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ORIGINAL ARTICLE

Electrochemical behavior of anthraquinone in aqueous solution in presence of a non-ionic surfactant

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Abstract Cyclic voltammetric behavior of anthraquinone in aqueous medium has been studied in presence of a non-ionic surfactant, Triton X-100 (TX-100) using sodium salt of anthraquinone-2-sulphonic acid (AQS) as the electro-active species. When cathodic potential is applied, the anthraquinone (AQ) group of AQS is reduced to its dianion. In the reverse scan, the oxidation of AQ^{2-} gives AQ. The electrochemical behavior shows a profound influence from the dissolved state of TX-100 in aqueous media. Spectrophotometric results indicate interaction between AQ and TX-100. A CEC (chemical–electrochemical–chemical) mechanism with the electrochemical reaction coupled with preceding interaction of AQS with TX-100 and following protonation reaction of reduced AQ has been proposed.

1. Introduction

Electrochemical switching has been a fascinating domain of modern research. An electrochemically switchable species displays differing affinity with a second species based on its redox state. In such a system host, guest or both, may be redox-active. The most promising application of electrochemical switching to supramolecular chemistry is the use of redox-active amphiphilic compounds, or redox-active substances in amphiphilic compounds for redox switching. This provides the easiest means for controlling the molecular architecture of redox-active supramolecular systems.

Surface active agents form supramolecular assemblies as micelles and vesicles in aqueous solution. If surfactants are redox-active, supramolecular assemblies may be reversibly formed and disrupted, depending on the redox state. Research to-date has witnessed a surge of interest on the electrochemistry of such redox-active surfactants as well as redox-active substances in conventional surfactants. Early studies, which include both the micelles of electro-active and electro-inactive surfactants, have been reviewed by Rusling (1994). The electro-

chemical behavior has been found to be controllable by changing concentration of surfactants in the works of Saji and co-workers, where the electrochemical properties of redox-active surfactants containing different electro-active groups were extensively studied (Saji et al., 1985a,b, 1991, 1994; Hoshino and Saji, 1987a,b, 1997; Saji, 1988, 1989; Saji and Ishii, 1989). Kozlecky et al. have investigated the effect of changes in the molecular structure and the environment around the azobenzene-containing surfactants on their self-aggregation behavior in aqueous media by means of surface tensiometry and cyclic voltammetric techniques (Kozlecky et al., 1997). Takeoka et al. studied the electrochemical behavior of a non-ionic ferrocenyl amphiphile in aqueous solution (Takeoka et al., 1996) and applied the concept of formation of disruption of micelles for the electrochemical control of drug release from the redox-active micelles (Takeoka et al., 1995). Susan et al. worked extensively on the electrochemical behavior of series redox-active non-ionic surfactants containing an anthraquinone group and a phenothiazine group (Susan et al.,1999, 2000a,b, 2004). They have correlated electrochemical responses to the dissolved states of the surfactants in aqueous solution. Yeh and Kuwana have estimated the diffusion coefficient of the micelles of an electro-inactive surfactant, Tween 20, by solubilizing a probe molecule, ferrocene in micelles (Yeh and Kuwana, 1976).

Despite numerous studies on redox-active surfactants, the electrochemical behavior of a redox-active species in an electro-inactive surfactant in aqueous solution is scarce. The area of research needs to be further explored to exploit the mechanism of electrochemical reactions in such organized media. In this study, we used anthraquinone (AQ) as an electro-active group and studied the electrochemical behavior of a water soluble sodium salt of anthraquinone-2-sulphonic acid (AQS) in aqueous media in presence of a non-ionic surfactant, p-(1,1,3,3-tetramethylbutyl) polyoxyethylene, commercially known as Triton X-100 (TX-100). We aimed at investigating how the concentration of the surfactant in aqueous media brings about changes in electrochemical properties to correlate electrochemical behavior with the dissolved states of the surfactant.

2. Experimental

2.1. Materials

Triton X-100 (BDH), sodium salt of anthraquinone-2-sulphonic acid (AQS) (TCI, Tokyo, Japan) and sodium chloride (BDH) were used as received without further purifications. All the stock solutions were prepared with Puric-S grade deionized water ($R = 2.0$ MΩ cm, Organo Co., Tokyo).

2.2. Measurements

Spectrophotometric measurements were made with a double-beam Shimadzu UV–visible spectrophotometer (model UV-1650 PC). Rectangular quartz cells of path length 1 cm were used throughout the investigation.

