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Conductivity Studies of Binary Mixtures of Ionic and Non-ionic Surfactants at different Temperatures and Concentrations.

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ABSTRACT: Conductivity studies of aqueous solutions of binary mixtures of sodium dodecyl sulphate (SDS), an ionic surfactant and n-decyl-n,n-dimethyl-3-ammonio1-propanesulfonate (DPS), a non-ionic surfactant have been carried out at different concentrations and temperatures. The results show that the conductivity of the solutions of SDS increased with increasing temperature but decreased as the concentration of DPS increased. It was also observed that the concentration at which SDS aggregates or micelles begin to form in solution, called critical micelle concentration (CMC) extrapolated from inflection points on the conductivity versus concentration curves increased with increasing temperature but decreased as the concentration of DPS increased. These results have been discussed in terms of the influence of the molecular architecture of SDS and DPS headgroups on mixed micelle formation. © JASEM

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The importance of surfactants in various applications such as agriculture, water treatment, oil recovery, cosmetics, pharmaceutical, food, detergency, wetting and micellar solubilisation (Briscoe *et al*., 2006; Briscoe *et al*., 2007; Sehgal *et al*., 2008 and Stubenrauch *et al*., 2008) has been greatly emphasised. However, mixtures of surfactants are now preferred over the single components in various areas of application (Gharibi *et al*. 2004). Depending on the molecular architecture of the mixing surfactants and solution conditions, mixtures of surfactants usually have enhanced fundamental and performance properties over the individual component surfactants. In view of this, studies of mixed surfactant systems have been on very high increase (Rosen and Sulthana, 2001). The general fundamental focus has been to relate the interfacial and solution behaviour of surfactant mixtures to the interaction between the component surfactants of the mixture. To this end, the choice of surfactant combinations becomes apparently important as mixing can be ideal or non-ideal. Generally, mixing surfactants of similar structures, e.g. similar headgroups and chain lengths, results in ideal behaviour (Rosen, 1991; Rosen and Sulthana, 2001; Stubenrauch *et al*., 2008) where the properties of mixed surfactants can be predicted from those of pure constituent surfactant molecules. Non-ideality is often exhibited by surfactants of dissimilar morphology e.g. ionic/non-ionic and zwitterionic/non-ionic (Rosen, 1991; Rosen and Sulthana, 2001) where mixed surfactants experience interactions between them. For instance, if strong attractive interactions exist between the mixing surfactants, it can lead to synergistic effect (Ruiz and Aguiar, 2003). This can be exploited to reduce the total amount of a component surfactant used in a particular application which in turn will reduce cost and environmental impact (Blankschtein and Shiloach, 1998; Stubenrauch *et al*., 2008) For this reason, it is important to understand the behaviour of such mixtures in order to tune their properties to a particular application.

Several techniques are used to determine parameters needed to evaluate the nature and strength of interactions between binary mixed surfactants. Among such techniques are surface tensiometry and conductometry (Gharibi *et al*., 2004; Kabir-ud-Din *et al*., 2008; Maeda, 2010). While surface tension measures the behaviour of surfactants and their mixtures at the air-water interface, conductivity measurements are vital in assessing bulk solution properties. However, both techniques are important in determining an invaluable parameter used to describe all surfactant solutions. This parameter is called critical micelle concentration (CMC), or the concentration at which micelles or surfactant aggregates begin to form in solution Micelle formation is so important in the chemistry of surfactant solutions since it is at CMC that abrupt changes in their solution and performance properties occur. Several studies (Rosen and Sulthana, 2001; Kallay *et al*., 2003; Marangoni *et al*., 2006; Pankaj *et al*., 2008) have shown that the CMC of single surfactants and their mixtures can easily be determined by measuring a physical property of surfactant solution against its concentration. CMC is usually indicated by an inflection point on the curve of the physical property plotted against solution concentration.

