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Voltammetry at C_{60}-modified electrodes

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Abstract

The reduction of electrodes coated with C_{60}-fullerene is examined in acetonitrile solution containing a wide variety of supporting electrolytes ($MClO_4$; M = Li, Na, $Ba_{0.5}$, NR_4). Electrochemical intercalation is observed with the formation of fulleride salts. Intercalation is typically irreversible except for the case of R = *n*-butyl where stable coats of fullerides may be formed into which charge can be passed with near chemical reversibility. Electron-transfer reactions at electrodes modified with C_{60} coatings were investigated for diverse substrates. With unreduced coats impeded diffusion to the metal surface was seen, whereas with films reduced in the presence of tetrabutylammonium perchlorate coat-mediated electron transfer to the substrate was possible.

INTRODUCTION

This paper is concerned with the electrochemical behaviour of thin coats of C_{60} deposited onto an electrode surface and studied voltammetrically using a non-aqueous solvent (acetonitrile) in which C_{60} is essentially insoluble. In a Preliminary note [1] we have reported that the reduction of such coats is strongly dependent on the nature of the supporting electrolyte employed, and that specifically with tetrabutylammonium perchlorate (NBu_4ClO_4, TBAP) reasonably stable coatings were achievable into which electrons could be (chemically) reversibly injected, presumably leading to the formation of tetrabutylammonium salts of $C_{60}^{\cdot -}$ anions. Intriguingly, this "electrochemical intercalation" was revealed by two separate voltammetric waves each associated with the uptake of one electron per two C_{60} molecules, suggesting the formation of the salts $NBu_4^+(C_{60})_2$ and $NBu_4^+C_{60}$. In this

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paper we (i) report these observations more fully, (ii) extend our voltammetric investigations of C_{60}-modified electrodes to examine a diversity of electrolytes, thus developing the work of Jehoulet et al. [2] and Chabre et al. [3], and (iii) examine some electrode reactions taking place at these electrodes. We note that prior work in ref. 2 was unfortunately unreferenced in our Preliminary note [1].

EXPERIMENTAL

Stable C_{60} coats with good adhesion characteristics were prepared by evaporation of a small quantity of a solution on a gold or platinum electrode. Optimal reproducibility was found to result from the rapid evaporation encouraged by the heating of the electrode achieved using an industrial hot air gun (H.J. Latham Ltd., Shoeburyness, UK). Typically, drops of solution (ca. 3 μl) containing C_{60} in dichloromethane (17 or 25 μM), were coated one at a time onto a small insulated metal disc (area, ca. 0.4 cm^2) and heated to dryness before the addition of subsequent drops to form a coat of the desired thickness. Other methods of preparation produced modified electrodes with distinctly less reproducible characteristics.

Standard voltammetric measurements were made using a Solartron Instruments 1286 electrochemical interface which was combined with a 1250 frequency response analyser for the purposes of ac impedance studies. Rotating-disc hydrodynamic voltammetry was pursued using Oxford Electrodes equipment. All experiments were conducted in outgassed acetonitrile containing 0.1 M supporting electrolyte of the chemical identity specified below. All potentials were recorded against a saturated calomel reference electrode (SCE).

TBAP, tetraethylammonium perchlorate (TEAP), tetrahexylammonium perchlorate (THAP), tetraoctylammonium perchlorate (TOAP), lithium perchlorate and barium perchlorate were obtained from Fluka. Sodium perchlorate and *N*,*N*,*N*′,*N*′-tetramethylphenylene diamine (TMPD) were supplied by Aldrich. Lancaster Synthesis provided tetrabromo-*p*-benzoquinone ("*p*-bromanil", PBA) and methylene blue (MB) was purchased from Sigma. 9,10-Anthraquinone (AQH) and *N*-phenyl-*p*-phenylene diamine (PPPD) were obtained from BDH Ltd.

RESULTS AND DISCUSSION

First we consider the cyclic voltammetric responses seen from gold electrodes modified by "thin layers" of C_{60} formed by the evaporation of no more than a total of 100 μl of 25 μM solution of fullerene under conditions fulfilling the experimental protocol described in the previous section. This leads to surface coverages of 6.5×10^{-9} mol cm^{-2} corresponding to coats of thickness of ca. 40 monolayers or less. The electrodes were examined in acetonitrile solution containing a wide variety of different supporting electrolytes present at a concentration of 0.1 M. The results are shown in Figs. 1, 2 and 6 which all relate to a voltage scan rate of 100 mV s^{-1} and can be summarized as follows.

