

Investigations on adsorption of paraquet radical cations on gold electrodes by voltammetry coupled with laser Raman spectroscopy

B S GARG* and N PARDEEP

Department of Chemistry, Delhi University, Delhi 110007, India

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Abstract. The electrochemical redox behaviour of paraquet has been studied by employing an advanced electrochemical technique at different concentrations. The conformation of adsorption of paraquet radical cation is characterised by cyclic voltammetry, laser Raman spectroscopy and a graph between i_p and $v^{1/2}$.

Keywords. Paraquet; Au electrode; radical cation; cyclic voltammetry; laser Raman spectroscopy.

1. Introduction

The paraquet radical cation is one of the most efficient electron relays used in water photolysis (Kiwi and Gratzel 1982). A common scheme for this process is the production of the 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 reduction of water to hydrogen is greatly enhanced by the presence of a noble metal catalyst (usually particles or deposits of noble metal) which acts as a micro-electrode (Meisel *et al* 1981). Recent studies by cyclic voltammetry have indicated the preferential adsorption of paraquet on silver, GCE, and platinum electrodes for both bulk and very low concentrations of this relay. In continuation of our previous studies on adsorption of paraquet using glassy carbon and platinum electrodes (Garg and Pardeep 1993), we have presently extended our investigations to gold electrodes. 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 (Bewick *et al* 1983). Raman spectral studies have been conducted on polished metal electrodes, especially metals associated with the surface-enhanced Raman effect (SERS). The gold electrode has been chosen as a test case because it is easily available and is commercially used for electrochemical investigations. Freeman and Jansson (1985) have successfully demonstrated the applicability of FTIR spectroscopy to determine the species adsorbed on it from aqueous solution. Moreover, there are some reports (Meisel *et al* 1981) on the *ex-situ* characterization of Raman spectra of materials deposited on gold electrodes and, to the best of our knowledge, no work has been done on the characterization of electrochemically generated species at gold electrode surfaces in solution.

* For correspondence

The electroreflectance spectroscopy in the UV-visible range, coupled with electrochemical measurements, was recently used to study the adsorption of cytochrome C at a silver electrode (Hinnen *et al* 1983). 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 adsorption of paraquet at a gold electrode by cyclic voltammetry and *in-situ* laser Raman spectroscopy. In order to achieve the high sensitivity necessary to detect monolayers or submonolayers of adsorbed species, the signal background (including adsorption from the bulk solution) was compensated by double beam detection and the reflectance adsorption signal at a fixed wavelength was averaged during fast voltammetric sweeps.

2. Experimental

2.1 Materials

KCl (0.1 M) was used as a supporting electrolyte and was prepared with triple-distilled deionised water. The hydrated paraquet (1,1'-dimethyl-4,4'-bipyridinium) obtained from Sigma was recrystallised from methanol or acetone. It was added to the supporting electrolyte in order to obtain low bulk concentrations. Nitrogen was passed through the solution to make it oxygen-free.

2.2 Cell designing

A three-electrode special cell has been designed for the spectroelectrochemical studies as shown in figure 1. A gold electrode was used as the working electrode, a calomel electrode as the reference electrode and a platinum gauze as the counter electrode. A voltammetric analyser with an *X-Y-T* recorder was used for voltammetric studies and for controlling the potential of the working electrode, while the Raman spectra were being recorded. The cyclic voltammograms were taken at different sweep rates varying from 100 mV/s to 500 mV/s between 0.0 and 0.95 V and 0.0 and 1.4 V.

2.3 Instrumentation

A Jasco Raman spectrophotometer based on the double monochromator was used for obtaining Raman scattering from the cell. No polarization analyser or scrambler

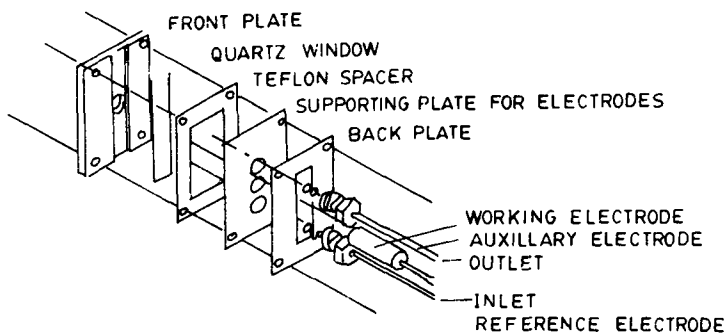


Figure 1. The electrochemical cell (schematic).

was used in the collection system. Raman spectra were generally detected with a phototube operating in the DC mode. The typical scanning conditions were 0.5 cm per second 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 subsequent data manipulation and display. A coherent radiation CR-3 argon ion laser was used as the excitation source and a Classen 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. The Raman spectra were recorded by controlling the potential of the working electrode by a computer interface.

