Methylene Green Voltammetry in Aqueous Solution: Studies Using Thermal, Microwave, Laser, or Ultrasonic Activation at Platinum Electrodes

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The voltammetry of the aqueous two-electron reduction of the phenothiazine dye methylene green, known to be passivating at platinum electrodes, is reported under simultaneous activation with each of the following techniques: thermal activation in the temperature range 15−80 °C, pulsed microwave activation with a modified 800 W, 2.45 GHz domestic microwave oven, 10 Hz pulsed laser activation with a Nd:YAG laser at 532 nm, sonication, or ultrasonic activation where a 20 kHz ultrasonic horn probe is employed to generate an aqueous/organic solvent emulsion. The relative merits of the five methodologies are compared and discussed in terms of surface activation and cleaning, mass-transport enhancement, and reduction mechanism elucidation. Comparisons are also drawn with the voltammetry of methylene blue, a dye of the same family. This is the first full report of both the effects of microwave heating on surface redox electrochemistry and of the sonoemulsion technique.

1. Introduction

The scope of electrochemical studies in aqueous systems where electrode passivation is commonplace can frequently be widely expanded by the use of *dual activation*, that is where a potential is applied to an electrode in tandem with some other mode of stimulation such as heating or photoexcitation. This work concentrates on four such secondary techniques, namely, thermal activation, microwave activation, laser activation, and ultrasonic activation. The first of these has been studied for many years, but recent advances have been made by examining the effects of very rapid local heating at wire electrodes by both Gründler et al.[1−3] and other workers. A second example of in situ activation of electrochemistry by external sources is by subjection to radiation. Until very recently, the interaction of microwave radiation with electrochemical processes[8] was entirely unexplored, despite the widespread interest in microwave enhanced chemistry. The use of low power microwave radiation in electrochemical systems is of considerable importance in areas of research such as in situ electrochemical EPR[9] (typically X-band, 9.5 GHz) and microwave reflectance characterization[10] of semiconducting electrodes. In these cases the activation of the electrochemical system due to absorption of microwave radiation can usually be ignored due to the low intensities used. However, microwave radiation is known to interact not only with molecules in the gas phase but also with condensed materials and interfaces with sufficient dielectric loss[11] and may therefore be employed to activate an electrochemical system.

The use of microwave radiation as an activation source leads to a considerable current enhancement, arising from a rapid heating effect which causes the temperature in the liquid phase at the electrode/solution interface to locally superheat.[8]

Laser irradiation of electrodes is becoming popular. McCreery and colleagues have utilized high-intensity infrared laser pulses to activate the surface and increase heterogeneous electron-transfer kinetics at glassy carbon and platinum electrodes,[12−18] while Watanabe and co-workers have subsequently employed a relatively high power infrared laser source to maintain clean platinum and gold electrodes by ablating the top layer of the electrode surface every other second.[19] Oltra et al. have additionally used pulsed laser irradiation to depassivate an iron electrode under channel flow hydrodynamic conditions,[20] while Hinoue et al. used an argon-ion laser to probe the effect of electrode heating on the electron-transfer process of aqueous Fe(II/III) species in a flow system.[21] Importantly, these[12−21] experiments used laser irradiation to activate or clean the electrode surface but not to provide direct photochemical or photoelectrochemical effects[22] which are not discussed here.

Last we consider the introduction of power ultrasound into electrochemical methodologies. This has been widely studied over the past decade[23−30] and has many benefits including extremely enhanced mass transport resulting from acoustic streaming[31] or microjetting[32] and electrode activation arising from cavitational erosion.[33] In addition ultrasound has been used to permit the electrochemical study of essentially water-insoluble organic species in aqueous solution.[34,35] Sonication is therefore a convenient and effective alternative to the use of high-speed stirring and/or detergents for the promotion of emulsions for electrochemistry.[36]

Many potentially viable electrode processes are inhibited if not entirely passivated by the adsorption, precipitation, or polymerization of reaction products or intermediates on the electrode surface. This work addresses one such reaction in aqueous solution, the two-electron reduction of the phenothiazine dye methylene green (MG shown in Figure 1)[37−39] to *leuco*-methylene green (*l*-MG) at platinum electrodes. This dye is similar to methylene blue (MB, also shown in Figure 1), which is studied for comparison. We report the use of the above activation techniques to explore and quantify the dual activation of a platinum electrode in the context of linear sweep and cyclic
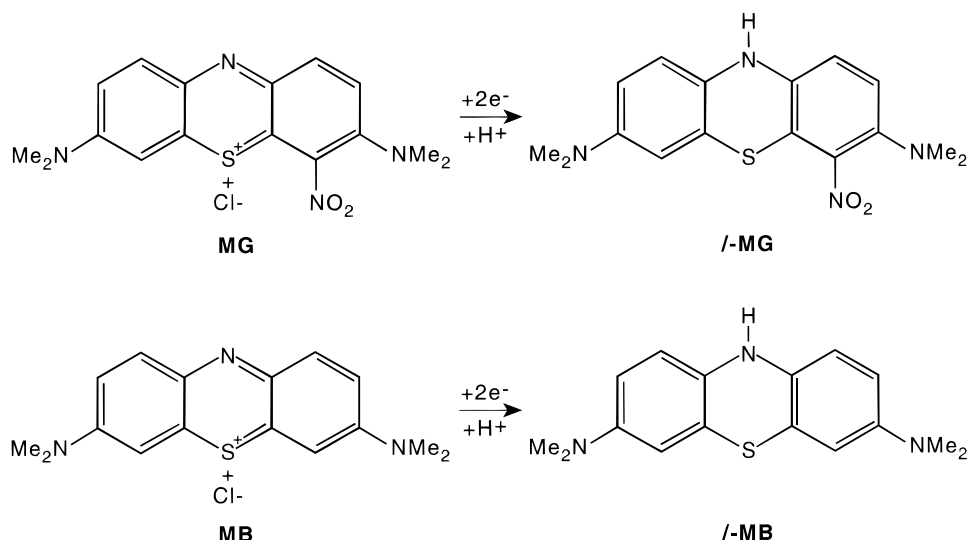
Figure 1. Structures of (a) methylene green (MG), (b) *leuco*-methylene green (*l*-MG), (c) methylene blue (MB), and (d) *leuco*-methylene blue (*l*-MB).

voltammetry of methylene green. Conventional thermostated voltammetry, microwave activated voltammetry (MAV) using a modified 800 W, 2.45 GHz domestic microwave, laser activated voltammetry (LAV) using a 10 Hz pulsed Nd:YAG laser at 532 nm, and sonovoltammetry using a 20 kHz ultrasonic horn are performed on aqueous solutions of methylene green to establish a comparison of the relative benefits of the different approaches.

