Formation of oligomers of methyl- and phenyl-pyrrole at an electrified liquid/liquid interface

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The formation of oligomers of 1-methylpyrrole and 1-phenylpyrrole has been initiated by a heterogeneous electron transfer (HET) step at the interface of two immiscible electrolyte solutions; the HET leads to the formation of a radical cation of the monomer in the organic phase.

In 1975 Guainazzi *et al.*[1] reported that a direct current applied across the liquid/liquid interface of a heterogeneous, unreactive $Cu^{2+}/[V(CO)_6]^-$ redox system, with $CuSO_4$ in the aqueous phase and tetrabutylammonium hexacarbonylvanadate in a 1,2-dichloroethane (DCE) phase, led to the deposition of a copper layer at the interface. More recently electrochemical–chemical (EC) type mechanisms have been reported for such liquid/liquid interfaces.[2,3] Here we report on a novel EC type reaction between an aqueous redox couple and a monomer in DCE leading to oligomer formation in the organic phase, where for the first time the electrochemical step is an electron transfer.

A general scheme for the equilibrium condition for the two phase electron transfer reaction [eqn. (1)] where a reducible

$$n^2O^{1(w)} + n^1R^{2(o)} \leftrightarrow n^1O^{2(o)} + n^2R^{1(w)} \qquad (1)$$

species O^1 in the aqueous phase reacts with an oxidisable species R^2 in the organic phase can be expressed in terms of individual ionic activities and the Galvani potential of each phase, leading to a Nernst type equation of the form shown in eqn. (2), where $E°_i$ is the standard potential of the couples in

$$\Delta^w_o\phi = E°_{R^2/O^2} - E°_{R^1/O^1} + (RT/n^1n^2F)\ln J_a \qquad (2)$$

each phase, R is the gas constant, T is the absolute temperature, F the Faraday constant and J_a is given by eqn. (3), where a is the

$$J_a = a^{n^2}_{R^1}a^{n^1}_{O^2}/a^{n^2}_{O^1}a^{n^1}_{R^2} \qquad (3)$$

activity of the species in each phase. As such, the position of equilibrium in a two phase redox system is dependent on the values of the standard potentials and also on the interfacial Galvani potential difference.[4] Hence for a given system the position of equilibrium can be determined by an externally imposed Galvani potential difference, using standard electrochemical instrumentation. A HET reaction can thus be observed in the available potential window by careful matching of the standard potentials of the redox couples in each phase.

Cyclic voltammetry (CV) was the main technique used. A flat water/1,2-DCE interface with an area of 0.125 cm^2 was formed in a four electrode cell. The potential difference at the interface was controlled using a four electrode potentiostat (Model 2000, Sycopel Scientific Ltd., Boldon).

DCE (Fluka 99.5% GC grade) was used as received as the organic solvent in all experiments. 18.2 MΩ water used throughout and was prepared using the Maxima ultra pure water system. Li_2SO_4 (Fluka $>$98.0%) was used as received as the aqueous supporting electrolyte. Tetraphenylarsonium chloride (TPAsCl) (Fluka, 95%) was used as received in the organic reference phase. Tetraphenylarsonium tetrakis(4-chlorophenyl)borate (TPAsTCPB) was the supporting electrolyte in the organic phase and was prepared using TPAsCl and sodium tetrakis(4-chlorophenyl)borate (NaTCPB) (Fluka $>$98.0%). Ferrous sulfate·7H_2O(Aldrich 99+%), ferric sulfate·5H_2O(Aldrich 97%), 1-methylpyrrole (MPy, Aldrich 99%) and 1-phenylpyrrole (PPy, Aldrich 99%) were also used as received.

To measure the half-wave potentials ($E_{1/2}$) of the aqueous redox couples and the oxidation potentials of the monomers in DCE a 10 μm platinum microelectrode was used. The $E_{1/2}$ of oxidation of 1-methylpyrrole and 1-phenylpyrrole, in the organic electrolyte system, were found to be 750 and 720 mV *vs.* SCE, respectively. Fe^{2+}/Fe^{3+} in the form of $Fe_2(SO_4)_3$/$Fe(SO_4)$ was chosen as the aqueous redox couple as it has a closely matching halfwave potential, with an $E_{1/2}$ of 650 mV *vs.* SCE in the aqueous electrolyte system.

The cell used to observe the electron transfer is shown in Scheme 1,where the monomer is 1-methylpyrrole or 1-phenylpyrrole and δ represents the interface.

Pt/10 mmol Li_2SO_4 + 10 mmol $Fe_2(SO_4)_3$ and 10 mmol
$FeSO_4$ (aq)/δ/1 mmol TPAsTCPB + 0.5 mmol monomer
(DCE)/1 mmol TPAsCl (aq)/AgCl/Ag

Scheme 1

When the aqueous redox couple is present and in the absence of monomer in the organic phase no charge transfer is observed in the potential window of interest and also no charge transfer is observed when the monomer is present but in the absence of the aqueous redox couple.

When both the aqueous redox couple and monomer are present a charge transfer reaction occurs, this is shown in Fig. 1(*a*). It was found that on continuous cycling the shape of the CV trace changes to give a characteristic S-shaped curve [Fig 1 (*b*)].

From eqn. (2) it can be seen that for a HET reaction, changing the ratio of concentrations of the aqueous redox couple should change the $E_{1/2}$ of the electron transfer reaction and, as can be seen from Tables 1 and 2, this is indeed the case.

Table 1 shows the variation of $E_{1/2}$ for the charge transfer reaction with varying Fe^{III}:Fe^{II} when the cell is: Pt/10 mmol Li_2SO_4 + x mmol $Fe_2(SO_4)_3$ and y mmol $FeSO_4$ (aq)/δ/1 mmol TPAsTCPB + 0.5 mmol MPy (DCE)/1 mmol TPAsCl (aq)/AgCl/Ag.

