

## ELECTROCATALYTIC OXIDATION OF BENZYL ALCOHOL ON A PLATINUM ELECTRODE MODIFIED BY UNDERPOTENTIAL-DEPOSITED HEAVY METAL ADATOMS

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Received October 8th, 1985

The oxidation of benzyl alcohol on platinum surfaces modified by foreign metal adatoms (Pb, Tl, Bi) deposited at an underpotential region was studied in both acid and alkaline media; it was found that Pb, Tl, and Bi submonolayers intensely catalyse the benzyl alcohol oxidation. The enhancement of the electrocatalytic activity of Pt for the benzyl alcohol oxidation in acid solutions has been explained through the mechanism of "third body" effect in electrocatalysis. On the other hand, the enhanced catalytic activity in alkaline media, which in the case of Bi adatoms yields current densities close to the diffusion-limited values, has been interpreted in terms of the bifunctional theory in electrocatalysis.

The deposition of a metal onto a foreign metal substrate at potentials more positive than its reversible Nernst potential, called underpotential deposition (UPD), has gained increasing interest due to its profound influence on the electrocatalytic properties of electrode substrates used for electrosynthesis and fuel cell reactions.

Many authors deal with the catalytic action of UPD on a large number of electrochemical reactions. Special interest has been given to the electrochemical reduction of oxygen<sup>1-5</sup>, evolution of hydrogen<sup>6,7</sup>, electrochemical reduction of nitro compounds<sup>8-11</sup>, and the electrooxidation of some organic fuels. The last group of the electrochemical reactions involves mainly the electrooxidation of formic acid<sup>12-14</sup>, methanol<sup>15-18</sup>, ethylene glycol<sup>1,19-21</sup>, and glucose<sup>22,23</sup>.

The electrooxidation of the above compounds on Pt leads to the formation of organic intermediates which are strongly adsorbed on the surface of the platinum electrode. The intermediate products poison the electrocatalyst surface by blocking multiple surface sites. It was found that the electrooxidation of these compounds is essentially catalysed by the UPD of lead, thallium, and bismuth on Pt. The catalytic effects are due to prevention of the electrode poisoning by strongly bound intermediates or to increased oxidation rate of the organic molecules by oxygen-containing species coadsorbed on the adatoms.

The works concerned with the catalytic oxidation of alcohols on these surfaces are restricted to methanol and ethylene glycol because of interest in fuel cells. Except for a comparative study of the catalytic oxidation of aliphatic alcohols<sup>18</sup>, nothing else has been reported in the literature on the oxidation of other alcohols.

In the present paper, the oxidation of benzyl alcohol on bare Pt and Pt surfaces modified by UPD of Tl, Pb, and Bi was investigated. The measurements were made

both in acid and alkaline aqueous media. Previous works were concerned with the kinetics of the electrochemical oxidation of benzyl alcohol on smooth Pt in  $\text{H}_2\text{SO}_4$  and the effective activation energy<sup>24,25</sup>. In addition, the oxidation of benzyl alcohol on Pt was studied in acetonitrile and an attempt was made to elucidate its reaction mechanism<sup>26</sup>.

## EXPERIMENTAL

The experimental procedure as well as the activation of electrodes were similar to those used in our previous works<sup>18,19</sup>. However, in the voltammograms and plots to follow, the potentials,  $E_{\text{H}}$ (V), refer to the normal hydrogen electrode.

All experiments were carried out at a constant temperature of  $298 \pm 0.1$  K except for the cases indicated below.

The electrolytic acid and alkaline solutions were prepared from triply distilled water and Merck "suprapure" 70%  $\text{HClO}_4$  and NaOH, respectively. Benzyl alcohol was from Fluka "puriss. p.a.". Solutions of the metal ions were prepared from the corresponding salts or oxides (Merck, "suprapure" or "p.a.") dissolved in a solution of a stoichiometric quantity of  $\text{HClO}_4$ .

