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Glassy carbon surface effects on the electroreduction of aromatic carbonyl compounds
Part III: Vanillin

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Voltammetric studies of vanillin reduction in aprotic (DMF) and aqueous media in three different pH ranges on glassy carbon electrodes (GCE's) are presented. The formation and stability of anion radicals and their reactivity towards protonating agents are discussed. On a partially polished or pretreated GCE in DMF as well as on a polished GCE in neutral aqueous media, a new time-dependent surface prewave is noticed. The evidence indicates that this prewave is due to the interaction of acidic functional groups present on the GCE surface with vanillin. In acidic, neutral and alkaline media, the main reduction process occurs at potentials close to the background reduction potential region.

1. Introduction

The oxidation of carbon materials creates surface oxides consisting mainly of carboxylic and phenolic groups in addition to a relatively smaller concentration of basic functional groups [1]. These surface functional groups have been identified by chemical, electrochemical and surface analytical methods [2, 3]. However, the interaction of these surface functional groups with aromatic carbonyl compounds has not been explored. Recently, the involvement of acidic functional groups present on Nafion® coated glassy carbon on the redox behaviour of organic molecules has been reported [4]. In this laboratory, a systematic investigation of the influence of surface functional groups on the reduction of carbonyl compounds was undertaken. The electrochemical reduction of benzaldehyde on glassy carbon electrode (GCE) shows some catalytic effects which depend greatly on the nature of surface pretreatment [5]. Compared to benzaldehyde, benzophenone is a stronger base and the surface effect on GCE is much stronger, reproducible and well defined [6]. The electroreduction behaviour of vanillin on mercury, lead and amalgamated electrodes are available in the literature [7–10]. However, its reduction behaviour on GCE has not been reported. In this part, the electroreduction of vanillin in aprotic (DMF) and protic media on GCE with emphasis on the influence of surface functional groups is presented.

2. Experimental details

The glassy carbon electrode (5 mm diameter, Tokai GC-A) was fabricated, polished, cleaned and activated through electrochemical cycling procedures as described elsewhere [11]. The electrode activity in aqueous solution was evaluated using the voltammetric response of ferricyanide–ferrocyanide redox couple in 0.1 M KCl media [12]. In non-aqueous solvents, the voltammetric response depended very much on the level of polishing and pretreatment. From a number of experiments it was found that a "perfectly polished" GCE surface for non-aqueous studies was obtained by polishing GCE from 1/0 to 4/0 emery paper for 10 min each, washing with water, degreasing with trichloroethylene and the solvent supporting electrolyte (SSE) solution and introducing it into the cell in a wet condition and electrochemically activating it by cycling in the potential region of interest at 10 mV s^{-1} for 15 min without adding the organic compound. The electrode activated according to this procedure produces voltammetric response of anthracene (An) reported in the literature for mercury [13] and platinum [14] electrodes in the potential region. Application of a lower level (i.e., less than 4 × 10 min) of polishing leads to small decrease in the peak current for An reduction and a ΔE_p value of $An/An^{\bar{\cdot}}$ couple greater than 59 mV. Such electrodes are referred to as "partially polished" electrodes in the present work.

An H-type cell with platinum counter electrode was used for voltammetric studies. The saturated calomel electrode (SCE) was connected to the working electrode compartment through a KCl – agar luggin capillary. For cyclic voltammetry in DMF, the Luggin capillary was equilibrated for one hour in the solvent + supporting electrolyte mixture just before use. Alumina was kept suspended in the solvent + supporting electrolyte mixture for 24 h and filtered just before use. The working electrode compartment was deaerated with purified nitrogen until dissolved oxygen was completely removed (as indicated by the absence of a reduction peak around – 0.8 V). All experiments were carried out at (25 ± 1)° C. 50% ethanolic solutions were used in aqueous studies. All chemicals were of AR grade.