Table 2 shows the variation of $E_{1/2}$ for the electron transfer reaction with varying Fe^{III}:Fe^{II} when the cell is: Pt/10 mmol Li_2SO_4 + x mmol $Fe_2(SO_4)_3$ and y mmol $FeSO_4$ (aq)/δ/1 mmol TPAsTCPB + 0.5 mmol PPy (DCE)/1 mmol TPAsCl (aq)/AgCl/Ag.

Table 1 Variation of $E_{1/2}$ with varying Fe^{III}:Fe^{II} for the charge transfer reaction with MPy

Ratio Fe^{3+}:Fe^{2+}	$Fe_2(SO_4)_3$/ mmol	$Fe(SO_4)$/ mmol	$E_{1/2}$/mV
1:5	1	10	565
2:1	10	10	640
4:1	10	5	660
10:1	10	2	No e-transfer

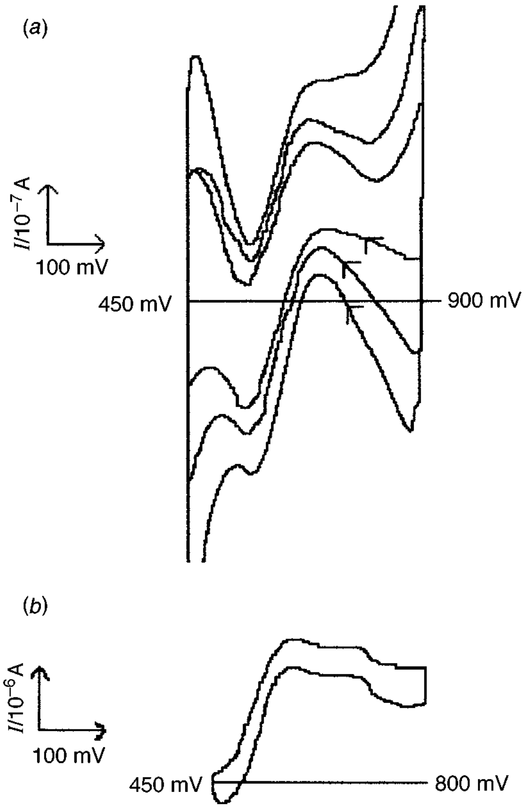

Fig. 1 (*a*) Cyclic voltammograms of the system: Pt/10 mmol Li_2SO_4 + 10 mmol $Fe_2(SO_4)_3$ and 10 mmol $FeSO_4$ (aq)/δ/1 mmol TPAsTCPB + 0.5 mmol MP (DCE)/1 mmol TPAsCl (aq)/AgCl/Ag. Sweep rates: 10, 25 and 50 mV s^{-1}. (*b*) Cyclic voltammogram of the system: Pt/10 mmol Li_2SO_4 + 10 mmol $Fe_2(SO_4)_3$ and 10 mmol $FeSO_4$ (aq)/δ/1 mmol TPAsTCPB + 5 mmol MP (DCE)/1 mmol TPAsCl (aq)/AgCl/Ag after cycling for 30 min at a sweep rate of 100 mV s^{-1}.

The changing shape of the cyclic voltammogram suggested that the electron transfer reaction is not reversible and that the organic phase changes throughout the experiment. UV–VIS spectroscopy was used to study the organic phase. The organic phase was removed from the cell and transferred to a quartz cuvette.

The 1-methylpyrrole monomer shows a characteristic peak at 247 nm when dissolved in DCE. On addition of the base electrolyte salt TPAsTCPB this characteristic monomer peak disappears and a new peak is detected at 271 nm. The disappearance of the monomer peak is probably due to the fact that this sample is blanked using 10 mmol TPAsTCPB, which absorbs in the region below 300 nm. After cycling for 10 min a peak is detected at 293 nm and after 20 min of cycling a peak is detected at 309 nm.

Table 2 Variation of $E_{1/2}$ with varying Fe^{III}:Fe^{II} for the electron transfer reaction with PPy

Fe^{3+}:Fe^{2+}	$Fe_2(SO_4)_3$/ mmol	$Fe(SO_4)$/ mmol	$E_{1/2}$/mV
1:5	1	10	No e-transfer
2:1	10	10	630
20:1	10	1	690

The 1-phenylpyrrole monomer shows a characteristic peak at 260 nm when dissolved in DCE. On addition of the base electrolyte salt TPAsTCPB a peak is observed at 292 nm. After cycling for 10 min a peak is detected at 304 nm, which does not change significantly with further cycling.

Rohde *et al.*[5] reported that the absorbtion maxima of oligomers of 1-methylpyrrole increase with increasing chain length. They found that 1-methylpyrrole monomer has a λ_{max} value of 250 nm increasing to λ_{max} of 290 nm for oligomers with eight methylpyrrole units. They extrapolated the λ_{max} of the insulating polymer, an oligomer of infinite chain length, to be 310 nm.

This change in λ_{max} is observed here for 1-methylpyrrole (and 1-phenylpyrrole) with increasing cycling time. This is an indication that oligomers are being formed in the organic phase.

We have shown for the first time that an electron transfer reaction can be brought about between an aqueous-based redox system and an organic-based monomer unit at an electrified liquid/liquid interface. It is presumed that the electron transfer results in the formation of a radical cation in the organic phase. This radical cation will then undergo various chemical steps leading to the formation of oligomers in the organic phase. Further research is investigating the nature of the oligomers formed and their conducting properties. The system is being expanded to look at other electroactive monomer and organic systems.

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Notes and References

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