

Electrochemical Behaviour of 5-Methyl-4-(2-Thiazolylazo)-Resorcinol in Micellar Media

Ahmet KARAÇELİK¹  Yeliz KARAMAN²  Saim TOPÇU^{1*} 

¹Giresun University, Sciences and Arts Faculty, Department of Chemistry, Giresun, Turkey.
²Sinop University, Sciences and Arts Faculty, Department of Chemistry, 57000 Sinop, Turkey

Geliş / Received: 24/05/2021, Kabul / Accepted: 26/06/2021

Abstract

In this study, surfactant effects on the spectroscopic and electrochemical behavior of 5-Methyl-4-(2-thiazolylazo)-resorcinol were studied in an aqueous solution at neutral pH. Dodecylpyridinium chloride (DDPC), cetylpyridinium chloride (CPC) (cationic), Triton X100, Tween 20 (nonionic), and sodium dodecyl sulfate (SDS) (anionic), were used in investigation. A large bathochromic shift of absorption maxima of the dye was observed upon the addition of surfactant. Electrochemical reduction of the dye was investigated by cyclic voltammetry (CV). The adsorption-controlled reduction reaction of the dye changed to a semi-reversible diffusion-controlled reduction peak at -0.43 V by the addition of CPC. Depending on the CPC concentration in the dye solution, the peak potential of the electrode reaction shifted about 120 mV in the cathodic direction and the peak current decreased up to ten times. These changes were interpreted depending on the type and concentration of surfactant present in the solution.

Keywords: Surfactant, critical micelle concentration, electrochemical, spectroscopic, 4-(2-thiazolylazo)resorcinol (TAO).

5-Methyl-4-(2-Thiazolylazo)-Resorcinol'ün Miselli Ortamdaki Elektrokimyasal Davranışı

Öz

Bu çalışmada, 5-Metil-4-(2-tiazolilazo)-resorsinolin spektroskopik ve elektrokimyasal davranışı üzerindeki yüzey aktif madde etkileri, nötr pH'ta sulu bir çözeltide incelenmiştir. Araştırmada dodesilpiridinyum klorür (DDPC), setilpiridinyum klorür (CPC) (katyonik), Triton X100, Tween 20 (noniyonik) ve sodyum dodesil sülfat (SDS) (anyonik) kullanılmıştır. Yüzey aktif maddenin eklenmesi üzerine boyarmaddenin absorpsiyon maksimumunda büyük bir kırmızıya kayma gözlemlendi. Boyanın elektrokimyasal indirgenmesi döngüsel voltametri (CV) ile araştırıldı. Boyarmaddenin adsorpsiyon kontrollü indirgeme reaksiyonu, CPC ilavesiyle -0,43 V'de yarı-tersinir difüzyon kontrollü bir indirgeme pikine dönüştü. Boyarmadde çözeltisindeki CPC konsantrasyonuna bağlı olarak elektrot reaksiyonunun pik potansiyeli katodik yönde yaklaşık 120 mV kaydı ve pik akımı on kata kadar düştü. Bu değişiklikler, çözeltideki yüzey aktif maddenin tipine ve konsantrasyonuna bağlı olarak yorumlandı.

Anahtar Kelimeler: Yüzey aktif madde, kritik misel konsantrasyonu, elektrokimyasal, spektroskopik, 4-(2-Tiazolazo)orsinol (TAO).

1. Introduction

Electrochemical studies of aromatic azo compounds have been the subject of many investigations because of (i) the importance of this group in the dyestuff industry (ii) interest in carcinogenic properties and (iii) the use of azo compounds for indirect determination of metal ions (Karaman et al 2015, Uçarlı 2020). Also, thiazolylazo derivatives have been used in chromatographic and spectroscopic studies (Wang 1999, Smolinska et al 2015).

*Corresponding Author: saim.topcu@giresun.edu.tr

Recently, attention has been devoted to micelles in developing analytical methods such as micellar liquid chromatography, surfactant sensitized spectroscopic determinations (Das et al, 1997, Amin A, 2000). Application areas of surfactants are not limited to analytical purposes, and they were added as catalysts for many reaction media. We previously investigated the catalytic decomposition mechanism of 5-Methyl-4-(2-thiazolylazo)-resorcinol (5-Me-TAR) in surfactant solutions (Menek et al, 2006).