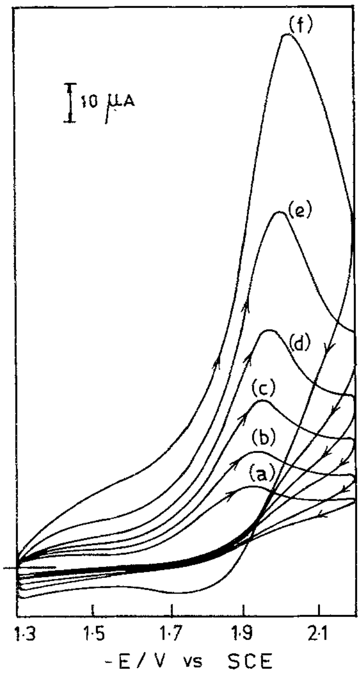

Fig. 1. Cyclic voltammogram for vanillin reduction on GCE (perfectly polished) in 0.1 M TBAI/DMF at various sweep rates. (Vanillin) = 1 mM: (a) 20, (b) 40, (c) 80, (d) 160, (e) 320 and (f) 640 mV s^{-1}.

Constant potential electrolysis was carried out at -1.1 V in aqueous alcoholic acidic medium. After electrolysis the electrolyte was neutralised with ammonium carbonate and vacuum distilled. The residue was extracted with ether and evaporated. The residue thus obtained was subjected to column chromatographic separation. Chloroform and acetone (1 : 1) mixture was used as eluent. Silica gel was used as an adsorbant. The solid separated by chromatographic method was recrystallised from alcohol and its melting point was 114° C, which is close to that of vanillyl alcohol reported in the literature. The product did not form a semicarbazone derivative. The product was also identified by i.r. spectral analysis by observing the absence of carbonyl frequency in the range of 1680 cm^{-1}.

3. Results and discussion

3.1. Electroreduction of vanillin in DMF

On a perfectly polished GCE vanillin gives two reduction peaks at around -1.9 V and -2.7 V corresponding to the anion radical and dianion, respectively. The second wave at extreme cathodic potential is diffuse and merges with the background reduction. The peak current of the first peak increases with sweep rate and concentration (Fig. 1). The peak potential shifts cathodically with increasing sweep rate and concentration. However, the peak current constant ($i_p/Acv^{1/2}$) continuously decreases with increase in concentration. At low sweep rates no anodic peak is observed. However, at higher sweep rates (around 600 mV s^{-1}) a small anodic wave corresponding to the first cathodic peak is observed. This type of irreversible voltammogram, becoming a reversible one at higher sweep rates, is also attributed to an EC reaction mechanism or, more specifically, a reductive dimerisation reaction in the present case. All the voltammetric response suggests that vanillin is reduced on a glassy carbon electrode as in the case of a mercury electrode. However, some adsorption/blocking effects are observed on GCE in the form of decreasing peak current constant and larger variation of $dE_p/d \log v$ values and $E_p-E_{p/2}$ values with concentration.

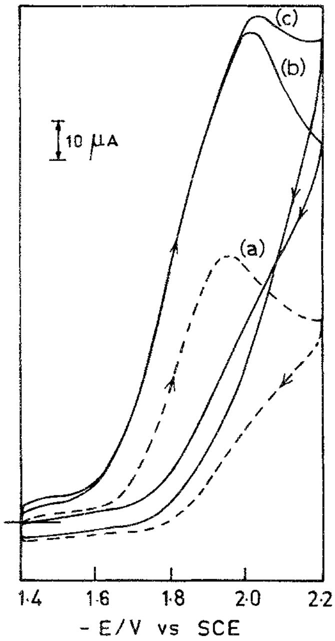

Fig. 2. Effect of benzoic acid on the reduction of vanillin on GCE in 0.1 M TBAI/DMF at 40 mV s^{-1}. (a) . . . 4.4 mM vanillin, (b) a + 4.8 M benzoic acid, (c) a + 6.7 mM benzoic acid.

