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Electrolytic reduction of vanillin to vanillyl alcohol at amalgamated copper, lead and zinc electrodes

P. L. SHARMA, J. N. GAUR

Chemical Laboratories, University of Rajasthan, Jaipur-302004, India

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The electrolytic reduction of vanillin to vanillyl alcohol was investigated as a function of temperature, pH and current density at a stationary amalgamated copper cathode. The results were compared with those for amalgamated lead and zinc electrodes.

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1. Introduction

This paper deals with the electrolytic reduction of an aromatic aldehyde group to the corresponding alcohol in an aqueous medium. The mechanism of such reductions has been studied extensively [1–7]; the reduction is found to depend on pH and temperature. 4-hydroxy-3-methoxy benzaldehyde, commonly known as vanillin, is widely used in perfumes, as a flavouring reagent and in pharmaceuticals. Similar uses have been found for its derivatives.

The electrolytic reduction of vanillin was investigated by Schepss [8] in 1913 at mercury, lead and cadmium electrodes in acid alcoholic medium and at high current density; he found a poor yield (28%) of alcohol along with other by-products. Shima [9] in 1929 studied the electrolytic reduction of aromatic aldehydes including vanillin at a mercury electrode in slightly acidic medium. He obtained hydrovanillin as a by-product with vanillyl alcohol in good yield (80%). The chemical method for vanillin reduction was studied by Carothers [10] in the presence of platinum oxide as catalyst in organic solvent. The reduction of various aromatic aldehydes was studied by Udupa *et al.* [11] and they reported the experimental conditions for different reduction products; the complete conversion of aldehyde into alcohol with no by-product was possible. Powers and Day [12] have further confirmed the role of pH by studying a number of aromatic aldehydes polarographically.

This paper reports the reduction of vanillin at amalgamated electrodes under controlled pH, temperature and current density. The amalgamation was done on a cheap substrate to avoid the large consumption of mercury.

2. Experimental technique

2.1. *Materials and apparatus*

The vanillin, anhydrous sodium sulphate, sodium bicarbonate, mercuric sulphate and sodium bisulphite used in the study were all BDH-grade chemicals. The electrolytic cell used was a 500 cm^3 beaker covered with a glass lid with openings for the cathode, a porous pot, a thermometer, a glass rod stirrer (rotated mechanically) and for a luggin capillary to measure electrode potential during the electrolysis. The current was controlled with a constant-current regulated power supply (0–10 A, 0–50 V). The working electrode potential was measured with an electronic voltmeter using the luggin capillary and an SCE.

The amalgamation of the cathodes (Cu, Pb and Zn) was carried out prior to the experiment by taking an amalgamating bath containing 10% mercuric sulphate and 5% H_2SO_4 and using a current density of 5 A dm^{-2} for a period of 5 minutes for the copper electrode (circular solid rod), 15 minutes for the zinc and 45 minutes for the lead (thin strip) electrodes. A strip of pure lead was used as the anode. After amalgamation the electrodes were washed with 2% H_2SO_4 and were used immediately for electrolysis.

The catholyte was prepared by taking 25 g of sodium sulphate (anhydrous) and 8 g of sodium bicarbonate in 250 cm^3 of doubly distilled water. To this solution vanillin (0.1 M) was added. The

Present address: Department of Chemistry, R.R. College, Alwar-301001, India.

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pH of the catholyte was adjusted with dilute HCl and the pH was maintained by bubbling a stream of CO_2 through it at a slow rate. The anolyte was 15% sulphuric acid in a porous pot with a lead strip as the anode. The whole assembly of the cell was then cooled to 15° C by surrounding it with ice. A total current equivalent to $2F\ \text{mol}^{-1}$ was passed during the electrolyses.

2.2. *Isolation and identification*

After electrolysis, the catholyte was treated with a saturated solution of sodium bisulphite to recover any unreduced aldehyde. The solution was filtered and the filtrate was extracted three times with ether. The dried solid product was recrystallized from petroleum ether. The melting point was 114° C, very close to the melting point of vanillyl alcohol (mp 115° C) as reported in the literature. Further identification of the product was carried out by following the usual physicochemical tests:

(a) The solid product was treated with Tollen's reagent to see if there was any aldehyde present as an impurity. A negative result was obtained.

(b) The product showed the usual test of alcohols with ceric ammonium nitrate reagent: a dark red colour was obtained. The parent compound does not show any such test.

(c) The product identification was confirmed by comparing the i.r. spectra with that for an authentic sample; the spectra were superimposable.

3. Results and discussion

3.1. *Polarization studies*

Polarization curves were drawn in the absence and presence of depolarizer to find the most suitable range of current densities. Fig. 1 is a plot of cathodic potential (with respect to SCE) versus log current density at amalgamated copper, amalgamated lead and amalgamated zinc electrodes with and without depolarizer. From the curves, it is apparent that the reduction of aldehyde is favoured only at low current density. The depolarization starts after 0.5 A dm^{-2} and remains effective up to 1.5 A dm^{-2}. More negative than -1.4 V a limiting current is observed and above this current density sodium amalgam or hydrogen gas is formed.