Determination of electroactive substances in the micellar medium has advantages over conventional methods in the view of selectivity, sensitivity, low toxicity and applicability (Sener et al 2020, Allahverdiyeva et al 2020). Also, micelles might significantly change the redox potential of electrode processes, as well as change diffusion coefficients, the stability of electrochemical intermediates or products (Topçu et al 2003, Wu et al 2016, Rajeev et al 2017).

Thiazolylazo compounds have been used successfully as chelating agents in adsorptive stripping voltammetric determination of trace metal ions (Gazarov et al 2016, Toncheva et al 2018, Genc et al 2020). Analog dyes 1-(2-Thiazolylazo)-2-naphthol (TAN), 4-(2-Thiazolylazo)-resorcinol (TAR) and 2-(2-Thiazolylazo)-p-cresol (TAC) have been investigated in different media (Croot et al 2000, Fraga et al 2000, Hamza et al 2021). Many researchers investigated the reduction mechanism and the number of electrons transferred in the reduction of azo dyes in aqueous and non-aqueous media (Karaman 2012, 2014).

Despite the importance of surfactant effects on electrochemical and spectroscopic properties of dyes, there is limited information available in the literature (Gomes et al 1999, Rahman et al 2013, Dash et al 2021). Our study discusses the effects of various surfactants on both the spectroscopic and electrochemical behavior of azo dye. Cationic, nonionic, and anionic surfactants, such as DDPC, CPC, Triton X100, Tween 20, and SDS, were used for comparison. The spectroscopic and electrochemical behavior of the dye is largely dependent on the surfactant concentration. The increase in surfactant concentration caused shifts in the peak potential and a decrease in the peak current of the dye. In the evaluation of absorption studies with voltammetric results, it was determined that Coulomb interactions play a primary role in the nature of dye-surfactant interactions. In particular, cationic surfactants have a more dominant effect on the electronic spectrum and electro-reduction.

2. Material and Methods

Absorption spectra were recorded with UNICAM UV/VIS Spectrometer UV2 from 300 nm to 600 nm at a concentration range $C_{\text{surfactant}} \gg C_{\text{dye}}$ by using 1cm quartz cuvette.

Voltammetric experiments were conducted using a computer-controlled electroanalysis system (Metrohm 757 VA Computrace Electrochemical Analyser). A three-electrode combination system was used. This consisted of a Multi-Mode electrode (HMDE), a Ag/AgCl reference electrode, and a Pt wire auxiliary electrode. All measurements were conducted at $20 \pm 1^\circ\text{C}$. The ionic strength of the solutions was adjusted to 0.1 with 1M KNO_3 . The solutions were purged with purified nitrogen for five minutes before the experiments to remove dissolved oxygen from the solution. After the nitrogen gas passage, it was waited for about 15 min for the foaming on the solution to be removed and the solution to become stagnant. Cyclic voltammetric experiments in micellar solutions were conducted at scan rates in the range of 20-2000 mV/s. Solutions at different surfactant concentrations were made in the electrochemical cell by adding appropriate volumes of stock surfactant solutions to the dye solution in KNO_3 using a microsyringe.

The dye solution, 5-Me-TAR (Aldrich), was prepared fresh prior to each determination (Fig. 1). 1×10^{-3} M stock solution was prepared by dissolving the compound at least amount of absolute ethanol. Surfactants (CPC, DDPC, Triton X100, Tween 20, SDS) used as purchased

and 0.1 M stock solutions were prepared in water. All the chemicals employed were of analytical grade and all solutions were prepared using ultrapure water (18.4 M Ω).

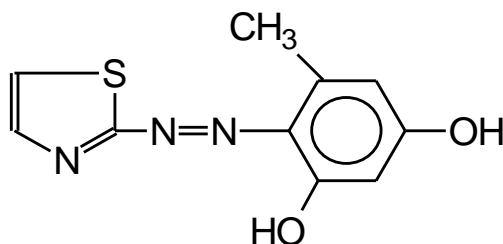


Fig. 1 The molecular structure of 5-Methyl-4-(2-Thiazolylazo)-Resorcinol.

