

Mohamed A. Ghanem · Frank Marken  
Barry A. Coles · Richard G. Compton

## Microwave-enhanced electrochemical processes in micellar surfactant media

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**Abstract** High intensity microwave radiation effects are demonstrated for electron transfer processes at 25 or 50- $\mu\text{m}$  diameter platinum electrodes immersed in micellar sodium dodecylsulfate (SDS) solutions. First, a solution containing 2 mM  $\text{Fe}(\text{CN})_6^{3-}$  and 2 mM  $\text{Fe}(\text{CN})_6^{4-}$  in aqueous 0.1 M NaCl with and without SDS is employed to calibrate the electrode temperature and mass transport conditions. Addition of 0.1 M SDS has only a small effect on the microwave enhanced voltammetry for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  system. Next, two highly water-insoluble redox systems are studied. A solution of 1 mM *tert*-butylferrocene in aqueous 0.1 M NaCl containing 0.1 M SDS is shown to give no current response in the absence of microwaves. In the presence of focused microwaves at a platinum disc electrode, a strong current for the one electron oxidation of *tert*-butylferrocene is detected presumably due to localized disruption of the micellar solution. Concentrations of *tert*-butylferrocene down to the micromolar level are detected.  $\alpha$ -Tocopherol, a lipophilic vitamin and antioxidant, is soluble in aqueous 0.1 M SDS/0.1 M NaCl. In the presence of microwave radiation, a strong and concentration dependent anodic current response consistent with the two-electron oxidation of  $\alpha$ -tocopherol is observed. A heptode array of seven individual 50  $\mu\text{m}$  diameter platinum microelectrodes placed in ca. 720  $\mu\text{m}$  distance of each other is shown to allow microwave enhanced currents to be increased sevenfold with each electrode exhibiting the same microwave effect.

**Keywords** Microwave · Electrochemistry · Voltammetry · Surfactants · Micelle · Ferrocene · Vitamin · Antioxidants · Cavitation · Array electrode · Heptode

### Introduction

Microwave radiation has been traditionally employed to activate digestion processes (see for example [1]) and many other chemical processes [2], but can also be employed to substantially enhance electrochemical processes and electroanalytical signals [3]. Electrochemical processes in the presence of microwaves have been studied in aqueous [4], organic [5], and ionic liquid [6] media. It has recently been shown that platinum microelectrodes immersed in degassed aqueous solution and placed into a microwave field give very interesting localized heating and extreme mass transport effects [7]. Under steady state conditions, temperatures at the electrode surface are consistent with liquid superheating and mass transport can be enhanced by upto three orders of magnitude. Here, these high temperatures—high shear force conditions induced by focused microwaves at the electrode surface are beneficially employed to conduct electrochemical experiments in micellar media containing highly water-insoluble redox systems.

Electrochemical processes in micellar solutions (see for example [8]) are important in emulsion electrosynthesis [9], in electrocatalytic processes [10], and potentially important in electroanalysis. Many chemical reagents, which are essentially insoluble in aqueous media, are readily dispersed in a micellar solution and are therefore available for electron exchange processes at suitable electrode surfaces. In contrast to the conventional often mass transport controlled electrode processes, electrode processes in micellar media are governed by solubility and the exchange of reagent from within the micelle and the electrode surface [11]. It is shown here that focused microwaves facilitate this

M. A. Ghanem · F. Marken (✉)  
Department of Chemistry, University of Bath,  
Bath, BA2 7AY, UK  
E-mail: f.marken@bath.ac.uk

B. A. Coles · R. G. Compton  
Physical & Theoretical Chemistry Laboratory, Oxford University,  
Oxford, OX1 3QZ, UK

*Present address:* M. A. Ghanem  
Science & Mathematics Department,  
Faculty of Petroleum & Mining Engineering, Suez, Egypt

process by disrupting or destabilizing the micellar solution prepared with sodium dodecylsulfate (SDS). The critical micelle concentration (here 1.46 mM SDS in 0.1 M NaCl at 25°C) is only weakly dependent on the temperature [12]. All experiments are carried out in 0.1 M SDS under conditions where micelles are present. However, a fast temperature change is shown to create non-equilibrium conditions which lead to more facile electron transfer at the electrode surface. The electrochemical disruption of (redox active) micellar media as a method for thin film deposition has recently been proposed by Saji et al. [13]. Here, a thermal disruption of a conventional SDS micellar solution is reported to lead to highly efficient water-based electrochemical processes even for highly water-insoluble materials.