A pH meter of model HM-26 S, TOA electronics Ltd., Japan was used for measurement of pH of the solutions. The solutions were bubbled with nitrogen to avoid any contribution in the measured pH from CO_2 dissolved from the atmosphere.

Cyclic voltammetric measurements were performed with a computer-controlled electrochemical analyzer (Model HQ

2040 by Advanced Analytics, USA). A glassy carbon electrode with a geometric area of 0.071 cm^2 (BAS) was used as a working electrode. The surface of the working electrode was polished with 0.05 μm alumina (Buehler) before each run. Prior to the electrochemical experiments, the surfactant solutions were purged with N_2 and inert atmosphere was kept during the course of the experiments. A platinum wire was used as a counter electrode. All potentials were reported vs. Ag/Ag$^+$ reference electrode. The measurements were carried out using 0.16 M NaCl aqueous solution as the supporting electrolyte. The potential sweep rate, (v), was between 10 and 500 mV s^{-1}. All the measurements were conducted at 25 °C. In every measurement, the concentration of AQS was kept constant at 0.2 mM.

3. Results and discussion

3.1. Aqueous electrochemistry of AQS

Cyclic voltammetric measurements were carried out for 0.2 M AQS at a glassy carbon electrode in aqueous media with 0.16 M NaCl as a supporting electrolyte in the range of −100 to 900 mV vs. Ag/AgCl. The pH of 0.2 M AQS in aqueous solution ion in the presence of the 0.16 M NaCl solution under such unbuffered condition was found to be 6.00. The voltammograms show one reduction peak and corresponding oxidation peak. The shape agrees with those reported in the literature (Hoshino and Saji, 1997; Susan et al., 1999, 2000a,b, 2004; Bailey and Ritchie, 1985). When cathodic potential is applied, AQ is reduced to its dianion, AQ^{2-}. In the reverse scan, the oxidation of AQ^{2-} gives AQ. The redox potential of AQ exhibits strong pH dependence (Hoshino and Saji, 1997; Susan et al., 2000b; Bailey and Ritchie, 1985; Revenga et al., 1994). Under unbuffered condition, the effective pH close to the electrode surface controls the potential of the electrode process. The changeover from the H$^+$-available to the H$^+$-depleted electrode process gives rise to a sudden jump in potential and the ionization for dihydroanthraquinone (AQH$_2$) to its dianion (AQ^{2-}) for a redox-active non-ionic surfactant, α-(anthraquinonyloxyhexyl)-ω-hydroxy-$oligo$(ethylene oxide) (ACPEG) could be observed at a pH of 4.14, above which only formation of only AQ^{2-} is apparent (Susan et al., 2000b). The electrode reaction of AQS in aqueous solution (pH 6.00) is, therefore, controlled merely by a two-electron-transfer process.

A satellite peak appeared at the cathodic side of the wave for the reduction of AQ of AQS (Fig. 1). Susan et al. (2000a) reported such a satellite peak to correspond to the formation of charge transfer complex for a redox-active anthaquinonyl surfactant, ACPEG under neutral condition, which disappear when the solution is made alkaline. In sharp contrast, the CV of AQS in alkaline solution also exhibited a similar satellite peak. This implies that the electro-active nature of the sulfonate group in AQS is responsible for the appearance of the satellite peak in the basic as well as in the neutral solution. The irreversible reduction of AQS is due to the reduction of the sulfonate group and influences the electrochemical behavior through an interaction between the carbonyl-oxygen of AQ moiety and the sulfonate group. The details of the reduction behavior will be reported elsewhere (Haque et al., submitted for publication).
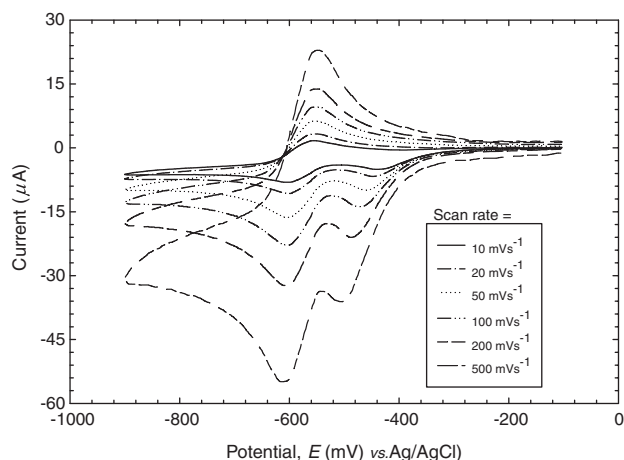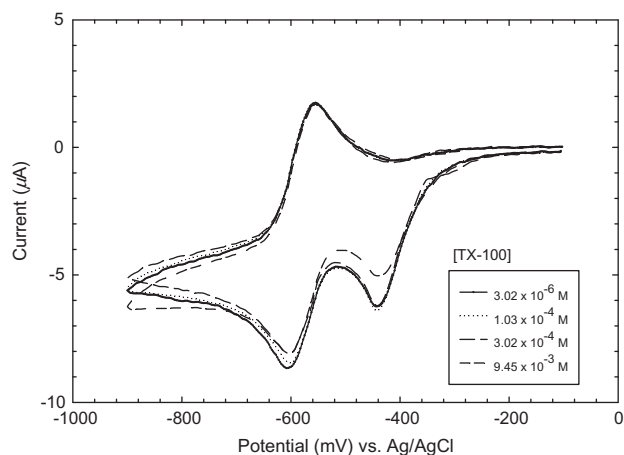
Figure 1 Cyclic voltammograms of 0.2 mM AQS aqueous solution (pH 6.00) at a glassy carbon electrode at different scan rates.

