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

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

Introduction

The requirement of green chemistry in eliminating or at least minimizing the toxic aprotic solvents has generated substantial interest in micelles and microemulsions ($\mu$Es). 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 $\mu$E). 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 $\mu$Es 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 \( \mu \mathcal{E} \) systems has been extensively investigated [24]. Electroreduction of benzyl chloride has also been achieved on Ni-tetrafluoroethylene oligomer (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 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.

Methyltrimethyl 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 (9.6x10^-4 M) [15].

The bicontinuous \( \mu \mathcal{E} \) was prepared by mixing CTAB, \( \mu \)-hexane, \( \mu \)-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, \( \mu \mathcal{E} \) 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 \( E_p(\text{micelle}) > E_p(\text{aqueous}) > E_p(\text{DMF}) \). 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 \( i_p(\text{aqueous}) > i_p(\text{DMF}) > i_p(\text{micellar}) > i_p(\text{HF}) \). 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
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. $\Delta E_p$ values decrease in the order $\Delta E_p(\text{DMF}) > \Delta E_p(\text{ME}) > \Delta E_p(\text{aqueous}) > \Delta E_p(\text{micelles})$.

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 $\mu$E. 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 $i_p(\text{micelles}) > i_p(\text{aqueous}) > i_p(\text{DMF}) > i_p(\text{ME})$. The peak potential values...
also shift in the more positive direction with increasing sweep rate and concentration. However, the general trend of anodic potential, $E_{P(DMF)} > E_{P(\mu E)} > E_{P(\text{aqueous})} > E_{P(\text{micelle})}$, is maintained 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].

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 $\mu E$ 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.

The $\mu E$ 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 decreases once again in the order $i_{p(\text{micelle})} > i_{p(\text{aqueous})} > i_{p(DMF)} > i_{p(\mu E)}$.

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 $\mu E$, 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 $\mu E$ 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 µE 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 µEs 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 µA/cm² 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 µEs 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 slower 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 µE. 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_p of ascorbic acid and hydroquinone shifts in the positive direction in micellar medium when compared with aqueous medium. The E_p of nitrobenzene is shifted to more 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 µE as well, no such catalytic effect is noticed. The electrode surface in µE...
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 $i_{p,\text{micelle}} > i_{p,\text{aqueous}} > i_{p,\text{DMF}} > i_{p,\text{ME}}$. 

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

![Graph showing the effect of concentration on peak current for the oxidation of ascorbic acid at 20 mV/s.]

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

![Graph showing the effect of concentration on peak potential for the oxidation of ascorbic acid at 20 mV/s.]

Thus, the study highlights the importance of medium effects on mass transport and peak currents in cyclic voltammetry, with implications for the design of more efficient electrochemical devices.
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)
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 μEs are always found to be significantly lower than those of all other media. This clearly suggests that the mass transport of organic reactants in μEs 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 μE 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 μE 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 μE may be necessary for a better understanding of the problem.

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

<table>
<thead>
<tr>
<th>Medium</th>
<th>Cathodic potential (V)</th>
<th>Anodic potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous (McIlvine buffer, pH 7.0)</td>
<td>-1.55</td>
<td>+1.10</td>
</tr>
<tr>
<td>CTAB micelles</td>
<td>-1.80</td>
<td>+0.55</td>
</tr>
<tr>
<td>CTAB microemulsion</td>
<td>-1.70</td>
<td>+0.53</td>
</tr>
<tr>
<td>Non-aqueous (DMF)</td>
<td>-2.80</td>
<td>+1.30</td>
</tr>
</tbody>
</table>

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

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)
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 \( \mu \)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 \( \mu \)Es 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 \( \mu \)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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**References**

The effect of structure of oil phase, surfactant and co-surfactant on the physicochemical and electrochemical properties of bicontinuous microemulsion

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Abstract
Efforts were made to prepare bicontinuous microemulsions with ten different oil phases involving aliphatic, linear, and aromatic hydrocarbons as oil phases, two co-surfactants (n-butanol and n-pentanol) and two surfactants: cationic (CTAB) and anionic (SDS). Different weight percentages were employed for the preparation of cationic and anionic surfactant based microemulsions as reported in the literature. Out of the 40 compositions (10 oil phases × 2 co-surfactants × 2 surfactants) thus selected only 28 systems showed stable bicontinuous microemulsion phase. This behavior is explained on the basis of the structures of various constituents present in the microemulsions. Viscosity variations of stable bicontinuous microemulsions are found to depend mainly on the nature of co-surfactant. Conductivity behavior on the other hand depends mainly on the weight percentage and composition of aqueous phase. The solubility of pyrene in the oil phase determines the excimer formation and fluorescence behavior in microemulsions. The electron transfer property of both the water-soluble and the oil-soluble redox systems does not depend on the oil phase and the co-surfactant. The significance and importance of characterizing well defined bicontinuous microemulsions is thus highlighted.

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Keywords: Bicontinuous microemulsion; Viscosity; Conductivity; Fluorescence; Electron transfer

1. Introduction
Bicontinuous microemulsions composed of dynamic intertwined microscopic networks of oil and water with surfactant at the interfaces. They are advantageous over the conventional medium with respect to the solubilization of the polar and the nonpolar substrates, the electro catalytic activity and the low toxicity [1].

Physicochemical and electrochemical characterization of microemulsion is receiving considerable current attention due to their potential implications in chemical, electrochemical and biochemical processes. During the past few years the chemical and electrochemical preparation of the nanomaterials employing microemulsions is emerging as a potential area of interest. Extensive reviews on the physicochemical and electrochemical characterization of microemulsions are available [2–6].

Investigations in microemulsions generally focus on the phase transitions from oil-in-water (O/W) to water-in-oil (W/O) through bicontinuous phase. Different experimental approaches are being employed to study the individual microemulsion phases and phase transitions [7]. These include the conductivity measurements [8–15], viscosity measurements [8,9,14], the fluorescence probe studies [15–17], the cyclic voltammetry [1,10,16,18–20], NMR self-diffusion studies [11], and the cryo TEM studies [11]. Conductivity for example tends to decrease with decrease in the water content that is from O/W through bicontinuous to W/O phase. Viscosity tends to increase with the oil content. Fluorescence and diffusion behavior depends on the partition of the probe between the water and the oil phases. Cyclic voltammetric behavior also depends on the relative solubility and the distribution of redox active molecule between the oil and the water phases. Cryo TEM technique enables direct microscopic observation of the phase changes.

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Practical applications of microemulsions and also bicontinuous microemulsions require more detailed characterization of the individual phases rather than phase transition. The influence of individual components of the microemulsion phases on the overall physicochemical behavior is also important. Only very few detailed investigations on the characterization of bicontinuous microemulsion are available. These include self-diffusion behavior by the NMR technique [21], the electrochemical studies of redox active species using cyclic voltammetry [22], and the fluorescence probe distribution between oil and water phases [23]. Brief discussions on the effect of the oil chain length [24], the viscosity variations [25] and the co-surfactant effect [21] on the behavior of bicontinuous microemulsions have also been reported.

The literature survey presented above suggests that many interesting questions can still be raised regarding the structure-property correlations, the stability and the physicochemical behavior of bicontinuous microemulsion phases. Under constant weight percentage of water, oil, surfactant and co-surfactant components, how does individual constituents and their molecular structure influence the overall stability of the microemulsions, for example will linear and cyclic compounds as oil phases exhibit similar stability? Can butanol and pentanol as co-surfactants influence the bicontinuous microemulsion stability under otherwise identical conditions? How does the oil phase structure influence the rheology of the microemulsions? Can the surfactant and the co-surfactant influence the viscosity of the bicontinuous microemulsion? Which component of the bicontinuous microemulsion significantly determines its overall conductivity? How is it influenced by the water content? How does the polarity of the microemulsion system compared with the individual polarities of the oil and the water phases? How does the molecular structure of the oil phase influence relative polarity? Does the oil phase have any influence on the electron transfer and the diffusion behavior of the redox active molecules? These are some of the issues that are addressed here.

