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Research Article

Cyclic voltammetric behavior of crystal violet in aqueous solution: Correlation with dissolved states of cetyltrimethylammonium bromide

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ABSTRACT

The cyclic voltammetric method was employed to study the electrochemical behavior of aqueous crystal violet in the presence of cetyltrimethylammonium bromide, both below and above the critical micelle concentration. The cyclic voltammograms were highly sensitive to solution pH, exhibiting well-defined oxidation and reduction peaks within the pH range of 1.76 to 2.29. The electrochemical potentials and currents indicate the involvement of a set of reactions responsible for the observed voltammograms. The fully oxidized diquinoid of N, N, N', N'- tetramethylbenzidine (TMBOx) was formed, which was reduced to N, N, N', N'- tetramethylbenzidine (TMB). The presence of CTAB profoundly influenced the electrochemical behavior, and responses were found to depend on the dissolved states of CTAB. The electrochemical process was diffusion-controlled and followed a chemical-electrochemical-chemical (CEC) mechanism.

Introduction

Triphenylmethane (TPM) dyes including malachite green (MG), ethyl violet, crystal violet (CV), and victoria blue B exhibit unique electrochemical activity (Perekotii et al., 2002; Xu et al., 2007; Song et al., 2010) and are extensively used in applications as antibacterial agents, antiseptics, and in industries like silk, textile, and paper (Arsalan et al., 2013). However, TPM dyes are recognized as potential environmental pollutants, prompting considerable research efforts to understand their physiochemical characteristics and devise effective strategies to mitigate their impact (Pillai et al., 2011; Petcu et al., 2016). In addition, they have gained attention in nontraditional usages, particularly in developing molecular devices by exploiting electrochemical switching (Ariga, 2006; Selvakumar, 2017; Toma, 2008; Ge et al., 2022).

Researchers have conducted studies under different electrochemical environments in pursuit of a deeper understanding of the electrochemical characteristics of TPM dyes and how to manipulate them. Perekotii et al. explored the electrochemical properties of CV using a glassy carbon electrode (GCE) to support electrolytes such as potassium salts of nitrate, chloride, and iodide. In KI solution, an electroactive complex with iodide forms on the surface of the electrode (Perekotii et al., 2002). Galus and Adams (1964) unveiled the complex nature of the electrochemical process of CV in acidic environments. They reported that the two phenyl fragments intramolecularly couple when the TPM moiety experiences expulsion of the central carbon residue. This sequence of reactions yielded fully oxidized a diquinoid of N, N, N`, N`-

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tetramethyl-benzidine (TMBOx). TMBOx is subsequently transformed into the reduced form, N, N, N`, N`- tetramethyl-benzidine (TMB) through a redox process involving a two-electron reduction process (Galus and Adams, 1964; Galas and Adams, 1962). When comparing the oxidation of TPM dyes in liquid SO_2 to that in the aqueous solution under acidic conditions, Hall et al. (1966) observed that the two environments showed very distinct redox activity. They proposed that the redox couple responsible for the voltammogram involved the carbonium ion and the free radical generation.

It would be interesting to find out if the distinct electrochemical activity of TMP dyes persists in surfactant-based organized media and to establish a correlation between dissolved states of the amphiphile and electrochemical responses. The surge in interest in redox-active species, especially TPM dyes in micellar systems, stems from the fact that a systematic change in the concentration of surfactants can control the electrochemical behavior of electroactive probes (Saji et al., 1985; Takeoka et al., 1996). The concept of switching by exploiting electrochemical changes of redox-active surfactants was pioneered by Saji et al. (1991, 1994) and Gokel and coworkers (Munoz and Gokel, 1993; Wang et al., 1996). Their work demonstrated that micelles can be disrupted into monomers through redox reactions, offering an efficient means for preparing thin films of water-insoluble organic dyes. Takeoka et al. investigated the electrochemical behavior of a nonionic surfactant containing a ferrocenyl group (Takeoka et al., 1995, 1996). They revealed that the oxidation state of the redox-active group and the dissolved states of the surfactant affect the features of the cyclic voltammograms of the surfactant solutions. According to Kozlecki et al. (1997), introducing an azo group to the hydrophobic tail of alkane carboxylates and linear alkane sulfonates improves their solubility in water, micellization, and adsorption. Susan et al. conducted extensive research on anthraquinonyl and phenothiazinyl nonionic surfactants (Susan et al., 2000a, 2000b, 2004). Their work demonstrated that these redox-active surfactants exhibit fascinating responses to electrochemical changes, with controllable (electrochemical) behavior achieved by manipulating factors such as the structure of the surfactants, concentration, pH, and redox potential.