## RESULTS AND DISCUSSION

### *Effect of UPD on Benzyl Alcohol Electrooxidation on Pt in Acid Solutions*

The effect of underpotential deposition of Tl, Pb, and Bi on the oxidation of benzyl alcohol in acid solutions can be seen from Fig. 1, showing cyclic voltammograms of benzyl alcohol on Pt in the absence (curve 1) and presence of  $\text{Tl}^+$ ,  $\text{Pb}^{2+}$ , and  $\text{Bi}^{3+}$  ions (curves 2–4) in  $\text{HClO}_4$  solution. In the inset figure the cyclic voltammograms for underpotential deposition of Pb, Tl, and Bi on Pt electrode are shown. The current density decrease in the hydrogen range is indicative of the suppression of hydrogen adsorption since underpotential monolayers of the metals are formed.

In the cyclic voltammogram of benzyl alcohol, in the absence of ions, there are two peaks (1 and 2) on the anodic branch. The oxidation actually occurs in the potential region where the electrode surface is partially covered with Pt—OH and totally with Pt—O. During the negative sweep the oxidation of benzyl alcohol starts in the potential region called "double layer region", where the platinum oxides are now reduced.

By varying the potential sweep rate,  $v$ , the peak current density varies linearly with  $v$  but non-linearly with  $\sqrt{v}$  (in the range from 25 to 400  $\text{mV s}^{-1}$ ). On the other hand, the dependence of the peak current density on benzyl alcohol concentration is non-linear. These facts suggest that the obtained currents exhibit distinctly kinetic character, which can be attributed to the formation and strong adsorption of intermediate products during the electrooxidation of benzyl alcohol. This gives rise to poisoning of the electrode surface.

The addition of  $Tl^+$ ,  $Pb^{2+}$ , and  $Bi^{3+}$  ions and their deposition in the underpotential region, forming two-dimensional submonolayers on the substrate, causes a remarkable enhancement of the electrocatalytic activity of the Pt electrode with respect to the benzyl alcohol oxidation. The most important characteristics of the catalytic activity are the shift of the first anodic peak to more negative potentials and the increase of the current density. In the case of  $Bi^{3+}$  ions, this enhancement is especially remarkable. The highest catalytic activity appears when their concentration is equal to  $5 \cdot 10^{-4} \text{ mol l}^{-1}$ . This value accords with that reported in previous studies on the oxidation of  $CH_3OH$ <sup>18</sup> and  $CH_2OHCH_2OH$ <sup>19</sup>.

