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EFFECT OF SOME BIOLOGICALLY IMPORTANT ORGANIC COMPOUNDS ON THE MICELLER PROPERTIES OF SODIUM DODECYL SULPHATE

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Abstract: The effect of some organic additives such as glucose, phenol, caffeine, urea and formamide on the critical micelle concentration (CMC) of an anionic surfactant sodium dodecyl sulfate (SDS) has been studied by conductance measurement. The investigation was performed in the additives concentration ranging from 0.01 M to 0.06 M. The presence of both urea and formamide cause a linear increase in the CMC from 8.10 mM to 9.5 mM and to 10.15 mM, respectively, while an exponential decreasing trend was observed with increasing the concentration of glucose, phenol and caffeine in the same range. In the latter case, the decreasing trend of the CMC values follows the order: caffeine > glucose > phenol.

***Keywords*:** Critical micelle concentration, micellization, denaturants, structure breakers, structure makers

Introduction

Surfactants are the amphiphilic molecules which undergo special type of self-assembly process, and the phenomenon is known as micellization. This type of morphology has provided vast scope for applications in biological systems, drug action mechanisms and also in many industries [1]. Over the last decade, interest in the molecular structure of biological membranes has dramatically increased. Model composed of amphiphilic materials and aggregated colloids provide a useful way of better understanding in many invaluable areas such as biochemistry, medicine, and pharmaceuticals as well as in catalysis [2,3]. Several research groups [4,5] have studied the kinetics of organic reactions in the presence of surfactant micelles as these can influence the rate of the chemical reaction incorporating the reactant molecules in micellar pseudophase [6].

The use of surfactants as detergent, stabilizer, and dispersing agent depends on the property which is known as solubilization. This occurs because the insoluble species can be incorporated into the micelle core and the micelle can act as the site for the dissolution of lipophilic molecules [7]. Surfactants are also widely used in studies on organic reactions in microemulsions, organic syntheses and also in nucleophilic aromatic substitution reactions [8-10].

Urea is considered as a well-known denaturant for proteins, polypeptides and biopolymers [11], as it weakens the hydrophobic interactions in aqueous solution [12]. The effect of urea is attributed to two different proposed mechanisms [13]. One is indirect mechanism, in which urea alters the structure of interfacial water surrounding the solute [14-16]. In the other, direct mechanism, urea replaces some of water molecules in the hydration shell of the solute [15, 17,18]. For these reasons, interest arises in studying the effect of urea on self-aggregation such as micelles [11,13,19-21], reversed micelles [22,23], and also on penicillin, which are extensively used with local anaesthetic and antibiotic action [1]. Although many researchers [14,24-26] reported that urea acts as a 'water-structure breaker', Kabir-ud-Din *et al.* [27] extensively studied the effect of urea at low concentration (≤0.25 M) on the micellization of 0.3 M SDS + Bu_4NBr with and without urea

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and interpreted SANS (Small Angle Neutron Scattering) and cloud point (CP) measurements, and presented that urea addition up to a certain concentration facilitates micellization.

The present work is an attempt to correlate the formation of micelles, for a series of organic additives which are urea, formamide, phenol, glucose and caffeine by measuring the conductivity since it is one of the widely used methods to locate the CMC's of ionic surfactants [28-32]. As the above organic compounds are biologically important and among them, urea is widely used in protein folding studies to explore the mechanism of denaturants in protein stiffening [28], interests has also grown in caffeine because of its potent pharmacological effects since alkaloids are the basis for many drugs.

Materials and Methods

SDS from Merck (Germany) was used after purification by recrystallization using absolute ethanol. Solutions of SDS in the desired range of concentrations were prepared from 50 mM stock solution in de-ionized water distilled previously with potassium permanganate. Solutions of organic additives such as caffeine, glucose, phenol (BDH, England), urea (M&B, England) and formamide (BDH, England) were prepared in the concentration range of 0.01 M to 0.06 M by the appropriate dilution of 0.1 M of the stock solutions. The conductivity data were measured with a digital conductivity meter (Model- DDS-607, China). The calibration of the instrument was done with 0.01M KCl solutions (specific conductance = 1.55×10^3 μS cm^{-1} at 30 ºC) at regular time intervals and the electrode was cleaned with distilled water after each measurement. The CMC of SDS was determined by measuring specific conductance containing a particular concentration of the organic additives by dipping the electrode in the solution. The temperature of the system was kept at 30 ± 0.1 ºC with the aid of a digital thermostat (Clifton, Nickel Electro, England).

Results and Discussion

Effect of caffeine, glucose and phenol on CMC of SDS

The effect of phenol, glucose and caffeine on the CMC of SDS is shown in Table 1 and the corresponding plot is shown in the Figure 1. In general, large amounts of water-miscible organics will increase the CMC by increasing the solubility of the tail, although the opposite effect may occur for highly ionized species where the lower dielectric constant reduces head group repulsion; as a result micelle formation is favored. Since glucose is polar and highly soluble in water, in its presence the water-water interaction is replaced with water-glucose interaction. As a result, the formation of water structure decreases and micelle formation is favored [33].

Addition of phenol, glucose and caffeine showed sharp decrease in CMC up to 0.01 and then CMC decreased steadily. It was found that increasing the amount of phenol decreased the value of CMC markedly as compared to glucose as well as caffeine. The descending trend of CMC was due to the action of phenol as a co-solute which can greatly increase the solubility of nonpolar additives in ionic SDS solutions. The mechanism is expected to be the insertion of polar additive molecules between adjacent surfactant molecules in the micelle. It was observed that the decreasing trend of CMC with increase in the concentration of caffeine was more pronounced than that of glucose at the additive concentration of 0.05 M or more as shown in Figure 1.

