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Molecular recognition in adsorption and electro-oxidation at chiral platinum surfaces

O.A. Hazzazi[1], G.A. Attard*, P.B. Wells

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff, CF10 3TB, UK

Abstract

Representatives of five classes of optically active compounds have been adsorbed at chiral single crystal Pt electrodes in order to assess the structural and other requirements for chiral/chiral molecular recognition in adsorption and in possible subsequent electro-oxidation. In some cases, analogous studies have been made using achiral stepped and flat Pt surfaces. Cyclic voltammetry in 0.1 M sulphuric acid, which reveals the presence of terraces, steps and kinks at the Pt surface, has been used to follow adsorption as a function of surface geometry and to detect electro-oxidation. For the alkaloids cinchonidine and codeine, and various aromatic compounds possessing chirality in the side-chain (including ephedrine) indiscriminate adsorption occurred at comparable rates at kinked, stepped, and flat surfaces; a proportion of the Pt remained exposed at maximum coverage due to the nature of the random ad-layer. Adsorption of anions of *R*,*R*-tartaric acid caused a shift to negative potential of the hydrogen underpotential features and the $\{1\,1\,1\}$ anion feature of the cyclic voltammograms, showing that tartrate ions were more strongly adsorbed than sulphate and bisulphate ions. Adsorption of *R*- and *S*-2-chloropropanol, *R*- and *S*-2-butanol, *R*-1,3-butanediol, and 2*R*,3*R*- and 2*S*,3*S*-butanediol was accompanied in each case by significant oxidation currents in the double layer potential range, indicating that electro-oxidative adsorption had occurred. However, both the magnitudes of the currents and the potentials at which maximum current was observed were independent of the chirality (*R*- or *S*-) of the Pt surfaces. This contrasts with the enantioselective response observed when D- and L-glucose were adsorbed at *R*- and *S*-Pt(3 2 1). The requirements for chiral recognition in adsorption appear to be (i) the dissociative adsorption of a weakly adsorbed precursor with the chiral surface and (ii) a geometry which is favoured by the adsorbate having a cyclic structure or containing an aldehyde moiety adjacent to a stereogenic centre. The importance of molecular sticking probability and/or adsorption enthalpy is also discussed. It is concluded that as the sticking probability approaches unity or the adsorption enthalpy becomes large relative to the difference in adsorption energy between *R*- and *S*-kinks, enantioselective effects will become more and more obscured.

Keywords: Chiral Pt surfaces; Chiral electrodes; Cyclic voltammetry; Molecular recognition; Chiral recognition; Enantiomeric response; Glucose adsorption; Glucose electro-oxidation; Alkanol adsorption; Alkanol electro-oxidation; Tartaric acid adsorption; Alkaloid adsorption; Cinchonidine adsorption; Codeine adsorption; Ephedrine adsorption; L-Dopa adsorption

1. Introduction

Interactions of chiral molecules with chiral surfaces is a subject of some importance; such interactions may have contributed to the development of life forms and to evolution, and in the immediate future they might contribute to the synthesis of chemicals and their medical application in living systems. In this investigation attention has focused on some simple adsorbents and adsorbates in the hope that the fundamentals of these interactions might be discerned. Chiral recognition has already been established in respect of the interactions of sugars (glucose, mannose, arabinose and xylose) with chiral Pt single crystal surfaces, where electro-oxidation accompanied adsorption and was the means whereby the enantomeric response was identified [1–3]. The objectives of the present investigation were to extend this work to simple alkanols and other classes of adsorbates.

Metal single crystal surfaces containing kink sites are inherently chiral [4]. Such crystals constitute ‘simple’ surfaces in the sense that all the atoms are of one elemental type and the geometry of the surface is well defined. Five classes of chiral compounds of increasing complexity have been studied as adsorbates: these are (i) aliphatic molecules having one chiral centre; (ii) aliphatic molecules having two chiral

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* Corresponding author. Tel.: +44-2920-874069;
fax: +44-1222-874030.
E-mail address: attard@cardiff.ac.uk (G.A. Attard).

[1] Present address: PO Box 2897, Makkah, Saudi Arabia.

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centres; (iii) aromatic molecules having one chiral centre in a side chain; (iv) an aromatic molecule having two chiral centres in a side chain; (v) two polycyclic alkaloids having several chiral centres, one having a rigid structure and the other a conformationally flexible structure.

Because the Pt(3 2 1) surface features prominently in the results presented, the interaction of D- and L-glucose with *R*- and *S*-Pt(3 2 1) is reported for the first time.

These choices of adsorbate were made in the context of our on-going investigations in two areas. First, our work on the enantioselective electro-oxidation of sugars has enabled us to adduce the required molecular geometry of the adsorbate [2]. A natural extension of this work was, therefore, towards the investigation of simpler adsorbates, hence, our choice of the alkanols in classes (i) and (ii). Our second area of interest concerns the enantioselective hydrogenation of α-ketoesters and related compounds catalysed by alkaloid-modified supported Pt catalysts [5–7]. These polycrystalline Pt surfaces have no net chirality but adsorption of certain optically active alkaloids confers an asymmetry on the surface that results, in the hydrogenation of a pro-chiral ketone or alkene, in the preferential formation of one enantiomer of the product. Some cinchona alkaloids are very effective 'modifiers' for this purpose, providing values of the enantiomeric excess in excess of 90% [6]. Some morphine, vinca and strychnos alkaloids also provide chiral environments at Pt or Pd surfaces, inducing modest enantioselectivities [6]. Thus, cinchonidine and codeine (class (v) compounds) have been included in the present study as adsorbates of particular interest. Compounds in classes (iii) and (iv) were selected because of their intermediate properties. Like cinchonidine and codeine, they are aromatic derivatives but, like the simpler adsorbates, they contain only one or two chiral centres in an alkyl side-chain. Finally, *R*,*R*-tartaric acid is an effective modifier in the enantioselective hydrogenation of β-ketoesters catalysed by Raney nickel [8] and has been included as a class (ii) adsorbate. Thus, by this choice of adsorbates, we have attempted to bridge our knowledge of chiral interactions in single-crystal-catalysed oxidations and in polycrystalline-catalysed hydrogenations.

