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Study of mixed micelles of Sodium dodecyl sulphate and nonionic surfactants polysorbates tween series:Their interaction and thermodynamic parameter using cyclic voltammetry

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Abstract

Mixed micellar systems of anionic surfactant sodium dodecyl sulphate and nonionic surfactants polyoxyethylene sorbitan fatty acid esters (polysorbates) such as tween 20 /tween 40/tween 60 /tween 80 have been studied by using cyclic voltammetry, Surface Tension and Conductivity measurements. Critical micellar concentration values have been determined for various micellar systems by using cyclic voltammetry measurements using $K_4Fe(CN_6)$ and KCl as an electroactive probe at 25 °C. Diffusion Coefficient has been computed from the peak current of the solution. Interaction parameter β has been calculated from regular solution theory. The negative values of interaction parameter suggest the synergistic behavior of all binary surfactant systems used in present study. Thermodynamic parameter free energy of micellization (ΔG°_m) computed for various mole fraction of tween series. Decrease in ΔG°_m with addition of tween series suggest spontaneous micellization.

Keywords: SDS-Tween, Cyclic voltammetry, Thermodynamic parameter, β Interaction parameter.

Introduction

In many cases a single surfactant cannot provide all the properties required and two or more surfactants can be mixed to obtain desired effect. Therefore the mixed surfactants are of greater importance due to their improved properties and extensive scientific and technological applications [1-5]. Like individual surfactant in micellization, mixed surfactants also undergo abrupt changes in physical properties which can be conveniently studied using suitable experimental methods. In the present study, surface tension, conductivity measurements, and cyclic voltammetry technique is used to study cmcs of mixed surfactant system. Aggregates formed by surfactant molecules are called micelles. The hydrocarbon tails of surfactant molecules form hydrophobic core of micelles and it is surrounded by the hydrophilic head group. Micelles formed by more than one surfactant species are called mixed micelles. The binary mixture of anionic-nonionic surfactants are of interest as this mixtures have low critical micellar concentration (cmc) than individual surfactants showing appreciable synergism[6-10].The synergism shown by these mixtures are important as it reduces the amount of surfactant required for application thereby reducing cost and environmental impact and enhance efficiency. In present study sodium dodecyl sulphate[11] is used as anionic surfactant and polyoxyethylene sorbitan fatty acid esters (polysorbates tween series) as nonionic surfactant. These nonionic surfactants are widely used as a detergent and as emulsifier in many domestic, scientific and industrial applications. They are nontoxic, hydrophilic nonionic surfactants and hence find widespread applications in pharmaceutical emulsion preparations as an emulsifying agent. For a variety of substances like essential oils oil soluble vitamins, they are used as solubilizing agent. Their compatible set of physical properties allow them to blend with many other surfactants.

Materials: Anionic surfactant sodium dodecylsulphate was procured from sigma and was of 98% pure. It was used as such. The nonionic surfactant –tween series, tween20 (polyoxyethylene sorbitan mono laureate n=12), tween40 (polyoxy ethylene sorbitan monopalmitate n=16), tween60 (poly oxy ethylene sorbitan mono stearate n=18), tween80 (poly oxy ethylene sorbitan mono oleate n=18) all of 98% purity were procured from Sisco Research laboratory. Deionised, doubly distilled water was used for preparation of solution.

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Method

1) Surface tension of all solutions was measured with a Dunoy tensiometer by ring detachment method. Care was taken to see that the solution under consideration attains a constant temperature before making measurements. The equipment was installed in a dust freeroom free from any air current.

2) Conductivity measurements

The conductivity measurements were made by using Elico digital conductivity meter model no. 660 at different temperatures i.e. 40 and 50 usingconstant temperature bath. The cell used was 1cm^{-1}. Precise conductance of SDS and tween series individually as well as the mixture of SDS and various mole fractions of tween series was measured.

3) Cyclic voltammetry measurements

In these measurements, the solutions were deoxygenated by bubbling Nitrogen gas. The measurements were performed by using a Potentiostat /galvanostat (Princeton Applied Research Model 273 with a IBM Computer) and a three necked electrolytic cell. A saturated calomel reference (SCE) electrode was employed in the study. The working electrode and counter electrode both were made up of platinum. The area of working electrode is 1cm^2. In the electrochemical measurements the potential sweep rate was 100mV/s. For determination of CMC of surfactant by cyclic voltammetry a series of solutions were prepared at a definite concentrations of the redox active material and supporting electrolyte (2.5x10^{-2} M $K_4Fe(CN_6)$ 0.5M and KCl , the concentration of surfactants were varied. The peak current i_p of each solution was measured and plotted against the concentrations of surfactant. The abrupt changes in the values of the initial slopes were considered as the cmc point.