3. Results and discussion

3.1 Electrochemical studies

Paraquet can be reduced at the cathode at a potential around 0.68 V through a one-electron transfer step to a semiquinone cation radical, whereas a two-electron reduction results in a quinone type molecule. Figure 2 shows the first sweep of a typical cyclic voltammogram on a gold electrode in deaerated paraquet (1 mM concentration) in 0.1 M aqueous KCl solution scanned between 0 and -0.95 V showing a single reduction peak. In contrast, sweeping from 0 to -1.4 V (figure 3) produces a more complexed cyclic voltammogram. At 1 mM concentration, the first and second reduction peaks are clearly seen. Another peak appears when the scan rate is reduced from 500 mV/s to 200 mV/s. It is more surprising to see that on further decrease in scan rate i.e. 100 mV/s, two more peaks appear. It is possible that there is more than one species present. There seems to be a cross-over loop around -1.3 V. A cross-over loop generally indicates nucleation and deposition of material on the electrode surface, since the single electron reduction cyclic voltammogram

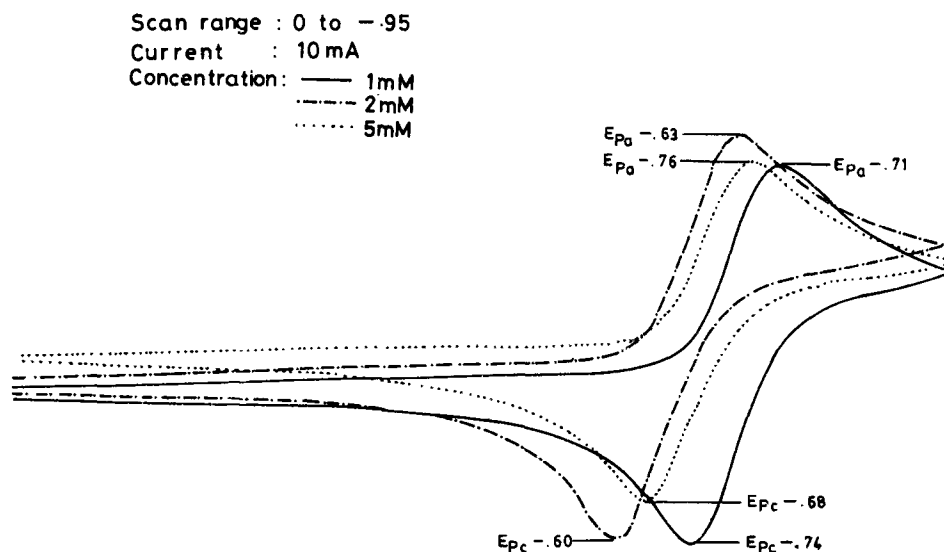


Figure 2. Cyclic voltammogram of paraquet at 100 mV/s, scan range = 0 to -0.95.