In this report, the electrochemical oxidation processes for *tert*-butylferrocene and for  $\alpha$ -tocopherol (vitamin E) are studied as two model redox systems for the case of highly water-insoluble molecules. Micellar solutions of these systems in SDS are readily prepared and stable. Cyclic voltammetric experiments for these redox systems show that in the absence of microwave radiation, only insignificant currents are detected while in the presence of microwave radiation substantially enhanced currents are recorded. The use of microwave activation in micellar systems provides a new and versatile approach to the electrochemical study of a wide range of water insoluble drugs or other organic or inorganic compounds.

## Experimental

### Reagents

Chemical reagents such as SDS, NaCl, *tert*-butylferrocene,  $\alpha$ -tocopherol, potassium ferrocyanide, potassium ferricyanide were obtained from Aldrich and used without further purification. Demineralized and filtered water of resistivity higher than 15 M $\Omega$  cm was taken from an Elga water purification system. Argon (Pureshield, BOC) was employed for de-aeration of the electrolyte solutions. Micellar solutions were equilibrated by vigorous stirring for at least 1 h prior to conducting experiments. All experiments were conducted in excess surfactant (0.1 M SDS; the critical micelle concentration in 0.1 M NaCl is 1.46 mM at 25°C [14]) where micelles of ca. 5 nm diameter are formed with an aggregation number of typically 100. Increasing the amount of supporting electrolyte slightly increases the aggregation number (due to Na<sup>+</sup> cations adsorbing onto the micelle surface) and increasing the temperature is expected to substantially decrease the aggregation number [15].

### Instrumentation

A conventional three electrode micro-Autolab potentiostat system (Eco Chemie, NL, USA) was employed to control the working electrode (a 25- $\mu$ m or 50- $\mu$ m

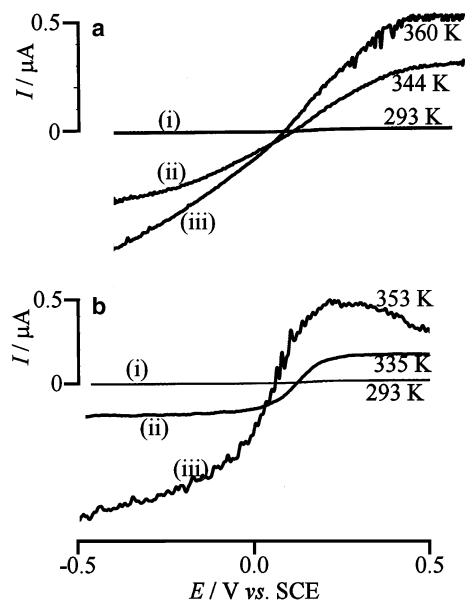
diameter platinum wire sealed in borosilicate glass to give well-defined platinum disc electrodes). Saturated calomel (SCE, Radiometer) was used as the reference electrode and platinum gauze as the counter electrode in a flow-through configuration [7]. The flow rate was typically 0.65 mL/min<sup>-1</sup> and did not affect the voltammetric current measurements. Prior to each experiment the working electrode was cleaned by polishing with 1  $\mu$ m alumina followed by thorough rinsing with de-ionized water. An electrochemical cleaning step (30 s to -1 V vs. SCE) was employed to activate the electrode in situ. A heptode configuration (vide infra) of microelectrodes was achieved by sealing platinum wire into a multi-barrel borosilicate capillary (World Precision Instruments, USA). Only the working electrode placed in a small volume Teflon cell was exposed to microwave radiation. Details of the cell design, vacuum-degassing, and application of microwaves have been reported previously [7]. A Panasonic multi-mode microwave oven (NN-3456, 2.45 GHz) with modified power supply, a water energy sink, and a port for the electrochemical cell was used. The microwave intensity was controlled via the anode current of the magnetron. *Special care is required when metal objects are placed into a microwave cavity. Before and during operation, the system was tested for leaking microwave radiation with a radiation meter.*

## Results and discussion

Microwave enhanced voltammetry in micellar media: Fe(CN)<sub>6</sub><sup>3-/4-</sup> Calibration

Micellar reaction media are of importance in many technical processes and may often be regarded as an alternative to the use of more hazardous organic solvents. Most water insoluble materials can be readily solubilized in a micellar solution in the presence of a suitable surfactant. In order to conduct electrochemical processes in micellar media, the solute has to be released to interact with the electrode surface. The presence of microwave radiation is shown here to strongly enhance this process.