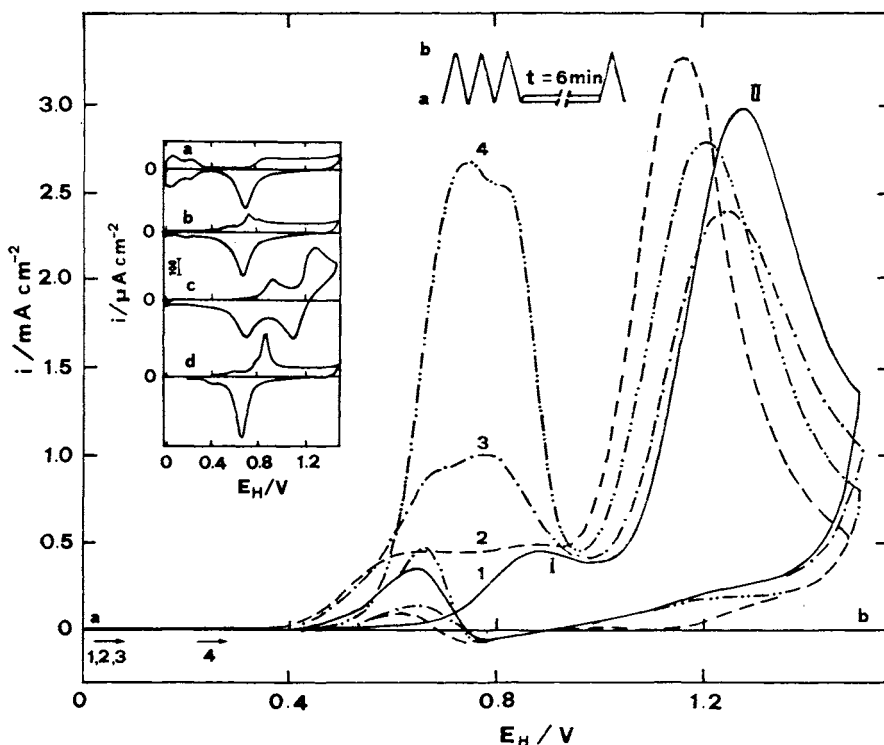


FIG. 1

Cyclic voltammograms for  $0.1 \text{ mol l}^{-1} C_6H_5CH_2OH$  oxidation on a Pt anode in  $0.5 \text{ mol l}^{-1} HClO_4$  in the absence (curve 1) and presence of:  $2.5 \cdot 10^{-4} \text{ mol l}^{-1} TlClO_4$ ;  $3.5 \cdot 10^{-4} \text{ mol l}^{-1} Pb(ClO_4)_2$ ;  $4.5 \cdot 10^{-4} \text{ mol l}^{-1} Bi(ClO_4)_3$ . Scan rate  $50 \text{ mV s}^{-1}$ . In the presence of  $Bi^{3+}$  the starting potential is  $0.2 \text{ V}$ . Inset: cyclic voltammograms for the underpotential deposition of heavy metals on Pt sheet in  $0.5 \text{ mol l}^{-1} HClO_4$ : a without any salt; b with  $5 \cdot 10^{-4} \text{ mol l}^{-1} Pb(ClO_4)_2$ ; c with  $5 \cdot 10^{-4} \text{ mol l}^{-1} TlClO_4$ ; d with  $5 \cdot 10^{-4} \text{ mol l}^{-1} Bi(ClO_4)_3$ . Scan rate  $50 \text{ mV s}^{-1}$ .

Competitive adsorption of the metal ions and benzyl alcohol in the underpotential region plays an important role in the oxidation process. To show this role, cyclic voltammograms were recorded at different holding times as well as at different starting potentials. Figs 2A, B give, as an example, cyclic voltammograms of benzyl alcohol in the presence of  $\text{Bi}^{3+}$  ions in the solution for different holding times at a starting potential of 0.2 V, and at a constant holding time 3 min and different starting potentials. It is seen that as the adsorption of Bi is stronger than that of benzyl alcohol (greater holding times and more negative starting potentials) the catalytic activity appears to be more intense. The same behaviour appears in the presence of  $\text{Pb}^{2+}$  or  $\text{Tl}^+$  ions in the solution.

The effect of temperature on the catalytic action of UPD of Pb and Bi on benzyl alcohol oxidation was also examined. The change of the current density caused by the temperature increase is much higher than that expected from the change of viscosity. This fact confirms the kinetic character of the obtained currents.

In our experiments the temperature was varied between 15°C and 55°C and the obtained data were correlated with the following Arrhenius-type equation:

$$\log i_p = \text{const.} + \frac{E_a}{2.303RT}, \quad (1)$$

where  $i_p$  is the peak current density in  $\text{A cm}^{-2}$  and  $E_a$  the apparent activation energy of the electrochemical process.