2. Experimental Section

The channel electrode cell employed consisted of a platinum electrode (4 mm × 4 mm) embedded in a Teflon base of width 6 mm and length 80 mm. This had walls approximately 0.8 mm high with an optically transparent silica cover plate located on top of this and sealed with a low melting inert wax.[40] The exact cell height was calibrated using the Levich equation,[41] using a value for the diffusion coefficient of ferrocene in acetonitrile as described previously.[42] A lead-out wire from the back of the Teflon base formed the connection to the poten- tiostat. The platinum gauze counter electrode was situated downstream of the cell, and the saturated calomel electrode (SCE, Radiometer, Copenhagen) acting as reference was located in a compartment out of the main flow but still in electrical contact with the solution. The solutions investigated flowed through the cell under gravity from a reservoir at a known height above the waste outlet, thus allowing the volume flow rate to be known at all times. All solutions were thoroughly degassed with nitrogen prior to and during experiments. All channel flow electrochemical measurements were carried out using an Oxford Electrodes potentiostat using scan rates appropriate for steady- state voltammetry. The possible ohmic distortion of the recorded voltammograms was negligible under the conditions employed.[43]

Thermal activation experiments were performed in a divided cell of approximately 50 cm³ total volume. This is shown in Figure 2 and employed a 25 μm diameter platinum disk as the working electrode in tandem with a combined reference and counter SCE connected via a solution bridge. The SCE was kept at a fixed temperature which was in the range 15 ± 2 °C for all experiments. All temperatures were measured with a Pt 102 resistance thermocouple thermometer. The temperature of the platinum electrode was raised in ca. 10 °C steps by means of a small heating coil in a surrounding water bath.
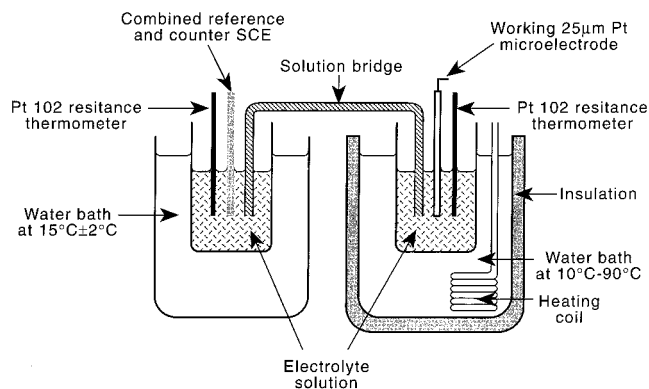
Figure 2. Apparatus used in thermally activated electrochemical experiments.
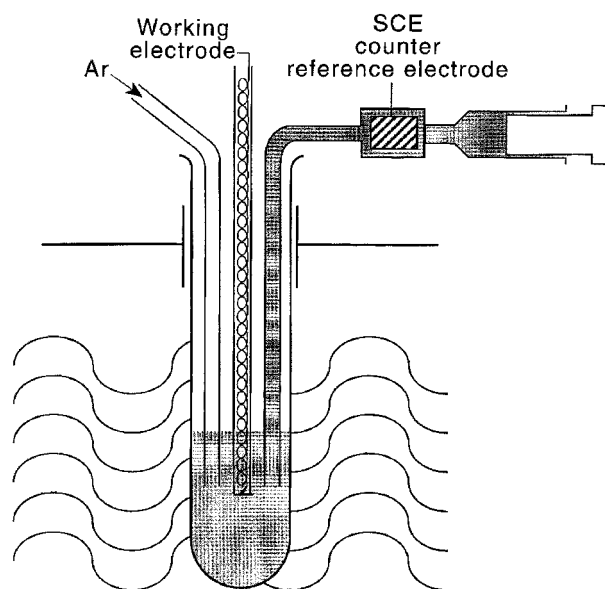
Figure 3. Apparatus used in microwave activated electrochemical experiments.

The two-electrode cell used in the microwave activated experiments is shown in Figure 3. The cell volume was approximately 5 cm³. In this cell, a platinum microelectrode was positioned at a specific height in the cell, the ideal height being found by optimizing the current response. In addition,
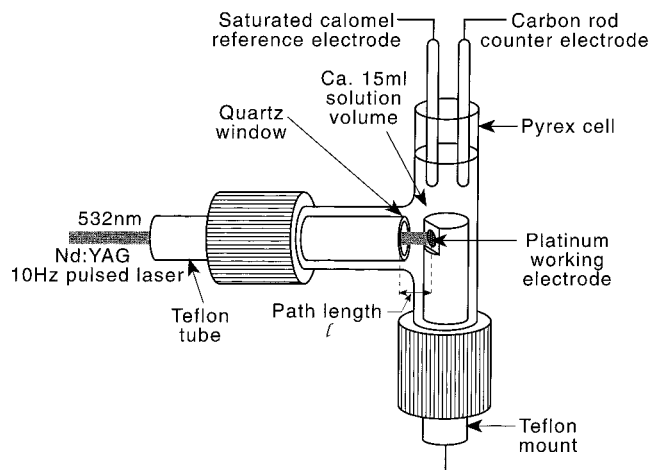
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Figure 4. Apparatus used in laser activated electrochemical experiments.

