

# Effect of Temperature on the Electrooxidation of Some Organic Molecules on Pt Doped Conducting Polymer Coated Electrodes

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Polymer modified electrodes are of importance as possible electrocatalysts for various electrode reactions, i.e., platinum incorporated into polypyrrole or polyaniline films are known to be good systems for the electrooxidation of various organic molecules. In this study, the effect of temperature on the electrooxidation of D. glucose and methanol on Pt doped films was investigated, apparent activation energies were calculated and the results were evaluated.

## Introduction

Recently, much research has been concentrated on incorporation of metal particles such as platinum by electrodeposition onto polymer films (1-4). These modified polymer electrodes seem very useful for synthesis of various organic molecules. Several polymeric films were tested as active electrode materials. Among these, polypyrrole and polyaniline have certain advantages over other conducting polymers such as simplicity and rapidity of preparation of the polymer by the chemical and electrochemical methods, chemical durability against aerial oxidation, possibility of being formed in aqueous electrolytic solutions and stability in such media (5). Oxidation of small organic molecules such as methanol, CO on Pt other noble metal electrodes has also been the subject of a number of investigations in the past few decades (6). Several authors (7-9) have investigated the oxidation of glucose. These studies were of particular interest due to the promising features of the organic fuels as potential energy sources. The reactions were also considered simple models for oxidation of larger organic molecules.

In this study, the effect of temperature on the electrooxidation of D. glucose and methanol on Pt doped polypyrrole and polyaniline electrodes, respectively, were studied and the resulting activation energies were derived from experimental data.

## Experimental

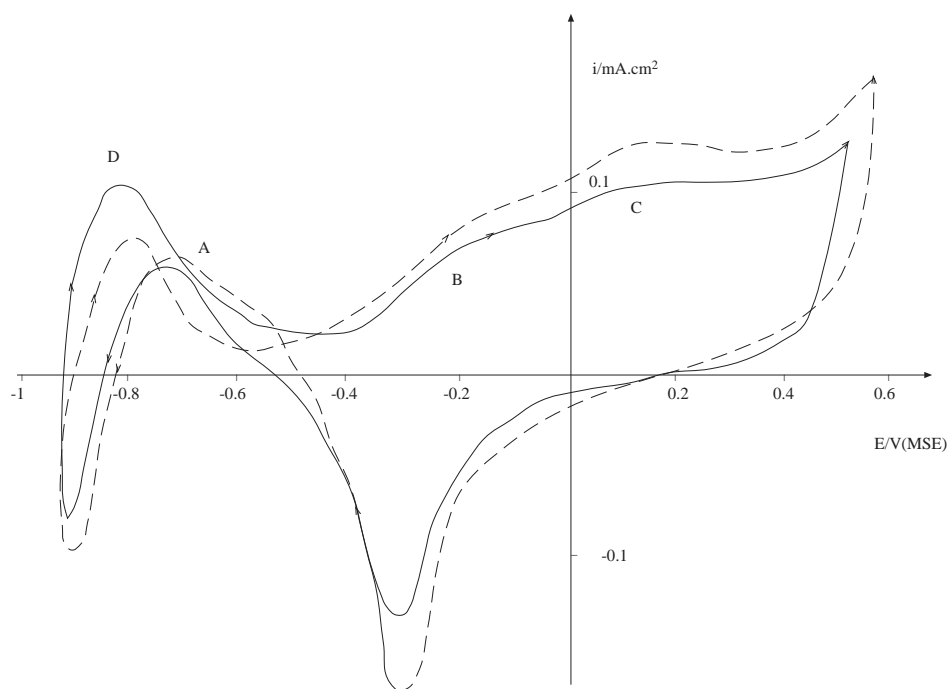
Voltammograms were recorded using standard equipment (a Wenking HP 88 High Power Potentiostat, a Tacussel GSTP 4 Signal Generator, and a BBC Goerz Metrawatt X-Y Recorder). Electrolytic solutions were

prepared from ultra-pure water (Millipore Milli Q System) and Merck reagents. Pyrrole and aniline were purified by vacuum distillation and other reagents were used as received. All experiments were performed under a nitrogen atmosphere in a classical three electrode cell with a Pt wire as the counter electrode and a Hg / Hg<sub>2</sub>SO<sub>4</sub> / K<sub>2</sub>SO<sub>4</sub> (sat.) electrode (MSE) as the reference. The working electrode was a Pt sheet. The electrochemical deposition of platinum particles on the polymer matrix was realized from solutions containing 0.01% H<sub>2</sub>PtCl<sub>6</sub> in phosphate buffer, by electrolysis at a constant potential, -0.56 V/MSE.

