Graph 3: Standardisation of AgNO₃ solution by KCl solution: See graph of experiment 7C. Convert drops related to end point into volume and calculate strength of AgNO₃.

Graph 4: Titration of halide mixture by AgNO₃ solution: Same as graph 3.

Calculation of the strengths of the halides in the mixture.

From graph 2,

the number of drops of NaOH solution required for neutralisation of HCl

$$= x = x \times \text{volume of 1 drop of NaOH} = \cdots \text{ cm}^3$$
.

: strength of HCl in the mixture =
$$\frac{\text{vol. of NaOH} \times \text{strength of NaOH}}{15}$$
 (N).

Again, the number of drops of NaOH required for neutralisation of $NH_4Cl = (y - x)$ drops = ... cm^3 .

$$\therefore \text{ strength of NH}_4\text{Cl in the mixture} = \frac{\text{vol. of NaOH} \times \text{strength of NaOH}}{15}(\text{N}).$$

From graph 4,

number of drops of $AgNO_3$ solution for equivalence of total chlorides in the mixture = z drops (say) = $z \times volume$ of 1 drop of $AgNO_3$ solution = \cdots cm³.

$$\therefore \text{ strength of total chlorides in the mixture} = \frac{\text{vol. of AgNO}_3 \times \text{strength of AgNO}_3}{15}(N)$$

∴ strength of KCl in the mixture
 = (total concentration of Cl⁻) - (strength of HCl + strength of NH₄Cl) = ···(N).

Conclusion

In the supplied solution,

strength of HCl = \cdots (N)

strength of $NH_4Cl = \cdots (N)$

strength of KCl = \cdots (N)

[Since NH₄Cl and KCl have been taken by weighing the salts, you may compare their analytical strengths to that obtained conductometrically].

Experiment 11

Determination of Critical Miceller Concentration (C.M.C.) of a surface-active agent (e.g., Sodium Lauryl Sulphate) conductometrically. [for P.G. courses]

Theory: Soaps, synthetic detergents, and a number of dyes are called surface-active agents. When added a very small amount to water, they decrease the surface tension of water (or a solvent) appreciably, retaining themselves mostly on the surface of the solvent than in the bulk. They form either emulsion (a colloidal system) at low dilution or in most cases remain as individual molecules forming ions. Such type of compounds have a hydrophobic and a hydrophilic parts in their structures. For example, in sodium lauryl sulphate, a detergent, the hydrocarbon part is hydrophobic and the sodium sulphonate part is hydrophilic.

$$\begin{array}{c} CH_3 - (CH_2)_{11} - O\overline{S}O_3Na^+ \equiv & \\ hydrophobic & hydrophilic & Alkyl \\ \hline & group & O\overline{S}O_3Na^+ \end{array}$$

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

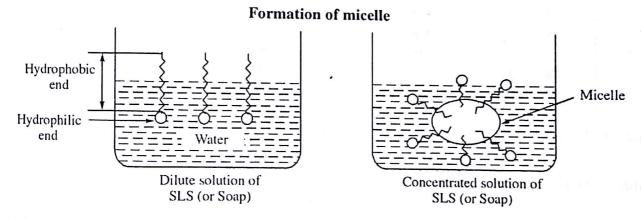
With increasing concentration, the hydrophilic portion are readily attracted by water, while the hydrophobic parts gradually stay away from water and approach each other to form an almost spherical ionic cluster inside the bulk, which is called **micelle**—an **association colloid**. A minimum concentration 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.



Appraratus: 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 condustance ($\kappa = C \times K_c$) and equivalent conductance $\left(\Lambda = \frac{1000 \, \kappa}{c}\right)$ 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)
			$\frac{w_1 - w_2}{7.2095} (0.05) M$

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, $K_{\perp} = \cdots$ cm⁻¹

No. of Vol. flask	Conc. of SLS solution (c) (M)	√c	Conductance (C) ohm ⁻¹	Sp. Cond. (κ) (ohm ⁻¹ cm ⁻¹) $\kappa = C \times K_c$	Eqv. conductance (A) (ohm ⁻¹ cm ² g-eqv ⁻¹) $\Lambda = \frac{1000 \text{ K}}{2}$
1	*		***		$\Lambda = \frac{1000 \text{ K}}{c}$
2			***		
3			•••	•	••
4	gain reference in	· · · · ·	60 f	***	
5	·		***		•
6	***		Company		
7	***		•••	•••	
			The state of the s	1	

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.

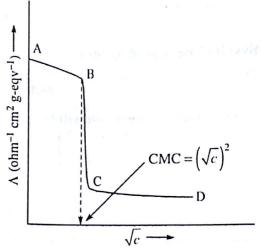
The nature of the graph:

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 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:

$$MeCOOMe + OH^- \rightarrow MeCOO^- + MeOH$$

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

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

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

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

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