

STUDY OF HYDROCARBON OXIDATION BY EXPERIMENTAL
SEPARATION OF REACTION STEPS - 1. THEORETICAL
ANALYSIS AND ETHANE ADSORPTION ON PLATINUM.

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INTRODUCTION

The study of electrochemical processes which involve two or more elementary reaction steps is at present of increased interest because of the development of fuel cells. The direct oxidation of hydrocarbons is a case in point since along with charge transfer, surface processes such as adsorption, desorption and possible conversion may take place. In addition to the above the effects of mass transfer may have to be taken into account. The analysis of such systems is difficult since most studies are undertaken with all of the processes occurring more or less simultaneously. Thus the surface reactions are all coupled with a diffusion step. Theoretical analysis is normally carried out under conditions either of semi-infinite linear diffusion or of known convection with all of the rate surface constants appearing as grouped constants in the resulting expressions. Separation of parameters is difficult and normally cannot be done without some degree of ambiguity. The work of Matsuda and Delahay¹ is an excellent example of the grouped parameter problem when relaxation techniques are employed. In addition the various mechanisms which have been proposed for the hydrogen evolution reaction and which all appear to provide at least partial explanations for this process are by now classic examples of parameter separation difficulties.

In order to study electrochemical reactions in which there is at least adsorption coupled with charge transfer such as the hydrogen evolution reaction, relaxation techniques have been extensively used. The main reason for their use is because they allow the quantity of hydrogen adsorbed at a given overvoltage to be evaluated. Charging curve²⁻¹², impedance measurements¹³⁻¹⁵ and the voltage sweep technique¹⁶⁻³⁰ have been employed. The determination of kinetic parameters using these methods is not, however, done without some degree of ambiguity, although the introduction of time as a variable normally renders the situation less complex since the number of simultaneous equations increases.

The fact, that the first step in the oxidation of gaseous reactants is normally one of adsorption allows the

possibility of separating this step from those succeeding it in time. This would allow independent analysis of the adsorption and possible conversion processes.

Such a technique necessarily involves time as a variable thus permitting a dynamic analysis of the reaction steps. It is thus a relaxation technique.

The direct electrochemical oxidation of hydrocarbons is receiving much attention at the present time³¹⁻⁴⁷. Probably the most important step in the oxidation and that most studied, is adsorption followed by possible conversion. Thus the aspect of catalysis in an electrochemical reaction is increasingly important. It is therefore of interest to be able to elucidate the process of adsorption so that the demand for new catalyst materials to be used in fuel cells may be, at least in part, met.

It is the purpose of this communication to describe a method whereby the reaction steps preceding charge transfer and desorption may be separated in time. A theoretical analysis of the method will be given and an example of its application will be made in a preliminary study of the adsorption of ethane and platinum.

THEORETICAL

In order to experimentally separate the reaction steps in the oxidation of a gaseous reactant it is necessary to allow the electrode to periodically be in the presence of gas then in the electrolyte. This may be carried out in the following way. The electrode under study is placed in a large circular insulated disc (making up only a small portion of this to avoid edge effects). The disc may then be rotated thus allowing the electrode to spend part of a rotation in the presence of the gaseous reactant and electrically insulated from the polarization circuit and the rest of the rotation immersed in the liquid where charge transfer and desorption may take place.

During the adsorption phase the electrode is covered with a thin film of liquid the thickness of which may be varied. There now exists a diffusion coupled adsorption process. Two methods by which this occurs may be envisaged. One is that in which the liquid film initially contains no gas so that this must first dissolve in the electrolyte then diffuse through the film with subsequent adsorption on the electrode surface. This case will be analyzed here. The second is to introduce on the electrode surface electrolyte previously saturated with the gas under study.

Adsorption then immediately starts with a diffusion layer gradually being created in the film. This case will be analyzed elsewhere.