## Results

### Electrooxidation of D. Glucose on Platinum Doped Polypyrrole Electrodes

Polypyrrole films (PPy) were formed on a Pt foil by means of electrochemical oxidation of pyrrole. Polymerization was achieved from solutions containing 0.1M pyrrole in phosphate buffer (0.1M Na<sub>2</sub>HPO<sub>4</sub>+0.1M KH<sub>2</sub>PO<sub>4</sub>) by electrolysis at a constant potential, +0.43 V/MSE. The thicknesses of the polymer layers were calculated as 0.15 and 0.35 μm (10). Then, the polymer electrode was modified with platinum particles by electrolysis at -0.56 V/MSE. It has been previously reported that the maximum current density of D. glucose oxidation on PPy films was obtained with a Pt loading of 100 μg/cm<sup>2</sup> at -0.56 V/MSE (11). It is known that a charge Q<sub>pt</sub> of 200 mC.cm<sup>-2</sup> corresponds to a Pt loading of 100 μg.cm<sup>-2</sup> (12). Therefore, in this study, Pt loading was kept at 100 μg.cm<sup>-2</sup>.

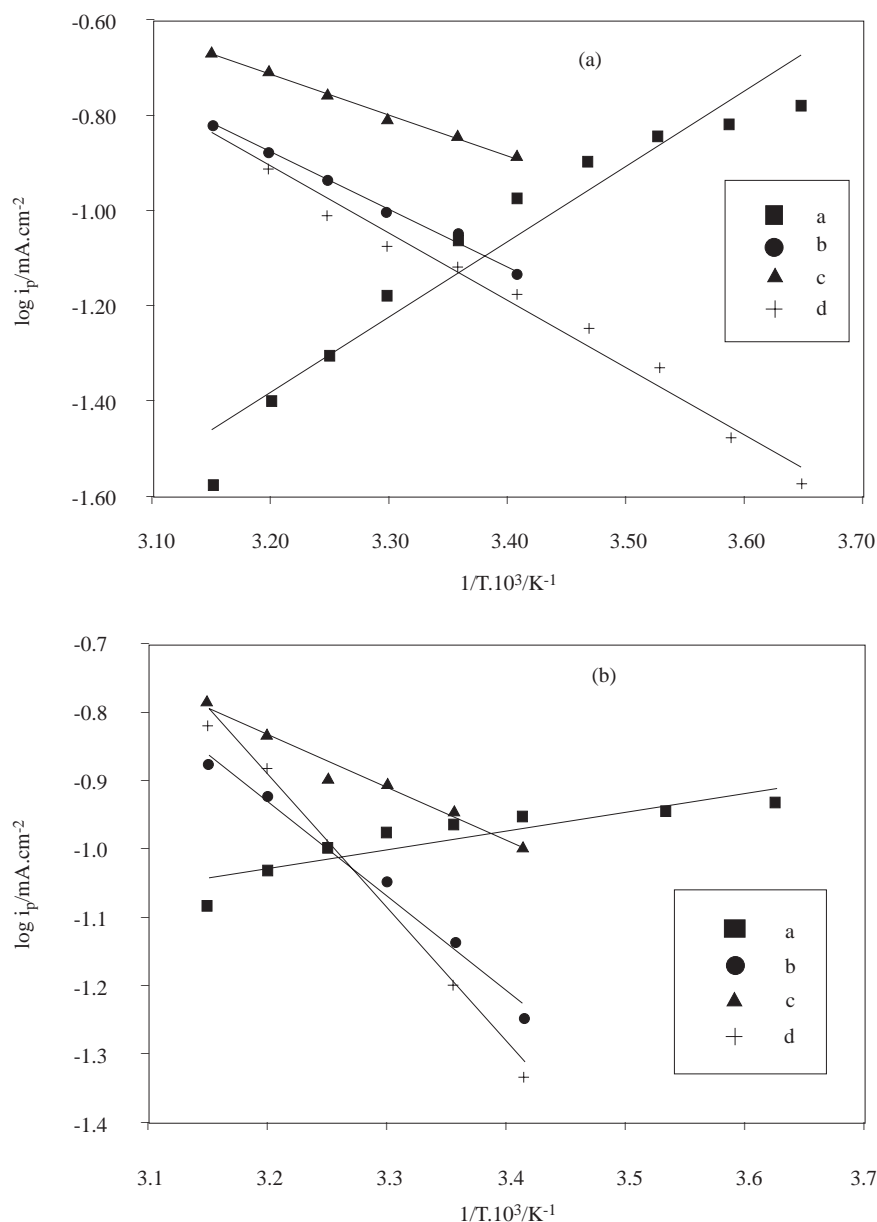


**Figure 1.** The Electrooxidation of D. Glucose on PPy-Pt Electrode,

0.1M Phosphate Buffer,  $v=50$  mV/s, 25°C,

— Film Thickness: 0.15 μm,

- - - - Film Thickness: 0.35 μm



**Figure 2.** Graph Used for the Determination of Activation Energy of D. Glucose

a) Peak A, b) Peak B, c) Peak C, d) Peak D

a) Film Thickness:  $0.15\ \mu\text{m}$ , b) Film Thickness:  $0.35\ \mu\text{m}$

Figure 1 shows the cyclic voltammogram of the polypyrrole electrode at two different thicknesses prepared under the conditions mentioned above, in the presence of 0.1M glucose. During the positive scan, three peaks, A, B and C were seen. During the reverse scan, oxidation of D. glucose occurred in the potential range in which the surface oxides were reduced. Previous investigations showed that while the peak A represents the dehydrogenation of the anomeric carbon, peaks B and C represent the further oxidation of glucose residues.