Theoretically, CMCs of aqueous solutions of binary mixtures of surfactants can be predicted from the knowledge of the CMCs of the single surfactant components assuming ideal mixing. Clint's model (Clint, 1975 and Joshi *et al*. 2005) relates the CMCs of the individual surfactants, C_1 and C_2, to the bulk solution compositions of the surfactants, α and $1-\alpha$ to obtain the CMC of the mixture, C_M as shown in the equation below. The values of the theoretical CMCs of the mixtures so calculated are usually compared with values determined experimentally for the same single surfactants.

$$\frac{1}{C_M} = \frac{\alpha}{C_1} + \frac{1-\alpha}{C_2}$$

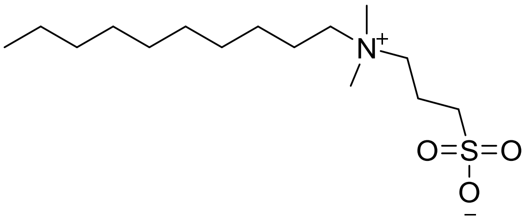
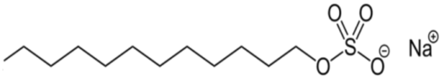
The ideality of mixing can then be estimated by considering the difference between these values. Clint's theoretical treatment of mixed surfactants has been useful especially in comparing ideal and non-ideal behaviours of mixed surfactant systems. Deviations from ideality are a function of the nature of interaction between the component surfactants. Interactions between mixing surfactants can be repulsive or attractive. Attractive interactions between surfactant mixtures may result in synergism, a case in which the fundamental properties e.g. surface tension reduction, critical micelle concentration (CMC) and performance properties e.g. foaming, detergency, and wetting of the mixture are superior to those of the single surfactants (Rosen and Kunjappu, 2012). The fundamental aim of mixed surfactant studies is therefore to seek for synergism.

CMCs of surfactants and their binary mixtures evaluated from surface tension and conductivity data are also important in predicting bulk solution compositions of mixed micelles. This can be achieved through the application of thermodynamic models to these data; Rosen's model for the mixed monolayer at the air-water interface and Rubingh's model for the mixed micelles in the bulk solution (Tsubone and Ghosh, 2003; Tsubone and Ghosh, 2004; Chakraborty and Ghosh, 2007; Ghosh and T. Chakraborty, 2007; Kabir-ud-Din et al., 2009; Khan *et al.*, 2010). The knowledge of the compositions of the individual mixed surfactants at these phases gives an understanding of the nature of the interactions between the mixture components and thus an insight on whether the mixing results in ideal or non-ideal solution. CMCs of mixed surfactants are also useful tools in predicting the strength of interactions between them in comparison to the interactions of the single surfactant molecules before mixing. These models will be applied and discussed in details in our next paper. The importance of CMC for both single and surfactant mixtures therefore, is an integral part of the study of any surfactant system. In this study, we have measured the conductivities of SDS at different temperatures in order to ascertain the influence of temperature on the conductivity of SDS solutions and thus the CMC. Secondly, we have progressively increased the concentrations of DPS in SDS solution at different temperatures so that the influence of this non-ionic surfactant on both conductivity and CMC of SDS can be determined.

MATERIALS AND METHODS

Sodium dodecyl sulphate (99%) was purchased from Lancaster synthesis while n-decyl-n,n-dimethyl-3-ammonio-1-propanesulfonate (97%) was a product of Sigma Aldrich. The surfactants were used without further purification. Their purity was checked by determining the CMCs of the pure surfactants, and these were in agreement with literature values. The molecular architecture of these surfactants are shown in the Table below.

Table 1: Molecular architecture of SDS and DPS surfactants studied.