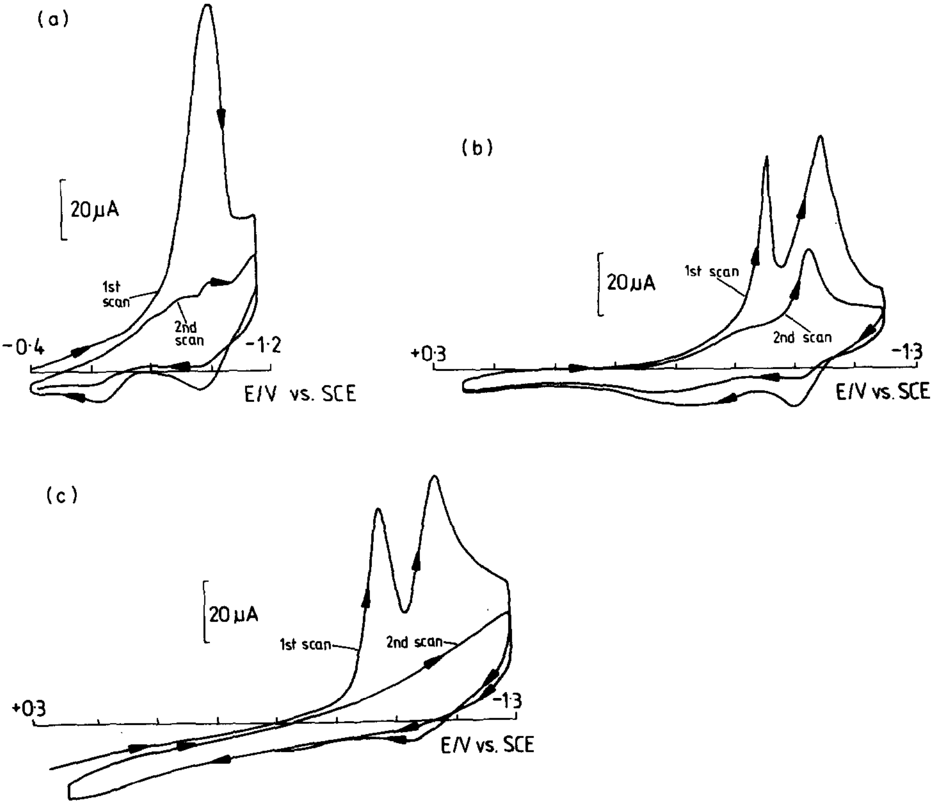

Fig. 1. Cyclic voltammograms showing the electroreduction of a "thin-layer" C_{60}-modified electrode in 0.1 M supporting electrolyte: (a) $LiClO_4$; (b) $Ba(ClO_4)_2$; (c) $NaClO_4$. In all three cases a scan rate of 100 mV s^{-1} was used.

Lithium, sodium and barium perchlorates

Figure 1 shows the first and second scans resulting from potential cycling within the windows encompassing all the fullerene-related faradaic features in each case. Large reduction waves are seen on the first negative scan, and integration of these curves shows that for all three systems a total of one electron (with a maximum error of ±10%) per C_{60} ball is passed; the shape of the voltammograms is suggestive of electron transfer to a surface-immobilized layer [4]. Only very small oxidative currents pass on the reverse (positive) voltage sweep and all faradaic activity is completely lost after a second potential cycle. We infer the (chemically) irreversible electrochemical intercalation of C_{60} with the formation of the salts $M^+C_{60}^-$ (M = Li, Na) and $Ba^{2+}(C_{60}^-)_2$. We return to these observations below.