the cell was filled with a solution to a specific height, the ideal solution height also being found by experimentation. Because of the use of a microelectrode and the small currents involved, the SCE reference electrode also acted as the counter electrode. This electrode was positioned outside of the oven. To prevent bulk heating of the solution and reduce thermal convection within the cell, the solution in the cell was connected to a pump system, which slowly and continually pumped solution around the system from a reservoir kept at room temperature. The inlet and outlet tubes were positioned near the top of the solution in the cell, again to reduce convection and movement of solution in the region of the electrode surface. An 800 W, 2.45 GHz domestic multimode microwave oven was modified to supply constant power or pulsed microwave radiation of variable power and to allow an electrochemical cell to be inserted into a high intensity region. To apply intense microwave radiation to the working electrode in a reproducible manner the intensity distribution in a Panasonic NN-3456 multimode microwave oven fitted with a water load was mapped. A hole through the cavity wall extended by a 14.7 mm inner diameter brass tube, 50 mm long, which acted as a waveguide below "cut off", allowed a 1.41 cm diameter electrochemical cell to be inserted into a high-intensity region. A special working electrode design with a range of Pt disk electrodes of 25, 50, and 1000 μm diameter sealed in glass was used to prevent both sparking and radiation escaping through the inlet. The lead-out from the microelectrode was in the form of a helix made by winding 0.19 mm diameter platinum wire on a 0.46 mm diameter mandrel with 28 turns per cm. A test with a radiation meter (Apollo XI microwave monitor, Apollo Ltd.) confirmed that this design acted as a filter to stop microwave radiation from being conducted out of the cavity. A capillary inlet and outlet connected to a peristaltic pump served to quickly renew the solution phase. The microwave power level of the modified oven was continuously adjustable. To calibrate the power of the microwave, temperature readings were taken at set time intervals during microwave exposure for each microwave setting. The temperature rise between each reading was then plotted against exposure time and the gradient calculated for a tangent taken through zero. The latter was converted to the power in watts by multiplying by the heat capacity and mass of the whole cell.

Laser activated voltammetry in nominally stationary solution was conducted in the three-electrode cell shown in Figure 4. This utilized a 2 mm diameter platinum disk working electrode embedded in a Perspex window set in a Teflon mount, an SCE reference electrode, and a graphite rod as the counter electrode.

The cell volume was approximately 15 cm^3. The bulk solution temperature was 20 $\pm$ 2 °C in all cases. The temperature during individual runs was found to increase by less than 0.2 °C, demonstrating a minimal overall bulk heating effect by the laser.

The light source employed was a LAB 130 Q-switched Nd: YAG laser (Spectra Physics Lasers, Inc., CA) operating in frequency doubled mode at a wavelength of 532 nm and pulsed at 10 Hz. Lenses and optics housings were supplied by the Newport Corporation and mirrors obtained from Comar Instruments (Cambridge, UK). The beam was reduced to 4.0 mm in diameter by means of passage through a fixed diameter aperture before being passed into the LAV cell. The average (not pulse) laser power was determined with a Gentec ED-200LA detector head in conjunction with a Gentec SUN Series EM-1 Energy Meter (Gentec, CA). Typical experiments were performed in the range 0.1–0.8 W cm^{-2}.

Sonovoltammetric experiments were conducted using a 6 mm diameter platinum working electrode in a 250 mL cell at 20 °C, which incorporated a 20 kHz titanium tipped ultrasonic horn probe of 13 mm diameter (Sonics & Materials). Ultrasound power levels up to 50 W cm^{-2} were employed.[44,45] Laser and ultrasonic electrochemical measurements were carried out using a commercial computer-controlled "μ-autolab" potentiostat (Eco-Chemie, Utrecht) with the horn probe electrically isolated as previously reported.[46] Full descriptions of similar "face on" sonoelectrochemical procedures have appeared elsewhere.[47]

The platinum working electrode in all cases was accurately measured with a travelling microscope and polished with diamond lapping compounds (Kemet, UK), from 25 μm down to 1 μm prior to use. Methylene green (as the salt $C_{16}H_{17}N_4O_2S^+\cdot Cl^-$) (Fluka 99%), methylene blue (as the salt $C_{16}H_{18}N_3S^+\cdot Cl^-\cdot 3H_2O$) (Aldrich, 99%), KH_2PO_4 (Aldrich, >99%), KCl (Aldrich 99.99%), KOH (Aldrich 99.9%), and HCl (Aldrich, 1.0 M) were used as received. Buffer solutions were made up over a range of pH using buffers consisting of 0.1 M HCl/KCl for pH values below 2.2 and 0.2 M phosphate plus HCl or KOH for higher pHs.

Atomic force microscopy (AFM) surface imaging of a platinum disk before and after *leuco*-methylene green deposition at various temperatures was performed on a TopoMetrix TMX 2010 Discoverer system in contact mode (typically 10 Hz scan rate) with TopoMetrix standard AFM probes (no. 15-20).

3. Results and Discussion

3.1. Voltammetry in the Absence of Dual Activation. The voltammetry of methylene green (MG)[37–39] and methylene blue (MB)[48–49] at pHs in the range 1.7–7.3 was investigated at platinum electrodes using buffered 0.2 mM aqueous solutions of dye under channel flow conditions at a flow rate of 0.0104 cm^3 s^{-1}. For methylene blue, a single mass transport limited reduction wave was observed at all pHs, though the half-wave potential of the wave increased with decreasing pH. Half-wave potentials over the above range of pH were measured, and there were three distinct observed pH ranges where the slope of the $E_{1/2}$ vs pH plot changed from ca. −90 to −60 to −30 mV decade^{-1}. This was directly analogous to the previously reported voltammetric behavior of toluidine blue dye.[50] For the two-electron reduction,

$$MB + mH^+ + 2e^- \rightleftharpoons l\text{-}MB \qquad (1)$$
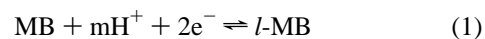
theory predicts that these gradients correspond directly to the uptake of three, two, then one proton(s) during reduction, respectively.[51] The pHs which marked the changeovers were
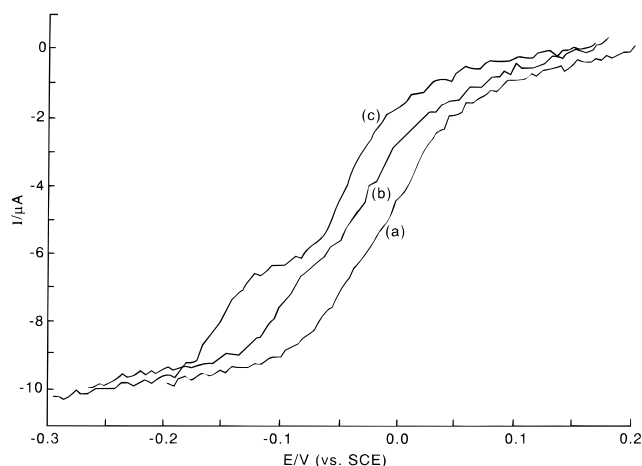
Figure 5. Linear sweep channel flow voltammograms on a 4 mm × 4 mm Pt electrode at a flow rate of 1.04×10^{-3} cm^3 s^{-1} for 0.2 mM MG buffered at (a) pH 3.86, (b) pH 4.39, and (c) pH 5.25.