Table 1. Variation of CMC of SDS at different concentrations of glucose, phenol and caffeine at 30 ˚C.

[Organic additive] (M)	CMC at different additive concentration (mM)		
	glucose	phenol	caffeine
0.00	8.10	8.10	8.10
0.01	4.85	4.00	5.20
0.02	4.55	3.80	4.98
0.04	4.15	3.50	4.60
0.06	3.85	3.15	3.40

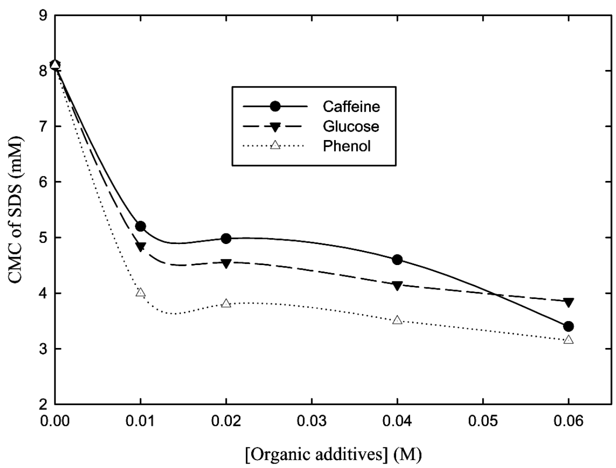

Figure 1. Variation of CMC of SDS (mM) against concentration of added organic additives: caffeine (●), glucose (▼) and phenol (Δ) at 30 °C**.**

Effect of urea and formamide on CMC of SDS

The effect of urea and formamide on CMC of SDS is shown in Table 2 and the corresponding plot is shown in Figure 2. It was observed that in the presence of urea, the CMC of SDS rose from 8.10 mM to 9.50 mM at the urea concentration up to 0.06 M. The results indicate that urea influenced the hydrophobic effect which is considered as the driving force of micelle formation. The results are in good agreement with the previous work of Constantino *et al* [15]. The CMC value is method dependent [34] and small amounts of organic material cause a sharp change in CMC from its pure state at a particular temperature, which is consistent with an earlier study [35]. Having different hydrogen bonding sites, urea is able to form bonds with water molecules. Figure 2 shows that when the concentration of the additives increased, the value of CMC increased sharply in the presence of formamide than with urea at 0.06 M concentration or more. This can be explained on the basis of dielectric constant of the medium. Since the dielectric constant of urea is lower (5-8 at 71 °F) than that of formamide (84.0 at 68 °F), urea addition increases the dielectric constant of the system [36,37]. Hence the degree of dissociation (α) of SDS increases. Increasing the dielectric constant of the polar solvent, the coulombic force between the ions of opposite charged Na^+ ion and DS^- decreases. As a result, the ion pair formation (*i.e.* micelle) is hindered. This effect is dominating for formamide than for urea at a concentration of 0.06 M or more. Thus, for a particular surfactant, the CMC decreases with increasing the dielectric constant of the polar solvents. Furthermore, micelle formation depends not only on the hydrogen bonding capability but also on the dispersion forces among the alkyl chains of the surfactant ions [38].

Table 2. Variation of CMC of SDS at different concentration of urea and formamide at 30 ˚C.

[Organic additive] (M)	CMC at different additive concentration (mM)	
	urea	formamide
0.00	8.10	8.10
0.01	8.60	8.70
0.02	8.80	9.05
0.04	9.00	9.75
0.06	9.50	10.15

Formamide is capable of forming strong hydrogen bond [35] and affect CMC by modifying the bulk water structure. Hence hydrophobic parts of SDS are weakly induced by lower amount of water structure. Thus, CMC increases with reduction in the entropy of micellization.

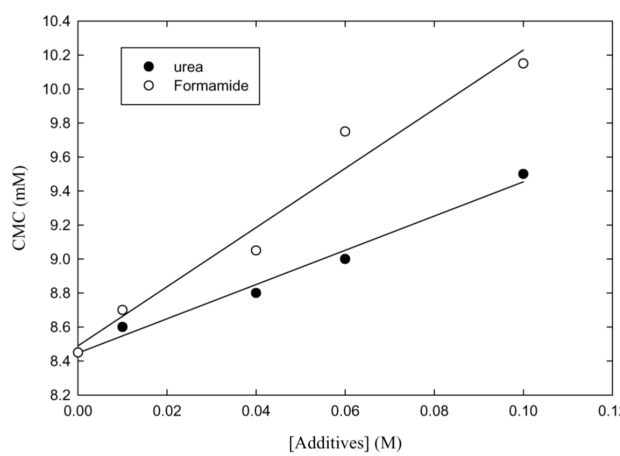

Figure 2. Variation of CMC of SDS (mM) against concentration of added organic additives (M) formamide (o) and urea (●) at 30 °C**.**

Conclusion

It can be concluded that micellization phenomenon is strongly affected by the addition of foreign substances, and the effect is strongly additive nature dependent. In case of urea and formamide, a linear upward trend in CMC occurs with the increased additive concentration. Hence, with increase in the additive concentration of urea and formamide in the experimental range of 0.01 to 0.06 M, CMC increases from 8.10 mM (pure state) to 9.5 mM and 10.15 mM, respectively, but in case of glucose, phenol and caffeine, CMC decreases exponentially.

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