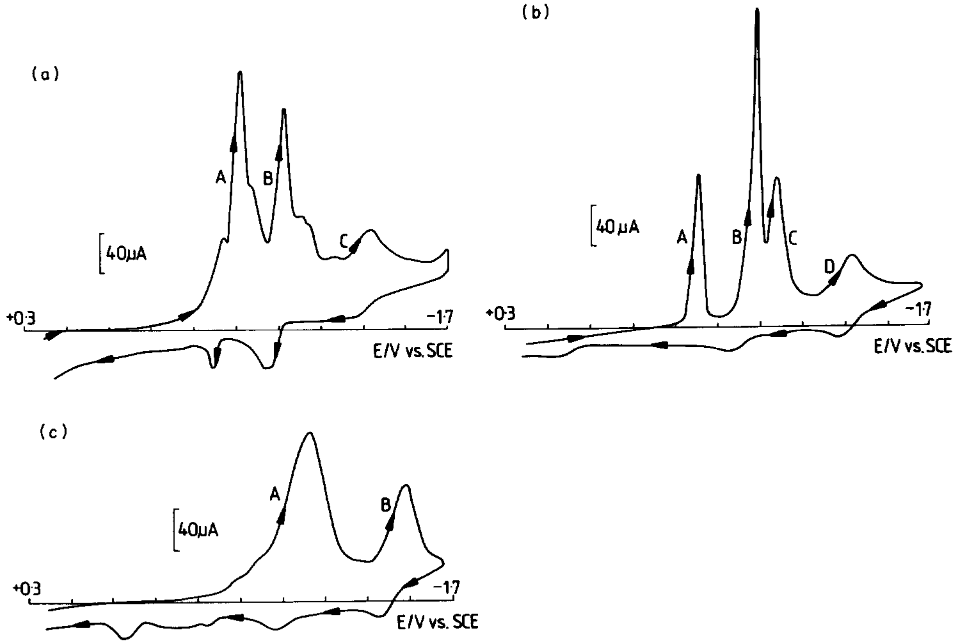

Fig. 2. Cyclic voltammograms showing the electroreduction of a "thin-layer" C_{60}-modified electrode in 0.1 M supporting electrolyte: (a) TEAP; (b) THAP; (c) TOAP. Scan rate, 100 mV s^{-1}.

Tetra-alkylammonium perchlorates $NR_4^+ClO_4^-$ *(R = ethyl, n-hexyl, n-octyl)*

Figure 2 shows the first potential cycle obtained in each case for potential limits embracing all C_{60}-related features; in subsequent cycles only negligible faradaic currents are visible. Significant oxidative processes are absent on the first reverse scan provided that the first reductive scan includes the final fullerene-related peak in each case, as in the voltammograms shown in Fig. 2. If the cyclic voltammogram is reversed before the final peak, one or more small oxidative features may be observed, but in all cases cycling the voltammogram a second time reveals no substantial reproducible faradaic electrochemistry (either reductive or oxidative). Integration of the total charge which may be injected into the coat (sum of all reductive voltammetric peaks) suggests that between two and three electrons per C_{60} are transferred. We note that superconducting salts of the stoichiometry M_3C_{60} (M = K, Rb, Cs) have been made by chemical synthetic routes [5,6].

For TEAP, integration of the three peaks seen (see Fig. 2(a)) shows that close to two electrons per C_{60} in total are passed into the coat. Figure 3 shows that this number is insensitive to the coat coverages in the range 1×10^{-9}–6×10^{-9} mol cm^{-2} and provides a good indication of the level of certainty which can be obtained in the measurements described and hence in the reproducibility of the method of preparing the C_{60} coatings. Also shown in Fig. 3 is an indication of the

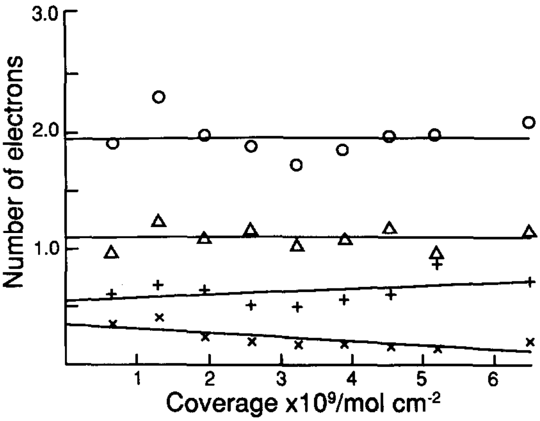

Fig. 3. The number of electrons injected into the C_{60} coat when reduced in acetonitrile + 0.1 M TEAP measured as a function of fullerene coverage in all voltammetric peaks (○), in peak A (△), in peak B (+) and in peak C (×).

charge passed in each of the peaks, although the level of voltammetric complexity revealed in Fig. 2(a) shows that these estimates are necessarily very approximate.