Rusling (1994) reviewed earlier research on the redox behavior of electrochemical probes in electro-inactive surfactants. Susan and his team used ferrocene, anthraquinone, and phenothiazine to explore their electrochemical behavior in various surfactant solutions. Their results demonstrated that redox probes, when dissolved in organized systems containing electro-inactive surfactants, can also be administered using the principle of electrochemical switching (Haque et al., 2011; Mahmud et al., 2011; Haque et al., 2012; Keya et al., 2014; Roy et al., 2020). Yeh (1976) also solubilized a redox probe in micelles to estimate micellar diffusion coefficients of Tween 20 (Yeh, 1976). Rahman et al. (2013) examined the electrochemical behavior of MG in an aqueous solution with cetyltrimethylammonium bromide (CTAB), a cationic surfactant, and sodium dodecyl sulfate (SDS), an anionic surfactant. Using a GCE in the experiments, they observed important interactions between MG and various surfactants. They demonstrated that, under ambient conditions, the redox process of MG is irreversible and diffusion-controlled.

Despite extensive studies, research on the redox behavior of TPM dyes in surfactant systems remains in its infancy; in particular, comprehensive studies on CV are still lacking. The CV in a surfactant system is of immense interest due to its unusual yet tunable electrochemical behavior (Galus and Adams, 1964) for the construction of electrochemical switchable molecular devices. To address this gap, Mahmud and coworkers documented the electrochemical characteristics of aqueous CV in the presence and absence of Triton X-100, a nonionic surfactant (Mahmud et al., 2023). Using platinum electrodes in the cyclic voltammetry method, they found the characteristics of the voltammograms of CV were complex and very sensitive to solution pH.

According to the literature (Galus and Adams, 1964, 1962), CV can exist in different forms in solution and give rise to different voltammograms based on the solution pH (Fig. 1). In acidic aqueous buffered solutions, Structure I could undergo complex reactions leading to TMBOx compounds, which, through a two-electron transfer process, form TMB (Fig. 1) (Galus and Adams, 1964). Mahmud and coworkers verified that the electrochemical reaction of the redox pair, TMBOx/TMB, is the basis of the shapes of the cyclic voltammograms at pH 1.76-2.29.

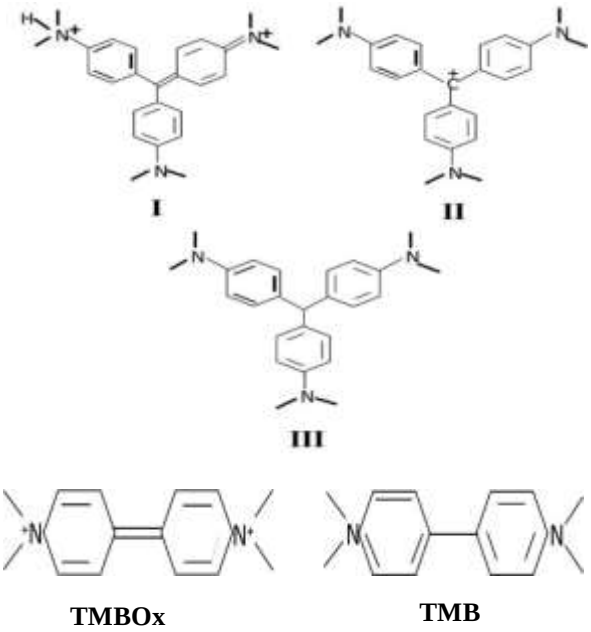


Fig. 1. Different forms of crystal violet in the aqueous electrochemical system at different pH values. Structure I, TMBOx, and TMB are present at low pH, and Structure II and III are at high pH.

