided an example for you to practice calculating the HLB. The answer will also be shown at the bottom.

In this example, we have a mono-oleic acid ester type of non-ionic surfactant. Here, ethylene oxide is the hydrophilic group, and the rest of the molecule is the hydrophobic backbone. We know that the molecular weight of the hydrophilic part is based on ethylene oxide, and the total molecular weight of the compound is 671. If you calculate the HLB, you will get a value of approximately 11.8.

Looking at this value in the table, it falls into the range for oil-in-water emulsifiers. Therefore, you can say that this particular surfactant, mono oleic acid ester, will most likely stabilize oil-in-water emulsions when used as an emulsifier.

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## Determination of average molecular weight of micelle using Debye plot



The light scattering data from aqueous solutions of dodecyltrimethylammonium bromide

$c \left( \frac{kg}{dm^3} \right)$	0.006	0.010	0.015	0.020	0.025	0.030
$\frac{H(c-c_{cmc})}{\tau} \times 10^4 \left( \frac{kmol}{kg} \right)$	0.83	1.07	1.63	2.02	2.35	2.76



□ Where  $\tau$  is Rayleigh scatter of solution,  $c$  and  $c_{cmc}$  are the concentration of surfactant and critical micelles.

$$\frac{H(c - c_{cmc})}{\tau} = \frac{1}{M} + 2B(c - c_{cmc})$$

Debye plot

$$H = \frac{4\pi n^2 \left( \frac{dn}{dc} \right)^2}{\lambda^4 N_A}$$

❖ Light scattering techniques are used to study the micelle size and shape of given surfactant.

Reference: Pallab Ghosh, NPTEL - Chemical En

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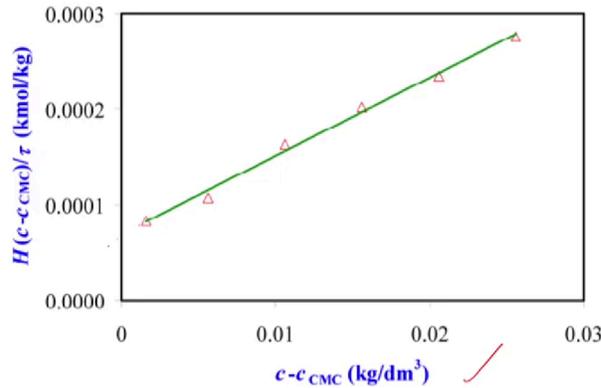
Next, we will look at the Debye plot. The Debye plot is obtained from light scattering data using a light scattering instrument. When you plot the Debye plot, with concentration on the x-axis and a specific parameter on the y-axis, you typically get a straight line. The slope of this line represents the second virial coefficient, denoted as  $2B$ , and the intercept is  $1/M$ , where  $M$  is the molecular weight.

This method was proposed by Debye and is commonly referred to as the Debye plot. The data for the plot can be obtained from light scattering experiments. The constant  $h/h$  is a function of the refractive index, wavelength, and Avogadro's number.

The quantity  $DN/DC$  can be obtained by constructing a graph of  $N$  versus concentration; the slope of this graph will be  $DN/DC$ . This data can often be provided by the manufacturer or obtained when operating a specific light-scattering instrument. When you plot these values on the y-axis, both  $c$  and  $\tau$  will vary depending on the concentration of the sample being analyzed. Based on this, you will get different y-values and x-values when plotting the data.

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## Determination of average molecular weight of micelle using Debye plot



Intercept  
 $\downarrow$   
 $\frac{1}{M} = 6.93 \times 10^{-5} \text{ kmol/kg}$

$M = 14430 \text{ kg/kmol}$

The molecular formula of dodecyltrimethylammonium bromide is  $C_{12}H_{25}N_3Br$ .  
 The molecular weight, therefore, is 308. Therefore, the aggregation number of the micelle is 47.

Reference: Pallab Ghosh, NPTEL - Chemical Engineering

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In this fashion, you will obtain a straight line, and the slope of the line will give you the second virial coefficient. However, what is important for us in this plot is the intercept. One can calculate the intercept from this data, which can be used to determine the molecular weight of the micelle.