3. Results and Discussion

3.1. Surfactant Effects on Visible Spectrum of Dye

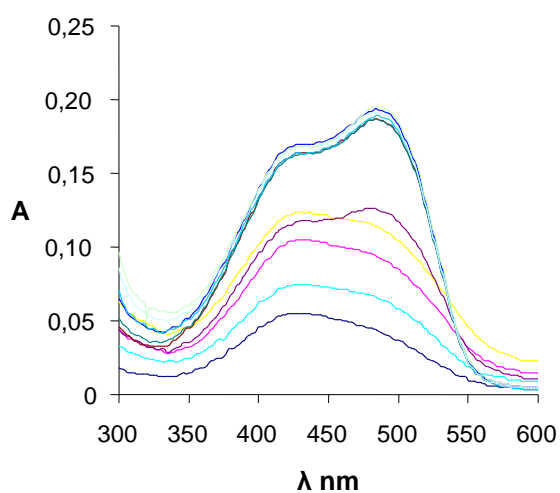
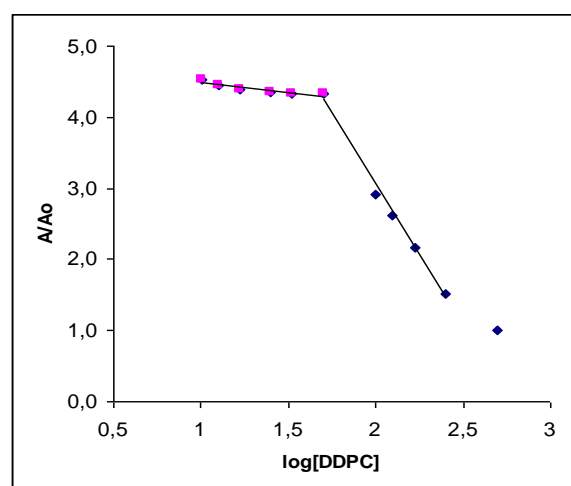
The visible spectra of the dye were investigated by mixing a fixed concentration of dye with various concentrations of the surfactant. The concentration range is arranged to include both below and above critical micelle concentration (CMC). The addition of surfactants caused large bathochromic shifts on λ_{max} of the dye.

As a representative, the change in the absorption spectra of 5-Me-TAR with varied concentrations of DDPC is shown in Fig.2. Without surfactant, an absorption maximum (π - π^*) was observed at 421 nm originating from the conjugated system of the dye. The first stage of surfactant addition caused a rise in the absorption peak, which indicates the solubilization effect of the surfactant. Further increase in the concentration of the surfactant, the intensity of the 421 nm band stabilized with a corresponding appearance of another absorption maximum at 486 nm. The 486 nm band can be attributed to the interaction of 5-Me-TAR with DDPC micelles, where the micelles start forming at around 4.0×10^{-4} mol dm $^{-3}$. The visible spectra are fixed after a specific surfactant concentration. The variation of A/A_0 values with the logarithm of surfactant concentration is shown in Fig. 3. The breaking point of the plot is considered the critical micelle concentration of surfactant (Hait et al 2001). Similar changes were observed with the addition of other surfactants, which are tabulated in Table 1.

Since the shift in the absorption spectrum results from the interaction between the dye and the surfactant, the shift in λ_{max} can be used to measure the interaction between molecules. The interaction between cationic surfactant micelles with dye, stronger than those anionic and nonionic ones. It has also been noticed that the shift in the absorption band of the dye is less in DDPC micelles (from 421 to 486 nm) compared to that in the CPC micelles (from 421 to 494 nm). This illustrates that the interaction between the dye and surfactant depends not only on ionic interactions but also hydrophobic nature of the surfactant used.

Table 1. Spectral properties of 5-Me-TAR in water and micellar solutions.

