Micellization of sodium dodecyl sulphate in the presence and absence of potassium sulphate and nickel sulphate

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Article Information:  
Received: May 07, 2022  
Accepted: June 17, 2022

Keywords:  
Surfactant  
CMC  
Electrolyte  
SDS

ABSTRACT

The effect of addition of salts on the micellization of anionic surfactant sodium dodecyl sulphate (SDS) in aqueous medium has been studied by conductance measurement at 298.15 K. The critical micelle concentration (CMC) as well as thermodynamic properties was evaluated. From the premicellar and postmicellar slopes, the degree of dissociation (α) of SDS was also calculated. On adding the salts, CMC decreased whereas degree of dissociation increased. Employing these CMC and α values, the standard free energy of micellization was also evaluated. The negative values of $\Delta G_m^\circ$ was decreased when $K_2\text{SO}_4$ was added but increased when $\text{NiSO}_4$ was added.

DOI: https://doi.org/10.3126/bibechana.v19i1-2.46830
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1. Introduction

Surfactants are surface-active molecules which possess both hydrophobic tail and hydrophilic head and are therefore amphiphilic in nature [1]. Due to amphiphilic nature, they exhibit various unique properties such as adsorption at interfaces, self-association and solubilization of hydrophobic molecules, so widely used in pharmaceutical, food, cosmetic, textile, paint and coating industries [2]. The narrow concentration range above which micelles are formed is called critical micelle concentration [3]. From the CMC value of a surfactant, fundamental information about the surface-
active properties can be known. Micelle formation plays a model role in biological, chemical and industrial processes [4]. The physicochemical properties of aqueous surfactants can be changed by external means, such as, concentration of reactants, type of additives, nature of the solvent and temperature [5]. In the present scenario, due to the increasing demand for novel materials with unique and enhanced properties has given priorities to the investigation of surfactant-additives system [6]. The aggregation behaviour of surfactants in aqueous solutions can be changed by altering the temperature of solution and also by changing the solvent. The addition of salts can also affect the aggregation behavior of anionic surfactants in aqueous solutions, which is crucial to different applications in detergency and emulsification [7].

When salts are added to surfactants, their properties change, which plays an influential role in many research fields. Conductivity measurements in aqueous and ethanol-water systems at 298.15 K, Niraula et al. investigated the influence of solvent permittivity and salt on sodium dodecyl sulphate micellization behavior [8]. Ren studied the mechanism of salt effect on micellization of sodiumdodecyl diamino sulphonate amphoteric surfactant in aqueous medium by tensiometry using the Wilhelmy plate method at 298.15 K [9]. Miyagishi et al. studied the salt effect on critical micelle concentration of nonionic surfactants, N-Acyl-N-methylglucamides using surface tension or a fluorescent probe method at 298.15 K [10]. No studies have been conducted on the effect of salts (K₂SO₄, NiSO₄) on SDS surfactant. Conductivity measurements have been used in the present study to determine sodium dodecyl sulphate’s thermodynamic properties.

The measurement was performed in aqueous system at room temperature. Additionally, salts have been studied for their effect on SDS, which is quite different from the previous studies.

2. Materials and Method

Materials

The materials that were used for the determination of CMC are conductivity meter, cotton, beaker, measuring cylinder, pipette, potassium sulfate, nickel sulfate and distilled water. Conductance measurements was carried out on 601/602/611 Digital conductivity meter purchased from ESICO International having cell constant of 1.0 cm⁻¹ from India. Various independent solutions were prepared and were carried out to check the reproducibility of the outcome. Sodium dodecyl sulfate [SDS] and Nickel (II) sulfate heptahydrate [NiSO₄.7H₂O] was purchased from Merck Life Science Private Limited, Mumbai, India. K₂SO₄ was purchased from Glaxo India limited, Mumbai. Distilled water was used in the experiments. The solutions were prepared at room temperature.

Methods

Determination of CMC of sodium dodecyl sulfate with and without salts

Since conductivity measurement is very simple to do in the lab, it is a very convenient way to determine CMC. At first sodium dodecyl sulfate of 0.05M was prepared by mixing 1.442gm of SDS in 100 ml of distilled water. It was kept for whole night to make homogenous solution. About 30 ml SDS was taken in one beaker. The conductivity meter was standardized at 298.15 K and the conductance of SDS solution was first measured. 2ml of SDS was pipetted out and 2 ml of distilled water was added each time after addition. Similarly, 100 ml of 0.05M SDS solution was prepared in 0.001M K₂SO₄ aqueous solution. 30 ml of the mixture was taken and its conductance was measured. 2ml of the mixture was pipetted out and 2ml K₂SO₄ was added in the beaker and conductance was measured each time after addition. Similarly, 100 ml of 0.05M NiSO₄.7H₂O in distilled water.
30 ml of the mixture was taken and its conductance was measured. 2 ml of mixture was pipette out and 2 ml NiSO\(_4\) solution was added followed by measurement of conductance each time. About 35 readings were taken for SDS in aqueous medium in absence and in presence of each salt. The graph of specific conductance versus concentration of SDS in aqueous medium was plotted by using easy plot program to get two straight lines with different slopes. The breaking point of these two lines was the CMC of the surfactant, the value of which is determined by solving two equations.

