Electroreduction of Benzylidene Aniline and P-Methoxy Benzylidene Aniline at Different Cathodes

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IN the present work, the electrochemical reduction of the titled two different schiff bases is investigated in acid medium at different cathodes formed by electrodeposition at different conditions to correlate the surface texture with the reducibility. The effect of the depolarizer concentration, the applied current density and the nature of the cathode material is investigeted. It is found that the reducibility (A) is higher, the higher the concentration of the depolarizer as well as the hydrogen overvoltage of the cathode and the lower the current density.

INTRODUCTION

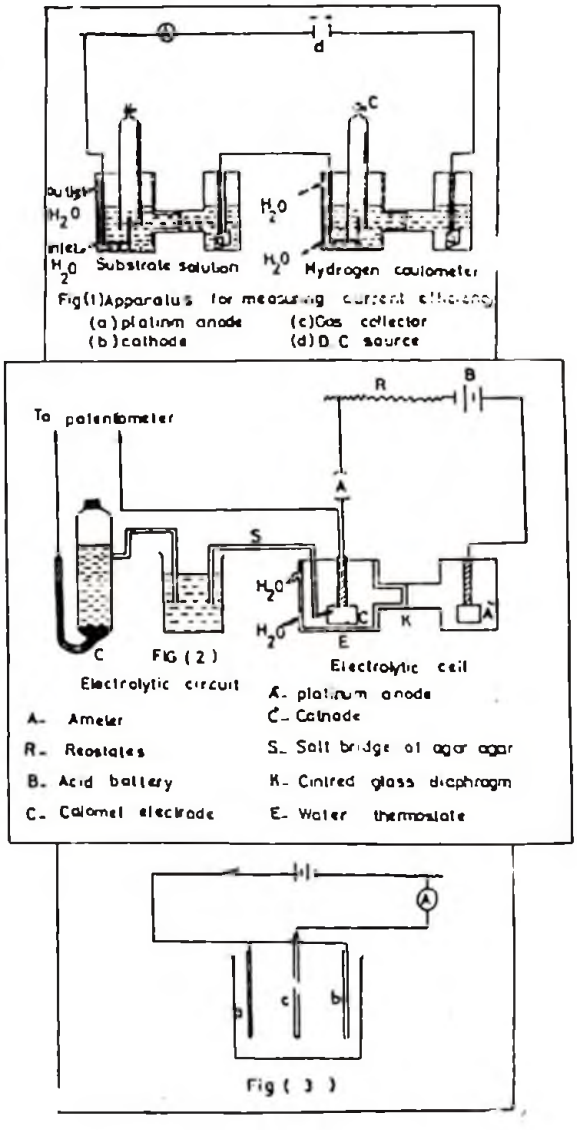
IN a recent communication it was found that the reduction efficiency of the schiff bases on copper cathodes depends to a great extent on the hydrogen overvoltage of the cathode([1]). It was suggested that, the reduction of organic compounds on metals with high hydrogen overvoltage takes place via an electronic mechanism before protonation([2,3]). The adsorbability of organic compounds plays a very important role in their reduction([4]). In this study cathodes of different surface texture and consequently the hydrogen overvoltage are formed by deposition of cathodes such as cadmium and copper from the usual plating bath on copper and the reducibility of the two schiff bases are examined

EXPERIMENTAL

The electroplanting circuit is shown in Fig. (3). Here we deposited copper and cadmium ions. Copper is deposited at 800, 100, 10 mA for 5, 10, 20 minutes. Cadmium is deposited at 100, 50, 10 mA for 5, 10, 20 minutes respectively. Two copper or cadmium sheets (a,b) were connected as anodes for plating. The cathodes of area 5.0 cm^2 were hung half way between the two anodes.

The used cathodes are: 1) Metallurgical copper. 2) Electrodeposited copper. 3) Amalgamated copper. 4) Electrodeposited cadmium.

0.1, 0.075, 0.05, 0.025, 0.01 M solutions were prepared by dissolving the appropriate amount of each of benzylidene aniline (I) and P-methoxy benzylidene aniline (II) in a 1 : 1 ethanol water mixture and made IN with respect to H_2SO_4. The cathodes were pretreted chemically before switching on the current. The circuit used for efficiency measurements is illustrated in Fig. (1). The reduction efficiency was estimated by measuring the quantity of hydrogen evolved on the cathode and comparing it with that evolved in the hydrogen coulometer connected in series with the electrolytic cell.