Aqueous solution	Micellar solution			
λ_{\max} (nm)	Surfactant	λ_{\max} (nm)	$\Delta\lambda_{\max}$ (nm)	CMC (mM)
421	DDPC	486	65	17.00
	CPC	494	73	0.90
	SDS	446	25	8.27
	Triton X100	460	39	0.24
	Tween 20	476	55	5.00

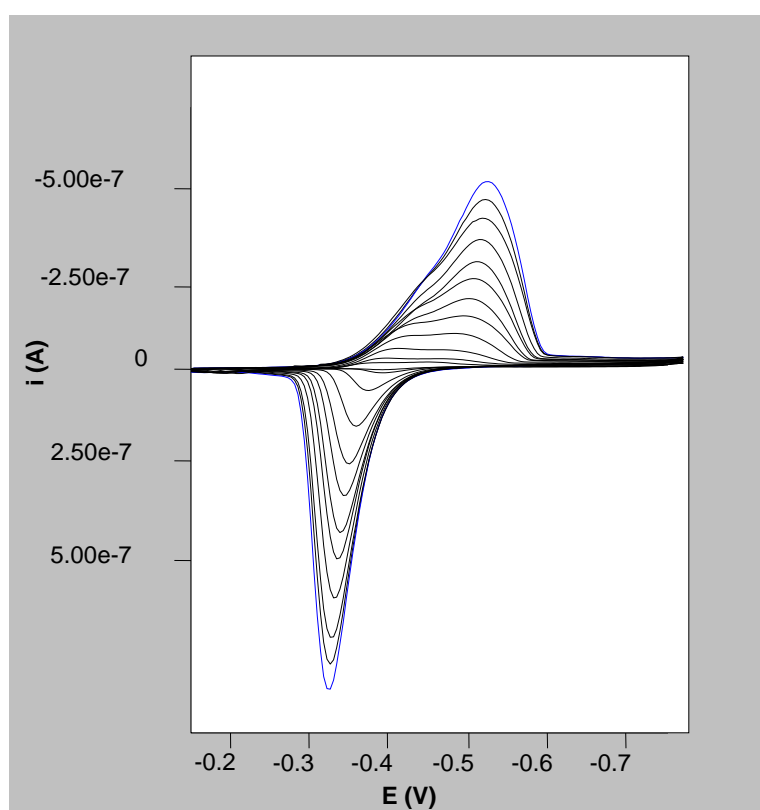
**Fig. 2.** VIS spectra of 1.10^{-5} M 5-Me-TAR in the presence of DDPC**Fig. 3.** The variation of A/A_0 (at $\lambda_{\max}=486$ nm) with the logarithm of DDPC concentration.

3.2. Surfactant Effects on Voltammetric Behaviour of Dye

Our previous study deals with a detailed electrochemical study of the dye and a reduction mechanism suggested for a broad pH range (pH 2-12). The study showed that 5-Me-TAR yields a single wave or peak in the range of pH 2-10 studied but two peaks were observed at higher than pH > 10 with the SWV, DPP, DCP, and CV techniques. The azo dye reduced reversibly to hydrazo form by taking two electrons and two protons at neutral pH region on the hanging mercury drop electrode (Menek and Topçu, 2003).

The CMC depends on the nature of surfactant (e.g. surfactant type, charge, and alkyl length vs) and solution medium (e.g. temperature, ionic strength vs) (Medel et al. 1986, Charlotte et al 2010). Since the CMC of surfactants has a different value when designating the worked concentrations the CMC of the surfactants are taken into account. A wide range of concentrations was used in the study, which covers concentrations both below and above CMC. Cyclic voltammograms of the dye were taken at a fixed dye concentration and ionic strength to determine the effects of surfactant type and concentration.

The cyclic voltammograms of the dye alone were shown at different scan rates between 20 to 1000 mV/s in 0.1M KNO₃ medium at pH 7.