3. Results and Discussion

The conductivities of sodium dodecyl sulphate in pure water and in presence of K\(_2\)SO\(_4\) and NiSO\(_4\) at room temperature is presented in Figure 1. SDS is more conductive when salts are added because salts have a higher mobility (Figure 1). SDS in the presence of K\(_2\)SO\(_4\) has less conductance than SDS in the presence of NiSO\(_4\). Since conductivity and resistivity have an inverse relationship. Small ions, therefore, have a high charge density. Because of this, smaller ions have more conductivity than larger ones. Atomic size of Ni is 163 pm which has the equivalent value 1.63 Å appears on p. 449 in the literature [11] whereas atomic size of K seems 275 pm which has the equivalent value 2.75 Å appears on p. 113 in the literature [12]. In other words, As ion size increases, ion mobility decreases and conductivity decreases.
There is the calculation of Gibbs free energy of micellization ($\Delta G_m^o$) \[8\] as

$$\Delta G_m^o = (2 - \alpha)RT \ln X_{cmc} \quad (1)$$

Here, R is the universal gas constant, T is the absolute temperature and $X_{cmc}$ is the mole fraction of surfactant at CMC. The critical micelle concentration (CMC), degree of micelle ionization ($\alpha$) and standard free energy of micellization ($\Delta G_m^o$) of SDS in the absence and presence of salts in water are given in Table 1.

Table 1: Table for CMC, degree of dissociation, Gibbs free energy of micellization, premicellar and postmicellar slopes

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Salts</th>
<th>CMC (mM)</th>
<th>$\alpha$</th>
<th>$\Delta G_m^o$ (kJ/mol)</th>
<th>$S_1$</th>
<th>$S_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>K$_2$SO$_4$</td>
<td>5.1</td>
<td>0.55</td>
<td>-33.40</td>
<td>51.2</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td>NiSO$_4$</td>
<td>2.2</td>
<td>0.51</td>
<td>-37.43</td>
<td>46.7</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 1 shows the decrease in the CMC values with the addition of salts (K$_2$SO$_4$, NiSO$_4$). The variation of the CMC of SDS in presence and absence of salts are in the order: SDS > K$_2$SO$_4$ > NiSO$_4$. Ni and K have ionic radii of 69 pm [13]and 133 pm [14], respectively, and the CMC increases as the ionic radii of counterions increase [15]. CMC of SDS decreases in the presence of salts (Figures 3 & 4) because salt ions interact with the surfactant's head group. As salts are added, the electrostatic repulsive force between polar head groups of SDS molecules is reduced by shielding micelle charge, resulting in more tightly packed spherical micelles, which reduces the CMC [16].

The increase in degree of dissociation after the addition of salts may be due to the increased in the number of unbound counterions in SDS solution [17]. In regard to standard free energy of micellization of SDS in the presence of salts, the standard free energy of micellization becomes less negative in presence of K$_2$SO$_4$ and more negative in presence of NiSO$_4$, indicating that micelle formation becomes less spontaneous in case of K$_2$SO$_4$ and more favourable in case of NiSO$_4$. Such type of behaviour infers that micellization becomes less favourable in presence of K$_2$SO$_4$ and more favourable in presence of NiSO$_4$ [18].

Table 1 also shows the values of premicellar ($S_1$) and postmicellar slopes ($S_2$) drawn from the graphs of specific conductance with the concentration of SDS with salts (K$_2$SO$_4$, NiSO$_4$) in aqueous system. With the addition of salts, these two slopes are changed which leads to difference in physicochemical properties of solution [19].

Conclusion

The micellization behaviour of sodium dodecyl sulphate in aqueous solution in presence and absence of salts was investigated conductometrically. The critical micelle concentration decreased when salts were added. This decreased in the values of the CMC is due to the interaction of salt ions with the head group of the surfactant. It was also found that degree of dissociation of SDS increased when salts were added. Also, $\Delta G_m^o$ was found less negative in presence of K$_2$SO$_4$ and more negative in presence of NiSO$_4$.

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