



## Effect of N-Decyl-N-N-Dimethyl-3-Ammonio-1-Propanesulfonate on the Solution Properties of Sodium Dodecyl Sulfate

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**ABSTRACT:** Conductivity measurements have been used to study the solution properties of mixtures of sodium dodecyl sulphate (SDS) and n-decyl-n,n-dimethyl-3-ammonio-1-propanesulfonate (DPS) at 35 and 40 °C and various concentrations of DPS. The critical micelle concentrations (CMCs) of the solution of SDS and its mixtures with DPS were extrapolated from the inflection points on conductivity versus concentration curves. The CMCs increased as the temperature of the solution increased but decreased with increasing concentration of DPS. The degree of ionization of the mixed micelles calculated from the slope before and after the inflection point on concentration versus conductivity plots increased with increasing concentration of DPS but decreased with temperature. These results have been fully discussed based on the effect of non-charged DPS headgroup on the charged SDS headgroup. © JASEM

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Surfactants are amphiphilic compounds i.e., they possess a hydrophilic headgroup covalently bonded to a hydrophobic alkyl chain in a single molecule. This dual chemical nature gives them unique interfacial and solution properties. As surface-active agents, they greatly reduce the surface tension of water and form aggregates in the bulk solution even at low concentrations. Most surfactants are usually synthetic but some biological substances mainly phospholipids that make up living cell walls are also amphiphilic. Surfactants are of different types depending on the nature of the hydrophilic headgroup. They can be anionic which have negatively charged headgroups such as sulphates, phosphates and carboxylates; cationic surfactants possess headgroups that terminate with a positive charge e.g., quaternary ammonium and pyridinium; non-ionic surfactants have neutral uncharged polar headgroups e.g. polyethylene glycol. The zwitterionic surfactants are special class of surfactants with two oppositely charged species within a headgroup and thus have net neutral charge (Shiloach and Blankshtein, 1997). Surfactants are very important in various industrial and household products such as detergents, dishwashing liquids, hair conditioners, toothpaste, food, paints, emulsions, inks, firefighting, shampoos, agrochemicals, lubrication, antifungal, antibacterial and antiseptics (Sehgal et al., 2008; Patil et al., 2008; Briscoe et al 2006; 2007). In fact, some surfactants such as dodecyltrimethyl ammonium bromide have been reported to interact favourably with DNA and lipids (Peyre et al., 2005; Arrigler et al., 2005).

As mentioned earlier, surfactants are unique surface-active agents in that they do not only adsorb at the air-water interface to reduce the surface tension of

water but also form aggregates in solution when the interface is fully saturated. The concentration above which surfactant aggregates otherwise called micelles begin to form in solution is called critical micelle concentration CMC (Peyre et al., 2006). Micelle formation is a very important concept in surfactant chemistry since surfactant molecules behave differently as monomers in solution and when present in micelles. Most striking and important changes in the properties of surfactant solutions occur at CMC (Arrigler et al., 2005). Moreover, the aggregation number or number of surfactants in a micelle and the shape of micelles formed are important in determining the properties of a surfactant solution. Therefore, the behaviour of surfactants in solution in terms of aggregation and factors influencing this behaviour are essential in understanding the performance and physical properties of surfactants.

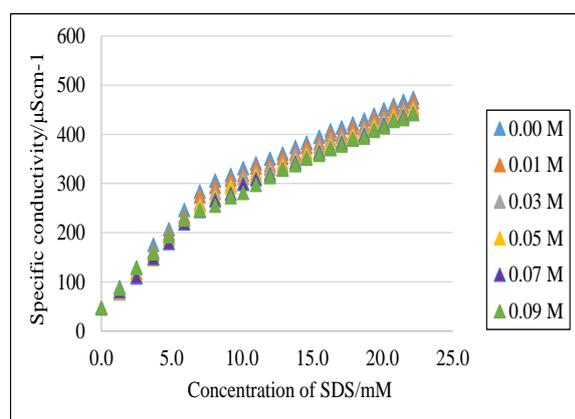
CMC of aqueous solution of a surfactant is greatly influenced by the molecular architecture of the surfactant i.e. the nature of the headgroup and alkyl chain. Ionic surfactants usually have higher CMC values than non-ionic surfactants of equal hydrophobic chain since repulsive interactions of the ionic headgroups will limit micelle formation and thus increase CMC (Rosen and Kunjappu, 2012). Ionic surfactants with higher headgroup charge will experience greater electrostatic repulsion and thus higher CMC. The more polar nature of amine-containing ionic headgroups will tend to interact more strongly with water molecules than the headgroups of other ionic surfactants with a resultant increase in CMC for the amine-containing surfactants. For ionic surfactants with constant alkyl chain, the degree of micelle ionization largely

determines the value of CMC. For complete ionization, no counterion is bound to the surfactant headgroup and electrostatic repulsion is greatest and CMC is increased. For incomplete ionization, micelle formation is dependent on the degree of counterion binding as this significantly influences the repulsive interactions between ionic headgroups.