Results and Discussions

1) Determination of cmc by using CV

Cyclic Voltammetry (CV) is the most versatile electroanalytical technique for the study of electroactive species. Its versatility combined with the ease of measurements results in extensive use of CV. Peak current of solution containing fixed amount $K_4Fe(CN_6)$ and KCl was measured using Pt electrode as working electrode at various surfactant concentration. Peak current thus obtained was plotted against the concentrations of surfactant to determine cmc. Cmc determined by cyclic voltammetry agrees well with cmc values obtained by surface tension and conductivity measurements. (Table1)The peak current i_p (μA) is related to $\sqrt{\nu}$(square root of sweep rate) by Randles sevcik equation [17]

$$I_p = \frac{0.4447F^{3/2}An^{3/2}D^{1/2}C\,\nu^{1/2}}{R^{1/2}\,T^{1/2}}$$

Where n is the number of electrons involved in oxidation or reduction, A is the area of electrode (cm^2), D is the diffusion coefficient of the electroactive species (cm^{2}S^{-1}) C is the concentration of electroactive species in the solution (moll^{-1}), ν is the sweep rate (Vs^{-1}), F is the faraday constant, R is the gas constant and T is the absolute temperature. Above equation is also used for computing diffusion coefficient. Diffusion coefficient was determined for various compositions of surfactant mixtures.

2) Surfactant – Surfactant interaction

Surfactant – Surfactant interaction result in various physicochemical changes in binary surfactant systems. The micellization of single surfactant differ from micellization of binary surfactant systems. Rubingh's [18] regular solution theory was applied to explain nonideality of binary surfactant mixture.

$$\frac{1}{cmc*} = \frac{\propto 1}{f1cmc1} + \frac{(1-\propto 1)}{f2cmc2} \quad \text{————————} \quad (1)$$

Where α1 is the mole fraction of Tween 20 and f1 & f2 are the activity coefficient of Tween20 & SDS respectively cmc1 and cmc2 are the cmcs of Tween 20 & SDS respectively. For ideal behaviour f1= f2 hence eq 2 is written as

$$\frac{1}{cmc*} = \frac{\propto 1}{cmc1} + \frac{(1-\propto 1)}{f2cmc2} \quad \text{————————} \quad (2)$$

For ideal behaviour mixed cmc* can be calculated by using Eq-2

The experimental values shows negative deviations from ideal cmc values. Rubingh regular solution theory explains the extent of non-ideality.

$$\left\{\frac{x_1^2}{1-x_1^2}\,\frac{\ln\left(\frac{cmc*\propto 1}{cmc1x1}\right)}{\ln\left(\frac{cmc*(1-\propto 1)}{cmc2(1-x1)}\right)}\right\} = 1 \quad \text{————————} \quad (3)$$

X_1& X_2 aremole fraction of Tween& SDS respectively

$$\beta = \ln\frac{\left(\frac{cmc*\propto 1}{cmc1x1}\right)}{(1-x)^2} \quad \text{————————} \quad (4)$$

The β interaction parameter values help in quantifying extent of interaction between two surfactants in a binary surfactant system. The interactions between the two surfactants result in deviation from ideal behavior. All the β interaction parameter values are negative. The negative β valuesreveals the existence of synergistic i.e. attractive interactions which favour micelle formation. In SDS-Tween binary system SDS+Tween20 composition shows less negative β parameter values. The lesser negative values of β is an indication of weaker synergistic interaction between the two surfactants. β values for SDS+Tween40 is comparatively more negative than SDS+Tween20. SDS+Tween60 and SDS+Tween80 show still more negative values of β parameter showing stronger synergism. Though Tween60 and Tween80 have same number of carbon atoms n=18, the presence of double bond (unsaturation) in Tween80 plays an important role. Thus synergism or favorable interactions increase with chain lengh and hydrophobic character of tail of polysorbates which interact with hydrophobic tail of SDS in this binary surfactant system.

3) Thermodynamics of micellization

The free energy of micellization ($\Delta G°_m$) is a measure of stability of micelles. The cohesive interactions between the tail of monomers and solvent molecule has an impact on the mechanism of micelle formation. It is evident that spontaneous micellization process has negative value of $\Delta G°_m$. $\Delta G°_m$ values decrease (become more negative) with the increase in mole fraction of nonionic surfactant, polysorbates in present study. More stable micelles are formed with increased proportion of polysorbate in SDS-tween binary surfactant system. The repulsive forces between the polar anionic heads of SDS do not favour micellization and hence ΔG°_{m} values are higher for pure SDS micellization. In binarymixture of SDS-tween these repulsive forces between polar heads of SDS become weaker due to presence of larger polar heads of tweens as they increase the distance between negatively charged heads of SDS and more stable micelles are formed. When the chain of polysorbate is increased from tween20 to tween60 the stability of micelles is enhanced.

