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Effect of additives on the micellar behaviour of aqueous alkaline earth metal dodecyl sulphates

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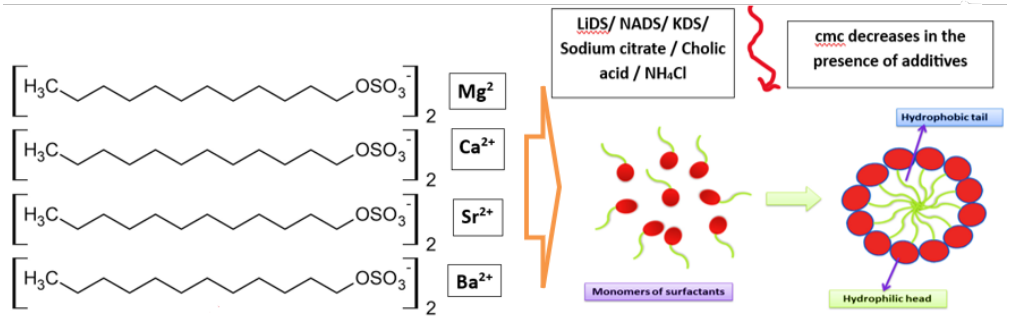
Article

ABSTRACT



The critical micelle concentrations (CMCs) of alkaline earth metal dodecyl sulfates have been determined in the presence of alkali metal dodecyl sulfates, cholic acid, ammonium chloride, and sodium citrate—key ingredients commonly found in various cough syrups. Two key observations emerge from the data obtained. First, the presence of these additives leads to a decrease in CMC values. Second, the efficiency of CMC reduction follows the order: sodium citrate > cholic acid > potassium dodecyl sulfate > sodium dodecyl sulfate > ammonium chloride (NH_4Cl) > lithium dodecyl sulfate. The decrease in CMC is attributed to the presence of added ions, such as sodium, which reduce electrostatic repulsion between the surfactant head groups, thereby facilitating micelle formation.

Keywords: Critical Micelle Concentration (CMC), sodium citrate, cholic acid, ammonium chloride, surfactants

INTRODUCTION

Micellization of anionic surfactants (e.g. metal soaps/soap) in aqueous solutions is generally affected by the presence of organic additives.[1,2] Research workers in the past have studied the observed effects of various additives on the micellization of different surfactants. CMC's are affected both and adversely i.e. lowered or raised with the addition of organic solvents. Mohsin et.al.[3] have however observed significant change in surface tension of surfactants in the presence of high salt concentrations. The effect of sorbitol and inositol on the cmc of non-ionic surfactants in water and in aqueous area was investigated by M. Ueda et.al.[4] Further, M.A. Motin et.al.[5] have studied the thermodynamic properties of Sodium Dodecyl Sulfate aqueous solutions with Methanol, Ethanol, n-Propanol and iso-Propanol at different temperatures. Conductance behaviour of soap solutions (anionic surfactants) in presence of varying amount of different alcohols has been observed by many researchers.[6] Research workers have however expounded the decrease in cmc for micellar solutions containing alcohols in terms of micellar solubilization. The interaction between the solubilization and the different parts of the surfactants chain seems to bring about the process of solubilization in surfactant solution.[7] Various parameters such as type of surfactants and of solubilizate, the temperature and the presence of additives (electrolyte and non-electrolyte) can influence these interactions. A study involving the effect of polar additives (water, ethylene glycol, phenol, ethanol, n-amyl amine, di-n-amyl ketone, picric acid and phenyl stearic acid) on the rheological properties of benzene solutions of sodium phenyl stearate has been carried out by another researcher. The strong ionic interaction of the sodium ions and carboxylate ions is supposed to promote filamentous or ribbon like micelles.

The effects of acids, bases and salts on the surface tension of the soap solution was however studied by several workers. A.J.M. Valente et.al.[8] have studied the aggregation and micellization of sodium dodecyl sulfate in the presence of Ce (III) at different temperatures. T.P. Niraula et.al.[9] have studied the micellization of sodium dodecyl sulphate in presence and

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absence of alkali metal halides at different temperatures in water and methanol-water mixtures.