Microwave radiation has been shown to enhance the magnitude of electrochemical currents in aqueous electrolyte media by upto three orders of magnitude [7]. This effect has been proposed to originate from (1) faster diffusion at increased temperatures and (2) convective flow caused by a vapour bubble in the vicinity of the electrode surface. Figure 1 shows typical current responses in the absence and presence of microwave radiation. For the oxidation of 2 mmol dm<sup>-3</sup> Fe(CN)<sub>6</sub><sup>4-</sup> and for the reduction of 2 mmol dm<sup>-3</sup> Fe(CN)<sub>6</sub><sup>3-</sup> at 293 K mass transport controlled limiting currents are observed of 9.0 and 8.5 nA. In the presence of microwave radiation, a characteristic shift in the equilibrium potential (the steady state potential at zero current) and an increase of the mass transport controlled current are observed. The shift in equilibrium potential is employed

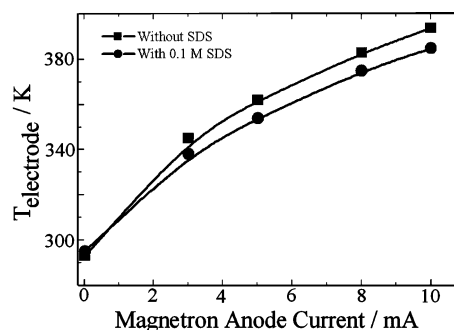


**Fig. 1** Voltammograms (scan rate  $50 \text{ mV s}^{-1}$ ) for the oxidation and reduction of  $2 \text{ mM Fe(CN)}_6^{4-}/2 \text{ mM Fe(CN)}_6^{3-}$  **a** in aqueous  $0.1 \text{ M NaCl}$  and **b** in aqueous  $0.1 \text{ M NaCl} / 0.1 \text{ M SDS}$  obtained at a  $25 \text{ }\mu\text{m}$  diameter platinum disc electrode in the presence of microwave radiation (magnetron current (i)  $0 \text{ mA}$ , (ii)  $3 \text{ mA}$ , (iii)  $5 \text{ mA}$ )

here to obtain an estimate of the temperature at the electrode surface,  $T_{\text{electrode}}$ , based on the expressions  $dE_{\text{equilibrium}}/dT = -1.6(\pm 0.1) \text{ mV K}^{-1}$  in aqueous  $0.1 \text{ M NaCl}$  and  $dE_{\text{equilibrium}}/dT = -1.8(\pm 0.1) \text{ mV K}^{-1}$  in  $0.1 \text{ M NaCl}/0.1 \text{ M SDS}$ . These values have been determined independently in a conventionally heated non-isothermal electrochemical cell and they are similar to the literature value for the  $\text{Fe(CN)}_6^{3-/4-}$  redox system determined in aqueous  $1 \text{ M KCl}$ ,  $dE_{\text{equilibrium}}/dT = -1.53 \text{ mV K}^{-1}$  [16].

From the data in Fig. 1, it is interesting to note that the presence of SDS has only a minor effect on the microwave enhanced mass transport for the aqueous  $\text{Fe(CN)}_6^{3-/4-}$  redox couple, presumably due to the insignificant interaction between the anionic micelles and the anionic redox system. Both in the presence and absence of SDS, currents of up to  $0.5 \text{ }\mu\text{A}$  are observed. Under extreme microwave conditions, a decrease in current at potentials positive of  $0.4 \text{ V}$  is observed and tentatively attributed to partial blocking of the platinum surface, e.g., with a layer containing oxidized forms of platinum (see Fig. 1b(iii)).

In order to obtain an estimate of the electrode temperature,  $T_{\text{electrode}}$ , as a function of the applied microwave power (magnetron anode current) a calibration plot was determined (see Fig. 2). It can be seen that the presence of  $0.1 \text{ M SDS}$  in  $0.1 \text{ M NaCl}$  has only a small effect on the temperature at the electrode surface. The slightly lower temperature in the presence of surfactant may in part be due to the effect of the surfactant on the vapour bubble [3] which has been proposed to be



**Fig. 2** Plot of the temperature at the electrode surface ( $T_{\text{electrode}}$ , obtained from the  $\text{Fe(CN)}_6^{3-/4-}$  equilibrium potential in aqueous  $0.1 \text{ M NaCl}$  with or without  $0.1 \text{ M SDS}$ ) versus the magnetron anode current (which determines the microwave power)

responsible for the fast mass transport and thermal conditions in the presence of microwave radiation.

