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Study on influence of Co-Solvent on the Critical Micelle Concentration (CMC) of aqueous sodium lauryl sulphate solution by conductance & surface tension measurement

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We have studied the critical micelle concentration (CMC) of sodium lauryl sulphate (SLS) in water and ethanol-water system by surface tension and conductance measurement method. The CMC obtained in aqueous solution is compared with those obtained in ethanol co-solvent solutions. Different concentrations of SLS in water and 10% and 20% ethanol solutions were prepared to study the influence of co-solvent on the CMC of SLS solution. The drop number method was used for the measurement of surface tension whereas direct conductance values are utilized in conductance measurement for determination of CMC. It is observed that the CMC of SLS solution decreases with increasing percentage of ethanol suggesting the formation of micelles are favored at lower concentration of ethanol.

Keyword: CMC, co-solvent, SLS, surface tension, drop number method, conductance.

1. Introduction

Surfactants, or surface-active agents, are compounds that accumulate at the interface between different phases, such as between a liquid and gas, two immiscible liquids, or a liquid and solid. Their primary function is to lower surface or interfacial tension hence having wide applications. Surfactants play a important role in various industries due to their versatile properties, offering significant practical value. They are extensively used in the manufacturing and processing of a wide array of products, including food items, agrochemicals, pharmaceuticals, personal care products, and laundry detergents. Surfactants also find applications in the petroleum industry, mineral ore processing, fuel additives, and lubricants. Additionally, they are crucial components in the formulation of paints, coatings, adhesives, and photographic films. Beyond industrial applications, surfactants are present in biological systems and medical treatments, as well as in environmental technologies like soil remediation and other health and safety-related fields [1]. As the concentration of surfactants in an aqueous solution increases, more surfactant molecules are adsorbed onto the surface, leading to a progressive decrease in surface or interfacial tension. At a certain concentration, known as the Critical Micelle Concentration (CMC), the surface and bulk of the solution become saturated with surfactant molecules. Beyond this point, further increase in surfactant concentration do not affect surface tension significantly. Instead, surfactant molecules aggregate to form micelles in the bulk solution. The surface tension decreases steadily as the concentration of the surfactant rises, until it levels off at the CMC, where the surface or interfacial tension reaches its minimum value. Any further addition of surfactant does not lead to additional decreases in surface tension. The CMC is important in various applications such as detergency, drug delivery, cosmetics, and food science. It helps determine the effective concentration for surfactants to exhibit their desired properties, like emulsification, cleaning, or solubilisation. Thus the CMC is a critical parameter for understanding and optimizing the behaviour of surfactants in solution, especially when they are used in systems requiring stable emulsions or micelle-based solubilisation.

The CMC is determined by monitoring changes in physical properties of a surfactant solution as its concentration increases. The physical properties those are measured are surface tension [2], conductivity [3], refractive index [4], osmotic pressure [5] and density [6]. Common techniques include measuring surface tension, where a sharp decrease occurs until the CMC, after which it remains constant; electrical conductivity, which increases significantly at the CMC due to micelle formation; fluorescence spectroscopy and light scattering**,** both of which show distinct changes when micelles begin to form; and viscosity, which may increase as micelles aggregate. Thus at the CMC, several physical properties of the surfactant solution undergo noticeable changes [7]. Therefore CMC is determined at the point where the extrapolated straight lines on either side of the curve intersect, marking the break in the physical property vs. concentration plot [8]. By measuring these properties, such as surface tension, electrical conductivity, or viscosity, and identifying the concentration at which these changes occur, the CMC of the surfactant in a given solvent system can be accurately determined. This point represents the concentration at which surfactant molecules begin to aggregate into micelles. Die and Tam investigated the influence of co-solvents, such as glycols, on the behavior of surfactants like sodium dodecyl sulfate (SDS) in mixtures of water and co-solvent. They found that the process of demicellization for SDS in these mixtures differed from that in pure water. This difference was attributed to the reduced polarity of the solvent and altered charge interactions between the surfactant molecules. Specifically, the CMC initially decreased with the addition of a small amount of co-solvent, indicating enhanced micelle formation. However, as the co-solvent concentration increased further, the CMC began to rise again, reflecting changes in the solvent environment that inhibited micelle formation at higher concentrations of co-solvent. [9]. K. Prajapati and S. Patel studied the micellization of the cationic surfactant hexadecyl trimethyl ammonium bromide (CTAB), anionic sodium dodecyl sulfate (SDS) and polyoxyethylene sorbitan monooleate (Tween-80) using a series of ethylene glycol-water and formamide-water mixed solvents using surface tension, viscosity and conductance measurements. The CMC shifts to lower values upon increasing the ratio of ethylene glycol in the ethylene glycol -water mixed solvent, while the CMC changes in an opposite way with increasing formamide. Contrary to ethylene glycol, the formamide-water mixed solvent seems to become a better solvent for the surfactant compared to water and thus disfavors the formation of micelles [10]. Glenn et al also studied the self-aggregation of binary mixtures of SDS and polyoxyethylene alkyl ethers in aqueous solution [11]. Literature survey reveals that the effect of ethanol as a co-solvent on CMC of SLS has been not reported therefore attempt have been made to study the influence of ethanol co-solvent on the CMC of SLS by conductance & surface tension measurement methods.