A perusal of literature shows that the effect of additives on alkaline earth metal dodecylsulphates is not well studied. In the present work, the effect of various additives such as LiDS/NaDS/KDS and cholic acid, ammonium chloride, sodium citrate on the micelllization behavior of aqueous alkaline earth metal dodecylsulphate solution has been studied (25-45°C).

EXPERIMENTAL

The conductivity of the surfactant solutions in absence and presence of additives was measured at different temperatures (25-45°C) in a thermostatically controlled condition. The specific conductance, k (mS cm-1) of alkaline earth metal (Mg/Ca/Sr/Ba) laurates in mixed solvent (50% methanol +50% chloroform) has been measured in order to look into the dissociation / association behaviour of these surfactant systems in presence or absence of additives. Extremely dilute aqueous solution (0.001 M) of these additives (LiDS, NaDS, KDS, Cholic acid, sodium citrate and ammonium chloride) were employed to test their efficacy in lowering the cmc.

RESULTS AND DISCUSSION

Both conductance and micelllization demeanour of aqueous alkaline earth metal dodecylsulphates have been studied in presence of 0.001 M of different additives (dodecylsulphates of alkali metals abbreviated as LiDS/NaDS/KDS); and cholic acid, ammonium chloride, sodium citrate (all of them being important ingredients of various cough syrups) at various temperatures (25-45°C). Extremely dilute aqueous solution (0.001 M) of these additives were employed to test their efficacy. The alcoholic solution of cholic acid (0.001M) was however used as the compound is not soluble in water. The figures (κ-C plots at 25°C) however serve as representatives in support of our observation about the change in micellization behavior brought about by the introduction of these additives to the present surfactant systems.

Two concrete observations may thus made from the perusal of the data. First, the cmc's are found to decrease in presence of these additives. Secondly, the efficacy of lowering of cmc's for all the additives used in the present study is found to follow the order as: sodium citrate, cholic acid, KDS, NaDS, NH_4Cl, LiDS.

The Critical Micelle Concentration (CMC) of alkaline earth metal dodecyl sulfates decreases in the presence of additives because the added ions, like sodium, reduce the electrostatic repulsion between the surfactant head groups, making micelle formation more favourable. Adding ions like sodium (Na^+) to the solution can reduce the electrostatic repulsion of the negatively charged head groups of alkaline Earth Metal Dodecyl Sulfates. The added ions, especially those with opposite charges to the surfactant head groups, can screen the electrostatic interactions between the surfactant head groups, effectively reducing the repulsion. This reduced repulsion makes it easier for the surfactant molecules to come together and form micelles, thus lowering the CMC.[9]

The findings of Martina Gudelj et.al.[10] indicate that the nature of the additive influences the micellar structure and properties of sodium dodecyl sulfate (SDS). He increased the mass fraction of propane-1,2-diol in binary mixtures, the c.m.c. values decrease because propane-1,2-diol is a polar solvent, which gives it the ability to form hydrogen bonds, decreasing the cohesivity of water and reducing the dielectric constant of the aqueous phase.

D. Bajani et.al.[11] also finds the similar results. He studied the influence of the addition of ethylenediamine and L-Lysine. HCL on the micellization process of sodium lauryl sarcosine (SLAS) in aqueous solution and he founds 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.

Table 1. The values of cmc's (mol dm^{-3}) of alkaline dodecylsulphates in pure solvent i.e. in the absence of additives at different temperature (25-45°C).

Compounds	cmc x 10^3				
	25°C	30°C	35°C	40°C	45°C
$Mg(DS)_2$	18.0	16.0	13.0	13.0	12.0
$Ca(DS)_2$	17.5	15.4	12.0	12.0	10.0
$Sr(DS)_2$	17.0	15.0	11.0	11.0	9.0
$Ba(DS)_2$	15.0	12.0	9.0	9.0	8.0

