Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2016, 8(10): 49-55

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Effect of Additives on the Aggregation Behavior of Sodium Lauroyl Sarcosine in Aqueous Solution

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ABSTRACT

The influence of the addition of ethylenediamine and L-Lysine.HCL on the micellization process of sodium lauroyl sarcosine (SLAS) in aqueous solution was studied using an electrical conductivity technique. The conductivity data were used to determine the critical micelle concentration (CMC) and degree of counter-ion dissociation (α) in the temperature range 288.15–318.15 K. Thermodynamic properties of micellization ($\Delta G°_{mic}$, $\Delta H°_{mic}$, and $\Delta S°_{mic}$) were evaluated using a mass action model. The results showed that the CMC values of SLAS decreased with increases in the ethylenediamine and L-Lysine.HCL concentrations in aqueous solution. The extent of this effect followed the order: ethylenediamine < L-Lysine.HCL. Furthermore, the CMC of SLAS enhanced with increases in temperature for all systems studied. The α values of SLAS increased in the presence of the ethylenediamine and L-Lysine.HCL. The calculated thermodynamic parameters indicated that the micellization of SLAS is spontaneous and entropy driven in the absence and in the presence of ethylenediamine and L-Lysine.HCL within the temperature range investigated.

Keywords: Thermodynamic of micellization; Sodium lauroyl sarcosine; CMC

INTRODUCTION

Surfactants are molecules that consist of an apolar long-chain hydrocarbon tail attached to a polar, or ionic, portion and are widely used in foods, paints, pharmaceutical products, agrochemicals, and in industrial processes [1]. Surfactants tend to form thermodynamically stable aggregates denominated micelles. The *core* of the micelle is composed of a hydrophobic part and the corona is formed by polar head groups. These micelles are formed above a specific concentration called the critical micelle concentration (CMC) [1].

Interactions between surfactants and additives in aqueous solutions have been studied for decades. In general, the addition of electrolytes and non-electrolytes affect the CMC values of surfactants, leading micelles to be formed at different monomer concentrations [2]. This behavior is usually interpreted in terms of the Gibbs energy change of micelle formation.

Several research groups have studied systems formed by surfactants and additives such as amines and amino acids because these systems are widely used in micro emulsions [3,4], biosciences, foods, cosmetics, and drug delivery [5]. These studies provided a better understanding of the effects of pH, temperature, nature of the amine molecules and amino acid, as well as their content, on the micellization process of ionic surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB) and cationic gemini surfactants [6-14].

Sodium lauroyl sarcosine (SLAS) is an amino acid-based surfactant widely used in shampoos, soaps, toothpaste, and skin cleansers [15,16]. Furthermore, it is used as a corrosion inhibitor and accelerator in the formation of hydrogels [17]. However, to our knowledge, there are few studies that have examined the influence of additives on the aggregation process of SLAS in aqueous solutions. Among the existing studies, Seagal et al. investigated the micellization processes of SLAS and SLAS/SDS mixtures in the presence of different amounts of cyclic oligosaccharides, namely, α, β, and γ-Cyclodextrins by means of conductivity, NMR, and fluorescence study [18-20]. Recently, Ghosh and Dey studied the interaction of SLAS and sodium N-lauroylglycinate with the bovine serum albumin (BSA) and discussed the effect of the headgroup in these surfactants in the binding to BSA [21].

The aim of this research was to study the influence of the amine molecule ethylenediamine and amino acid L-Lysine.HCl on the aggregation behavior of sodium lauroyl sarcosine (SLAS) in aqueous solutions.

EXPERIMENTAL SECTION

Materials

The surfactant sodium lauroyl sarcosine (SLAS) was acquired from Sigma-Aldrich. The amino acid L-Lysine monohydrochloride (L-Lysine.HCL) was purchased from Sigma-Aldrich. Ethylenediamine was obtained from Vetec (Brazil). Doubly distilled water (specific conductance, $\kappa = 2 - 4\ \mu S.cm^{-1}$) was used to prepare all solutions. All reagents were used as received. The chemical structures of the molecules investigated are depicted in Figure 1.