Addition of water and *o*-cresol in millimolar concentration does not affect the voltammogram of vanillin reduction. But benzoic acid, a powerful protonating agent increased the peak current of the first peak while the peak potential remains unchanged (Fig. 2). Benzoic acid protonates the anion radical of vanillin which is further reduced at the same potential. In contrast to the prior protonation of benzaldehyde by benzoic acid in DMF, (as indicated by a distinct prewave) reported earlier [5], such a process is not noticed in the case of vanillin. This is in spite of the fact that the -CHO group in vanillin should be more basic. The exact cause for this anomalous behaviour is not known. This may however, be connected with the acid-base properties of the phenolic–OH group present in vanillin and/or the difference in adsorption effects of benzaldehyde and vanillin on GCE. The overall reaction scheme follows an ECE mechanism:

$$\mathrm{RCHO} + e^- \rightleftharpoons \mathrm{RCHO}^{\overline{\cdot}} \qquad (1)$$

$$\mathrm{RCHO}^{\overline{\cdot}} + e^- + 2\mathrm{H}^+ \longrightarrow \mathrm{RCH_2OH} \qquad (2)$$

where R is the 4-hydroxy-3-methoxyphenyl group.

3.2. *Surface effects in DMF*

On a partially polished GCE vanillin gives a prewave and a main wave (Fig. 3). The prewave starts approximately 200 mV (less negative) to the main peak.

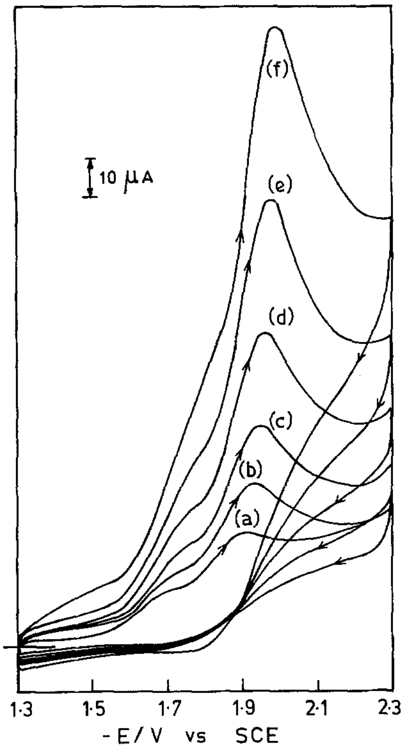

Fig. 3. Cyclic voltammograms for vanillin reduction on a partially cleaned GCE in 0.1 M TBAI/DMF at various sweep rates (vanillin) = 3 mM: (a) 10, (b) 20, (c) 40, (d) 80, (e) 160 and (f) 320 mV s^{-1}.

Beyond a critical concentration of vanillin (which depends in this case on the extent of polishing of the GC electrode) the prewave becomes independent of concentration. However the prewave current increases with sweep rate. The prewave potential also shifts in the cathodic direction with increase in sweep rate. Another interesting observation regarding the prewave is presented in Fig. 4. In the multisweep cyclic voltammetry the prewave is totally absent in the second and the subsequent sweeps. Many quantitative features of the prewave in aprotic media such as the peak potential, peak current, their dependence on sweep rate and concentration depend greatly on the level of polishing and pretreatments. Hence more quantitative analysis of these data is not attempted here.

The real surface of any solid electrode, even under the most stringent experimental conditions, can still contain some surface imperfections and surface chemical functional groups. Hence even a "perfectly polished" GCE prepared according to the procedure described in the experimental section can still contain some small concentrations of surface functional groups [1].