In the present work the effect of the oil phases, the surfactants and the co-surfactants on the physicochemical and the electrochemical properties of the bicontinuous microemulsions are investigated. Oil phases having different structures and co-surfactant with varying chain length were taken as variables. A cationic surfactant cetyl trimethylammonium bromide (CTAB) and an anionic surfactant sodium dodecyl sulfate (SDS) were used for the preparation of microemulsions. The compositions of microemulsions were kept constant. The microemulsions thus prepared were characterized by measuring the viscosity, the conductivity, the fluorescence behavior of the probes and the cyclic voltammetry of the redox active species. Some interesting observations and generalizations are summarized here.

2. Materials and methods

2.1. Materials

The surfactants CTAB (Merck) and SDS (BDH) were used as received. The medium chain alcohols such as n-butanol (Merck) and n-pentanol (Acros) were used as co-surfactants. Aliphatic oil phases such as n-hexane (Merck), n-heptane (SRL), isooctane (Merck), dodecane (Merck), tetradecane (Merck), hexadecane (Merck), benzene (Merck), toluene (Ranbaxy), and p-xylene (SRL fine chem.) were employed. Fluorescence experiments were carried out using the molecular probe pyrene (Alfa Aesar). In electrochemical experiments hydroquinone (Merck) and ferrocene (Alfa Aesar) were chosen as electrochemical probes for the cationic and the anionic surfactant based microemulsions, respectively. Double distilled water was used for the preparation of solutions.

2.2. Preparation of microemulsion

Microemulsions were prepared by mixing the appropriate components and stirred vigorously until clear. The basic composition for cationic bicontinuous microemulsion containing CTAB (17.5 wt%), oil (12.5 wt%), co-surfactant (35 wt%), water (35 wt%) and anionic bicontinuous microemulsion containing SDS (8 wt%), oil phase (13.3 wt%), co-surfactant (26.7 wt%), water (52 wt%) were taken from the literature [26]. Typically 50 g of the cationic microemulsion was prepared by dissolving 8.75 g of CTAB in 17.5 g water and 6.25 g oil then the liquid became turbid. To this 17.5 g co-surfactant was added with constant stirring until the solution became clear and stable. Similarly the anionic microemulsion was prepared by dissolving 4 g of SDS in 26 g water and 6.65 g oil then the liquid became turbid. To this 13.35 g co-surfactant was added with constant stirring until the solution became clear and stable. Those microemulsions, which are clear and stable at room temperature, are chosen for studies.

2.3. Physicochemical measurements

The relative viscosity of microemulsions was measured with an Ostwald viscometer at 20 ± 0.1 °C. The electrical conductivity of the microemulsions was measured using a DCM-200 conductivity meter equipped with a CD-06 platinum conductance electrode coated with platinum black. The conductivity was measured at 25 ± 0.1 °C.

Fluorescence measurements were done with a Varian eclipse fluorescence spectrophotometer. The fluorescence emission spectrum of pyrene (excitation at 337 nm) was used to obtain the ratio of intensities of the first to the third vibronic peaks (I1/I3). The concentration of pyrene was 9.89 μM. Good resolution of the bands was obtained at the slit width 5 × 2.5 nm. The intensities for I1 and I3 are taken at 372 and 383 nm, respectively.

2.4. Cyclic voltammetry measurements

Cyclic voltammetry measurements were carried out in an Auto Lab model PGSTAT30 potentiostat/galvanostat controlled with the (GPES) soft ware version 4.9 (ECO Chemie, B.V., The Netherlands). An undivided cell with glassy carbon (Tokai GC 3 mm dia) as working electrode and platinum foil as counter
n-butanol interact positively with linear as well as cyclic oil phases except hexane, all other oil phases formed stable microemulsions as a co-surfactant. In the case of n-pentanol as a co-surfactant n-butanol microemulsions the viscosity increases only slightly with oil phase chain length. The effect of structure of oil phases is not significant with respect to its solubility in microemulsion phases and the microemulsions highly depend upon the nature of co-surfactant, co-surfactants (Table 1).

3. Results and discussion

3.1. Stability of bicontinuous phases

In the present study ten oil phases, with two co-surfactants (n-butanol and n-pentanol) and two surfactants—cationic (CTAB) and anionic (SDS) were considered for the preparation of the stable bicontinuous microemulsions. Among the 40 combinations that were selected, 12 systems did not lead to a stable microemulsion at room temperature (Tables 1–3). There appears to be a compatibility requirement between the chain length of the oil phase (alkane) and the chain length of the co-surfactant [28]. Among the linear alkanes stable bicontinuous microemulsions were formed up to tetradecane with n-butanol as a co-surfactant. In the case of n-pentanol as a co-surfactant except hexane, all other oil phases formed stable microemulsions.

Cyclohexane and aromatic compounds tend to form stable bicontinuous microemulsions with co-surfactant n-butanol. However, with these oil phases stable microemulsions are not formed with the co-surfactant n-pentanol. It appears that n-butanol interact positively with linear as well as cyclic oil phases thus minimizing the interfacial tension and stabilizing the bicontinuous phases. n-Pentanol as a co-surfactant appears to have a destabilizing effect with the oil phases containing p-Xylene.

Table 1

<table>
<thead>
<tr>
<th>Oil phases used</th>
<th>n-Butanol as co-surfactant</th>
<th>n-Pentanol as co-surfactant</th>
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</thead>
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<tr>
<td></td>
<td>CTAB</td>
<td>SDS</td>
</tr>
<tr>
<td>Hexane</td>
<td>4.9180</td>
<td>5.1242</td>
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Table 2

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<th>n-Pentanol as co-surfactant</th>
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Table 3

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<th>n-Pentanol as co-surfactant</th>
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<td>0.9618</td>
<td>1.0880</td>
<td>0.9976</td>
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</table>

Note. Pyrene concentration 9.89 μM; excitation wavelength: 337 nm; slit width 5 × 2.5 nm; I1/I3 values of pure alcohols in similar conditions; n-butanol: 1.1550; n-pentanol: 1.0358; I1/I3 value for water = 1.81.

3.2. Viscosity

Viscosity is a characteristic property of any fluid. In microemulsions it is a macroscopic property, which largely depends upon the type of aggregates present, on their interactions and on the concentration. Thus it is mainly used to monitor the microstructure of the system.

The present study reveals that the viscosity of bicontinuous microemulsions highly depend upon the nature of co-surfactant, with respect to its solubility in microemulsion phases and the chain length. The effect of structure of oil phases is not significant in the viscosity of microemulsions. The structural effect of the surfactant is very low in the case of n-butanol-based microemulsions. n-Butanol based microemulsions exhibit significantly lower viscosity as compared to that of n-pentanol based microemulsions (Table 1, Fig. 1). The solubility of n-pentanol in water (0.30 g ml⁻¹) is significantly lower than that of n-butanol (1.05 g ml⁻¹). This variation reflects itself in the viscosity of microemulsions prepared employing these two co-surfactants (Table 1).

Both the cationic and anionic surfactants in n-butanol based microemulsions show almost similar viscosity behavior (Fig. 1). In general the viscosity values are found to increase slightly with increasing chain length of the oil phase. In n-pentanol microemulsions the viscosity increases only slightly with oil phase chain length when anionic surfactant is employed. For cationic surfactant however the viscosity values increase substantially with increasing oil phase chain length. In CTAB systems, the amphiphile hydrocarbon chain length is higher (CI6) when compared to SDS (CI2). Thus higher surfactant–oil interaction leads to higher viscosity values in CTAB based microemulsions.

The viscosity value for systems containing isocetane (oil phase) slightly deviate from the trend observed (Table 1 and
Fig. 1. Viscosity variations with the increase in chain length of the linear oil phase employed. CB, CTAB/n-butanol/oil phase/water system; CP, CTAB/n-pentanol/oil phase/water system; SB, SDS/n-butanol/oil phase/water system; SP, SDS/n-pentanol/oil phase/water system. Viscosities measured at 20 ± 0.1°C.

