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A study of adsorption characteristics of the paraquet using stationary electrode

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Paraquet has been reduced at cathode and cyclic voltammograms have been recorded. The adsorption studies on electrode surface reveals that new species has been formed which is characterised by cyclic voltammetry and Raman spectroscopy. The plot i_p vs $\sqrt{v}$ gives a linear curve which further supports our conclusion.

The 1,1′-dimethyl-4,4′-bipyridinium radical cation (paraquet) is one of the most efficient electron relays used in water photolysis[1]. A common scheme for this process is the production of blue coloured cation radical by electron transfer from an excited state of a photosensitiser. The back conversion of the reduced form of the relay to its initial state through water reduction to hydrogen is greatly enhanced by the presence of a noble metal catalyst (usually particles or deposits of noble metal) which acts as a microelectrode[2]. Recent studies[3] by cyclic voltammetry indicated the preferential adsorption of paraquet on silver and gold electrodes, for both bulk and as low as 10^{-5} *M* concentrations of this relay. A similar strong interaction between 1,1′-dimethyl-4,4′-bipyridinium radical cation and a metal surface was also observed in case of silver electrode by CV and Laser Raman spectroscopy[4]. The formation of electrochromic multilayer deposits of diheptyl and diethylbipyridinium salts have recently been studied by voltammetry coupled with rapid time resolved UV-visible spectroscopy[5]. A number of Raman studies have been conducted on polished metal electrodes, specifically to metals associated with the surface enhanced Raman effect (SERS). The commercially important electrode materials are rarely shiny metals, so glassy carbon was chosen as a test case since it is a typical industrial electrode material. Freeman *et al.* have successfully demonstrated the applicability of FTIR spectroscopy to determine the species adsorbed from aqueous solution on it. Moreover, there are some reports[4] on the *in situ* characterization of Raman spectra of materials deposited on glassy carbon substrate and to the best of our knowledge no work has been done on the characterization of electrochemically generated species at glassy carbon electrode surfaces in solution.

The electroreflectance spectroscopy in the UV-visible range coupled with electrochemical measurements was recently used to study the adsorption of cytochrome C at a gold electrode[6]. However, due to the potential modulation technique, differential electroreflectance curves were obtained as a function of either the wavelength of the incident light (at fixed potential) or vice versa.

This paper describes a preliminary study on the absorption of 1,1′-dimethyl-4,4′-bipyridinum salt at a noble metal electrode. In order to achieve the high sensitivity necessary to detect monolayers or submonolayers of adsorbed species, voltammetric sweeps were recorded.

Materials and Methods

A supporting electrolyte solution (0.1 *M*, KCl) was prepared with triply distilled deionised water. The hydrated 1,1′dimethyl 4,4′bipyridinium dichloride (from Sigma) was recrystallised from methanol or acetone. It was added to the supporting electrolyte in order to obtain low bulk concentrations. The solution was deareated by bubbling nitrogen gas.

The spectroelectrochemical measurements were made in a special cell. The working electrode consisted of a smooth micro GCE (flat disc) electrode, polished with 0.05 μm alumina. A calomel electrode was used as the reference electrode and a platinum gauze as the counter electrode. A Jasco Raman spectrometer based on the double monochromator was used for obtaining Raman scattering from the cell. No polarisation analyser or scrambler was used in the collection system. Raman spectra were generally detected with a phototube operating in the