For THAP, integration of all four peaks gives a total electron injection close to three electrons per fullerene as shown in Fig. 4. Also shown are the charge injections for peaks A, B + C and D. In the case of TOAP just two peaks are discernable. Figure 5 shows the charge injected per peak and the total charge injection as a function of surface coverage. Ac impedance measurements made before reduction of the coat in the presence of THAP revealed essentially

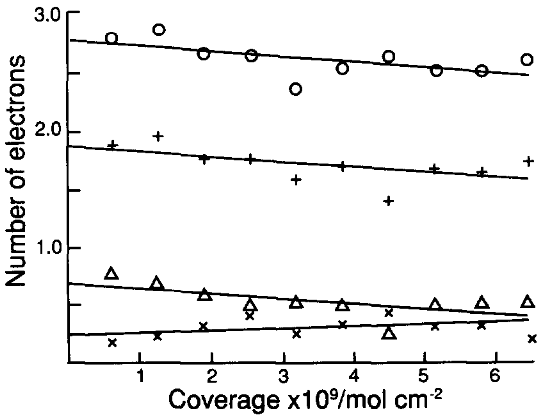

Fig. 4. The number of electrons injected into the C_{60} coat when reduced in acetonitrile + 0.1 M THAP measured as a function of fullerene coverage in all voltammetric peaks (○), in peak A (△), in peaks B + C combined (+) and in peak D (×) where the peaks are identified in Fig. 2(b).

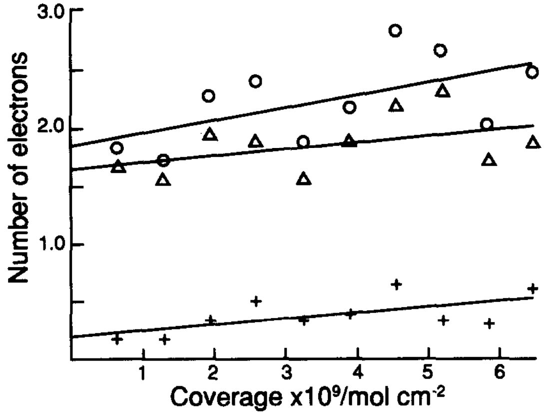

Fig. 5. The number of electrons injected into the C_{60} coat when reduced in acetonitrile + 0.1 M TOAP measured as a function of fullerene coverage in all voltammetric peaks (○), in peak A (△) and in peak B (+) where the peaks are identified in Fig. 2(c).

capacitative behaviour, whereas after reduction the complex plane impedance plot was altered qualitatively and consistent with the addition of a parallel *RC* component in series with the interfacial capacitance, again suggesting the formation of a salt which adheres to the electrode surface.

In all three cases—TEAP, THAP and TOAP—(chemically) irreversible electrochemical intercalation is suggested.

Tetra-butylammonium perchlorate

Figure 6 shows the behaviour found if the potential cycle is reversed at a potential negative to peak C. In subsequent scans only negligible electroreduction

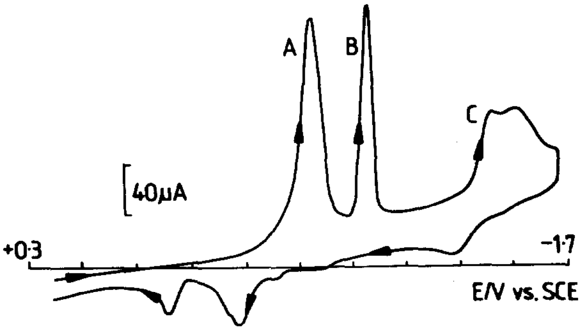

Fig. 6. Cyclic voltammograms showing the electroreduction of a "thin-layer" C_{60}-modified electrode in 0.1 M TBAP supporting electrolyte. Scan rate, 100 mV s^{-1}. The labels A, B and C correspond to the peaks defined in Fig. 3.

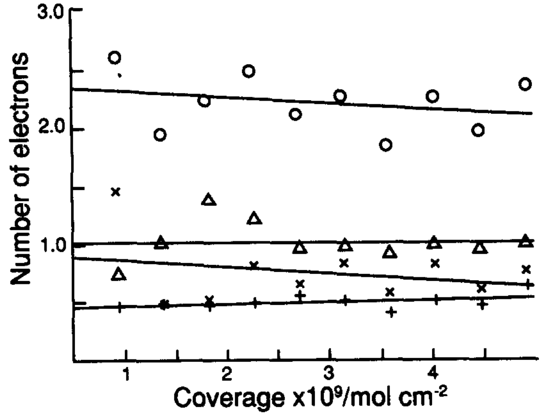

Fig. 7. The number of electrons injected into the C_{60} coat when reduced in acetonitrile + 0.1 M TBAP measured as a function of fullerene coverage in all voltammetric peaks (o), in peak A (△), in peak B (+) and in peak C (×) where the peaks are identified in Fig. 6.

