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# 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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## 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 elec-

trochemical 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.

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), and cyclic systems such as cyclohexane (Merck), benzene (Merck), toluene (Ranbaxy), and *p*-xylene (Sd 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 $20 \pm 0.1\,°C$.

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 $25 \pm 0.1\,°C$.

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 ($I_1/I_3$). The concentration of pyrene was 9.89 μM. Good resolution of the bands was obtained at the slit width $5 \times 2.5$ nm. The intensities for $I_1$ and $I_3$ 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

Table 1
Relative viscosity (cP) of microemulsions measured at $20 \pm 0.1\,°C$

| Oil phases used | *n*-Butanol as co-surfactant | | *n*-Pentanol as co-surfactant | |
|---|---|---|---|---|
| | CTAB | SDS | CTAB | SDS |
| Hexane | 4.9180 | 5.1242 | – | – |
| Heptane | 5.4161 | 5.3343 | 10.1898 | 10.1232 |
| Isooctane | 4.7457 | 5.5177 | 9.9616 | 9.7130 |
| Dodecane | 6.2911 | 6.0962 | 13.1359 | 12.0283 |
| Tetradecane | 6.5573 | 6.2671 | 14.1237 | 11.7726 |
| Hexadecane | – | – | 14.3000 | 11.8246 |
| Cyclohexane | 6.8532 | 6.592 | – | – |
| Benzene | 5.8970 | 6.695 | – | – |
| Toluene | 7.1383 | 6.695 | – | – |
| *p*-Xylene | 6.0688 | 6.592 | – | – |

Table 2
Conductivity (mS cm$^{-1}$) measurements of microemulsions measured at $25 \pm 0.1\,°C$

| Oil phases used | *n*-Butanol as co-surfactant | | *n*-Pentanol as co-surfactant | |
|---|---|---|---|---|
| | CTAB | SDS | CTAB | SDS |
| Hexane | 5.356 | 7.004 | – | – |
| Heptane | 3.708 | 7.828 | 0.927 | 4.429 |
| Isooctane | 3.708 | 8.034 | 0.927 | 4.326 |
| Dodecane | 4.944 | 6.901 | 1.442 | 5.974 |
| Tetradecane | 4.841 | 7.725 | 1.545 | 6.180 |
| Hexadecane | – | – | 1.751 | 6.489 |
| Cyclohexane | 3.708 | 6.592 | – | – |
| Benzene | 4.017 | 6.695 | – | – |
| Toluene | 4.017 | 6.695 | – | – |
| *p*-Xylene | 3.914 | 6.592 | – | – |

Table 3
Fluorescence measurements ($I_1/I_3$) of molecular probe pyrene in bicontinuous microemulsions

| Oil phases used | For pure oil phases alone | *n*-Butanol as co-surfactant | | *n*-Pentanol as co-surfactant | |
|---|---|---|---|---|---|
| | | CTAB | SDS | CTAB | SDS |
| Hexane | 0.6561 | 1.0292 | 0.9236 | – | – |
| Heptane | 0.6438 | 0.9742 | 0.9186 | 1.0206 | 0.8937 |
| Isooctane | 0.6789 | 1.006 | 0.9203 | 0.9996 | 0.9355 |
| Dodecane | 0.6007 | 0.9532 | 0.8592 | 0.9595 | 0.8700 |
| Tetradecane | 0.6232 | | 0.8324 | 0.9522 | 0.8762 |
| Hexadecane | 0.6074 | – | – | 0.9516 | 0.8826 |
| Cyclohexane | 0.6068 | 0.9999 | 0.9346 | – | – |
| Benzene | 1.1677 | 1.0832 | 0.9841 | – | – |
| Toluene | 1.0844 | 1.0925 | 1.0149 | – | – |
| *p*-Xylene | 0.9618 | 1.0880 | 0.9976 | – | – |

*Note*. Pyrene concentration 9.89 µM; excitation wavelength: 337 nm; slit width $5 \times 2.5$ nm $I_1/I_3$ values of pure alcohols in similar conditions; *n*-butanol: 1.1550; *n*-pentanol: 1.0358; $I_1/I_3$ value for water = 1.81.

electrode was used. Saturated calomel electrode (SCE) served as the reference electrode. The pretreatment procedure adopted in this work for glassy carbon electrode to give reproducible voltammetric responses in microemulsion medium was already explained in an earlier communication [27].

## 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 cyclic structure.

### 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 (C16) when compared to SDS (C12). Thus higher surfactant–oil interaction leads to higher viscosity values in CTAB based microemulsions.

