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Voltammetric analysis of hydroquinone, ascorbic acid, nitrobenzene and benzyl chloride in aqueous, non-aqueous, micellar and microemulsion media

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Abstract Voltammetric behaviour of hydroquinone, ascorbic acid, nitrobenzene and benzyl chloride in aqueous, micellar, microemulsion and aprotic media on glassy carbon electrode under identical experimental conditions was compared. A general trend of decreasing peak currents in the order $i_{p(\text{micelle})} > i_{p(\text{aqueous})} > i_{p(\text{DMF})} > i_{p(\mu\text{E})}$ was noticed. The only exception was hydroquinone, which exhibited a slightly lower current in micellar medium. The peak potentials for each of these compounds varied in the order $E_{P(\text{DMF})} > E_{P(\mu\text{E})} > E_{P(\text{aqueous})} > E_{P(\text{micelle})}$ with due consideration for the two oxidation and reduction processes (negative E_P values for reduction). In micellar systems, which contain a

predominantly aqueous phase where the cationic surfactant exhibits a catalytic effect, lower peak potentials and higher current are obtained. The peak potential and peak current is lower in microemulsion when compared to aprotic medium. The causes for such systematic variations and their analytical implications are discussed.

Keywords Organic compounds · Aqueous · DMF · Micelles · Microemulsion · Cyclic voltammetry

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Introduction

The requirement of green chemistry in eliminating or at least minimizing the toxic aprotic solvents has generated substantial interest in micelles and microemulsions (μEs). In electrochemistry itself, some significant contributions have been made towards the utilization of micelles and microemulsions in electroanalysis, electrosynthesis and electrochemical detoxification [1–5]. Protic and aprotic media have so far been commonly used for the analysis of water-soluble and water-insoluble organic compounds, respectively. The behaviour of organic compounds in homogeneous media (aqueous and non-aqueous) is different from heterogeneous media (micellar and μE). However, a quantitative comparison of voltammetric data

of organic compounds in all four media, namely, micelles, microemulsions, aqueous and non-aqueous solvents, has not been reported in the literature. Such a quantitative comparison is the objective of the present work.

Four compounds, namely, hydroquinone, ascorbic acid, nitrobenzene and benzyl chloride, were selected for comparative evaluation in all four media. The oxidation of hydroquinone, ascorbic acid and reduction of nitrobenzene and benzyl chloride were selected. Another criteria for selection of these compounds are the significant variation in solubility of the compounds in the four media. Ascorbic acid and hydroquinone are highly soluble in aqueous systems. The solubility of nitrobenzene and benzyl chloride is significant only in μEs and non-aqueous solvents. Among the compounds chosen, hydroquinone and nitro-

benzene exhibit quasi-reversible charge transfer, ascorbic acid exhibits irreversible oxidation, and benzyl chloride exhibits irreversible reduction.

The compounds selected for the present investigation has already been investigated in one or two media. Hydroquinone generally exhibits a quasi-reversible two-electron redox behaviour [6]. Similar two electron oxidations are noticed on gold [7, 8], boron-doped diamond (BDD) [8] and other electrodes. Recently, electrochemical oxidation of hydroquinone has been investigated on polyaniline films [9] and self-assembled monolayers [10].

Ascorbic acid has received considerable attention in recent times due to its antioxidant activity. A variety of modified surfaces, including metal oxides [11], polymer [12] and clay-modified glassy carbon electrodes, have been investigated [13]. This compound has also been investigated in anionic, cationic and nonionic micellar media [14–16].

Electroreduction of aromatic nitro compounds has been compared in aqueous and non-aqueous media [17], and also in anionic, cationic and nonionic micellar systems [18, 19]. Effect of surface orientation of single crystal gold electrode [20] and clay-modified glassy carbon electrodes [21] have also been reported. The mass transfer effect of ultrasound on this process has also been studied [22].

The electrochemical reduction of benzyl chloride is inherently more difficult when compared to benzyl bromide [23]. Electrogeneration of benzyl radicals from benzyl bromide in μ E systems has been extensively investigated [24]. Electroreduction of benzyl chloride has also been achieved on Ni-tetrafluoroethyleneoligomer (TFEO) electrode [25]. Electrochemical [26] and photoelectrochemical [27] generation of benzyl radical from benzyl chloride and its reactivity has also been reported.

Voltammetric oxidation and reduction of these four organic compounds in all the four media mentioned above on glassy carbon electrode under identical experimental conditions are compared in this work. McIlvaine buffer (pH 7.0) served as aqueous media. Dimethyl formamide (DMF) containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) and tetrabutyl ammonium iodide (TBAI) was used as the aprotic media for oxidation and reduction, respectively. A solution containing 100 mM cetyl trimethyl ammonium bromide (CTAB) prepared in McIlvaine buffer (pH 7.0) served as the micellar medium. A bicontinuous μ E containing CTAB, *n*-hexane, *n*-butanol and water in the composition 17.5, 12.5, 35, and 35%, respectively, was used, which has already been reported in the literature [28]. These voltammetric investigations indeed provide some common features and general trends as discussed below.

Experimental

Chemicals and solutions

The chemicals used in this work were of high purity obtained from standard manufacturers. CTAB (Aldrich), benzyl chloride (Ranbaxy), nitrobenzene (Ranbaxy), ascorbic acid (SD fine chem), hydroquinone (Merck), dimethyl formamide (Merck), TBAP (SRL), TBAI (SRL), *n*-butanol (Qualigens) and *n*-hexane (Ranbaxy) were used.

McIlvaine buffer (pH 7.0) was used as an aqueous medium. Stock solutions of ascorbic acid and hydroquinone were prepared in buffer. Nitrobenzene is sparingly soluble in this buffer; the stock solution was prepared in 50% methanolic solution.