The concentration of these surface functional groups may be increased by partial polishing or incomplete polishing or chemical or electrochemical activation. Let us denote the surface functional groups by a common formula namely S-COOH, always remembering that this can denote any other functional groups (such as quinonoic or phenolic group) which can show acid-base properties. These surface functional groups can serve as protonating agents for vanillin.

$$\text{S-COOH} + \text{RCHO} \longrightarrow \text{S-COO}^- \ldots {}^+\text{CH(OH)R} \tag{3}$$

This type of surface protonated species can be reduced easily when compared to RCHO itself. Hence, wherever such a surface protonation becomes possible a prewave before the main reduction would be noticed. The surface protonation process in the prewave region is found to be a time-dependent slow process, as seen from the response of the multi-sweep voltammogram. To our knowledge, such prewaves have not so far been reported for carbonyl compounds for mercury or any other electrode in the absence of protonating agents. This surface protonation model presented here is also similar to that proposed to explain similar observation on Nafion® coated GCE for different organic molecules of lower basicity [4].

3.3. *Surface effects in aqueous media*

On a perfectly polished GCE, vanillin gives one reduction wave in acidic and alkaline media. The reduction peak occurs at potentials close to the hydrogen evolution potential. Apparently the peak current increases with sweep rate and concentration. Since the reduction process occurs at the hydrogen evolution potential region, quantitative cyclic voltammetric analysis is not possible. In neutral pH medium, in addition to the main wave, a prewave at about 200 mV less cathodic to the main wave is observed (Fig. 5). In neutral medium also, the main reduction process occurs at extreme cathodic potentials in the region of hydrogen evolution.

Constant potential electrolysis in acid medium yields a two electron reduction product, namely vanillyl alcohol. In neutral and alkaline medium constant potential electrolysis yields no product. This may be due to hydrophobic film formation on the GCE surface which hinders the electrochemical process.

In the neural pH medium the observed wave cannot

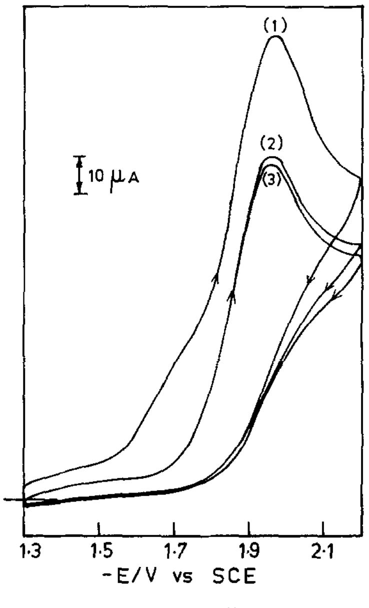

Fig. 4. Cyclic voltammograms for vanillin reduction on a partially cleaned GCE in 0.1 M TBAI/DMF in multisweep (vanillin) = 4 mM at 80 mV s^{-1}. (Numbers indicate the sweeps)

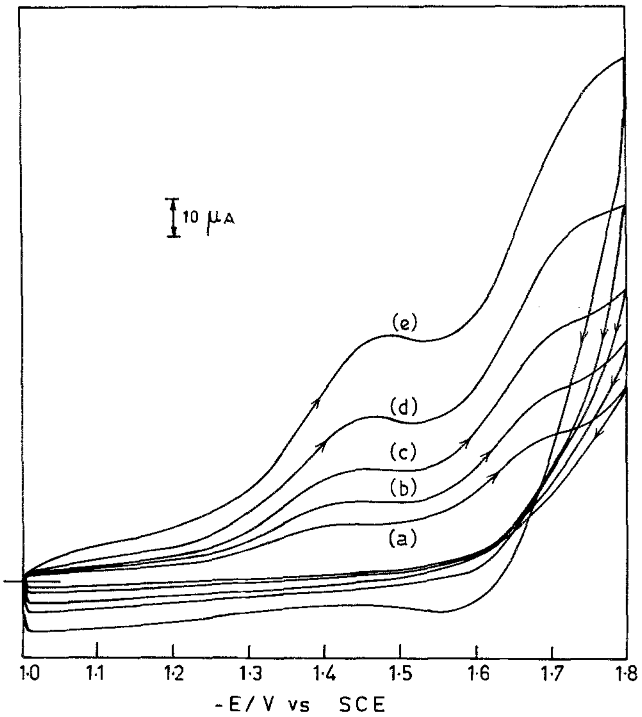

Fig. 5. Cyclic voltammograms for vanillin reduction on GCE in 0.1 M Tetraethylammonium-toluene-4-sulphonate/50% EtOH at various sweep rates (vanillin) = 1 mM: (a) 20, (b) 40, (c) 80, (d) 160 and (e) 320 mV s^{-1}.