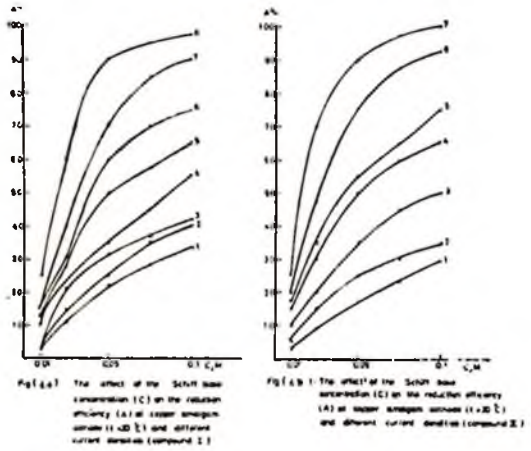


$$\text{Efficiency}\% = \frac{\left(\begin{matrix}\text{H}_2 \text{ evolved in} \\ \text{coulometer}\end{matrix}\right) - \left(\begin{matrix}\text{H}_2 \text{ evolved during} \\ \text{reduction}\end{matrix}\right)}{(\text{H evolved in coulometer})} \times 100$$

The volume of the evolved hydrogen in both the coulometer and the electrolytic cell were corrected to S.T.P. conditions. The circuit used for potential measurements is represented in Fig. (2). Reduction is carried out at constant current.

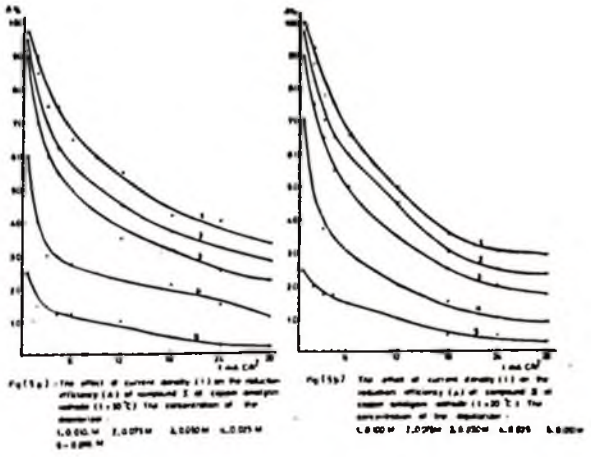
RESULTS AND DISCUSSION

a) *The effect of the depolarizer concentration :* The reducibility (A) for compounds (I) and (II) increases by increasing their concentration at all the electrodes. A representative curve for copper amalgam electrode is presented in Fig. (4).

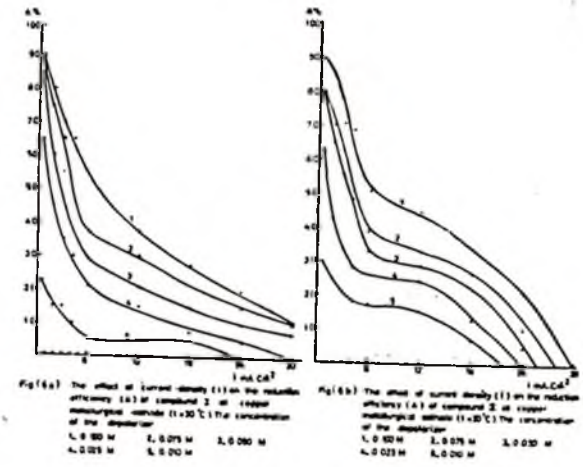


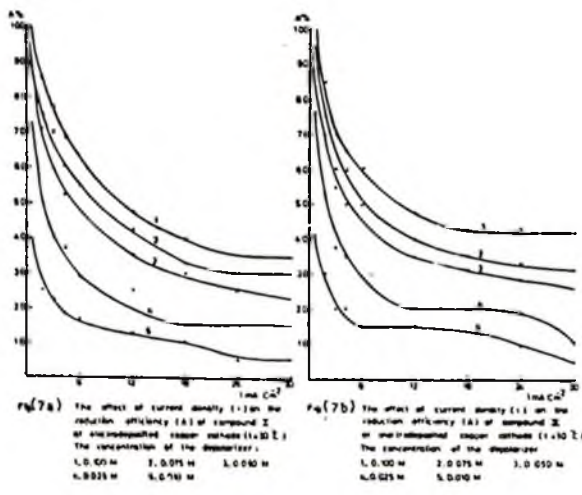
The increase in (A) for compounds (I) and (II) at the above mentioned electrodes is attributed to the dependence of the surface concentration on the bulk cancentration of the depolarizer[5]. The plateau on the (C-A) curves corrosponds to the surface saturation with the depolarizer molecules.