The voltammogram changes shape at high pH (alkaline condition) because TMBOx is not formed under this condition, and leucocrystal violet is produced via an electrochemical reduction reaction involving the carbocationic form (Structure II) of CV (Structure III), which is then oxidized to CV. Although complex, the redox process did not change in Triton X-100 in aqueous medium. It is, therefore, interesting to investigate whether the electrochemical behavior is unique for a nonionic surfactant system and whether electrostatic interactions of an ionic surfactant influence the electrochemical behavior similarly. In this study, to correlate the available knowledge of the electrochemical reaction of CV with the dissolved states of a surfactant, we investigated the cyclic voltammetric behavior of the aqueous solution of CV in the presence of a cationic surfactant, CTAB.

Materials and Methods

Sodium chloride (NaCl), CTAB, and crystal violet were purchased from BDH and used without further purification. Puric-S (Organo Co., Tokyo) grade deionized water with a specific resistance of 2.00 MΩ cm was used to prepare all of the stock solutions. The concentration of CV was maintained at 1.00×10^{-6} M for all experiments conducted to investigate its electrochemistry, regardless of the presence of CTAB. The stock solution was properly diluted to produce CTAB solutions in different concentrations.

A pH meter (Model HM-26S; TOA Electronics, Japan) measured the solution pH. The cyclic voltammograms were recorded using a computer-controlled electrochemical analyzer (model HQ 2040; Advanced Analytics, USA). 0.16 M NaCl aqueous solution was used as the supporting electrolyte. A single-compartment three-electrode cell was used. A platinum electrode (area of 0.021 cm^2) served as the working electrode, while a Pt-wire was the counter electrode, and an Ag/AgCl was the reference electrode. Before each measurement, the surface of the working electrode was cleaned and polished with 0.05 µm alumina (Buehler) to render it mirror-polished. The potential was scanned at a scan rate (v) ranging from 10 to 500 mVs^{-1}. To remove the influence of ambient CO_2 and dissolved oxygen, all the pH and electrochemical measurements experiments were performed in an inert atmosphere by purging the solution with N_2 gas at 25^oC.

Results and Discussion

Electrochemical responses of crystal violet in a micellar solution of CTAB: The cyclic voltammetric behavior of CV was studied in CTAB with 0.16 M aqueous NaCl solution as the supporting electrolyte.

CTAB concentration varied in a wide range, including concentrations below, above, and far above the CMC, with the CMC value of CTAB being 9.2 $\times 10^{-4}$ M at 25.0 ºC (Rahman et al., 2013). Due to the salting out effect (Shahid et al., 2009), the addition of NaCl brings about a decrease in the CMC of CTAB in aqueous solutions, and the concentrations of 1.5×10^{-3} M or above of CTAB used in this work can be regarded as concentrations above the CMC (Haque et al., 2011).

Fig. 2 presents the characteristics of the shape, potentials, and current of the cyclic voltammograms of 1×10^{-6} M CV at different CTAB concentrations at the v of 10 mVs^{-1}. The cyclic voltammograms in aqueous solution maintain their shape when CTAB is present, as demonstrated in Fig. 2(a). As reported earlier, the electrochemical reaction involves a two-electron transfer process (Mahmud et al., 2023). One reduction peak and its corresponding oxidation peak are observed in these voltammograms. Nonetheless, it has been revealed that the electrochemical reactions rely on the CTAB concentration. The potential data presented in Fig. 2(b) shows the change in half-wave potential ($E_{1/2}$) and cathodic peak potential (E_{pc}) with [CTAB]. While the $E_{1/2}$ is minimally affected, the E_{pc} increases with the concentration of CTAB. This increase in the E_{pc} with CTAB concentration suggests that the formation of TMBOx may be favored in the micellar core or enhanced by the surface activity of CTAB. Figure 2(c) depicts the change in the cathodic peak current, $i_{pc,}$ with [CTAB]. As demonstrated in Fig. 2(c), the i_{pc} decreases as the concentration of CTAB rises, followed by a minimum before increasing again.

Surfactant species exist as free monomers at concentrations lower than the CMC, allowing reducible TMBOx to diffuse freely to the electrode interface. This results in relatively high i_{pc} at low surfactant concentrations. Micelles, in other words, thermodynamically stable aggregates of colloidal dimension, are formed by the aggregation of surfactant species above the CMC. The decrease in the i_{pc} is caused by the solubilization of CV inside the micellar core and the ensuing decreased diffusion to the electrode interface. As the concentration of CTAB reaches far above CMC, the i_{pc} is found to increase. This could be attributed to the solubilization effect, where all the electroactive species are trapped in the micellar cores.