The model used for the mathematical analysis given below is as follows. The film of electrolyte is of thickness δ such that finite linear diffusion is the sole mode of mass transfer. The dissolution of gas in the film occurs at $x = 0$ and is considered infinitely rapid, i.e. a concentration step function of time exists at the gas liquid interface.

The adsorption process occurs at $x = \delta$ following Langmuir kinetics which appears to hold for many adsorption processes in electrochemistry. The case in which Temkin kinetics prevail will be analyzed elsewhere. Thus the adsorption process is assumed to be given by:

$$\frac{d\Gamma(t)}{dt} = k_a (\Gamma_m - \Gamma(t)) C(\delta, t) - k_d \Gamma(t) \quad (1)$$

In order to take the diffusion process into account the Fick equation written for linear diffusion will be used.

$$\frac{\partial C(X, t)}{\partial t} = D \frac{\partial^2 C(X, t)}{\partial X^2} \quad (2)$$

This equation must be integrated using equation (1) from which the principal boundary conditions will be derived. The use of (1) as written prohibits the obtention of a closed form solution. This work is now in progress. Two cases which allow (1) to be simplified may be envisaged. If $\Gamma(t) \ll \Gamma_m$, then:

$$\frac{d\Gamma(t)}{dt} = k_a \Gamma_m C(\delta, t) - k_d \Gamma(t) \quad (3)$$

This simplification is probably fairly reasonable as far as hydrocarbons are concerned since their solubility in the aqueous solutions normally employed in fuel cells is small.

Further, the experimental technique, which is described in more detail below, allows measurements to be made at times sufficiently short so that this simplification may be fulfilled. If, in addition the adsorption process is sufficiently rapid, then:

$$k_a \Gamma_m C(\delta, t) = k_d \Gamma(t) \quad (4)$$

This, of course, is probably not true for hydrocarbon adsorption, but the case is of general interest and will be presented here.

a) Low coverage, rapid adsorption: The integration of (2) is carried out using the following initial and boundary conditions.

$$\begin{array}{ll} X = 0, t \geq 0 & C(0, t) = C_0 \\ X = \delta, t = 0 & C(\delta, t) = 0 \\ X = \delta, t > 0 & C(\delta, t) = \frac{D}{k} \Gamma(t) \end{array}$$

Since the surface concentration $\Gamma(t)$ is a function of the flux of the diffusing species at the electrode surface, then:

$$\Gamma(t) = D \int_0^t \frac{\partial C(\delta, t)}{\partial X} dt \quad (5)$$

The use of Laplace transformation leads to:

$$C(X, s) = \frac{C_0}{s} \left[\frac{\lambda \cosh \gamma(\delta - X) + \sinh \gamma(\delta - X)}{\lambda \cosh \gamma\delta + \sinh \gamma\delta} \right] \quad (6)$$

where $\gamma = s^{1/2}/D^{1/2}$ and $\lambda = D\gamma/Ks$.

This equation represents, in transformed state, the complete solution of equation (2) for these particular initial and boundary conditions. It can in principle be used in this form as was shown by Wynen^{4b} in a general study. Inverse transformation may be carried out by a method which has already been described elsewhere^{4a}. If, for a given film thickness observation is made at relatively short times, then:

$$\cosh \gamma(\delta - X) = \sinh \gamma(\delta - X) = 0.5 \exp \gamma(\delta - X) \quad (7)$$

and

$$\cosh \gamma\delta = \sinh \gamma\delta = 0.5 \exp \gamma\delta \quad (8)$$

Inverse transformation then gives:

$$C(X, t) = C_0 \operatorname{erfc} \left(\frac{X}{2D^{1/2}t^{1/2}} \right) \quad (9)$$

Equation (9) indicates that there is a certain time required before the adsorbant reaches the electrode surface since no adsorption parameter are present in the expression. The time constant for this process is approximately given by, $\tau = \delta^2/4D$. It is to be noted that this result is the same as would be obtained if the liquid film were of infinite thickness, thus attributing to the generality of the solution given by equation (6).