Cetyl trimethyl ammonium bromide micellar solution was prepared by dissolving the surfactant in buffer solution under vigorous stirring for 2 days. The concentration of micellar solution was 100 mM, and it is well above the critical micelle concentration (CMC) value reported (9.6×10^{-4} M) [15].

The bicontinuous μ E was prepared by mixing CTAB, *n*-hexane, *n*-butanol and water in the composition 17.5, 12.5, 35, and 35%, respectively, and stirred until clear as per the procedure outlined earlier [28].

Apparatus

A Wenking LB75L potentiostat coupled with a Wenking VSG72 voltage scan generator was used for cyclic voltammetry. A Rikadenki 101T XY/T recorder was used to record the voltammograms. An H-type glass cell was used for voltammetric studies. The working electrode was a glassy carbon disc of 5-mm diameter obtained from Tokai GC-A. A platinum foil was used as a counter electrode. A saturated calomel electrode (SCE) was used as reference electrode. All other experimental details were given elsewhere [29].

Results

Voltammetric behaviour of hydroquinone

The cyclic voltammograms of hydroquinone in aqueous media recorded at different sweep rates shows well-defined quasi-reversible redox response. The peak separation value ($\Delta E_p = E_{pa} - E_{pc}$) was found to increase significantly with increase in sweep rate.

Quite similar voltammetric responses were obtained for hydroquinone in the other three media as well. However, the peak potential and peak current values were found to be significantly different. The cyclic voltammograms for 2 mM hydroquinone in the aqueous, micellar, μ E and

aprotic media at a constant sweep rate of 40 mV/s are shown in Fig. 1a,b. The anodic peak potentials are found to differ by as much as 490 mV between aqueous and aprotic media. The peak potentials of hydroquinone increases in the order $E_{P(\text{micelle})} > E_{P(\text{aqueous})} > E_{P(\mu\text{E})} > E_{P(\text{DMF})}$. The anodic peak potentials in all the media tend to move in the more positive direction with increasing concentration (Fig. 2). Quantitatively, the anodic peak current values

obtained for different concentrations of hydroquinone in all four media are compared in Fig 3. At constant sweep rate, anodic peak current increases linearly with concentration and decreases in the order $i_{p(\text{aqueous})} > i_{p(\text{DMF})} > i_{p(\text{micellar})} > i_{p(\mu\text{E})}$. However, for each concentration of hydroquinone, the anodic peak current was found to increase linearly with the square root of sweep rate. Hence, the diffusion-limited

Fig. 1 **a** Cyclic voltammograms for the oxidation of 2 mM (40 mV/s) hydroquinone on GCE aqueous (a) and CTAB micelles (b). **b** Cyclic voltammograms for the oxidation of 2 mM (40 mV/s) hydroquinone on GCE CTAB microemulsion (c) and DMF (d)