Cyclic voltammetry has been used to characterise single crystal Pt surfaces. The cyclic voltammograms (CVs) of Pt single crystal electrodes in 0.1 M sulphuric acid electrolyte are now well understood [9]. Interactions of adsorbates which result in the displacement of adsorbed-H or adsorbed-anions from the terraces, steps and kink sites at these Pt surfaces can now be investigated as the features in the CVs change with changes in experimental variables.

2. Experimental

Crystals were prepared in-house from 99.999% Pt wire (Goodfellow Metals). Clean spherical single crystal beads 3 mm in diameter were formed by Clavilier's method [10] and were cut, polished and annealed. Confirmation that the crystals were of the required symmetry was obtained in each case by low energy electron diffraction [3].

The two compartment electrochemical cell has been described [11]. The single crystal working electrode and a Pt mesh counter electrode were housed in one compartment and a Pd/H reference electrode in the other. The electrolyte was 0.1 M sulphuric acid. The electrodes were regulated by a potentiostat and current/voltage information fed to a computerised data handling system. Cyclic voltammograms or linear sweep voltammograms (LSVs) were obtained at a sweep rate of $50\,\mathrm{mV\,s^{-1}}$. A carefully regulated stream of pure nitrogen was passed over the electrolyte to ensure reproducibility in measurements of adsorption rates.

All apparatus was rigorously cleaned and all solutions were made up with ultra pure water (Milli-Q plus system, resistivity $18.2\,\mathrm{M\Omega\,cm^{-1}}$, organic content <10 ppb).

In addition to D- and L-glucose, which have been studied previously, the following five classes of optically pure adsorbates were investigated.

Class (i): Aliphatic molecules having one chiral centre: *R*- and *S*-2-chloro-propanol (**I**,**II**); *R*- and *S*-2-butanol (**III**,**IV**); *R*-1,3-butanol (**V**).
Class (ii): Aliphatic molecules having two chiral centres: 2*R*,3*R*- and 2*S*,3*S*-2,3-butanediol (**VI**,**VII**): *R*,*R*-tartaric acid (**VIII**).
Class (iii): Aromatic molecules having one chiral centre in a side chain: *N*-acetyl-L-phenylalanine, $PhCH_2C^*H(NHAc)COOH$ (**IX**); *N*-acetyl-L-tyrosine, $HOPhCH_2C^*H(NHAc)COOH$ (**X**); 3-(3,4-dihydroxy-phenyl)-*S*-alanine $(HO)_2PhCH_2C^*H(NH_2)COOH$ (L-dopa) (**XI**).
Class (iv): An aromatic molecule having two chiral centres in a side chain: 1*R*,2*S*-ephedrine, $PhC^*H(OH)C^*HMeNHMe$ (**XII**).
Class (v): Alkaloids having several chiral centres: the morphine alkaloid codeine (**XIII**); the cinchona alkaloids cinchonidine (**XIV**) and its 10,11-dihydro-derivative (**XV**) (Fig. 1).

Platinum surfaces studied are listed in Table 1. The 'flat' surfaces were the basal planes Pt(1 0 0), Pt(1 1 1) and Pt(1 1 0). The stepped surfaces contained terraces and monatomic steps. Pt(5 1 1), (7 1 1), (9 1 1), (11 1 1) and (13 1 1) were all of the type $n(1\,0\,0)_{\mathrm{terrace}} \times (1\,1\,1)_{\mathrm{step}}$ where the terrace width n = 3, 4, 5, 6 and 7 atoms, respectively,

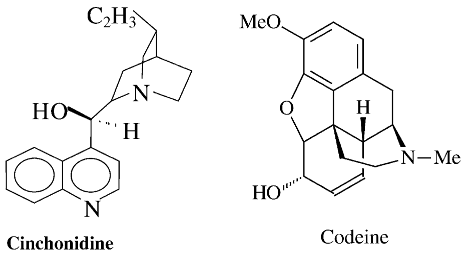

Fig. 1. Structures of the alkaloids cinchonidine and codeine.

