

Micellar Effect of Anionic, Cationic and Nonionic Surfactants on Electron Transfer Process of Methylviologen Measured by UV-Visible Spectroscopy

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Summary: The reductive electrochemistry of methyl viologen (MV^{2+}) was surveyed in the presence of sodium dodecyle sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), Dodecyl ethyl dimethyl ammonium bromide (DEDAB) and Sorbitane monolaurate (SPAN 20) micelles, by considering the UV-visible technique. The effect of different surfactants on the reduction of methyl viologen radical was studied by using the UV-visible technique. The possible interactions of the anionic, cationic and nonionic surfactants with the reduced methyl viologen in the micellar and pre-micellar phase were discussed. In a definite range of concentration it was suggested that MV^{\bullet} (Methyl viologen radical) resides particularly in non-aqueous environment, such as micellar hydrocarbon core. Detection of MV^{\bullet} in the presence of anionic surfactant is possible through the peak heights of the UV-visible spectra, while in case of cationic and non-ionics, no observable changes occurred in the pre-micellar as well as in micellar concentrations.

Introduction

Micellar systems have been widely investigated and used in a variety of Chemical applications [1]. The nature of the structure of micelles has still not been determined completely probably because of the dynamic nature of these assemblies as compared to other highly organized lipid bilayer structures, such as vesicles. However, the micelle is considered to be primitive although a simple model for biological membranes [2]. There have been a few reports in the chemical literature on electrochemistry in micellar solutions [3, 4]. Saveant *et al.* [5] has reported a model stabilization of the electro generated anion radical of pthalonitrile in the presence of cationic micelles, and suggested that the observed 250 fold decrease in the rate of protonation of anion radical was due to the association with the positively charged micelles.

According to Wroblewski and Verkade [6], the electron transfer reactions of phenothiazine derivatives for physiological and photoionisation, examined in both aqueous [7] and non-aqueous [8] media, by solubilising this substrate in anionic, cationic and non-ionic surfactants and concluded that the $MPTH^+$ (10-methylphenothiazine) resides on the polar part of the micelles rather than hydrocarbon core of micelles. Kaifer and Bard [9] investigated the micellar effects on the reductive electrochemistry of MV^{2+} dication and it shows more pronounced hydrophobic character, so that hydrophobic interaction postulated to create the interactions between the cation radical and the micelles.

Methyl viologen radical has been used frequently as an electron acceptor in photochemical

energy conversion schemes in which micelles, vesicles and other organized assemblies play an important role as spacers intended to decrease the rates of detrimental charge recombination reaction. Since reports described the use of MeV^{2+} as a probe of the structure of Nafion films and clay layers on electrodes, utilizing electrochemical and ESR Methods [10, 11].

In the present work the methyl viologen radical has been exploited to see the effect of anionic, cationic and nonionic surfactants in the micellar and pre-micellar phases. UV-Visible spectroscopy has been used as analytical tool for this study. The surfactant used to see the effects on MV^{2+} (SDS & SDBS), DEDAB and SPAN as anionic, cationic and non-ionic surfactants respectively.

Results and Discussion

The UV-visible spectra of MV^{2+} 1mM under nitrogen atmosphere is similar to the once reported previously [9-11] i.e. the λ_{max} is $\approx 399\text{nm}$ and a band at 601nm , which is diagnostic value for MeV^{2+} .

The spectra of MV^{2+} as shown in Fig.1 & 2 in micellar free and SDS micellar solution respectively. It has been considered that by increasing the concentration of SDS in solution, the absorbance decreases while no other spectral features like shifts in absorption bands are observed. Similarly, Fig. [3] shows the behavior of SDBS in the same trend like SDS with the different absorbance at different concentrations of the surfactants.

By starting from $100\mu\text{M}$ to 5mM the decrease in absorbance is gradual. Above 5mM SDS concentration up to 50mM the absorbance is substantially decreased as shown in the Fig. [2]. For SDBS the Fig. [3] shows that in the concentration range $100\mu\text{M}$ up to $750\mu\text{M}$ the decrease in the absorption is less and when it increased from $750\mu\text{M}$ up to 1.5mM SDBS the absorption decreased very abruptly. The comparison of the decrease in absorbance by SDS and SDBS can be seen in Fig. [4]. It shows that at low concentration SDS causes more %decrease in absorbance as compared to SDBS. However above 1mM the trend is reversed i.e. SDBS becomes more efficient than SDS to decrease absorbance. Maximum decrease in absorbance i.e. 93.57% appears at 1.5mM SDBS concentration while in case of SDS to cause 94.8% .