ca. pH 5.0 and pH 6.0. This compares with previously reported work for methylene blue reduction on carbon fiber microdisk electrodes which gave three slopes as above at changeovers of ca. pH 5.4 and 6.0.[52]

In contrast, the channel flow voltammetry of methylene green presented some interesting differences. At low pHs up to about pH 4.5, a single mass transport limited wave was seen on reduction of an aqueous solution of the dye. In this pH region, the slope of $E_{1/2}$ vs pH was ca. -60 mV decade^{-1}, indicating the involvement of only two protons in the reduction process of eq 1 with MB replaced by MG. This may reflect the increased acidity of the protonated molecule owing to the nitro group on the ring. At higher pHs, however, the wave splits into two. Some typical cathodic sweep voltammograms at pHs 3.86, 4.39, and 5.25 are shown in Figure 5 and illustrate this phenomenon. The plots of these separate half-wave potentials for the split wave against pH both have slopes of ca. -30 mV decade^{-1} at pHs higher than about 5.5, suggesting the uptake of a single proton during the reduction to form *l*-MG. Although the voltammetric response splits into two separate processes as discussed below, the total current observed in Figure 5 remains the same, indicating an *overall* two-electron process in all cases. Treating the total current passed as representing a two-electron reduction, the value of the diffusion coefficient, D, for methylene green was found to be $(3.6 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1}. The possibility that the split wave might be due to two one-electron processes as hypothesised by Dong et al.[38] was discounted both by the lack of any ESR signal which would be produced by the radical formed at intermediate potentials and also by virtue of Tafel analysis of the split wave which gave Tafel slopes of ca. 30 mV for each wave. The value of the gradients is that expected for a two-electron electrochemically reversible process. It is likely that because a two-electron reduction accompanied by the uptake of a single proton results in the formation of a neutral organic species that the wave is split because one process takes place in solution and the other on the electrode surface. Thus, at pHs above about 4.5, the relevant equations for dilute concentrations of methylene green are

$$MG(aq) + H^+ + 2e^- \rightleftharpoons l\text{-}MG(s) \qquad (2)$$

$$MG(aq) + H^+ + 2e^- \rightleftharpoons l\text{-}MG(aq) \qquad (3)$$
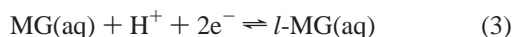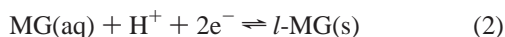
Further evidence for the above processes is suggested by the nonequality of the two waves in terms of current as has been reported previously.[38]
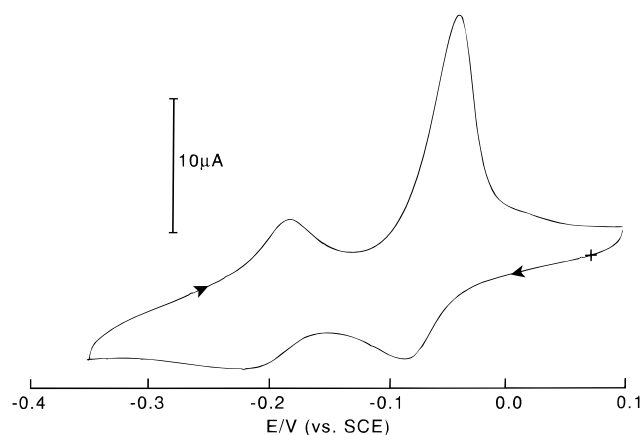

Figure 6. "Silent" cyclic voltammogram of 0.2 mM MG in 0.1 M KCl/0.2 M KH$_2$PO$_4$(aq) at pH 6.5. Scan rate was 10 mV s^{-1} and the working electrode was a 6 mm diameter Pt disk.

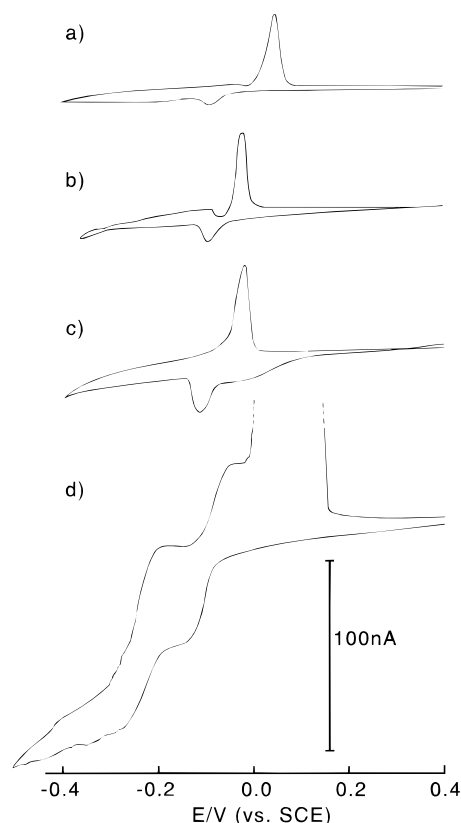**Figure 7.** Cyclic voltammograms at 10 mV s^{-1} at a 30 μm Pt disk electrode for 1.0 mM MG in 0.1 M KCl/0.1 M KH$_2$PO$_4$(aq) (pH 6.5) at (a) 17 °C, (b) 41 °C, (c) 59 °C, and (d) 79 °C.

