

## Biphasic Voltammetry of $\alpha$ -Tocopherol Studied as Femtolitre Droplets Immobilized onto Graphite Electrodes

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Charge transfer across the interface between two immiscible liquids has significant roles in biology and chemistry and, as such, has been the focus of much electrochemical investigation. One methodology which allows the interrogation of such biphasic systems involves the immobilization of random arrays of micron-sized droplets of water-immiscible liquids onto a basal plane pyrolytic graphite (bppg) electrode. Immersion of droplet modified electrodes into aqueous electrolyte media then allows the probing of the liquid\*liquid interface using voltammetric methods. This technique has been used to study a plethora of redox "switchable" liquids in this biphasic environment [1].

$\alpha$ -Tocopherol ( $\alpha$ -TOH) is a naturally occurring, lipophilic liquid belonging to the vitamin E family and has a variety of functions in biological systems [2,3]. One of its major roles is as an antioxidant within the phospholipid bilayer of living cells, which derives from its ability to inhibit free radical chain peroxidations by donating its phenolic H-atom, yielding a relatively stable radical species. The biological importance of this vitamin makes it an interesting subject for electrochemical investigations which, combined with its hydrophobic nature, makes it an ideal liquid to study using the microdroplet technique.

In this work, the voltammetric behaviour of immobilized microdroplets  $\alpha$ -TOH in supported aqueous media is reported. Under these conditions, the electrochemical oxidation is shown to involve two competing pathways initially involving either one or two electrons, the products of which undergo chemical reactions to form electroactive species (figure 1).

The proposed two electron pathway generates a quinone via ring opening hydrolysis at the electrode |  $\alpha$ -TOH | aqueous electrolyte three-phase boundary of the femtolitre volume droplets which undergoes reduction on the reverse sweep (scheme 1). The single electron oxidation produces a dimer, via the coupling of  $\alpha$ -Tocopherol derived radicals, which can be oxidized further to produce cyclized spiro-dimer (scheme 2). Both processes involve the deprotonation of the starting material, suggesting that the initial electrochemical steps are preceded by proton expulsion from the  $\alpha$ -TOH into aqueous solution in order to maintain charge neutrality in the droplet phase.

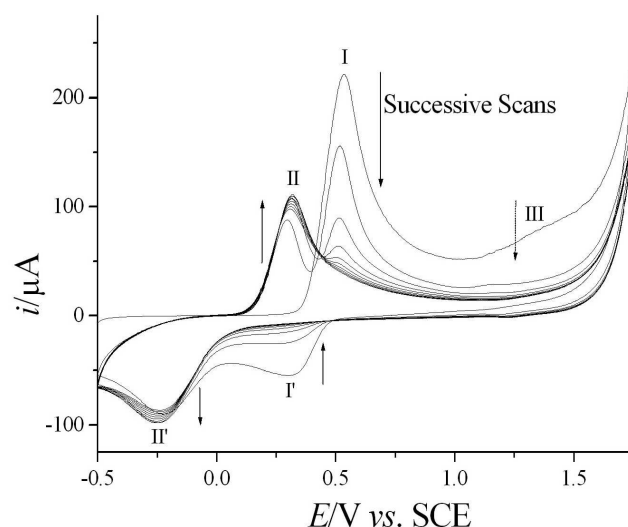
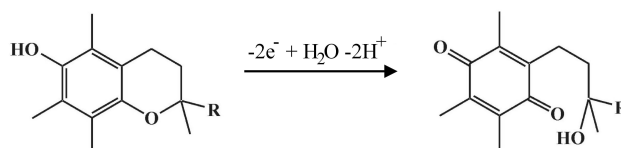
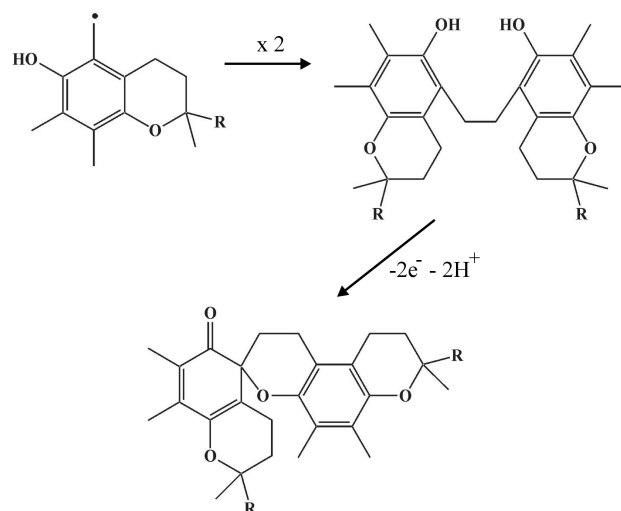


Figure 1. CV at  $200 \text{ mV s}^{-1}$  of  $\alpha$ -TOH droplets immobilized on a bppg electrode immersed in 0.1 M aqueous Britton-Robinson buffer solution (pH2).



Scheme 1. Proposed mechanism for the two electron oxidation and hydrolysis of  $\alpha$ -TOH.



Scheme 2. Suggested mechanistic pathway following the single electron oxidation of  $\alpha$ -TOH (after proton expulsion).

[1] C. E. Banks, T. J. Davies, R. G. Evans, G. Hignett, A. J. Wain, N. S. Lawrence, J. D. Wadhawan, F. Marken, R. G. Compton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 4053.

[2] L. J. Machlin, *Vitamin E*, Marcel. Dekker, New York, 1980.

[3] G. W. Burton, K. U. Ingold, *Acc. Chem. Res.*, 1986, **19**, 194.