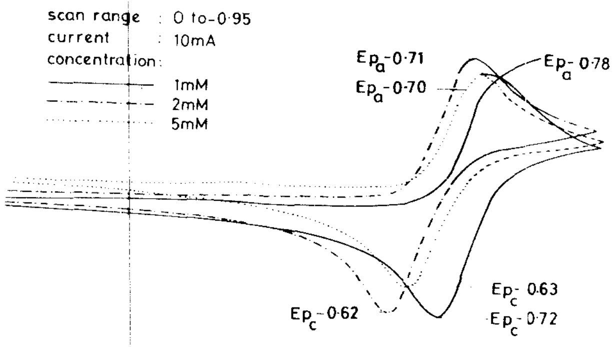

Fig. 1—Linear sweep voltammogram of paraquet in 0.1 *M* KCl at 100 mV/sec

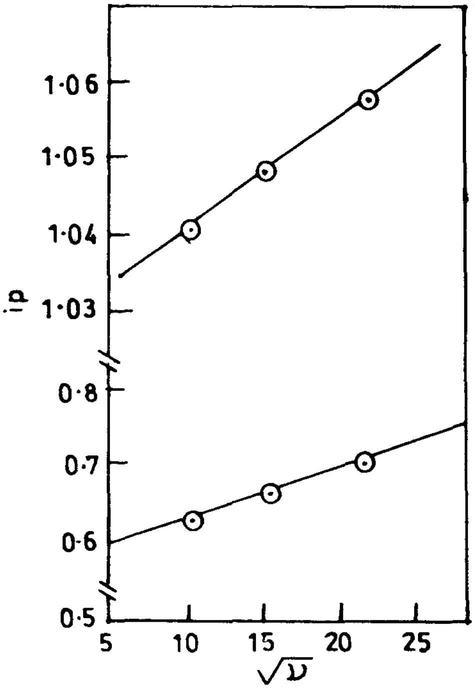

Fig. 2—Plot of *ip* versus $\sqrt{v}$

DC mode. The typical scanning conditions were 0.5 cm/sec with slits set for a 0.6 cm bandpass. A computer system was interfaced to the spectrometer for controlling the data collection and storing the recorded spectra for the subsequent data manipulation and display. A coherent Radiation CR-3 argon ion laser was used as the excited source and a claassen filter was used to remove unwanted argon ion emission lines from the laser beam. The laser power was measured with a coherent radiation power meter. The output of the laser was generally adjusted to 100 mW at the surface of the electrochemical cell.

A voltammetric analyser with a X-Y-T recorder was used for voltammetric studies and for controlling the potential of the working electrode while the Raman spectra were being acquired. The cyclic voltammograms were taken at different sweep rates varying from 50 mV/sec to 500 mV/sec between 0.0-0.95 V and 0.0-1.4 V.

Result and Discussion

The 1,1'dimethyl 4,4'bipyridinium salt can be reduced at a cathode through a one electron transfer step to a semiquinone cation radical, whereas a two electron reduction results in a quinone type molecule. Figure 1 shows the first sweep of a typical cyclic voltammogram on a glassy carbon electrode in deaerated 0.1 *M*(1,1'-dimethyl-4,4'-bipyridinium) (1 m*M*) in aqueous KCl solution scanned between 0 and −0.95 V showing single peak reduction and reoxidation. By contrast, sweeping from 0 to −1.4 V produces a more complexed cyclic voltammogram. At 1 m*M* concentration, the first and second reduction peaks are clearly seen. An other peak appears when the scan rate is reduced to 200 mV/sec. It is rather more surprising to see that on further decrease in scan rate i.e. 100 mV/sec, two more peaks. appear. It may be possible that there are more than one species present.

It is notable that the precursor must be a neutral species, since the single electron reduction cyclic voltammogram does not show concentration and sweep rate dependency. In our case, apart from the fact that, cyclic voltammetry indicates the presence of more than one species, it also shows that the adsorption at electrode surface and dimer formation is taking place. In Fig.1, we have taken the voltammogram at upto −0.95 V and could get a single redox peak. At a potential upto −1.4 V, and holding at this potential for 10 sec, it is evident that during the anodic sweep, there is practically no return peak for the oxidation whereas more than two peaks appear due to adsorption of the species at electrode surface and the splitting of peaks into two at the same potential indicating it to be a dimer (at −0.77 V). The plot of *ip* versus. $\sqrt{v}$ (Fig.2) indicates that it is increasing rapidly with the increasing scan rate, confirming the adsorption at the electrode surface. In addition to cyclic voltammetry, some spectral informations are also needed to confirm the dimer formation.

Investigations were undertaken to detect the adsorbed intermediate with *in situ* Raman spectroscopy and compared these spectra with the known solution species. While there are a number of reports in the literature on the measurements of the Raman spectra of this compound in solution, evidences for the adsorbed species on the electrode is not so clear. Regis and Corset[7] reported the

Table 1—Raman spectral bands (in cm^{-1}) of 1,1′ – dimethyl – 4,4′ – bipyridinium and its radical cation

Electrochemically generated

2 mM			1 mM		
50 mM	−0.7V	−0.9V	−0.7V	−0.9V	Chemically generated from 2 mM
				$^{\Delta}$664	—
662	682 m	682 m	682 w	682 w	682 w
—	—	—	—	798	—
842	820 m	820 m	820 m	820 m	820 m
—	—	$^{\Delta}$ 997 m	—	997 vs	—
1060 w	1028 s	1028 s	1028 s	1028 s	1028 s
—	1048 sh	1048 sh	1048 sh	1048 sh	1048 sh
—	$^{+}$1195 w	$^{+}$1195 w	—	—	—
1194 vs	1215 w	1215 w	1215 w	1215 w	1215 w
1234 m	1250 m	1253 m	1250 m	1250 m	1253 m
—	—	—	—	$^{\wedge}$1294	—
—	$^{+}$1345 sh	$^{+}$1345 sh	—	$^{\wedge}$1349 ms	—
1302 vs	1356 ms	1356 ms	1356 ms	$^{\wedge}$1364 ms	1356 m
—	—	$^{\wedge}$1406 vw	—	$^{\wedge}$1406 ms	—
1345 w	—	1430 w	1430 w	1430 w	1430 w
1371 w	1430 w	—	—	—	—
—	$^{+}$1515 ms	$^{+}$1515	—	—	—
1539 s	1534 vs	1534 vs	1534 vs	1534 vs	1534 vs
—	$^{+}$1610 w	—	—	$^{\Delta}$1545 vs	—
—	1662 s	$^{+}$1610 w	—	—	—

vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw= very weak, sh = shoulder, $^{+}$ = dimer, $^{\Delta}$ = adsorbed

adsorption on the surface of a silver electrode, but could not detect the same adsorbate on platinum. Ohsawa *et al.*[8] and Foster *et al.*[9] have reported the spectrum of electrochemically and chemically generated paraquet species in the solution. The band positions are similar to those ascribed by Regis and Corset[7] to adsorbed paraquet species. Melendres *et al.*[4] have also studied the Raman spectra of paraquet species generated on a silver electrode at potentials of −0.8 and −0.9 V, and found them to be essentially identical to the one reported earlier[9]. They found a different spectrum at −0.6 V after cycling the electrode between anodic dissolution and cathodic redeposition potentials in the presence of added KCl, and ascribed the new spectrum to adsorbed paraquet species. It appears, therefore, that while the Raman spectrum of electrogenerated paraquet in the solution has been well characterized, there is a doubt whether there is such an adsorbed species. Therefore, a special effort was made to determine if it is possible to detect and identify species adsorbed on GCE. The Raman spectra of 1,1′dimethyl 4,4′bipyridinium dichloride in aqueous solution were recorded. The positions of the major bands in these spectra are in good agreement with those reported by other workers[10,11]. The bands have been tentatively assigned on the basis of the data available in literature (Table 1). Our assignments are similar to those assigned by Hester and Suzuki's[12] except for the 1194 and 1060 cm^{-1} bands. In the case of the radical cation, Raman enhancement of the order of 25 cm^{-1} relative to the Raman lines was observed. The Raman spectra show some additional bands at 662, 798, 997, 1294, 1406, 1545 and 1676 cm^{-1} and the bands at 1253 cm^{-1} appeared to gain intensity. These bands suggest the presence of more than one species at a more negative potential.

To confirm the presence of species adsorbed at the electrode surface, we investigated the effect of flow rate on the Raman spectrum. We took the Raman spectra at two different potentials and three flow rates. At −0.7 V the bands are flow rate independent, but it can be seen from Table 1 that the relative intensities of bands ascribed to the surface confined

Table 2—Effect of flow rate on relative intensity of Raman lines

Flow rate * A.U	Peak areas					
	997 cm		1534 cm		1610 cm	
	E	E	E	E	E	E
0.0	0.0	2.14	2.80	3.88	1.22	2.1
5.0	0.0	5.10	2.91	7.32	1.27	4.3
10.0	0.0	5.70	2.91	8.87	1.22	4.7

* Arbitrary Unit

species increase relatively to the solution band at 1028 cm^{-1} with increasing flow rate. This is most marked for the new bands at 997 cm^{-1} but is also true for others (1534 and 1610 cm^{-1}). The ratios are presented in Table 1.

The concentration of species in solution phase must be flow rate dependent, since it is the result of the balance between the rate of generation, rate of reaction and rate of convections. Therefore, we would expect the ratio of band intensities of surface confined species to solution, to increase with flow rate. We further investigated the nature of the adsorbed species by sweeping the potential to -1.4 V and holding at this potential for a time period of 10 sec. It is evident that during the anodic sweep there is practically no return peak for the oxidation, whereas a large peak corresponding to the oxidation of 1,1'dimethyl 4,4'bipyridinium is observed. At the same time, since the intensity of the band at 997 cm^{-1} and other bands assigned to the adsorbed species also increase with time, it appears that the adsorbed species is a radical salt of paraquet.

Paraquet has been found to be significant for its use as a mediator and $-$ ve redox potential. It has two $1e^{-1}$ reduction steps. The radical cation of paraquet has been used as an electron transfer mediator for various biological molecules such as cytochrome C, ferrodoxin NADP-reductase system and the flavoprotein flavodoxin. Thus this technique has helped us to characterize the electrochemically generated radicals, dimer radicals with Raman spectroscopy in solution.

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