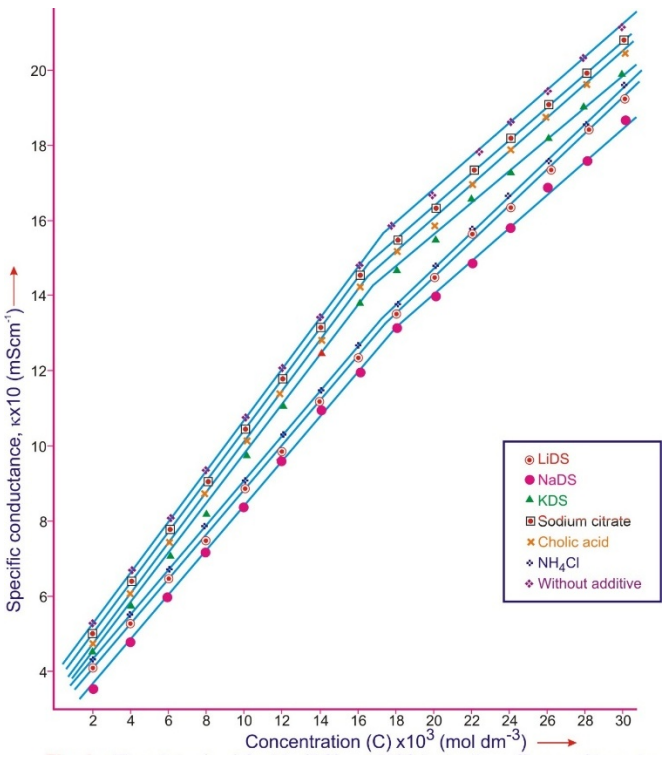

Figure 1. The plots of **(κ - C)** for Mg $(DS)_2$ at 25^0C indicating efficacy of lowering of cmc's by different additives used.

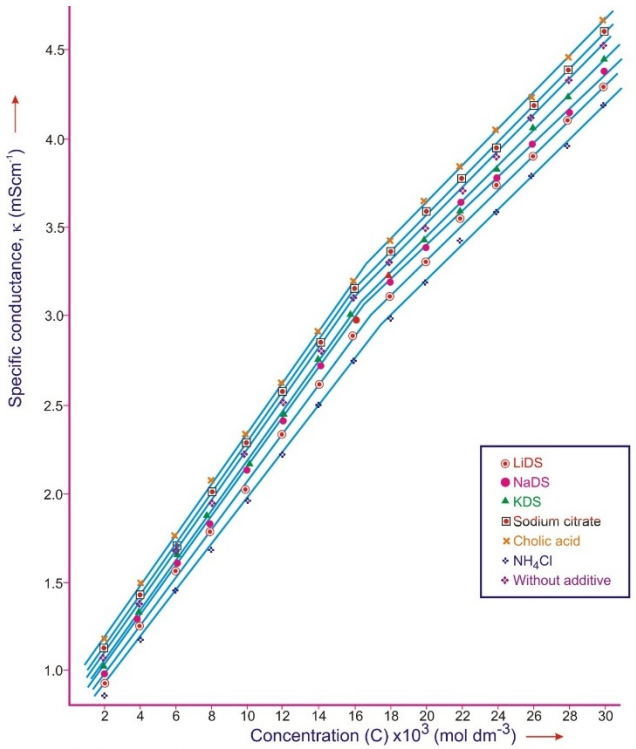

Figure 2. The plots of **(κ - C)** for Ca $(DS)_2$ at 25^0C indicating efficacy of lowering of cmc's by different additives used.

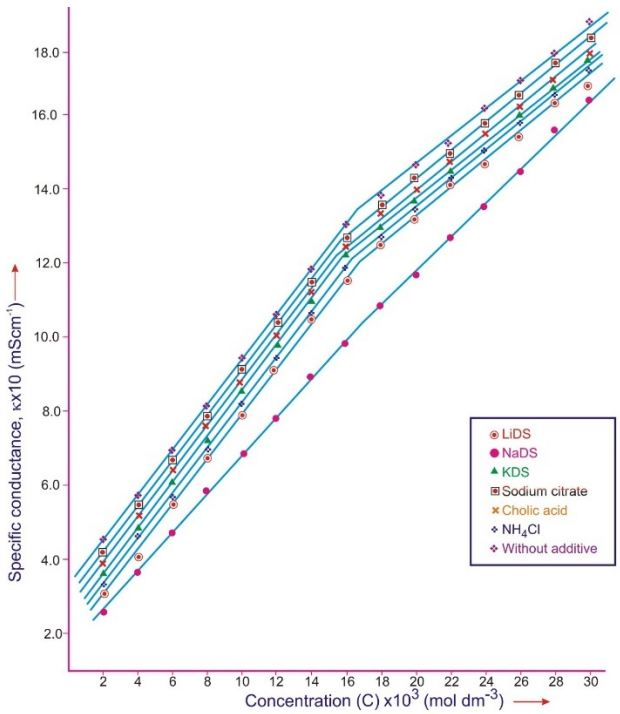

Figure 3. The plots of **(κ - C)** for Sr $(DS)_2$ at 25^0C indicating efficacy of lowering of cmc's by different additives used.

