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Method for Measurement of Critical Micelle Concentration

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Introduction:

Micelle:

The aggregation of a single molecule of a certain type [e.g., the molecule of a surface active agent like- Na-lauryl sulphate, $CH_3 (CH_2)_{12} SO_4Na$] when dissolved in water to form a particle of colloidal dimension is called a micelle. Micelles are thermodynamically stable colloids. The single molecule which takes part in this process is characterized by possessing two regions in its chemical structure. This dual nature is responsible for the properties of micellization, surface activity, and solubilization.

Critical Micelle Concentration (CMC):

In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles. The CMC is an important characteristic of a surfactant. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant. After reaching the CMC, the surface tension remains relatively constant or changes with a lower slope. The value of the CMC for a given dispersant in a given medium depends on temperature, pressure, and (sometimes strongly) the presence and concentration of other surface active substances and electrolytes.

Knowledge of the CMC is very important when using surfactants. As the surface tension does not reduce further above the CMC, in many processes the CMC specifies the limiting concentration for meaningful use, and the same is applied for pesticide formulation.

Important Methods for Measuring CMC:

The methods for measuring CMC can be classified into two types. The first methods detect abrupt changes in the monomolecular concentration, such as the surface tension and electric conductivity methods. The second type detects micelles and includes the dye adsorption method and the solubilization method.

1. Surface tension method

For assaying CMC by measurement of surface tension, a graph of surface tension versus log concentration is produced. The CMC is found as the point at which two lines intersect; the baseline of minimal surface tension and the slope where surface tension shows the linear decline. Various techniques are available; one of which is the Will Helmy side method where force is required to detach a thin microscopic slide of known thickness and width from the surface of the liquid is measured. A few advantages of this method are –

- simple and convenient
- Applicable to all kinds of surface-active agents. i.e.; it can be used for ionic and non-ionic surfactants.
- Can be used for very low concentrations.
- The sensitivity is not affected by the surfactant type concentration, activity level, or the effect of inorganic salts and other factors.
- It is generally believed that the surface tension method is the standard method for the determination of surfactant CMC.

2. Conductivity method

In this method, the relationship between the conductivity of ionic surfactant solution and concentration is studied and a curve of conductivity versus concentration or molar conductivity is prepared on which the turning point is the CMC. Below the CMC, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers and consequently, an increase in the conductivity. Simultaneously, above the CMC, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant at the CMC level. Since a micelle is much larger than a monomer it diffuses more slowly through the solution and so is a less efficient charge carrier.

3. Dye Method

For the dye micellization method, it has been reported that certain dyes can be used to determine the CMC of surfactants in one of two ways: through a shift in the wavelength maximum in the presence of micelles or by absorbance at a set wavelength to measure the extent of dye uptake by the surfactant. For nonionic surfactants, graphing a range of concentrations against their absorbance at a set wavelength will give an increase in absorbance and then eventually flatten again as the dye fully moves into the micelle interior depleting the continuous-phase dye. As long to find a suitable dye, this method is very simple. But sometimes the colour change is not obvious, so the CMC is not easy to determine. It is used for various ionic and non-ionic surfactants.

4. Turbidity method

In this method, the surface activity is observed by adding the proper amount of hydrocarbon solution with surfactant concentration, the concentration of turbidity point mutation is the surface-active agent CMC. The experiment can use visual or turbidimetric endpoints. This means that there is a solubilizing effect of surfactant CMC, the general is to enable CMC to reduce, reduce the degree of difference for different types of hydrocarbons.

5. Light scattering method

Usually, the determination of CMC by light scattering technique (static) is performed to measure the change in average intensity of scattered light with an increase in micelle concentration. It shows the change in the average intensity of scattered light as a function of the concentration of surfactant. It has been observed that the intensity of light due to the monomer concentration of surfactant did not change up to a certain concentration, but beyond this concentration, it began to increase rapidly because of the aggregation of surfactant molecules. Therefore, the CMC by the light scattering measurement was determined from the concentration at which the intensity of scattered light changes rapidly.

Conclusion:

It is significant to notice that the various approaches to calculating the CMC differ systematically. In particular, surface tension is an indirect technique with the determination of the surface concentration of all surface-active species while conductimetry and absorption measure the bulk properties and then the presence of micelles. Surface-active particles have a tremendous impact on the surface tension method. The surface tension vs. concentration curve will therefore exhibit a minimum rather than a sharp break, which makes it hard to figure out the value of CMC. So the CMC of commercial surfactants, especially SDS and nonionic surfactants, represents the surface concentration of all surface-active components only at the surface rather than the abundance of micelles in the bulk solution. Caution is needed when estimating the CMC of these substances. The surface tension approach is more prone to contaminants than the electrical conductance method, which can only be used with ionic surfactants. The overall number of micelles in a system determines how easily a dye or any other hydrophobic species will dissolve in it. When the CMC of a surfactant is less than 5.10-4mol/L, determining the CMC of that substance becomes nearly impossible. Nevertheless, under all experimental conditions of electrolyte or nonelectrolyte concentration, this approach is sufficient for determining the CMC of an anionic, cationic, or nonionic surfactant. The fact that the added material may impact the CMC and cause a measured value to be less than the actual value is a significant drawback of this approach. Although this procedure is straightforward, in actuality colour and fluorescence changes are frequently difficult to distinguish, especially when working with unrefined or mixed samples. Because of the continual variations in monomolecular concentration around the CMC, the surface tension and conductimetry methods did not typically produce good findings when used to test the CMC of mixed systems.

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