is observed, an observation in agreement with that reported by Jehoulet et al. [2]. Figure 7 shows the approximate charges injected during the first potential cycle in each of the three peaks seen. Again, irreversible electrochemical intercalation would seem to take place with a total electron injection per fullerene of between two and three. However, if the first voltammetric scan is reversed after peak B but before peak C (see Fig. 6), then reversible intercalation becomes apparent. Figure 8 reveals that, after the first potential cycle, under these conditions close to half an electron per C_{60} is injected into the coats in each of peaks A and B and removed in each of peaks C and D as previously reported [1]. Interestingly, on the first cycle, the charge passed in peak A approximates to one electron per C_{60} whilst the charge associated with the other three peaks is close to half an electron per C_{60}. Additionally, the shape of the reductive voltammetric peaks (A and B) is markedly broader on the first scan. These observations suggest substantial structural change accompanying the first formation of fulleride salts. Importantly, after peak A in the first cycle, all subsequent charge associated with each of peaks A B, C and D corresponds to half an electron which is injected reversibly, including the case where the negative extreme of the potential cycle is attained immediately after peak A as displayed in Fig. 9. Impedance measurements, as above, were again consistent with the formation of an adherent layer of fulleride salt.

These voltammetric observations can be summarized as follows.

(i) Electrochemical intercalation of C_{60} coats with a wide range of cations is possible.

(ii) Intercalation is typically chemically irreversible, particularly if large amounts of charge are injected. This may result from the increased C_{60}–C_{60} separation concomitant with increased influx of charge-compensating cations into the coat.

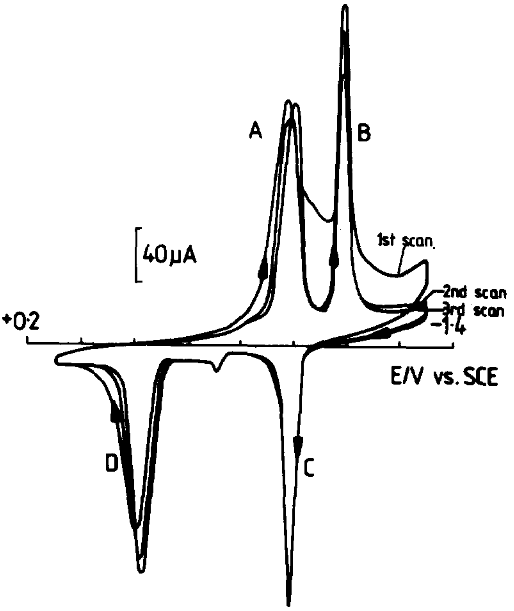

Fig. 8. Cyclic voltammogram (three potential cycles) showing the electroreduction of a "thin-layer" C_{60}-modified electrode in 0.1 M TBAP supporting electrolyte but reversed after peak B. Scan rate, 100 mV s^{-1}.

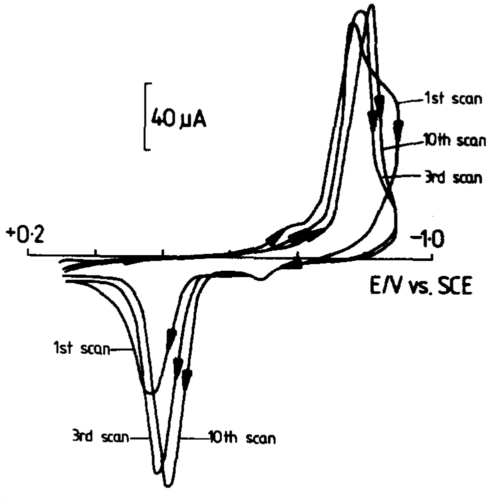

Fig. 9. Cyclic voltammogram showing the electroreduction of a "thin-layer" C_{60}-modified electrode in 0.1 M TBAP supporting electrolyte but reversed after peak A. The first, third and tenth cycles are presented. Scan rate, 100 mV s^{-1}.

