



Influence of polyelectrolyte on micellar behaviour of non-ionic surfactant using dye solubilization technique

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ABSTRACT

The change in critical micellar concentration of Tween-80 has been studied through the influence of additive PVSA in aqueous medium by measuring the absorbance of the pure surfactant and with PVSA in presence of water insoluble dye Orange-OT by using dye solubilization technique. The absorbance was found to be increased with increased concentration of pure surfactant Tween-80. The absorbance of the mixed systems with PVSA also shows the same trend. The CMC of pure surfactant get decreased with increased concentration of additive PVSA. The influence of additive PVSA on the absorbance of Tween-80 suggests that the dye micellization is associated with the different micelles coalescing.

Key Words: Dye Micellization, Dye Solubilization, Absorbance (A), Tween-80 (TW-80), Polyvinylsulphonic acid (PVSA), 1-o-tolyl azo- 2-naphthol (Orange-OT), Critical Micelle Concentration (CMC).

INTRODUCTION

The concentration above which micelles form is called the *critical micelle concentration* (CMC). Above the CMC, monomers and micelles exist in dynamic equilibrium. The critical micelle concentrations (CMC's) of surfactants in aqueous solutions have so far been determined by various methods such as surface tension, electroconductivity, and dye absorption spectral measurements, UV absorption spectroscopy method Fluorescence spectroscopy method [1, 2, 3]. The critical micelle concentration of technical grade non-ionic surfactants has been determined in the past by three different methods [4], viz., from the break in the turbidity Vs. concentration curve, from the break in the static surface tension Vs. logarithm of concentration curve and by the iodine solubilization technique [5]. Thus CMC determinations are usually on the basis of sharp change in the colligative properties like clouding, surface tension, iodine solubilization technique. Since these methods due to different reasons [6] cannot be reliable w.r.t. dye solubilisation technique. The solubilizing power is one of the most important properties of surfactants. The solubilization of water insoluble dye Orange- OT in the surfactant micelles was studied in order to determine CMC of the surfactants. The amount of the dye solubilized was insignificant up to the CMC of each surfactant or with additive and thereafter a sudden steep rise was observed with the formation of micelles.

Tween-80 is ethoxylated hydrophilic non-ionic surfactant. Which is used for various purposes; tween-80 was used as sensitizer to determine trace of As(V) in human hair and tea samples [7], tween-80 used for the preparation of oil-in-water emulsions in pharmaceutical products, cosmetics, and industrial detergents [8], Tween 80 used in the formulation of biotherapeutic products for both preventing surface adsorption and as stabilizers against protein aggregation [9], Tween-80 is a nonionic surfactant, with a carbohydrate moiety. Such surfactants are usually ecofriendly and biodegradable and hence can be used in several cosmetics, dish washings, pharmaceuticals and food industries [10,11].

Poly (vinylsulfonic acid, sodium salt) (PVSA) has negatively chargeable sulfonate groups and it is a blood-compatible material. Many researchers have reported that the incorporation of sulfonate groups into the substrates reduces protein adsorption or platelet adhesion, due to the negatively charged character of these groups in aqueous solutions [12].

Since last decades the interactions between polymers and surfactants has more scientific attraction due to the fundamental properties in intermolecular interactions/ phenomena. Water soluble polymer/surfactant systems are important for a variety of industrial applications in the areas of cosmetics, personal-care, food, pharmaceuticals, detergents, and mineral processing [13].

This article presents the preliminary results regarding the influence of PVSA on CMC of pure non - ionic surfactant Tween-80 at various concentrations of PVSA by dye solubilization technique since these studies plays a vital role in the field of medicinal preparations, agrochemicals, detergents etc.

EXPERIMENTAL SECTION

The non-ionic surfactant Tween- 80 (M.W.1310) and the polymer PVSA (M.Wt.5000) were the products of Sigma-Aldrich, USA and these were used as received. The dye Orange-OT (1-o-tolyl azo- 2-naphthol, M.W. 262.3) prepared from o-toluidine and 2-naphthol was purified twice by precipitating it from acetone solution with water followed by recrystallization from ethyl alcohol. The dye Orange-OT is characterized by LC-MS as in Figure 1.