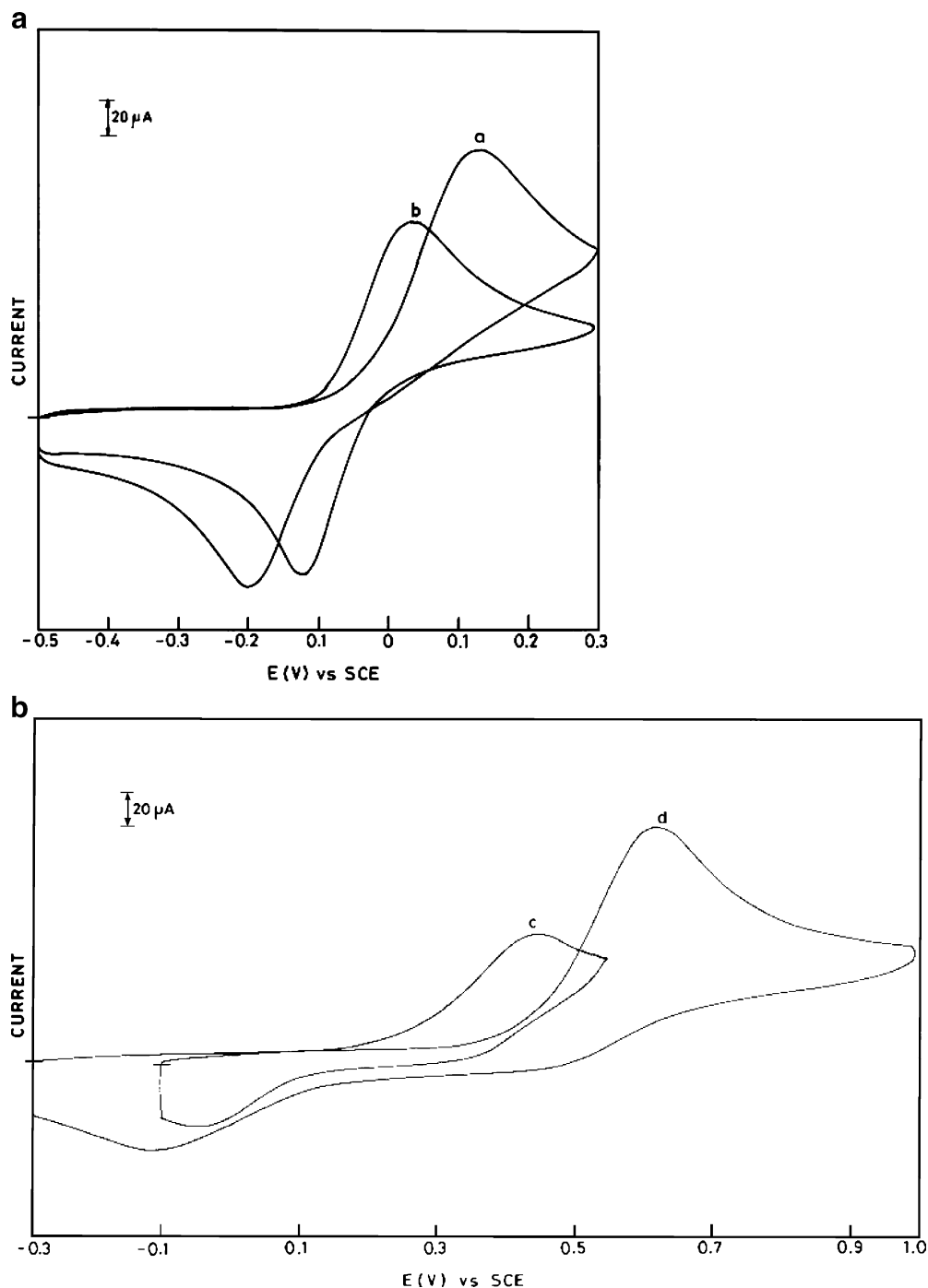
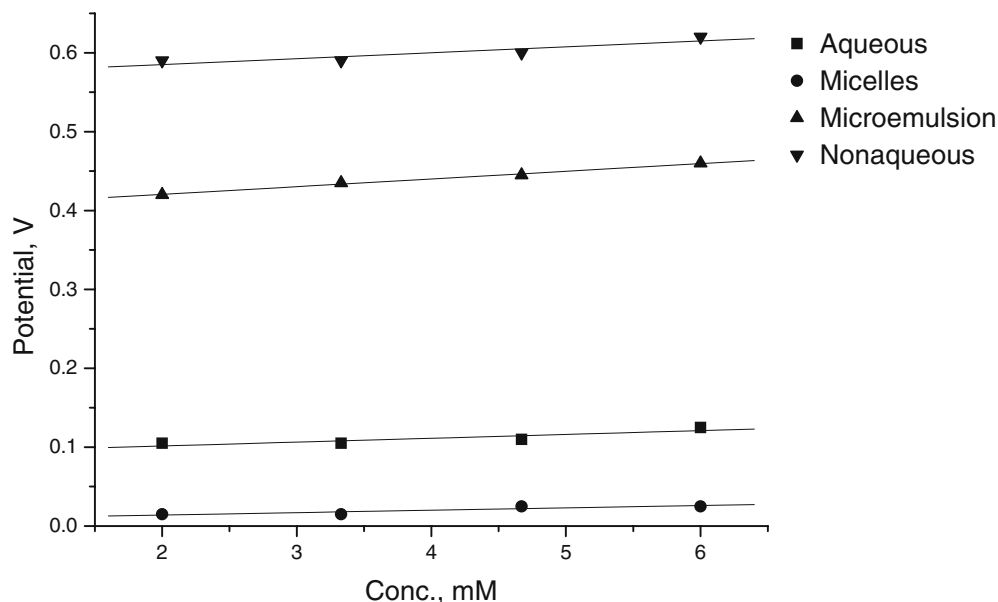


Fig. 2 Effect of concentration on peak potential for the oxidation of hydroquinone at 10 mV/s



currents for hydroquinone are indeed found to be significantly different in different media investigated.

The peak separation values also tend to increase slightly with an increase in concentration of hydroquinone (Fig. 4). However, the general trend of peak separation values among the four media does not change with reactant concentration. ΔE_p values decrease in the order $\Delta E_{P(DMF)} > \Delta E_{P(\mu E)} > \Delta E_{P(aqueous)} > \Delta E_{P(micelle)}$.

Voltammetric behaviour of ascorbic acid

The cyclic voltammograms of ascorbic acid in all four media shows a well-defined irreversible peak (Fig. 5). The anodic peak current increases with increasing concentration and square root of sweep rate. However, the peaks were much broader in μE . Quantitatively, the anodic peak current values obtained at different concentrations in all the media at the sweep rate of 20 mV/s are compared in Fig. 6. The peak current values decreases in the order $i_{p(micelle)} > i_{p(aqueous)} > i_{p(DMF)} > i_{p(\mu E)}$. The peak potential values

Fig. 3 Effect of concentration on peak current for the oxidation of hydroquinone at 10 mV/s