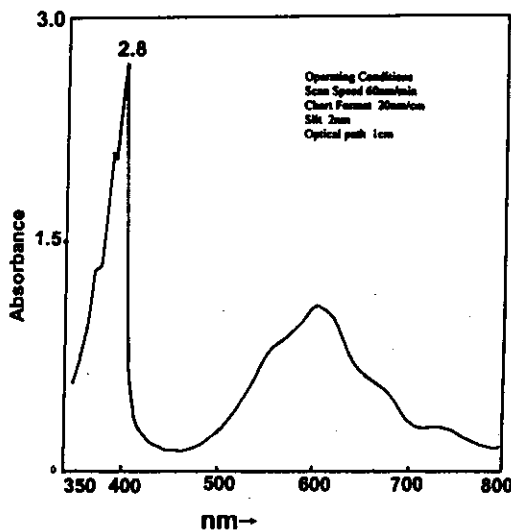


Fig.1. Absorption spectrum of $1 \times 10^{-3}\text{M}$ MV^{2+} without surfactant.

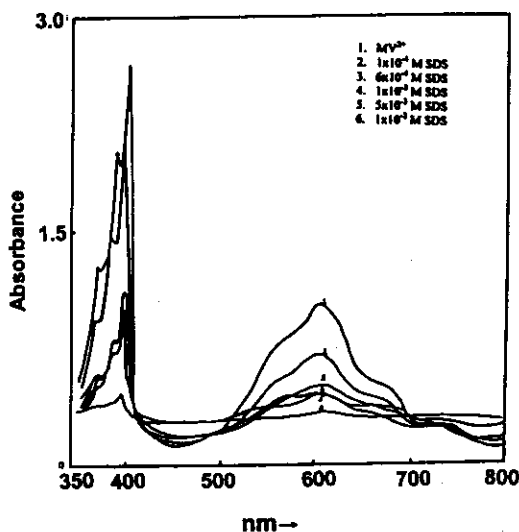


Fig.2. Absorption spectrum of $1 \times 10^{-3}\text{M}$ MV^{2+} in the presence of varying concentration of SDS surfactant.

Since electron transfer process under investigation was $\text{MV}^{2+} + e^- \rightarrow \text{MV}^{2+}$ and the decrease of intensity of absorption simply indicates decrease in concentration of MV^{2+} . It may either be due to the association of MV^{2+} with surfactants or it may be expected that radical (MV^{2+}) was produced but undergoes with a specific association with surfactant molecules.

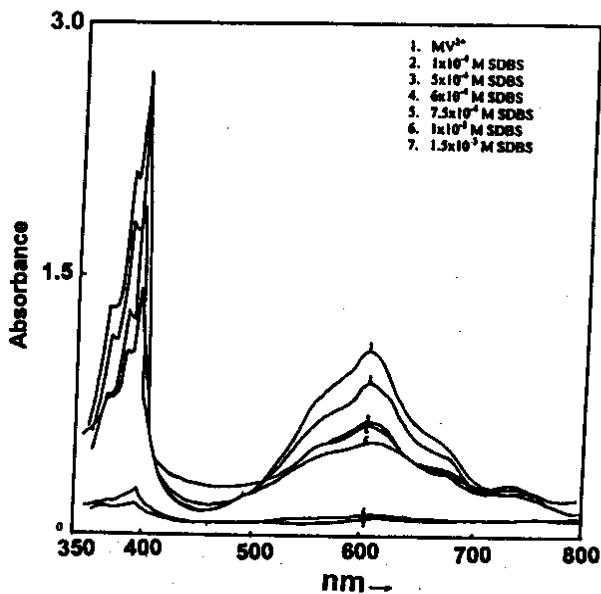


Fig.3. Absorption spectrum of 1×10^{-3} M MV^{2+} in the presence of different concentration of SDBS surfactant.

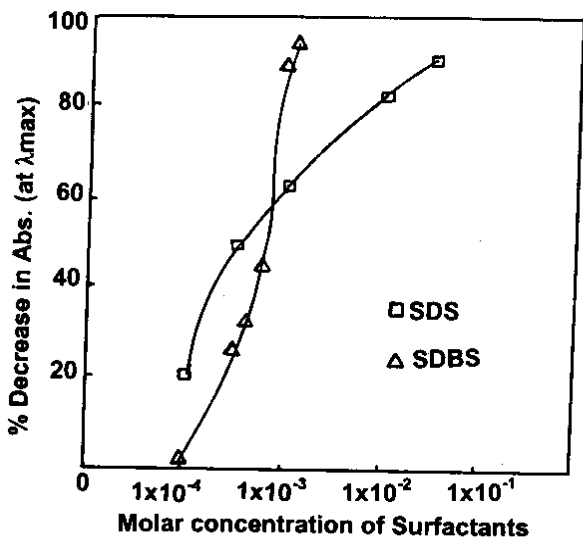


Fig.4. Percent decrease in absorbance at λ_{max} Vs molar concentration of surfactant.