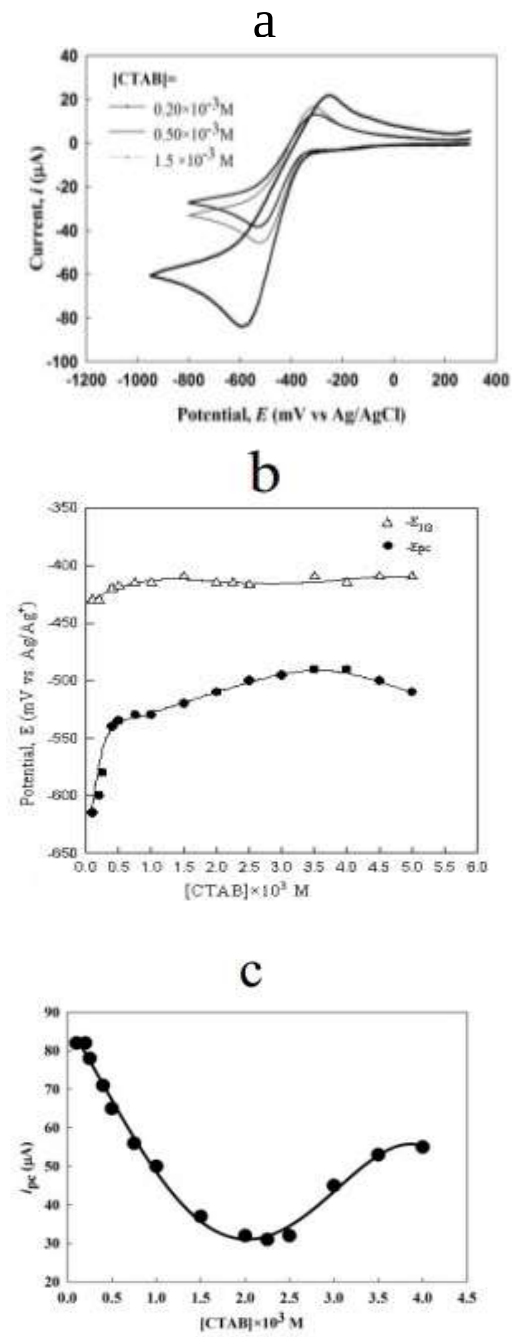
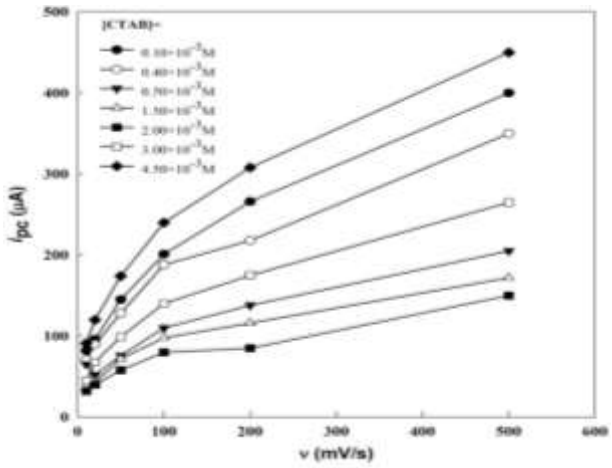


Fig. 2. Cyclic voltammetric results for 1×10^{-6} M crystal violet at various CTAB concentrations at the v of 10 mVs^{-1} in 0.16 M NaCl aqueous solution: a. characteristic shape of the voltammograms, b. E_{pc} and $E_{1/2}$ vs. [CTAB] plots, and c. i_{pc} vs. [CTAB] plots.

The concentration of CV in the micellar pseudo phase decreases as surfactant concentration rises since more micelles are produced. Since micelles are in dynamic equilibrium with their monomers, diffusion of CV becomes higher to the electrode interface to cause an increase in the i_{pc}. The observations are reminiscent of those for CV in an aqueous solution of TX-100, and the overall trend of the electrochemical behavior is not changed for the cationic surfactant.