If for the same film thickness given above observation times are now longer, then, transforming (6) for $\Gamma(s)$:

$$\Gamma(s) = \frac{KC_0}{s} \left[\frac{\lambda}{\lambda \cosh \gamma\delta + \sinh \gamma\delta} \right] \quad (10)$$

and assuming that:

$$\sinh \gamma \delta = \gamma \delta + \frac{(\gamma \delta)^3}{6} \quad (11)$$

and

$$\cosh \gamma \delta = 1 + \frac{(\gamma \delta)^2}{2} \quad (12)$$

inverse transformation may be carried out giving:

$$\Gamma(t) = KC_0 \left[1 - \frac{6D}{\delta(6K+\delta)} \left(\frac{\delta^2 e^{-\frac{6Dt}{\delta^2}}}{6D} - \frac{\delta(3K+\delta) e^{-\frac{3Dt}{\delta(3K+\delta)}}}{6D} \right) \right] \quad (13)$$

Taking the first term of the series given in (11) and using (12) as is, one obtains:

$$\Gamma(t) = KC_0 \left(1 - \exp - \frac{2DT}{\delta^2 + 2K\delta} \right) \quad (14)$$

A still simpler expression may be obtained when the first term of both of the series given in (11) and (12) are used.

Thus:

$$\Gamma(t) = KC_0 \left(1 - \exp - \frac{DT}{K\delta} \right) \quad (15)$$

Equations (9) and (13) are the complete solutions for this particular diffusion adsorption process. They progressively characterize a pure diffusion then a diffusion - adsorption process. The transition between these two behaviors is particularly evident in equation (13) where it may be seen that the first exponential term contains only diffusion parameters, where as the second contains both diffusion and adsorption parameters. For relatively thinner and thinner films equation (6) is valid for only very short times, becoming effectively nonexistent for the thinnest films. Equation (13) may conveniently be replaced by (14) and then (15) for the thinner films indicating, as might be expected that the electrode surface becomes saturated with the adsorbing species more rapidly as the electrolyte film becomes smaller.

b) Low coverage, finite adsorption rate: This case is of greater interest here since it has been reported⁴⁷ that the rate of hydrocarbon adsorption is relatively slow. To integrate equation (2) the same initial and boundary conditions as those used previously will be assumed to be valid, except for the following:

$$X = \delta, t > 0 \quad C(\delta, t) = \frac{k_d}{K} \frac{d\Gamma(t)}{dt} + \frac{\Gamma(t)}{K}$$

In addition, equation (5) is also employed.

Laplace transformation results in an equation of the same form as that given in (6) where $\gamma = s^{1/2}/D^{1/2}$ and,

$$\lambda = \frac{(k_d + s)D\gamma}{k_d k_s}$$

Inverse transformation using the simplifications given in (7) and (8) results in equation (9), which is to be expected. Using the series expansions given in (11) and (12) the following equation results:

$$\Gamma(t) = KC_0 \left[1 - \frac{mn}{m-n} \left(\frac{e^{-mt}}{m} - \frac{e^{-nt}}{n} \right) \right] \quad (16)$$

where

$$m = \frac{6D^2 + 3D\delta^2 k_d + 6D\delta K k_d}{6D\delta^2 + K k_d \delta^3} - \frac{1}{2} \left[\left(\frac{6D^2 + 3D\delta^2 k_d + 6D\delta K k_d}{6D\delta^2 + K k_d \delta^3} \right)^2 - \frac{24D^2 k_d}{3D\delta^2 + K k_d \delta^3} \right]^{1/2}$$

Finally the series expansion used to obtain equation (15) gives:

$$\Gamma(t) = KC_0 \left[1 - \exp - \frac{Dk_d t}{D + k_d k \delta} \right] \quad (17)$$

It may be seen that essentially the same comments as those given earlier concerning the effect of the time of observation and the film thickness apply here. The main difference occurs of course in the time constant of the diffusion coupled adsorption process.

