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Micellization of sodium dodecyl sulphate in the presence and absence of potassium sulphate and nickel sulphate

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ABSTRACT

The effect of addition of salts on the micellization of anionic surfactant sodium dodecyl sulphate (SDS) in aqueous medium has been studied by conductance measurement at 298.15 K. The critical micelle concentration (CMC) as well as thermodynamic properties was evaluated. From the premicellar and postmicellar slopes, the degree of dissociation (α) of SDS was also calculated. On adding the salts, CMC decreased whereas degree of dissociation increased. Employing these CMC and α values, the standard free energy of micellization was also evaluated. The negative values of ΔG_m^o was decreased when K_2SO_4 was added but increased when $NiSO_4$ was added.

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1. Introduction

Surfactants are surface-active molecules which possess both hydrophobic tail and hydrophilic head and are therefore amphiphilic in nature [1]. Due to amphiphilic nature, they exhibit various unique properties such as adsorption at interfaces, self-association and solubilization of hydrophobic molecules, so widely used in pharmaceutical, food, cosmetic, textile, paint and coating industries [2]. The narrow concentration range above which micelles are formed is called critical micelle concentration [3]. From the CMC value of a surfactant, fundamental information about the surface-

active properties can be known. Micelle formation plays a model role in biological, chemical and industrial processes [4]. The physicochemical properties of aqueous surfactants can be changed by external means, such as, concentration of reactants, type of additives, nature of the solvent and temperature [5]. In the present scenario, due to the increasing demand for novel materials with unique and enhanced properties has given priorities to the investigation of surfactant-additives system [6]. The aggregation behaviour of surfactants in aqueous solutions can be changed by altering the temperature of solution and also by changing the solvent. The addition of salts can also affect the aggregation behavior of anionic surfactants in aqueous solutions, which is crucial to different applications in detergency and emulsification [7].

When salts are added to surfactants, their properties change, which plays an influential role in many research fields. Conductivity measurements in aqueous and ethanol-water systems at 298.15 K, Niraula et al. investigated the influence of solvent permittivity and salt on sodium dodecyl sulphate micellization behavior [8]. Ren studied the mechanism of salt effect on micellization of sodiumdodecyl diamino sulph-onate amphoteric surfactant in aqueous medium by tensiometry using the Wilhelmy plate method at 298.15 K [9]. Miyagishi et al. studied the salt effect on critical micelle concentration of nonionic surfactants, N-Acyl-N-methyl-glucamides using surface tension or a fluorescent probe method at 298.15 K [10].
No studies have been conducted on the effect of salts (K_2SO4, NiSO4) on SDS surfactant.
Conductivity measurements have been used in the present study to determine sodium dodecyl sulphate's thermodynamic properties.

The measurement was performed in aqueous system at room temperature. Additionally, salts have been studied for their effect on SDS, which is quite different from the previous studies.

2. Materials and Method

Materials

The materials that were used for the determination of CMC are conductivity meter, cotton, beaker, measuring cylinder, pipette, potassium sulfate, nickel sulfate and distilled water. Conductance measurements was carried out on 601/602/611 Digital conductivity meter purchased from ESICO International having cell constant of 1.0 cm^{-1} from India. Various independent solutions were prepared and were carried out to check the reproducibility of the outcome. Sodium dodecyl sulfate [SDS] and Nickel (II) sulfate heptahydrate [$NiSO4.7H_2O$] was purchased from Merck Life Science Private Limited, Mumbai, India. K_2SO4 was purchased from Glaxo India limited, Mumbai. Distilled water was used in the experiments. The solutions were prepared at room temperature.

Methods

Determination of CMC of sodium dodecyl sulfate with and without salts

Since conductivity measurement is very simple to do in the lab, it is a very convenient way to determine CMC. At first sodium dodecyl sulfate of 0.05M was prepared by mixing 1.442gm of SDS in 100 ml of distilled water. It was kept for whole night to make homogenous solution. About 30 ml SDS was taken in one beaker. The conductivity meter was standardized at 298.15 K and the conductance of SDS solution was first measured. 2ml of SDS was pipetted out and 2 ml of distilled water was added each time and the conductance of diluted SDS solution was noted. Again100 ml of 0.05M SDS solution was prepared in 0.001M K_2SO4 aqueous solution.
30 ml of the mixture was taken and its conductance was measured. 2ml of the mixture was pipette out and 2ml K_2SO4 was added in the beaker and conductance was measured each time after addition. Similarly, 100 ml of 0.05M SDS solution was prepared in 0.001M $NiSO4.7H_2O$ in distilled water.