Activation energies were determined by studying the oxidation of D. glucose at different temperatures between 1 and 45 °C on platinum dispersed polypyrrole for two different thicknesses of PPy films. Activation energies were calculated from the slope of the plots of  $\log i$  vs  $1/T$  for certain potential values by the use of the following equation:

$$[\delta \ln i_p / \delta(1/T)]_{E,C} = -\Delta H^* / R$$

The values of activation energies -5.1, 26.7, 14.7, 58.8 kJ/mol for peaks A, B, C, D respectively for polypyrrole film thicknesses of 0.15  $\mu\text{m}$  and -29.8, 22.7, 0.8, 26.9 kJ/mol for peaks A, B, C, D respectively for those of 0.35  $\mu\text{m}$  thicknesses were obtained (Figure 2). By comparing the activation energies of peak A for two different film thicknesses of PPy electrode, it is seen that when the film thickness was increased, the activation energy value for peak A decreased which means that the reaction was controlled by diffusion instead of adsorption. According to the previous results on the influence of temperature (13), the transformation of D. glucose into fructose begins to take place at an appreciable rate, when the temperature is increased, i.e. the current density of peak A increases, when the temperature decreases, giving a negative activation energy.

If we compare the activation energy values of peaks A, B, C, D for two different thicknesses of polypyrrole, the decrease of activation energies of peaks A, C, D indicate that the rate-determining step is diffusion, increasing the film thickness. The activation energy remains approximately constant for peak B in both cases of the film thicknesses, which means that the rate-determining step is adsorption for both of the film thicknesses of the PPy electrode. The increasing porosity with film thicknesses allows the platinum particles to be deposited in a regular style giving higher possible surface area for the oxidation of D. glucose. Thus, the diffusion of molecules to the surface of the electrode determines the rate of reaction. However, the rate-determining step was always adsorption in the case of peak B.