Fig. 1. In n-butanol based microemulsions the viscosity values for the cyclic systems are substantially higher than those for the linear systems. This may be due to the higher penetration of cyclic oil phases into the surfactant palisade layer than the linear alkyl chain oil phases. These observations indicate the importance of the structure of the oil phase on the overall microstructure of microemulsions.

3.3. Conductivity

Conductivity is also another important indication of structural variation in bicontinuous microemulsion. n-Butanol based bicontinuous microemulsions generally exhibit higher conductivity when compared to n-pentanol based microemulsions (Fig. 2, Table 2). This may again be attributed to the higher miscibility of n-butanol–water system and the transport of ionic species in such miscible medium. CTAB microemulsions generally exhibit lower conductivity when compared to SDS microemulsions. It should be noted that in the weight percentage composition selected for these microemulsions, SDS microemulsion have substantially higher water content (52%) than CTAB microemulsions (35%), which may lead to higher conductivity of SDS systems. Hexane based microemulsions which show stability only in n-butanol systems, are found to deviate from the linear correlation indicated above (Fig. 2). The cationic microemulsion involving hexane show higher conductivity, when compared to the observed trend.

During the phase transitions some correlations between the viscosity and the conductivity changes have been frequently reported in the literature. For example increase in conductivity is normally associated with corresponding decrease in viscosity. This type of inverse relationship is not noticed in a well-defined bicontinuous system. For example, the viscosity changes depend on the co-surfactant (higher viscosity for n-pentanol systems) whereas the conductivity changes depend more on the surfactant (higher conductivity for SDS system). This is also understandable because the viscosity depends on the rheology of the overall microemulsion phase whereas the conductivity depends on the total volume fraction of aqueous phase and its composition.

3.4. Fluorescence measurements

Fluorescence measurements of the hydrophobic probe mainly depend on the polarity of the medium and hence in bicontinuous microemulsions it is a good indication of the polarity of the microenvironment in the microemulsion structure.

The fluorescence data for pyrene molecule in water, individual oil phases, individual co-surfactants and all the bicontinuous microemulsions are presented in Table 3. In this data the intensity $I_1$ at 372 nm is considered to be due to the excitation of pyrene monomer, the intensity $I_3$ at 383 nm is considered to be due to the excimer formed between excited pyrene molecule and the ground state pyrene molecule. The ratio of $I_1/I_3$ is a measure of polarity of the medium. Since pyrene reactant is substantially more soluble in oil phases, excimer signal $I_3$ is expected to be higher and $I_1/I_3$ is expected to be lower in these phases [29]. In the present work also for all alkane oil phases including cyclohexane, the $I_1/I_3$ value is closer to 0.65 (Table 3). In relatively polar n-butanol and n-pentanol medium $I_1/I_3$ value where found to be 1.15 and 1.04, respectively. Aromatic compounds benzene, toluene and p-xylene may interact with the photo-excited monomer as well leading to slightly higher $I_1$ value. Water is a highly polar solvent; the solubility of pyrene in this solvent is less than 2 μM. Hence the possibility of formation of excimer leading to $I_3$ signal is extremely low in water. Experimentally $I_1/I_3$ value is closer to 1.8 was obtained for this medium.
The following generalizations may be made regarding the fluorescence probe behavior in bicontinuous microemulsions. The $i_1/i_3$ values obtained by fluorescence measurements for all the stable bicontinuous microemulsions are closer to 1.0. This proves the partition of pyrene in the nonpolar oil phase and the polar interfacial layer. The present study also reveals that the $i_1/i_3$ value depends very little upon the co-surfactant in conformity with the earlier reports [30]. The slight decrease in $i_1/i_3$ value with increase in chain length almost in most of the cases is due to the increase in microviscosity and also due to the decrease of the distance over which the probes diffuse to form an excimer. In isooctane there is a slight variation from the normal trend observed for other oil phases. This proves that the structure of oil phase is also an important factor in the $i_1/i_3$ values. Excimer concentration generally decreases with increase in the surfactant concentration. Between the two types of microemulsions cationic surfactant based microemulsions have higher surfactant concentration (17.5%) when compared to anionic surfactant based microemulsions (8%). Thus the excimer formation is lower in CTAB based microemulsions and thereby higher $i_1/i_3$ values. The $i_1/i_3$ values in aromatic oil phase systems are closer to the respective pure oil phases. This is due to complete solubility of pyrene in oil phases of the bicontinuous microemulsions.

3.5. Cyclic voltammetry

The structural effects on the electrochemical behavior of microemulsions were investigated using cyclic voltammetry. In general, ferrocene soluble predominantly in oil phase is employed as the electrochemical probe in the phase transition studies. However, in the present work in addition to ferrocene, it was decided to investigate one more electrochemical probe hydroquinone, which is soluble predominantly in the aqueous phase. It may also be noted that hydroquinone is a quasi-reversible system which would be more sensitive to electron transfer kinetics when compared to ferrocene.

Typical cyclic voltammogram obtained for ferrocene in SDS/hexane/n-butanol/water system is shown in Fig. 3a. The anodic peak potential $E_{pa}$, the anodic peak current $I_{pa}$ and the peak separation $\Delta E_p$ values were obtained for this redox probe employing all the oil phases in n-butanol and n-pentanol medium under identical conditions. Except in the case of p-xylene based microemulsions these voltammetric data vary only slightly with change in oil phase as well as co-surfactant. There is only a small noticeable increase in $\Delta E_p$ (60 ± 4 mV) values with alkyl chain length of the oil phase. The peak separation is significantly higher for ferrocene in p-xylene based microemulsions (Fig. 3b). It appears that at least in such high molecular weight aromatic systems, the oil phase (p-xylene) adsorbs on the electrode surface and retards the electron transfer process.

Fig. 4a shows the first quasi-reversible redox peak for hydroquinone in hexane/n-butanol/CTAB microemulsion. The peak current, peak potential and the peak separation values were obtained for this compound in CTAB microemulsions. There is no systematic variation in the peak current values with alkyl chain length. The peak separation values are found to increase slightly with increasing alkyl chain length (for example, 327 mV for hexane to 405 mV for dodecane) in n-butanol systems. The peak current values are also slightly lower for n-pentanol based microemulsions when compared to n-butanol based microemulsions. These observations suggest that some blocking effect of the oil phase toward electron transfer is noticeable in a quasi-reversible system like hydroquinone. p-Xylene based microemulsions once again are found to give significantly higher $\Delta E_p$ values as shown in Fig. 4b suggesting inhibitive adsorption of this molecule on the electrode surface.

The cyclic voltammetric data obtained for all the bicontinuous microemulsions indicate broader similarity for both the reversible and the quasi-reversible redox systems. Bicontinuous microemulsions contain fairly uniform and completely connected aqueous domain network. The electron transfer processes occur predominantly on the electrode-aqueous electrolyte interface and the electrode-surfactant interface. The electrode-oil interface does not contribute to the electron transfer. Hence the overall electrochemical responses for redox systems do not depend significantly on the molecular structure of the oil phase or the co-surfactant.

4. Conclusions

Physicochemical and electrochemical measurements need not be confined to phase transition studies in microemulsions.
The present study clearly illustrates the importance of physicochemical and electrochemical characterization of stable bicontinuous microemulsion systems without any special consideration for phase transitions. It is possible to achieve desirable physicochemical properties by appropriately varying the constituent molecules of oil phases, surfactant or co-surfactant, while retaining the overall weight ratio of the bicontinuous microemulsion. Some such interesting potentialities emerging from the present studies include the following.

The oil phase of bicontinuous microemulsions need not be restricted to linear alkanes. Even an aromatic hydrocarbon can be used as oil phase. Such systems may be of interest for chemical processes involving aromatic molecules and conducting polymer synthesis. Of course the viscosity of the media involving long chain length oil phases and aromatic hydrocarbons are relatively higher, which may also have favorable impact on relatively slow organic phase reactions.