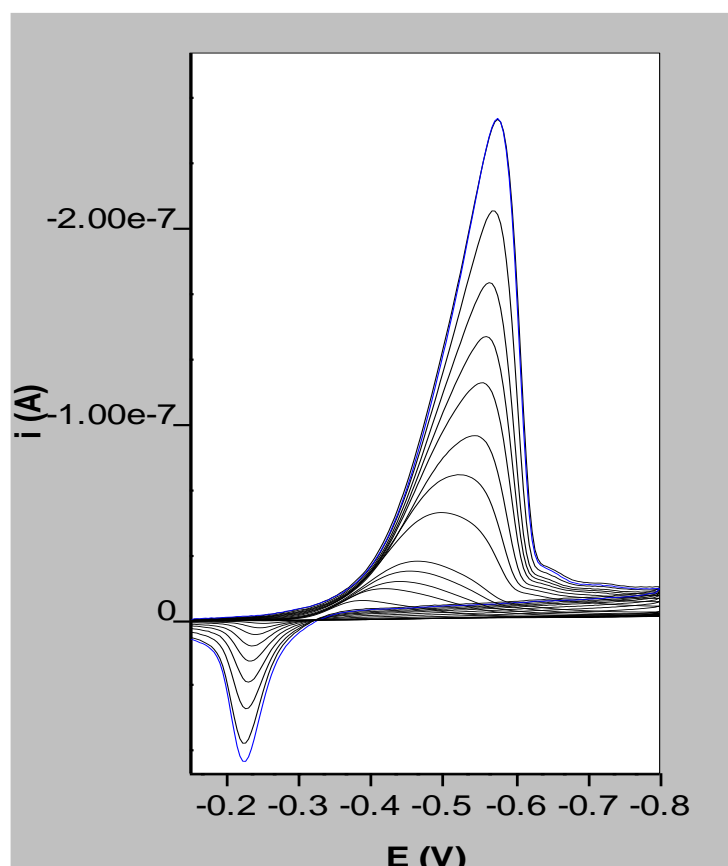
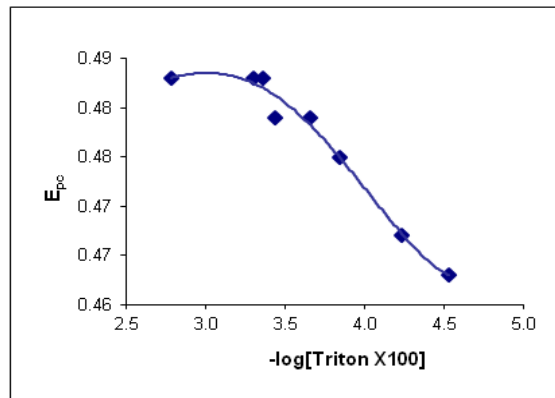
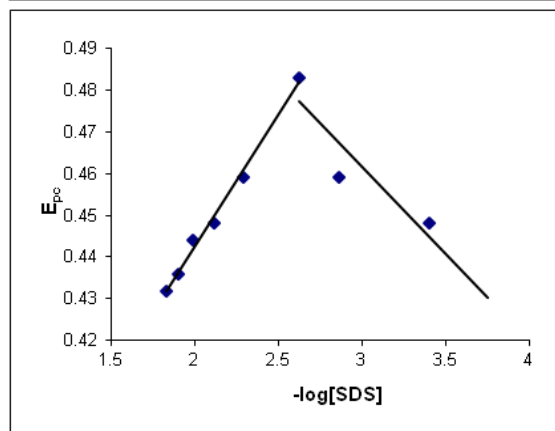
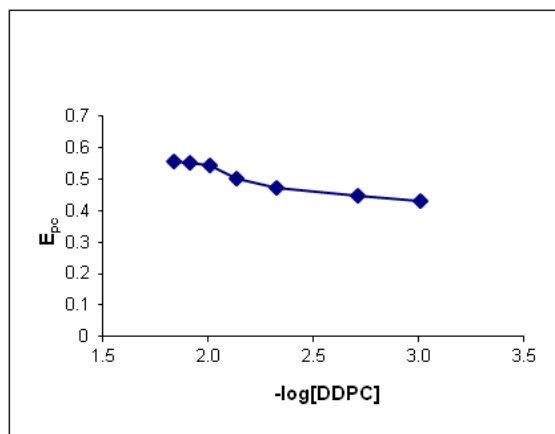
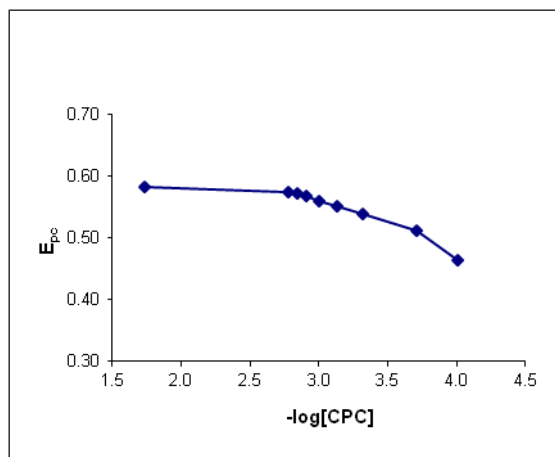