Table1: showing CMC of mixed micelles,anodic peak current,Diffusion coefficient of probe, βInteractionparameter, free energy change of micellization (ΔG°)

CMCs ofmixed micelles of SDS and Tween 20						
Mole fraction of tween	**CMC(Moles/dm^3)By surface Tension**	**CMC(Moles/dm^3)By CV**	**I_{pa}(mA)**	**Diff. Coeff. of Probe**	**βInteractionparameter**	**ΔG°KJ/mol**
0.0	8.01×10^{-3}	8.00×10^{-3}	0.45	4.68×10^{-8}	--------	-12.16
0.2	4.83×10^{-4}	3.74×10^{-4}	0.52	6.00×10^{-8}	-8.63	-19.91
0.4	2.00×10^{-4}	1.83×10^{-4}	0.58	7.56×10^{-8}	-10.58	-21.68
0.6	9.00×10^{-5}	7.60×10^{-5}	0.63	8.78×10^{-8}	-3.87	-23.89
0.8	$8.50. \times 10^{-5}$	7.70×10^{-5}	0.64	9.09×10^{-8}	-3.39	-23.86
1.0	7.10×10^{-5}	8.50×10^{-5}	0.53	6.30×10^{-8}	--------	-23.61
CMCs ofmixed micelles of SDS and Tween 40						
0.0	8.01×10^{-3}	8.00×10^{-3}	0.45	4.68×10^{-8}	--------	-12.16
0.2	3.44×10^{-4}	3.33×10^{-4}	0.61	8.23×10^{-8}	-6.26	-20.09
0.4	1.15×10^{-4}	1.00×10^{-4}	0.61	8.20×10^{-8}	-7.25	-22.85
0.6	7.42×10^{-5}	8.00×10^{-5}	0.58	7.52×10^{-8}	-5.87	-23.95
0.8	5.56×10^{-5}	5.36×10^{-5}	0.55	6.76×10^{-8}	-6.53	-24.68
1.0	4.50×10^{-5}	4.71×10^{-5}	0.63	8.78×10^{-8}	--------	-25.21
CMCs ofmixed micelles of SDS and Tween 60						
0.0	8.01×10^{-3}	8.00×10^{-3}	0.45	4.68×10^{-8}	--------	-12.16
0.2	1.20×10^{-4}	1.41×10^{-4}	0.66	9.73×10^{-8}	-4.80	-22.74
0.4	5.70×10^{-5}	5.00×10^{-5}	0.67	9.91×10^{-8}	-6.52	-24.62
0.6	3.50×10^{-5}	2.58×10^{-5}	0.65	9.26×10^{-8}	-8.01	-25.85
0.8	3.70×10^{-5}	2.57×10^{-5}	0.65	9.32×10^{-8}	-7.07	-25.71
1.0	4.00×10^{-5}	4.00×10^{-5}	0.70	1.09×10^{-8}	--------	-25.51
CMCs ofmixed micelles of SDS and Tween 80						
0.0	8.01×10^{-3}	8.00×10^{-3}	0.45	4.68×10^{-8}	--------	-12.16
0.2	7.62×10^{-5}	9.56×10^{-5}	0.65	9.32×10^{-8}	-6.74	-23.89
0.4	3.62×10^{-5}	5.00×10^{-5}	0.41	3.79×10^{-8}	-8.31	-25.78
0.6	3.54×10^{-5}	3.28×10^{-5}	0.45	4.47×10^{-8}	-7.25	-25.85
0.8	2.52×10^{-5}	2.50×10^{-5}	0.47	4.90×10^{-8}	-9.52	-26.67
1.0	3.42×10^{-5}	2.00×10^{-5}	0.43	4.07×10^{-8}	--------	-25.91