The analyses given above are of a very general nature and indicate that it may be possible to determine kinetic parameters specific to the adsorption process of any gaseous reactant. The experimental conditions may be chosen so that the simplest of the equations may be valid for most of the observation time, thus

facilitating the final calculations. In addition a theoretical study which will be presented elsewhere for the case in which the liquid film is initially saturated with gas shows that the equation valid for times during which equation (9) holds may be used in the calculation of $\Gamma(t)$ thus increasing the number of simultaneous equations.

EXPERIMENTAL TECHNIQUE

The exploitation of the equations given above necessitates an experimental determination of the amount of reactant adsorbed on the electrode after a given exposure time. This is most easily done by applying a potentiostatic pulse to the system once the electrode is immersed in the liquid. Integration of the resulting current-time curve allows $\Gamma(t)$ to be evaluated. Error due to double layer capacity current is greatly minimized because of the potentiostatic nature of the experiments.

The actual experimental cell will only briefly be described here. A detailed description will be given elsewhere. The electrode under study is placed in a non conducting disc, such as plexiglass or teflon, making up only a small portion of this so that the time between initial and complete immersion of the sample is negligible compared to the disc rotation speed. The level of the electrolyte in the cell may be varied so that many different exposure times may be obtained. Provision is made to vary the film thickness by means of a windshield wiper type arrangement. In addition it is possible to dry the electrode with a suitable hydrophilic material. A platinum counter electrode of large surface area is placed so that the working electrode is in a uniform potential field. Two auxiliary electrodes are placed in the cell such that any gas which enters the electrolyte is immediately oxidized, thus ensuring that the liquid film initially contains no gaseous reactant. A gold reference electrode found to be suitable for this work, is placed approximately 0.1 mm from the sample allowing potentiostatic conditions to be obtained rapidly. A saturated calomel electrode is also placed in the cell for standard comparison purposes.

The electronic circuit is shown in Fig. 1. The potentiostat P is a Tacussel PIT type having an amplifier rise time of about 30 nsec. In the work described below typical in circuit rise times are of the order of 700 nsec. The oscilloscope employed is a Tektronix type 555 having a dual beam and a dual time base. Plug in unit L is used to record the potential-time transient across the working electrode, W, and the reference electrode, S. Plug in unit D is used to record the current-time transient across resistance R. S₁ is a mechanical switch which operates as the electrode totally enters the solution. It serves to close the battery circuit which activates the mercury wetted Clare relay, S₂, thus allowing the pulse to be applied. It also triggers the oscilloscope slightly before the relay closes due to its approximately 2 m sec. reaction time. Proper synchronization of the two time bases allows pulses of the

type shown in Fig. 2 to be obtained. C is the counter electrode.

ETHANE ADSORPTION

To illustrate the method described above a preliminary study was made of the adsorption of ethane on a platinum electrode. Ethane was chosen since it is a relatively simple hydrocarbon and because it shows significant activity at low temperatures. In addition it has been studied by other workers³⁵⁻⁴⁷ thus allowing comparisons to be made.

The experiments were carried out using 5N phosphoric acid prepared from reagent grade acid and triply distilled water. The electrode was highly polished platinum of 0.5 cm² area. Ethane is obtained from "Société Air Liquide" and is of 99.99% purity. All measurements were made at 25^o ± 0.2^oC.

In order to ascertain that the quantity of current measured is actually that due to the adsorbed ethane pulses were applied to the system in an Argon atmosphere. The maximum pulse voltage always attained the same value as that employed for the ethane oxidation although the voltage difference was variable. This correction is rather important since there is a considerable amount of faradaic current even in the so-called double layer region indicating that the platinum electrode is certainly not inert. The difference between the current-time traces in argon and ethane may be seen in Fig. 3.