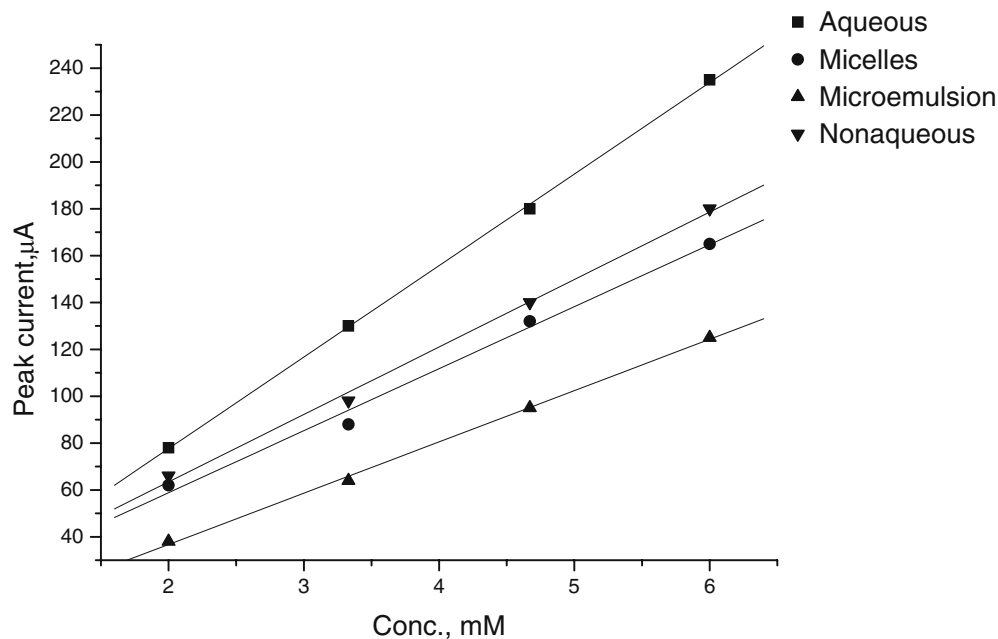
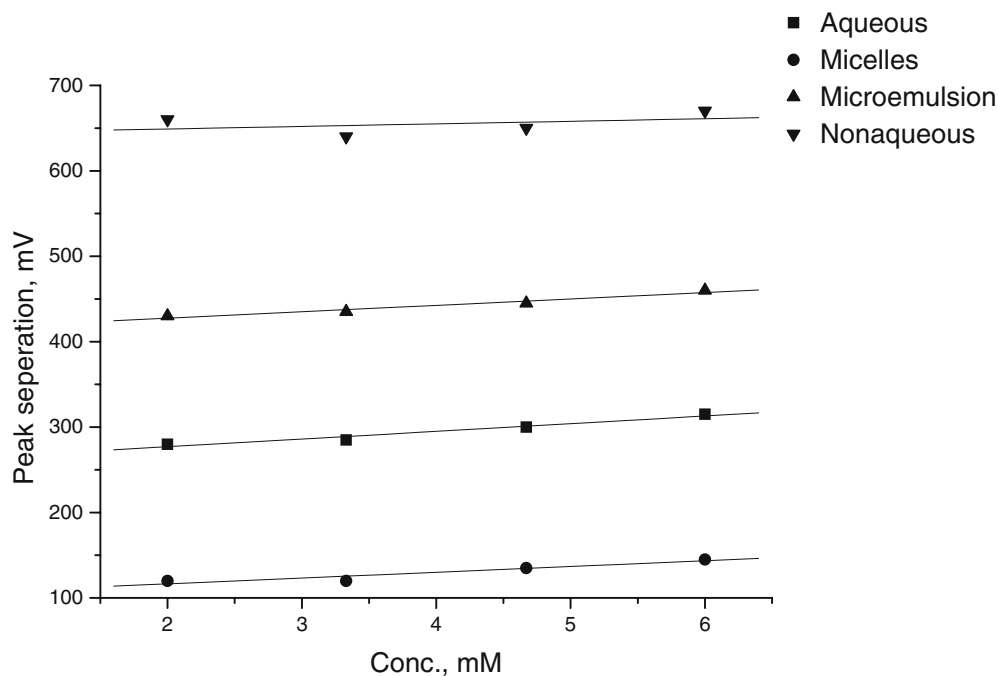


Fig. 4 Effect of concentration on peak separation for the oxidation of hydroquinone at 10 mV/s



also shift in the more positive direction with increasing sweep rate and concentration. However, the general trend of anodic potential, $E_{P(DMF)} > E_{P(\mu E)} > E_{P(aqueous)} > E_{P(micelle)}$, is maintaining in the whole concentration 2–7 mM and also in the sweep rate 10–640 mV/s range. Typical data at a constant sweep rate of 20 mV/s are compared in Fig. 7. The peak potential in the cationic micellar medium is indeed lesser than that of aqueous medium. This is obviously due to the catalytic effect of cationic surfactant adsorbed on the electrode surface. Similar results and explanations have already been reported [15].

The μE also contains the same cationic surfactant (CTAB). It appears that the CTA^+ species is highly dispersed in the microheterogeneous aqueous–non-aqueous interface; hence this cationic species is not available at the electrode–electrolyte interface for exhibiting the stabilizing effect similar to micellar medium (Figs. 9a,b).

The first cathodic peak current value obtained for nitrobenzene in all four media at different concentrations is presented in Fig. 10. The cathodic peak currents increase linearly with increasing concentration. The peak current values decrease once again in the order $i_{p(micelle)} > i_{p(aqueous)} > i_{p(DMF)} > i_{p(\mu E)}$.

Voltammetric behaviour of nitrobenzene

The cyclic voltammograms of nitrobenzene in all four media are presented in (Figs. 8 and 9). Two cathodic peaks at –1.25 and –1.85 V, corresponding to the formation of nitrobenzene anion radical (one electron reduction) and phenyl hydroxyl amine (three further electron reductions), are observed in DMF (Fig. 8). Similarly, in μE two cathodic peaks at –0.92 and –1.09 V are noticed (Fig. 9).

A single peak around –0.86 V is observed in aqueous medium, and also, a single cathodic peak around –0.8 V is noticed in the micellar solution. Because aqueous and micellar media contain significantly higher concentration of water molecules in the interface, further reduction of nitrobenzene anion radical generated in the first peak region also occurs at the same potential, giving rise to an overall four-electron reduction process.

Voltammetric behaviour of benzyl chloride

Benzyl chloride is practically insoluble in the aqueous medium even in the presence of 50–75% methanol. In micelles and μE , no solubility problem for benzyl chloride was encountered. The cyclic voltammograms for benzyl chloride in micellar medium at different sweep rates show a small prewave followed by a distinct cathodic peak at –1.1 V, whereas at higher concentrations, the cathodic peaks become much broader. Quantification of peak current and potential also becomes more difficult. It appears that significant blocking-type adsorption of benzyl chloride occurs on electrode surfaces, thus complicating voltammetric response.