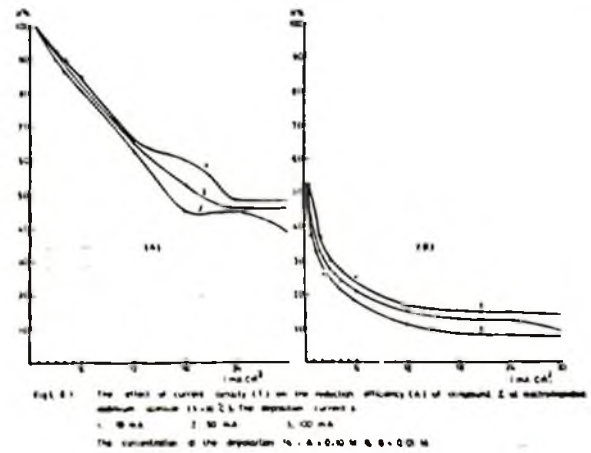
B) *The effect of current density :* From the plots constructed for the variation of (A) with the applied current density (i) it can be concluded that (A) decreases with increasing the current density (i) for both the compounds at all concentrations examined. Representative curves are presented in Fig. (5) for copper amalgam electrode. The increase of the current density (i) leads to a shift of the cathode potential to more negative values. So the hydrogen evolution accompanying reduction of the schiff bases become easier as the cathode potential increases. The efficiency (A) thus, decreases by increasing the current density.

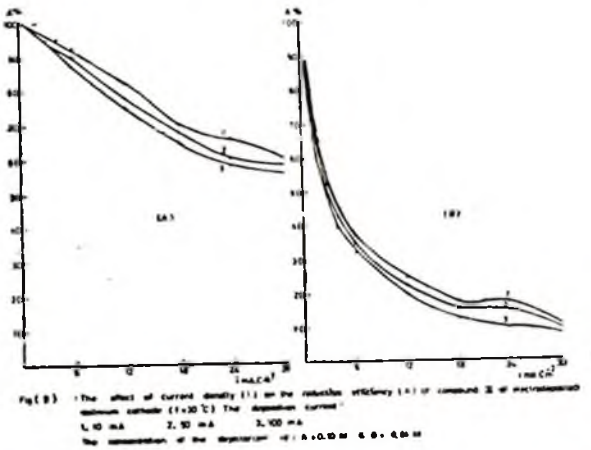


C) *The effect of the cathode material :* The reducibility (A) for compounds (I) and (II) at different cathodes is illustrated in Fig. (5-9). It clearly illustrates the effect of hydrogen overvoltage and the surface structure on the reducibility of organic compounds. The variation in the hydrogen









overvoltage of the cathodes is the main factor responsible for the difference in the reduction efficiencies of organic compounds. The higher the hydrogen overvoltage and the greater the degree of dispersion of the cathode surface, the higher is the reduction efficiency of organic compounds. S,o (A) for the two compounds at copper amalgam cathode are expected to be much higher than thal at the metallurgical one. The comparison of (A) for the two compounds at copper metallurgical and at electrodeposited copper cathodes with Cd. ot 800 mA.cm^{-2} reveals that for all the studied concentrations (A) is always greater at the electrodeposited that at the metallurgical cathodes. Between the two electrodes, the actual surface area of the electrodeposited copper cathode is probably greater than the geometric area. Thus, the applied current density is less than the rea value. On the other hand, the adsorption of organic molecules is known to be enhanced at the dispersed metal surface[6]. The higher reducibility at the electrodeposited cadmium cathodes are obtained when cadmium deposits are formed at 10mA.cm^2. At this value of current density the cadmium deposits are relatively of good quality and considerable dispersion[7]. The deposition of cadmium at higher current densities leads to the codeposition of basic salts together with the metal and the behaviour of the cathode is no more that of pure cadmium.