2. Material and Methods

2.1 Materials

Sodium lauryl sulfate (SLS), Sodium hydroxide, oxalic acid and absolute ethanol were procured from SD fine chemicals and were used as obtained without further purification. Freshly prepared sodium hydroxide solution is standardized against standard oxalic acid solution for everyday experiments. The solutions were prepared in conductivity water for conductance measurement experiments.

The surface tension of SLS surfactant at various concentrations was determined by using the drop number method. All measurements were carried out at 30 °C. The CMC values were determined at sharp break point in surface tension against concentration curves for surfactant.

Conductometric measurements were made with a digital microprocessor based conductivity meter, model EQ-660B, Equiptronics, India, using a dip-type cell at 30 °C. All measurements were done in a jacketed vessel, which was maintained at the appropriate temperature (± 0.1 ^{o}C). The errors in the conductance measurements were within ± 0.5%. The conductance was measured after thorough mixing and temperature equilibrium at each dilution.

2.2 Preparation of stock and experimental solutions of SLS

5% stock solution of SLS were prepared in distilled water and 10%, 20% ethanol separately. Care was taken so that, no bubbles or frothing appeared. A series of concentration of SLS ranging from 50 to 400 mg/100 ml with difference of 50 mg/100 ml were prepared by diluting the stock solution with distilled water and different composition of ethanol for experimental purpose as per the following Table 1.

Table 1: Experimental systems of varying SLS concentrations

Solution number	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Volume of 5% SLS solution (ml)	1	2	3	4	5	6	7	8
Volume of total solution (ml)	100	100	100	100	100	100	100	100
Concentration of SLS solution (mg/100ml)	50	100	150	200	250	300	350	400