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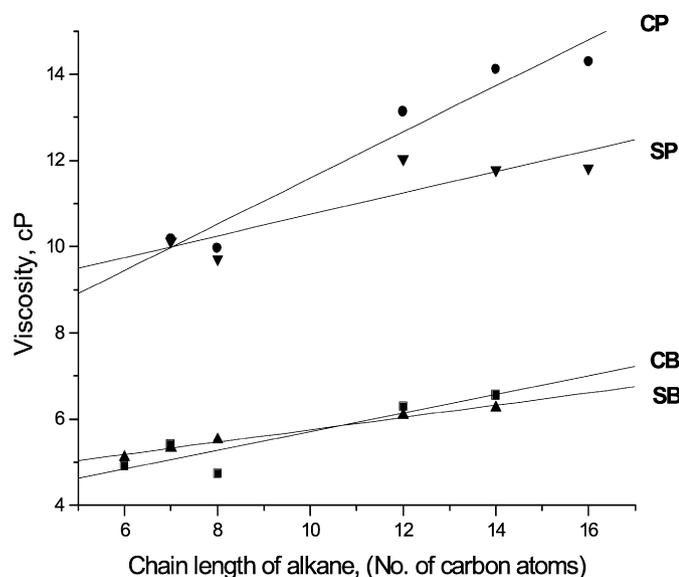
Fig. 1. Viscosity variations with the increase in chain length of the linear oil phase employed. CB, CTAB/*n*-butanol/oil phase/water system; CP, CTAB/*n*-pentanol/oil phase/water system; SB, SDS/*n*-butanol/oil phase/water system; SP, SDS/*n*-pentanol/oil phase/water system. Viscosities measured at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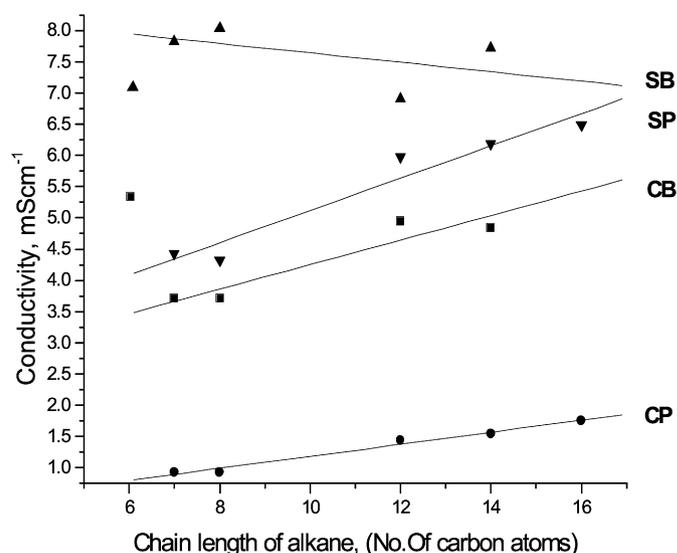


Fig. 2. Conductivity variations with the increase in chain length of the linear oil phase employed. CB, CTAB/*n*-butanol/oil phase/water system; CP, CTAB/*n*-pentanol/oil phase/water system; SB, SDS/*n*-butanol/oil phase/water system; SP, SDS/*n*-pentanol/oil phase/water system. Conductivities measured at $25 \pm 0.1\,°C$.

Fig. 1). In *n*-butanol based microemulsions the viscosity value 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 $\Delta E_p$ ($60 \pm 4$ 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
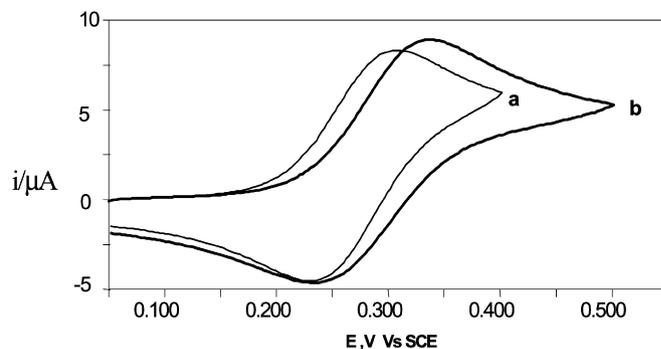


Fig. 3. Cyclic voltammograms of 2 mM ferrocene on GCE in microemulsions at 20 mV s$^{-1}$: (a) SDS/hexane/$n$-butanol/water, (b) SDS/$p$-xylene/$n$-butanol/water.
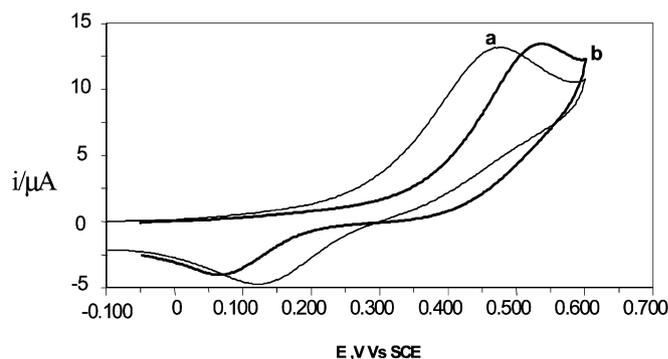


Fig. 4. Cyclic voltammograms of 2 mM hydroquinone on GCE in microemulsions at 20 mV s$^{-1}$: (a) CTAB/hexane/$n$-butanol/water, (b) CTAB/$p$-xylene/$n$-butanol/water.

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 physico-chemical 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 ionic 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.

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