Electrochemical Oxidation of Guaiacol at Platinum Electrode

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The anodic oxidation of guaiacol at a platinum wire electrode in aqueous solutions by cyclic voltammetry and chronoamperometry has been studied. The data have been utilized in the evaluation of transfer and diffusion coefficients of the electroactive species under consideration. Mechanism of the oxidation process has been proposed and is consistent with the electrochemical data. The nature of the adsorption involved is discussed.

LITERATURE on the electrochemical oxidation of guaiacol is scanty. Papouchoudo *et al.*[1] have reported the cyclic voltammetric studies of the oxidation of guaiacol in a solution of pH 2·3 and identified the product as *o*-benzoquinone, formed by the removal of two electrons. In the present investigation, an attempt is made to elucidate the nature and mechanism of the electrochemical oxidation of guaiacol at a platinum electrode in aqueous solutions of different pH values using cyclic voltammetric and chronoamperometric techniques. The data have also been utilized in the evaluation of transfer and diffusion coefficients of the electroactive species under consideration. The nature of the adsorption involved is discussed.

The theoretical principles and various applications of the cyclic voltammetric and chronoamperometric techniques have been described in detail in the literature[2,3].

Materials and Methods

Riedel grade sample of guaiacol was purified by distillation. The distillate collected at 204-5° was used for the preparation of solutions, first by dissolving the guaiacol in methanol and making up the solution with water.

Supporting electrolytes used were: (i) Clarks and Lubs buffer of pH 1·3, prepared by mixing 0·1N hydrochloric acid (200 ml) and 0·2N potassium chloride (250 ml) and diluting to 1000 ml; (ii) phosphate buffer of pH 6·6, prepared by mixing 0·1N sodium hydroxide (178 ml) and 0·1N potassium dihydrogen phosphate (500 ml) and making up the resulting solution up to 1000 ml. Other supporting electrolytes (0·1N sodium carbonate, 0·1N sodium hydroxide and 1N sulphuric acid) were prepared using BDH analar grade samples.

The details of the instrument used and the experimental procedure have been discussed elsewhere[4].

Results and Discussion

Typical cyclic voltammograms of guaiacol in the different media studied are presented in Figs 1 and 2. In sulphuric acid and Clarks and Lubs buffer, a reduction peak is noticed at $+0·30$ V vs SCE. This is possibly due to the reduction of the oxidation product formed. This reduction peak is not noticed in other media in the potential range used. Table 1 presents the cyclic voltammetric data for guaiacol (peak potential values at different sweep rates). The variation of peak potential with sweep rate observed in the different media studied indicates the process to be irreversible. i_p vs $v^{1/2}$
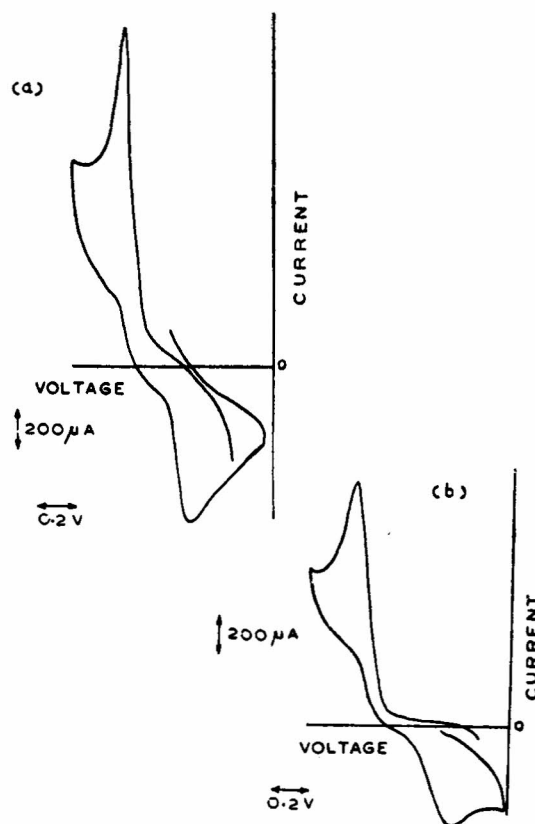