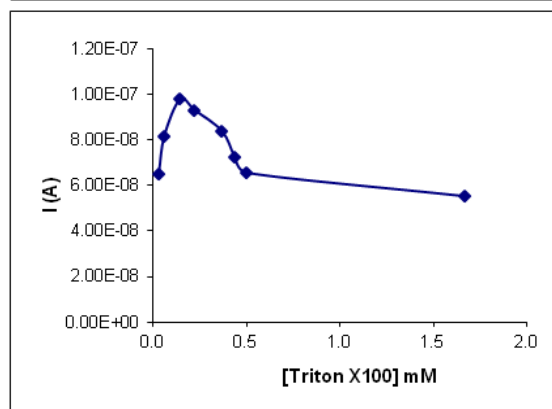
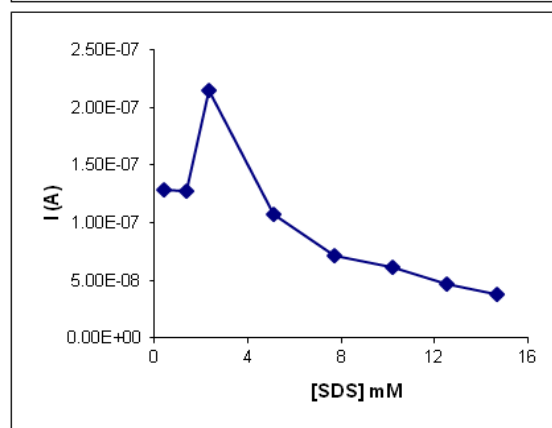
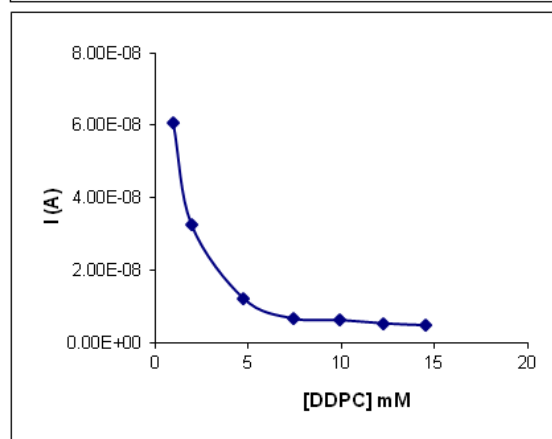
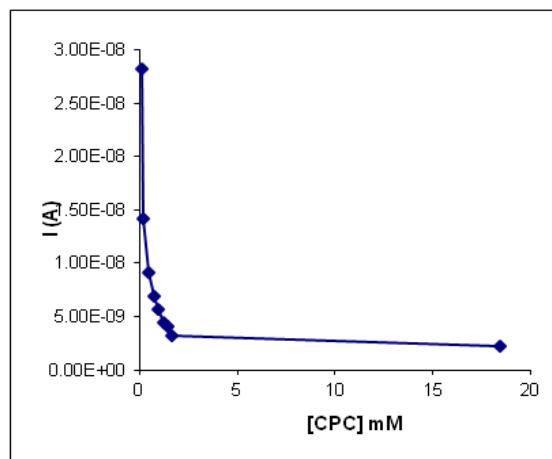
Fig. 4 Cyclic voltammograms of (a) 5-Me-TAR alone $9 \times 10^{-6} \text{M}$ and (b) in the presence of 0.1 mM CPC (scan rate: 20-1000 mV/s).