The (shaded area Fig. 3) charge, Q_E , corresponding to various ethane adsorption times is shown in Fig. 4. It may be seen that the adsorption times are relatively long, however, they follow to a good approximation an exponential curve. This would appear to indicate that the theory given above is obeyed. However, integration of equation (1) taking $C(\delta, t) = \text{const.}$ would also lead to exponential time behavior. In order to decide between pure adsorption control; or coupled diffusion-adsorption control experiments were carried out in which the film thickness was varied. In every case and even for the longest adsorption times Q_E depended upon the film thickness. It thus appears that the adsorption of ethane is partly diffusion controlled even when relatively thin films are present. It is to be noted that this does not indicate that there would be a limiting diffusion controlled current for all overpotentials in steady state fuel cell operation. It does, however, indicate that diffusion contributes to some extent to the total observed polarization and that higher hydrocarbon solubility would greatly increase performance.

It has been shown⁵⁰ that knowledge of the evolution of open circuit potential with adsorption time can provide information concerning adsorption especially if surface conversion exists. The experiments performed here give this data. Analysis of the potential-time curves for different exposure times indicates that the observed voltage difference is a direct measure of the equilibrium potential since the voltage base line varies with adsorption time and, because of the set up of the electric circuit, can only be due to different equilibrium potentials. A typical curve is shown in Fig. 5. It may be seen that there appears to be a slight arrest in the curve after approximately 10 min. exposure time. This function is a measure of

the extent of electrode surface coverage and indicates that there are probably two surface species one corresponding to low coverages and the other to high coverages. They are very probably related to the two peaks observed in the voltage sweep experiments used in similar studies and reported by Gilman⁴⁷.

In order to examine the behavior of these surface species and to obtain some indication of the processes which follow adsorption it is then necessary to examine the current-time curve obtained after application of the potential step function.

The first observation is that it appears fairly evident that the charge transfer and desorption processes take place much more rapidly than the adsorption and conversion processes. These latter then comprise the global rate limiting steps in the oxidation of ethane at these temperatures and indicate the importance of catalysis in this process.

Exploitation of the current-time curves may be carried out in the following way. If the current is due to the concentration of surface species then this should be an exponential function of time, thus:

$$i = A \exp - \beta t \quad (18)$$

where A contains electrochemical and proportionality constants and β represents the time constant for the charge transfer and desorption process. Semi logarithmic plots of the current time curves obtained in the presence of ethane show good linearity after the first 100 μ sec. No such linearity occurs for the curves obtained in an Argon atmosphere. These results indicate that diffusion control is nonexistent.

Examination of equation (18) shows that the intercept of the semi logarithmic plot should result in consistent values for the same surface species (taking into account surface concentration and overpotential).

Two sets of values were obtained corresponding to low and high coverages (See Fig. 5) indicating the presence of two surface species.

The study presented above is a preliminary one serving to give some indication of the potentialities of the method described in this work. It may be seen that a large variety of data may be obtained and that it is indeed possible to separate the two global processes occurring in the electrochemical oxidation of hydrocarbons. The results obtained are less ambiguous and it is hoped that future work will elucidate the phenomenon of catalysis in electrochemical processes.

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LIST OF SYMBOLS

- $\Gamma(t)$ = Surface concentration of adsorbing species at time t .
- Γ_m = Maximum surface concentration of adsorbing species.
- k_a = Adsorption rate constant.
- k_d = Desorption rate constant.
- $C(\delta, t)$ = Concentration of adsorbing species at electrolyte-solid interface.
- $C(X, t)$ = Concentration of adsorbing species at a point X within the liquid film.
- D = Diffusion coefficient of adsorbant.
- δ = Liquid film thickness and coordinate of electrolyte solid interface.
- X = Point within liquid film.
- K = $k_a \Gamma_m / k_d$.
- s = Laplace transform parameter.
- $C(X, s)$ = Concentration of adsorbing species after Laplace transformation at a point X within the liquid film.
- erfc = Error function.
- erfc = $1 - \text{erf}$.
- $\Gamma(s)$ = Surface concentration of adsorbant after Laplace transformation.
- C_0 = Initial gas concentration.
- Q_E = Charge corresponding to ethane surface concentration.