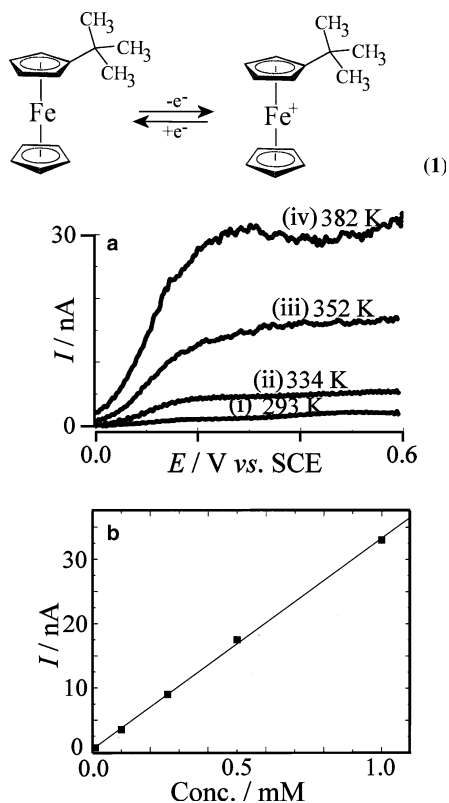
In conclusion, it can be stated that microwave activation of electrochemical processes is effective in the presence of surfactant-rich micellar solutions. The minimal changes in mass transport and electrode temperature due to the surfactant suggest that extreme conditions can be achieved to disrupt the micellar solution and to enhance electrochemical processes of redox systems dissolved within the micelles.

#### Microwave enhanced voltammetry in micellar media: oxidation of *tert*-Butylferrocene

The *tert*-butylferrocene redox system is highly water insoluble in the reduced form and soluble to some degree after oxidation. The system has been studied in micellar media, e.g., for the mediation of glucose oxidase catalyzed redox processes [17]. *Tert*-butylferrocene is readily dissolved into a  $0.1 \text{ M SDS}$  surfactant solution. The electrode process corresponds to a one-electron oxidation (see Eq. 1) but due to the low solubility of *tert*-butylferrocene in water, no direct voltammetric signal is observed at a  $25 \text{ }\mu\text{m}$  diameter platinum disc electrode at ambient temperature (see Fig. 3a(i)).

In the presence of microwave radiation the oxidation of *tert*-butylferrocene becomes immediately detectable. Figure 3a shows how microwave power increases the anodic current response and temperature at the electrode surface.

Varying the concentration of *tert*-butylferrocene results in a linear change in the observed limiting current in the presence of microwave radiation (see Fig. 3b). With sufficiently high microwave intensity, concentrations down to a micromolar level can be determined. Varying the concentration of  $\text{NaCl}$  from  $0.1 \text{ M}$  to  $0.5 \text{ M}$ , a minor change in voltammetric characteristics was observed (not shown). When plotted in the form of an Arrhenius plot, the observed increase in the limiting current is consistent with an apparent activation energy of ca.  $20 \text{ kJ mol}^{-1}$ . However, due to the unknown



**Fig. 3** **a** Voltammograms (scan rate  $50 \text{ mV s}^{-1}$ ) for the oxidation of  $1 \text{ mM}$  *tert*-butylferrocene in aqueous  $0.1 \text{ M NaCl}/0.1 \text{ M SDS}$  at a  $25 \text{ }\mu\text{m}$  diameter platinum electrode in the presence of microwave radiation generated with (i)  $0$ , (ii)  $3$ , (iii)  $5$ , and (iv)  $10 \text{ mA}$  magnetron anode current. **b** shows the linear change in Faradaic current (with  $10 \text{ mA}$  magnetron anode current) observed upon changing the concentration of *tert*-butylferrocene

mechanism for the electrode process, this value does not have a clear physical interpretation.