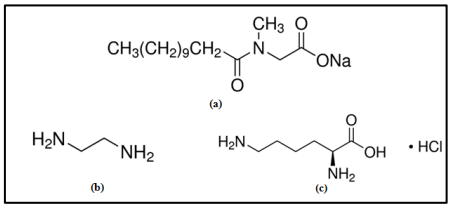

Figure 1: Chemical structure of (a) sodium lauroyl sarcosine, (b) ethylenediamine and (c) L-Lysine.HCL

Methods

The conductivity measurements of the surfactant solutions were carried out with a digital conductivity meter (Gehaka CG1800). A dip-type conductivity cell with a double-walled jacket to circulate the thermostated water was used for all of the measurements. An automatic thermostat bath (Tecnal TE-184) was used to maintain the appropriate temperature. The conductivity measurements were performed in the temperature range from 288.15 to 318.15 K. Before starting each experiment, the system was equilibrated in the respective temperature for at least 25 minutes. The accuracy of the conductance measurement was well within ± 0.5 %.

RESULTS AND DISCUSSION

Effect of additives on the CMC of SLAS

The conductometric titration method is one of the most widely used techniques to investigate the aggregation process of ionic surfactants. The physicochemical parameters of micellization can be obtained from the plots of specific conductance (κ) and surfactant concentration ([S]) such as the degree of counter-ion dissociation (α) and the critical micelle concentration (CMC) of the surfactant. In general, the κ vs. [S] plot shows a linear variation of specific conductance (κ) with the surfactant concentration both in the pre-micellar and post-micellar regions. The abrupt change in κ at a determined concentration of surfactant ([S]) leads to a sharp break point in the plot. The intersection point between the two straight lines provides the CMC value of the surfactant. Furthermore, the degree of counter-ion dissociation (α) can be calculated by the equation:

$$\alpha = \frac{S_2}{S_1} \qquad (1)$$

Where S_1 and S_2 are the slopes of the linear portion below and above the break point in the conductivity profiles, respectively

In order to understand the effect of additives on the micellization process of SLAS, the CMC and α of SLAS were initially obtained without the additives. Figure 2 shows the change in specific conductance (k) with the SLAS concentration at 298.15 K. In the absence of additives (ethylenediamine and L-Lysine.HCl), the profile exhibits a CMC value of 13.9 $mmol.L^{-1}$ at 298.15 K. The degree of counter-ion dissociation was determined from the slopes of the linear conductivity of the premicellar (S_1) and postmicellar (S_2) regions. The obtained value was 0.56. The CMC and α values found in this research are in agreement with the values reported in the literature [18,19,22].

Figure 3 shows the plot of specific conductance of the SLAS solution in the presence of additives at 298.15 K. The CMC values obtained for SLAS at different concentrations of ethylenediamine and L-Lysine.HCl at 298.15 K are shown in Figure 4. The results show that the CMC value of SLAS is influenced by the presence of both the additives.

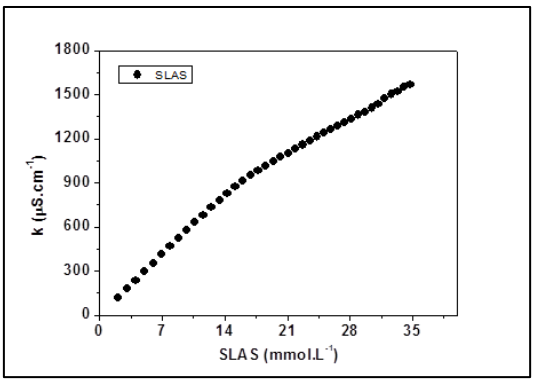

Figure 2: Specific conductance as a function of SLAS concentration (mmol.L^{-1}) in aqueous solution at 298.15 K

In addition, the CMC value of the SLAS decreased with increasing additive concentrations and the extent of the reduction of CMC followed the order: ethylenediamine < L-Lysine.HCl. A decrease in the CMC of SLAS occurs to the maximum extent with the L-Lysine.HCL, probably caused by the zwitterionic nature of the amino acid [5], which promotes a higher interaction with the SLAS in aqueous solution than ethylenediamine. Amino acids can facilitate the formation of micelles, decreasing the thickness of the electrical double layer of ionic micelle (electrostatic interaction) and acting as a water structure breaker [6,8]. This result can be better understood by acquiring the thermodynamic parameters of micellization of SLAS in aqueous solutions containing these additives, which is discussed in the next section.