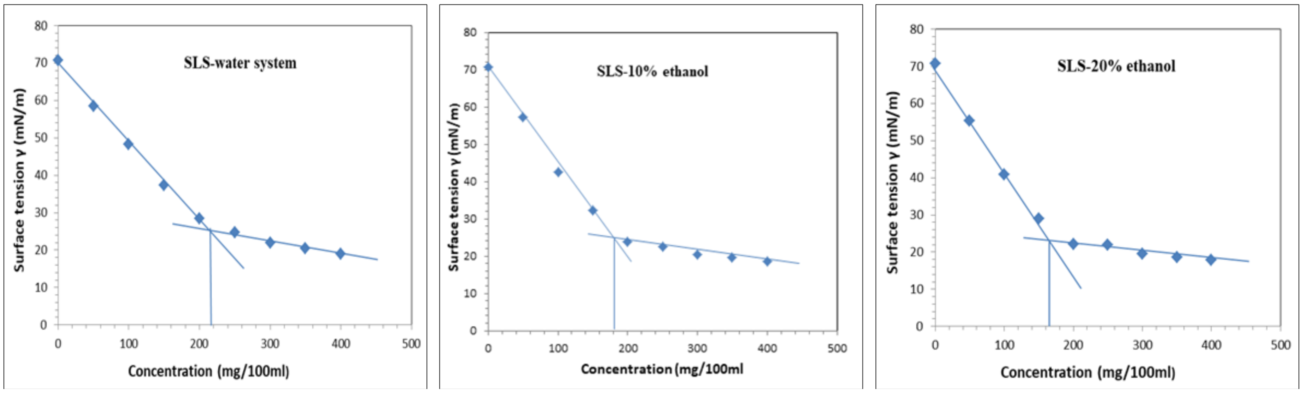
3. Results and Discussion

3.1 Surface tension

The experimental values of surface tension for SLS solution of varying concentrations in water, 10% ethanol and 20% ethanol are reported in Table 2. The plots of surface tension versus concentration of SLS (Figure 1a, 1b & 1c) show a gradual decrease in surface tension with an increase in surfactant concentration, reflecting the surface activity and amphiphilic nature of SLS. The CMC was obtained from the break point in the surface tension-concentration plots. This is a common behavior shown by surfactants in solution and is used to determine their purity and CMCs. This is due to the fact that, when SLS dissolved in water, the hydrocarbon chain of SLS breaks the intermolecular hydrogen bonds in water, increasing the free energy of the system. This increased free energy is minimized by expelling the SLS molecules to the surface of water, where the hydrophilic group is attached to water, and the hydrophobic group is oriented away from water into the air [12-14]. Due to decrease in the dissimilarity between the two phases, i.e., the air and hydrocarbon chains, both being non-polar, the surface tension of water become lowered. It can further be seen that the surface activity of the SLS enhances with the addition of ethanol as a co-surfactant. The effect can be attributed to the overall increase in the hydrophobicity of the solution. The increasing composition of ethanol in water reduces the hydrophobicity and increases the solubility of surfactant. This in turn lowers the interfacial tension between the hydrophobic chains and the solvent, so that shrinking and disruption of micelles becomes more energetically favorable than in plain water. The values of CMC observed for SLS surfactant in water, 10% ethanol and 20% ethanol are reported in Table 4.

Table 2: Surface tension values of varying SLS concentrations

Soluitions	**Concentration (mg/100ml)**	**Surface tension γ (mN/m)**		
		Water	**10% Ethanol**	**20% Ethanol**
Water	0	70.7	70.7	70.7
SLS-1	50	58.57	57.21	55.32
SLS-2	100	48.32	42.61	40.77
SLS-3	150	37.41	32.18	29.02
SLS-4	200	28.35	23.85	22.15
SLS-5	250	24.66	22.64	21.84
SLS-6	300	21.91	20.48	19.48
SLS-7	350	20.39	19.67	18.64
SLS-8	400	18.93	18.53	17.85

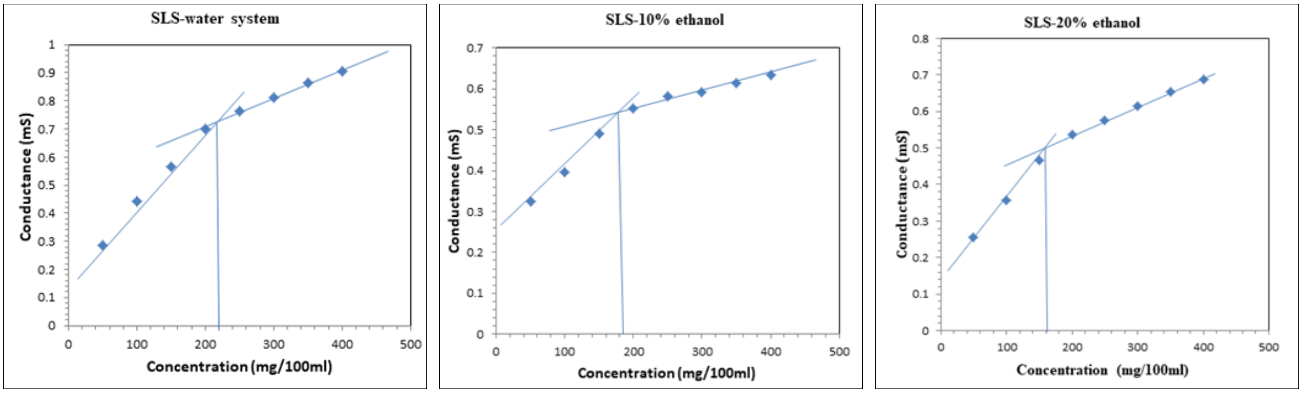


a b c

Fig: 1: Plot of surface tension against concentration of SLS for a SLS-water system, b SLS-10% ethanol and, c SLS-20% ethanol