Table 1
Combinations of adsorbent and adsorbate investigated

Adsorbates			Flat[a]	Stepped[b]	Adsorbent surfaces				
Class	Compound	Concentration (μM)			Chiral[c]				
i	**I**	5000	No	No	{3 2 1}	{5 3 1}	{6 4 3}	{9 7 6}	{11 7 1}
i	**II**	10000	No	No		{5 3 1}	{6 4 3}	{9 7 6}	
i	**III**	5000	No	No			{6 4 3}	{9 7 6}	
i	**IV**	5000	No	No		{5 3 1}	{6 4 3}	{9 7 6}	
i	**V**	1000	No	No	{3 2 1}	{5 3 1}		{9 7 6}	
ii	**VI**	1000	No	No	{3 2 1}	{5 3 1}			
ii	**VII**	1000	No	No	{3 2 1}	{5 3 1}		{9 7 6}	
ii	**VIII**	1,10	No	No	{3 2 1}[d]				
		100	No	No		{5 3 1}			
		500	No	No	{3 2 1}[e]				
iii	**IX**	5	Yes	Yes		{5 3 1}	{6 4 3}		
		1	Yes	Yes[f]				{9 7 6}	
iii	**X**	1	Yes	Yes[g]	{3 2 1}	{5 3 1}	{6 4 3}	{9 7 6}	{11 7 1}
iii	**XI**	1	Yes	Yes	{3 2 1}	{5 3 1}	{6 4 3}	{9 7 6}	{11 7 1}
iv	**XII**	1	Yes	Yes	{3 2 1}	{5 3 1}	{6 4 3}	{9 7 6}	{11 7 1}[h]
v	**XIII**	1	Yes	Yes	{3 2 1}	{5 3 1}	{6 4 3}		{11 7 1}
v	**XIV**	1	Yes	Yes[i]	{3 2 1}	{5 3 1}	{6 4 3}	{9 7 6}	{11 7 1}
v	**XV**	1	Yes	Yes[j]	{3 2 1}		{6 4 3}	{9 7 6}	

[a] No = not studied; yes = {1 1 1}, {1 0 0} and {1 1 0} studied.

[b] No = not studied; yes = {7 5 5}, {5 3 3}, {2 1 1}, {3 1 1}, {5 1 1}, {7 1 1}, {9 1 1}, {11 1 1}, {13 1 1} and {3 3 2} studied.

[c] Adsorption was studied at both *R*- and *S*-surfaces in separate experiments.

[d] *S*-{3 2 1} not studied.

[e] *R*-{3 2 1} not studied.

[f] {7 1 1} and {13 1 1} not studied.

[g] {7 1 1}, {13 1 1} and {3 3 2} not studied.

[h] {8 4 1} also studied.

[i] {7 1 1} and {3 3 2} not studied.

[j] {7 1 1} not studied.

whereas Pt(2 1 1), (5 3 3) and (7 5 5) were of the type $n(1\,1\,1)_{\text{terrace}} \times (1\,0\,0)_{\text{step}}$ where $n = 3$, 4, and 6 respectively. Pt(3 3 2)≡6(1 1 1) × (1 1 1). Pt(3 1 1) can be regarded as either 2(1 1 1) × (1 0 0) or 2(1 0 0) × (1 1 1). In the case of the chiral (kinked) surfaces, each kink consisted of the junction of two steps and a basal plane, these three elements being of (1 0 0), (1 1 1) and (1 1 0) configuration. Where these elements, viewed from the electrolyte, run in descending order of surface atom density (i.e. (1 1 1)(1 0 0)(1 1 0)) in a clockwise fashion the kink site and the surface are designated *R*-; where this sequence is anti-clockwise the designation is *S*- [1]. Pt(3 2 1), Pt(6 4 3) and Pt(9 7 6) contained (1 0 0) and (1 1 0) step components on (1 1 1) terraces, the terraces being, respectively, 2, 3 and 6 atoms in width; Pt(11 7 1) and Pt(8 4 1) contained (1 1 1) and (1 0 0) step components on (1 1 0) terraces. Pt(5 3 1) is at the centre of the stereographic triangle and contains only steps and kinks. Hard sphere models of these surfaces are shown in reference [3].

3. Results

CVs were obtained for all systems listed in Table 1. Representative results are presented in the figures here; reference [12] contains a wider selection.

Compounds of classes (i) and (ii) were adsorbed onto chiral surfaces only. Compounds of classes (iii), (iv) and (v) were adsorbed onto the flat surfaces and onto a range of stepped and chiral surfaces.

For glucose and the compounds of classes (i) and (ii) it was necessary to use adsorbate concentrations in the millimolar range whereas, for the compounds of classes (iii), (iv) and (v) effects were observed at micromolar concentrations. The first group (except for tartaric acid) were saturated compounds for which chemisorption must be dissociative, whereas the second group all contained an aromatic moiety and hence were, in principle, able to undergo chemisorption without dissociation. This demarcation extended to the type of interactions observed. The first group (again with the exception of tartaric acid) underwent electro-oxidation whereas the second group did not.

3.1. Adsorption of glucose

Since results featuring *R*- and *S*-Pt(3 2 1) are reported below the interaction of D- and L-glucose over these surfaces is reported for the first time.

Fig. 2 shows the voltammograms obtained when D- and L-glucose were each adsorbed onto Pt(3 2 1)^{R} and Pt(3 2 1)^{S}. The enantiomeric response is seen in the close similarity of