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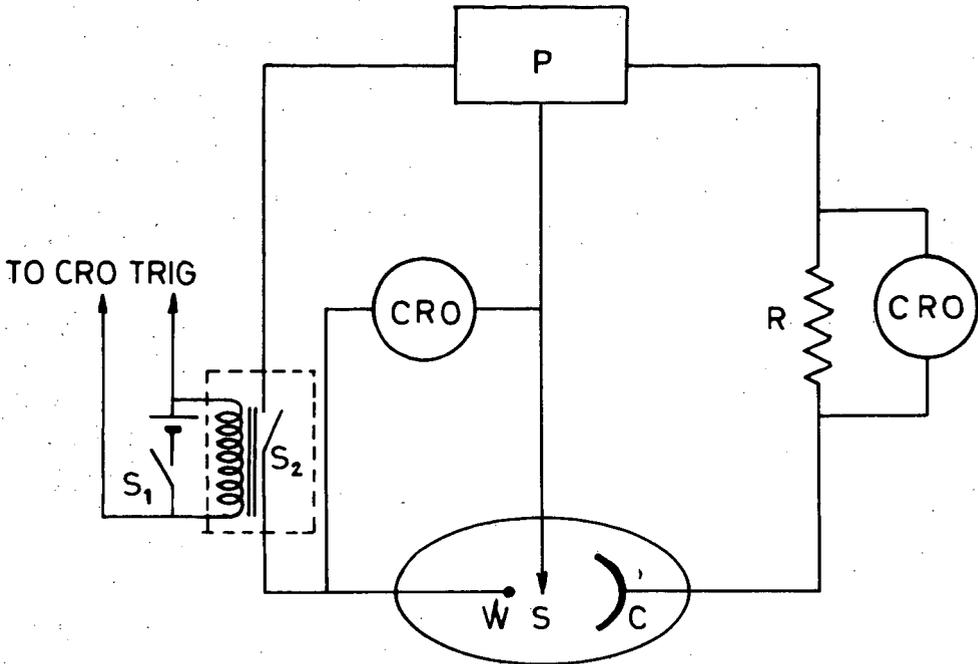


Fig. 1 - Electronic circuit for application of potential-time step functions.

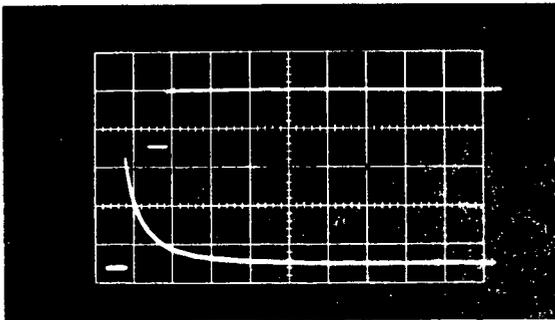


Fig. 2 - Upper curve : potential-time trace.
Lower curve : current time trace. Horizontal axis 1 m sec/cm, vertical axis 50 mV/cm.