The voltammetric behaviour of benzyl chloride in μE and in aprotic media is much more well defined and reproducible (Fig. 11). The cathodic reduction peak occurs

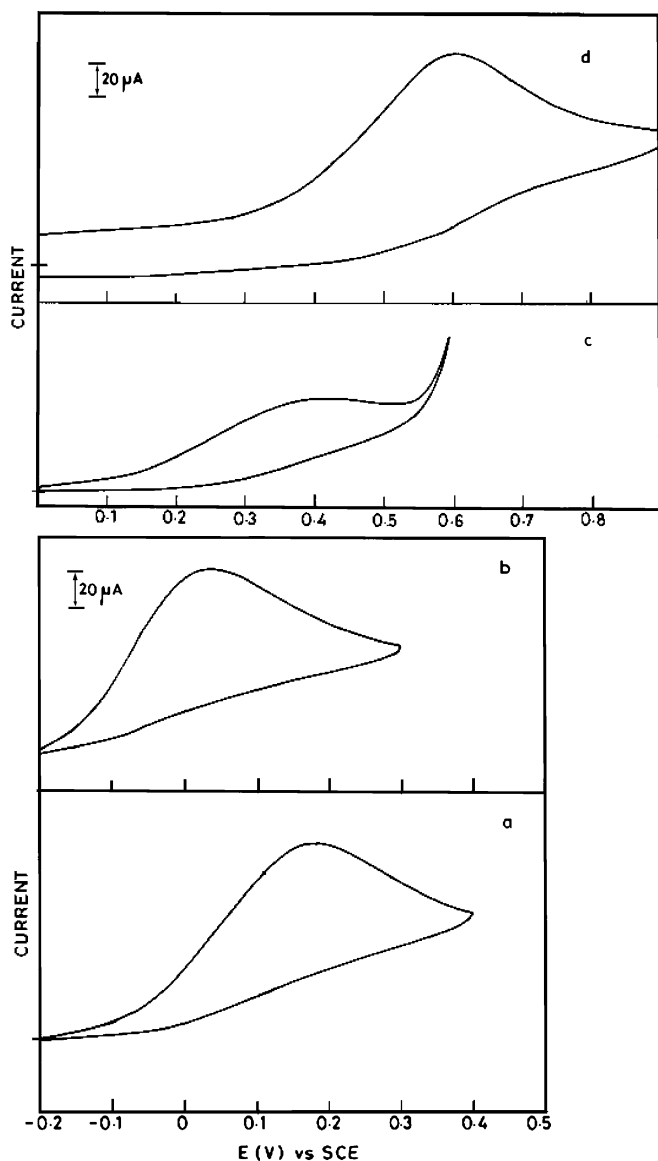


Fig. 5 Cyclic voltammograms for the oxidation of 2 mM ascorbic acid at 40 mV/s on GCE aqueous (a), CTAB micelles (b), CTAB microemulsion (c), and DMF (d)

at around -1.9 V in μ E when compared with -2.3 V in aprotic media. The peak currents in both cases tend to increase linearly with concentration and square root of sweep rate.

Discussion

Medium effect on electrode processes and peak potentials

The above results indicate that the behaviour of organic compounds is different in homogeneous and heterogeneous media. It is generally known that non-aqueous systems

have much wider potential range, with more positive anodic limits and more negative cathodic limits, when compared with aqueous medium. Micelles and μ Es contain increasingly higher non-aqueous phase when compared with water. Hence, their anodic and cathodic limits also lie in between aqueous and aprotic media. The anodic limits are also sensitive to the anion used (e.g., lower anodic limit for bromide when compared with chloride). Typical anodic and cathodic limit values at a constant current density of $101.83 \mu\text{A}/\text{cm}^2$ on all four media are summarized in Table 1.

The oxidation and reduction potentials of organic compounds in aprotic solvents are much higher than those in water. The peak potential in μ Es generally falls in between these two limiting values. The oxidation and reduction potentials of hydroquinone (Fig. 1a,b), ascorbic acid (Fig. 5), first reduction peak of nitrobenzene (Figs. 8 and 9) and benzyl chloride (Fig. 11) clearly establish this trend.

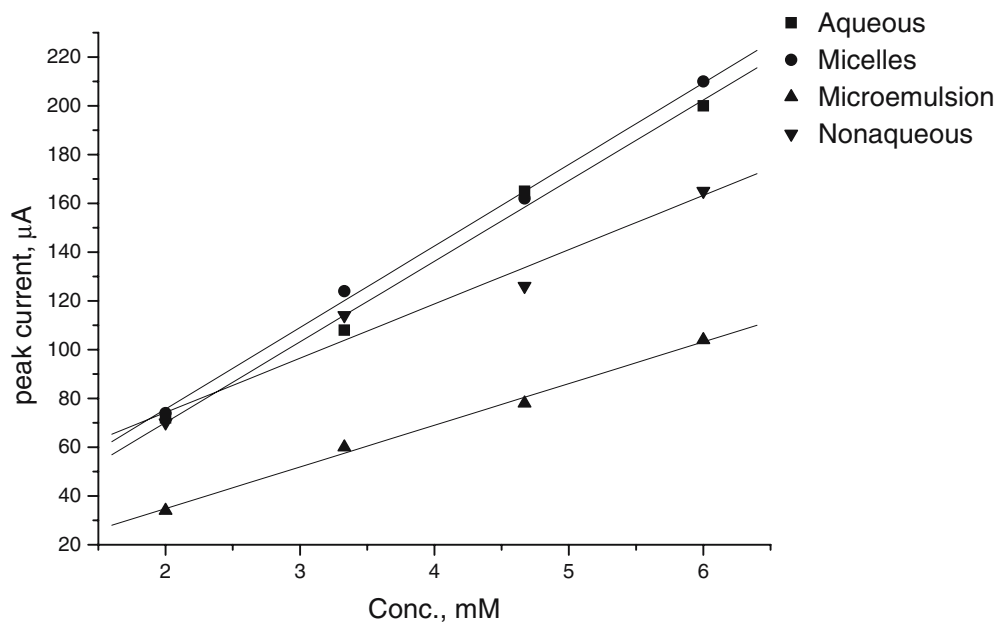
It appears that the electro-oxidation and reduction of organic compounds generally require higher potentials and, thus, higher energy with increasing content of organic phase in the solvent supporting electrolyte system.