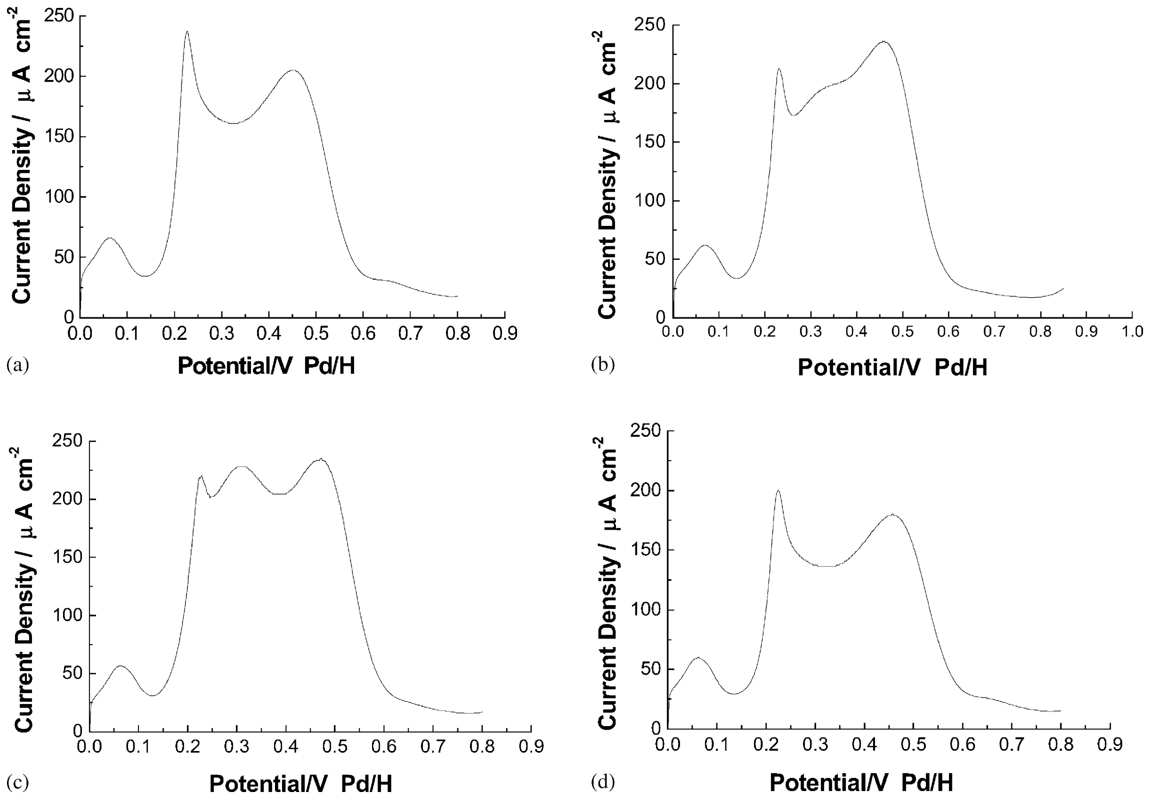

Fig. 2. Linear sweep voltammograms for the electro-oxidation of 5 mM D- and L-glucose on Pt(3 2 1)^R and Pt(3 2 1)^S. (a) Pt(3 2 1)^R + D-glucose, (b) Pt(3 2 1)^R + L-glucose, (c) Pt(3 2 1)^S + D-glucose, (d) Pt(3 2 1)^S + L-glucose. Electrolyte = 0.1 M H_2SO_4. Sweep rate = 50 mV s^{-1}.

the (*R*- + L- and *S*- + D-) and of the (*S*- + L- and *R*- + D-) combinations. When compared with more kinked (Pt{5 3 1}) or less kinked (Pt{6 4 3}) surfaces, the extent of chiral recognition (as measured by differences in electro-oxidation current densities at 0.3 V) is found to be intermediate between these two extremes. These results correspond to those reported for various other chiral Pt surfaces [1–3].

3.2. *Adsorption of compounds of classes (i) and (ii)*

Fig. 3(c) and (d) shows the CVs obtained when *R*,*R*-2,3-butanediol was adsorbed onto Pt(3 2 1)^R and Pt(3 2 1)^S. Closely similar CVs were obtained for *S*,*S*-2,3-butanediol on the same surfaces. Thus, although the features indicate that electro-oxidation occurred (see discussion below) the enantiomeric response was absent. It was also absent when *R*,*R*- and *S*,*S*-2,3-butanediol were adsorbed on the other *R*- and *S*-chiral surfaces listed in Table 1. This absence of an enantiomeric response extended to the behaviour of *R*- and *S*-chloropropanol and of *R*- and *S*-2-butanol on the chiral surfaces listed and was, therefore, a general phenomenon. It should be pointed out that the desorption and reaction of 2-butanol on Ag{6 4 3} has been studied by Gellman with the conclusion that the adsorption energy is not sensitive to which enantiomer is adsorbed [4]. There were, however, measurable differences between the orientation of the butanol enantiomers on the chiral metal surface [13].

However, electro-oxidation was sensitive both to the structure of the adsorbate and that of the surface. Comparison of Fig. 3(a)–(c) shows how electro-oxidation over Pt(3 2 1)^S varied on adsorption of *S*-2-butanol, *R*-1,3-butanediol and *R*,*R*-2,3-butanediol, and Fig. 3(d)–(f) show how *R*,*R*-2,3-butanediol oxidation varied over Pt(3 2 1)^R, Pt(6 4 3)^R and Pt(9 7 6)^R.

3.3. *Adsorption of compounds in classes (iii), (iv) and (v)*

Fig. 4 shows the effect of the adsorption of cinchonidine on *R*- and *S*-Pt(6 4 3), of codeine on *R*- and *S*-Pt(3 2 1) and of ephedrine on *R*- and *S*-Pt(5 3 1). The first sweep in each CV is closely similar to that shown by the clean surface (clean surface CVs not shown). The effect of adsorption in each case was to diminish each feature without any shift in potential. Adsorption occurred at a measurable rate, and each feature of a given CV diminishing at a comparable rate. Thus, not only did the sense of the chiral kink not influence the rate of cinchonidine adsorption, but the adsorption was indiscriminate. Similar effects were observed for the adsorption of codeine and of ephedrine and have been reported in the literature for naphthylethylamine [14].