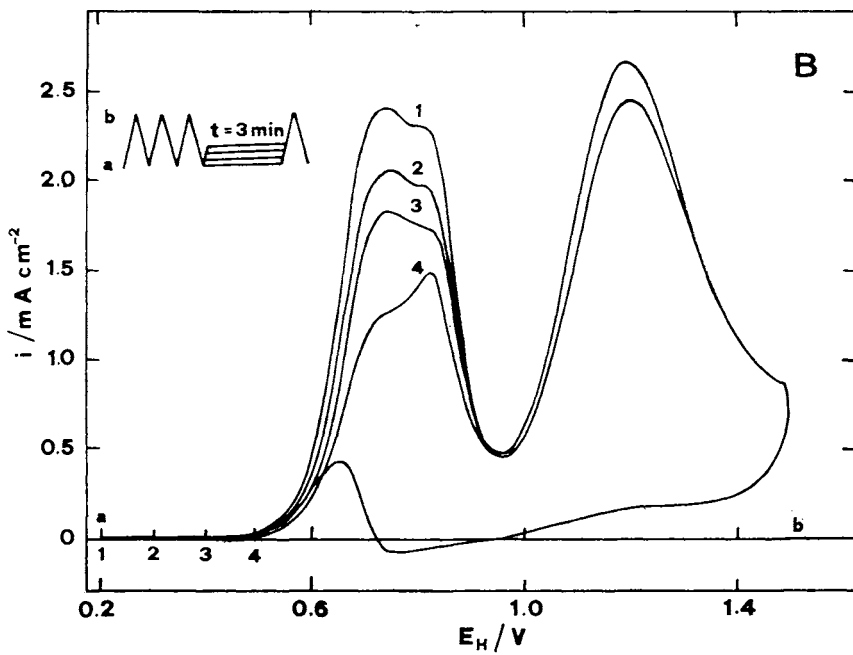
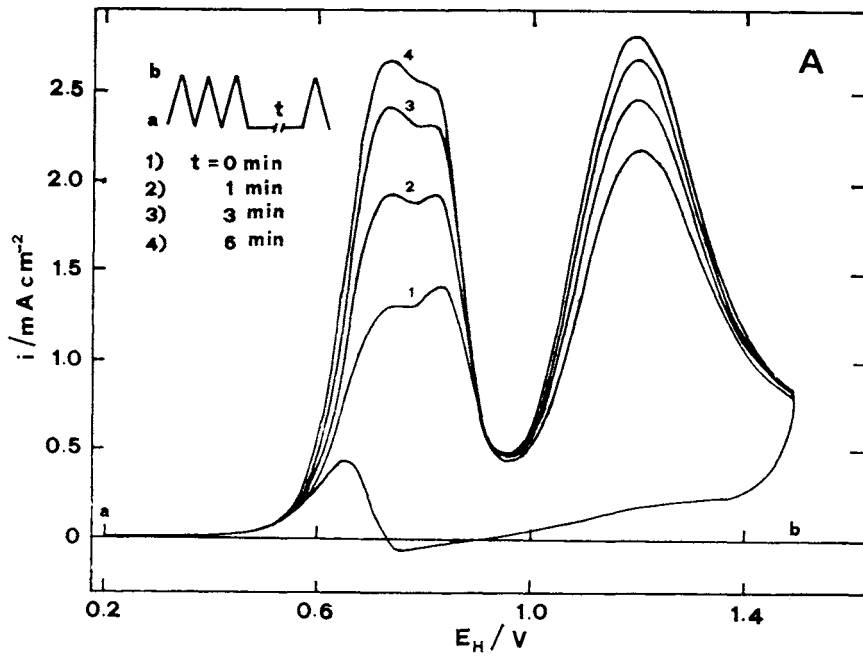
The values of  $\log(i_p)_I$  for the first anodic peak on Pt and on Pt modified by the UPD of Pb and Bi have been plotted against  $1/T$ ; the calculated values of the apparent activation energy are as follows:

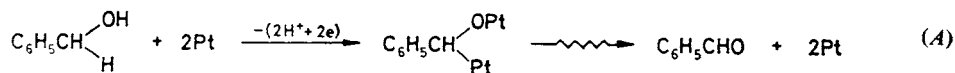
System	Pt	$5 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Pt/Pb}^{2+}$	$5 \cdot 10^{-4} \text{ mol l}^{-1} \text{ Pt/Bi}^{3+}$
$E, \text{ kJ mol}^{-1}$	30.2	27.3	27.6

The small decrease of the apparent activation energy observed in the systems  $\text{Pt/Pb}^{2+}$  and  $\text{Pt/Bi}^{3+}$  can be ascribed to a decrease of the adsorption energy of benzyl alcohol on the modified surfaces.