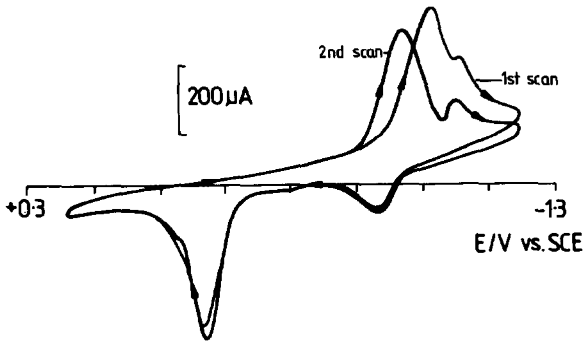

Fig. 10. Cyclic voltammogram showing the electroreduction of a "thick-layer" C_{60}-modified electrode in 0.1 M TBAP supporting electrolyte. The surface coverage of C_{60} was 6.5×10^{-8} mol cm^{-2}.

(iii) Uniquely, in the case of tetrabutylammonium cations, stable coats of fullerides may be formed into and from which charge can be passed with near chemical reversibility (Fig. 9).

Having characterized the voltammetry of electrodes coated with C_{60}, we next consider the properties of such structures as modified electrodes. First we examine the response of gold electrodes coated with substantially thicker layers than those discussed above. Figure 10 shows a cyclic voltammogram for a coverage of 6.5×10^{-8} mol cm^{-2}. Essentially similar behaviour is observed as for the thin coats except that peaks A and B merge into one single feature on the first cycle but become resolved on subsequent scans. Again, cycling more negative than peak C leads to irreversible behaviour and the cessation of subsequent faradaic activity. It was found on progressively increasing the coat depth that the number of electrons injected per C_{60} fell, as displayed in Fig. 11 which relates to charge transferred to peaks A and B in the first voltammetric cycle. We assume that this indicates that sections of the coating are effectively insulated from the electrode substrate because of structural imperfections in the coat. This almost certainly implies that the coat has a substantial porosity.

We now examine how electrode modification with "thick layers" of C_{60} influences electrolytic reactions taking place at gold electrodes. We investigated two reductions and two oxidations which were known to occur at potentials more positive than that required for the reduction of the C_{60} coat. The specific systems studied using rotating-disc voltammetry were as follows.

(a) The one-electron oxidations of TMPD and PPPD (to the corresponding radical cations).

(b) The one-electron reductions of PBA and MB (to the corresponding radical anions).

In all four cases excellent Levich plots (of transport-limited current against square root of rotation speed [7]) were found in the absence of C_{60} coatings with 0.1 M TBAP or $LiClO_4$ as supporting electrolyte. Analysis revealed the following

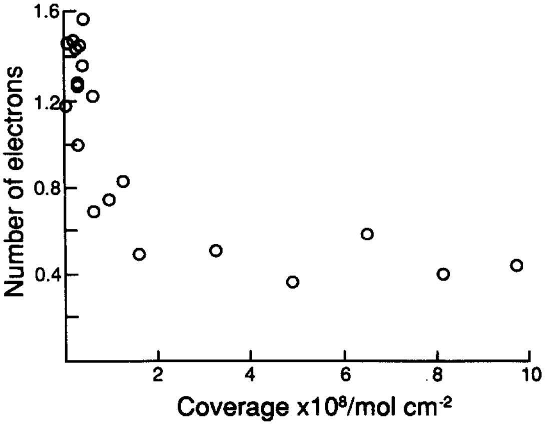

Fig. 11. Plot demonstrating the decrease in the electron injection as a function of surface coverage (i.e. coat thickness).