The behaviour of ephedrine (one phenyl ring, one side chain, two chiral centres) was mirrored by *N*-acetylphenyl-

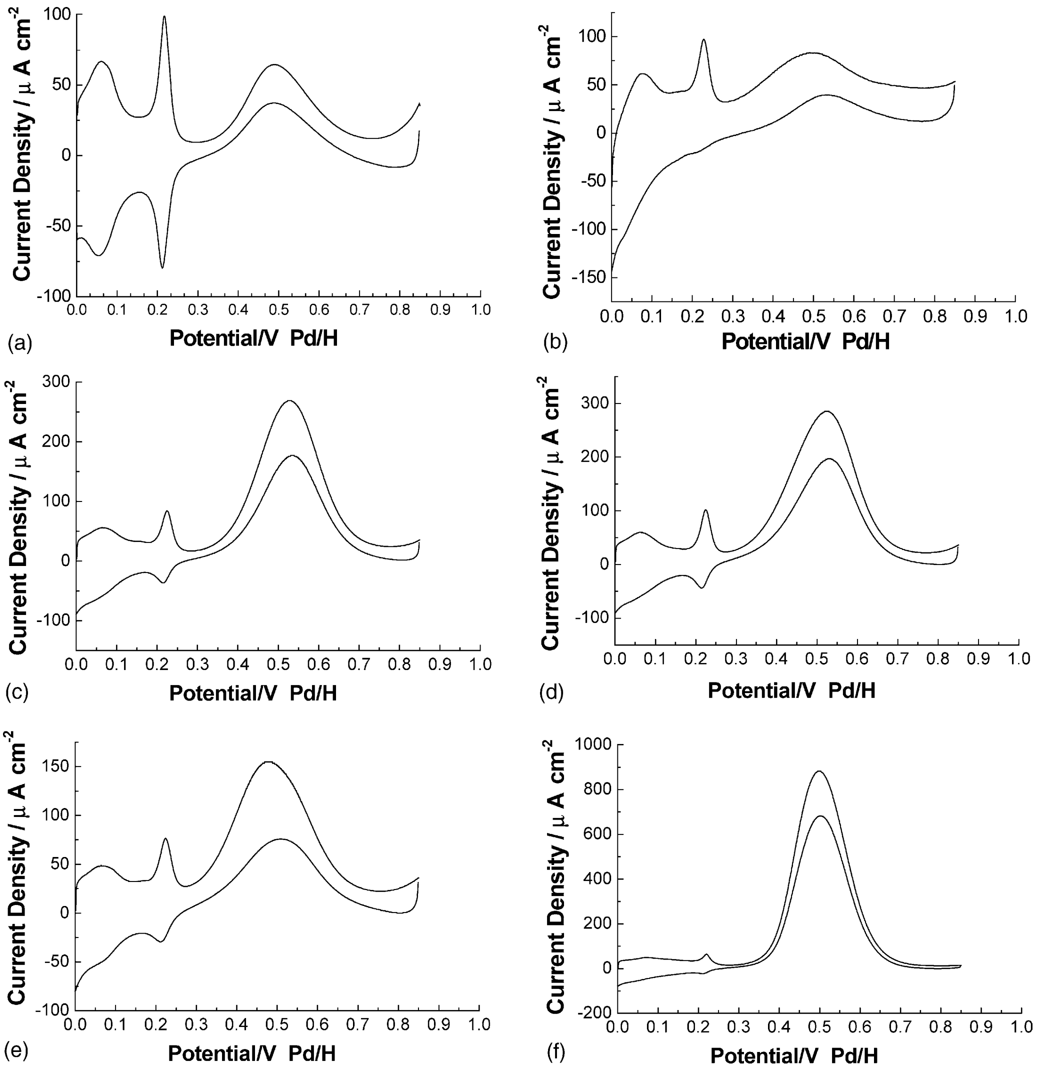

Fig. 3. CVs for the adsorption of 5 mM *S*-2-butanol (*S*-2-B), 1 mM *R*-1,3-butanediol (*R*-1,3-BD), and 1 mM *R*,*R*-2,3,butandiol (*R*,*R*-2,3-BD) at chiral Pt surfaces. (a) *S*-2-B/Pt(3 2 1)^S, (b) *R*,1,3-BD/Pt(3 2 1)^S, (c) *R*,*R*-2,3-BD/Pt(3 2 1)^S, (d) *R*,*R*-2,3-BD/Pt(3 2 1)^R, (e) *R*,*R*-2,3-BD/Pt(6 4 3)^R, (f) *R*,*R*-2,3-BD/Pt(9 7 6)^R. Electrolyte = 0.1 M H_2SO_4. Sweep rate = 50 mV s^{-1}.

alanine, *N*-acetyltyrosine and L-dopa (one phenyl ring, one side chain, one chiral centre) as shown in Fig. 5.

3.4. Adsorption of tartaric acid

Although tartaric acid is formally included in class (iii), its reactivity as an acid was expected to differ from that of the other members of the class. Furthermore, although tartaric acid effectively modifies Raney nickel for the enantioselective hydrogenation of β-ketoesters [i] it is not an effective modifier of Pt. At 1 μM tartaric acid had no effect on the clean surface CV of any of the surfaces studied. At 100 μM it behaved as an anion reversibly adsorbed at the electrode surface, causing a shift (∼20 mV) to more negative potentials of the {1 1 0} and {1 1 1} × {1 0 0} step features and the {1 1 1} terrace feature. A shift to more positive potential also occurred in the oxide feature at ∼0.8 V.