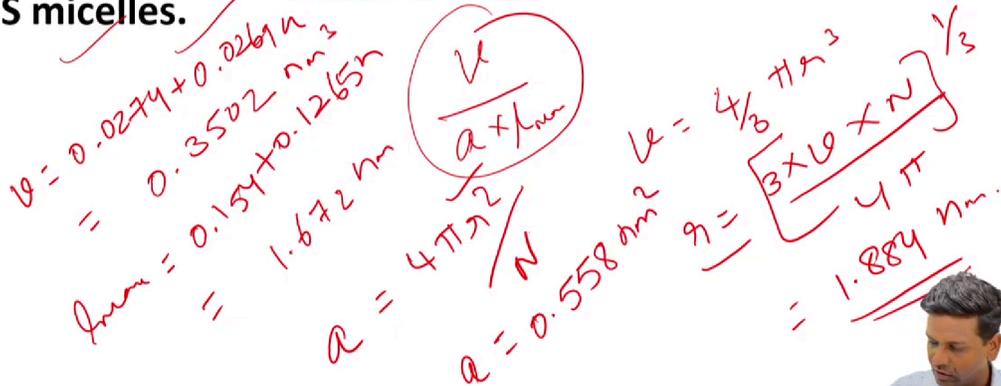
The molecular weight of the micelle can be thought of as indicative of the size of the micelle itself. When you divide this molecular weight by the molecular weight of the individual compound, such as the CTAB-type surfactant used in the experiment, you can calculate the aggregation number. The molecular weight of the CTAB surfactant is 308. By dividing the molecular weight of the micelle by this value, you obtain the aggregation number.

This aggregation number represents the number of monomers that make up the micelle. You can understand that this aggregation number is derived from the data obtained through scattering experiments. Once you know the aggregation number, it is straightforward to calculate, for example, the packing factor.

Sometimes, knowing the aggregation number allows you to comment on whether the micelle formed is spherical, cylindrical, or another shape.

Timestamp: 13.42 mins

The aggregation number of SDS micelle in water is 80. Calculate the packing parameter and predict the shape of the SDS micelles.



$$V = 0.0274 + 0.0269n$$

$$= 0.3502 \text{ nm}^3$$

$$L_{max} = 0.154 + 0.1265n$$

$$= 1.672 \text{ nm}$$

$$a = \frac{V}{a + L_{max}}$$

$$a = \frac{4\pi r^3}{3N}$$

$$a = 0.558 \text{ nm}^2$$

$$r = \left[ \frac{3 \times V \times N}{4\pi} \right]^{1/3}$$

$$= 1.884 \text{ nm}$$

Reference: Pallab Ghosh, NPTEL - Chemical En



Now, based on this information, we can proceed to solve the tutorial problem. In this exercise, we are given the aggregation number of the SDS micelle and asked to calculate the packing parameter and predict the shape of the SDS micelles.

In this case, the shape of the micelle is not specified. Therefore, we need to calculate the value of  $\frac{V}{A \cdot L_{max}}$  To comment on the shape of the micelles. This calculation is essential for understanding the micelle's structure.

As you may recall from previous lectures, we use the Tanford equation, which is an empirical equation used to calculate  $V$  and  $L_{max}$ . These values are functions of the number of carbon atoms in the surfactant chain. For a surfactant with 12 carbon atoms, we can use the Tanford equation to find  $V$  and  $L_{max}$ .

The Tanford equation is given by:

$$V = 0.0274 + 0.0269nL_{max} = 0.154 + 0.1265n$$

Substituting  $n = 12$  Into these equations gives us:

$$V = 0.0274 + 0.0269 \times 12 = 0.3502 \text{ nm}^3 \quad L_{max} = 0.154 + 0.1265 \times 12 = 1.672 \text{ nm}$$

If we assume the micelle is spherical, we can calculate its radius using the formula:

$$r = \left( \frac{3Vn}{4\pi} \right)^{1/3}$$

Given that  $n = 80$  and  $V = 0.3502 \text{ nm}^3$ , we find:

$$r = \left( \frac{3 \times 0.3502 \times 80}{4\pi} \right)^{1/3} = 1.884 \text{ nm}$$

With the radius known, we can calculate the optimum head group area.  $A$  Using:

$$A = \frac{4\pi r^2}{n}$$

$$\text{Substituting the values gives: } A = \frac{4\pi(1.884)^2}{80} = 0.5576 \text{ nm}^2$$

Now, we can calculate  $\frac{V}{A \cdot L_{max}}$ :

$$\frac{V}{A \cdot L_{max}} = \frac{0.3502}{0.5576 \times 1.672} = 0.3756$$

This value helps us understand the shape and packing characteristics of the micelle.

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**Tutorial**

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The aggregation number of SDS micelle in water is 80. Calculate the packing parameter and predict the shape of the SDS micelles.

*Handwritten:*

$$\frac{V}{A \cdot L_{max}} = \frac{0.3502}{0.558 \times 1.672}$$

$$= 0.375$$

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$$0.375 > 0.33$$

Non-spherical



Reference: Pallab Ghosh, NPTEL - Chemical Engineering

If you look at the packing parameter, which is  $V/AL$  for this problem, it is approximately

0.375. Remember, for a micelle to be spherical in shape, the packing parameter must be less than or equal to 1/3 (0.333). However, if you examine the value of the packing parameter we calculated for this case, based on the aggregation number and the Tanford equation, it is 0.375. This value is slightly greater than 0.333.

Therefore, we can conclude that the shape of the micelle will be non-spherical to some extent. It will not be perfectly spherical. This is the observation we can make from this exercise. We will stop here and continue from the next lecture.

Thank You