The micellar systems are predominantly aqueous systems containing very small regions of micellar phase. The oxidation and reduction potentials are indeed lower in micellar systems when compared with aqueous systems (Figs. 2 and 7). This may be due to the catalytic influence of the surfactant at the electrode surface.

The peak potential for an irreversible process may be influenced by charge transfer kinetics and other factors such as change in the formal electrode potential due to change in media, the associated preceding or following chemical reaction, and blocking and non-blocking adsorption effects [30]. Hence, the change in the oxidation potential or reduction potential with medium cannot be directly linked to the kinetics of electron transfer. In the case of quasi-reversible processes, however, the ΔE_p values may be taken as a measure of electron transfer rate. Higher ΔE_p values indicate lower charge transfer kinetics. As one can infer from Fig. 4, the ΔE_p values in non-aqueous medium are very high, indicating slower electron transfer kinetics. A slightly better charge transfer rate is observed in μ E. The ΔE_p values in aqueous solutions are higher than in micellar media. The ΔE_p values in micellar systems are always lower, suggesting the catalytic interfacial effect of the cationic surfactant.

The catalytic influence of surfactant is generally noticed in micellar systems alone. The E_{pa} of ascorbic acid and hydroquinone shifts in the positive direction in micellar medium when compared with aqueous medium. The E_{pc} of nitrobenzene is shifted to less negative potential in micellar medium when compared with aqueous medium (Figs. 8 and 9). However, for all the three compounds, although the same cationic surfactant is present in the μ E as well, no such catalytic effect is noticed. The electrode surface in μ E

Fig. 6 Effect of concentration on peak current for the oxidation of ascorbic acid at 20 mV/s



thus exhibits a more hydrophobic environment similar to aprotic media.

Medium effects on mass transport and peak currents

Cyclic voltammetric peak current values generally depend on the rate of diffusion of reactive species. In special cases, it may also depend on associated chemical reactions and

weak or strong adsorption [30]. In the present study, the anodic and cathodic peak currents of all the four compounds investigated generally increased with increasing concentration and square root of sweep rate, suggesting that diffusion-like processes generally control the peak current values.

Quantitatively, anodic and cathodic peak currents decrease in the order $i_{p(\text{micelle})} > i_{p(\text{aqueous})} > i_{p(\text{DMF})} > i_{p(\mu\text{E})}$.

Fig. 7 Effect of concentration on peak potential for the oxidation of ascorbic acid at 20 mV/s

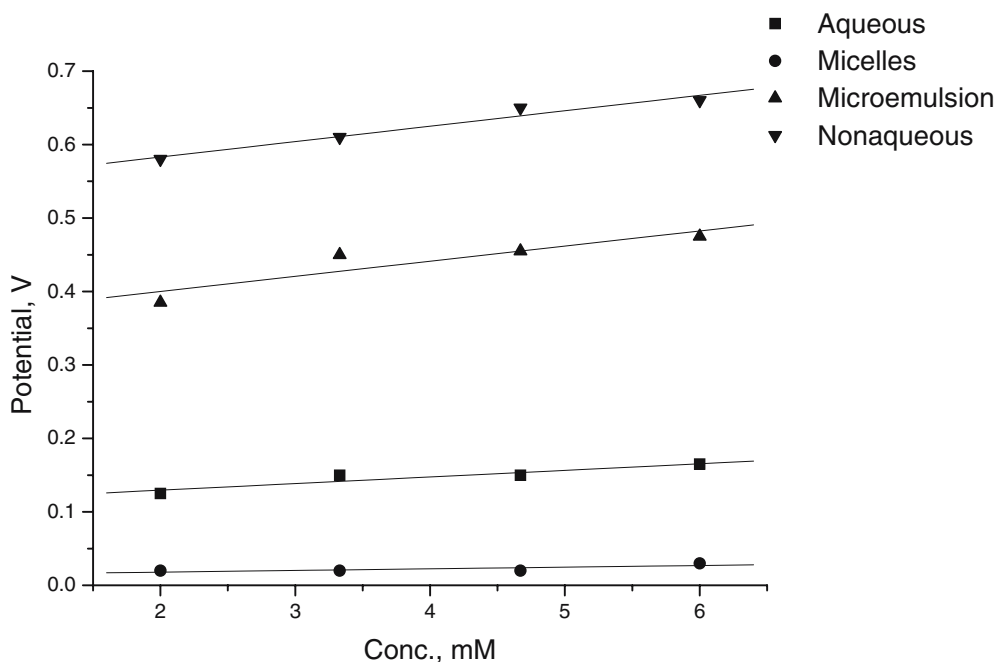


Fig. 8 Cyclic voltammograms for the reduction of 3.9 mM nitrobenzene at 40 mV/s on GCE aqueous (a) and DMF (b)