3.2. Electrochemistry of AQS in presence of TX-100 in aqueous solution

Cyclic voltammetric behavior of 0.2 mM AQS has been studied in aqueous solution of TX-100 with 0.16 M NaCl as the supporting electrolyte. The shapes of the CV's in aqueous solution are retained in the presence of TX-100 (Fig. 2). The cyclic voltammograms in TX-100 also give a reduction peak due to the reduction of AQ and the corresponding oxidation peak. The separation of peak potentials is less than 50 mV (Table 1) which indicates that the system is almost reversible. The cathodic peak potential shifts to more negative values with increase in scan rate (Fig. 3) which indicates a slow electron-transfer process (Hoshino and Saji, 1997) and the system might be considered as a quasi-reversible one (Nicholson and Shain, 1964).

Electrochemical study in aqueous solution was made with a wide range of surfactant concentrations in the range of 0.0032–9.5 mM. It is worth noting that the addition of TX-100 did not change the pH of aqueous solution of AQS and pH value of

Figure 2 Cyclic voltammograms of 0.2 mM AQS at a glassy carbon electrode in presence of varying TX-100 concentrations at the scan rate of 10 mV s^{-1}.

Table 1 The redox potential (vs. Ag/AgCl) ($v = 10$ mV s^{-1}) and separation of peak potential (ΔE_p) and slope of the plot of log i_{pc} vs. log v of 2×10^{-4} M AQS in 0.16 M NaCl aqueous solution (pH 6.00).

[TX-100] (M)	$E_{1/2}$ (mV vs. Ag/AgCl)	ΔE_p (mV vs. Ag/AgCl)	Slope of plot of log i_{pc} vs. log v
3.02×10^{-6}	491	55	0.51
3.02×10^{-4}	500	47	0.50
1.51×10^{-3}	501	48	0.57
3.78×10^{-3}	508	40	0.56
9.45×10^{-3}	494	52	0.48
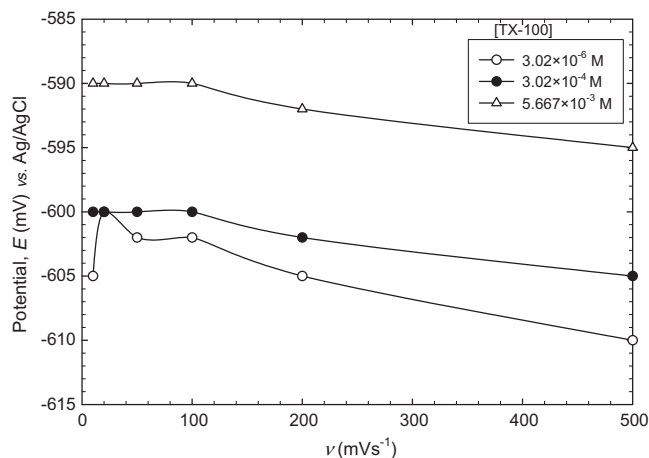
Figure 3 Cathodic peak potential as a function of scan rate for 0.2 mM AQS at a glassy carbon electrode with different TX-100 concentrations.

