The electrolytic reduction of acetaldehyde, benzaldehyde, and furfural in ethanol-water mixture (1:1) and in the presence of 1.0 N H₂SO₄ has been investigated. The reductions have been carried out at metallurgical copper, electrodeposited copper, copper amalgam and electrodeposited cadmium cathodes. The structures of the aldehydes seem to play a definite role in their reducibility. The dipole moments (i.e., polarities) of the aldehydes influence the adsorbability and hence the reduction efficiency to a great extent. The cathode potentials at which the reduction takes place are highly dependent on the dipole moments of the aldehydes. It is found that on (i) increasing the aldehyde concentration, (ii) lowering the current density, (iii) raising the temperature of the solution and (iv) addition of some salts, the current efficiency of electrochemical reduction increases. On the other hand, on increasing the ethanol content of the solvent a parallel increase in the reducibility of the aldehydes studied is noticed till a certain limit after which the reducibility decreases.

The activity of carbonyl compounds towards electrochemical reduction depends to a great extent on their structure. The effect of substituents on the reducibility and the extent of reduction of aldehydes and ketones has also been investigated. In the present work, an attempt has been made to investigate the role of the simple differences in the dipole moments of the aldehydes, viz., acetaldehyde, benzaldehyde and furfural on their reducibility. Benzaldehyde and furfural are aromatic but have sufficient structural differences. Hence the study has been extended to differentiate between the cathodic behaviour of these compounds.

**Materials and Methods**

The electrolytic cell used consisted of two compartments, separated by a porous diaphragm of sintered glass. The anode consisted of a platinum sheet of 4.2 cm² surface area. The cathode was made of a copper spiral of 5.0 cm² surface area. Aqueous ethanol (1:1) containing 27.8 ml conc. H₂SO₄/litre was used as the electrolyte. The cathode was pretreated chemically before each run and then kept in solution under investigation for about 15 min without polarizing current. When small amounts of some salts (0.001M) were added, polarization was carried out for about 5 min at 40 ma/cm². This cathodic treatment allowed the deposition of a thin layer of metal of the added salt on the copper spiral cathode. Electrodeposited copper and cadmium cathodes were obtained by electrodeposition of these metals on the spiral copper cathode for 30 min at 25° from the following baths: (i) copper bath — CuSO₄·5H₂O (220 g/litre), conc. H₂SO₄ (60 g/litre) and current density 1.5 a/dm²; (ii) cadmium bath — CdSO₄·8H₂O (65 g/litre), (NH₄)₂SO₄ (35 g/litre), Al₂(SO₄)₃·18H₂O (30 g/litre), glue (0.7 g/litre) and c.d., 1.0 a/dm². Amalgamation was carried out from a bath containing NH₄Cl (1 g) + HgCl₂ (1 g) per litre for 30 sec.

The amount of hydrogen gas evolved at the cathode was compared with that evolved in a hydrogen coulometer, connected in a series to the electrolytic cell containing ethanol-water solvent and H₂SO₄ (1.0N). In the case of experiments with added salts, same salts at low concentrations were also added to the coulometer. The difference between the quantities of hydrogen evolved was considered to be equivalent to the quantity of electricity consumed in the reduction process of the carbonyl function.

The temperature during electrolysis was kept at 25° and the cathodic potentials were measured against a saturated calomel electrode.

**Results and Discussion**

In the present work the current efficiency of reduction (A) was taken as a measure of the ease of reduction of the carbonyl function. This is given by $A = (V' - V)/V$ where $V$ and $V'$ are the corrected volumes of hydrogen evolved over the coulometer and the working cathode respectively.

Effect of chemical structure of the aldehyde — The dipole moments of acetaldehyde, benzaldehyde and
furfural are 2.69, 3.0 and 3.6 respectively. The potentials of reduction of these aldehydes under identical conditions (concentration, temperature, current density and electrode material) are found to become less negative as the dipole moment increases (Fig. 1). Thus, acetaldehyde is reduced at the highest negative potential, while furfural at the least negative potential at the same cathode. This fact confirms the well known rule in polarography on the relation between \( \mu \) (dipole moment) and \( E_{1/2} \) for the different ketones. The higher dipole moment assists the adsorption of the organic compound. Thus, the potential at the same cathode. Figure 2 shows that an increase in concentration (furA) is accompanied by an increase in the current efficiency. However, at higher concentrations the increase in \( J \) becomes less noticeable, especially at low current densities. This behaviour may be explained on the basis of aldehyde adsorption. At low concentrations the amount of aldehyde adsorbed is proportional to its concentration. At higher concentrations, the electrode surface becomes more saturated and further increase in \( C \) does not affect the adsorption as noticeably as at low concentrations. When the degree of surface coverage is small, more aldehyde molecules can be adsorbed.

Effect of varying current density — The effect of increasing the current density on current efficiency is the same for all the compounds studied. On increasing the applied current, the efficiency decreases and at higher current values it is found to approach a more or less constant value. This behaviour is quite common for many organic depolarizers and may be explained by the competitive reduction of the organic molecules and the hydrogen ions at the cathode.

Representative curves for the variation of the current efficiency (A) with current density (i) in the case of furfural reduction at metallurgical copper cathodes are given in Fig. 2.

Generally, the reducibility of the aldehydes studied is higher at copper amalgam and electrodeposited cadmium cathodes than at electrodeposited or metallurgical copper at the same values of current density. This phenomenon can be attributed to the difference in the hydrogen overvoltage of these cathodes. In acidic medium, Tafel's constants for hydrogen evolution on copper, copper amalgam and electrodeposited cadmium are respectively 0.800, 1.406 and 1.40 V. The hydrogen evolution at copper amalgam and cadmium cathodes is more difficult than at copper cathode. This must lead to higher reduction efficiencies of the organic depolarizer at copper amalgam and cadmium cathodes.

Effect of added metal salts — Representative curves of furfural reduction in the presence of small amounts of some metal salts (Fig. 3), show that the addition of metal salts increases the reducibility of the aldehydes as compared to that in their absence. The function of the added metal ions in solution is mainly the formation of a very thin layer of their deposits on the copper cathode. In the case of mercuric sulphate,
amalgamation of the copper takes place. The formed deposit is highly dispersed, very fine-grained and of spongy film type. The adsorption of organic matter on such metal films is much greater than on compact surfaces. Also the real surface area of spongy metal deposits is much greater than that of the compact surfaces. This in turn leads to lower current densities on spongy surfaces than on compact smooth cathodes.

Solvent effect — The reducibility of aldehydes increases with increase in alcohol content of the solvent, reaches a maximum and then decreases with further increase in alcohol content. Such a behaviour of the current efficiency with the solvent composition may be due to two factors: (i) different solubilities of the reduction products, and (ii) competitive adsorption at the cathode surface by alcohol and aldehyde molecules. The decrease in current efficiency on increasing alcohol content may be attributed to the blocking of the cathode surface by alcohol molecules inhibiting the adsorption and consequently the reduction of aldehydes.

Effect of varying temperature — The reduction efficiency of furfural at different temperatures is graphically shown in Fig. 4. The other aldehydes studied reveal the same characteristics. As can be seen from Fig. 4 raising of temperature leads to a parallel increase in the reduction efficiency of the aldehyde. This behaviour is noticed at different cathodes studied and over a wide range of applied current densities. This phenomenon may be attributed to the different effect of temperature on the competing reactions of hydrogen evolution and aldehyde reduction.

References