The CMC and degree of micelle ionization of ionic surfactants and their mixtures are usually determined from conductivity versus concentration curves of the conductivity data of the surfactant solution. The CMCs are determined at the point of intersection of lines extrapolating the conductivity-concentration curve of the solution from below and immediately above the region in which an inflection point in the slope is observed and the degree of micelle ionization from the ratio of the slopes before and after CMC (Holmberg et al., 2003; Rosen and Kunjappu, 2012). In this work, conductivity measurements of aqueous solutions of sodium dodecyl sulphate have been done at 35 and 40 °C and different concentrations of DPS. The conductivity data was used to extrapolate the CMCs and degree of micelle ionization of SDS and its mixtures with DPS. These results have been used to discuss the influence of temperature and concentration of DPS on the micellization of SDS.

#### MATERIALS AND METHODS:

**Materials:** Sodium dodecyl sulphate (99%) was purchased from Lancaster synthesis and n-decyl-n,n-dimethyl-3-ammonio-1-propanesulfonate (97%) was purchased from Sigma Aldrich. There was no further purification on the surfactants but their purity was checked by determining their CMCs at 298 K. The experimental CMCs were in agreement with the literature values.

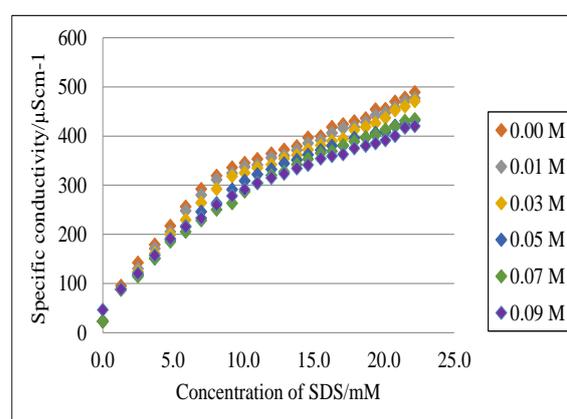


**Fig. 1:** Plots of specific conductivity vs. molar concentration of SDS and its mixtures with DPS at various concentrations of DPS and at 35 °C.

**Methods:** Aqueous stock solutions of SDS were prepared at concentrations approximately ten times the literature value of its CMC. For the mixtures, such aqueous stock solutions of SDS were first prepared and used to prepare mixed solutions of SDS and DPS at concentrations of 0.0, 0.01, 0.03, 0.05, 0.07 and 0.09 M DPS. The conductivity of solutions of single SDS and the mixtures was measured at 35 and 40 °C with a JENWAY 4510 conductivity meter (027013) with a cell constant 1.02 cm<sup>-1</sup>. The first procedure was to measure the conductivity of a known volume of deionized water and for each solution (single SDS or mixtures) successive addition of the stock solution of a precise volume into the water was made using an Eppendorf pipette, from which the concentration of SDS or mixtures was calculated. Conductivity versus concentration plots were linear at lower concentrations until a break (or inflection) point was observed. Beyond this point, the curves became linear again with a smaller gradient

#### RESULTS AND DISCUSSIONS:

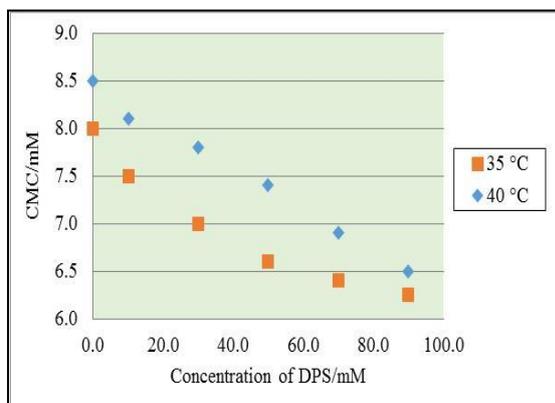
Figures 1 and 2 illustrate the conductivity of solution of SDS and its mixtures with DPS at various concentrations DPS and at 35 and 40 °C respectively. Here conductivity increases with increasing solution concentration before the break or inflection point (CMC). The inflection point becomes less well defined as the concentration of DPS increases due to reduced charge density on mixed micelles. Ionic surfactants are like strong electrolytes that dissociate completely in aqueous solution into its ions. Before CMC, conductivity increases linearly with concentration. Above CMC, the rate of conductivity increase with concentration or the gradient decreases. This indicates that the mobility of free surfactant ions in solution before micelles are formed is greater than that of the micellar aggregates.



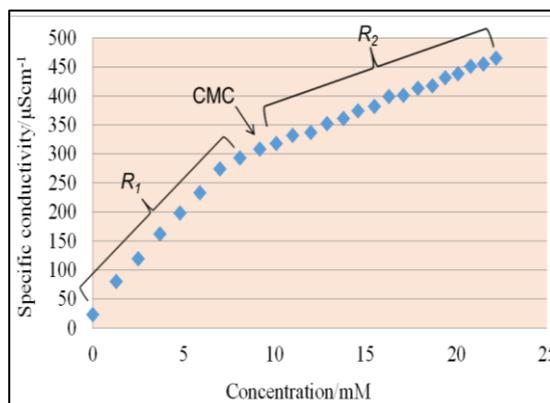
**Fig. 2:** Plots of specific conductivity vs. molar concentration of SDS and its mixtures with DPS at various concentrations of DPS and at 40 °C.