It is interesting to discuss the likely mechanism for the observed electrode process. Micellar systems show two distinct relaxation times in response to temperature jump experiments [18]. The first and relatively fast

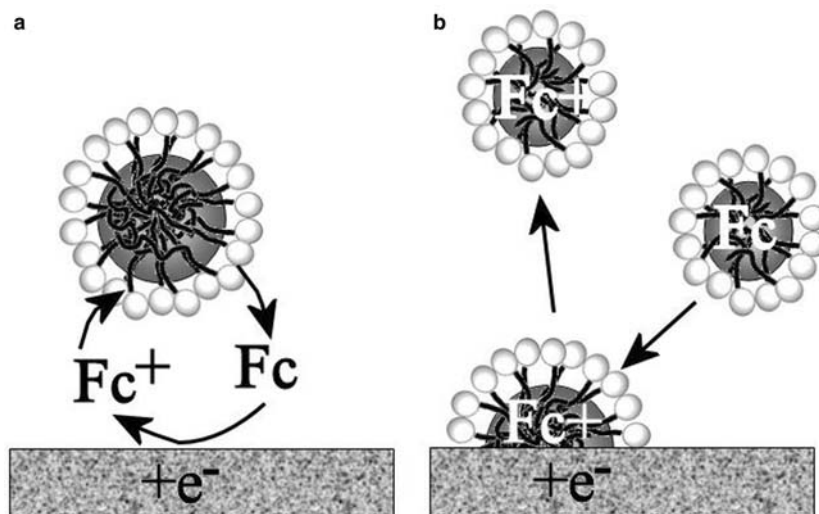
relaxation process (typically  $< 1 \text{ ms}$ ) occurs within micelles which re-equilibrate with the surrounding solution phase by shedding surfactant molecules (lowering the aggregation number). A second and much slower relaxation process (in the order of  $100 \text{ ms}$ ) is observed, during which the number of micelles in the solution changes. The reaction time within the microwave heated reaction zone is convection- and diffusion-controlled and can currently only be estimated. Diffusion within the diffusion layer thickness ( $< 1 \text{ }\mu\text{m}$ ) occurs on a sub-millisecond timescale and if an overall reaction time in the order of milliseconds is assumed, the micellar solution at the electrode surface cannot be in equilibrium. As a result, the interaction of the micelles with the electrode surface may be affected. In Fig. 4, two plausible pathways for the electrochemical process are depicted. In Fig. 4a, an equilibrium between inside and outside the micelle allows the neutral ferrocene derivative to diffuse into the electrode. This mechanism has been proposed for many room temperature processes involving micelles at electrode surfaces [19]. In Fig. 4b, the direct interaction of micelles with the electrode surface is postulated. This latter pathway may be possible, in particular, under non-equilibrium or under high shear force conditions.

An experimental approach to distinguish these two mechanistic pathways can be based on comparing the oxidation currents for different types of redox systems. Next, the oxidation of  $\alpha$ -tocopherol as an extremely lipophilic system is investigated under microwave conditions.

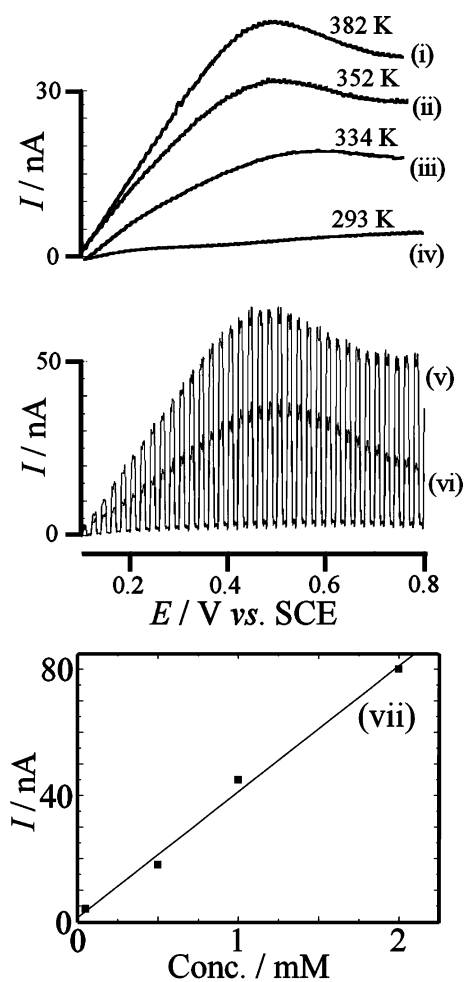
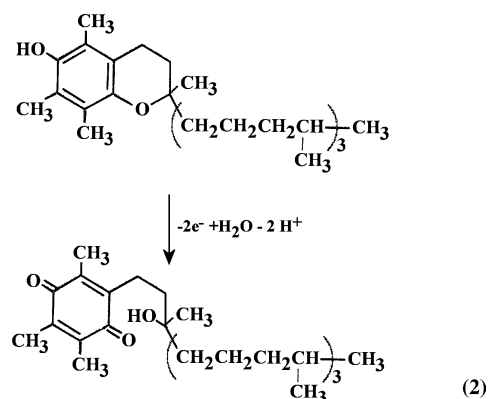
#### Microwave enhanced voltammetry in micellar media: oxidation of $\alpha$ -tocopherol