4. Discussion

The five classes of adsorbates presented in Table 1 are regrouped into three categories for the purposes of discussion: (a) *R*,*R*-tartaric acid, which showed the simplest interaction with Pt surfaces, causing only a displacement of the features in the CVs, (b) all compounds containing an aromatic moiety which adsorbed causing a reduction in all the features of the voltammograms but no potential shifts, and (c) all saturated alcohols which produced new features in the voltammograms which indicate the occurrence of electro-oxidation.

Fig. 2 shows molecular recognition in the adsorption and subsequent electro-oxidation of glucose on Pt(3 2 1). It is of the type previously published for other chiral crystal surfaces [1], and it provided the impetus for our studies of the compounds in classes (i) and (ii). The voltammogram for D-glucose on the *R*-surface pairs with that for L-glucose on the *R*-surface, and that for L-glucose on the *R*-surface pairs

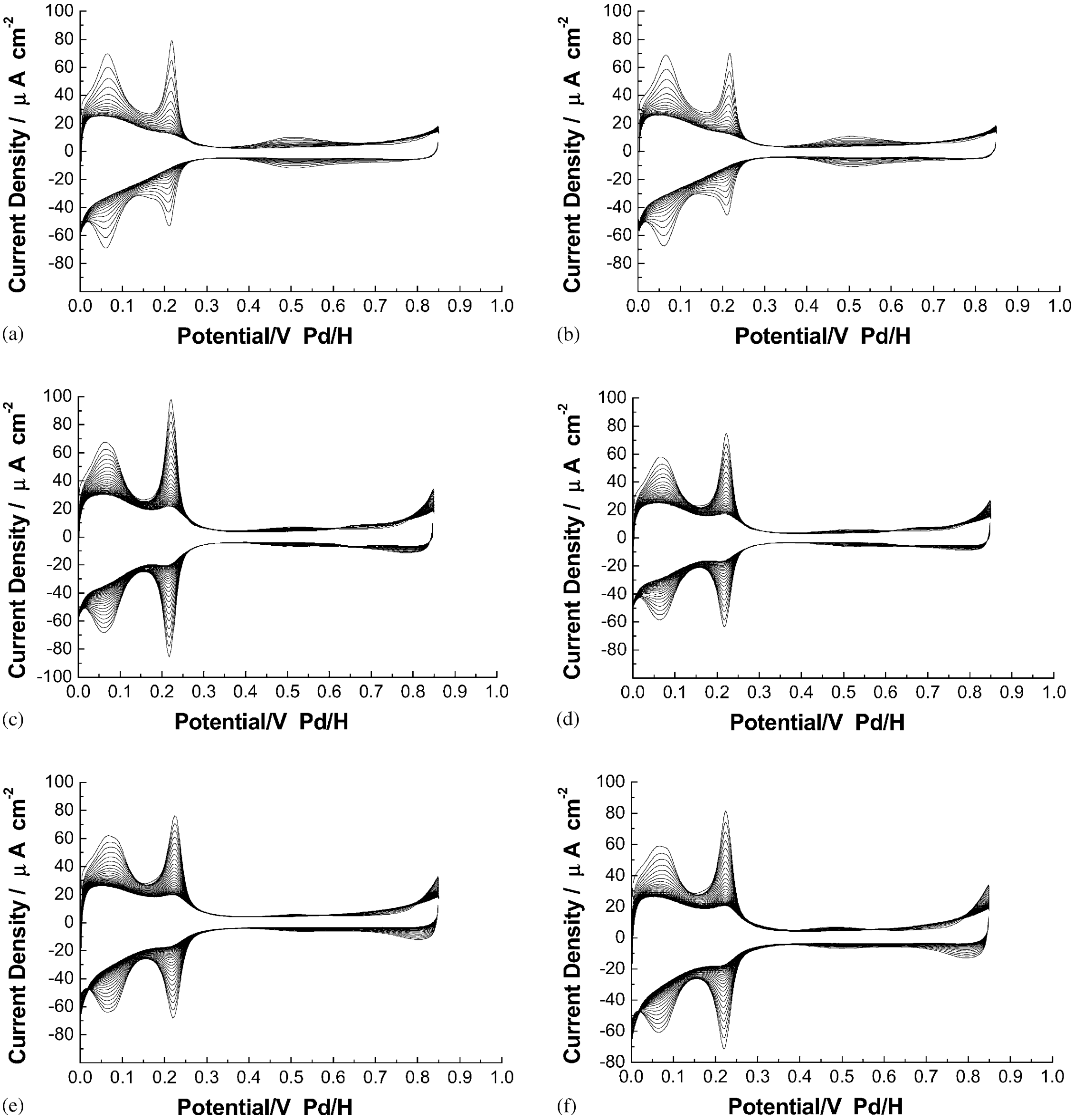

Fig. 4. CVs for the adsorption of 1.0 µM cinchonidine (CD), codeine (C) and ephedrine (E) at chiral Pt surfaces. (a) CD/Pt(6 4 3)^R; (b) CD/Pt(6 4 3)^S; (c) C/Pt(3 2 1)^R; (d) C/Pt(3 2 1)^S; (e) E/Pt(5 3 1)^R; (f) E/Pt(5 3 1)^S. Electrolyte: 0.1 M H_2SO_4. Sweep rate: 50 mV s^{-1}.

with that of D-glucose on the *S*-surface (enantiomeric pairings). The features at 0.06, 0.21 and 0.48 V relate to the step and terrace features shown by the clean surfaces [1]; the new feature at 0.31 V for the L-/*R*- and D-/*S*- pair results from a specific adsorbate/adsorbent interaction achieved only by this mirror-image pair which has been discussed in detail and tested by reference to the behaviour of various pyranoses [2].