be removed by any amount of polishing or pretreatment. This prewave is similar to that obtained in DMF on a partially polished electrode. The peak current of the prewave increases with increasing sweep rate. In multi-sweep cyclic voltammetry the prewave is totally absent in the second and the subsequent sweeps, as in the case of DMF (similar to Fig. 4). This indicates that the prewave is due to a slow time-dependent process involving vanillin and surface functional groups on GCE. To evaluate this time effect, cyclic voltammograms in the prewave region were recorded at the same sweep rate after various time intervals between each sweep. Such time dependent voltammograms are presented in Fig. 6. The maximum limiting current of the prewave is observed when the time interval between the sweeps is equal to or greater than 5 min. The linear sweep voltammogram itself may be considered as an i–t transient since the potential axis is directly related to time. The charge accumulated for each time can be obtained by direct integration with the appropriate background correction. The charge varies with time linearly before reaching a limiting value in about 5 min. The maximum charge in the prewave region was found to be 43 μC cm^{-2}. If we assume that the "n" value for the reduction of vanillin in the prewave region is one (dimerisation) as in the main wave region leading to the same product and a monolayer coverage would approximately correspond to 175 μC cm^{-2} for a 1e^- process [15], the maximum surface coverage of surface bound species is about 25%.

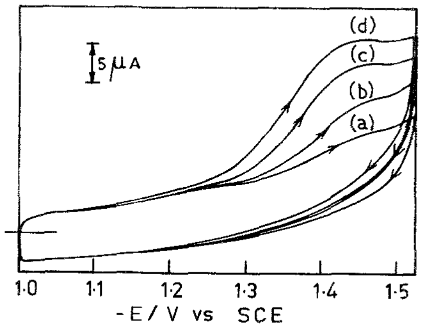

Fig. 6. Time effect on cyclic voltammetric adsorption prewave for vanillin reduction on GCE in 0.1 M Tetraethylammonium-toluene-4-sulphonate/50% EtOH at 80 mV s^{-1} (vanillin) = 1 mM. (a) 30, (b) 60, (c) 90 and (d) 150 s time intervals.

In the aqueous acidic pH region, the carbonyl compound can undergo protonation in the bulk and hence the surface protonation is not observed. In the alkaline pH region, the surface acidic groups exist in basic form (for example -COO$^-$ instead of -COOH) and so no catalytic effect is noticed again. Only in aprotic solvents and neutral aqueous media are both criteria of the presence of acidic groups on the surface of the electrode and of unprotonated carboxylate groups in solution satisfied. Hence the prewave occurs only in aprotic and neutral media.

Also the prewave cannot be due to the "product adsorption" wave extensively discussed in the polarographic literature [16]. Such adsorption–desorption processes are rapid equilibrium processes. In contrast, the surface protonation reaction suggested here is essentially time-dependent.

4. Conclusions

Vanillin on GCE in aprotic media is reduced to the anion radical and dianion. The anion radical undergoes fast dimerisation. Vanillin gives a surface prewave on a partially pretreated GCE in aprotic media. This prewave is quite sensitive to the pre-treatment of the electrode. Available evidence suggests that the surface functional groups on the electrode surface are responsible for this prewave.

In aqueous media, the reduction occurs at the extreme cathodic potential which merges with the background reduction. Constant potential electrolysis experiments in acid medium gives vanillyl alcohol. In neutral medium vanillin gives a slow time-dependent surface protonation wave in the form of a prewave in addition to the main reduction wave.

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