The oxidation of benzyl alcohol on Pt in aqueous acid solutions furnishes as main product benzaldehyde, while benzoic acid is formed in small amounts<sup>24</sup>. Benzaldehyde in acid solutions is hardly oxidized to benzoic acid, since its solutions do not give any oxidation peak on both pure Pt and Pt modified by UPD.

As with the oxidation of aliphatic alcohols and glycols, the oxidation of benzyl alcohol on Pt most probably begins with a dissociative chemisorption and an oxidative dehydrogenation which lead to the formation of a strongly adsorbed intermediate product which occupies at least two sites on Pt, poisoning in this way the electrocatalytic surface.





An adsorbed molecule may occupy multiple active sites, two with real chemisorption bonds and possibly one or two more since the benzene ring exhibits a certain steric hindrance.

The catalysis of the electrooxidation process by the UPD of metal adatoms may be elucidated on the assumption that the poisoning of the electrode surface is limited. The role of the large metal adatoms is to prevent the formation and the strong adsorption of the poisoning intermediate. The greatest electroactivity (based on current densities) is obtained at medium degrees of coverage of the electrode surface by the metal adatoms; so the distribution of free sites allows the dissociative chemisorption in order to start the oxidation process. Furthermore, at these degrees of coverage, the adatoms prevent adsorption of the intermediate, since the occurrence of two or more adjacent Pt sites, which are needed for this adsorption, is statistically very limited.

Consequently, the catalysis of the benzyl alcohol oxidation in acid solutions can be explained in terms of the "third body" effect in electrocatalysis<sup>12,13</sup>.

#### *Effect of UPD on Benzyl Alcohol Electrooxidation on Pt in Alkaline Solutions*

Electrooxidation of benzyl alcohol on a pure platinum electrode in 0.2M-NaOH is shown in Fig. 3. During the positive sweep, an oxidation peak appears in the potential range where the electrode surface is partially covered with Pt—OH. During the negative sweep, the electrode sites are almost blocked by the surface oxide layer until it begins to be reduced, so that the oxidation of benzyl alcohol occurs again. This behaviour is similar to that observed in acid medium except that in the positive sweep only one wave appears and the current densities obtained are about 6 times higher. Moreover, in alkaline solutions, during both the positive and negative sweeps the oxidation curves are practically superimposed in the potential range of benzyl alcohol oxidation. This fact shows that no poisoning species is present, in contrast to what happens in acid solutions.

The variation of the peak current densities with the potential sweep rate is linear (in the range from 25 to 400 mV s<sup>-1</sup>), i.e. the obtained currents are kinetic in character as in acid solutions.

FIG. 2

Cyclic voltammograms for 0.1 mol l<sup>-1</sup> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OH oxidation on a Pt anode in 0.5 mol l<sup>-1</sup> HClO<sub>4</sub> in the presence of 5 · 10<sup>-4</sup> mol l<sup>-1</sup> Bi(ClO<sub>4</sub>)<sub>3</sub>; A for different holding times at the starting potential 0.2 V; B for constant holding time (3 min) at different starting potential values. Scan rate: 50 mV s<sup>-1</sup>

The influence of the UPD of Pb, Tl, and Bi adatoms on the electrocatalytic activity of Pt electrode for benzyl alcohol electrooxidation is shown in Fig. 4; the cyclic voltammograms of benzyl alcohol oxidation were recorded in the absence and presence of Pb, Tl, and Bi perchlorates. The ions of Pb and Bi are hydrolysed in strongly alkaline media ( $\text{pH} \approx 13$ ) to form complex ions  $\text{HPbO}_2^-$  and  $\text{BiO}_2^-$  or  $\text{BiO}^+$ .