The impact of co-surfactant in influencing a variety of physicochemical interactions is another significant highlight of the present investigation. When relatively higher viscosity and lower ionic conductivity is desired n-pentanol turns out to be a better co-surfactant. This co-surfactant cannot be used for the preparation of microemulsions containing aromatic hydrocarbons. In general for applications requiring low viscosity and higher conductivity n-butanol turns out to be a better candidate. This co-surfactant also provides stability to a much broader variety of oil phases.

The electrical conductivity and ion-transport behavior of bicontinuous microemulsions are determined by the weight percentage and the composition of aqueous phase. The structure of the oil phase has practically no role in this property.

Stable bicontinuous microemulsions behave as a well-defined electrolytic medium for redox electrochemistry. The electron transfer property as measured by the peak separation value as well as the apparent mass transport property as measured by the limiting peak current value are found to exhibit very little variations in all the bicontinuous microemulsions investigated except one system. This is indeed true whether we employ a predominantly water soluble reactant or an oil soluble reactant. This observation is true only for simple redox reactions. The medium effects may be significant for coupled chemical processes involving electrogenerated cation or anion radicals. Such questions definitely deserve further investigation.

The present study thus opens up a new window of opportunity to fine-tune the properties of bicontinuous microemulsions by proper choice of individual molecular components with predictable property variations. There is considerable scope for further research efforts in this direction.

Acknowledgments

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References

Electrochemical destruction of p-chlorophenol and p-nitrophenol – Influence of surfactants and anode materials

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Abstract

The electrochemical oxidative removal of p-chlorophenol and p-nitrophenol was studied by cyclic voltammetry (CV) and constant current electrolysis on commercially available graphite and titanium substrate insoluble anodes (TSIA). The effect of cationic cetyl trimethylammonium bromide (CTAB), anionic sodium dodecyl sulphate (SDS) and non-ionic polyoxyethylene(23)lauryl ether (Brij-35) surfactants, which prevent adherent film formation on the electrode surface were also studied. CV experiments indicate that p-chlorophenol exhibits a relatively higher tendency for film formation on graphite and that sodium chloride is a better medium for the destruction of phenols. The electrochemical oxidation of phenols under galvanostatic conditions in chloride medium with CTAB enhanced the detoxification process with significantly lower fouling effects on TSIA. The surfactants, however, did not improve phenol removal on graphite under identical experimental conditions. A charge of 2.5 F per mol was found to be sufficient to achieve 44–48% removal of phenol on both the electrodes in the absence of the surfactants. A 55–65% removal was achieved in the presence of the cationic surfactant on the TSIA electrode. Phenol was removed as a low molecular weight polymer (MW ~ 4450).

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Keywords: Phenols; Surfactants; Electrochemical destruction; Graphite; Oxide-coated electrode

1. Introduction

Detoxification of phenols using electrochemical (EC) methods (Rajeshwar and Ibanez, 1997) is an active area of current interest. Recent work in this area is centered on the choice of suitable experimental conditions to avoid fouling and passivation effects of anodes. A variety of electrode materials including platinum (Ezerskis and Jusys, 2001; Torres et al., 2003), lead – dioxide (Wu and Zhou, 2001; Borras et al., 2004), graphite (Korbahti et al., 2002; Ortiz et al., 2003), glassy carbon (Ureta-Zanartu et al., 2002), boron-doped diamond-BDD (Hagans et al., 2001; Iniesta et al., 2001), gold (Ureta-Zanartu et al., 2001) stainless steel (Canizares et al., 2002) and oxide-coated titanium (Polcaro et al., 1999; Chozhan et al., 2004) have been investigated as anodes. The fouling and passivation of electrode materials is normally not observed at very low concentrations of phenols whereas it is a major challenge at higher concentrations.

Though some initial reports suggested BDD as a potential non-fouling electrode (Hagans et al., 2001), further studies did not confirm this (Iniesta et al., 2001). Chemically modified electrodes involving aluminosilicate and other complexes (Mohan et al., 2004; Obirai et al., 2005) have also been tried, although with limited success. Photo-electrochemical degradation on platinum (Davies et al., 2002) and TiO₂ particulate systems (Pandiyan et al., 2002) has also been reported recently.

Besides anode fouling effect, energy consumption in EC processes is a serious issue. Complete EC oxidation of phenols to CO₂ is a multi-electron, energy-intensive process.
They contaminate the eco-system by bio-accumulation et al., 2002). Further efforts to minimize energy consumption cause severe environmental contamination. Chlorophenols explosives, dyes and plasticizers (Spain. 1995) and they mainly used in the production of pesticides, herbicides, the role of surfactants in addressing the above challenges. of phenols. The present investigation was initiated to evaluate energy or faradic charge for removal of phenols. Hence, sur­

(ii) avoidance of electrode fouling and (iii) reduction in the oxidation followed by bio-degradation (Szpyrkowicz et al., 2005). However, the influence of surfactants on detoxification of phenols has not been reported so far.

A study of the literature indicates that the EC detoxification of phenols is brought with the following challenges: (i) removal of phenols in significantly high concentrations; (ii) avoidance of electrode fouling and (iii) reduction in the energy or faradic charge for removal of phenols. Hence, surfactants can adsorb on the electrode surface and influence the fouling. They may also influence oligomerization and coagulation processes initiated by electrogenerated cation radicals of phenols. The present investigation was initiated to evaluate the role of surfactants in addressing the above challenges. Nitrophenols and chlorophenols are rated as priority pollutants (Keith and Telliard, 1979). Nitrophenols are mainly used in the production of pesticides, herbicides, explosives, dyes and plasticizers (Spain. 1995) and they cause severe environmental contamination. Chlorophenols are used in plastics, pesticides and wood preservatives. They contaminate the eco-system by bio-accumulation (Ezerskis and Jusys, 2001). Hence in the present work p-chlorophenol (PCP) and p-nitrophenol (PNP) were chosen for the EC destruction studies. Titanium substrate insoluble anodes (TSIA) with an RuO$_2$-IrO$_2$-TiO$_2$ coating (Subbiah et al., 1990) and graphite anodes were employed since these electrodes are commercially available and are well known anode materials for use in neutral chloride media. A fairly high concentration of phenols, around 50 mM was taken for detoxification. The influence of cationic, anionic and non-ionic surfactants was assessed using cyclic voltammetry (CV) and constant current electrolysis.

2. Experimental

2.1. Reagents

PNP and PCP were obtained from SRL. Cationic surfactant cetyl trimethylammonium bromide (CTAB), anionic surfactant sodium dodecyl sulphate (SDS), non-ionic surfactant polyoxyethylene(23)lauryl ether (Brij-35) were purchased from BDH. Potassium ferrocyanide was obtained from Merck. All the chemicals were of reagent grade. Double distilled water was used for the preparation of solutions.

2.2. Voltammetric measurements

Voltammetric measurements were carried out using an Autolab model PGSTAT 30 potentiostat/galvanostat controlled with a General Purpose Electrochemical Syste...
consistent with an increase in the number of cycles in both the media. After 7-8 cycles the voltammetric response turns out to be similar to that of the background CV response (Fig. 1a1 and a2 and also Fig. 1b1 and b2). It should be noted that the substantial decrease in the oxidation peak currents is due to passive polymer film formation, which is quite different from the slight decrease in peak currents normally noticed in conventional diffusion-controlled voltammetric responses.

The oxidation potential for PNP on graphite is higher by 200-300 mV as compared to that for PCP. The oxidation peak for PNP occurs closer to the oxygen evolution potential region (Fig. 2a and b). Hence, distinct anodic peaks are not observed in these media. However, the passivation effect leading to substantial decrease in the peak current during the second and subsequent sweeps is clearly noticed in the CV responses (Fig. 2a and b).

Electrode fouling after the multi-sweep cycling for both the compounds was found to be substantial. This effect was further confirmed by recording the CV response of potassium ferrocyanide before and after multi-sweep cycling in phenolic solutions. A CV reversible response for potassium ferrocyanide on a freshly polished graphite electrode at a sweep rate 40 mV s⁻¹ is shown in Fig. 3a1. After multi-sweep cycling in NaOH solution containing PCP (as seen in Fig. 1a2) both anodic and cathodic peak currents decreased. The film-covered electrode surfaces seem to block even the background surface redox processes (Fig. 3a2 and a3). The electrode fouling effect after multi-sweep cycling of graphite in NaOH containing PNP (as seen in Fig. 2a) appears to be similar (Fig. 3a3). These results indicate that in the absence of surfactants both PCP and PNP form insulating polymer films on the electrode surface, which inhibit further electron transfer.