The microwave enhanced voltammetry methodology was applied to the case of  $\alpha$ -tocopherol oxidation.  $\alpha$ -tocopherol (or vitamin E) is highly water-insoluble and in sufficiently dilute conditions known to undergo a two-electron oxidation with ring opening hydrolysis (see Eq.

**Fig. 4** Schematic representation of (a) a mechanism based on the diffusion of the ferrocene derivative through the aqueous phase to the electrode and (b) a mechanism based on the direct interaction of the micelle with the electrode surface



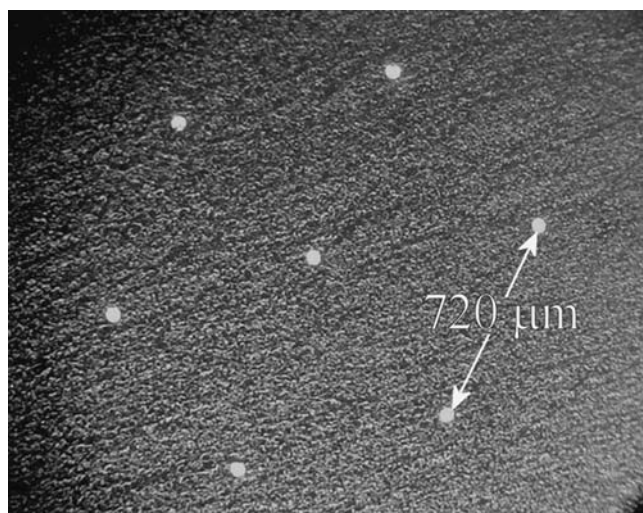
2) [20, 21]. In nature,  $\alpha$ -tocopherol is present in lipophilic membranes and acts as an antioxidant by transferring electrons to reactive and toxic reaction intermediates.



**Fig. 5** Voltammograms (scan rate  $50 \text{ mV s}^{-1}$ ) for the oxidation of  $1 \text{ mM}$   $\alpha$ -tocopherol in aqueous  $0.1 \text{ M NaCl}/0.1 \text{ M SDS}$  at a  $25 \mu\text{m}$  diameter platinum electrode. The microwave intensity was controlled by the magnetron anode current of (i) 10, (ii) 5, (iii) 3, (iv) 0, (v) 20, and (vi) 10 mA and the effect of applying short 200 ms pulses is demonstrated. The plot in (vii) shows the current at  $0.5 \text{ V}$  vs. SCE detected with a magnetron current of 10 mA as a function of the  $\alpha$ -tocopherol concentration

$\alpha$ -tocopherol, when dissolved in aqueous  $0.1 \text{ M NaCl}/0.1 \text{ M SDS}$ , exhibits only a weak room temperature oxidation response at a  $25 \mu\text{m}$  diameter platinum disc electrode (see Fig. 5). It can be observed that in the presence of microwave radiation, a strong increase in current occurs. With applied potential, a gradual increase in current and a peak feature are observed rather than a limiting current. The peak shape is very likely to be due to the modification of the platinum surface, e.g., with an oxide layer (vide supra). Currents observed for the  $\alpha$ -tocopherol system are very similar in magnitude compared to those for the tert-butylferrocene system which is not inconsistent with the mechanism B in Fig. 4. Mechanism A appears very unlikely due to the low water-solubility of  $\alpha$ -tocopherol. The magnitude of the limiting current is only apparently low when compared to the currents observed with the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox system. However, SDS micelles are known to have an approximate diameter of  $5 \text{ nm}$  and therefore exhibit a considerably slower rate of diffusion. Indeed, the observed currents could be close to those expected for a diffusion-controlled process, but further experimental work is required to confirm this hypothesis.