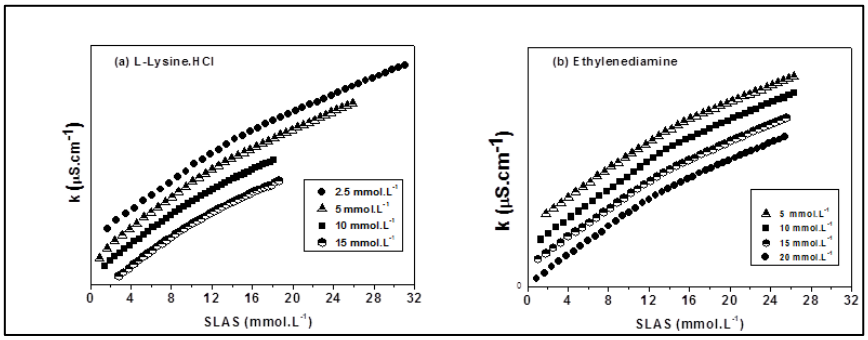

Figure 3: Specific conductance as a function of SLAS concentration (mmol.L^{-1}) in aqueous solutions containing different contents of (a) L-Lyssine.HCl and (b) ethylenediamine at 298.15 K. All plots are shifted for clarity

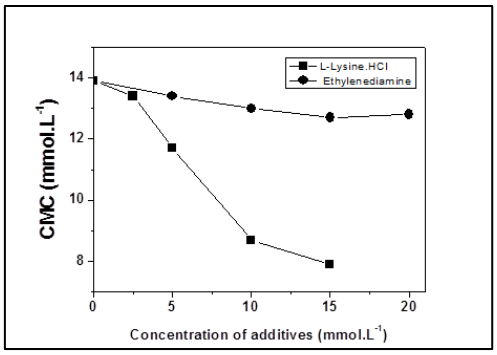

Figure 4: Values of critical micelle concentration (CMC) of SLAS in aqueous solutions as a function of (■) L-Lysine.HCl and (●) ethylenediamine contents at 298.15 K

The degree of counter-ion dissociation (α) is an important parameter for understanding of the micellization process of an ionic surfactant. Figure 5 shows the α values calculated by taking the ratio between the slopes of the linear portion above and below the break point in the conductivity profile for SLAS in the absence and presence of additives at 298.15 K. It is clear from Figure 5 that the α value of SLAS is higher upon addition of ethylenediamine and L-Lysine.HCl and its value depends on the concentration of the additives in the solution. This behavior can be attributed to the interaction of SLAS micelles with the additives, which promotes a

decrease of Na^+ ions bound to the SLAS micelles. As can be observed from Figure 5, this trend is more pronounced with L-Lysine.HCl than ethylenediamine.

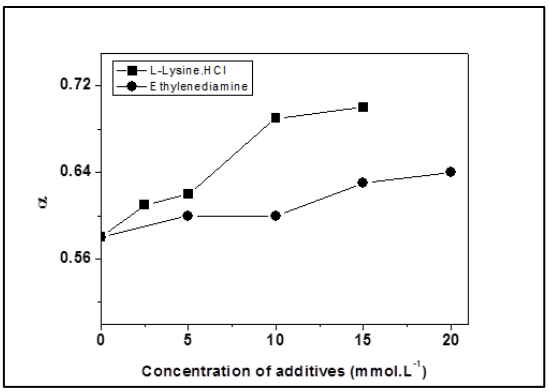

Figure 5: Values of degree of counter-ion dissociation (α) of SLAS in aqueous solution as a function of (■) L-Lysine.HCl and (●) ethylenediamine amounts at 298.15 K

Thermodynamic of micellization of SLAS

Conductivity measurements were performed at various temperatures (288.15–318.15 K) to investigate the effect of temperature on the CMC value and the degree of counter-ion dissociation (α) of SLAS in water and when ethylenediamine and L-Lysine.HCl were present. Figure 6 shows the plot of specific conductance as a function of SLAS concentration for SLAS in water and in the presence of additives (10 $mmol.L^{-1}$) at different temperatures.