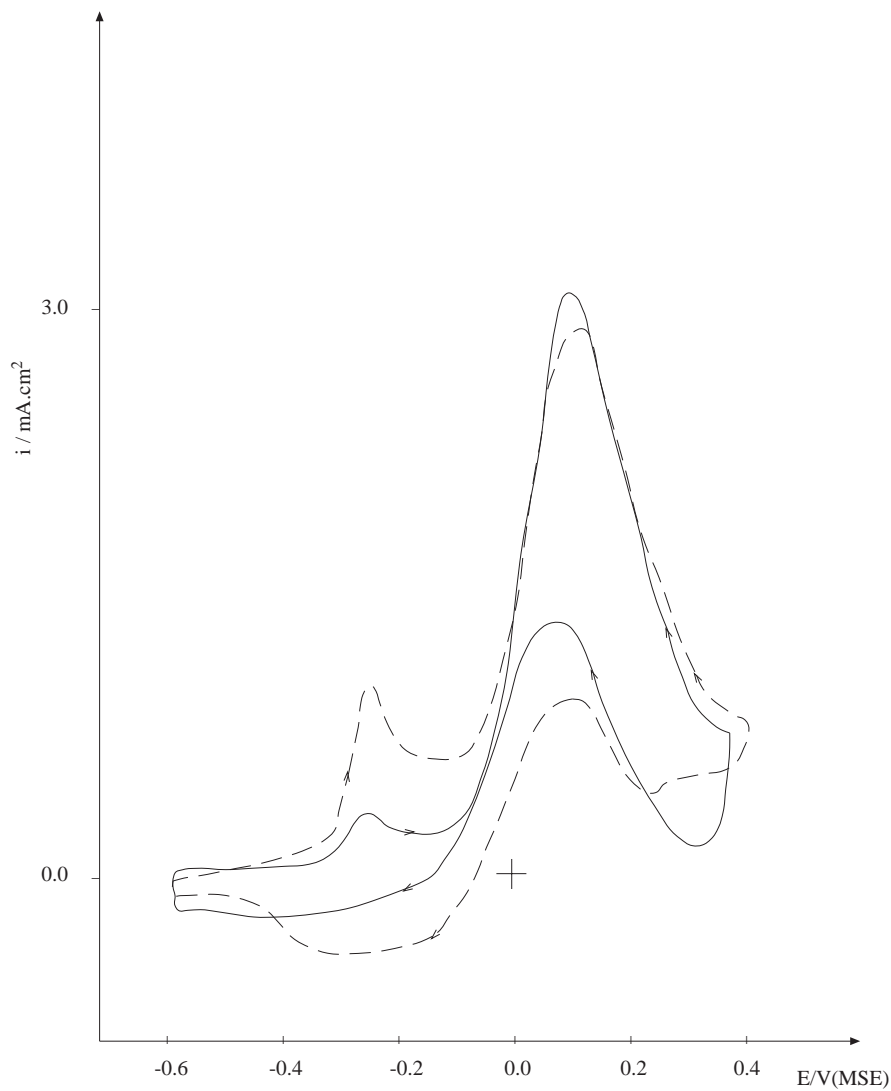
## The Electrooxidation of Methanol on Platinum Doped Polyaniline Electrodes

Polyaniline films (PANI) were formed on a Pt foil by means of electrochemical oxidation of aniline. Polymerization was achieved from solutions containing 0.1M aniline in 0.5M  $\text{H}_2\text{SO}_4$  by sweeping the potential continuously between -0.6 and 0.4V until a film of certain thickness was obtained. Film thickness was determined using the charge value of the first anodic peak of the last growth cycle during polyaniline film formation (13). After that, platinum was deposited onto the PANI films. The maximum current density of methanol oxidation on PANI films was obtained with a Pt loading of 70-100  $\mu\text{g}/\text{cm}^2$  (1). Hence, Pt loading was kept at 100  $\mu\text{g}/\text{cm}^2$  and electrodeposition was realized at -0.365 V/MSE (14).

A voltammogram of methanol oxidation on an electrode thus formed is given in Figure 3. The voltammogram shows that the oxidation of methanol on platinum modified polyaniline starts in the double layer region of platinum (at -0.1V/MSE). The oxidation rate increases at more positive potentials, reaching its maximum at 0.1 V/MSE. During the negative variation of the potential, platinum sites are almost blocked by the surface oxide layer until the reduction takes place. The methanol oxidation starts again reaching a weak current peak at 0.9 V/MSE.

Activation energies were determined by studying the oxidation of methanol on PANI-Pt electrodes of two different polyaniline film thicknesses between 20 and 45 °C (Figure 4). The potential shift between positive and negative sweeps was not very significant with increasing temperature. The apparent activation energies were determined from the slopes of the plots of  $\log i$  vs  $1/T$  for certain potential values. Activation energies of 51 and 25 kJ/mol were calculated for polyaniline film thicknesses of 0.11 and 0.38  $\mu\text{m}$ , respectively. For a 0.11  $\mu\text{m}$  thick polyaniline film, the activation energy value of 51 kJ/mol might indicate that the

rate determining step is the adsorption step, conversely to pure platinum for which the diffusion process determines the total reaction rate, whereas an activation energy value of 25 kJ/mol for the polyaniline film of 0.38  $\mu\text{m}$  thickness suggests that the reaction is diffusion controlled. This may be explained by the higher surface area provided by the 0.38  $\mu\text{m}$  thick film.