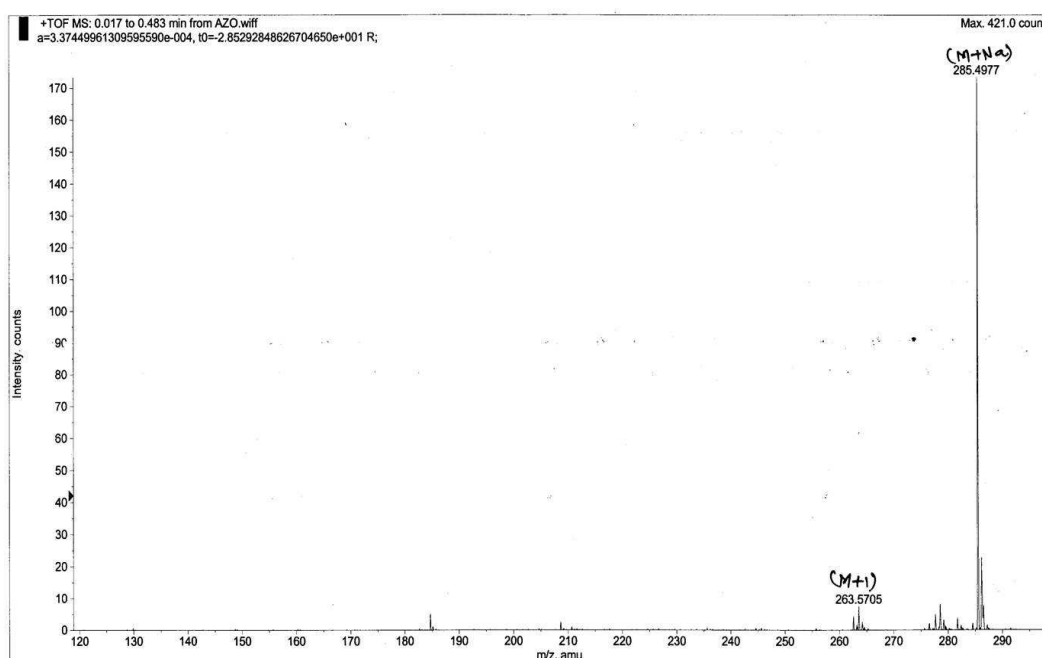


Figure 1 - LC-MS of Orange-OT

Doubly distilled water having specific conductance 2- 4 μScm^{-1} at 303.15K is used for the preparation of all the solutions of different concentrations. The structures of molecular species involved in dye micellisation method are shown in Figure 2.

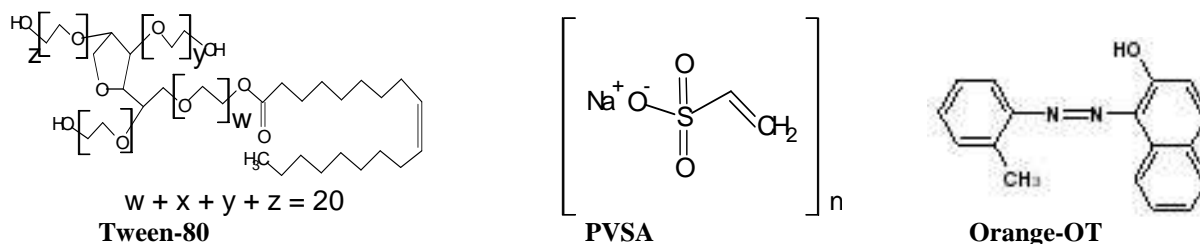


Figure 2- Structures of molecular species

DYE SOLUBILIZATION METHOD- In this method, the insoluble dye Orange-OT was shaken with an aqueous solution of the surfactant Tween-80 for 48 hours at room temperature by using mechanical stirrer and then the residue was removed by means of centrifugation and filtration. The absorbance of the filtered solution was measured by using Equiptronics Digital Spectrophotometer Model: EQ-820 at $\lambda_{\max} = 470\text{nm}$ and at 303.15K

RESULTS AND DISCUSSION

The absorbance for pure surfactant Tween-80 increases with increase in its concentration. The absorbance values of surfactant solutions were measured at 470nm wavelength are plotted as a function of surfactant concentration in weight percentage to measure the extent of dye uptake (Figure 3). Below the CMC, the rise in absorbance is small, where as above the CMC, the rise in absorbance is sharp. For non-ionic surfactant the micellization process is known to be less sharp than for ionic surfactant hence the rise in absorbance varies strongly over a range of surfactant concentration. The absorbance Vs concentration curve get flattened at high enough surfactant concentration as most of the dye forms micelles, depleting the continuous-phase dye. The linear portion near the inflection point is extrapolated to the point where the absorbance matches that of the dye in the absence of any surfactant. This concentration is defined as the CMC. The observed CMC value for surfactant Tween-80 was 0.091 mM in pure water which is very close to reported value 0.093 mM [14]. The CMC of ionic or non-ionic surfactants get affected (decreased) by the addition of salts [15].

TWEEN-80 AND PVSA SYSTEM

The absorbance for mixed system also increases slowly with increase in concentration up to CMC and then increases sharply with increase in concentration above CMC. The absorbance values of mixed systems of Tween-80 and PVSA at $\lambda_{\max} = 470\text{nm}$ wavelength are plotted as a function of surfactant concentration in millimole to measure the extent of dye up take (Figure 4), The logarithmic value of both co-ordinates are considered. The Surfactant Tween-80 in presence of additive PVSA shows that the amount of dye solubilized rise slowly up to the CMC, thereafter a sudden and sharp rise was observed with the formation of micelles in the bulk. The CMC of Tween- 80 surfactant was found to be decrease with increase in the concentration of added solute PVSA. Thus the solubilizing power of surfactants increases due to addition of PVSA. The CMC values obtained for Tween-80 and PVSA mixed systems are shown in Table 1.

Table 1: Influence of [PVSA] on CMC of detergent at $\lambda_{\max} = 470\text{nm}$ at 303.15K

Surfactant Tw-80 with [PVSA] wt%	CMC(mM) of Tw-80 in presence of PVSA
0.05	0.030
0.10	0.025

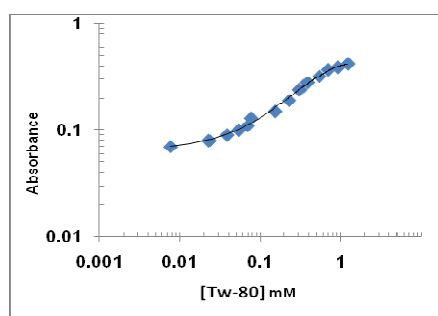


Figure 3

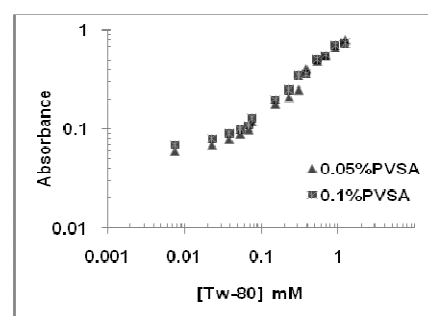


Figure 4

The influence of additive PVSA on the absorbance of Tween- 80 is clear indication that the phenomenon of dye micellization is associated with the different micelles coalescing.

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