Voltammograms show that the electrode process involves adsorption complications (Fig. 4a). The presence of adsorption is verified by the difference between anodic-cathodic peak potentials and anodic to cathodic peak ratio, which is greater than 1. Also, the slope of the $\log i_{pc} - \log v$ graph of the dye was found to be 0.98 and higher than 0.5. These results indicate that 5-Me-TAR is adsorbed to the electrode surface at this concentration. Moreover, cyclic voltammograms were recorded to make a comparison in the ethanole-water mixture. The peak ratio i_p^a/i_p^c of the ethanole-water mixture (%30 v/v) smaller than 1 showed that the absence of adsorption in this medium. The presence of strong intermolecular interaction of dye and ethanol molecules prevents the adsorption of dye as expected.

The presence of a surfactant molecule in the dye solution leads to a similar electrochemical response in ethanole-water media. The stepwise manner addition of surfactant into dye solution leads to a sharp decrease in the anodic peak to cathodic peak current ratio. A representative cyclic voltammogram of cationic CPC solution was shown in Figure 4b. In all surfactant solutions, similar voltammograms were observed. These changes are attributed to the adsorption of the surfactant to the electrode surface and therefore inhibit the adsorption of the dye.

The variation in peak potential and peak current of 5-Me-TAR in surfactant solutions are shown in Figures 5 and 6, respectively. In the presence of SDS and Triton X100, the peak current of the dye slightly increased in the early stage of surfactant addition. Further addition of these surfactants caused a sharp decrease in the peak current. CPC, DDPC, and Tween 20 reduced the peak current as soon as they were added to the solution.





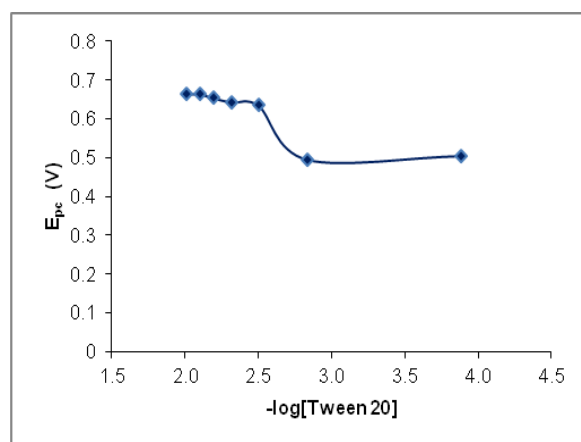


Fig. 5. The peak potential ($-E_{pc}$) versus the logarithm of surfactant concentration

The negative shift of the peak potential means that reduction of the dye becomes more difficult to occur with increasing surfactant concentration.

Triton X100 addition into the dye solution barely changed the reduction potential (25 mV). It remained in the range of 0.46-0.48 V. The peak current raised until the CMC of the surfactant (0.24 mM) and then decreased and become constant.

CPC, DDPC, and Tween 20 showed similar behavior in the electrochemical reaction. The peak potentials shifted to more negative values with increasing concentration and then fixed around a certain potential value. CPC and DDPC changed the peak potential from 0.46 V to 0.58 V and 0.43 V to 0.55 V, respectively. Tween 20 leads to a greater shift (160 mV) from 0.50 V to 0.66 V. Although equal variation (120 mV) is observed both in CPC and DDPC, these changes occurred at much lower concentrations in CPC. The peak current of the dye sharply decreased until the CMC of the used surfactant (Table 1). Then approach to a lower limit value (Fig. 6). Moreover, these three surfactants also caused a larger bathochromic shift in absorption spectra (Table 1).