We next focus on this split-wave voltammetry at higher pHs. Experiments were conducted in stationary solution using a 0.2 mM aqueous solution of methylene green in 0.1 M KCl buffered at pH 6.5 $\pm$ 0.1 with 0.1 M KH$_2$PO$_4$. Under dark conditions, two reduction peaks are seen which can be attributed to the above processes. On the reverse scan, a single large stripping peak is observed as shown in Figure 6 corresponding to the reoxidation of the surface bound *l*-MG. At high concentrations (>ca. 2 mM in stationary solution), the second aqueous reduction wave largely disappears, and this can be explained by the formation of a thick insulating surface bound layer of solid *l*-MG which largely passivates the electrode. This is shown for a microelectrode at room temperature in Figure 7a.
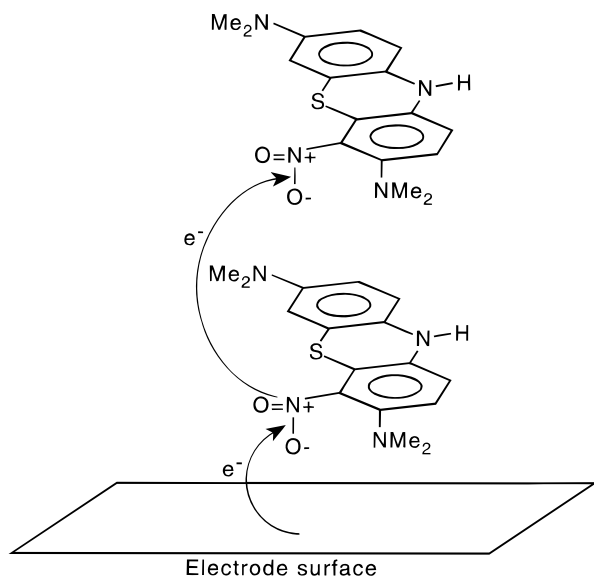
Figure 8. Schematic diagram of a possible "electron hopping" mechanism for *leuco*-methylene green.

3.2. Thermal Activation of Methylene Green Voltammetry. Cyclic voltammetry for a 2 mM aqueous solution of methylene green in KCl buffered at pH 6.5 ± 0.1 with 0.2 M KH_2PO_4 was performed in the apparatus shown in Figure 2. The temperature of the platinum electrode was raised in ca. 10 °C steps by means of a small heating coil in a surrounding water bath. Typical voltammograms at 17, 41, 59, and 79 °C are shown in Figure 7a−d. Initially, below ca. 70 °C, as the temperature is raised the magnitude of the forward and backward peaks increases, corresponding to greater surface coverage probably as a result of increased mass transport and rates of nucleation and solid growth at the electrode. However, as the temperature rises to ca. 80 °C, two waves are clearly seen in the reduction sweep of the cyclic voltammogram recorded, as well as an extremely large "stripping" peak upon reoxidation (Figure 7d). Comparison with the results shown in Figure 6 leads to the conclusion that the second peak corresponds to the two-electron reduction of methylene green to form *leuco*-methylene green in the solution phase as given by eq 3.

A possible explanation of why this second solution phase reaction is able to occur at higher temperatures is that the surface-bound *leuco*-methylene green becomes conducting via the thermally activated electron-hopping mechanism illustrated in Figure 8. This type of mechanism has been reported in liquid nitrobenzene,[53] and the hypothesis is supported by AFM measurements taken after 60 s deposition at −0.14 V vs SCE (just beyond the potential for the surface reaction) at a range of temperatures (see Figure 9a−d). These images show that the higher the temperature the greater the surface coverage, and hence further reactions which occur must do so in the presence of this covered surface. Further evidence comes from the large stripping peak observed at high temperatures which shows that the surface species is still present in large amounts after the second process has occurred.

3.3. Microwave Activated Voltammetry. The activation of electrochemical systems by microwave radiation was until recently entirely unexplored except for a preliminary report[8] concerning methodology and the effect of microwave heating on the voltammetry of soluble redox systems. In this section, we first report the optimization of this technique with respect to a simple well-characterized system before addressing the passivating system of methylene green reduction. This is the

first report of the effect of microwave heating on the electrochemistry of a surface redox process.

3.3.1. Optimization. Initially it was necessary to optimize the microwave experimental setup to ensure that good reproducible results were obtained. First, the effect of solution depth in the microwave cell shown in Figure 3 was investigated. This was carried out by allowing the cell to slowly fill up with solution while applying pulsed microwave radiation and recording the current response for anodic linear sweep voltammetry of a 2 mM aqueous solution of $K_4[Fe(CN)_6]$ in 0.1 M KCl. The voltammogram is shown in Figure 10 and clearly shows two solution levels where the current response due to microwave activation is greatest. The first volume was chosen as the experimental solution depth, for at this level the current response was appreciable and fairly uniform over a small range of depth; therefore, small deviations would not result in large current deviations. Thus, this level was marked on the cell wall and all following experiments were carried out with the solution up to this mark.

One further modification was made to the experimental procedure as a result of problems arising in reproducibility due to gas bubbles rising through the solution during scans. To eliminate this, the solution was thoroughly degassed by bubbling argon through the solution via a thin capillary under high vacuum. This process removed most of the dissolved gases from the solution, leaving only a small amount of inert argon gas dissolved.

Current enhancement seen under microwave activation was ca. 10-fold for 2.5 W activation compared with "dark" voltammetry and can be shown to be a result of rapid heating of the liquid phase at the solution/electrode interface by comparison with thermally activated ferrocyanide voltammetry. The shift of half-wave potential with temperature (ca. -1.53 mV K^{-1}) has been previously reported.[54] Microwave activation at increasing powers also reduced the half-wave potential of the ferrocyanide voltammetry. A plot of $E_{1/2}$ against microwave power had a slope of ca. -23 mV W^{-1}, which can be equated to an electrode temperature increase of approximately 15 °C W^{-1}. By applying ca. 3.6 W of microwave power, we estimate that temperatures of about 80 °C were reached at the electrode−solution interface.