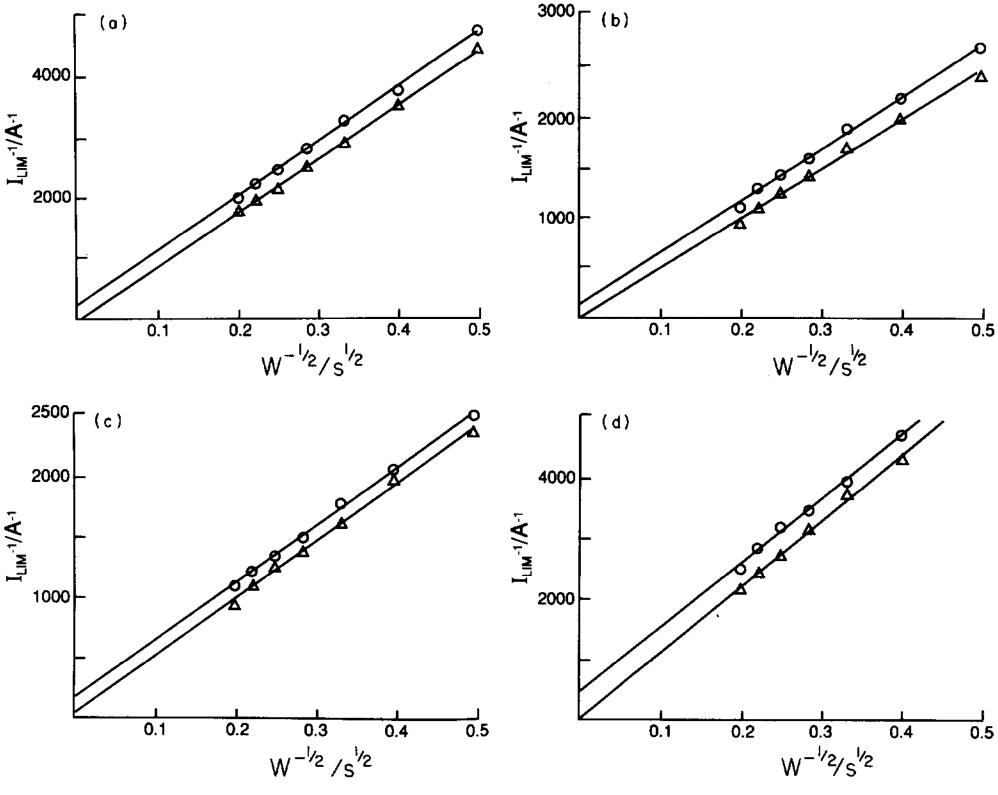

Fig. 12. Koutecky–Levich plots (see text) summarizing the results of rotating disc voltammetry for the systems (a) TMPD, (b) PPPD, (c) PBA and (d) MB studied at a gold rotating disc electrode with (○) and without (△) thick layers of C_{60}. In each case the fullerene coverage was 6.5×10^{-8} mol cm^{-2}.

diffusion coefficients and formal potentials: TMPD, 2.2×10^{-5} cm^2 s^{-1}, +0.41 V/SCE; PPPD, 1.65×10^{-5} cm^2 s^{-1}, +0.67 V/SCE; PBA, 1.7×10^{-5} cm^2 s^{-1}, +0.06 V/SCE; MB, 1.1×10^{-5} cm^2 s^{-1}, +0.28 V/SCE. In all cases these values were in very good agreement with data in the existing literature [8–11]. On modification of the electrode with thick coats of C_{60} the transport-limited current was partially suppressed. Albery and Hillmann [12] have shown that such behaviour can be analysed via Koutecky–Levich plots to yield values of an overall electrochemical rate constant k_{ME} for the modified electrode:

$$j = k_{\mathrm{ME}}[\mathrm{X}]_s \tag{1}$$

where j is the flux of electroactive material X being discharged at the rotating electrode and $[\mathrm{X}]_s$ denotes the concentration of X at the interface between the electrolyte and the outside of the layer which modifies the electrode surface. In particular

$$j = k_{\mathrm{D}} k_{\mathrm{ME}}[\mathrm{X}]_\infty/(k_{\mathrm{D}} + k_{\mathrm{ME}}) \tag{2}$$

where k_{D} is the mass transfer rate constant related to the rotation speed W/Hz of the electrode and $[\mathrm{X}]_\infty$ is the bulk concentration of X. Analysis plots of reciprocal transport limited current I^{-1} versus $W^{-1/2}$ are shown in Fig. 12 from which the following values of k_{ME} were found: TMPD, 0.14 cm s^{-1}; PPPD, 0.09 cm s^{-1}; PBA, 0.08 cm s^{-1}; MB, 0.05 cm s^{-1}.

We interpret k_{ME} as arising from impeded diffusion through the C_{60} layer to the gold substrate electrode [12]. This notion is supported by the plot shown in Fig. 13 which reveals that k_{ME} correlates with the bulk diffusion coefficient of the electroactive substrate in acetonitrile as might be expected if X approaches the electrodes surface through a porous or locally porous C_{60} coat.

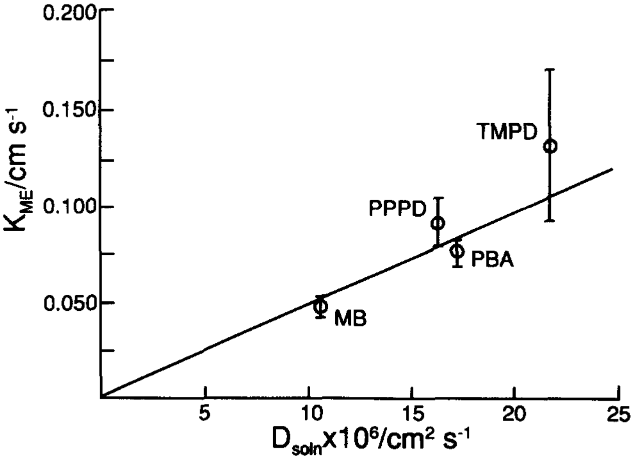

Fig. 13. Plot showing the approximate linear relationship between measured values of k_{ME} and the bulk diffusion coefficients of the four substrates studied in Fig. 12.

