Sulfide accumulation and sensing based on electrochemical processes in microdroplets of N^1-[4-(dihexylamino)phenyl]-N^1,N^4,N^4-trihexyl-1,4-phenylenediamine

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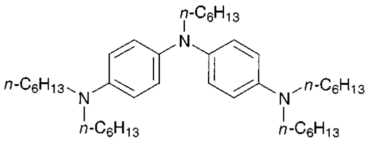
Electroanalytical sulfide detection *via* oxidation of N^1-[4-(dihexylamino)phenyl]-N^1,N^4,N^4-trihexyl-1,4-phenylene diamine (DPTPD) deposited in form of microdroplets onto basal plane pyrolytic graphite electrodes immersed in aqueous 0.1 M $NaClO_4$ containing sulfide is proposed to be associated with two consecutive reversible one electron processes accompanied by ClO_4^- uptake, sulfide accumulation, and formation of a methylene blue derivative.

Voltammetric experiments at microdroplets of electrochemically active materials deposited on suitable types of electrode surfaces in form of an organic oil have recently been shown to result in unique electrochemical characteristics.[1,2] An organic redox system such as phenylenediamine can be made highly insoluble in aqueous media by introducing several hexyl chains into the molecular structure. With this kind of derivatisation the resulting material shows as a further useful property an extremely low tendency to crystallise or freeze into a solid glass. Surprisingly, the liquid nature of the material at room temperature remains even after oxidation and the associated uptake of anions from the solution phase to achieve charge neutrality. The material resulting from this type of redox process, a room temperature ionic liquid, is of considerable interest for electrochemical applications requiring ion accumulation and/or ion conduction.

Redox processes in microdroplets of organic oils proceed *via* exchange of anions with the surrounding solution phase and for chemically reversible processes, such as the first oxidation of tetrahexylphenylenediamine,[1] the ion exchange process has been shown to be very fast. Usually the most hydrophobic anion crosses from the aqueous into the organic liquid phase most readily. In cases in which secondary chemical processes are coupled to the redox process much more complicated conditions arise. Voltammograms become chemically irreversible and products mix with the original oil phase or escape into the aqueous solution phase. The presence of a product with a redox potential different to that of the starting material may interfere with the mass and charge transport in the microdroplet and therefore considerably change the voltammetric characteristics. The rate of the chemical follow up step is a crucial parameter which determines whether (i) the redox process can be driven to completion before reaction or (ii) the chemical step is fast and directly proceeds thereby effectively stopping any charge transport by electron hopping in the zone close to the electrode.

In the present study a novel redox system, N^1-[4-(dihexylamino)phenyl]-N^1,N^4,N^4-trihexyl-1,4-phenylenediamine (DPTPD, structure **I**) is deposited in form of microdroplets onto basal plane pyrolytic graphite electrodes, immersed in aqueous electrolyte media, and used in voltammetric experiments. A key feature of this type of molecule is its ability in the presence of sulfide to undergo a nucleophilic substitution reaction at the aromatic rings to yield phenothiazine type derivatives.[3] This type of process is known as the 'methylene blue reaction'[4] and used for the selective and highly sensitive analytical determination of traces of sulfide with *N*,*N*-dimethylphenylenediamine and a chemical oxidant, Fe^{3+}. The preliminary work described here is aimed at coupling the highly selective chemical sulfide detection method *via* the methylene blue process to the electrochemical process in the microdroplet deposit at the electrode surface.



I

DPTPD deposited onto a basal plane pyrolytic graphite electrode surface and immersed into aqueous 0.1 M $NaClO_4$ undergoes two well defined and reversible oxidation processes shown in Fig. 1. Based on the comparison of the amount of material deposited, 1.7×10^{-9} M corresponding to 0.17 mC per electron transferred, and the charge under the first and second oxidation responses (combined 0.34 ± 0.03 mC), the processes may be identified as the first and the second oxidation of DPTPD [eqn. (1) and (2)]. For this amount of deposit present on

$$\mathrm{DPTPD_{oil}} + \mathrm{ClO_4^-{}_{solution}} \rightleftarrows [\mathrm{DPTPD^+ClO_4^-}]_{\mathrm{oil}} + e^- \quad (1)$$

$$[\mathrm{DPTPD^+ClO_4^-}]_{\mathrm{oil}} + \mathrm{ClO_4^-{}_{solution}} \rightleftarrows [\mathrm{DPTPD^{2+}(ClO_4^-)_2}]_{\mathrm{oil}} + e^- \quad (2)$$

the surface of the graphite electrode the charge under the voltammetric response for the oxidation (Fig. 1) is essentially independent of the scan rate over the range of 1–100 mV s^{-1} and therefore a nearly complete conversion of the material even at moderately fast scan rate appears to be possible. However, the lack of symmetry in the observed voltammetric responses[5] suggests that mass transport effects are present and affect the shape. Voltammetric data are summarised in Table 1. The comparison of the voltammetric characteristics with results obtained for the oxidation of THPD under similar conditions[1] suggests that DPTPD is chemically much more stable in the dicationic oxidation state because of delocalisation of the