ca. 6.00 could be noted for all cases. The peak potentials (Table 1) and peak currents, obtained from the voltammograms vary with change in surfactant concentration. It is apparent from Fig. 4 that the reduction potential increases with increasing concentration of the surfactant. When the concentration of TX-100 reaches at ca. 4 mM, the reduction potential decreases with further increase in [TX-100] to give more negative values. The reduction potential is expected to decrease when micellization commences (ca. 4 mM in Fig. 4) and consequently diffusivity lowers (vide infra). The reported CMC value of TX-100 in aqueous solution is 8.75×10^{-4} M in aqueous solution at 25.0 °C (Datta et al., 1988), which is likely to further lower in presence of a supporting electrolyte (0.16 M NaCl solution) and a redox-active species (AQS) (Kabir and Susan, 2008). However, the electrochemical behavior indicates a relatively larger value of CMC under the identical experimental condition. In fact, this is not surprising. The CMC measured by surface tension measurements by using a Wilhelmey plate method reflects the adsorption saturation at the air/water interface, whereas the electrochemical reaction occurs at the solid/water interface. The difference in the two concentrations indicates that TX-100 adsorbs more strongly at the solid/water interface than at the air/water interface (Takeoka et al., 1996; Susan et al., 2000a).
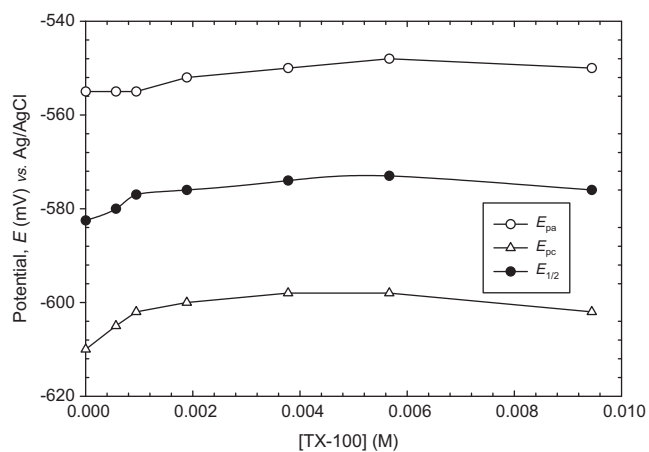
The plot of logarithm of cathodic peak current vs. logarithm of scan rate gives a straight line. This allows us to
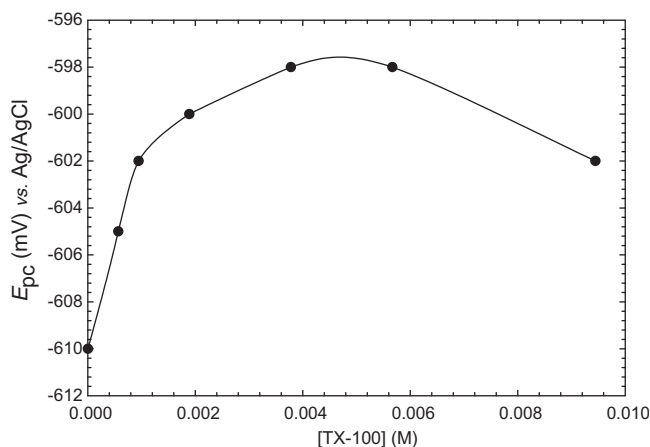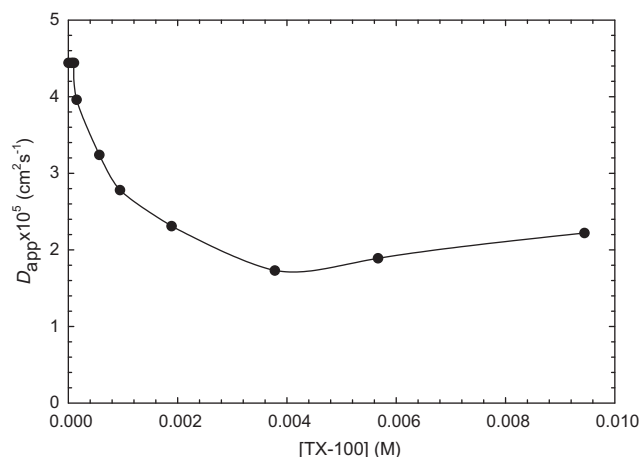
Figure 4 Cathodic peak potential vs. concentration of TX-100 for 0.2 mM AQS in 0.16 M NaCl aqueous solution.