3.2 Conductance

Conductivity measurements were carried out for SLS surfactant at a controlled temperature of 30 °C to determine the CMC. The experimental conductivity data for SLS solutions at varying concentrations in water, 10% ethanol, and 20% ethanol are presented in Table 3. The plots of conductivity versus surfactant concentration, are shown in Figures 2a, 2b, and 2c. The progressive increase in conductance with increasing SLS concentration was observed. It is established that conductivity is directly proportional to surfactant concentration both in the pre-micellar and post-micellar regimes. In the pre-micellar region, the slope of the conductivity-concentration curve is greater than in the post-micellar region due to the formation of micelles, which alters the ionic dissociation and aggregation behavior of the surfactant molecules. The point of intersection between the two linear regions of the conductivity-concentration curve corresponds to the CMC, signifying the concentration at which surfactant molecules begin to self-assemble into micelles. The observed CMC values for SLS in water, 10% ethanol, and 20% ethanol are summarized in Table 4.



a b c

Fig: 2 Plot of conductance against concentration of SLS for a SLS-water system, b SLS-10% ethanol and, c SLS-20% ethanol

Table 3: Conductance values of varying SLS concentrations

Solutions	Concentration (mg/100ml)	Conductance ($ohm^{-1}cm^{-1}$)		
		Water	10% ethanol	20% ethanol
SLS-1	50	0.287	0.325	0.255
SLS-2	100	0.443	0.397	0.358
SLS-3	150	0.567	0.491	0.467
SLS-4	200	0.701	0.553	0.536
SLS-5	250	0.764	0.581	0.575
SLS-6	300	0.811	0.592	0.615
SLS-7	350	0.866	0.615	0.654
SLS-8	400	0.907	0.635	0.688

CMC values for a SLS in water and ethanol co-solvent systems are reported in Table 4 and are in good agreement.

Table 4: Comparative values of CMC of different SLS-solvent systems by surface tension method and conductance method

Systems	CMC (mg/100ml)	
	Surface tension method	Conductance method
SLS-water	218	220
SLS-10% ethanol	183	181
SLS-20% ethanol	165	162

4. CONCLUSION

From the above results, it can be concluded that an increase in the concentration of SLS leads to a corresponding decrease in surface tension and an increase in conductivity. These trends are characteristic of surfactant behaviour, where the reduction in surface tension is attributed to the adsorption of surfactant molecules at the air-water interface, while the rise in conductivity reflects the increased ionic dissociation of surfactant molecules in solution. The presence of a co-solvent, such as ethanol, significantly influences the behaviour of the surfactant in aqueous solution. Specifically, the co-solvent enhances the relative permittivity (dielectric constant) of the aqueous phase. The increased permittivity results in a more favourable environment for the electrostatic interactions between the ionic heads of the surfactant molecules. This effect promotes the aggregation of surfactant molecules into micelles, which reduces the CMC, as observed in the experimental results. The reduction in CMC indicates that less surfactant is required to initiate micellization, which can be attributed to the improved solubilisation properties and stronger electrostatic interactions in the modified solvent system.

These findings are important as they demonstrate how the presence of co-solvent, such as ethanol, can be used to modulate the surfactant’s behaviour, particularly its CMC and micellization properties. This information can be utilized to tailor surfactant properties for specific applications, such as in the formulation of cleaning agents, pharmaceuticals, or cosmetic products, where control over micelle formation and surfactant efficiency is critical. By adjusting solvent composition, one can fine-tune the surfactant's performance to meet the needs of various industrial and research applications.

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Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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