E) *The cathodic polarization* : A representative galvanostatic cathodic polarization curves of the different studied cathodes for compound (II) are illustrated in Fig. (10–13). The reduction

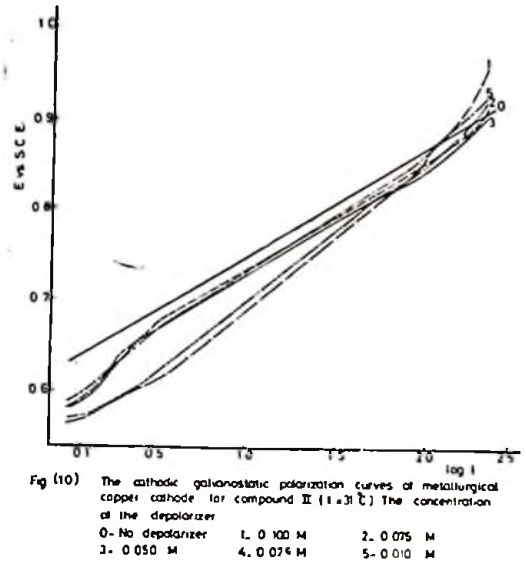


Fig (10) The cathodic galvanostatic polarization curves of metallurgical copper cathode for compound II (t = 31 °C) The concentration of the depolarizer
0- No depolarizer 1. 0.100 M 2. 0.075 M
3- 0.050 M 4. 0.025 M 5- 0.010 M

potentials are near the hydrogen evolution potentials on copper cathodes Fig. (10, 12). On the other hand at copper amalgam electrode, the hydrogen evolution process proceeds at sufficiently higher cathodic potentials than those of the reduction potentials Fig. (11). The polarization curve of the eleotrodeposited copper cathode are similar and close enough to those of the metallurgical copper. The fact that the reduction potentials are near the hydrogen evolution potentials on the copper cathodes is an evident explanation for the low reduction efficiencies at these cathodes. On the other hand cadmium and copper amalgam electrodes are capable of separating the potentials at which the hydrogen evolves and the depolarizer is reduced. This is the reason behind the higher reduction efficiencies at cadmium and copper amalgam electrode. From Fig. (11), it is obvious that, at low values of (i) the compounds behaves as depolarizers. The higher its concentration, the

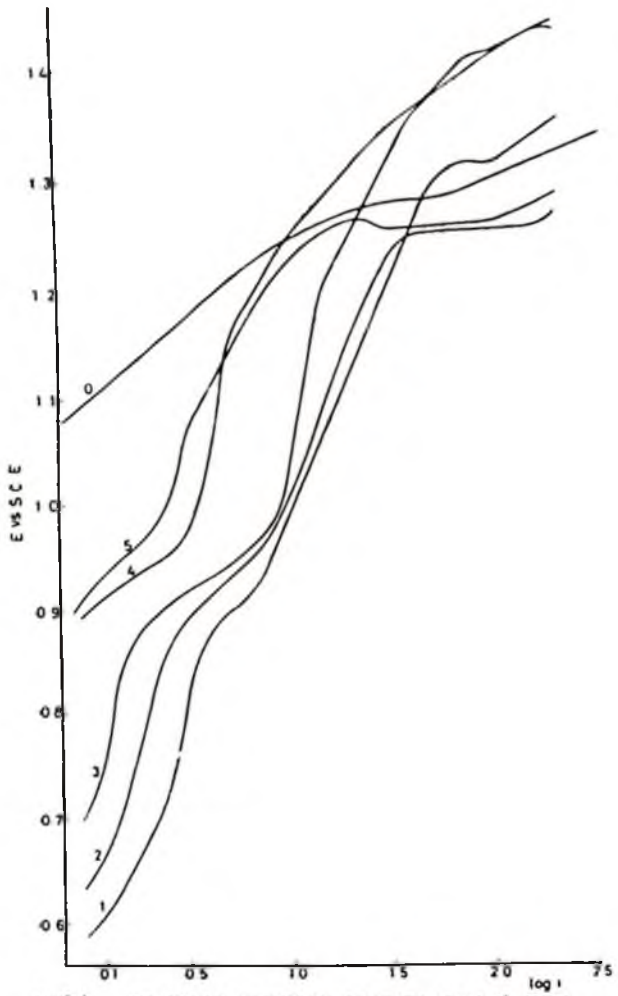


Fig (11) The cathodic galvanostatic polarization curves of copper amalgam cathode for compound II, (t = 31 °C) The concentration of the depolarizer
0- No depolarizer 1- 0.100 M 2- 0.075 M
3- 0.050 M 4- 0.025 M 5- 0.010 M

