

Cetyltrimethylammonium bromide (CTAB), Cetylpyrriidumchloride (CPC) are some examples of detergents, while sodium stearate, sodium oleate, etc are examples of soaps.

With increasing concentration, the hydrophilic portion are readily attracted by water, while the hydrophobic parts gradually stay away from water and approach each other to form an almost spherical ionic cluster inside the bulk, which is called **micelle**—an **association colloid**. A minimum concentration of the surface-active agent is required to form micelle. In the micelle, the hydrocarbon ends remain in the interior and the ionic functional groups project outward in the solution.

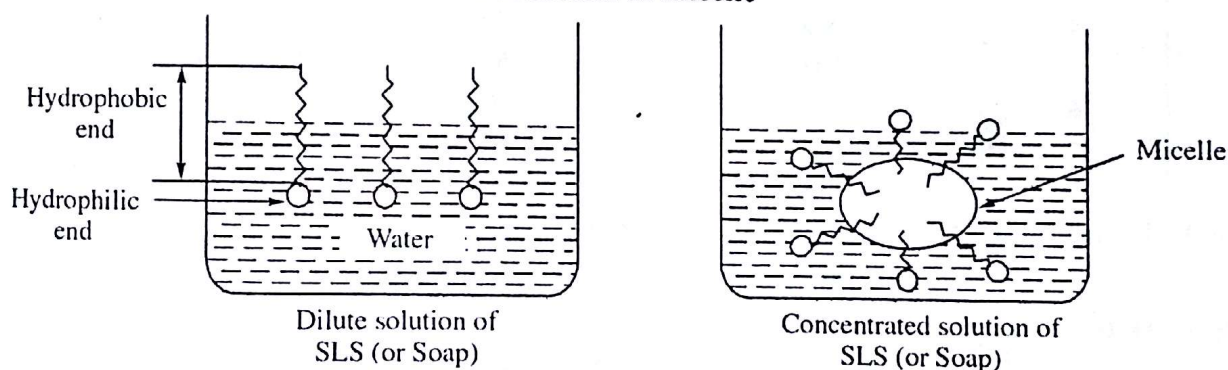
At a definite temperature, the minimum concentration at which a surface-active agent begins to form micelle, is called the 'critical micellar concentration' or 'critical micellization concentration' (CMC) of the particular agent at that temperature.

For example, a soap is unlikely to form micelle below 10^{-3} M concentration of it at normal temperature.

Micelle may be cationic or anionic in nature. At the point of formation of micelle, many properties of the solution like surface tension, conductances, osmotic coefficient, etc suffer a sudden change, which so far changed regularly with concentration. Measuring the conductance, the CMC value can be estimated.

Increase in temperature lowers the CMC value. A number of solutions of SLS is prepared and their equivalent conductances (Λ) are measured following the usual procedure. Now a plot of Λ vs \sqrt{c} is drawn, which shows a minima. The corresponding concentration is the value of CMC for SLS.

Formation of micelle



Apparatus: Conductivity bridge, 7-8 numbers of 50 ml volumetric flasks, one 500 ml volumetric flask, a 50 ml burette.

Materials: Sodium Lauryl Sulphate (SLS) AR, conductivity water, KCl.

Procedure

1. Prepare a standard 500 ml 0.05 M SLS solution. Weight required = 7.2095 g (MW 288.38).
2. Prepare a number of SLS solutions (50 ml each) of different concentrations from the stock solution. [You may use the stock solution as it is, even its concentration may not be 0.05 M, but the concn. should be exact one].
3. Prepare 100 ml 0.1 N KCl solution and determine the cell constant (K_c) of the experimental conductivity cell following experiment 1.
4. Determine the conductance of each solution by conductometer.
5. Calculate the specific conductance ($\kappa = C \times K_c$) and equivalent conductance ($\Lambda = \frac{1000 \kappa}{c}$) of each solution.

6. Plot Λ vs. \sqrt{c} .

7. CMC value will be $(\sqrt{c})^2$ at the corresponding point.

Results and Calculations:

Table 1: Preparation of 500 ml standard 0.05 M SLS solution

Weight required = 7.2095 g

| 1st weight of SLS w_1 (g) | 2nd weight of SLS w_2 (g) | Weight taken $w_1 - w_2$ (g) | Strength of SLS solution, (M) |
|--------------------------------|--------------------------------|---------------------------------|---|
| ... | ... | ... | $\frac{w_1 - w_2}{7.2095} (0.05) \text{ M}$ |

Table 2: Preparation of various SLS solutions from the stock solution

| Volumetric flask no. | Vol. of stock solution (ml) | Final volume after making up with water (ml) | Conc. of the soln. (c) (M) |
|-------------------------|--------------------------------|---|-------------------------------|
| 1 | 1.0 | 50 | ... |
| 2 | 2.0 | 50 | ... |
| 3 | 4.0 | 50 | ... |
| 4 | 8.0 | 50 | ... |
| 5 | 10.0 | 50 | ... |
| 6 | 15.0 | 50 | ... |
| 7 | 20.0 | 50 | ... |

Table 3: Preparation of 100 ml 0.1 N KCl solution

See Table 2 of experiment 1.