Figure 6 Dependence of the apparent diffusion coefficient on the concentration of TX-100.

diagnose the electrochemical process in aqueous media. The theoretical slope for a diffusion-controlled voltammogram is 0.5 and for ideal adsorption it is 1 (Susan et al., 2000b; Bard and Faulkner, 2001). In the concentration range of TX-100 the value of slope, a (Table 1), is close to 0.5 for reduction of AQ in aqueous solution with surfactant concentration and the process therefore has been found to be a diffusion-controlled one.

The voltammetric peak potentials (E_{pa}, $E_{1/2}$, E_{pc}) plotted against the concentration of TX-100 at the scan rate of 10 mV s^{-1} are revealed in Fig. 5. At concentrations lower than the CMC, the peak potentials are almost constant. The half wave potential ($E_{1/2}$) increases with increasing concentration but when the concentration reaches to ca. 4 mM, the potential ($E_{1/2}$) is found to decrease with further addition of the surfactant. Addition of surfactant up to a concentration of ca. 4 mM causes shift in potential to less negative values. This may be explained in terms of solubilization or interaction of AQS with the surfactant (vide supra). At low TX-100 concentrations, AQS can move freely to the electrode surface to reduce AQ to AQ^{2-} upon application of the reduction potential. When

the concentration of TX-100 reaches ca. 4 mM, all the AQS species are likely to be trapped inside the hydrophobic core of the micelle. The hydrophobic interaction may cause such solubilized AQS species to be less diffusive and potential, thereby, shifts to more negative values.

The apparent diffusion coefficients (D_{app}) of AQS in TX-100 solutions have been estimated using *Randles Sevcick* equation (Bard and Faulkner, 2001) from the plot of i_{pc} vs. $v^{1/2}$. The diffusion coefficient decreases with increasing surfactant concentration, passes through a minimum and then increases (Fig. 6). The decrease in D_{app} above CMC is not surprising. As the micelles are formed, AQS is solubilized inside the core of micelles and diffusion of AQS to the electrode interface lowers. Below CMC, the diffusion coefficient increases with decreasing surfactant concentration and should attain the diffusivity of AQS in the absence of TX-100. The diffusivity increases after reaching a minimum with increasing TX-100 concentration. This may be attributed to an increase in the number of micellar aggregates, which lowers the density of AQS in the micellar pseudophase. The distance between the electrode surface and AQS inside the core of micelle is too long to undergo the electron-transfer reaction. It is, therefore, reasonable to consider that the electrochemical reaction occurs in the monomeric form. Prior to reduction, the micelles are diffused to the electrode surface, which is followed by the dynamic equilibrium of the formation-disruption of micelles.

The i_{pa}/i_{pc} decreases with increase in scan rate (Fig. 7) to coincide with the behavior of a reversible electrochemical reaction coupled with a preceding chemical reaction (Takeoka et al., 1996; Susan et al., 2000a; Nicholson and Shain, 1964). It should be mentioned here that unlike redox-active surfactants, the preceding chemical reaction is not the disruption of micelles into monomers (Hoshino and Saji, 1997; Takeoka et al., 1996; Susan et al., 2000a). Interestingly, even at low concentrations of TX-100 (where micellization does not occur), the value of i_{pa}/i_{pc} decreases with increasing scan rate. The preceding chemical reaction may therefore, be considered as the strong hydrophobic interaction of AQS in the core of micelle or interaction of AQS with monomeric surfactant. This is supported by spectrophotometric results. In aqueous solution UV spectrum of AQS shows two peaks at 256 and 330 nm. As the