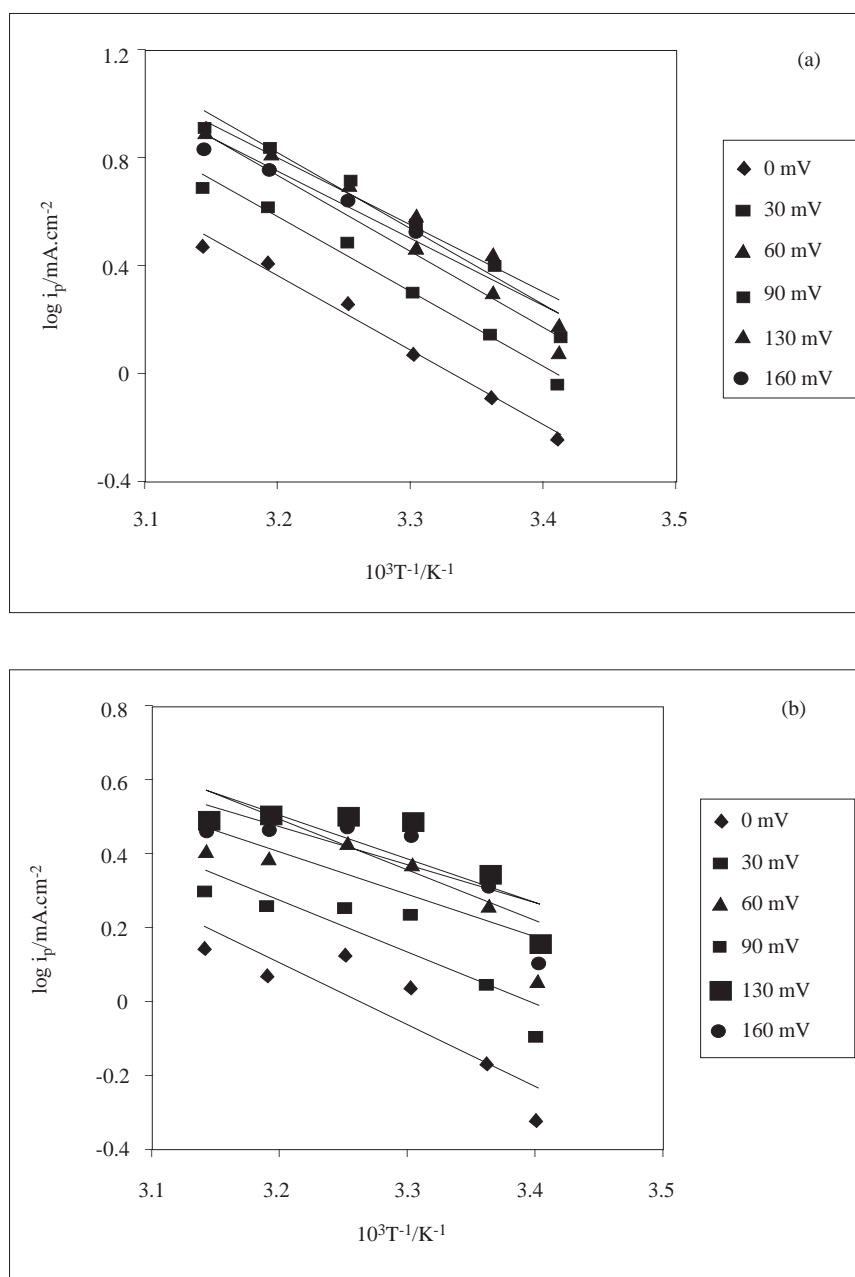


**Figure 3.** The Electrooxidation of D. Methanol (0.1M) on PANI-Pt Electrode,

0.5M  $\text{H}_2\text{SO}_4$ ,  $v=10$  mV/s,  $25^\circ\text{C}$ ,

——— Film Thickness:  $0.11\mu\text{m}$ ,

- - - - - Film Thickness:  $0.38\mu\text{m}$



**Figure 4.** Graphs Used for the Determination of Activation Energy of Methanol

a) Film Thickness:  $0.11 \mu\text{m}$ ,

b) Film Thickness:  $0.38 \mu\text{m}$

## Conclusion

These results show that the mechanism of the rate-determining step is modified as a function of the PPy and PANI film thicknesses in the case of electrooxidation of methanol and D. glucose. Generally, it is

observed that the rate-determining step becomes diffusion controlled by increasing the conductive polymer film thickness. This may be explained by the higher surface area and porosity provided by the thicker film which allows the platinum particles to be deposited in a regular style giving the maximum possible surface area for the oxidation of organic molecules. Thus, the conductive polymer thickness control may offer an alternative control over the oxidation mechanism of organic molecules, leading to changes in the electrical and catalytic properties of the surfaces. Such results may be promising for the direct oxidation of G. glucose and methanol.

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