To diagnose if diffusion regulates the entire electrochemical process or if the change in CTAB concentration impacts adsorption at the electrode surface, the i_{pc} of 1×10^{-6} M CV at 10 mVs^{-1} was further examined.

a.



b.

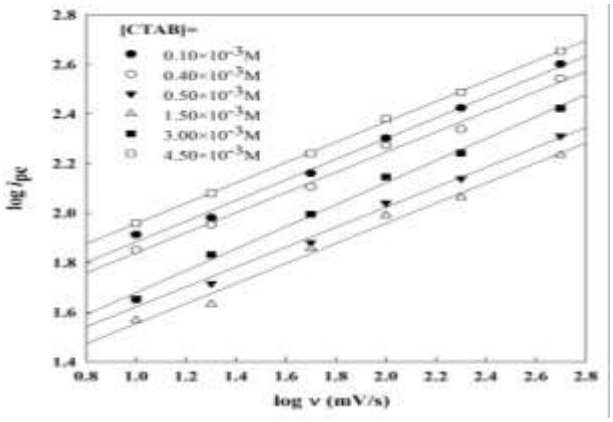


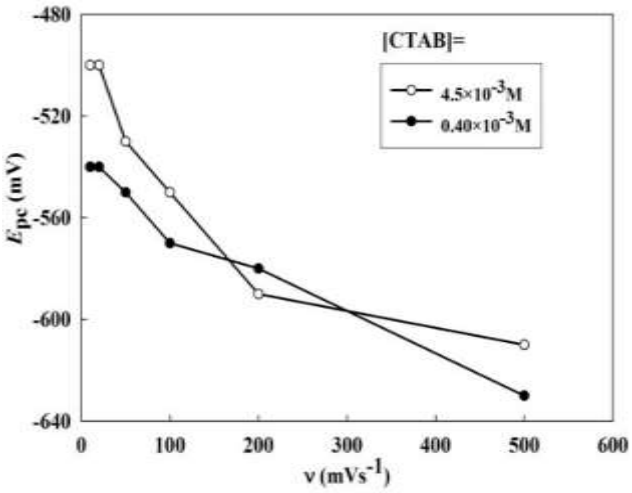
Fig. 3. The variation of the i_{pc} with v for various CTAB concentrations for 1×10^{-6} M crystal violet solution in the presence of 0.16 M NaCl aqueous solution; a. i_{pc} vs. v; b. log i_{pc} vs. log v.

Table 1. Slopes of the plots of log i_{pc} vs. log v at various CTAB concentrations for 1×10^{-6} M CV in 0.16 M NaCl aqueous solution.

[CTAB]×10³ (M)	Slope
0.10	0.42
0.40	0.41
0.50	0.41
1.50	0.40
3.00	0.44
4.50	0.41

Fig. 3 provides insight into the v dependence of the i_{pc}, revealing that the i_{pc} increases in a non-linear fashion with the v, which indicates a *quasi-reversible* process. It is apparent [Fig. 3(a)] that some other process significantly influences the electrochemical process instead of adsorption. When log i_{pc} vs. log v is plotted, the slopes [Fig. 3(b)] at all CTAB concentrations have values closer to 0.5 than 1 (Table 1), suggesting a diffusion-controlled process (Bard et al., 2022). Furthermore, given that the slope is somewhat less than 0.5, a chemical reaction likely precedes the electrochemical reaction, in this instance, the generation of TMBOx from CV and protonation of the carbocationic dye, even in the presence of CTAB.

a.



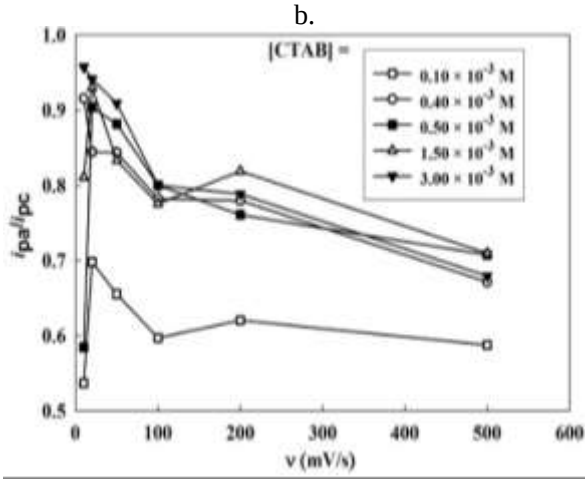


Fig. 4. Variation of the peak potential and currents with *v* for 1×10^{-6} M CV at various concentrations of CTAB in 0.16 M NaCl aqueous solution; a. E_{pc} vs. *v*; b. i_{pa}/i_{pc} vs. *v*.