Figure 5 Cathodic, anodic and half wave potentials (vs. Ag/AgCl) plotted against surfactant concentration for 0.2 mM AQS in 0.16 M NaCl aqueous solution.
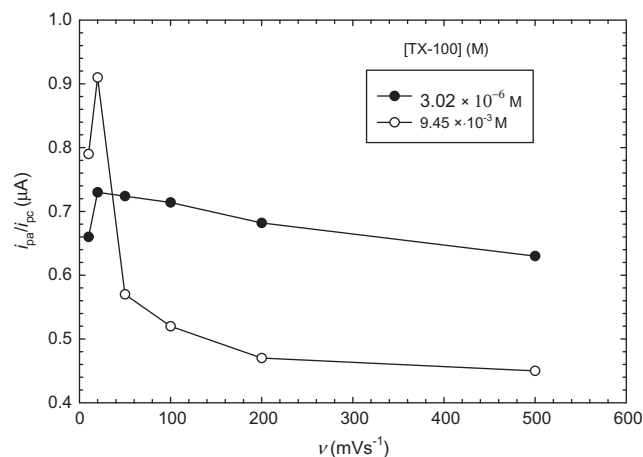
Figure 7 Ratio of anodic peak and cathodic peak current vs. scan rate for different TX-100 concentration for 0.2 mM AQS in 0.16 M NaCl aqueous solution.

TX-100 is added to aqueous solution of AQS, absorbance at 256 nm is noticeably changed. As apparent from Fig. 8, the absorbance decreases up to a concentration of ca. 4 mM (below CMC), but further addition of the surfactant results in a sharp fall in absorbance.

The ratio of i_{pa}/i_{pc} is smaller than 1, which indicates that the electrochemical reaction is also complicated by some other processes like a following chemical reaction (Nicholson and Shain, 1964). At lower scan rate the ratio has been found to increase with increasing scan rates to support this consideration. Upon reduction, the AQ is changed to its dianion, AQ^{2-}, which is very sensitive to H^+ ion concentration in the solution. AQ^{2-} can undergo two-step protonation to yield AQH^- and AQH_2 in resemblance to an electrochemical behavior of ACPEG (Susan et al., 2000a; Bailey and Ritchie, 1985; Revenga et al., 1994). The following chemical reaction accompanying the electrochemical reaction is the protonation reaction of AQ^{2-}. Although the effective pH at the electrode interface under such an unbuffered condition controls the overall electrode process, the influence of the following protonation on the mechanism of the electrochemical reaction at a
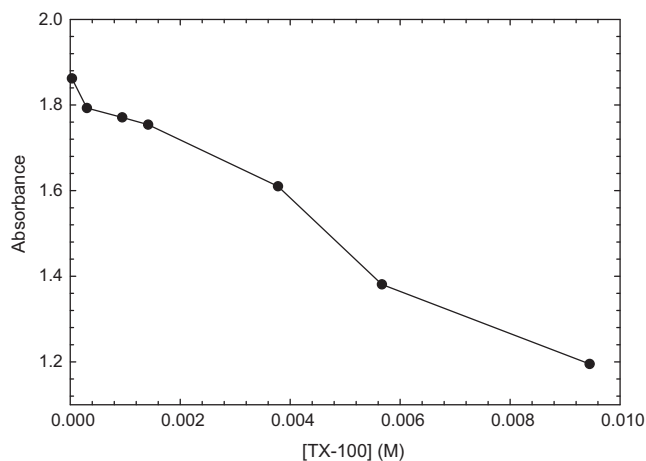
pH of ca. 6.00 is apparent. A CEC mechanism with the electrochemical reaction coupled with preceding interaction of AQS with the surfactant or the micelle (CE) and the following protonation reaction of the reduced state of AQ (EC) could be visualized.

4. Conclusions

Cyclic voltammetric behavior of AQS is fairly dependent on the concentration TX-100 in aqueous medium. The electrochemical responses at concentrations below and above CMC of TX-100 are distinctly different. The electrochemical results indicate a strong interaction between AQS and TX-100, below and above the CMC value. The apparent diffusion coefficient of the micellar solution changes continuously with TX-100 concentration. Below the CMC, apparent diffusion coefficient approaches the monomeric diffusion coefficient while with increasing concentration it approaches the micellar one. A CEC mechanism with the electrochemical reaction coupled with preceding interaction of AQS with the surfactant or the micelle (CE) and the following protonation reaction of the reduced state of AQ (EC) could be visualized.

The electrochemical behavior of AQS in presence of TX-100 in aqueous solution established anthraquinone as a fascinating electro-active group. Electrochemical reactions can be effectively used to reversibly control the state of these anthraquinone and may lead to the understanding of biological processes and to the development of new materials. The present study thus opens up a new window of opportunity to design an electrochemically switchable molecular device. There is considerable scope for the development of supramolecular structures and their dynamics on electrode surfaces for further progress in this direction.

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Figure 8 Absorbance at 256 nm of 0.2 mM AQS vs. TX-100 concentration.

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