3.3.2. Microwave Activation of Methylene Green Voltammetry. Cyclic voltammograms were then recorded for a 0.2 mM aqueous solution of methylene green in 0.1 M KCl buffered at pH 6.5 ± 0.1 with 0.2 M KH_2PO_4 under microwave activation as outlined above. The scans show evidence of a sustained mass transport limited current and two waves at negative potentials (see Figure 11 for an example). This agrees with the high-temperature results above, as is expected from the thermal activation arising from the application of microwave radiation.

A similar experiment was carried out for a 1 mM aqueous solution of methylene blue in 0.1 M KCl buffered at pH 6.5 ± 0.1 with 0.2 M KH_2PO_4. Figure 12 shows the cyclic voltammogram for methylene blue with no thermal activation, while Figure 13 shows the cyclic voltammogram under microwave activation. Comparison of these results with those obtained for methylene green shows that in the case of methylene blue no sustained mass transport limiting current is seen under microwave activation. Instead, as in the absence of microwave activation, the current is seen to fall off at negative potentials due to surface passivation. This suggests that the surface bound *leuco*-methylene blue does not become conducting at high temperature, unlike *l*-MG. This may arise from the absence of the nitro group (NO_2) on the ring system of methylene blue,
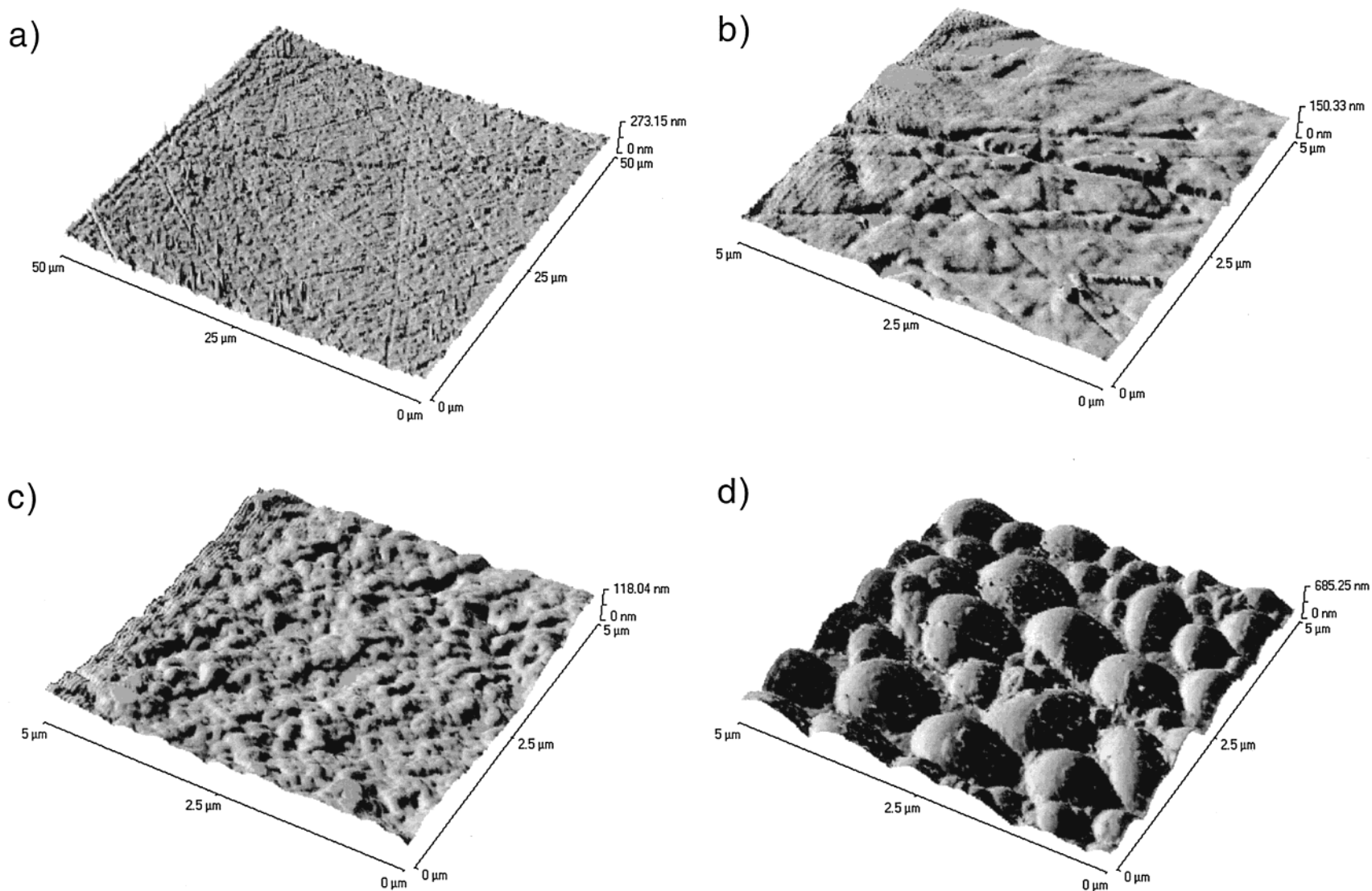
Figure 9. AFM images of (a) a polished 4 mm diameter Pt disk electrode and the same electrode held at −0.14 V (vs SCE) for 60 s in 1.0 mM MG at (b) 17 °C, (c) 30 °C, and (d) 85 °C.
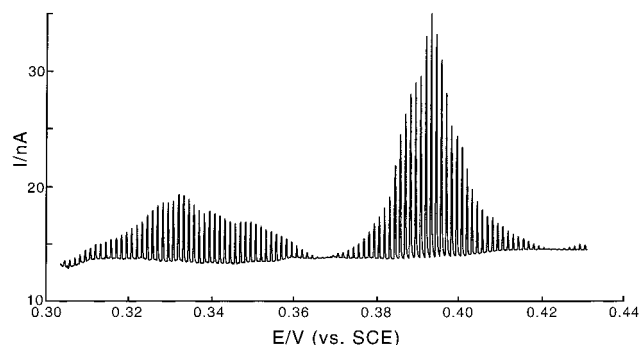
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Figure 10. Linear sweep voltammogram at 20 mV s^{-1} for 2 mM K$_4$-[Fe(CN)$_6$] in 0.1 M KCl(aq) at a 50 μm Pt disk electrode during slow solution depth increase under pulsed microwave irradiation.