Fig. 1 — Cyclic voltammograms of guaiacol (1·5 mM) in (a) H$_2$SO$_4$ (sweep rate = 0·05 V sec^{-1}), (b) Clarks and Lubs buffer (sweep rate = 0·04 V sec^{-1})
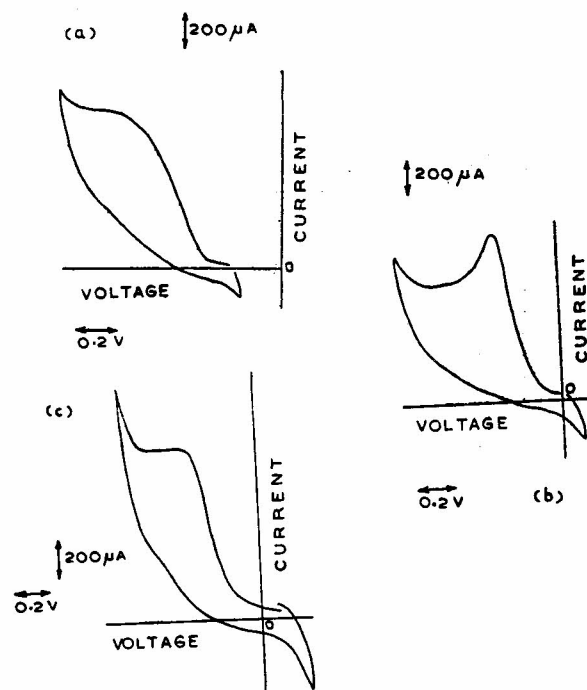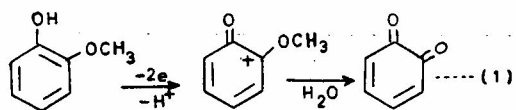
Fig. 2 — Cyclic voltammograms of guaiacol (1·5 mM) in (a) phosphate buffer (sweep rate = 0·05 V sec⁻¹), (b) Na₂CO₃ (sweep rate = 0·05 V sec⁻¹) (c) NaOH (sweep rate = 0·04 V sec⁻¹)

Fig. 3 — i_p vs $v^{1/2}$ plot for guaiacol (1·5 mM) in Clarks and Lubs buffer

plot (Fig. 3) for guaiacol suggests that the electrode process is diffusion-controlled.

The number of electrons involved in the oxidation of guaiacol is evaluated to be two. This is evaluated by assuming the diffusion coefficient of guaiacol to be same as that of p-methoxyphenol, and calculating $i_p/v^{1/2} c$ values and comparing these values with the values obtained for guaiacol experimentally (given in Table 2). αn_a values employed are calculated from the cyclic voltammetric data. A single two electron peak has been observed for its oxidation and the process involving the formation of o-benzo-quinone may be represented by Eq. (1).

The chronoamperometric data for the electro-chemical oxidation of guaiacol in the different media studied are given in Table 3. $it^{1/2}$ vs t plots of guaiacol (Fig. 4) show that in the media of higher pH, 0·1N sodium carbonate and 0·1N sodium hydroxide, $it^{1/2}$ values exhibit decreasing trend with time. This is indicative of the presence of adsorption, probably weak adsorption of the product which reduces the effective area of the electrode resulting in lower current values. The absence of pre- or post-peaks in the cyclic voltam-mograms of guaiacol in these media indicate the absence of any strong adsorption of guaiacol or the product of oxidation.
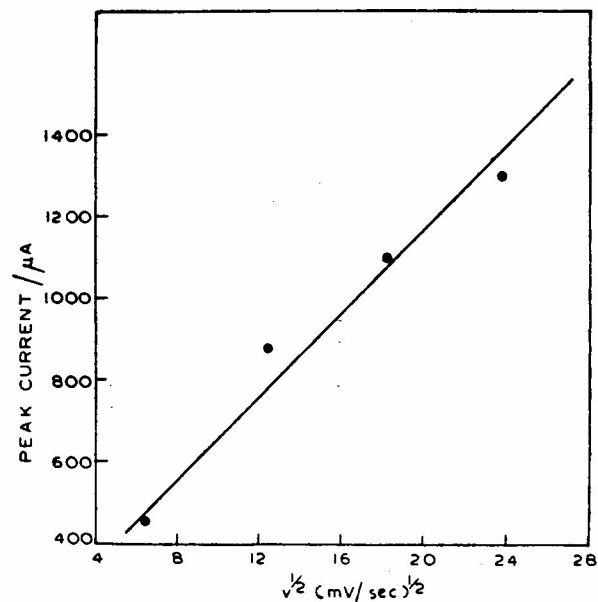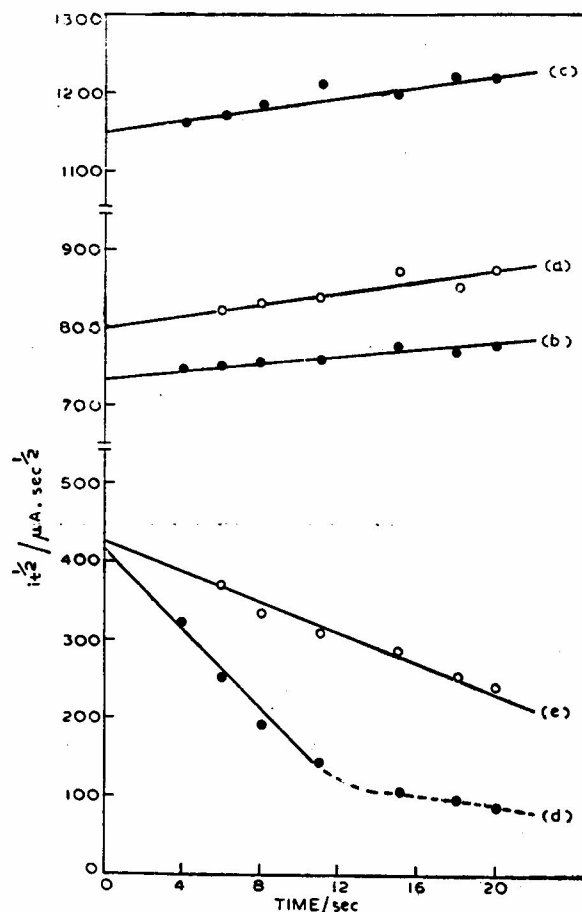

