

Micellization behaviour of sodium dodecyl sulphate in presence and absence of sodium sulphate and zinc sulphate in distilled water by surface tension measurement

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Abstract

The accurate measurements of surface tension of sodium dodecyl sulphate (SDS) in distilled water and in presence of 0.01M Na₂SO₄ and 0.01M ZnSO₄ at room temperature were reported by drop weight method using a stalagmometer. The critical micelle concentration (cmc) of sodium dodecyl sulphate (SDS) in distilled water was obtained higher than in presence of Na₂SO₄ and ZnSO₄. The decrease of cmc of sodium dodecyl sulphate in the presence of salts has been discussed.

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1. Introduction

Due to the different environment of molecules located at an interface compared to those from either bulk phase, an interface is associated with a surface free energy. At the air-water surface for example, water molecules are subjected to unequal short-range attraction forces and, thus, undergo a net inward pull to the bulk phase. Minimization of the contact area with the gas phase is therefore a spontaneous process, explaining why drops and bubbles are round. The surface free energy per unit area, defined as the surface tension (γ). Another, but less intuitive, definition of surface tension is given as the force acting normal to the liquid-gas interface per unit length of the resulting thin film on the surface.

Surfactants reduce the amount of work necessary to create unit surface area i.e. surface tension of a solution is lowered when surfactants are present [1]. The limiting value of surfactant concentration that produces a surface tension decrease is the critical micelle concentration [2]. Furthermore, the steeper decrease in surface tension is evident only at high surfactant concentrations. Since, due to the surface activity of the surfactant, surface tension measurement is the major method for the determination of cmc. In tensiometric determination of the surfactant, surface tensions (γ) are plotted as a function of logarithm of the surfactant concentration. The following equation is used to calculate the surface tension of required solution.

$$\gamma_{soln} = \left(\frac{n_{solv}}{n_{soln}}\right) \left(\frac{d_{soln}}{d_{solv}}\right) \gamma_{solv} \tag{1}$$
where,

 $\gamma_{soln} = surface tension of solution$ $\gamma_{solv} = surface tension of solvent$ $n_{soln} = number of drops of solution$ $n_{solv} = number of drops of solvent$ $d_{soln} = density of solution$ $d_{solv} = density of solvent$

Sodium dodecyl sulphate (SDS) is an anionic surfactant. One end of the molecule is charged and therefore has an affinity for water, and the other end is non polar and soluble in fat/oil. SDS has a negatively charged sulfonate group as its "hydrophilic" end and a saturated 12-carbon for its "lipophilic" end. Sodium dodecyl sulphate has significant application as very effective surfactant in a number of industrial products and in recent studies it is considered as a novel microbicide against different viruses [3, 4].

In this paper, we report a study of the micellization behaviour of sodium dodecyl sulphate (SDS) at room temperature in absence and in presence of Na_2SO_4 and $ZnSO_4$ by surface tension method in aqueous media.

2. Experimental

Sodium dodecyl sulphate was purchased from Loba Chemical, India. $ZnSO_4$ and Na_2SO_4 were purchased from Ranbaxy Chemical, India. The water used in the experiments was doubly distilled. The solutions prepared at room temperature.

For the preparation of experimental solution of SDS in distilled water, 2.8838g of pure SDS was weighed accurately with digital balance and was dissolved in 100 ml of distilled water to get 0.1M SDS solution. 0.1 M SDS solution was used as stock solution (s_0) for the preparation of different eight solutions of different concentrations viz. 0.08M (s_1), 0.06M (s_2), 0.04M (s_3), 0.024M (s_4), 0.018M (s_5), 0.012M (s_6), 0.00725M (s_7), 0.0054M (s_8). These different solutions were prepared by diluting the appropriate volume of stock solution (s_0) with distilled water in 50 ml volumetric flasks.

Similarly, as described above the same weight of pure SDS was weighed and was dissolved in 100 ml of 0.01M Na₂SO₄ and 0.01M ZnSO₄ separately to get 0.1M SDS in non-aqueous environments. Here also eight different solutions were prepared for each of solvents with stock solutions: A_0 , A_1 , A_2 , A_3 , A_4 , A_5 , A_6 , A_7 , A_8 and D_0 , D_1 , D_2 , D_3 , D_4 , D_5 , D_6 , D_7 , D_8 respectively with equivalent concentrations.