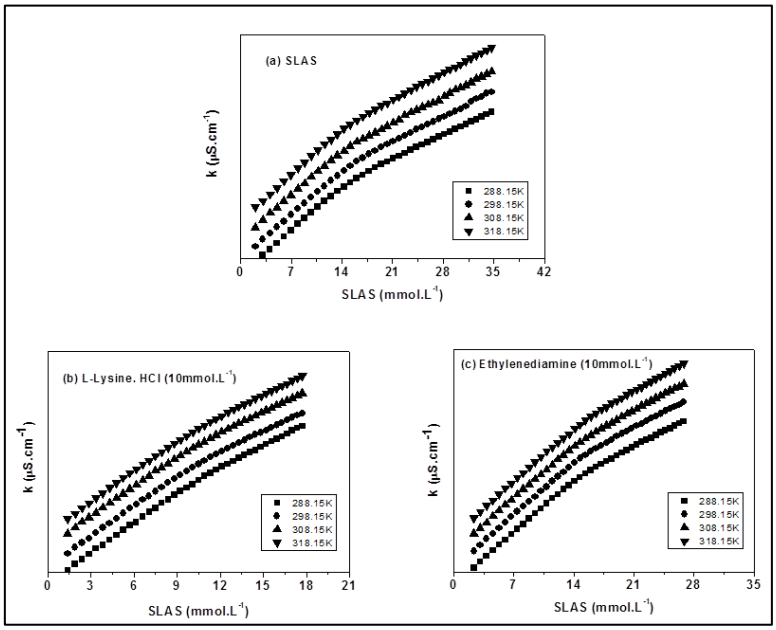

Figure 6: Specific conductance vs. concentration (mM) plot for: (a) SLAS, (b) SLAS + L-Lyssine.HCl (10 $mmol.L^{-1}$), and (c) SLAS + ethylenediamine (10 $mmol.L^{-1}$) at different temperatures. All plots are shifted for clarity

From the experimental data reported in Figure 6, the micellization parameters of SLAS at different temperatures were determined. The values of CMC and α at various temperatures for pure SLAS and with an additive concentration of 10 $mmol.L^{-1}$ are presented in Table 1. As can be observed, CMC and α values of SLAS enhance for all the systems (SLAS + water, SLAS + ethylenediamine, and SLAS + L-Lysine.HCL) in the temperature range investigated. Temperature was found to have two effects on the CMC of surfactant in aqueous solution: (i) the rise of temperature decreases the degree of hydration of the hydrophilic, which delays the micelle formation; and (ii) an increase in temperature causes the disruption of the water structure surrounding the hydrophobic group of surfactant, disfavoring micelle formation [23,24]. Therefore, the results demonstrate that the aggregation process for pure SLAS and in the presence of the ethylenediamine and L-Lysine.HCL are most influenced by the second of these effects in the temperature range studied.

Table 1: Values of critical micelle concentration (CMC) and degree of counter-ion dissociation (α) of SLAS in aqueous solution and in the presence of L-Lysine.HCl (10 mmol.L^{-1}) and ethylenediamine (10 mmol.L^{-1}) at different temperatures

Systems	Temperature			
	288.15 K	298.15 K	308.15 K	318.15 K
SLAS + Water				
CMC (mmol.L-1)	13.6	13.9	14.2	14.7
α	0.56	0.58	0.61	0.61
SLAS + 10 mmol.L-1 aqueous L-Lysine.HCl				
CMC (mmol.L-1)	8.5	8.7	9.1	9.3
α	0.77	0.69	0.7	0.71
SLAS + 10 mmol.L-1 aqueous ethylenediamine				
CMC (mmol.L-1)	12.9	13	13.3	13.5
α	0.6	0.6	0.63	0.63

In order to investigate further information about additive–SLAS interactions, thermodynamic parameters of micellization were calculated and examined using the mass action model [25]. The standard free energy of micellization was obtained using the equation:

$$\Delta G^{\circ}_{mic} = (2-\alpha)RT\ln X_{CMC} \qquad (2)$$

Where *R* is the gas constant, *T* is the temperature in Kelvin scale, α is the degree of counter-ion dissociation, and X_{CMC} is the CMC value expressed in terms of mole fraction.

