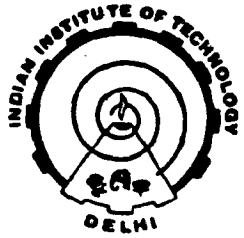
SOME STUDIES ON ELECTROCHEMICAL SENSORS

by

ANITA

THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY



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JULY, 1994

.. to my parents, my husband & my son

CERTIFICATE

This is to certify that thesis entitled **"SOME STUDIES ON ELECTROCHEMICAL SENSORS"** being submitted by **Anita** for the award of the degree of **"Doctor of Philosophy"** in Chemistry is a record of bonafide research work carried out by her. Anita has worked under my guidance and supervision and has fulfilled the requirements for submission of the thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree.

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Care has been taken to give proper credit for the work of other authors in the literature. The author would like to apologise for any unintentional omissions which might have occurred by oversight.

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ABSTRACT

Mediated electrochemistry offers a generic route to the development of sensors for different analytes. The use of p-benzoquinone as an electron transfer mediator has been considered in the glucose/glucose oxidase (GOD) coupled reaction in homogeneous solution. At a pyrolytic graphite (PG) electrode [basal plane (BPG) and edge plane (EPG), but edge plane in particular], p-benzoquinone exhibits high reversibility unlike on metal or carbon paste electrodes. Such an electrochemical reversibility on PG electrodes is advantageous because it lends itself for immobilization either by the mediator or enzyme or both for future sensor development. A second order rate constant for the reaction between p-benzoquinone and GOD has been obtained from cyclic voltammetric data, which is comparable to that reported in the literature for ferrocene derivatives. In solution at a pH 7.0, the measured catalytic current is linearly related to glucose concentration in the range 1-10 mM.

There are a large number of NAD^+/NADH dependent dehydrogenase enzymes which are useful for sensor development specific for different substrates. The oxidation of NADH at metal electrodes requires large overpotentials. Mediators in solution or mediator modified electrodes could be employed to oxidise NADH electrocatalytically at lower potentials. The thesis describes investigations on the

modification of a EPG electrode by dip coating and electro-deposition procedures. The TCNQ modified electrodes were characterized by cyclic voltammetric technique and found to be quite stable.

TCNQ modified electrodes prepared by dip coating or electro-deposition procedure were found to be electrocatalytic to NADH oxidation. The rate constant data and the calibration plots indicate that TCNQ modified electrode can be effectively used for NADH sensing over an extended concentration range. The results are significant for the development of amperometric enzyme sensors for subrtrates which are enzymatically coupled to NAD^+/NADH.

The electrocatalytic oxidation of L-ascorbic acid (AH_2) on TCNQ modified electrode has also been examined in detail. The surface coverage was $\sim 6.1 \times 10^{-9}$ mol cm^{-2}. The electrocatalytic activity of the modified electrode for AH_2 oxidation in phosphate buffer (pH 7.0) was shown by cyclic voltammetry at a potential of 0.08V vs. Ag/AgCl. The catalytic current varies linearly with concentration of AH_2 in the range 1-10 mM. The estimated rate constant for the reaction between AH_2 and immobilized TCNQ is 1.8×10^6 M^{-1} s^{-1}. The electro-oxidation of AH_2 by tetrathiafulvalene (TTF) has also been examined at carbon electrodes by employing cyclic voltammetric technique. In solution phase,

the oxidation of AH_2 was observed at ~0.25 V vs. SCE and linearity is seen in the range 0.5-10.0 mM. The rate constant for the reaction between AH_2 and TTF^+ is estimated to be $1.1x10^5$ M^{-1} s^{-1}. Electrocatalysis of AH_2 was also examined at TTF modified carbon paste electrode at a potential of ~0.23 V vs. Ag/AgCl. The modified electrode shows linear variation of current with concentration of AH_2 over the range 0.05 to 1.00 mM. Therefore, the method is ideally suited for quantitative determination of AH_2.

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