The underpotential monolayers of Pb, Tl, and Bi on Pt electrode in alkaline solutions strongly enhance the electrocatalytic activity for the benzyl alcohol electrooxidation. The current densities in the presence of Pb, Tl, and Bi are respectively about 6, 7, and 10 times higher at the optimum salt concentrations. The electrocatalytic activity is observed at very low ion concentrations. The optimum concentration for  $\text{Tl}^+$  was found equal to  $5 \cdot 10^{-6} \text{ mol l}^{-1}$  and for  $\text{HPbO}_2^-$  and  $\text{BiO}_2^-$  or  $\text{BiO}^+$  equal to  $1 \cdot 10^{-5} \text{ mol l}^{-1}$ .

From Fig. 4 it follows that in the presence of  $\text{BiO}_2^-$  or  $\text{BiO}^+$  (curve 4) a hysteresis equal to about 150 mV appears between the ascending (during the positive scan) and descending (during the negative scan) segment of the oxidation curve of benzyl alcohol. This seems to be consistent with the fact that the adsorption isotherm of Bi underpotential deposition is shifted towards more negative potentials during the negative sweep.

The lower part of the cyclic voltammogram of benzyl alcohol oxidation is almost independent of the sweep rate (in the range from 25 to  $400 \text{ mV s}^{-1}$ ). This fact allows the foots of these waves to be considered as quasi-stationary current-potential curves. Therefore, Tafel plot analysis of the ascending portion of the cyclic voltammogram

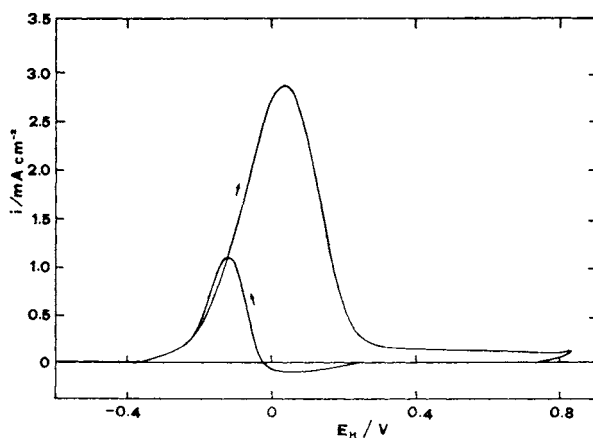


FIG. 3

Cyclic voltammogram for  $0.1 \text{ mol l}^{-1} \text{ C}_6\text{H}_5\text{CH}_2\text{OH}$  oxidation on a Pt anode in  $0.2 \text{ mol l}^{-1} \text{ NaOH}$ . Scan rate:  $50 \text{ mV s}^{-1}$