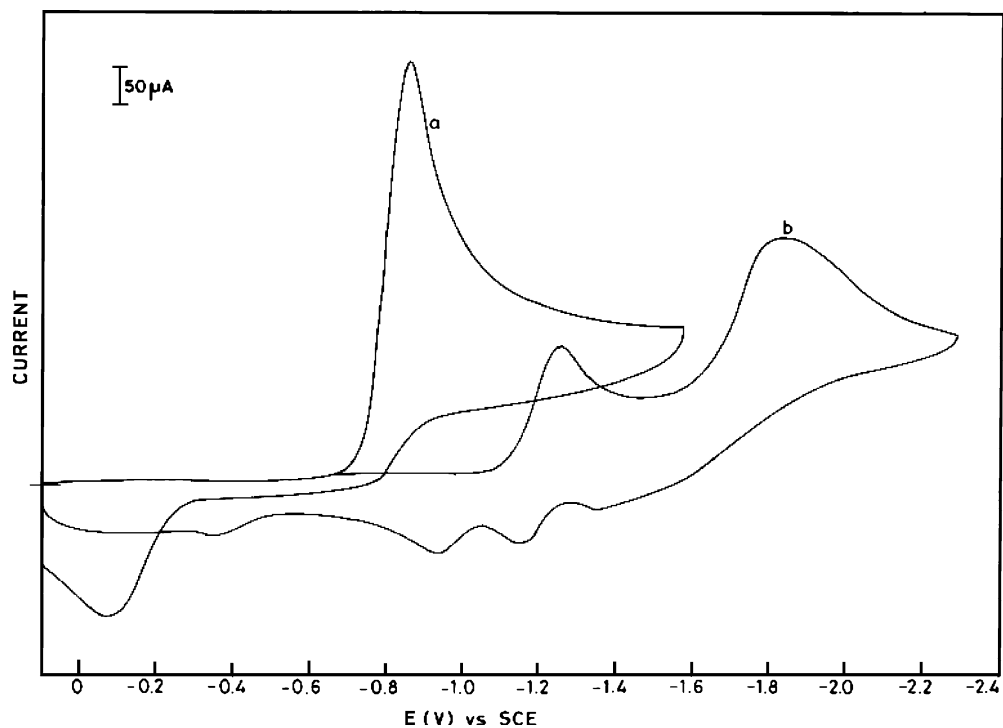


Fig. 9 Cyclic voltammograms for the reduction of 3.9 mM nitrobenzene at 40 mV/s on GCE CTAB micelles (a) and CTAB microemulsion (b)

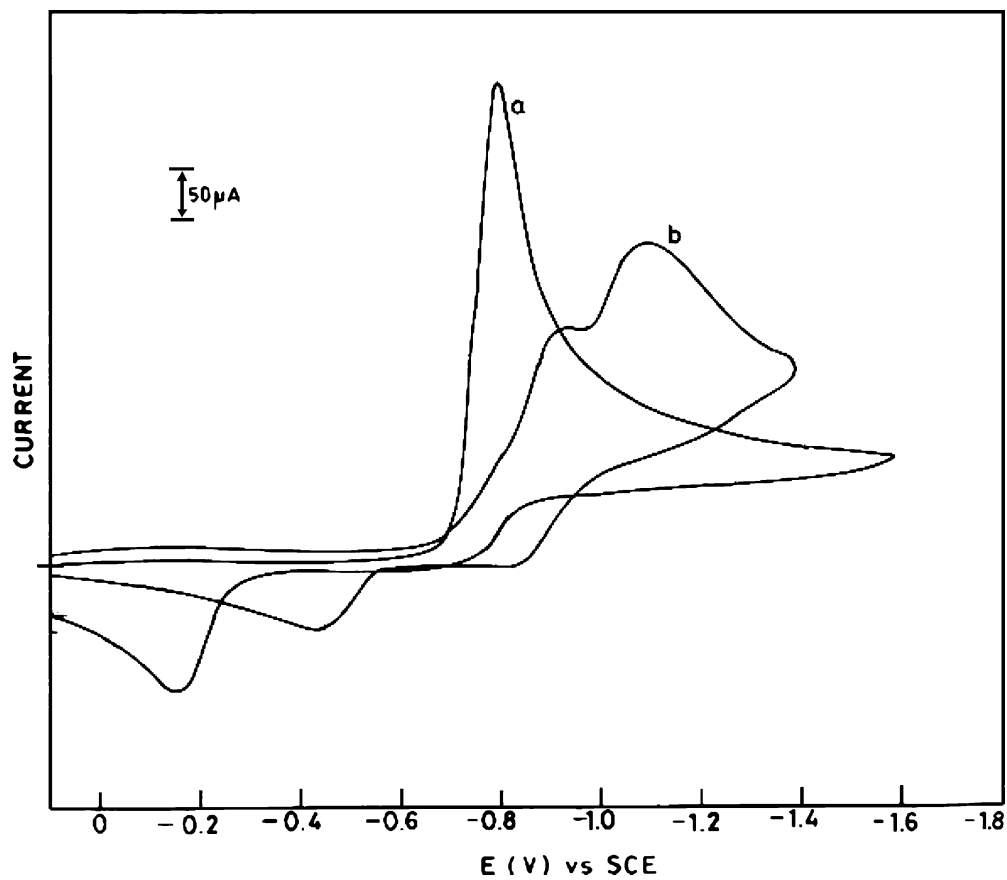
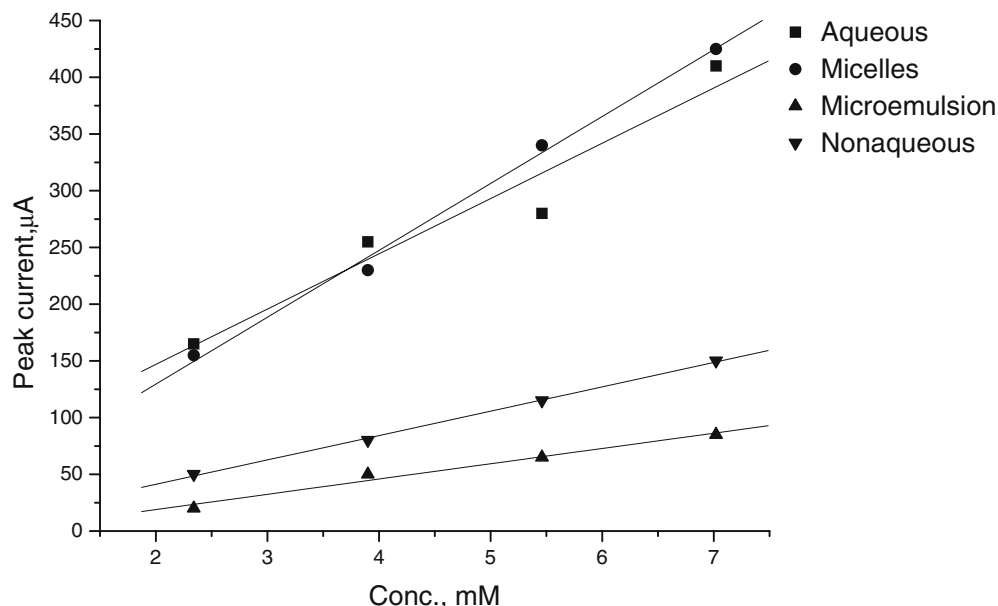