CV responses obtained for PCP during multi-sweep experiments in the presence of cationic, anionic and nonionic surfactants in 0.1 M NaCl are shown in Fig. 4a2, b2, and c2 respectively. The peak currents during multi-sweep cycling decreased significantly in the presence of surfactants, suggesting film formation on the electrode surface even in the presence of surfactants. Similar surfactant effects were noticed also for PNP in NaCl. It is clear that polymeric film formation occurs in the presence of the surfactants for both PCP and PNP. Quite interestingly, however, these polymer layers were not adherent or passivating. This is evident from the voltammogram recorded for potassium ferrocyanide on the electrodes subjected to multi-sweep cycling (Fig. 4a2, b2 and c2), without polishing or cleaning the electrode surface. The CV recorded
Fig. 3. Cyclic voltammograms of 4 mM potassium ferrocyanide in 0.1 M KCl on graphite under various electrode conditions, (a) Freshly polished (1), after multi-sweep cycling in 2 mM phenolic compound in 0.1 M NaOH solution; PCP (2) and PNP (3). (b) After multi-sweep cycling in 2 mM PCP in 0.1 M NaCl containing 0.1%; (1) CTAB (2) Brij-35 and (3) SDS. (c) After multi-sweep cycling in 5.67 mM PNP in 0.1 M NaOH containing 0.1%; (1) CTAB (2) Brij-35 and (3) SDS. Scan rate = 40 mV s⁻¹.

for potassium ferrocyanide are shown in Fig. 3a1, b2 and b3; both the anodic and cathodic peaks can distinctly be seen. The voltammograms are also similar to that recorded in pure 0.1 M KCl solution on a freshly polished electrode (Fig. 3a1). These results suggest that the surfactants prevent the formation of adherent passive films on the graphite electrode.

Similar trends could be noticed for the phenolic compounds in NaOH medium as well. In alkaline media, the background currents are significantly higher even below 1 V in the presence of the cationic, anionic and non-ionic surfactants as given in Fig. 5a1, b1 and c1 respectively. The oxidation of phenols occurs as a competitive process in this region as may be seen from Fig. 5a2, b2, and c2 for PNP. In multi-sweep cycling experiments the anodic peak currents continuously decreased and retraced the background current after 5–6 cycles. Even after multiple cycling, the electrode surface doesn’t get passivated as may be noticed from CV responses recorded for ferrocyanide (Fig. 3c1, c2 and c3). The electrode activity in the alkaline medium remained unaffected, which may either be due to unstable polymer film formation or due to poor efficiency of phenol oxidation as compared to oxygen evolution.

The voltammetric studies on graphite presented so far indicate the following:

(a) Oligomerization/polymerization process is generally favourable in NaCl medium as compared to that in NaOH medium. In NaOH medium oxygen evolution reaction occurs competitively in the same potential region.

(b) Polymerization leading to fouling of the electrode surface is more significant for the more easily oxidizable PCP as compared to PNP. It appears that the cation (Ar–OH⁺) radical generated from PCP undergoes a more facile radical-substrate coupling leading to oligomerization/polymerization. Another cause may be the closeness of the PNP oxidation region to the background oxygen evolution region. Oxygen bubbles may inhibit film formation and thereby prevent fouling of electrode surface to some extent.

CV responses were also recorded on the TSIA working electrode. However, the background currents due to chlorine evolution in NaCl medium and oxygen evolution in NaOH medium were found to be substantially higher on this electrode. Hence the voltammetric peaks for PCP and PNP, the surfactant effect on the background current and the relative influence of graphite and TSIA electrodes could not be quantified from voltammetric studies. However, the possibility of oxidative polymerization of phenols through electrogenerated species such as Cl₂, Cl⁻ and OH⁻ does exist. Hence, this electrode was also selected for constant current electrolysis.

3.2. Constant current electrolysis

Constant current electrolysis was carried out to further evaluate the influence of surfactants on the removal of PCP and PNP. As mentioned in the introductory section, it is essential to achieve detoxification with a minimum electric charge. In this work, 2.5 F per mol of phenol (2 F per mol + 25% excess current) was chosen as the amount of charge passed during a single batch of electrolysis. Around 40–50 mM of PCP and PNP were initially dissolved in the electrolyte medium, and subjected to constant current electrolysis. During electrolysis the average cell voltage was found to vary between 1.8 and 3.1 V. In general, the electrolyte solution turned yellow to brown in colour depending on the nature of the compound and operating conditions. After electrolysis the solution was filtered to remove the insoluble coloured polymer. The amount of phenol present in the clear solution and thus the percentage of phenol removed during constant current electrolysis was obtained from HPLC analysis. Data
showing the influence of medium, electrode material and surfactant are summarized in Table 1.

3.3. Effect of medium and anode material

In the absence of surfactants only a very low quantity of PCP was removed from NaOH (run 1) and NaCl (run 2) on the TSIA electrode. However a higher level of phenol removal could be realized in neutral NaCl medium. Comparatively better results were obtained for the removal of PNP in NaOH (run 3) as well as in NaCl medium (run 4). NaCl was found to be a better medium for PNP as well. On the TSIA electrode as much as 48% PNP could be removed in the first batch itself from the NaCl solution (run 4). Although phenols undergo oxidation in both NaOH and NaCl media, the background oxidation processes are different in these two media. In NaOH, oxygen evolution is the parallel process, while in NaCl it is chlorine evolution. The chlorine generated at the anode is also likely to assist in the oxidative polymerization of phenol. This probably accounts for the higher efficiency in NaCl as compared to that in NaOH. Hence, all further constant current electrolysis experiments were confined to the NaCl medium.

Similar results were obtained for the removal of PCP and PNP on graphite electrode in NaCl solution. The removal of PNP was substantially higher in this case (run 6) as compared to that of PCP (run 5). Quite interestingly in the absence of surfactants PNP removal was found to be around 48% on TSIA (run 4) and graphite electrodes (run 6). This, despite the fact that TSIA assists the oxidation of phenol predominantly through chlorine evolution, while graphite directly oxidizes the phenols, as suggested by the voltammetric behavior.

3.4. Effect of surfactants

On graphite both cationic and anionic surfactants are found to exhibit a negative influence on the removal of PCP (runs 7 and 8) and PNP (runs 9 and 10). The negative influence of the anionic surfactant is relatively higher than that of the cationic surfactant. For example in the case of PNP the removal efficiencies in the absence of surfactant and in the presence of cationic and anionic surfactants were found to be 48%, 44% and 26% respectively (runs 6, 9 and 10). It appears that surfactants adsorbed on graphite electrodes prevent oxidation of organic compounds significantly through a blocking effect, as may be inferred from our CV results (Figs. 4 and 5).

On TSIA electrode, the cationic surfactant has a favourable impact on the removal of PCP (run 11) and PNP (run 14). In the case of PCP the oxidative removal efficiency increases remarkably from 14% to 57% while with PNP it
improves moderately from 48% to 64%. However for both PCP and PNP the anionic and non-ionic surfactants exhibit an either insignificant positive effect (run 13) or a negative effect (runs 12, 15 and 16).

Since no distinct oxidation peak was observed for phenol oxidation on TSIA electrode, chlorine evolution followed by chemical oxidation is probably an important parallel pathway for the oxidative removal of phenols on these electrodes. The cationic species CTA$^+$ builds up the surface concentration of chloride ions through formation of CTACl, facilitating the chlorine evolution reaction. The cation radical generated during phenol oxidation may also be prevented by the cationic surfactant from adsorbing on to the electrode surface. This may prevent electrode fouling, thereby contributing to a higher rate of removal of phenols. This type of catalytic influence is possible only in the case of cationic surfactants.