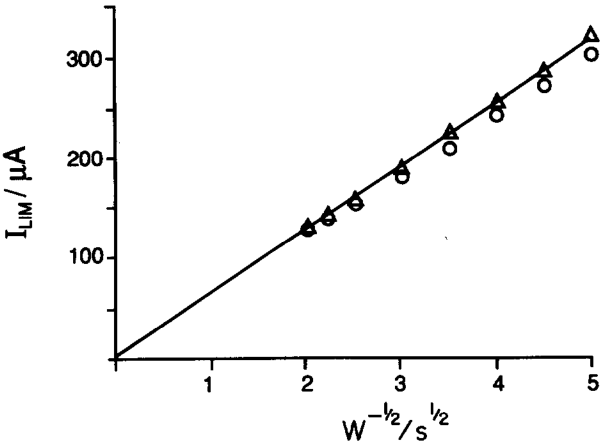

Fig. 14. Levich plots showing that the reduction of AQH on bare gold electrodes (△) and on electrodes modified with coats of C_{60} that had been reduced in the presence of TBAP with the formation of (conducting) TBA^+ salts of fulleride anions (○).

The voltammograms shown in Figs. 6, 8, 9 and 10 demonstrate facile electron transfer within C_{60} coats reduced in the TBAP + acetonitrile medium. Therefore we investigated such reduced coats with respect to the reduction of AQH (to its radical anion) which occurs at a formal potential of −0.84 V/SCE. Figure 14 shows that transport-limited reduction for this process is almost Levich like and closely approaches the behaviour seen on a bare electrode. In particular, no Koutecky–Levich behaviour was seen, in contrast with the results for processes examined at *un*reduced coats despite the fact that the diffusion coefficient of

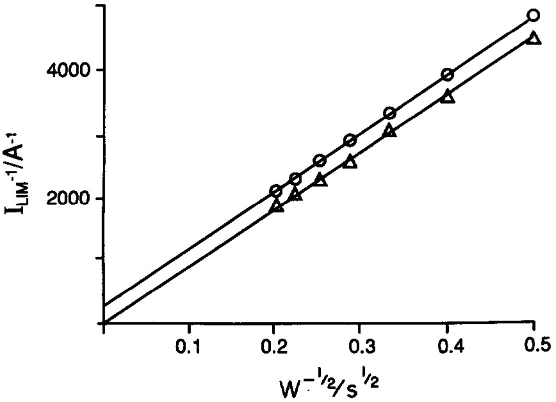

Fig. 15. Koutecky–Levich plot for the reduction of AQH at a gold rotating disc electrode with (○) and without (△) "thick-layers" of C_{60} prereduced in the presence of TEAP. The intercept of this plot permits the evaluation of $k_{ME} = 0.11$ cm s^{-1}. The coverage of fullerene was 6.5×10^{-8} mol cm^{-2}.

AQH in acetonitrile was found to be 2.0×10^{-5} cm^2 s^{-1} (in good agreement with the literature [13]) which, on the basis of Fig. 13, would suggest restricted diffusion within the coat. On these grounds, together with the observed levels of electron injection into the C_{60} coats, we suggest that TBA$^+$ salts of C_{60} anions coated on electrodes can mediate reductive electron transfer from the electrode to a suitable substrate. This notion was confirmed by the observation that for analogous C_{60} coats reduced in the presence of TEAP—for which intercalation is irreversible implying negligible coat conductivity—the reduction of AQH again revealed Koutecky–Levich behaviour (Fig. 15).

In conclusion, intercalation of C_{60}-coated electrodes with tetrabutylammonium cations is almost chemically reversible and leads to a conducting layer of salt which can mediate electron transfer between the electrode and electroactive species in solution. In contrast, C_{60} layers that are unreduced or have been (chemically) irreversibly reduced in the presence of other cations provide no mediation and simply present an impeded diffusional pathway for the transport of the electroactive species to the electrode surface.

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