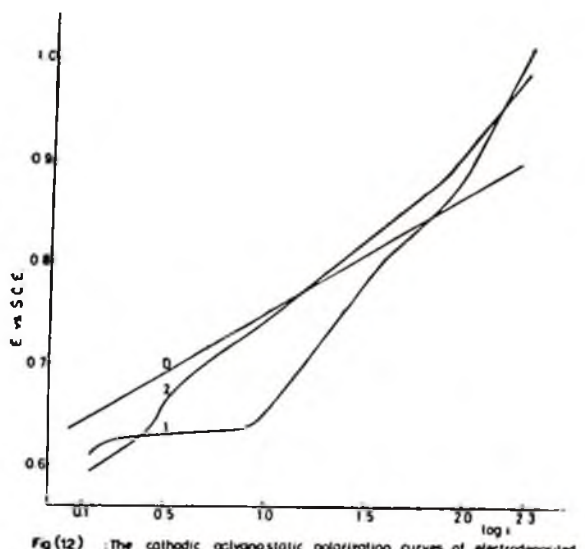


Fig (12) The cathodic galvanostatic polarization curves of electrodeposited copper cathode at current density = 100 ma Cm^{-2} for compound II (t = 31 °C) The concentration of the depolarizer
0- No depolarizer 1- 0.10 M 2- 0.01 M

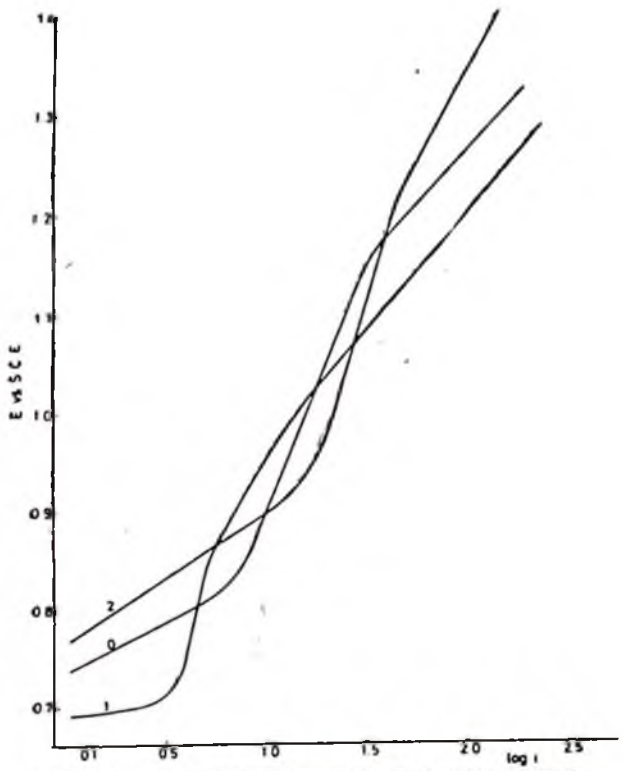


Fig (13) The cathodic galvanostatic polarization curves of electrodeposited cadmium cathode at current density = 10 ma Cm^{-2} for compound II. (t = 31 °C) The concentration of the depolarizer.
0- No depolarizer 1- 0.10 M 2- 0.01 M

lower is the cathodic potential of the electrode. At higher values of (i), the higher the concentration, the more negative is the potential. This phenomenon illustrates the double role of the studied compounds. They behave as depolarizers and inhibitors. A similar behaviour is reported for other organic compounds during their reduction at different cathodes[8]. At metallurgical and electrodeposited copper cathodes the potentials at which hydrogen evolves very between −0.5 and −0.9 V vs. S. C. E. One straight line is obtained when E is plotted against log (i) with b (Tafles slope) = 0.125v. In case of copper amalgam cathode, the potentials of hydrogen evolution are much more negative than those of copper cathode (−1.10 −1.35). Two straight lines are obtained when plotting E against log (i) for copper amalgam and cadmium cathodes. This behaviour is not reported for mercury and cadmium cathodes. The cathodic polarization curves in presence of depolarizers are found to consist of two main parts. At low values of (i), where a depolarization phenomenon takes place, the cathodic potentials corrospond to the schiff base reduction. At higher values of (i), over the limiting values, the potentials are those of

hydrogen evolution in presence of schiff base and their reduction products.

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