N-decyl-n,n-dimethyl-3-ammonio-1-propanesulfonate (DPS)	
Sodium dodecylsulfate (SDS)	

Stock solutions of single SDS surfactant were prepared at concentrations ten times the literature values of its CMC. For the mixtures, aqueous solutions of SDS were first prepared at concentrations ten times its CMC. Stock solutions of the mixtures were then prepared by using these SDS stock solutions to prepare 0.01, 0.03, 0.05, 0.07 and 0.09 M concentrations of DPS. All solutions were prepared with deionized water. The conductivity of the solutions of single and mixed surfactants was measured with JENWAY 4510 conductivity meter of cell constant 1.02 cm^{-1} at 25 and 30 ± 1°C. Each temperature was maintained fairly constant with a thermostated temperature bath before the conductivity of the solutions was measured. This was done by measuring the conductivity of a known volume of deionized water first, and then successive addition of an exact volume of SDS or mixture stock solution into the water was made using an Eppendorf pipette. Conductivity at each addition was measured. Conductivity versus concentration plots were linear at lower concentrations until a break point was observed. Beyond this point, the curves became linear again.

RESULTS AND DISCUSSION

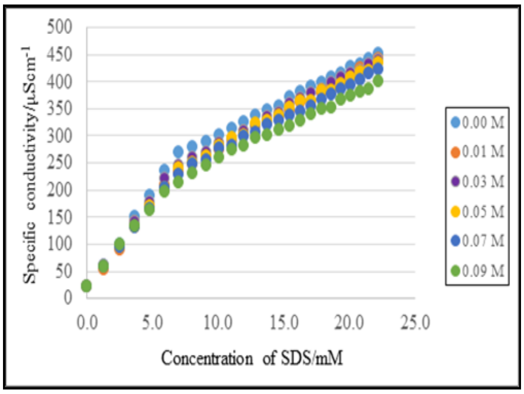


Fig: 1: Plots of specific conductivity vs. Molar concentration of SDS and its mixtures with DPS at various concentrations of DPS at 25 ^{0}C.

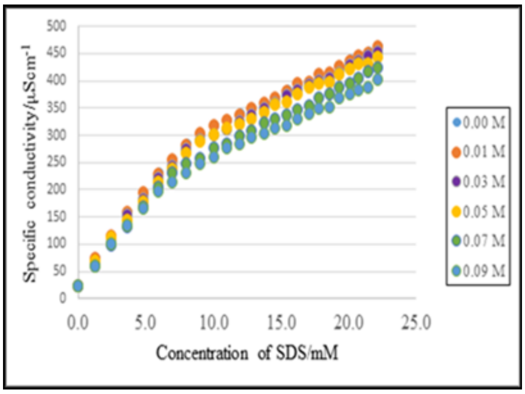


Fig: 2: Plots of specific conductivity vs. molar concentration of SDS and its mixtures with DPS at various concentrations of DPS at 30 ^{0}C.

Figures 1 and 2 show the specific conductivity versus concentration curves of SDS and DPS mixtures at 25 and 30 ^{0}C respectively and at various concentrations of DPS. These curves show increase of conductivity as the concentration of DPS increases with corresponding increase in gradient until an inflection point (CMC) is observed. Above this point, conductivity still increases with concentration but with a decrease in gradient. The abrupt change at the CMC has been reported in several literatures (López-Díaz, and Velázquez, 2007) as due to different degree of ionization of surfactants below and above CMC, *i.e*., below CMC, ionic surfactants behave as strong electrolytes and dissociate completely into its ions according to Kohlrausch's Law of independent mobility of ions (Domínguez *et al*., 1997; López-Díaz and Velázquez, 2007). At CMC, aggregates begin to form and mobility of ions is slowed down. Above CMC, dissociation becomes weaker as micelles are partially ionized. Electrical conductivity then dependents on the degree of micelle ionization (Tyowua1 *et al*., 2012).