The standard enthalpy of micellization can be determined by equation [26]:

$$\Delta H^{\circ}_{mic} = -(2-\alpha)RT^2\left(\frac{d\ln X_{CMC}}{dT}\right) \qquad (3)$$

Where $d(\ln X_{CMC})/dT$ was determined as the slope of the straight line obtained by plotting $\ln X_{CMC}$ against T.

Figure 7 shows the variation of $\ln X_{CMC}$ with the temperature (T) for all the systems studied. The curves were fitted using the following equations:

For SLAS+ water:

$$\ln X_{CMC} = (3.75 \times 10^{-5} K^{-2})\,T^2 - (0.02\ K^{-1})T - 5.59\ (R= 0.99) \qquad (4)$$

For SLAS + L-Lysine.HCl:

$$\ln X_{CMC} = (2.5 \times 10^{-5} K^{-2})\,T^2 - (0.012\ K^{-1})T - 7.38\ (R= 0.97) \qquad (5)$$

For SLAS + Ethylenediamine:

$$\ln X_{CMC} = (2.5 \times 10^{-5} K^{-2})\,T^2 - (0.013\ K^{-1})T - 6.57\ (R= 0.99) \qquad (6)$$

The standard entropy of micellization was calculated using the relation:

$$\Delta S^{\circ}_{mic} = \left(\Delta H^{\circ}_{mic} - \Delta G^{\circ}_{mic}\right)/T \qquad (7)$$

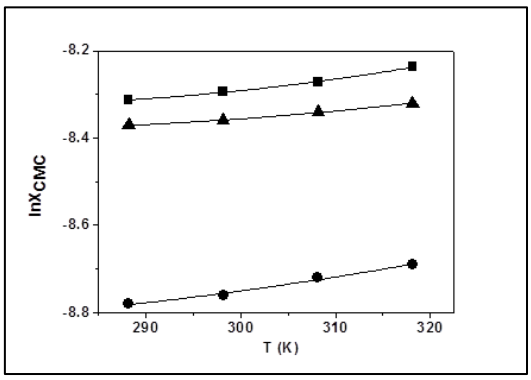

Figure 7: Plot of $\ln X_{CMC}$ vs. temperature for (■) SLAS, (▲) SLAS + ethylenediamine (10 mmol. L^{-1}), and (●) SLAS + L-Lysine.HCl (10 mmol.L^{-1})

Figure 8 shows the thermodynamic parameters obtained for SLAS in water and in the presence of the ethylediamine and L-Lysine.HCl (10 mmol.L^{-1}). As can be seen from Figure 8 (a), $\Delta G°_{mic}$ values are negative for all the systems, indicating that the micellization process of SLAS is spontaneous. Furthermore, $\Delta G°_{mic}$ values decrease with the rise in the temperature and are higher in the presence of the additives than in water, demonstrating that the micellization of SLAS is less favorable in the presence of the additives. Ali and Ansari also reported a rise in the $\Delta G°_{mic}$ values of SDS in the presence of 0.10 mol.Kg^{-1} aqueous glycine, alanine, and glycylglycine [27]. This effect can be explained considering that the higher α for SLAS in the presence of additives decreases the Na^+ content available for interaction with SLAS micelles, enhancing the electrostatic repulsion between the head groups of SLAS, increasing the standard free energy of micellization. Thereby, $\Delta G°_{mic}$ values follow the sequence: water < ethylenediamine < L-Lysine.HCL in the temperature range investigated.