Fig. 4 — $it^{1/2}$ vs t plots of guaiacol (2·4 mM) in (a) H₂SO₄, (b) Clarks and Lubs buffer, (c) phosphate buffer, (d) Na₂CO₃ and (e) NaOH

TABLE 1 — CYCLIC VOLTAMMETRIC DATA FOR GUAIACOL

[Conc. of guaiacol = 1·5 mM]

Sl No.	Sulphuric acid		Clarks and Lubs buffer		Phosphate buffer		Sodium carbonate		Sodium hydroxide	
	v/V sec^{-1}	E_p/V	v/V sec^{-1}	E_p/V	v/V sec^{-1}	E_p/V	v/V sec^{-1}	E_p/V	v/V sec^{-1}	E_p/V
1	0·05	+0·76	0·04	+0·79	0·05	+0·72	0·05	+0·28	0·05	+0·33
2	0·16	+0·78	0·15	+0·77	0·16	+0·78	0·14	+0·32	0·15	+0·36
3	0·34	+0·78	0·33	+0·80	0·29	+0·80	0·32	+0·35	0·34	+0·37
4	0·41	+0·79	0·38	—	0·40	+0·88	0·40	+0·35	0·39	+0·37
5	0·58	+0·80	0·57	+0·81	0·59	+0·98	0·60	+0·35	0·57	+0·40
6	0·62	+0·80	0·83	+0·82	0·80	+1·00	0·80	+0·36	0·82	+0·44

TABLE 2 — CYCLIC VOLTAMMETRIC DATA FOR GUAIACOL AT DIFFERENT CONCENTRATIONS

Sl No.	Medium	pH	Sweep rate V sec^{-1}	[Guaiacol] mM	Current (μA)	$i_p/v^{1/2}c$
1	Sulphuric acid		0·05	1·5	650	1958
				2·4	780	1471
				3 5	1355	1711
2	Clarks and Lubs buffer	1·3	0·05	1·5	450	1479
				2·4	540	1111
				3·5	800	1102
3	Phosphate buffer	6·6	0·05	1·5	320	964
				2·4	520	981
				3·5	750	947
4	Sodium carbonate	11·4	0·05	1·5	380	1181
				2·4	475	924
				3·5	635	827
5	Sodium hydroxide	13·0	0·05	1·5	393	1260
				2·4	440	885
				3·5	620	835

TABLE 3 — CHRONOAMPEROMETRIC DATA FOR GUAIACOL

[Conc. of guaiacol = 1·5 mM]

Time sec	Current/μA in				
	Sulphuric acid	Clarks and Lubs buffer	Phosphate buffer	Sodium carbonate	Sodium hydroxide
2	360	337	515	262	426
4	271	266	361	149	279
5	249	224	330	140	240
6	225	205	305	97	201
7	216	192	286	83	172
8	213	183	267	67	148
9	194	171	248	56	128
11	181	156	237	47	100
13	173	147	220	36	78
15	165	136	204	30	63
16	155	134	195	26	59
18	145	126	183	23	49
20	136	121	174	19	41
Potentials employed/V	+0·80	+0·80	+0·90	+0·40	+0·50

TABLE 4 — DIFFUSION COEFFICIENT DATA FOR GUAIACOL AT 24°

[Conc. of guaiacol = 1·5 mM]

Sl No.	Medium	αn_a	Diff. coeff. × 10⁵ (cm² sec⁻¹)	
			Cyclic voltammetric	Chronoamperometric
1	1N sulphuric acid	0·80	0·876	0·604
2	Clarks and Lubs buffer	0·68	0·680	0·525
3	Phosphate buffer	0·20	3·396	1·141
4	0·1N sodium carbonate	0·69	0·433	0·260
5	0·1N sodium hydroxide	0·53	0·816	0·870

αn_a values and diffusion coefficient data for guaiacol are presented in Table 4. The low value of the transfer coefficient may be attributed to the drawn out wave obtained for guaiacol in the phosphate buffer (Fig. 2a). The diffusion coefficient values obtained by chronoamperometric method are preferred to cyclic voltammetric values for the following reasons: (i) Cyclic voltammetric evaluation of the diffusion coefficient requires the knowledge of αn_a and $i_p/v^{1/2} c$ values. αn_a is extremely sensitive to the surface state of the electrode and $i_p/v^{1/2}c$ values are also influenced by adsorption. (ii) Chronoamperometric evaluation of the diffusion coefficient requires a knowledge of $(it^{1/2})_0$ values. Since these values are evaluated by extrapolation to zero time, diffusion coefficient values are not likely to be affected by adsorption.

References

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