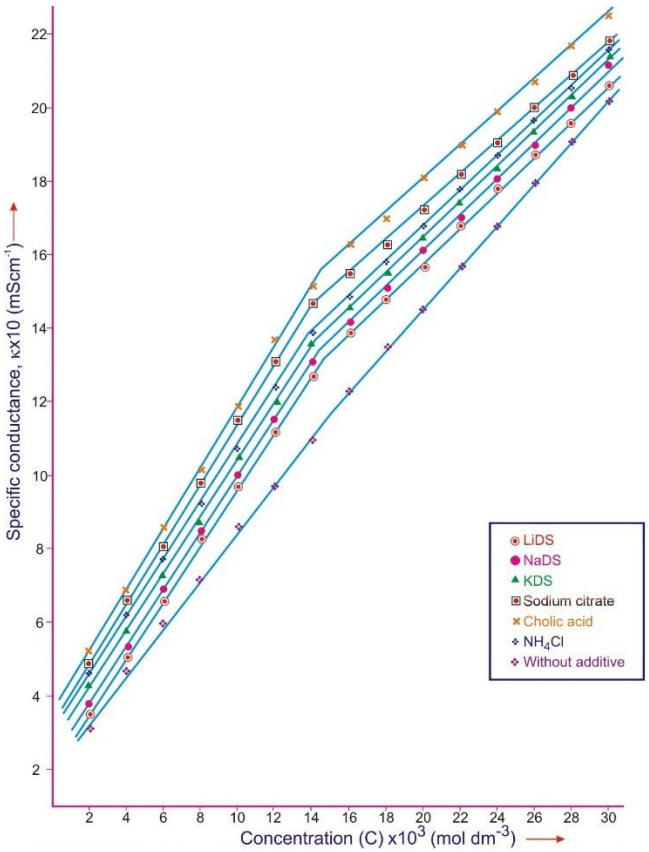

Figure 4. The plots of **(κ - C)** for Ba $(DS)_2$ at 25^0C indicating efficacy of lowering of cmc's by different additives used.

Md. Sahidul Islam et.al.[12] studied the effect of NaCl and KCl on the Micellization of Sodium Dodecyl Sulfate and Sodium Dodecyl Benzene Sulfonate in presence of Cephradine Monohydrate and found similar results. He concluded that the presence of CPDM in an aqueous solution decreases the critical micelle concentration (CMC) of surfactants, thereby increasing the degree of micellization, also the CMC values were found to favorable with an increase of salt NaCl and KCl concentrations.

Jay Narayan Mitruka et.al.[13] findings also observed that the effect of addition of salts on the micellization of anionic surfactant sodium dodecyl sulphate (SDS) in aqueous medium by conductance measurement at 298.15 K He founds that on adding the salts, CMC decreased whereas degree of dissociation increased.

Biyong Zhu et.al.[14] findings analyzed the effect of inorganic salt additives (NaCl, $CaCl_2$, $AlCl_3$, Na_2SO_4, Na_2CO_3, and $NaHCO_3$) on the surface tension of a sodium dodecylbenzene sulfonate (SDBS) solution

One may therefore easily conclude that sodium citrate (an important ingredient of cough syrup) is the most efficacious additive in bringing down the cmc's (a favourable change) among all the additives used LiDS however comes last in this context, i.e. it is the least efficacious additive amongst.[15]

Conclusion

Two concrete observations may thus made from the perusal of the data. First, the cmc's are found to decrease in presence of these additives. Secondly, the efficacy of lowering of cmc's for all the additives used in the present study is found to follow the order as: sodium citrate, cholic acid, KDS, NaDS, NH_4Cl, LiDS. The Critical Micelle Concentration (CMC) of alkaline earth metal dodecyl sulfates decreases in the presence of additives because the added ions, like sodium, reduce the electrostatic repulsion between the surfactant head groups, making micelle formation more favorable.

Conflict-of-interest statement

All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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