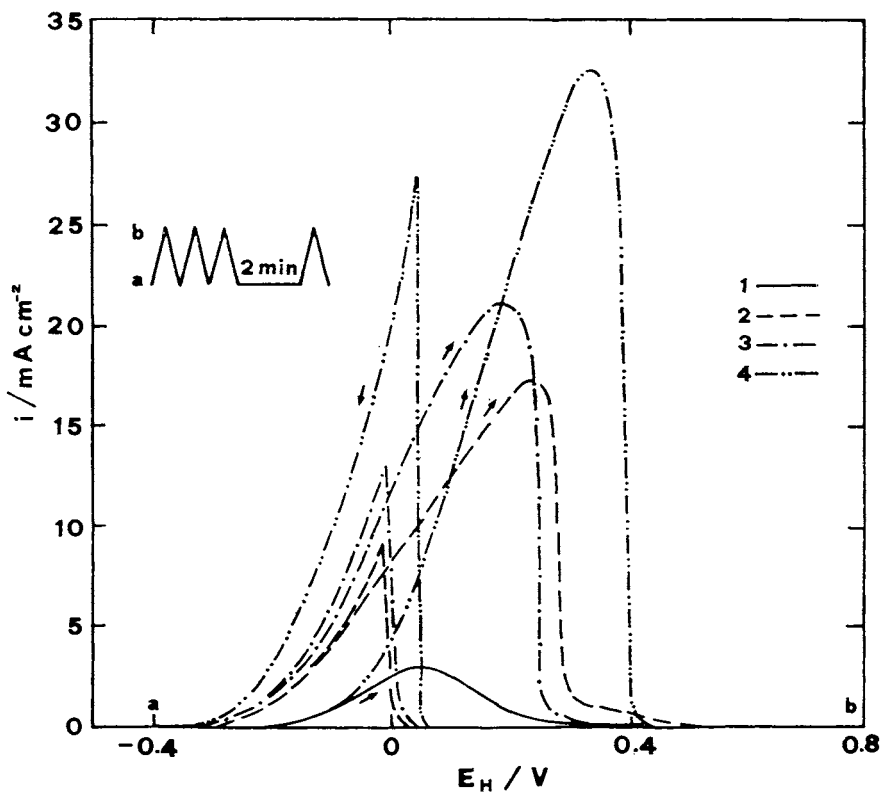


FIG. 4

Cyclic voltammograms for  $0.1 \text{ mol l}^{-1} \text{ C}_6\text{H}_5\text{CH}_2\text{OH}$  oxidation on a Pt anode in  $0.2 \text{ mol l}^{-1} \text{ NaOH}$  in the absence (curve 1) and presence of:  $2 \cdot 10^{-5} \text{ mol l}^{-1} \text{ Pb}(\text{ClO}_4)_2$ ;  $3.5 \cdot 10^{-6} \text{ mol l}^{-1} \text{ TiClO}_4$ ;  $4 \cdot 10^{-5} \text{ mol l}^{-1} \text{ Bi}(\text{ClO}_4)_3$ . Scan rate  $50 \text{ mV s}^{-1}$

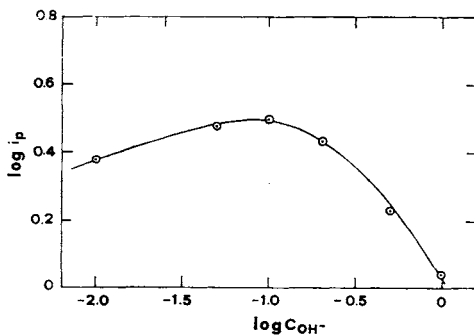


FIG. 5

Plot of  $\log i_p$  ( $\text{mA cm}^{-2}$ ) vs  $\log C_{\text{OH}^-}$  ( $\text{mol l}^{-1}$ ) for  $0.1 \text{ mol l}^{-1} \text{ C}_6\text{H}_5\text{CH}_2\text{OH}$  oxidation on a Pt anode



was carried out for the positive sweep. In the presence of  $\text{Bi}^{3+}$  ions, the analysis was carried out for the negative sweep on the descending part. The Tafel plots in the absence and presence of metal ions for the benzyl alcohol oxidation give curves with slopes ranging between 135 and 140 mV. These slopes lead to the transfer coefficient,  $az$ , equal to 0.44 independent of the coverage with the underpotential-deposited foreign metal atoms.