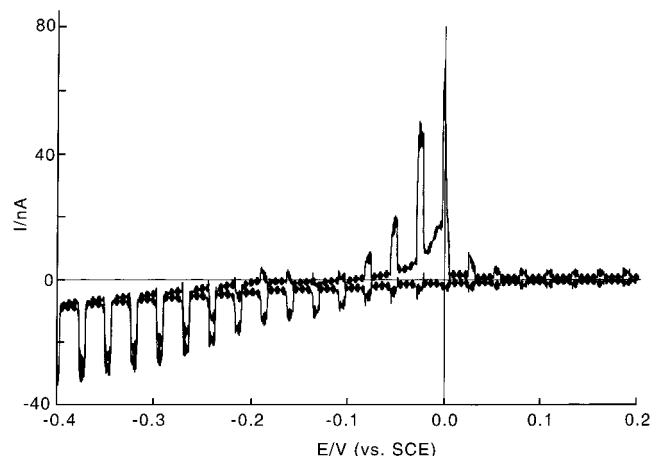**Figure 11.** Cyclic voltammogram at 20 mV s^{-1} for 0.2 mM MG in 0.1 M KCl(aq) at pH 6.5 at a 50 μm Pt disk electrode under 3 W pulsed microwave irradiation.
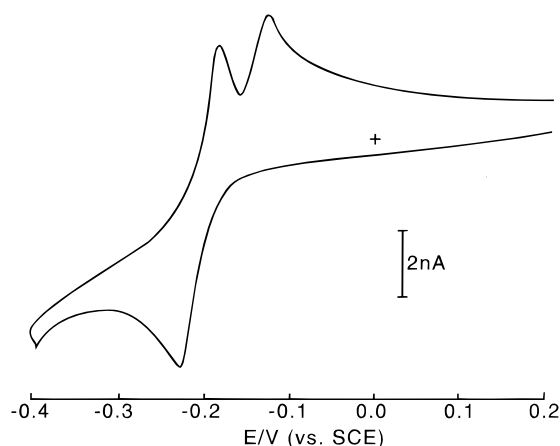

Figure 12. Cyclic voltammogram at 20 mV s^{-1} at a 50 μm Pt disk electrode for 1.0 mM MB in 0.1 M KCl/0.1 M KH$_2$PO$_4$(aq) at pH 6.5.

which may preclude the electron hopping mechanism. The structures of all four molecules are given in Figure 1.

3.4. Laser Activated Voltammetry. For laser activated cyclic voltammetry experiments a 0.2 mM aqueous solution of methylene green in 0.1 M KCl buffered at pH 6.6 ± 0.1 with 0.2 M KH$_2$PO$_4$ was used and scans were taken at 50 mV s^{-1}. Attention was focused on the first reduction wave attributed to the formation of surface bound *leuco*-methylene green given in eq 2. Figure 14 shows the voltammetry at a 2 mm platinum disk electrode under (a) dark conditions, (b) 160, (c) 295, (d) 445, and (e) 560 mW cm^{-2} laser illumination. It is evident that when greater laser activation is applied both the reduction and
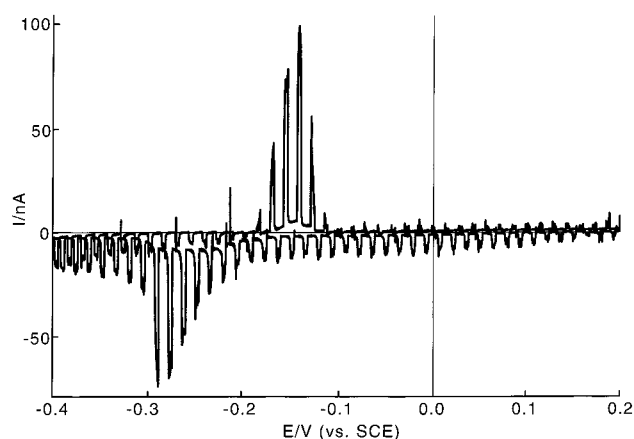

Figure 13. Cyclic voltammogram at 20 mV s^{-1} for 0.2 mM MB in 0.1 M KCl(aq) at pH 6.5 at a 50 μm Pt disk electrode under 3 W pulsed microwave irradiation.

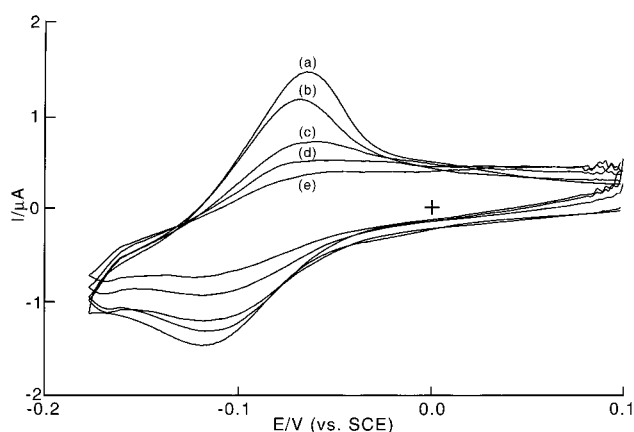**Figure 14.** Cyclic voltammograms at 50 mV s^{-1} at a 2 mm Pt disk electrode for 0.2 mM MG in 0.1 M KCl/0.1 M KH$_2$PO$_4$(aq) at pH 6.6 under (a) dark conditions, (b) 160, (c) 295, (d) 445, and (e) 560 mW cm^{-2} laser illumination (smoothed traces).

reoxidation peaks are increasingly diminished, in contrast with the above results for thermal and microwave activation. A possible explanation of this is that the laser pulses remove methylene green nuclei on the surface preventing the growth of solid *l*-MG. Thus, these results provide good evidence for the surface cleaning effects of laser illumination.