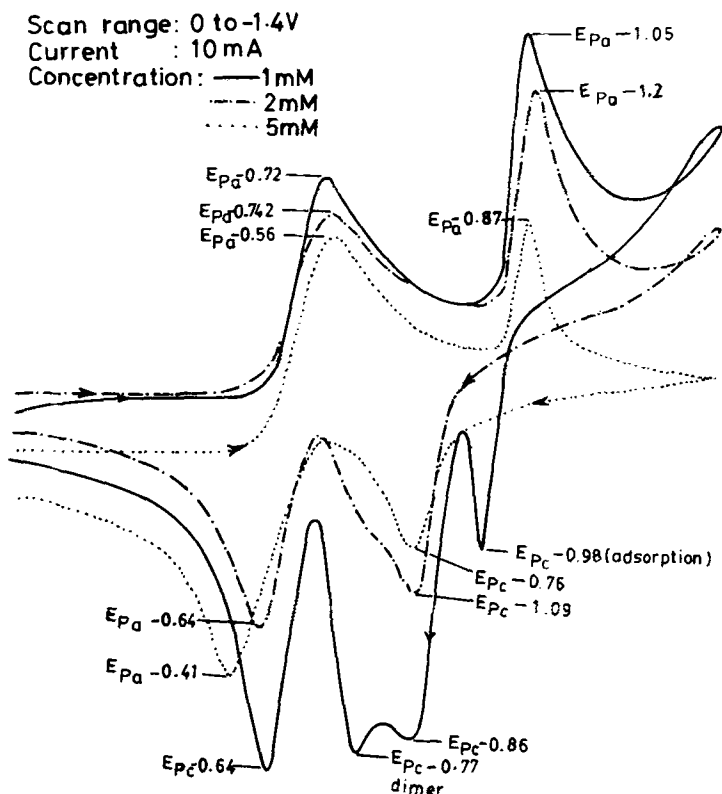


Figure 3. Cyclic voltammogram of paraquat at 100 mV/s, scan range = 0 to -1.4.

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 adsorption at the electrode surface and dimer formation are taking place. In figure 2, we have recorded the voltammogram upto -0.95 V but could get a single oxidation-reduction peak. At a potential upto -1.4 V, and holding it at this potential for 10 s, it is evident that during the anodic sweep, there is practically no reverse peak for oxidation whereas more than two peaks appear due to adsorption of the species at the electrode surface and the splitting of peaks into two at the same potential, thus indicating that it is a dimer (at -0.77 V). The plot of i_p versus $v^{1/2}$ (figure 4) shows that it increases rapidly with increasing scan rate, confirming adsorption at the electrode surface. In addition to cyclic voltammetry, some spectral information is also needed to confirm the dimer formation.

3.2 Spectrochemical studies

Investigations were undertaken to detect the adsorbed intermediate *in situ* with Raman spectroscopy and compare these spectra with known solution species. While there are a number of reports in the literature on the Raman spectra of this compound in solution, evidence for the species adsorbed on the electrode is not so clear. Regis and Corset (1981) reported adsorption on the surface of a silver electrode, but could not detect the same adsorbate on gold. Ohsawa and Nishijima (1981) and Foster *et al*

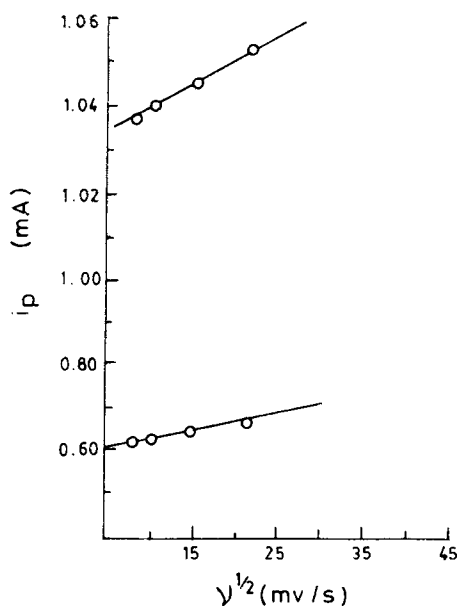


Figure 4. Plot of i_p vs $v^{1/2}$.

(1982) have reported the spectra of electrochemically and chemically generated paraquet species in solution. The band positions are similar to those ascribed by Regis and Corset (1981) to the adsorbed paraquet species. Melendres *et al* (1983) have also studied the Raman spectra of paraquet species generated on a silver electrode at potentials of -0.8 and -0.9 V, and have found them to be essentially identical to the one reported earlier. Foster *et al* (1982) 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 electro-generated paraquet species in the solution has been well characterized, there is doubt about whether there is such an adsorbed species. Therefore, a special effort was made to detect and identify species adsorbed on gold electrodes. The Raman spectra of paraquet in aqueous solution were recorded. Diagnostic bands given in table 1 and the representative spectra are shown in figure 5. The positions of the major bands in these spectra are in good agreement with those reported by other workers (Lee *et al* 1991). Our assignments are similar to those by Hester and Suzuki (1982) except for the 1200 and 1050 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 , 961 , 1294 , 1406 , 1545 and 1676 cm^{-1} , and the bands at 1253 cm^{-1} appeared to gain intensity with flow rate. 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 (table 2), but it can be seen from table 1 that the relative intensities of bands ascribed to the surface-confined species increase relatively to the solution band at 1028 cm^{-1}

Table 1. Raman band positions (cm^{-1}) for 1,1-dimethyl 4,4'-bipyridinium (paraquet) and its radical cation.