The weights of the different solutions of SDS with different strengths were measured by the pyknometer (specific gravity bottle). For this purpose, the cleaned pyknometer was taken and was first filled with airfree distilled water in it, then the stopper was inserted into its mouth so that the small amount of water flowed out the capillary then the outer surface of it was wiped out with a tissue paper ensuring that outer surface was completely dried. Finally, the bottle was weighed and then emptied and dried. Then, the same process was repeated for every type of solutions under investigations. After collecting the weights, the densities of related solutions were calculated and tabulated with reference to the standard density of water at $30^{\circ}C$ (room temperature) i.e. 0.99571 g/cm³.

Surface tension measurements were carried out on a stalagmometer. The surface tension of SDS in absence and presence of salts was measured by drop count method using a stalagmometer. It was designed by Troube and consists of a pipette with a capillary outflow to be the end of which is flattened out. This is done to give a larger dropping surface. The surface is carefully ground flat and polished. Before using the stalagmometer was first carefully washed with a solution of chromic acid and then with

distilled water. Finally it was washed with acetone and dried. The stalagmometer was held vertical and was not shaken because otherwise the drop will fall out even before attaining its maximum size. In this process, first the stalagmometer was filled with distilled water as above without changing the pressure. Then the drop count was started. By following the same process all the liquids or solutions of varied strength of SDS in presence and absence of Na₂SO₄ and ZnSO₄ was measured.

3. Results and Discussion

The surface tension of SDS in distilled water and in aqueous solution of Na_2SO_4 and $ZnSO_4$ were calculated from equation (1) and were tabulated in Table 1A, 1B and 1C. The graphical representations of the surface tension of SDS in distilled water and in aqueous solution of Na_2SO_4 and $ZnSO_4$ with log [SDS] are shown in Figs. 1-3. Since, there was sharp decrease of surface tension on increase of surfactant concentrations. According to the experimental calculations and determinations, the surface tension was found to be decreased in presence of salts .i.e. Na_2SO_4 and $ZnSO_4$.

The surface tension value was high in case of water because of absence of externally added salts. Since, on the addition of inorganic salts, affect surfactant aggregation mainly through reducing the electrostatic interaction among the surfactant head groups and consequently decrease the surface tension of the surfactant molecules.

In the case of Na₂SO₄ and ZnSO₄, the sodium ion (Na⁺) is larger than the Zinc ion (Zn²⁺) because, the Zinc cation, Zn²⁺, has a greater cationic charge than the Na⁺ cation. The surface tension of SDS in presence of Na₂SO₄ is more than in presence of ZnSO₄ because the smaller ions are strongly hydrated, so they need to pull more water molecules with them which make them less mobile. Thus, due to zinc ions (Zn²⁺) i.e. counter ions reduced largely the electrostatic interaction among the surfactant molecules and decreased surface tension largely.

When surface tension of a solution is plotted against $\log[C]$, where C is the concentration of surfactant then it gives a curve. The two fitted lines meet in the curve at the particular point. That point of intersection is known as cmc of the solution.

Concentration (mol/l ⁻¹)	Surface tension (dyne/cm)	
0.02402	31.80359	
0.01801	32.11061	
0.01351	32.42408	
0.01013	32.74436	
0.00760	33.40919	
0.00570	35.97611	
0.00428	37.62764	
0.00321	38.96942	
0.00241	39.91825	
0.00180	40.40978	
0.00135	40.91390	
0.00102	41.43103	
	0.01801 0.01351 0.01013 0.00760 0.00570 0.00428 0.00321 0.00241 0.00180 0.00135	

Table 1A: Surface tensions of SDS in distilled water.

Solvent	Concentration (mol/l ⁻¹) Surface tension (dyne/cm)	
Na ₂ SO ₄	0.02400	29.83293
	0.02000	30.10266
	0.01667	30.66151
	0.01389	31.54318
	0.01157	32.15982
	0.00965	33.13277
	0.00804	33.81490
	0.00670	34.16566
	0.00558	40.99797
	0.00465	43.73001
	0.00388	44.92753
	0.00323	47.53145
	0.00269	50.45586
	0.00224	53.76411
	0.00187	56.54468
	0.00156	58.56345
	0.00130	59.62791

Table 1B: Surface tensions of SDS in the presence of Na₂SO₄.

Our calculation of cmc of SDS in distilled water at room temperature found to be 8.29 mM which is almost matching with 9.00 mM by surface tension method [5]. When surfactant and salt are mixed in solution, salting-out phenomenon often happens [6-9].