30 ml of the mixture was taken and its conductance was measured. 2 ml of mixture was pipette out and 2 ml $NiSO_4$ solution was added followed by measurement of conductance each time. About 35 readings were taken for SDS in aqueous medium in absence and in presence of each salt. The graph of specific conductance versus concentration of SDS in aqueous medium was plotted by using easy plot program to get two straight lines with different slopes. The breaking point of these two lines was the CMC of the surfactant, the value of which is determined by solving two equations.

3. Results and Discussion

The conductivities of sodium dodecyl sulphate in pure water and in presence of K_2SO_4 and $NiSO_4$ at room temperature is presented in Figure 1. SDS is more conductive when salts are added because salts have a higher mobility (Figure 1). SDS in the presence of K_2SO4 has less conductance than SDS in the presence of NiSO4. Since conductivity and resistivity have an inverse relationship. Small ions, therefore, have a high charge density. Because of this, smaller ions have more conductivity than larger ones. Atomic size of Ni is 163 pm which has the equivalent value 1.63 Å appears on **p. 449** in the literature [11] whereas atomic size of K seems 275 pm which has the equivalent value 2.75 Å appears on **p. 113** in the literature [12]. In other words, As ion size increases, ion mobility decreases and conductivity decreases.

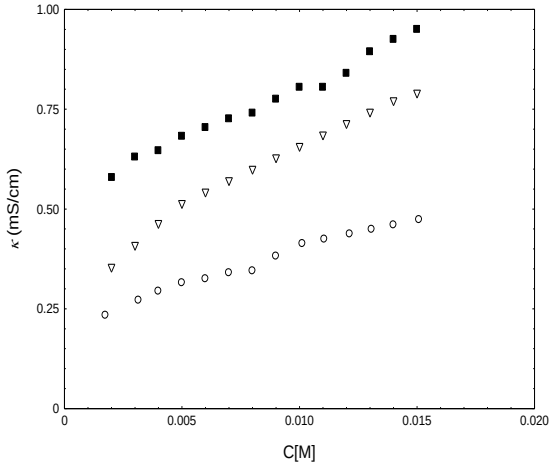

Fig. 1: Specific conductance of SDS as a function of concentration in aqueous system (circles) and in the presence of K_2SO_4 (opposite triangles) and $NiSO_4$ (closed squares)