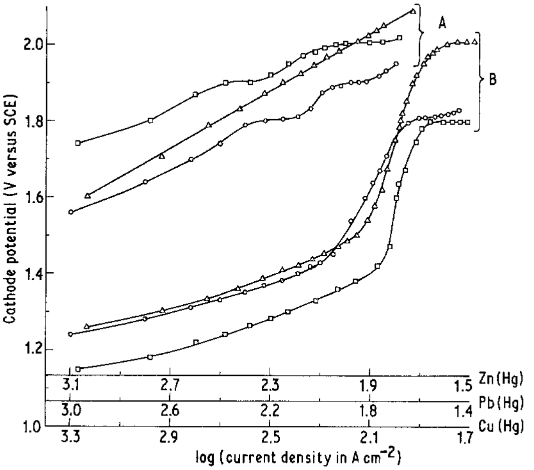

Fig. 1. Electrolytic reduction of vanillin. Polarization curves at amalgamated electrodes: △, Cu(Hg); ○, Pb(Hg); □, Zn(Hg). A, without depolarizer; B, with depolarizer.

Preparative studies showed the yield of vanillyl alcohol at Pb(Hg) and Zn(Hg) electrodes to be low compared to amalgamated copper electrode. Therefore, amalgamated copper was chosen as the most effective cathode to study the effect of other variables, e.g. the effect of current density, pH and temperature. The results are summarized in Table 1.

3.2. *Effect of current density*

From Table 1 it is apparent that as the current density increases the current efficiency decreases. This may be attributed to sodium-ion discharge at higher negative potentials [13]. At such potentials other products of reduction can be formed as reported by Allen [14] and others [15, 16]. At low current densities, the cathode behaves as a mercury cathode [17], i.e., as an electrode of high hydrogen overvoltage, which leads to the conditions for complete reduction.

3.3. *Effect of pH*

From the results shown in Table 1 it is evident that for alcohol preparation, an increase in pH has an adverse effect on current efficiency, although base catalysis causes an increase in the current with increase in pH due to enhancement of the dehydration rate [18]. The most suitable range of pH is 7.5–7.8.

Table 1. Results. Cathode: amalgamated copper, catholyte: aqueous sodium sulphate (250 cm^3) containing vanillin (0.1 M), anode: lead strip, anolyte: 15% H_2SO_4, pH of the catholyte: 7.5 ± 0.2, temperature: 15–18°C

Current density (A dm^{-2})	*Current efficiency (%)*
0.8	96.1
1.2	92.2
1.5	83.1
pH of the catholyte†	*Current efficiency (%)*
7.5	91.0
7.8	96.1
8.6	88.3
8.5	81.8
Temperature (° C)‡	*Current efficiency (%)*
15–18	96.1
25–28	83.1
35–38	74.0
Cathodes §	*Current efficiency (%)*
Cu(Hg)	96.1
Pb(Hg)	65.9
Zn(Hg)	60.0

† Current density: 0.8 A dm^{-2}.
‡ Current density: 0.8 A dm^{-2}, pH: 7.5 ± 0.2.
§ Current density: 0.8 A dm^{-2}, pH: 7.5 ± 0.2, temperature: 15–18° C.

3.4. *Effect of temperature*

The current efficiency decreases with a rise in temperature. This may again be attributed to an enhancement of the dehydration process. At low temperature, not only is the process of dehydration slowing down [19], but H^+ or Na^+ ion reduction is also suppressed. Also, at elevated temperature the possibility of self-condensation or dimerization cannot be ignored [20, 21].

3.5. *Depolarization with time*

To understand the course of reduction with time, the cathode potential was noted during the electrolysis. Fig. 2 is a plot of cathode potential (SCE) versus time at a Cu(Hg) electrode. The electrolysis was conducted at 0.8 A dm^{-2}. At the start of the electrolysis, a drop in cathode potential was observed, then the cathode potential rose to reach a limiting value near the end of the theoretical electrolysis time.

4. Conclusion

The electrolytic reduction of vanillin to vanillyl alcohol in aqueous medium was found to be dependent on pH and temperature. The choice of cathode also played an important role in determining the yield of the product. In our investigations, amalgamated copper was found to be the best cathode for this reduction. The current density must be low (below 1.5 A dm^{-2}) for high yields of alcohol. The maximum current efficiency was 96%.

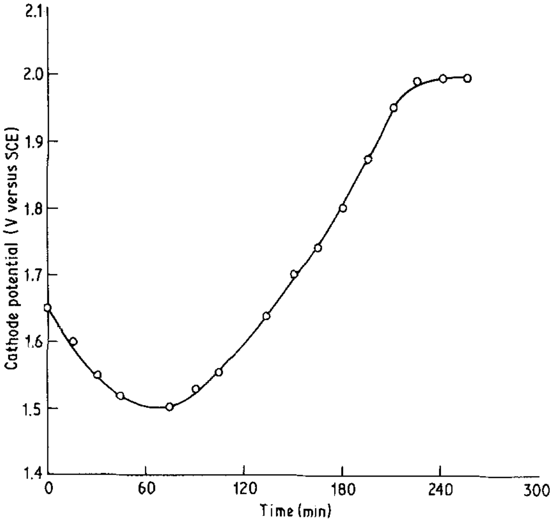

Fig. 2. Variation of cathode potential with time at Cu(Hg). Current density: 0.8 A dm^{-2}.

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