3.5. Sonoemulsion Voltammetry. When 25 W cm^{-2} of power ultrasound is introduced to the cyclic voltammetry of a 0.2 mM aqueous solution of methylene green in 0.1 M KCl buffered at pH 6.6 ± 0.1 with 0.2 M KH$_2$PO$_4$, it changes markedly from the "silent" behavior seen in Figure 6 due to significantly enhanced mass transport. A cyclic voltammogram at a 6 mm platinum disk electrode at 20 mV s^{-1} is shown in Figure 15. First, it can be observed that a much larger stripping peak is seen corresponding to the greater deposition resulting from the enhanced currents flowing due to the increased mass transport. Second, while there is a mass transport limited current relating to the two-electron processes, reflecting the constant flux of material due to steady-state convection/diffusion, the wave at the more negative potential shows a progressive decrease of signal at potentials negative of ca. −0.23 V (vs SCE). This electrode passivation was also seen earlier both under silent conditions at higher concentrations and during hydrodynamic voltammetry at a channel electrode, effectively precluding the electrosynthetic generation of useful quantities of *leuco*-methylene green. However, when voltammetry is conducted using a 20% (v/v) solution of toluene in water and 18 W cm^{-2}
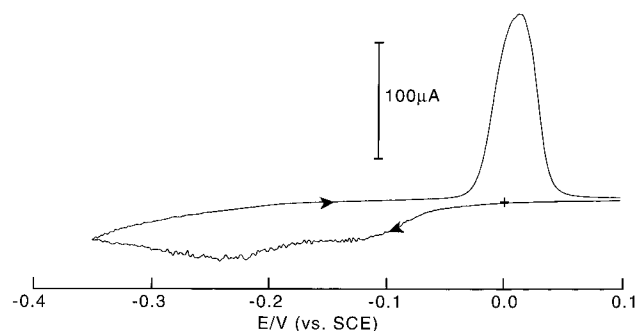
Figure 15. Cyclic voltammogram of 0.2 mM MG in 0.1 M KCl/0.2 M KH$_2$PO$_4$(aq) at pH 6.5. 25 W cm^{-2} ultrasound was employed at a horn-to-electrode distance of 22 mm. Scan rate was 10 mV s^{-1}, and the working electrode was a 6 mm diameter Pt disk.

Figure 16. Cyclic voltammogram of 2 mM MG in 0.1 M KCl/0.2 M KH$_2$PO$_4$(aq) at pH 6.5 and 20% (v/v) toluene (emulsified). 18 W cm^{-2} ultrasound was employed at a horn-to-electrode distance of 19 mm. Scan rate was 10 mV s^{-1}, and the working electrode was a 6 mm diameter Pt disk.
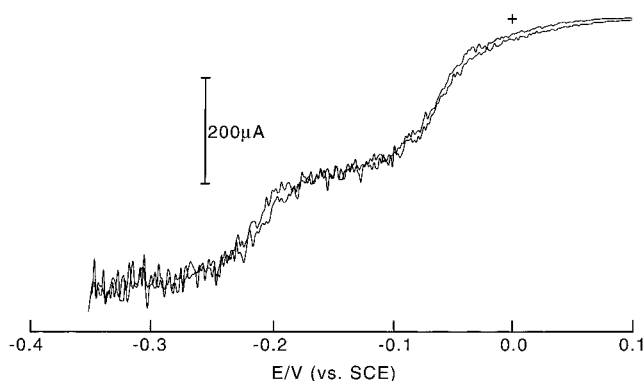
ultrasound is utilized to form an emulsion, the sonovoltammetry is very different as shown in Figure 16. Now, two steady-state sigmoidal reduction waves are observed with no evidence of a stripping peak on sweeps to positive potentials. Similar effects were seen using *n*-octane instead of toluene. We attribute this to the solubility of the reduction product in the emulsified organic phase that bathes the electrode surface. This was confirmed by employing a 30 min sonoelectrolysis experiment during which the potential of the solution (200 mL of 2 mM MG in 0.1 M KCl/0.2 M KH$_2$PO$_4$ at pH 6.5 and 50 mL of toluene) was maintained at −0.35 V vs SCE under 18 W cm^{-2} ultrasound. The toluene reaction mixture was then isolated under argon and evaporated to dryness, and the product was dissolved in octane for UV−visible characterization of the leuco base via the peak at 263 nm.[55]

Scrutiny of Figure 16 shows two nonequal waves attributed to the two-electron reduction of methylene green to give solid *l*-MG and aqueous phase *l*-MG, respectively. The former, of course, is rapidly removed by the emulsion. The relative sizes of the two waves reflect the amount of material that can nucleate and adsorb in the case of the first wave, and the fact that the overall magnitude of the two waves taken together reflects the total rate of mass transport of MG to the electrode surface. Tafel analysis of the two waves gave gradients of ca. 30 mV for each, again consistent with the two-electron reversible processes suggested in eqs 2 and 3 above. The scope for "clean" electrochemical measurements in the presence of passivating redox species by using ultrasound is evident.

4. Conclusions

The comparison of the five dual activation methodologies gives insight into the nature of methylene green reduction at platinum electrodes. Below pH 4.5, reversible two-electron voltammetry is observed, but at higher pH, a neutral, surface-active product is generated giving rise to both surface and solution reduction processes. Both high concentrations and large rates of mass transport (for example as produced by power ultrasound) accelerate electrode passivation. This can be overcome by means of laser irradiation of the electrode surface which removes surface adsorbed reactants before reduction can take place. In contrast, sonication of the electrode by means of 20 kHz ultrasound emitted from a horn probe located opposite to the electrode surface is, in itself, unsuccessful even at intensities as high as 52 W cm^{-2} in depassivating the methylene green system. However, the use of the novel sonoemulsion technique in which a small quantity of organic material is emulsified in the presence of ultrasound and used to dissolve the insoluble reduction product is shown to permit quantitative voltammetry. This technique promises much for synthetic, mechanistic, and analytical studies and can be expected to considerably broaden the range of chemical systems amenable to electrochemical study.

The use of electrode heating (up to ca. 80 °C) by either conventional or microwave heating is, unlike laser activation or the sonoemulsion method, unsuccessful at removing insoluble material formed in the reduction of methylene green. However, the heating allows the surface-deposited layer (as evidenced by AFM) to become sufficiently conducting, possibly through an electron hopping mechanism, to resurrect the second aqueous reduction wave. This use of microwave heating to change reaction surface electrochemistry is thought to be entirely novel.

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