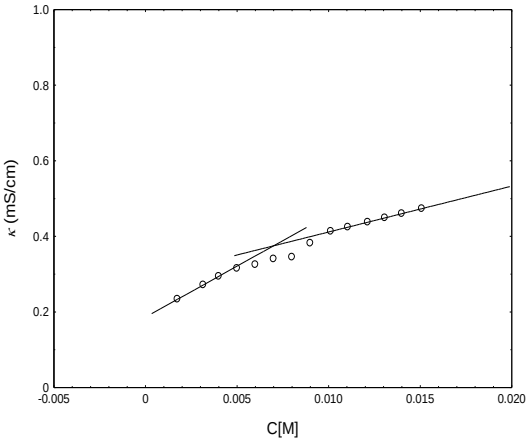

Fig. 2: Plot of conductivity of SDS in water versus concentration of SDS

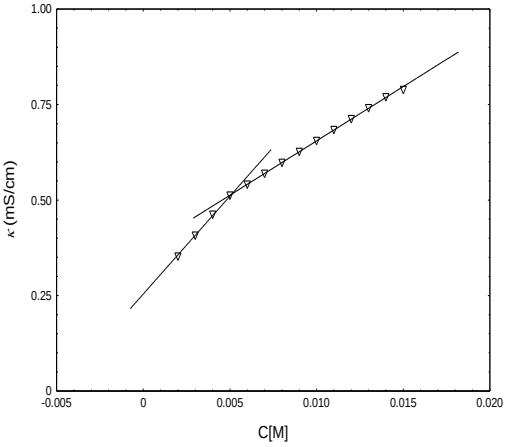

Fig. 3: Plot of conductivity of SDS in presence of K_2SO_4

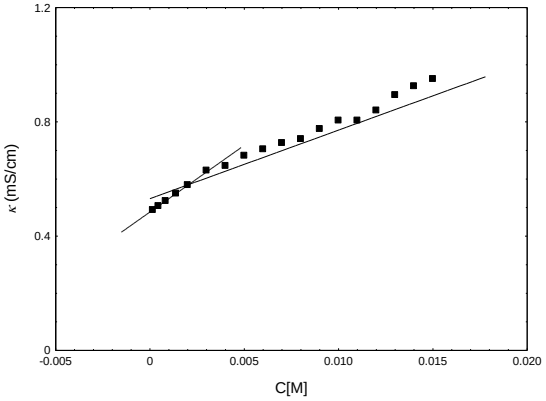

Fig. 4: Plot of conductivity of SDS in presence of $NiSO_4$

There is the calculation of Gibbs free energy of micellization (ΔG_m^o) [8] as

$$\Delta G_m^o = (2-\alpha)RT \ln X_{cmc} \quad (1)$$

Here, R is the universal gas constant, T is the absolute temperature and X_{cmc} is the mole fraction of surfactant at CMC. The critical micelle concentration (CMC), degree of micelle ionization (α) and standard free energy of micellization (ΔG_m^o) of SDS in the absence and presence of salts in water are given in Table 1.

Table 1: Table for CMC, degree of dissociation, Gibbs free energy of micellization, premicellar and postmicellar slopes

Surfactant	Salts	CMC (mM)	α	ΔG_m^o (kJ/mol)	S_1	S_2
	K_2SO_4	5.1	0.55	-33.40	51.2	28.4
	$NiSO_4$	2.2	0.51	-37.43	46.7	24
SDS		7.0	0.45	-34.49	27	12.1

Table 1 shows the decrease in the CMC values with the addition of salts (K_2SO_4, $NiSO_4$). The variation of the CMC of SDS in presence and absence of salts are in the order: SDS > K_2SO_4 > $NiSO_4$. Ni and K have ionic radii of 69 pm [13]and 133 pm [14], respectively, and the CMC increases as the ionic radii of counterions increase [15]. CMC of SDS decreases in the presence of salts (Figures 3 & 4) because salt ions interact with the surfactant's head group. As salts are added, the electrostatic repulsive force between polar head groups of SDS molecules is reduced by shielding micelle charge, resulting in more tightly packed spherical micelles, which reduces the CMC [16].

The increase in degree of dissociation after the addition of salts may be due to the increased in the number of unbound counterions in SDS solution [17]. In regard to standard free energy of micellization of SDS in the presence of salts, the standard free energy of micellization becomes less negative in presence of K_2SO_4 and more negative in presence of $NiSO_4$, indicating that micelle formation becomes less spontaneous in case of K_2SO_4 and more favourable in case of $NiSO_4$. Such type of behaviour infers that micellization becomes less favourable in presence of K_2SO_4 and more favourable in presence of $NiSO_4$ [18].

Table 1 also shows the values of premicellar (S_1) and postmicellar slopes (S_2) drawn from the graphs of specific conductance with the concentration of SDS with salts (K_2SO_4, $NiSO_4$) in aqueous system. With the addition of salts, these two slopes are changed which leads to difference in physicochemical properties of solution [19].

Conclusion

The micellization behaviour of sodium dodecyl sulphate in aqueous solution in presence and absence of salts was investigated conducto-metrically. The critical micelle concentration decreased when salts were added. This decreased in the values of the CMC is due to the interaction of salt ions with the head group of the surfactant. It was also found that degree of dissociation of SDS increased when salts were added. Also, ΔG_m^o was found less negative in presence of K_2SO_4 and more negative in presence of $NiSO_4$.

References

[1] A. Aliet et al., Critical micelle concentration and self_aggregation of hexadecyltrimethyl-ammonium bromide in aqueous glycine and glycylglycine solutions at different temperatures, Russ. J. Phys. Chem. A.86 (2012)1923-1929. https://doi.org/10.1134/S0036024412130031

[2] M. C. Celia et al., Mixed micelle formation between an amino acid-based anionic gemini surfactant and Bile Salts, Ind. Eng. Chem. Res. 53(2014)10112−10118. https://doi.org/10.1021/ie5003735

[3]E.Mohajeri, G.D. Noudeh, Effect of temperature on the CMC and micellization thermodynamics of nonionic surfactants: Polyoxyethylene Sorbitan Fatty Acid Esters, J. Chem. 9 (2012) 2268-2274.