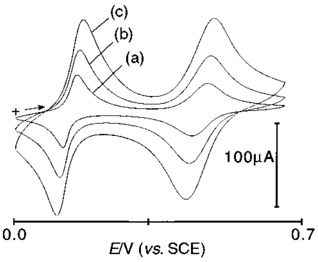


Fig. 1 Cyclic voltammograms obtained for the oxidation of 1.7×10^{-9} mol DPTPD deposited onto a 4.9 mm diameter basal plane pyrolytic graphite electrode and immersed in aqueous 0.1 M $NaClO_4$. The third cycle from a multicycle experiment is shown for scan rates of (a) 20, (b) 50 and (c) 100 mV s^{-1}.

Table 1 Voltammetric data for the oxidation of 1.7 × 10^{-9} mol DPTPD deposited onto a 4.9 mm diameter basal plane pyrolytic graphite electrode and immersed in aqueous 0.1 M $NaClO_4$

Scan rate/ V s^{-1}	E_p^{ox}/ V(*vs.* SCE)	I_p^{ox}/ μA	E_p^{red}/ V (*vs.* SCE)	I_p^{red}/ μA	ΔE^a/ mV	$E_{1/2}{}^b$/ V (*vs.* SCE)	ΔE_{hh}/ mV
First oxidation process: $DPTPD^{0/+}$							
0.02	0.158	44	0.124	−44	34	0.141	66
0.05	0.165	75	0.116	−80	49	0.140	80
0.10	0.173	109	0.110	−124	63	0.141	100
Second oxidation process: $DPTPD^{+/2+}$							
0.02	0.498	34	0.457	−28	41	0.477	120
0.05	0.505	68	0.452	−62	53	0.478	133
0.10	0.515	113	0.444	−106	71	0.480	165

[a] Peak-to-peak separation of the voltammetric responses associated with oxidation and the reduction. [b] The half wave potential, $E_{1/2}$, corresponds to the mid-potential given by $1/2(E_p^{ox} + E_p^{red})$.

positive charge over both aromatic rings (see structure **I**). Changes in shape or width at half height, ΔE_{hh}, of the voltammetric response, may be interpreted as a measure of the interaction of redox centres in the organic oil.[6] The wider peak for the second oxidation process is consistent with a better mixing or repulsive interaction in the regular solution model[7] of the $DPTPD^{2+}$ and $DPTPD^+$ containing ionic liquids compared to the mixing of the $DPTPD^+$ containing ionic liquid and the neutral oil.

The experiment shown in Fig. 1 has been conducted with 1.7 × 10^{-9} mol deposit. It can be calculated, based on the geometric area of the electrode and a hypothetic density of DPTPD of 0.5 g cm^{-3}, that this amount corresponds to a layer of *ca.* 57 nm height. However, owing to the surface morphology of the basal plane pyrolytic graphite microdroplets of *ca.* 0.1 μm size are anticipated. Changing the amount of deposited material causes a corresponding change in the charge under the voltammetric signals, although for high coverages corresponding to a layer of more than *ca.* 1 μm height the time for the redox process to go to completion becomes long (several minutes).

When the concentration of the supporting electrolyte is changed or other types of anion such as nitrate are used characteristic changes in form of shifts in the reversible potential, $E_{1/2}$, following the same trend observed in earlier studies are detected. However, in the presence of SH^- ions, the voltammetric response for the oxidation of DPTPD changes dramatically. Fig. 2 shows voltammetric responses for the oxidation of a deposit of 4.2 × 10^{-9} mol DPTPD on a 4.9 mm diameter basal plane pyrolytic graphite electrode immersed in aqueous 0.1 M $NaClO_4$ containing 2 mM HS^-. It can be seen that the main response at $E_{1/2}$ = 0.14 V *vs.* SCE drastically changes over consecutive potential cycles. A new broad response at E_p^{ox} = *ca.* 0.3 V *vs.* SCE can be detected on the first positive scan of a multi-cycle voltammogram and a product response gradually appears at $E_{1/2}$ = *ca.* −0.1 V *vs.* SCE. Qualitatively, the rate at which the change in the voltammogram occurs depends on the concentration of sulfide present in the solution phase and the experimental conditions such as the scan rate.