Both the surfactants i.e. SDS and SDBS are anionic and their association may be considered as



or



Another association may be considered which causes to decrease the concentration is as under



and therefore, the cation radical undergoes dimerization[12]. This possibility is ruled out because the absorption spectra gave a defined peak [12] at 560nm (due to dimerization) but no such peak was observed here.

The absorptivity (ϵ) is the intensity of absorption, which is dependent on the changes in molecular environment around chromophores (MV^{*+}).

From Fig. [5] and table-I it can be seen that at lower concentration the ϵ values are lower for SDS as compared to SDBS, however the trend is reversed above 1mM concentration of SDS and SDBS. Simply it can be suggested that above this concentration, ϵ decreases up to a greater extent when SDBS molecules are present in the environment around MV^{*+} rather than SDS molecules.

Table. I. Absorbance A and absorptivity ϵ of 1×10^{-3} M MV^{*+} in different concentration of SDBS and SDS surfactants at $\lambda_{max} = 396$ nm

SDBS (mol/dm ³)	Absorbance A	ϵ	SDS (mol/dm ³)	Absorbance A	ϵ
0.00	2.8	2800	0.00	2.8	2800
1×10^{-4}	2.76	2760	1×10^{-4}	2.2	2200
5×10^{-4}	2.10	2100	5×10^{-4}	1.4	1400
6×10^{-4}	1.89	1890	1×10^{-3}	1.02	1020
7.5×10^{-4}	1.55	1550	5×10^{-3}	1.02	1020
10×10^{-4}	0.285	285	1×10^{-2}	0.48	480
15×10^{-4}	0.183	183	5×10^{-2}	0.45	145

The other observation is that the reported value of CMC is 8mM for SDS, which shows that associations of MV^{*+} with SDS micelles would be started at this concentration, but in present work decrease in absorption appears even below 8mM, which is pre-micellar phase. This indicates that due to electrostatic interactions MV^{*+} may start associating with single DS^{-} surface-active path and this association continues and increase as the SDS concentration in solution becomes higher and higher where solution contains micelles. At 8mM the decrease in intensity is suddenly increased showing enhanced association because the MV^{*+} is more

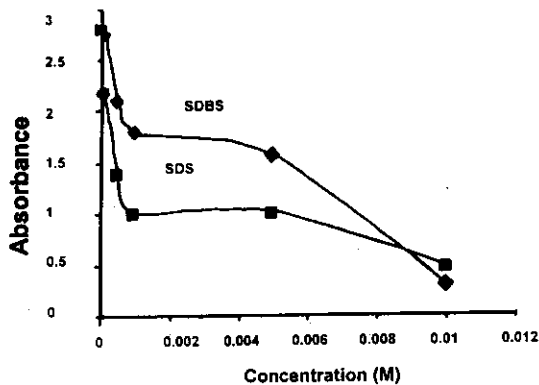


Fig.5. Effect of SDS and SDBS on the absorbance of MV^{2+} by increasing concentration.

hydrophobic as compare to MV^{2+} and core of the SDS micelles is predominantly water free [7] and thus MV^{2+} penetrates into the micelles and resides due to the association with hydrocarbon core [9] via hydrophobic interactions.

In case of SDBS, the similar trend of association of MV^{2+} and DBS has been observed by the variation of SDBS concentration. Since the CMC observed from $30\mu\text{M}$ to $50\mu\text{M}$ and below this concentration the decrease in absorbance may be attributed to electrostatic association of MV^{2+} and DBS^- . So by comparing the CMC of SDS and SDBS, the association of MV^{2+} with SDBS appears lesser than that of MV^{2+} and SDS because of steric hindrance of the benzene ring. Fig. [5] shows the trend of SDS and SDBS effects on the absorbance of Methyl Viologen radical at different concentrations.

The effect of cationic and nonionic surfactants on methyl viologen can be seen in Fig.6 and 7 respectively. The UV-visible spectra as shown in Fig. 6 of MV^{2+} in the presence of DEDAB cationic surfactant and SPAN 20, nonionic surfactant, in Fig.7, no effect of decreasing or increasing intensity of absorption was observed as compared to SDS and SDBS which show a prominent effect on the absorbance of MV^{2+} . The cationic and nonionic surfactants produced no marked difference in the spectra both in the micellar and pre-micellar concentrations, indicating that there is no concentration effect on the absorbance of the MV^{2+} . Due to the positive charge on the surface of DEDAB micelles, creates repulsion for the MV^{2+} and shows no associations [11].