Fig. 10 Effect of concentration on peak current for the reduction on nitrobenzene at 10 mV/s



An exception to this general trend is noticed only in the case of hydroquinone in micellar medium.

The voltammetric peak current values for all other cases, which follow the general trend, mentioned above may be due to similar mass transport and related properties of each medium. Micellar systems once again predominantly contain water; hence, the diffusion coefficients of organic reactants in both the micellar and aqueous media are likely to be similar. This explains the general trend of relatively small differences in the peak current values of all organic compounds in aqueous and micellar medium.

The peak current data also suggest significantly lower diffusion coefficient values for organic compounds in non-aqueous medium. Literature data also suggest lower value of diffusion coefficient in aprotic media when compared with aqueous media [31].

For all the compounds investigated, the peak current values in μ E are always found to be significantly lower than those of all other media. This clearly suggests that the mass transport of organic reactants in μ E are considerably lower than aqueous and aprotic phases. Microemulsions are defined as clear thermodynamically stable dispersions of two immiscible liquids containing an appropriate amount of surfactants or surfactants and cosurfactants. In bicontinuous μ E of the type used in the present study, small organic microparticles are dispersed in similar microaqueous phases. The organic reactant molecules should move from non-aqueous phase to ionic-conducting aqueous phase for electron transfer. Attempts have been made to understand mass transport in μ E media. Two approaches are essentially used. Transport between the two phases with different viscosities may be related to two different diffusion coefficients [32]. In another approach, the distribution of organic reactant between the two phases may be described by a partition coefficient [33]. Further measurements of physicochemical parameters in individual μ E may be necessary for a better understanding of the problem.

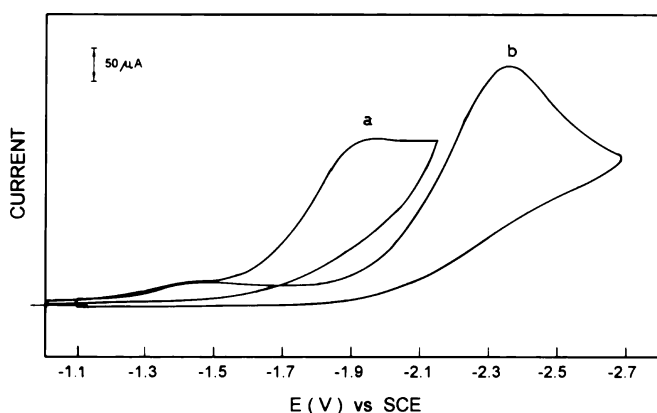


Fig. 11 Cyclic voltammograms for the reduction of 6.26 mM benzyl chloride at 40 mV/s on GCE CTAB microemulsion (a) and DMF (b)

Table 1 Limiting potential of GCE in different media at 10 mV/s and 101.83 μ A/cm²

Medium	Cathodic potential (V)	Anodic potential (V)
Aqueous (McIlvaine buffer, pH 7.0)	-1.55	+1.10
CTAB micelles	-1.80	+0.55
CTAB microemulsion	-1.70	+0.53
Non-aqueous (DMF)	-2.80	+1.30

From an analytical standpoint, as long as the reactant is soluble, linear relation between current and concentration may be obtained at least up to 8- to 10-mM solutions in all four media. Voltammetric sensing of organic compounds in micelles and μ Es may thus be taken up. Such possibilities exist in pollution monitoring and electrochemical detoxification.

Conclusions

In the absence of unusual adsorption, changes in reaction sequence and other blocking effects, the electro-oxidation and electro-reduction of organic compounds seem to follow a general trend. The ease of electron transfer, both for oxidation and reduction, is higher in aqueous medium. It becomes increasingly difficult as the content of aprotic phase increases in the solvent-supporting electrolyte. The

mass transport rate in these four media, as measured by the peak current values, also exhibit a uniform trend. It appears that the transport rate for organic reactants in μ E is significantly lower when compared with both protic and aprotic media. A more quantitative modelling of transport processes in these media would be worthwhile. The influence of individual surfactants, cosurfactants and aprotic component in the micelles and μ Es also deserves further investigation. Electroanalysis on a quantitative basis in individual media is indeed possible. However, quantitative comparison and extrapolation to other media appears a more interesting but challenging task now.

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