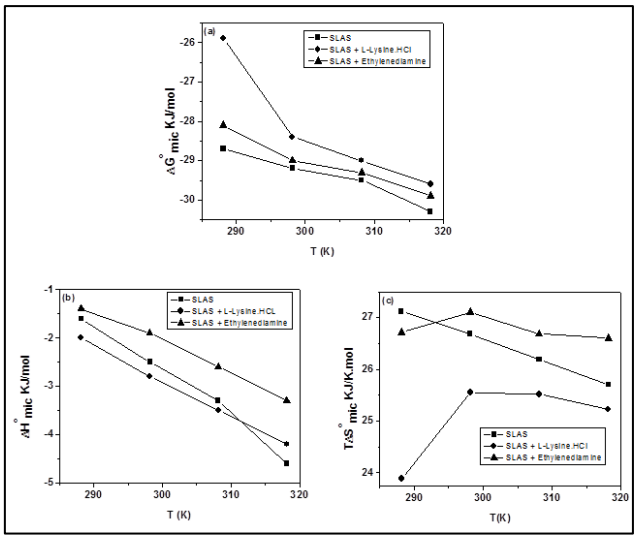

Figure 8: Thermodynamic parameters of micellization of SLAS as a function of temperature in the absence and in the presence of additives

The $\Delta G°_{mic}$ can be divided into two contributions: (1) $\Delta H°_{mic}$ and (2) $\Delta S°_{mic}$, as defined by thermodynamic relationship, $\Delta G° = \Delta H° - T\Delta S°$. Figure 8 (b) shows $\Delta H°_{mic}$ values calculated from Equations 3-6 as a function of the temperature for SLAS in water and upon the addition of ethylenediamine and L-Lysine.HCl. All the $\Delta H°_{mic}$ values are negatives, indicating that the formation of micelles of SLAS is exothermic. With a rise in temperature, $\Delta H°_{mic}$ values become more negative, indicating a decrease in the hydrogen bonds between the water molecules and hence of the energy needed to break up the water cluster [28]. However for SLAS + L-Lysine.HCl, the $\Delta H°_{mic}$ value increases at 318.15 K. From 288.15 K to 308.15 K, the relative order of $\Delta H°_{mic}$ values is L-Lysine.HCL < water < ethylenediamine. Above 308.15 K this trend is modified to: water < L-Lysine.HCL < ethylenediamine. The rise of the $\Delta H°_{mic}$ value for SLAS in the presence of the amino acid can be explained by a higher α of SLAS at 318.15 K (Table 1), which enhances the contribution of the electrostatic repulsion between the head groups of SLAS in the $\Delta H°_{mic}$ value. Figure 8 (c) exhibits $T\Delta S°_{mic}$ values of the aggregation process of SLAS at various temperatures. The results show that $T\Delta S°_{mic}$ values decrease with the rise of temperature, except for SLAS + ethylenediamine and SLAS + L-Lysine.HCl, which only decrease above 298.15K. This tendency can be explained by increases of the molecular motion at higher temperatures, which leads to the higher CMC values of surfactant [8]. The reduction of $T\Delta S°_{mic}$ values with the rise of temperature follow the order: L-Lysine.HCL < water < ethylenediamine. A similar effect of temperature on $T\Delta S°_{mic}$ and $\Delta H°_{mic}$ has been reported in the literature [6,8,29]. Considering that $\Delta_{tr}G°$ values are negative (Figure 8 (a)) and that $T\Delta S°_{mic}$ values are higher than $\Delta H°_{mic}$ values as shown in Figure 8 (b) and (c), it is possible to conclude that entropic factors govern the micellization process of SLAS in water and in the presence both additives in the temperature range studied. Thereby, positive $T\Delta S°_{mic}$ values show that the micellization of SLAS occurs with greater disruption of the water structure.

CONCLUSION

In this research, the effect of the addition of ethylenediamine and L-Lysine.HCL on the micellization of SLAS was investigated. The results derived from the conductivity measurements showed that the CMC values of SLAS decreased in the presence of ethylenediamine and L-Lysine.HCL. The zwitterionic nature of L-

Lysine.HCl contributed to the higher reduction of the CMC value. The thermodynamic parameters of the micellization of SLAS in both the absence and presence of ethylenediamine and L-Lysine.HCL showed that the micellization process is spontaneous and entropy driven in the temperature range between 288.15 K and 318.15 K.

ACKNOWLEDGEMENTS

The authors acknowledge the Brazilian funding agency FAPERJ for its financial support.

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