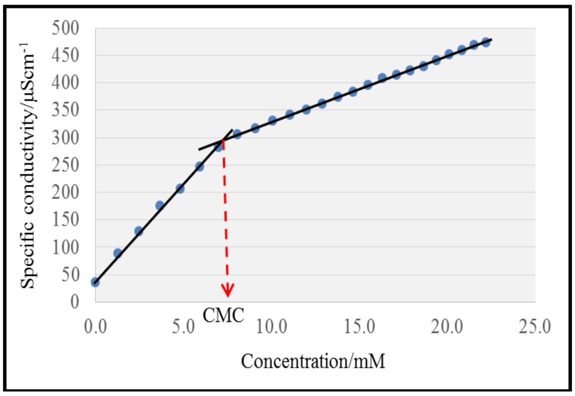


Fig: 3: Specific conductivity versus surfactant solution concentration showing linear fits below and above the inflection point and the extrapolated intercept, which is the CMC

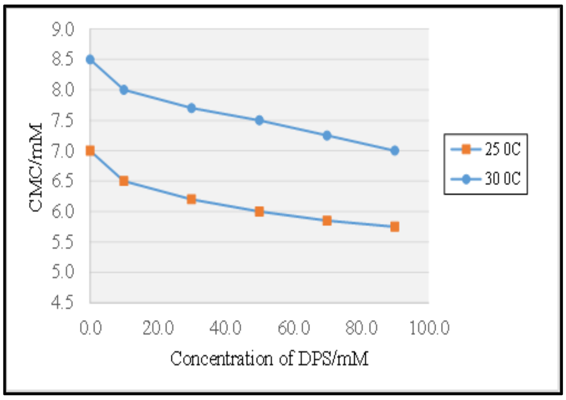


Fig: 4: The CMCs of SDS and its mixtures with DPS at different concentrations of DPS and 25 and 30 ^{0}C. Data points in orange are CMC values at 25 ^{0}C and those in blue are for 30 ^{0}C.

Figure 3 shows how the CMC of a surfactant solution can be extrapolated from specific conductivity versus concentration curve. The intercept of two linear fits above and below the inflection point corresponds to the CMC[17]. The CMCs so extrapolated from the conductivity versus concentration curves for solutions of SDS and the binary mixtures are plotted against the concentrations of DPS and illustrated in Figure 4.

Figure 4 shows the critical micelle concentrations of SDS and its mixtures with DPS at the various concentrations of DPS and temperatures. It is observed that the CMCs of both SDS single surfactant and those of the mixtures increase with increasing temperature. Such observation has also been reported by Noudeh *et al.*, 2007 who studied the effect of temperature on thermodynamic parameters of micellization of sodium dodecyl sulphate, benzalkoniumchloride, tetradecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide through conductivity measurements. The working temperatures were 15, 25, 30 and 35 K. It was reported that the CMC of all the surfactants decreased at 15 K but progressively increased at all other temperatures. These results were suggested to mean that the micellization of the surfactants was entropy-dominant at low temperatures and enthalpy-dominant at high temperatures. CMC is dependent on the balance of forces between electrostatic repulsion of charged headgroups and attractive forces of alkyl chain length (López-Díaz and Velázquez 2007). Repulsive interactions oppose aggregation and therefore increase CMC. Increase in temperature would enhance thermal agitation of ionic headgroups. Thus, electrostatic repulsion is stronger leading to reduced aggregation and resulting in increased CMC. Figure 4 also shows that CMC of SDS decreases with increasing concentration of DPS. DPS possess a positive and negative charge on the headgroup. Therefore, its headgroup has an overall neutral charge. So, an uncharged non-ionic surfactant introduced between same charged ionic headgroups will tend to keep the charged headgroups further apart and hence reduce the electrostatic repulsion between them. Micelle formation is thus favoured resulting in lower CMC.

SUMMARY AND CONCLUSIONS: The mixing behaviour of binary mixtures of SDS and DPS surfactants in aqueous solution has been studied at different temperatures and concentrations of DPS through conductivity measurements. The conductivity of SDS increased with increasing temperature but decreased as the concentration of DPS increased. The CMCs of solutions of SDS and its mixtures with DPS extrapolated from the conductivity versus concentration curves increased with increasing temperature but decreased as the concentration of DPS increased. The decrease in CMC of SDS with increase in the concentration of DPS is an indication of greater stability of the mixed micelles over micelles of single SDS. These observations have been attributed to the difference in the molecular architecture of the mixing surfactants.

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