Fig. 4(a) displays a negative shift in the cathodic peak potential with increasing *v*, implying again that the system is likely *quasi*-reversible (Greef et al., 1985). Meanwhile, Fig. 4(b) displays the ratio of the anodic peak current (i_{pa}) to the i_{pc} (i_{pa}/i_{pc}) as a function of *v* at varying concentrations of CTAB. In Fig. 4(b), it can be observed that the i_{pa}/i_{pc} values are smaller than 1 at all experimental concentrations of CTAB, indicating that other processes, such as a following chemical reaction, complicate the electrochemical reaction (Nicholson and Shain, 1964). The i_{pa}/i_{pc} value initially increases, reaches a maximum, and then decreases with increasing *v*. At lower *v* values, an increase in the ratio with increasing *v* is apparent, supporting the existence of a following reaction (Susan et al., 2000b). At higher *v* values, the decrease in the i_{pa}/i_{pc} with *v* corresponds to the property of a reversible electrochemical reaction coupled with a preceding chemical reaction. This behavior is similar to what is observed with CV in the aqueous solution without any CTAB (Mahmud et al., 2023). During the cathodic scan, the Pt electrode interface exhibits H_2 gas evolution in the presence of CTAB, leading to pH change at the interface. As a result, all TMB produced from the reduction of TMBOx may not be reoxidized, resulting in a decrease in the i_{pa} and hence in the i_{pa}/i_{pc}.

In CTAB solutions, the apparent diffusion coefficient (D_{app}) of CV could be estimated using the Randles-Sevcick equation (Eq. 1).

$$i_{pc} = (2.69\times10^5)n^{3/2}AD_{app}^{1/2}v^{1/2}C \qquad (1)$$

Here, A is the geometric area of the electrode surface in cm^2, D_{app} is in cm^{2}s^{-1}, *v* is in Vs^{-1}, *C* is the concentration of the reactive species in the bulk of the solution in mol cm^{-3}, and i_{pc} is in ampere. The number of electrons participating in the electrochemical reaction is represented by *n*.

Fig. 5 illustrates D_{app} versus [CTAB] for 1×10^{-6} M aqueous CV solution. The D_{app} decreases, reaches a minimum, and then increases with increasing [CTAB]. The D_{app} is expected to decrease above the CMC since the solubilization of CV within the micelle core upon micelle formation reduces the rate of diffusion of CV or TMBOx to the interface. The D_{app} increased as the surfactant concentration decreased at concentrations lower than the CMC, eventually reaching the same diffusivity as CV when CTAB was absent. The diffusivity increased with increasing [CTAB] after reaching a minimum because increasing micelle concentration reduces CV concentration in the micellar pseudo phase, making it easier for CV or its counterpart TMBOx to diffuse to the electrode interface.

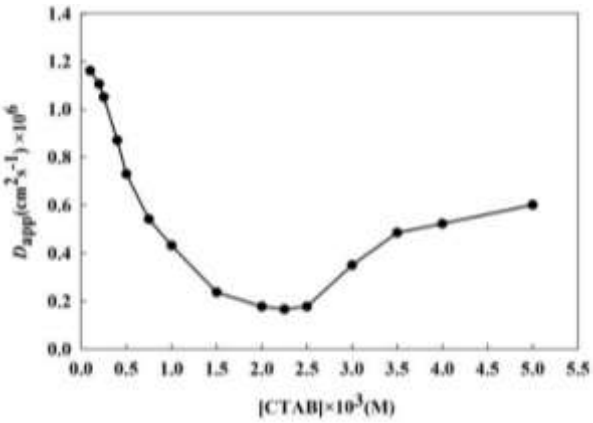


Fig. 5. Electrochemically estimated D_{app} plotted against the concentration of CTAB for 1×10^{-6} M CV aqueous solution.