### 3.5. Recycling and product characterization

The results summarized in Table 1 correspond to single batch constant current electrolysis. The electrolyte after filtering the polymeric material can be subjected to a subsequent constant current electrolysis under the same experimental conditions. A further removal of phenol was achieved after passing charge of 2.5 F per mol for the remaining concentration. In a typical experiment involving PNP on TSIA in 0.1 M NaCl solution [conditions similar to run 4], 98% removal could be achieved in three successive stages. This removal may be achieved in two stages in the presence of surfactants. Essentially, a

---

**Table 1**

Electrochemical destruction of PNP and PCP on graphite and TSIA electrodes

<table>
<thead>
<tr>
<th>Run</th>
<th>Compound</th>
<th>Electrolyte</th>
<th>Surfactant</th>
<th>Anode</th>
<th>Removal efficiency (%)</th>
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<td>NaOH</td>
<td>CTAB</td>
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<td>6</td>
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<td>NaCl</td>
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<td>48</td>
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</table>

**Effect of surfactants**

<table>
<thead>
<tr>
<th>Run</th>
<th>Compound</th>
<th>Electrolyte</th>
<th>Surfactant</th>
<th>Anode</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
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<tr>
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<tr>
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<tr>
<td>16</td>
<td>PNP</td>
<td>NaCl</td>
<td>Brij-35</td>
<td>TSIA</td>
<td>34</td>
</tr>
</tbody>
</table>

Conc. PNP = 47.9 mM and PCP = 40.63 mM.
continuous EC oxidative removal involving electrolysis, simultaneous filtration and recycling may be a feasible approach for a large-scale EC removal of these phenols. The polymeric products isolated during constant current electrolysis were subjected to FTIR analysis and GPC. The polymer formed is aromatic in nature (–C=C– stretching vibrations at 1450–1600 cm⁻¹) they also have an ether linkage (–C–O–C– stretching vibrations at 1100–1300 cm⁻¹) (Ezerskis and Juysys, 2002). The C–Cl bond is retained as such in the polymer (C–Cl bond at 1100 cm⁻¹). The intensity of the hydroxyl bands is weak and broad. This proves the presence of polymeric stretched –OH groups in the polymer. The molecular weight $M_n$ and $M_w$ were determined as 4390 and 4492, respectively. It is inferred from the molecular weight data that the polymer formed is monodispersed. The molecular weight obtained in the present work is close to the value reported in the literature (Zhang et al., 2006).

The electrolyte solution after the filtration of polymeric material was ether extracted and analyzed for other organic constituents, especially chlorinated products. At least in the case of PNP this ether phase did not contain any compound with aromatic C–Cl bond. Recent investigations on phenol degradation also indicate the absence of new nuclear chlorinated carcinogenic molecules (Comninellis and Nerini, 1995; Polcaro et al., 1999). However, this aspect may require further confirmation in scale-up investigations.

4. Conclusions

Significant amounts of substituted phenols (PCP and PNP) can be removed from effluents by simple galvanostatic electrolysis with commercially available graphite or CTAB. In the absence of surfactants, the behavior at both the electrodes are similar. In the presence of CTAB, the TSIA electrode performs much more efficiently. The phenols are removed mainly through oxidative polymerization. Cationic surfactants favour polymerization in the liquid phase by blocking the adsorption of electro generated cation radical of phenol on the electrode surface. About 55–65% reduction in phenolic content may be achieved in a single batch by passing electric charge of 2.5 F per mol. Complete removal is possible through recycling the same solution after filtration of the polymeric product. The experiments also suggest the feasibility of a flow cell operation with a filtration step for the removal of solid polymer.

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References


Electrochemical homolytic and heterolytic coupling of activated olefins in the absence and presence of benzyl bromide in microemulsion

R. Sripriya • M. Chandrasekaran • M. Noel

Abstract

Electrochemical reduction of four activated olefins namely cyclohexenone (CH), cyclopentenone (CP), methacrylate (MMA), acrylonitrile (AN) in the absence and presence of benzylbromide (BBr) were investigated in CTAB/n-hexane/n-butanol/water based bicontinuous microemulsion (µE). Both cyclic voltammetric studies and galvanostatic preparative electrolysis were carried out. Cyclic voltammetric results in µE were also compared with those in N,N-dimethylformamide (DMF) medium. Adsorption effects are observed both in DMF and µE. AN undergoes one electron reduction in aprotic solvent and two electron reduction in µE. CH, CP, BBr undergo one electron reduction and yield significant homolytic coupled products under galvanostatic conditions. AN and MMA lead to two electron reduction under identical conditions. In the presence of BBr, CH and CP alone yield significant heterolytic coupled products with simultaneous competitive resin formation. Reduction of AN leads to the formation of a identifiable quantity of propylamine and 3-phenylpropylamine in the absence and in the presence of BBr, respectively.

Keywords
Coupling reactions • Benzyl bromide • Activated olefins • Microemulsions • Electrochemistry

1 Introduction

Electroreductive coupling of acrylonitrile (AN) to adiponitrile is one of the major successful industrial processes. This type of coupling process has received considerable attention and has been reviewed from time to time [1–3]. Mechanistic investigations have been carried out to understand the highly selective hydrodimerisation even in the aqueous medium in the presence of surfactants [4, 5]. Cross coupling or heterolytic coupling would be of significant interest in the carbon–carbon bond formation reactions. Successful electrochemical heterolytic coupling of activated olefins in the presence of organic halogen compounds have also been achieved in N,N-dimethylformamide (DMF) media with vitamin B12 as catalyst [6]. Activated olefins like cyclohexenone (CH) [7, 8] and cyclopentenone (CP) [9] have led to reasonable yields of dimeric products in DMF. However in this medium the formation of polymeric by-products invariably occurs even under potentiostatic conditions. Activated olefins like methacrylate (MMA) and AN mainly lead to polymer films in DMF and acetonitrile [10]. There are considerable challenges and opportunities in the synthetic chemistry of such coupling processes in aprotic solvents.

Microemulsions (µEs) are emerging as interesting greener synthetic media for a wide variety of organic processes [11, 12]. Rusling and coworkers have investigated some interesting electro organic processes in µEs [13, 14]. Inter and intra molecular coupling between activated olefins and alkyl halides have been the main reactions studied extensively [15–17]. Debromination [18] leading to the alkene formation in µE has been reported. Electrogeneration of carbene intermediate from dibromodihalomethane and subsequent coupling with activated olefins have also been investigated [19]. Apart from carbon electrodes used in the above reactions nano TiO2 electrodes have also been employed [20]. Redox catalysts like vitamin B12 are invariably employed as a mediator in µE media. To facilitate product separation, these redox centers may also be covalently bonded to the electrode surface [21–25]. All the
above synthetic investigations by Rusling and coworkers have been carried out under potentiostatic conditions. There is only one report from this group, which employs the galvanostatic method for such synthesis, where the yield was found to be low [26]. Further confirmation of the feasibility of electro organic synthesis in µEs is yet to emerge. Recently a report on the coupling reactions from ionic liquids has been published [27].

In some recent investigations from this laboratory the systematic physicochemical and electrochemical characterization of bicontinuous µEs [28], comparative voltammetric investigations of electro organic processes in aqueous, aprotic, micellar and µE media [29] and electrochemical detoxification processes [30] have been reported. In continuation a feasibility study of homolytic and heterolytic reductive coupling reactions in µE was taken up. Electroreduction of benzyl bromide (BBr), CH, CP, MMA and AN were studied. The heterolytic coupling processes of electrogenerated benzyl radical with all other activated olefins were also investigated. The main objective of this work was to study the possibility of carrying out these processes under galvanostatic conditions without employing any homogeneous or surface bound redox mediator, since such conditions would be ideal for practically feasible scaling up and process development. Cyclic voltammetric (CV) studies were also carried out in DMF and µE to compare the medium effect and identify the reaction pathways.