In contrast to acid media, where benzyl alcohol is oxidized mainly to benzaldehyde, in alkaline solution the benzyl alcohol oxidation, involving four electrons per molecule gives mainly benzoic acid. The presence of the metal adatoms causes, as already noted, an enhanced activity which can reach very high values close to diffusion-limited current densities with the best foreign metal (*i.e.* Bi). According to the equation for the peak current density of the irreversible charge transfer,

$$i_p = 3.01 \cdot 10^5 n(az)^{1/2} D^{1/2} C v^{1/2}; \quad (2)$$

for  $n = 4$ ,  $az = 0.44$ ,  $D \approx 6.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (footnote\*);  $C = 10^{-4} \text{ mol cm}^{-3}$ ,  $v = 0.05 \text{ V s}^{-1}$ , the theoretical value of  $i_p$  is determined as  $45.5 \text{ mA cm}^{-2}$ . The experimental value of the peak current density in the case of Bi adatoms was found to be equal to  $32.8 \text{ mA cm}^{-2}$ . This value is close to the theoretical for an electrode reaction governed by diffusion.

The experimental findings in the alkaline medium favour another mechanism for the explanation of the catalytic effects excluding the "third body" effect, since there is no evidence for the formation and strong adsorption of organic intermediates.

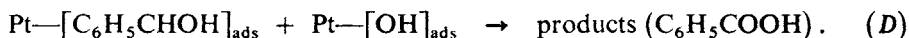
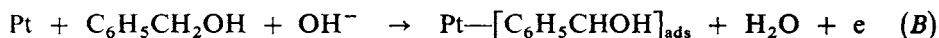
The dependence of the current density on both benzyl alcohol and hydroxyl ions concentration suggests that adsorbed hydroxyl ions participate in the oxidation process. Fig. 5 shows the variation of the logarithm of peak current density with the logarithm of concentration of hydroxyl ions. From this plot it is seen that the peak current density for constant concentration of benzyl alcohol attains its maximum value when the concentration of hydroxyl ions is equal to that of benzyl alcohol. This curve has a typical "volcano" shape, and the current density decreases when the ratio  $C_{\text{C}_6\text{H}_5\text{CH}_2\text{OH}}/C_{\text{OH}^-}$  becomes smaller than unity. Similar curves are also obtained by varying the benzyl alcohol concentration.

On the other hand, for constant hydroxyl ions concentration, the maximum value of the current density shifts towards more positive potentials with increasing benzyl alcohol concentration. The above experimental findings suggest a competitive adsorption of benzyl alcohol and hydroxyl ions.

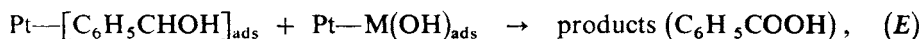
In conclusion, on the basis of the above discussion and the results which have previously been disclosed from similar studies on  $\text{CH}_3\text{OH}$  (ref.<sup>17</sup>) and  $\text{CH}_2\text{OHCH}_2\text{OH}$

\* This value was determined for  $\text{C}_6\text{H}_5\text{CHO}$  from polarographic data in alkaline medium<sup>27</sup>. We assumed that  $\text{C}_6\text{H}_5\text{CHO}$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  have approximately equal values of  $D$ .

(ref.<sup>21</sup>) oxidation, a possible reaction mechanism is suggested as follows:



In the presence of foreign metal adatoms, reaction (D) may be replaced by the following:



where M denotes the metal adatom.

The maximum electrocatalytic activity of a Pt electrode in alkaline media for benzyl alcohol oxidation seems to appear when the degree of coverage of the electrode surface with the organic residue and OH radicals is about equal to 0.5 (*i.e.*  $\theta_{\text{org}} = \theta_{\text{OH}} \approx 0.5$ ). This is a typical case in favour of the bifunctional theory of electrocatalysis<sup>14,15</sup>. The enhanced catalytic activity, which leads to current densities close to the diffusion-limited values with the best foreign metal (*i.e.* Bi), may be explained by the bifunctional character of the modified electrodes: the noble component, which in our case is platinum, furnishes the sites for adsorption of organic molecules and intermediates, while the non-noble components (Pb, Tl, and Bi) increase the coverage with oxidizing OH radicals.

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