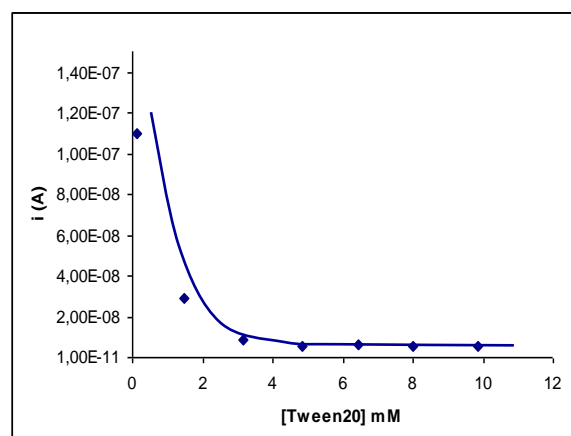


Fig. 6. The peak current (I_{pc}) of 5-Me-TAR in surfactant solutions

SDS and Triton X100 showed an increase in peak currents below their CMC values, suggesting that a surfactant-induced surface process has caused this change.

The surfactant concentration dependency of the reduction potential in SDS deviated from others. While the anionic surfactant initially increased the reduction potential from 0.43 V to 0.48 V, then decreased it to 0.44 V at higher concentrations. The electrode reaction becomes more difficult due to the interaction of SDS, which is strongly adsorbed on the electrode surface, with the anionic form of the dye. Further increase in the bulk concentration of SDS leads to anion-anion interactions that alter the protonation equilibria of the dye and thus convert the anionic dye to its neutral form. Thus, electro-reduction of 5-Me-TAR, which involves protonation of the dye on the electrode surface, occurs more easily (Uçar et al, 2002, Menek et al 2003).

The electrode reaction of 5-Me-TAR is highly sensitive to the presence of surfactants in the dye solution. The variation of peak potential and peak current of the dye with the surfactant concentration showed rapid changes in specific concentration ranges. These changes indicate that surfactant monomers begin to aggregate to form a micellar structure. Evaluation of peak potentials and currents together showed that critical micelle concentrations of surfactants in 5-Me-TAR solution can also be found by voltammetry. The critical micelle concentrations were in agreement with those found by the spectroscopic method (Table 1).

The peak current of the dye almost stayed constant after this surfactant concentration. As the surfactant concentration is increased there is a considerable decrease in the slope of the I_{pc} vs. $v^{1/2}$ plot. This may be due to an increase in effective size and high viscosity of the micellar solutions, which retard the diffusion of the encapsulated dye (Das et al 1997, Davis et al 1998).

4. Conclusion

The presence of surfactant in the dye solution significantly changed the electronic absorption spectra and electro-reduction of the dye reaction on the mercury electrode. The increase in the absorption spectrum before the critical micelle concentration indicates that the dye dissolves better in the presence of surfactant. However, it has been found that it effectively prevents the adsorption of the dye to the mercury electrode surface up to the critical micelle concentration and makes the electrode reaction diffusion-controlled. When the critical micelle concentration was exceeded, the formation of a new peak in the absorption spectrum showed that the dye remained within the micelle structure and its immediate surroundings changed from a hydrophilic structure to a hydrophobic structure. The trapping of 5-Me-TAR in micelles significantly reduced the diffusion rate to the electrode. The peak current of the electrochemical reaction gradually decreased in micellar media. These effects were more pronounced with cationic surfactants than others. It shows that cationic surfactants and the dye interact with each other beyond Van der Waals forces. Considering the acidic nature and ionization of 5-Me-TAR in aqueous media, the Coulomb force plays an active role in the interaction between cationic surfactants and dye anions.

This study showed that surfactant-dye interactions could be used to separate overlapping peaks of different dyestuffs in voltammetric determination (Kumar et al 2021). Tween 20 provided the largest peak shift (160 mV), followed by CPC and DDPC with 120 mV. SDS caused a change of about 50 mV, while the Triton X100 was found to have an effect of only 25 mV. A peak shift above around 100 mV can be useful in many overlap situations (Selcuk et al 2021). The use of excess surfactant to achieve good peak separation can become the limiting factor since it reduces the peak currents.

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