According to hydration theory [10] salting-out is the result of preferential movement of water molecules, which immobilize and quench their role as solvents, from coordination shells of surfactant molecules to those of salts. The effects of halide salts on the growth of micelles in ionic surfactant solutions have been systematically studied [11,12].

With the addition of inorganic salts, the reduced electrostatic repulsion among the surfactant head groups is a key factor to influence the morphology of aggregates in ionic surfactant solutions. For conventional single-chain cationic surfactants, micelles may change from global to rod like or wormlike with the addition of inorganic salts [13,14].

Salts decrease the cmc in the order: $ZnSO_4 < Na_2SO_4$. Here Zn^{++} is least effective in decreasing the cmc due to small size and large hydrated radius and would act as a water-structure promoter decreasing the availability of water to the micelles. Therefore, upon addition of $ZnSO_4$ and Na_2SO_4 in SDS, Na_2SO_4 is more effective in reducing the cmc of SDS. Hence in our case Na_2SO_4 decreases the cmc of SDS more than $ZnSO_4$ (Table 2).

Solvent	Concentration (mol/l ⁻¹)	n (mol/l ⁻¹) Surface tension (dyne/cm)	
ZnSO4	0.06017	27.16200	
	0.05014	27.37816	
	0.04179	27.59907	
	0.03482	28.06390	
	0.02902	28.29980	
	0.02418	28.79153	
	0.02015	29.56571	
	0.01679	30.10506	
	0.01399	30.66502	
	0.01166	30.95195	
	0.00972	31.24480	
	0.00810	31.54408	
	0.00675	31.84879	
	0.00562	34.89688	
	0.00469	37.27535	
	0.00391	40.00185	
	0.00325	41.00095	
	0.00271	41.51947	
	0.00226	41.51852	
	0.00188	41.51804	

Table 1C: Surface tensions of SDS in the presence of ZnSO₄.

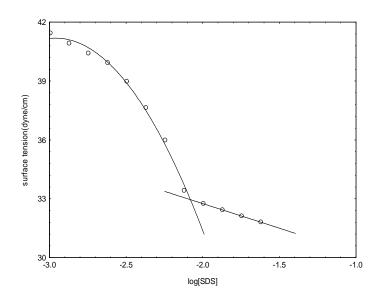
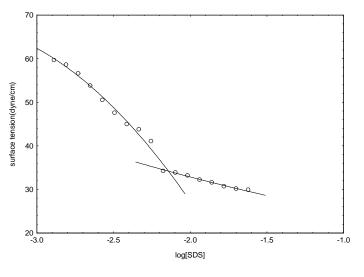


Figure 1: Variation of surface tension of SDS with log [SDS] in distilled water at room temperature.



K. Limbu et al. / BIBECHANA 11(1) (2014) 79-85: (Online Publication: March, 2014) p.84

Figure 2: Variation of surface tension of SDS with log [SDS] in aqueous solution of Na_2SO_4 at room temperature.

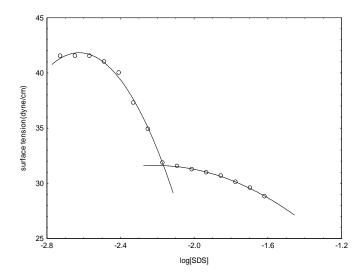


Figure 3: Variation of surface tension of SDS with log [SDS] in aqueous solution of $ZnSO_4$ at room temperature.

 Table 2: Critical micelle concentrations of SDS obtained from surface tension measurement in distilled water, aqueous solution of Na₂SO₄ and ZnSO₄.

Solvent	Distilled water	0.01M ZnSO ₄	0.01M Na ₂ SO ₄
	<i>Cmc</i> (mM)	<i>Cmc</i> (mM)	<i>Cmc</i> (mM)
Surface tension	8.29	7.01	6.02

4. Conclusion

The following conclusions have been drawn from above results and discussion. The results showed the decrease in surface tension of sodium dodecyl sulphate (SDS) at room temperature in presence of Na_2SO_4 and $ZnSO_4$. The surface tension of sodium dodecyl sulphate is found less in presence of $ZnSO_4$ than Na_2SO_4 in aqueous media and the cmc of sodium dodecyl sulphate decreases more in Na_2SO_4 comparison with presence of $ZnSO_4$.

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