4.1. *Adsorption of R,R-tartaric acid*

Tartrate ions (100 µM in the electrolyte) adsorbed at all Pt surfaces, displacing sulphate/bisulphate ions (0.1 M) at the same sites. Adsorbed tartrate perturbed hydrogen adsorbed at the step sites thereby causing the potential shift in the H UPD features; the {1 1 1} terrace feature was similarly shifted because of anion substitution. The shift to more positive potentials observed in the onset of oxide electrosorption is a common feature when anions more strongly adsorbed than sulphate/bisulphate (e.g. chloride) are present [15]. It is to be expected that H desorption/adsorption during the cycle was accompanied by additional adsorption/desorption of the acid. This reversible adsorption of *R,R*-tartrate ions did not distinguish between *R*- and *S*-Pt surfaces, i.e. there was no chiral recognition.

4.2. *Adsorption of chiral compounds containing an aromatic moiety*

The adsorption of compounds containing an aromatic moiety (Figs. 4 and 5 and similar results for adsorptions on

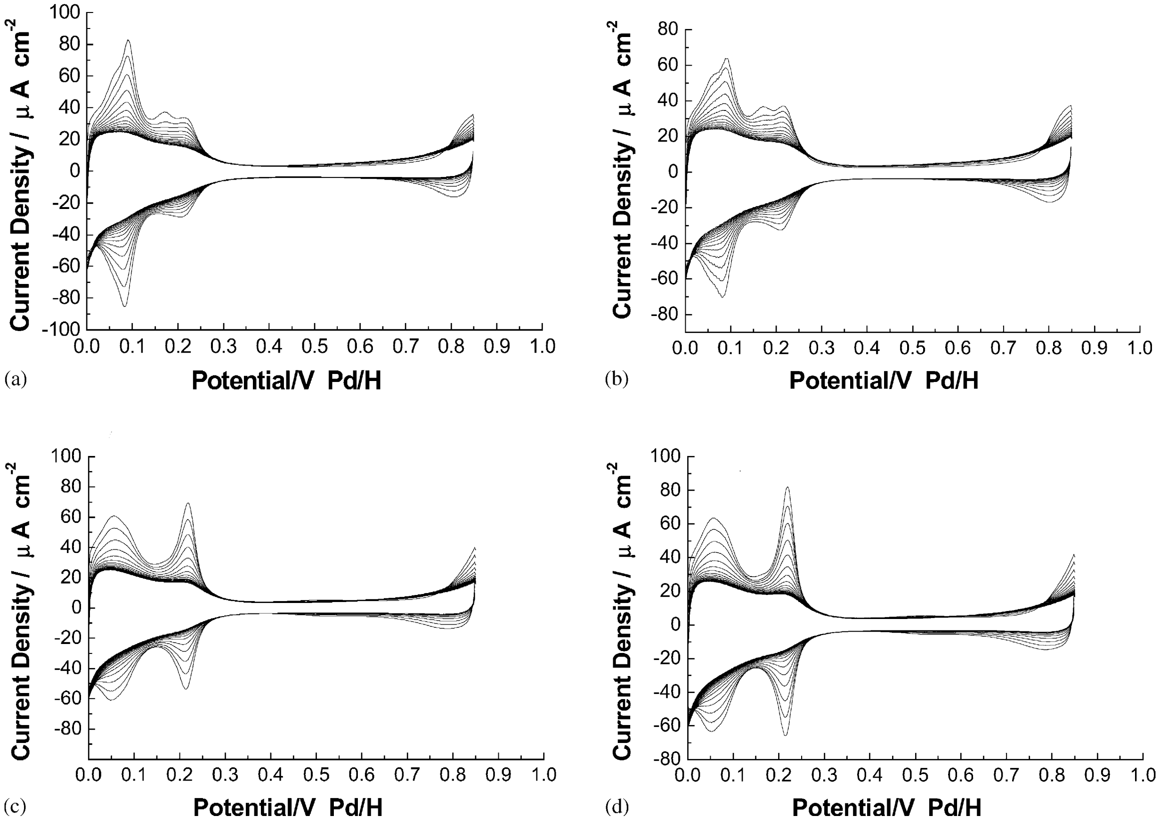

Fig. 5. CVs for the adsorption of 1.0 μM L-dopa (L-D) and *N*-acetyltyrosine (*N*-AT) at chiral Pt surfaces. (a) L-D/Pt(11 7 1)^R, (b) (L-D)/Pt(11 7 1)^S, (c) *N*-AT/Pt(5 3 1)^R, (d) *N*-AT/Pt(5 3 1)^S. Electrolyte = 0.1 M H_2SO_4. Sweep rate = 50 mV s^{-1}.