2 Experimental

2.1 Reagents

The high purity chemicals cetyl trimethylammonium bromide (CTAB) (Aldrich), n-hexane (Merck), n-butanol (Merck) was used for the preparation of µE. Dimethylformamide (Merck) containing 0.1 M tetra-n-butylammonium iodide (TBAl) (SRL) served as the aprotic media. The other chemicals were purchased from standard manufacturers benzylbromide (Alfa-Aesar), cyclohexenone (Acros), cyclopentenone (Acros), methylmethacrylate (Merck) and acrylonitrile (Merck).

2.2 Preparation of microemulsion

Bicontinuous µE was chosen in the present investigation to ensure sufficient electrical conductivity (through continuous aqueous phase) and adequate radical stability for coupling (through continuous organic phase). The µE was prepared by mixing CTAB, n-hexane, n-butanol and water in the composition 17.5, 12.5, 35, 35 wt%, respectively and then stirred vigorously until a clear solution is obtained.

2.3 Voltammetric studies

The voltammetric measurements were carried out in an Autolab PGSTAT-30 potentiostat/galvanostat controlled with the GPES 4.9 software (Eco-Chemie B.V., The Netherlands). An H-type glass cell with 15 ml capacity in the working electrode compartment was used for the voltammetric studies. The working electrode was a glassy carbon disc of 5 mm diameter obtained from Tokai GC-A. The counter and the reference electrodes were a platinum foil and a saturated calomel electrode, respectively. The glassy carbon electrode was polished with 1/0-4/0 emery sheets, washed with water and trichloroethylene prior to every experiment.

2.4 Galvanostatic experiments

A single compartment cell of 12 ml volume was used for all the galvanostatic experiments. Both the cathode and anode (3.5 cm² each) were graphite electrodes. A constant current of 10 mA cm⁻² was passed using a galvanostat. The charge corresponding to 2 F per mole was passed for AN and MMA, since clear indication of two electron reduction was obtained from CV experiments for these compounds. In other homolytic and heterolytic coupling reactions 1 F per mole was passed. In all cases 25% excess charge was also passed to ensure exhaustive electrolysis and enable product isolation. Constant stirring was given throughout the electrolysis. After electrolysis the reaction mixture was evaporated under vacuum and the surfactant was removed using ethylacetate/heptane in the ratio 7:3.

The product formed was characterized by High performance liquid chromatography (HPLC). An LC-10AT pump and an SPD-10A UV-detector (Shimadzu, Japan) at 254 nm with a Shim pack CLC ODS-18 column were used. A 70:30 (v/v) mixture of methanol/water was used as the mobile phase. The flow rate was 1.0 ml min⁻¹. IR spectrum was recorded as a liquid film (Perkin Elmer Paragon-500) and NMR spectrum was recorded using CDCl₃ as the solvent (Bruker-400 MHz).

Typically in the homolytic coupling reaction of BBr apart from the minor peak for the reactant a major peak corresponding to the product was obtained in HPLC. The coupled product bibenzyl was confirmed by IR (1,100-1,300 cm⁻¹, sharp peak due to —CH₂Br absent) and NMR [7.4 (aromatic proton), 2.9 (—CH₂—CH₂—)]. In the heterolytic coupling of CH and BBr, the major peak corresponding to the coupled product was obtained in HPLC. The product was further confirmed by IR (1,600 cm⁻¹ —C=C— absent, reduction in the intensity of —CH₂Br peak, 1,660 cm⁻¹ —C=O— present) and in NMR [7.2 (aromatic protons), 1-2 (alicyclic protons), 4.5 (proton adjacent to —C=O)]. The IR and NMR signals were also matched with standard spectrum.
3 Results and discussion

3.1 Voltammetric studies of individual compounds

Typical cyclic voltammograms of BBr in DMF and µE media are presented in Fig. 1. The peak current values after background correction vary within 10% in both the media. The cathodic peak potential in µE (−1.45 V) is more negative than in DMF (−1.25 V). This is quite contrary to the general trend of less negative potentials for a few molecules in the µE reported earlier [29] and for other organic molecules reported here Figs. 2, 3. This may be due to the presence of large concentration of Br⁻ ions from the surfactant (17.5 wt%) at the electrode-electrolyte interface exerting a negative influence for the production of additional bromide ions during the electro reduction of BBr.

CH and CP give two distinct reduction peaks in DMF. Typical CV along with the background current for CH in DMF is presented in Fig. 2a. CH gives two reduction peaks around −2.0 V and −2.75 V. The second cathodic reduction process occurs very close to the background reduction process. The exact quantification of this peak current thus becomes difficult. However, if one assumes that the background current also increases exponentially in this peak region, we may at least qualitatively conclude that the first and the second cathodic peak currents are quite similar.

The background current due to the hydrogen evolution increases significantly at less negative potentials in µE Fig. 2b. Hence only one cathodic peak (−1.65 V) is observed in µE. The peak current value in µE is similar to the first cathodic peak in DMF.

Typical CVs for MMA in DMF and µE media are shown in Fig. 3a. The cathodic peak currents are found to be similar in both the media. The cathodic peak potential in

![Fig. 1 Cyclic voltammograms for benzyl bromide reduction on GCE at 20 mV s⁻¹; (a) 5.4 mM BBr in (a) DMF containing 0.1 M TBAI, (b) µE](image1)

![Fig. 2 Cyclic voltammograms for cyclohexenone reduction on GCE at 20 mV s⁻¹; (a) 2.7 mM CH in DMF containing 0.1 M TBAI, (b) 2.7 mM CH in µE](image2)

![Fig. 3 Cyclic voltammograms for the reduction of (a) 4.17 mM MMA in (a) DMF containing 0.1 M TBAI, (b) µE; (b) 4.86 mM AN in (a) DMF containing 0.1 M TBAI, (b) µE at 20 mV s⁻¹](image3)
μE (−2.0 V) is found to be less negative when compared to DMF (−2.2 V).

The cathodic peak current for AN in DMF (Fig. 3ba) is found to be almost half the peak current value observed for the same compound in μE. The cathodic peak potential value is found to be lower in μE.

The first cathodic peak current value per unit concentration (Ip/C) at a constant sweep rate for all the individual compounds in DMF and μE are compared in Fig. 4a and b, respectively. For simple reductive processes without adsorption effects Ip/C value should remain constant. In the present work BBr, CH, CP in μE and BBr in DMF exhibit this behavior. The Ip/C value for CH in DMF show a slight decrease with increase in concentration, indicating weak adsorption effects especially at higher concentrations. In other cases Ip/C value decreases with increasing reactant concentration. This is a clear indication of weak adsorption of reactants on the electrode surface for AN, MMA in μE and DMF, CP in DMF.

The Ip/C values vary within a narrow range for BBr, CH, CP and AN in DMF medium. The Ip/C values for MMA at all concentrations investigated are found to be significantly higher than the Ip/C values for other compounds. It appears that in DMF, MMA undergoes two electron reductions, while all the other compounds undergo one electron reduction.

\[
\text{Ar-CH}_2\text{-Br} + \text{e}^- \rightarrow \text{Ar-CH}_2^+ \text{Br}^- \quad (1)
\]

\[
\text{Ar-CH}_2^+ + \text{Ar-CH}_2^- \rightarrow \text{ArCH}_2\text{CH}_2\text{Ar} \quad (2)
\]

The relative peak current values in μE media are compared in Fig. 4b. In this medium BBr, CH and CP appear to undergo one electron reduction. The Ip/C values for MMA in μE as well as DMF remain similar, indicating that this compound also undergoes a two electron reduction in μE. Relatively lower peak currents in DMF when compared to μE may be due to blocking type adsorption effects. The relative Ip/C values for An in DMF and μE once again indicate one electron reduction in DMF and two electron reduction in μE.

\[
\text{R}_1\text{R}_2\text{C} = \text{CR}_3\text{R}_4 + 2\text{e}^- \rightarrow \text{R}_1\text{R}_2\text{CH-CHR}_3\text{R}_4 \quad (4)
\]

3.2 Voltammetric studies of activated olefins in the presence of BBr

Typical cyclic voltammograms obtained for different concentrations of AN in the presence of 2.2 mM BBr in DMF media are presented in Fig. 5. There is a slight decrease in the peak current in the peak potential region corresponding to benzylbromide reduction, probably due to blocking adsorption with increase in total concentration of organic reactant (2.2 mM BBr + AN). The peak current due to the reduction of AN continues to increase with increase in concentration. Similar trends were noticed for CH, CP and
MMA in DMF medium. There is also an interesting split in the cathodic peak especially at higher concentrations of AN indicating stronger adsorption effects.