In Fig. 5v and 5vi it can be seen that pulsing the microwave power causes current pulses with very rapid rise and decay time. This behavior is consistent with a highly localized microwave effect affecting only the immediate vicinity of the electrode surface [22]. Arrhenius plot of the current data is consistent with an apparent activation energy of approximately  $20 \text{ kJ mol}^{-1}$ . Varying the concentration of  $\alpha$ -tocopherol in the micellar medium at constant microwave intensity causes a linear change in the observed voltammetric currents (see Fig. 5vii).

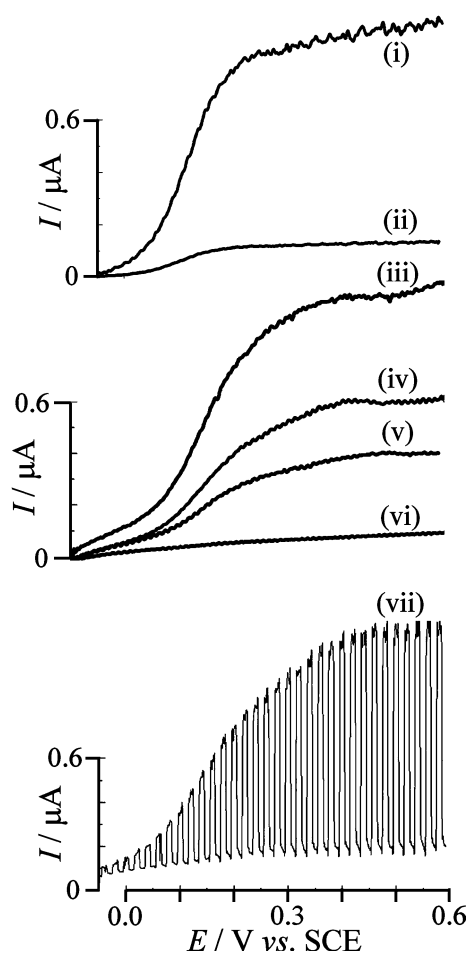


**Fig. 6** Photographic image of a heptode with seven individual  $50 \mu\text{m}$  diameter platinum disc electrodes placed at a distance of ca.  $720 \mu\text{m}$  from each other

## Microwave enhanced voltammetry at array electrodes

It is well known that arrays of microelectrodes can be employed to improve the signal-to-noise ratio and the overall current response in electroanalytical processes (see for example [23]). Microwave effects have been observed only at relatively small electrodes and it is interesting to explore the effect of employing an array of microelectrodes or a "heptode" arrangement of microelectrodes under microwave conditions. Figure 6 shows the electrode surface and the symmetric arrangement of electrodes.

The microwave field is affected by metal objects and when employing an array of electrodes, interference effects have to be avoided. However, voltammetric responses shown in Fig. 7i and 7ii clearly demonstrate that in the presence of microwave radiation, all seven electrodes give independent current signals of similar mag-



**Fig. 7** Voltammograms (scan rate  $50 \text{ mV s}^{-1}$ ) for the oxidation of  $1 \text{ mM}$  *tert*-butylferrocene in aqueous  $0.1 \text{ M NaCl}/0.1 \text{ M SDS}$  with a  $10 \text{ mA}$  magnetron current and (ii) at a single  $50 \text{ }\mu\text{m}$  diameter platinum electrode and (i) at seven combined  $50 \text{ }\mu\text{m}$  diameter platinum electrodes. The effect of the microwave intensity on the oxidation current at seven combined  $50 \text{ }\mu\text{m}$  diameter platinum electrodes is shown for (iii)  $10$ , (iv)  $5$ , (v)  $3$ , and (vi)  $0 \text{ mA}$  magnetron anode current and (vii) with  $200 \text{ ms}$  microwave pulses and  $10 \text{ mA}$  magnetron anode current

nitude. By combining the currents from individual electrodes a seven-fold increase in the overall current is observed. Therefore, a further improvement in signal-to-noise and current magnitude can be achieved simply by increasing the number of electrodes.

## Conclusions

It has been demonstrated that electrochemical processes in aqueous micellar media are strongly enhanced in the presence of microwave radiation. Even highly water-insoluble redox systems, such as *tert*-butylferrocene and  $\alpha$ -tocopherol, give well-defined current responses proportional to their concentration in the micellar solution. The mechanism for the electrode process is likely to involve disruption of the micelles and direct interaction of micelles and the electrode surface. Further studies are required to confirm this mechanism for a wider range of redox systems. An important development is the use of arrays of microelectrodes in the presence of microwaves to further increase currents and the signal-to-noise ratio.

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