flat and stepped surfaces, not shown) showed a reduction in the step and terrace features which proceeded smoothly on the time scale of the experiment, i.e. over about 20 scans or 10.7 min. The rate of adsorption (which equalled the rate of exclusion of hydrogen and anions from the surface and was indicated by the rate of decrease in the area under the voltammogram) decreased in a gradual, first-order manner, the coverage finally achieving a value of ∼60%. This behaviour was in good agreement with previous measurements of alkaloid uptake curves [2]. For example, for dihydrocinchonidine adsorption on stepped Pt(7 5 5) the rate coefficient was 0.0024 s^{-1}. The failure entirely to exclude H from the surface is consistent with random adsorption of these large irregularly-shaped molecules at a surface [16]. Adsorption of cinchona alkaloids at Pt single crystal surfaces has been shown to occur by interaction of the quinoline ring with the surface [17], the plane of the ring being parallel with a {1 1 1} surface [18], and we take this mode of associative π-adsorption via the aromatic moiety as the model for the compounds in classes (iii) to (v). However, each of these compounds adsorbed at comparable rates at *R*- and *S*-kink sites, i.e. there was no kinetic distinction in adsorption based on the chirality of the surface (and rates were similar on the flat and stepped surfaces studied). Thus, there was no evidence for the interaction of the chiral centres adjacent to these aromatic moieties with the chiral kink sites at the surface. This was surprising in the cases of cinchonidine and ephedrine; these molecules each contain a hydroxyl group at or adjacent to the chiral carbon atom associated with their directing influence as modifiers of Pt for enantioselective hydrogenation, and it is the interaction of suitably located hydroxyl groups with kink sites which facilitates the enantiomeric pair effect in glucose adsorption [2]. It is, therefore, concluded that chiral recognition may be suppressed by the presence in the molecule of a reactive grouping that provides a competitive mode of adsorption: specifically, the presence of the aromatic moiety may actually have *prevented* the desired interaction of the chiral entity in the adsorbate with the chiral kink site at the surface. A test of this conclusion would be to examine the adsorption behaviour of dodecahydrocinchonidine or of hexahydroephedrine.

4.3. *Adsorption and electro-oxidation of chiral alkanols*

The adsorption of each of the alkanols in classes (i) and (ii) resulted in a gross perturbation of the clean-surface CVs for chiral surfaces (Fig. 3) and for flat and stepped surfaces. As for glucose adsorption, the H UPD features remain, and there is a broad bell-shaped feature centred at ∼0.5 V indicative of the occurrence of electro-oxidation which masks the {1 1 1} terrace anion feature. The lower curves, which relate to the return sweeps, show lower maximum current densities and reduced H UPD features, indicating that electro-oxidation in the forwards sweep was accompanied by the formation of surface poisons and that a reduced number of active sites contributed to the features recorded in the return sweep. This is a well know phenomenon in fuel cell research [19].

These chiral alkanols showed no enantioselective response in their adsorptions on *R*- and *S*-Pt surfaces (compare Fig. 3(c) and (d)). However, as the terrace width was decreased, so the magnitude of the oxidation peak at 0.5 V decreased: {9 7 6} > {6 4 3} > {3 2 1} > {5 3 1} (Fig. 3(d)–(f); for step sizes, see Section 2). This behaviour *is* observed in glucose electro-oxidation [2] and in this sense these alkanols showed behaviour consistent with that observed where chiral recognition is evident.

These alkanols and glucose share another feature in common in that they are all saturated molecules for which chemisorption is most likely to occur by fission of either a carbon–hydrogen or an oxygen–hydrogen bond [20]. Adsorption was probably weaker than that of the aromatics, as evidenced by the higher concentrations of alkanol required to obtain measurable effects in the CVs (no effects were observed for the alkanols at 1 μM). Thus, it appears that a relatively weak dissociative adsorption may be a favourable but not sufficient condition for the achievement of molecular recognition at chiral surfaces.

4.4. In conclusion

Adsorption at an electrochemical interface is always a displacement process in which the components of the electrical double layer such a neutrals, monopoles and dipoles are replaced by the adsorbate. Such processes are strongly dependent on electrode potential, bulk concentration, and the adsorption bond strengths of all the double layer components including the adsorbate itself [21]. It is argued above that strong adsorption of the type shown by the aromatic compounds militates against chiral recognition. The differences in adsorption energy expected for the adsorption of a chiral molecule at *R*- and *S*-kink sites will be small relative to the absolute value of the adsorption energy of strongly chemisorbed molecules, and hence strong chemisorption may ‘swamp’ any subtle and weak interactions that may be present under reaction conditions. An alternative approach is to recognise that sticking probabilities will tend to be high for strongly adsorbed molecules and, as a sticking probability of unity would tend to millitate against chiral recognition [22], chiral effects would become obscured. It is interesting that hydrogen bonding interactions tend to be favoured both in nature [23,24] and in chemistry designed to achieve a chiral outcome [6].

So, having achieved weak dissociative adsorption (and electro-oxidation) of the chiral alkanols, why was an enantiomeric response not observed? Glucose, mannose, arabinose and xylose all belong to the same class of weakly adsorbed molecules as the alkanols but, in contrast to the alkanols, they all show strong chiral responses at chiral Pt surfaces [2]. We note that they are distinguished by their ability to form cyclic (pyranose) rings in solution, and we are currently testing the hypothesis that this provides the crucial geometrical element in the adsorption by investigating the behaviour of suitable linear and non-linear carbohydrate molecules. There are previous reports of chiral influence on the kinetics of adsorption and desorption from a chiral metal surface and in many cases the adsorbate was a weakly adsorbed cyclic hydrocarbon [25–29]; this supports our view that molecules having cyclic structures are more likely to meet the necessary geometrical conditions for the observation of enantiomeric effects in adsorption, and hence, in subsequent reaction. However, it may also be that the aldehydic carbonyl function on glucose and related molecules holds the key to differences in enantioselectivity. This idea may afford a possible link to other enantioselective reactions involving prochiral carbonyl groups [6,7].

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