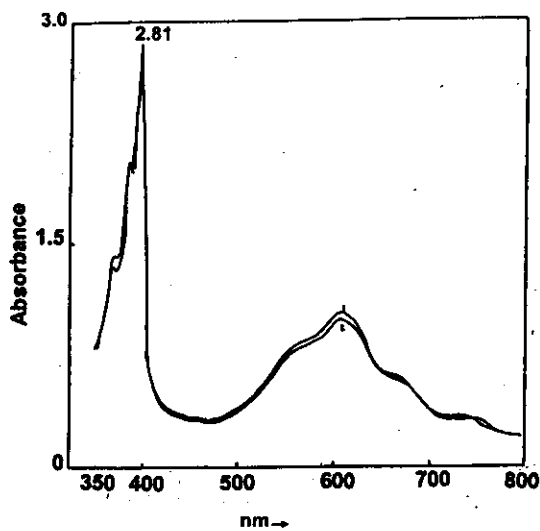


Fig.6. Absorption spectra of MV^{2+} in micellar-II and pre-micellar-I solutions of DEDAB cationic surfactant.

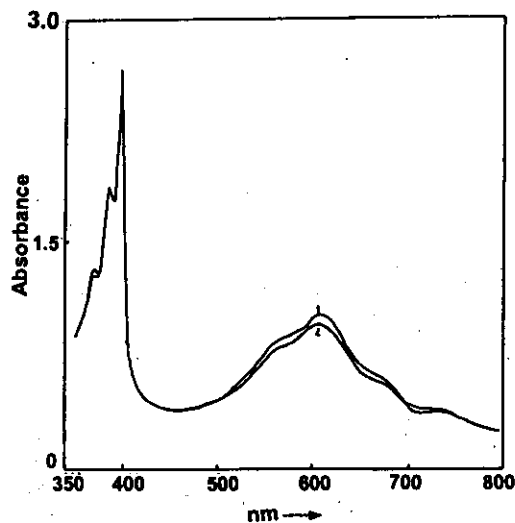


Fig.7. Absorption spectra of MV^{2+} in micellar-II and pre-micellar-I solutions of SPAN 20 nonionic surfactant.

Similarly, for non-ionic micelles (SPAN 20) having no electrostatic charges in the hydrocarbon core, the water-soluble MV^{2+} remains in the aqueous solutions. This suggested that cationic and nonionic molecules show association neither in monomer form nor in the micellar form.

MV^{2+} as compared to the MV^{2+} has stronger electrostatic interactions, with the anionic micelles

than the cationic and nonionic. MV^{2+} shows more pronounced hydrophobic character, so those hydrophobic interactions are postulated to play an important role in the interactions between the cation radical and micelles [12-14]. This conclusion is supported by the decrease in absorbance in the presence of SDS micelles as determined by spectroscopy. These effect were not observed in the DEDAB and SPAN 20 solutions.

Experimental

Materials

Methyl viologen MV^{2+} (1,1'- dimethyl-4, 4'-bipyridinium dichloride) was obtained from ICI U.K. SDS from BDH of high purity (99%), the surfactant such as SDBS, DEDAB and Span 20 were all from Fluka. Zinc dust was obtained from Merck. These chemicals were used without further purification, because all the reagents were of analytical grade. Doubly distilled water was used to prepare all solutions.

Procedure

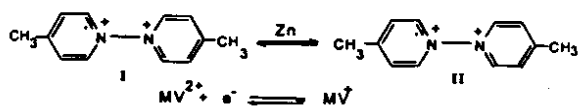
Absorption Spectra were recorded on Hitachi Model 220S UV-Visible double beam Spectrophotometer; at room temperature i.e. 25°C.

Stock solutions of anionic, cationic and nonionic surfactants were prepared with doubly distilled water. In case of nonionic surfactants gentle heating along with continuous stirring was carried out.

For experimental work, UV-visible spectra were recorded by the following procedures.

In the optical cell of 15mg of Zn powder and 4cm³ of sample solution were taken and nitrogen gas was purged for 45 minutes from the reaction mixture. Then optical cell was sealed and kept over night a blue coloration of methyl viologen cation radical was developed. The optical spectra of sample were recorded at conditions indicated, using water as in reference [12,13].

The reaction of methyl viologen may be represented as



The reduced product-II i.e. methyl viologen cation radical gave blue coloration in the solution and scanned between the range of 300nm to 800nm. The spectra were recorded first in the absence and then in the presence of the varying concentrations of anionic, cationic and nonionic surfactants.

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