The voltammetric responses were also similar in μE medium. Typical cyclic voltammograms of different concentrations of CH in the μE containing 5.4 mM BBr are shown in Fig. 6. Again there is a slight decrease in cathodic peak current in the BBr reduction region. The cathodic peak current due to CH reduction continues to increase with increasing concentration of this compound. The voltammetric responses of CP, MMA, AN were found to be quite similar.

The general trend noticed for all the four activated olefins indicate that the electro reduction process in the BBr reduction region is not significantly influenced by the addition of activated olefins. The benzyl radical generated in this potential region however may be available for the coupling in the reduction potential regions of activated olefins. The results of coupling between these molecules can only be ascertained by constant potential or constant current electrolysis and product characterization.

The Ip/C values for all the four activated olefins in the absence and in the presence of BBr in both μE and DMF media are compared in Figs. 7 and 8, respectively. The same scale for Ip/C values is employed in both the figures to enable easier differentiation of Ip/C values for individual compounds. In this comparison one may encounter variations in Ip/C values, either due to the variation in the overall number of electrons transferred (one electron versus two electron) or due to other effects such as weak adsorption, variation in diffusion coefficient, transfer coefficient. It may however be presumed that the variations due to the latter factors may be lower whereas the effect of the number of electrons involved would be substantially higher;
and at least two electron reductions occur in DMF and µE, respectively. On addition of BBr, Ip/C values decrease substantially in DMF suggesting significant blocking effects. In contrast, Ip/C values increase significantly in the presence of BBr in µE media suggesting partial reduction of the cyano group in addition to the double bond reduction.

\[ \text{Ar-CH}_2 + \text{CH}_2 = \text{CH-CN} + 4e^- + 2H^+ \rightarrow \text{Ar-CH}_2 \text{-CH-CN} \]  

Some of the observations regarding product distribution, blocking effects and polymerization were further confirmed by galvanostatic preparative electrolysis.

### 3.3 Galvanostatic preparative electrolysis

The experimental conditions employed for the reduction of BBr and all the four activated olefins in µE and the main products obtained for each reactant are summarized in Table 1. BBr gave 45.6% yield of the dimer bibenzyl. CH and CP gave dimeric products with 28% and 27% yields. As suggested by voltammetric studies it appears that MMA undergoes a two electron reduction to methyl isobutyrate in µE. AN also undergoes two electron reduction to propionitrile as indicated by CV. IR and NMR data have also indicated the formation of an identifiable quantity of propylamine under galvanostatic conditions. Since all these products are low boiling they could not be quantitatively traced out in the residual portion after vacuum concentration.

In the homolytic coupling process discussed above the yield of the product was low. However, no significant quantities of polymeric or resinous material were detected either in the bulk solution or on the electrode surface as a film. The cross coupling products obtained for all the four activated olefins under galvanostatic conditions and their yields are summarized in Table 2.

Significant polymerization and resinous material formation was observed during the electrochemical reduction of CH and CP, correspondingly the yield of heterolytically coupled products was found to be around 10% and 19% for

### Table 1 Homolytic reductive coupling of the compounds in µE

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Charge passed/F</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl bromide</td>
<td>1.25</td>
<td>Bibenzyl</td>
<td>45.6</td>
</tr>
<tr>
<td>Cyclohexenone</td>
<td>1.25</td>
<td>Dimer</td>
<td>28.08</td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>1.25</td>
<td>Dimer</td>
<td>26.98</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>2.5</td>
<td>Propylamine</td>
<td>–</td>
</tr>
<tr>
<td>Methylmethacrylate</td>
<td>2.5</td>
<td>Methyl isobutyrate</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature: 25 °C, Current density 10 mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTAB µE: 17.5 wt% CTAB + 12.5 wt% n-hexane + 35 wt% n-butanol + 35 wt% water</td>
</tr>
</tbody>
</table>
in CV and galvanostatic preparative electrolysis. MMA exhibit direct two electron reduction behavior both reduction peaks in CV, also leads to significant yields of excess of BBr, CH and CF, which show one electron group can occur simultaneously leading to poor selectivity. Conditions electro reduction of BBr and activated olefin reduction region or in the reduction region of redox mediator.

Constant potential electrolysis can be carried out in the BBr potential regions separated by approximately 300 mV. During electrode processes can show variation between blocking effects at higher concentrations required for electro synthesis. This is probably one of the reasons for decrease with increase in reactant concentration indicating the success of electrochemical coupling processes in the presence of BBr. The yields of heterolytic coupling products obtained in these two cases were also quite low especially in the case of MMA. It is interesting to note that in the case of AN the coupled product was 3-phenylpropylamine rather than 3-phenylpropionitrile.

4 Conclusions

The present investigation brings out some insights into the scope and limitations of electrochemical coupling processes in μEs. CV data indicate that Ip/C values generally decrease with increase in reactant concentration indicating blocking effects at higher concentrations required for electro synthesis. This is probably one of the reasons for the success of electrochemical coupling processes in μEs in the presence of redox mediators like Vitamin B12 [21-25].

CVs indicate that even the number of electrons transferred during electrode processes can show variation between aprotic and μE media. For example AN undergoes one electron reduction in DMF and two electron reduction in μE.

BBr (−1.45 V) and other activated olefins (−1.7 to −1.9 V) undergo electro reduction in different distinct potential regions separated by approximately 300 mV. Constant potential electrolysis can be carried out in the BBr reduction region or in the reduction region of redox mediator (for e.g. −0.75 V for Vitamin B12). Under galvanostatic conditions electro reduction of BBr and activated olefin group can occur simultaneously leading to poor selectivity.

Despite the above limitations homolytic coupling process of BBr, CH and CP, which show one electron reduction peaks in CV, also leads to significant yields of coupled products under galvanostatic conditions. AN, MMA exhibit direct two electron reduction behavior both in CV and galvanostatic preparative electrolysis.

One electron reduction leading to free radical formation of the activated olefin (CH, CP) appears to be an important determining factor for achieving heterolytic coupling. Under galvanostatic conditions both benzyl radicals and reduced activated olefin radicals would be present. It appears that simultaneous formation of resinous products also occurs to a significant extent in these conditions.

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Table 2 Heterolytic coupling of activated olefins in the presence of BBr in μE

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Ratio of activated olefin: BBr</th>
<th>Product</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexenone</td>
<td>5:1</td>
<td>2-Benzyl cyclohexanone</td>
<td>9.85</td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>5:1</td>
<td>2-Benzyl cyclopentanone</td>
<td>19.07</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>5:1</td>
<td>3-Phenylpropylamine</td>
<td>14.88</td>
</tr>
<tr>
<td>Methylmethacrylate</td>
<td>5:1</td>
<td>3-Phenylmethylbutyrate</td>
<td>&lt;2</td>
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</tbody>
</table>

Temperature: 25 °C, Current density: 10 mA cm⁻², Charge passed: 1.25 F

CTAB μE: 17.5 wt% CTAB + 12.5 wt% n-hexane + 35 wt% n-butanol + 35 wt% water

these two compounds. The competitive two electron reduction in the case of AN and MMA lead to low boiling volatile products as discussed above. Hence no resinous material was obtained during the galvanostatic electrolysis of these compounds in the presence of BBr. The yields of heterolytic coupling products obtained in these two cases were also quite low especially in the case of MMA. It is interesting to note that in the case of AN the coupled product was 3-phenylpropylamine rather than 3-phenylpropionitrile.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>14.88</td>
</tr>
<tr>
<td>Cyclohexenone</td>
<td>9.85</td>
</tr>
<tr>
<td>Cyclopentenone</td>
<td>19.07</td>
</tr>
<tr>
<td>Methylmethacrylate</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>

References