50 mM	Electrochemically generated				Chemically generated from 2 mM
	2 mM		1 mM		
	-0.7 V	-0.9 V	-0.7 V	-0.9 V	
—	—	—	—	$\Delta 664$	—
662	682 m	682 m	682 w	682 w	682 w
—	—	—	—	798	—
842	820 m	820 m	820 m	820 m	820 m
—	—	$\Delta 997m$	—	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
—	—	—	—	$\Delta 1294$	—
—	*1345 sh	*1345 sh	—	$\Delta 1349ms$	—
1302 vs	1356 ms	1356 ms	1356 ms	$\Delta 1364ms$	1356 m
—	—	$\Delta 1406vw$	—	$\Delta 1406ms$	—
1345 w	—	1430 w	1430 w	1430 w	1430 w
1371 w	1430 w	—	—	—	—
—	*1515 ms	*1515	—	—	—
1539 s	1546 vs	1546 vs	1546 vs	1546 vs	1534 vs
—	*1619 w	—	—	$\Delta 1545vs$	—
—	*1662 s	*1619 w	—	1667 s	—

vs = very strong*s* = strong*ms* = medium strong*m* = medium*w* = weak*vw* = very weak*sh* = shoulder

* = dimer

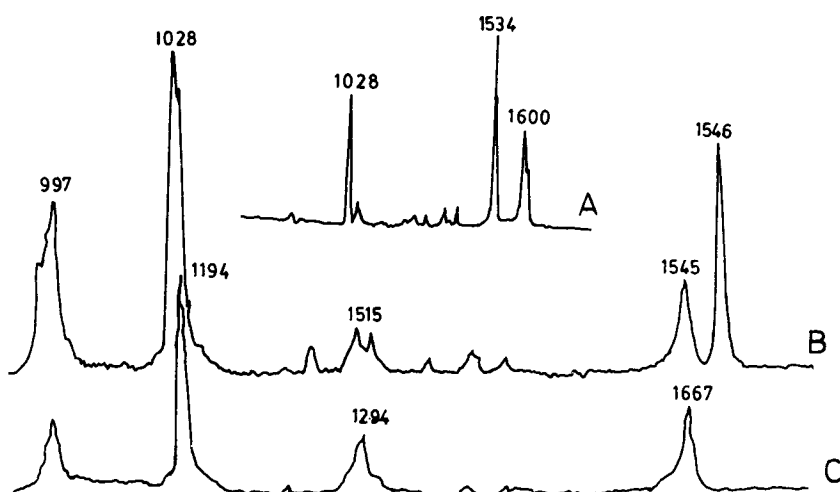
 Δ = adsorbed**Figure 5.** Raman spectra of paraquet chemically generated (A) and at concentrations of 2 mM (B) and 1 mM (C).

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

Flow rate (*A.U.)	Peak areas (cm^{-1})					
	961		1546		1619	
	E_1	E_2	E_1	E_2	E_1	E_2
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

with increasing flow rate. This is most marked for the new bands at 961 cm^{-1} but is also true for others (e.g. 1546 and 1619 cm^{-1}). The ratios are presented in table 2.

The concentration of species in the 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 convection. Therefore, we would expect the ratio of band intensities of surface-confined species to that of 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 s. It is evident that during the anodic sweep there is practically no reverse peak for the oxidation, whereas a large peak corresponding to the oxidation of paraquet is observed. At the same time, since the intensity of the band at 961 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. The intercept in figure 4 is not zero, indicating the adsorption of redox species on the electrode surface.

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

4. Conclusions

In conclusion, *in-situ* laser Raman spectroscopy appears to be a very useful and sensitive technique, able to detect the presence of a coloured species (i.e. Pq^+ in this case) adsorbed on a noble-metal electrode (i.e. gold here). By analysis of the spectral parameters (intensity, line-width etc), it should be possible to obtain quantitative information about the interactions in the adsorbed layer. This would be very useful in elucidating the role played by electron relays (such as Pq^{+2}) used in water photolysis.

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