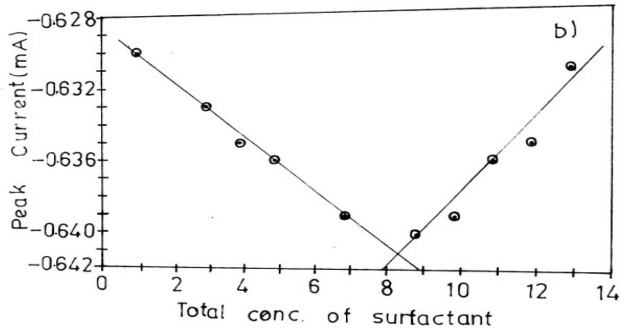

Fig 1: Plot of peak current vs concentration of surfactant

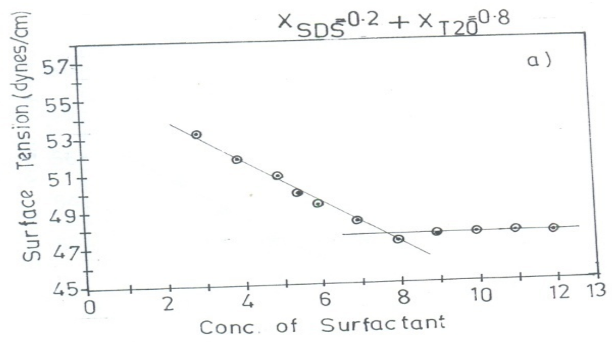

Fig 2: Plot of surface Tension vs concentration of surfactant

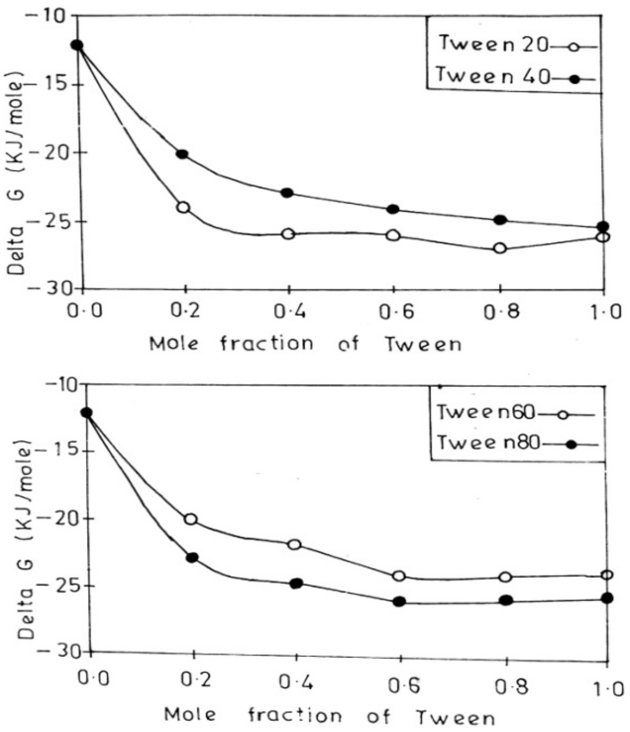

Fig 3: Plot of ΔG° vs mole fraction of Tween

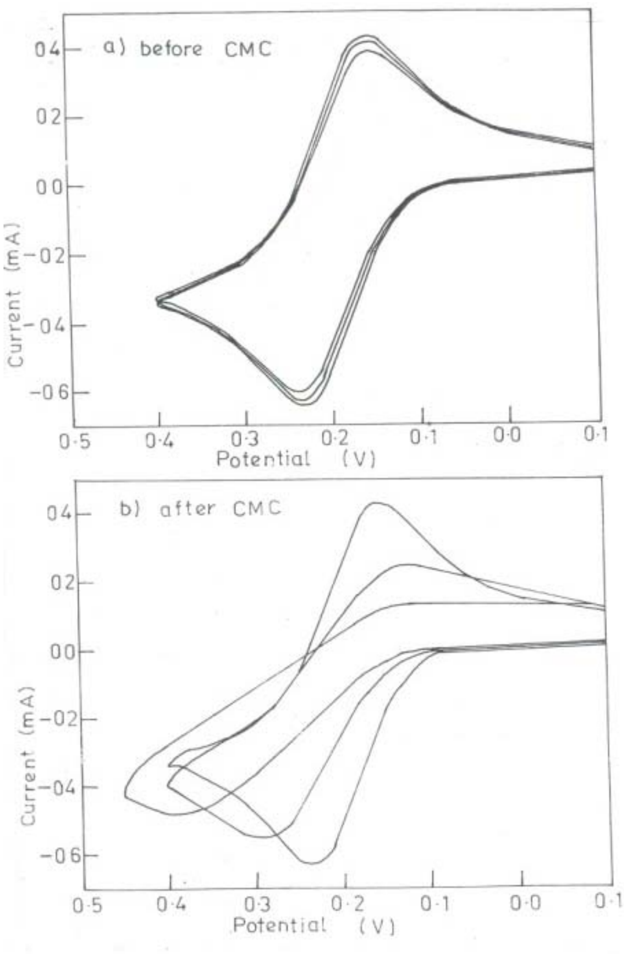

Fig 4: Overlay of cyclic voltammogram before & after cmc

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