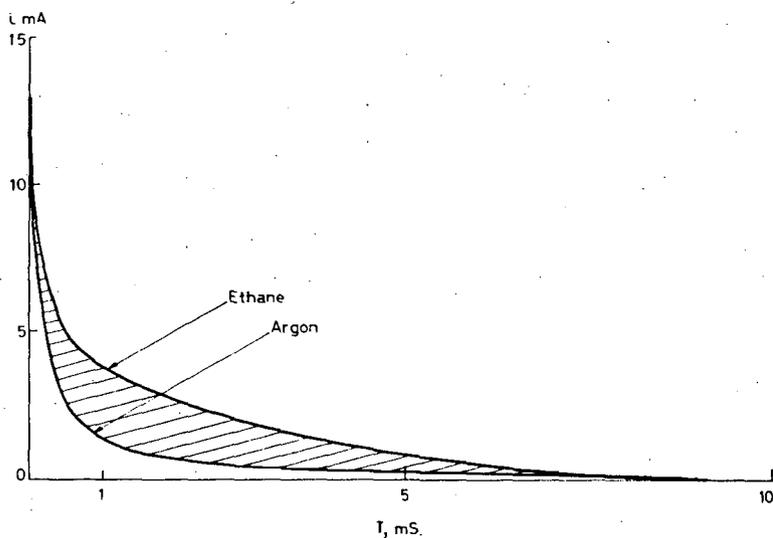


Fig. 3 - Current-time traces for Argon and ethane. Shaded area represents Q_E .

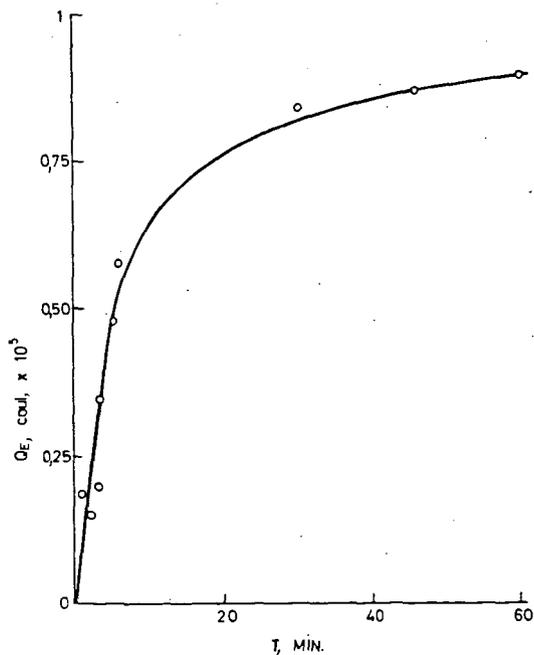


Fig. 4 - Variation of ethane surface coverage with time in adsorption phase.

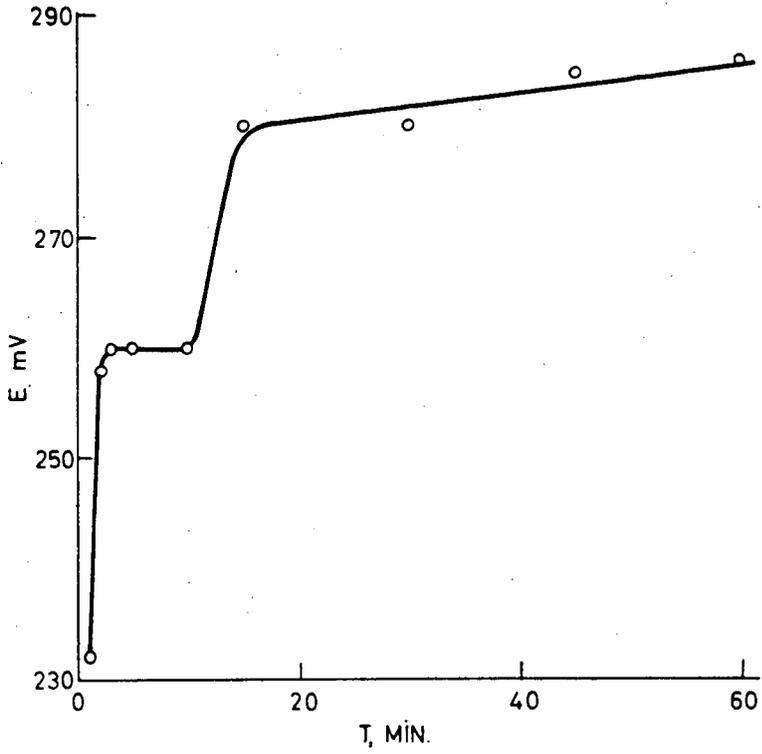


Fig. 5 - Variation of equilibrium potential with coverage.