Electrochemistry of aqueous crystal violet: The electrochemical behavior of aqueous CV solution was examined without CTAB while maintaining other conditions identical to the experiments conducted in the presence of CTAB at pH 2.29. The primary objective was to compare the results obtained in the presence of CTAB with those obtained in its absence. Under the current experimental conditions, cyclic voltammograms showed single reduction waves and their corresponding oxidation waves, similar to those recorded in the presence of CTAB (*vide supra*). These findings were consistent with the works of Galus and Adams (1964) and Mahmud and coworkers (2023). The separation of potentials for the cathodic and anodic peaks (ΔE) for the cyclic voltammograms was greater than 59/n mV (where n = 2), indicating that the electrochemical process was not entirely reversible under the experimental conditions. The greater ΔE is likely attributed to the sluggish transfer of electrons, which is accompanied by a chemical reaction. Furthermore, the logarithmic relationship between peak current and v exhibits a linear relationship with an acceptable regression coefficient (>0.9997) (Fig. not shown). The slope is 0.44, which suggests that the electrochemical process under the current experimental condition is also controlled by diffusion, as observed in the presence of CTAB. Furthermore, reduction current and v were evaluated using Eq. (1), which further supports a diffusion-controlled process.

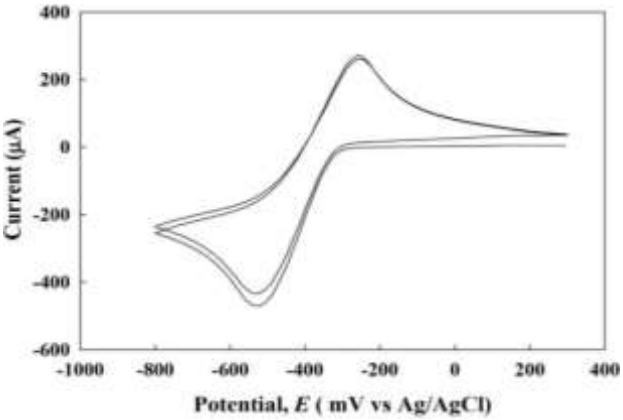


Fig. 6. Cyclic voltammograms of 1×10^{-6} M CV in 0.16 M aqueous NaCl solution during successive scans (pH= 1.86; v = 10 mVs^{-1}).

Cyclic voltammograms were also obtained to measure i_{pa} immediately after cathodic reduction. The system showed a significant current in the ensuing scan, indicating the existence of oxidized species. Notably, however, our observation differs from that reported by Galus and Adams (1964). As the potentials were scanned to obtain multiple cyclic voltammograms consecutively, the i_{pc} increased in the subsequent scan, as depicted in Figure 6. This increase suggests a rise in the relative number of reducible species at the electrode surface during the subsequent scan, suggesting that TMBOx, i.e., the reducible species, will diffuse faster to the interface.

Conclusion

Crystal violet demonstrates pH-dependent electrochemical responses in an aqueous solution, showing distinct cyclic voltammograms between 1.76 and 2.29. The TMBOx/TMB redox couple is primarily accountable for the voltammograms and resembles a diffusion-controlled process. The electrochemical process involves two-electron transfer, and a preceding chemical reaction is coupled with it. In the prior reaction, TMBOx is formed from the dication form of CV. Similar to a nonionic surfactant, CTAB does not affect the shapes of the voltammograms.

Nonetheless, an alteration in CTAB concentration has a major impact on the electrochemical behavior of CV since it results in a change of the surfactant from monomeric to self-assembled species. The voltammogram displays a relatively high peak current at concentrations lower than the CMC since CTAB is a free monomer, allowing the reducible TMBOx to diffuse freely to the electrode interface. However, increasing the concentration of CTAB leads to greater micelle formation, reducing the diffusivity of CV and causing a decrease in peak current. The electrochemical process is coupled with a preceding chemical reaction and a following reaction in the presence of CTAB. These findings contribute to the understanding of the

electrochemical properties of CV in the presence of a cationic surfactant. They may have implications in diverse fields, including electrochemistry and molecular switching. These results advance our knowledge of the electrochemistry of triphenylmethane dyes in the presence of cationic surfactants and may find applications in molecular switching and electrochemistry, among other areas.

Conflict of Interests

The authors declare no conflicts of interest.

Acknowledgments

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