Secondly, before the formation of micelles, counterions are fully dissociated from the surfactant headgroup and above CMC, they are partially dissociated. So, some fractions of the counter ions are bound to the micellar headgroup thus reducing the effective charge on the micelle (Tyowual *et al.*, 2012), therefore, conductivity is no longer linear to solution concentration. As micelles form, conductivity of the ionic solution does not depend on

the free surfactant ions and counterions alone but also on the charged micelles (Kallay *et al.*, 2003). The fraction of counter ion unbound to the micelle, which is equivalent to the degree of micellar ionization is determined from the ratio of the slope after and before CMC (Rosen, 1989). Figure 4 shows the inflection point corresponding to CMC, the slope before and after CMC,  $R_1$  and  $R_2$  respectively.



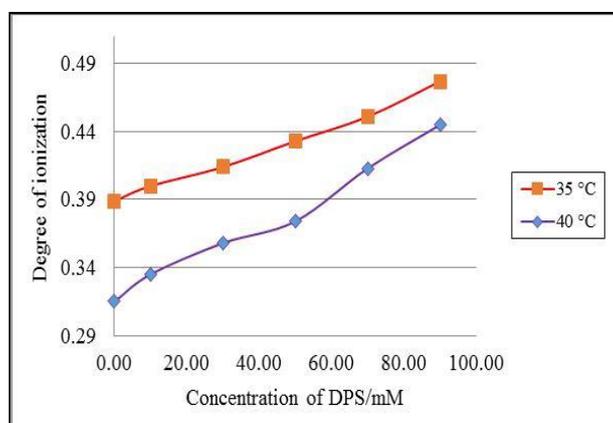
**Fig 3:** The CMCs of SDS and its mixtures with DPS at different concentrations of DPS and 35 and 40 °C Data points in orange are CMC values at 35 °C and those in blue are for 40 °C.



**Fig 4:** Specific conductivity versus solution concentration showing CMC, slopes before and after CMC,  $R_1$  and  $R_2$  respectively.

Figure 3 shows the variation of CMC of the binary mixtures of SDS and DPS as a function of DPS concentration and temperature. CMC decreases as the concentration of DPS increases but increases with increasing temperature. This implies that the incorporation of DPS non-ionic surfactant headgroup into the headgroup of SDS ionic surfactant reduces the electrostatic repulsion between the ionic headgroups and thus favours micelle formation. Recall that CMC is dependent on the balance of forces between electrostatic repulsion of charged headgroups and attractive forces of alkyl chain length (Domínguez *et al.*, 1997). As the concentration of the non-ionic surfactant is increased, the ionic

headgroups are further apart and the electrostatic repulsion between them becomes more reduced. Thus aggregation of surfactant molecules is enhanced resulting in lower CMC. This is reflected in Figure 3 where the CMCs of the mixtures are observed to decrease with increasing concentrations of the non-ionic surfactant. Interestingly, the CMCs of the mixtures at 35 °C are lower than those at 40 °C at all DPS concentrations. Noudeh *et al.*, 2007 have also reported increase in CMC at temperatures of 25 °C and above for the conductivity of aqueous solutions of cationic and anionic surfactants and attributed this behaviour as due to enthalpy effect at high temperature.



**Fig 5:** Plots of the degree of ionization of mixed SDS and DPS micelles versus concentration of DPS at 35 and 40 °C.

The influence of DPS and temperature on the degree of ionization of SDS micelle is illustrated in Figure 5. Here, the degree of ionization is observed to increase as the concentration of DPS increases but decreases with increasing temperature. It is well known that both physical and performance properties of ionic surfactants and their mixtures are dependent on the nature of the interactions of the polar headgroups and non-polar hydrophobic chain. For ionic surfactants, while interactions of the chain length are mainly Van der Waals attractive forces, which favour surfactant aggregation, headgroups interactions are often governed by charge density. A good understanding of the behavioural pattern of the micellar ionic headgroup is therefore essential. The degree of micellar ionization is one of the important parameters that influence headgroup-headgroup interactions and so influences micelle formation and hence CMC. Figure 5 indicates that the degree of ionization of SDS micelle can be increased by the addition of DPS molecules but decreases with increasing temperature. It becomes pertinent that for applications involving SDS, where the CMC needs to be reduced, addition of DPS is very important. However, for such applications, increased temperature is not favourable.

#### SUMMARY AND CONCLUSIONS:

Conductivity measurements have been used to study the influence of DPS on the aqueous behaviour of SDS at different temperatures and concentration of DPS. Results show that DPS, a non-ionic surfactant greatly reduce the attachment of counterions to the ionic micellar headgroup of SDS and thus increase the degree of micelle ionization. In addition, the CMC of SDS is greatly reduced in the presence of DPS signifying that DPS enhances micelle formation in SDS molecules and the tendency increases with increasing concentration of DPS. Increasing the temperature of aqueous solution of SDS was also found to disfavour the formation of SDS micelles.

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