Table 4: Determination of Cell Constant.

See Table 3 of experiment 1 (use only 0.1 N KCl solution).

Table 5: Determination of C , κ and Λ of different solutions. Cell constant, $K_c = \dots \text{cm}^{-1}$.

| No. of Vol. flask | Conc. of SLS solution (c) (M) | \sqrt{c} | Conductance (C) ohm^{-1} | Sp. Cond. (κ) ($\text{ohm}^{-1} \text{cm}^{-1}$) $\kappa = C \times K_c$ | Eqv. conductance (Λ) ($\text{ohm}^{-1} \text{cm}^2 \text{g-eqv}^{-1}$) $\Lambda = \frac{1000 \kappa}{c}$ |
|----------------------|-------------------------------------|------------|---|--|---|
| 1 | ... | ... | ... | ... | ... |
| 2 | ... | ... | ... | ... | ... |
| 3 | ... | ... | ... | ... | ... |
| 4 | ... | ... | ... | ... | ... |
| 5 | ... | ... | ... | ... | ... |
| 6 | ... | ... | ... | ... | ... |
| 7 | ... | ... | ... | ... | ... |

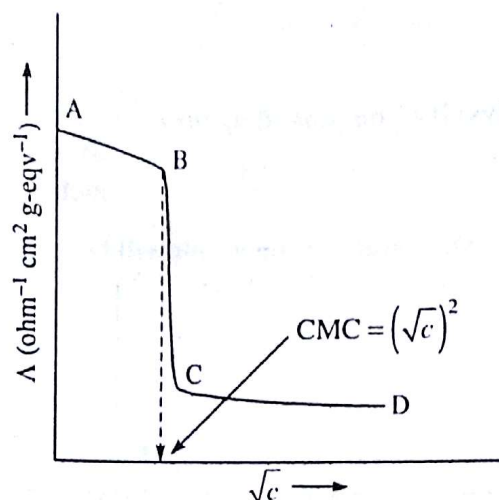
Table 6: Recording of room temperature.

Conclusion: From the graph, it is seen that the CMC for Sodium Lauryl Sulphate is ... M at ... °C temperature.

The nature of the graph:

- N.B.:**
1. First, there is a gradual fall of equivalent conductance with increase in concentration (AB).
 2. With the formation of micelle, Λ falls suddenly (BC).
 3. The CD portion indicates the completion of micellization. Due to absence of any free molecule in ionic form, no change in conductance is observed.

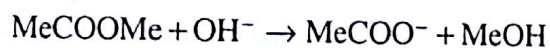
[CMC may also be determined by surface tension measurement, See Expt. 3 in the surface chemistry section].



Experiment 12

Conductometric determination of the rate constant of alkaline hydrolysis of methylacetate. [for P.G. courses]

Theory: In presence of a strong alkali, like NaOH, the hydrolysis of methyl acetate takes place as follows:



Such alkaline hydrolysis of ester is called *saponification reaction*.

Thus OH^- ions are successively replaced by acetate ions, having much lower ion conductance (41.2) compare to that of OH^- ion (198). Hence there will be a decrease of conductance of the reaction mixture with the progress of the reaction.

The reaction is second order — first order each with respect to ester and alkali. If the reaction is carried out with same initial concentrations of both the reactants, then the rate constant may be written as

$$k = \frac{x}{ta(a-x)}, \quad (1)$$

which is the result of integration of the second order rate equation, $\frac{dx}{dt} = k(a-x)^2$,

where a = initial molar concentration of the ester and the alkali,

x = concentration of the product at time t

Let the conductance of the reaction mixture at $t = 0$ is C_0 (which is in fact the conductance of only NaOH solution); that at any intermediate time t be C_t and that after completion of the reaction be C_α .

Hence equation (1) may be written as

$$k = \frac{C_0 - C_t}{ta(C_t - C_\alpha)}$$

$$\text{or, } (C_t - C_\alpha) = \frac{C_0 - C_t}{kat}$$