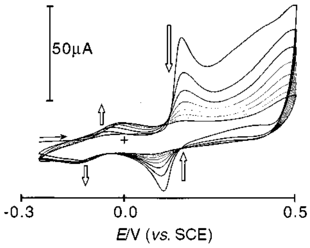
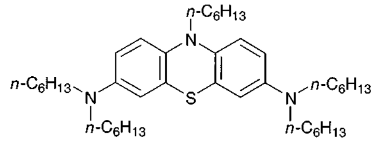


Fig. 2 Cyclic voltammograms obtained for the oxidation of 3.4 × 10^{-9} mol DPTPD deposited onto a 4.9 mm diameter basal plane pyrolytic graphite electrode and immersed in aqueous 0.1 M $NaClO_4$ containing 2 mM HS^- (scan rate: 20 mV s^{-1}).

Based on the known redox chemistry of dimethylphenylenediamine[4] it is proposed that the product of the chemical reaction step in the microdroplet is a hexyl derivative of methylene blue (PHPD, structure **II**). A hypothesis for the overall mechanism of



II

this reaction, which involves DPTPD in the monocationic state, is given in eqn. (3). The voltammetric response associated with the formation of the product with $E_{1/2}$ = *ca.* −0.1 V *vs.* SCE may be proposed to result from the reversible one electron redox process given in eqn. (4). The range of organic oils giving room

$$[DPTPD^+ClO_4^-]_{oil} + HS^- \rightarrow [PHPD^+ClO_4^-]_{oil} + 3\ H^+ + 4\ e^- \qquad (3)$$

$$[PHPD^+ClO_4^-]_{oil} + e^- \rightleftharpoons PHPD_{oil} + ClO_4^- \qquad (4)$$

temperature ionic liquids can be easily extended by derivatising the core redox molecule with long chain alkyl groups and chemical systems of high analytical value can be employed. The novel electroanalytical procedure based on sulfide accumulation in oil microdroplets by ion-exchange and selective detection by a chemical reaction sequence promises to combine high selectivity and sensitivity and is open to the use of combined spectroelectroanalytical techniques.

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Notes and references

† The redox active reagent N^1-[4-(dihexylamino)phenyl]-N^1,N^4,N^4-trihexyl-1,4-phenylenediamine (DPTPD) was prepared *via* refluxing N^1-[4-aminophenyl]-1,4-phenylenediamine (200 mg) with sodium hydride (192 mg, 8 equiv.) and hexyl bromide (1.32 g, 8 equiv.) in DMF (20 ml) at 90 °C for 12 h. The crude reaction mixture was purified by pouring into water (20 ml), extracted with ethyl acetate (3 × 20 ml), dried ($MgSO_4$), and the solvent removed in vacuum, and the resulting crude oil purified by chromatography over silica gel (2% Et_2O–98% hexane) to afford the title compound (142 mg) pure in 23% yield. ^1H NMR(d^8-toluene,200 MHz); 0.87 (15H, br t), 1.15 (30H, br), 1.48 (8H, br), 1.65 (2H, br), 3.10 (8H, br t), 3.55 (2H, br t), 6.61 (4H, br d), 6.95 (4H, br d); *m/z* (CI) 620 (M + 1); HRMS, calc. for $C_{42}H_{74}N_3$ 620.5883, found 620.5891.

Electrochemical experiments were conducted in a conventional three-electrode cell with a 4.9 mm diameter basal plane pyrolytic graphite working electrode, a gold wire counter electrode and a saturated calomel (SCE, Radiometer, Kopenhagen) reference electrode. A potentiostat (Autolab PGSTAT 20, Ecochemie, Netherlands) was used for cyclic voltammetric experiments. The procedure for the deposition of DPTPD microdroplets on the surface of the basal plane pyrolytic graphite electrode was based on evaporation of a solution of 0.1 mM DPTPD in acetonitrile. Solutions were degassed with argon (Pureshield, BOC) for at least 15 min prior to experiments. All studies were carried out at 20 ± 2 °C.

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