https://doi.org/10.1155/2012/961739

[4] D. Kumar, M.K. Rub, Influence of dicationic quaternary ammonium Gemini surfactant system on metal-amino acid complex-ninhydrin reaction,Mater. Chem. Phys. 248(2020)122926. https://doi.org/10.1016/j.matchemphys.2020.122926

[5] A. Bhattarai et al., Analysis of interaction between glutamic acid and ninhydrin in the presence of acetate buffer solvent: Impact of gemini (twin-headed) surfactants, Colloids Surf. A Physicochem. Eng. Asp. 626 (2021) 127061. https://doi.org/10.1016/j.colsurfa.2021.127061

[6] B. Kumar et al., Effects of electrolytes on micellar and surface properties of some monomeric surfactants, J. Dispers. Sci. Technol. 33 (2012) 265-271.

https://doi.org/10.1080/01932691.2011.561178

[7] H. Hooshyar, R. Sadeghi, Influence of Sodium salts on the micellization and interfacial behaviour of cationic surfactant dodecyl-trimethyl ammonium bromide in aqueous solution, J. Chem. Eng. Data. 60 (2015) 983-992.https://doi.org/10.1021/je501058a

[8] T. P. Niraula et al., Influence of solvent permittivity and divalent salt on micellization behaviour of sodium dodecyl sulfate: Conductivity measurement and simulation study, J. Mol. Liq. 349 (2022) 118186.

https://doi.org/10.1016/j.molliq.2021.118186

[9] Z. H. Ren, Mechanism of salt effect on micellization of an aminosulfonate amphoteric surfactant, Ind. End. Chem. Res. 54 (2015)9683-9688.
https://doi.org/10.1021/ie503888t
https://doi.org/10.1021/acs.iecr.5b00137
https://doi.org/10.1021/acs.iecr.5b02169
https://doi.org/10.1021/acs.iecr.5b03069
https://doi.org/10.1021/acs.iecr.5b01267
https://doi.org/10.1021/acs.iecr.5b02139

[10] S. Miyagishi et al., Salt effect on critical micelle concentrations of nonionic surfactants, N-Acyl--N-methylglucamides,J.Colloid Interface Sci. 238 (2001) 91-95.

https://doi.org/10.1006/jcis.2001.7503

[11]A. Bondi. Van der Waals Volumes and Radii, J. Phys. Chem.68 (1964) 441-451.
https://doi.org/10.1021/j100785a001

[12]Yu. V. Zefirov. Comparative Analysis of Systems of van der Waals Radii, Crystallogr. Rep. 42(1997)111-116.

[13]T.Chen et al., Ion Association and Hydration in Aqueous Solutions of Nickel(II) and Cobalt(II) Sulfate, J. Solution Chem. 34(2005)1045-1066.
https://doi.org/10.1007/s10953-005-6993-5

[14]A. Kvist, The Electrical Conductivity of Pure Molten Alkali Sulphates and Molten Equimolar Alkali Sulphate Mixtures, Z. Naturforsch. 22(1967) 467-470.

https://doi.org/10.1515/zna-1967-0408

[15] H.N. Singh et al., Effect of electrolytes on the micellization of ionic surfactants in n-alkanol-water mixtures, J. Colloid Interface Sci. 68 (1979) 128-134.

https://doi.org/10.1016/0021-9797(79)90264-9

[16]P. Bhattarai et al., Thermodynamic properties of cetyltrimethylammonium bromide in ethanol-water media with/without the presence of the divalent salt, J. Oleo Sci. 70 (2021) 363-374.

https://doi.org/10.5650/jos.ess20207

[17] G. A. Cookey, C. C. Obunwo, Effects of sodium bromide salt and temperature on the behaviour of aqueous solution of cetyltrimethylammonium bromide, J. Appl. Chem. 7 (2014) 34-38.

https://doi.org/10.9790/5736-071213438

[18]Y.Ghimire et al., Thermodynamic

properties and contact angles of CTAB and SDS in acetone-water mixtures at different temperatures, SN Appl. Sci.2(2020)1295.

https://doi.org/10.1007/s42452-020-3036-1

[19] S. K. Shah et al., Micellization of cationic surfactants in alcohol-water mixed solvent media, J. Mol. Liq. 222 (2016) 906-914. https://doi.org/10.1016/j.molliq.2016.07.098