

Title: Studies on the electrochemistry of organic compounds: process development in electro reduction of nitroso and nitro compounds and oxidation of sugars

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Abstract: The present study deals with the basic voltammetric investigations, preparative experimental works and cell design aspects in the development of electrochemical processes for the preparation of unsymmetrical dimethyl hydrazine (UDMH), p-phenetidine (PP), Calcium gluconate (CG) and Calcium Lactobionate (CLB).

The main cause for this state of affairs is primarily due to lack of a unified approach involving voltammetric studies, preparative experimental and proper cell design for each electrochemical process is necessary. The proper methodology for process development emphasizing the role of each of the three steps mentioned above is presented. The experimental details involved in the present research work are presented.

Voltammetric studies of the organic reactants used in the present electrochemical processes studied are dealt with. Results of voltammetric studies on the electrochemical reduction of nitroso dimethyl amine (NDMA) on lead electrode in H_2SO_4 medium are discussed. The reduction is found to be diffusion controlled with four electron transfer process under the experimental conditions. The presence of excess UDMH, the product of the electrochemical reaction, however, results in a competitive catalytic hydrogen evolution process which may greatly reduce the efficiency of the process.

Voltammetric studies of the direct reduction of nitrobenzene in aqueous alcoholic as well as absolute alcoholic H_2SO_4 solutions on copper cathode are presented. In both cases nitrobenzene is reduced in a 4-electron step. Slight differences in the adsorption effects, however, are noticed. The direct reduction of p-nitro phenetole (PNP) as well as its indirect reduction using Ti^{4+}/Ti^{3+} redox system are also discussed. Redox catalytic influence of Ti^{4+}/Ti^{3+} redox system is clearly established in these studies.

Glucose as well as lactose are not directly oxidized on glassy carbon electrode in near neutral pH conditions. The Br_2/Br^- redox couple shows quasireversible charge transfer behavior under these conditions. Voltammetric studies also indicate that the rate of chemical oxidation of glucose by electro generated Br_2 or hypobromite is much slower when compared to the electrochemical generation rate of bromine. Adsorbed lactose is much more easily oxidized when compared to solution phase lactose by reacting with electro generated bromine.

Based on the voltammetric studies mentioned above, comprehensive preparative works to optimize the conditions were carried out. The optimum experimental conditions and the difficulties encountered in the electro reduction of NDMA to UDMH are presented. p-Phenetidine is easily obtained by indirect electro reduction of p-nitrophenetole using Ti^{4+}/Ti^{3+} redox system. It may also be obtained by reducing nitrobenzene in absolute alcoholic H_2SO_4 medium. Although the latter process is more attractive some technical difficulties still remain. Preparative aspects of p-phenetidine from both these routes are considered. The preparative aspects of calcium-gluconate and lactobionate from glucose and lactose

respectively in NaBr medium containing CaCO_3 suspensions using graphite electrodes are discussed. The influence of various experimental parameters including fluid flow is discussed.

Among the three processes mentioned above the oxidation of sugars is certainly the most attractive one from the commercial point of view. Hence the cell design studies were mainly confined to this process. Tank cells have been conventionally employed for this process. The present study indicates that space time yield improves substantially in the rotating cylindrical electrode cell or more popularly known as Udupa Cell. Even greater efficiency in terms of space time yield as well as energy saving are discussed in a bipolar flow cell. A comparative discussion on both the cell designs is also presented.

The scope for further development in these three processes is presented. Some recent trends in electro organic process development are also indicated.