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CHRONOCOULOMETRY OF REACTIONS GOVERNED BY THE TEMKIN ADSORPTION ISOTHERM^{*})

By

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Abstract

The current transient during the controlled potential electrolysis in which a preceding adsorption step is in quasi equilibrium and the rate of whole reaction is controlled by the succeeding surface step has been analysed. Both the Temkin and Langmuir isotherms were taken into consideration for describing the adsorption equilibrium. The equations derived were compared with the experimental results of electrocatalytic hydrogenation of maleic acid on a platinum electrode in an aqueous sulfuric acid solution.

Introduction

The adsorption phenomena appearing in electrode systems are often described by the Temkin adsorption isotherm, which is best known in the approximate form¹⁾

$$\theta = k_a \ln c \quad (1)$$

This is quite reasonable because, in the adsorption particularly at the metal electrode surface, lateral interaction among adsorbed species is significant and the simple assumption of constant heat of adsorption, as is used in the Langmuir isotherm, is no more applicable. Although many examples are known, no report has been published for analysing the transient behavior of current during the electrolysis in which the preceding adsorption step is in equilibrium and the rate is controlled by the follow-up reactions. One of the best example of this type of reaction is the electrocatalytic hydrogenation of phenol at the platinum electrode in aqueous acid solutions.²⁾ The reaction is expressed by the following sequential steps

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Experimentally, adsorption step (3) was found to obey the empirical equation (1) over the concentration range $10^{-6} \sim 10^{-3}$ mole \cdot ℓ^{-1} of phenol. In addition, the overall rate of the reaction was also found to be a linear function of logarithmic concentration of phenol.

This may suggest that either the reaction is controlled by the rate of phenol adsorption or the adsorption step is in equilibrium and the succeeding hydrogenation is rate determining. In order to distinguish the correct mechanism, it is necessary to analyse the behavior of current transient during the course of controlled potential electrolysis, to which the present paper mainly concerns.

A preliminary report with use of several phenols have been reported already.²⁾ In this paper, we should like to describe the procedure of analysis more fully. The results obtained will be compared with the experimental findings obtained for the electrocatalytic hydrogenation of maleic acid.

1. Experiments

1.1 General description

Adsorption behavior of both acetone and maleic acid has been studied in this paper. A similar work on the catalytic hydrogenation of phenol has already been reported previously.²⁾ Both acetone and maleic acid were used as purchased without further purifications. Base solution was aqueous sulfuric acid of 1.0 N. A thorough caution was necessary to lower the concentration level of dissolved oxygen. All the measurements other than the current transient during the catalytic hydrogenation reaction were made with a platinum wire of 1 mm in diameter and 12 mm in length (0.4 cm²). The reaction product from maleic acid is solely succinic acid. This was confirmed by melting point measurement and IR spectroscopy for isolated product. Acetone was found to be inactive to catalytic hydrogenation.

1.2 Measurements of transient current

Measurements of transient current, which we define as the decaying current due to the consumption of starting material during the course of electrolysis, was not an easy matter. This is because the current flowing was generally so small to be able to complete the reaction within a finite time. Accordingly, it was necessary to use a cell system having a large

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ratio of the electrode surface area to the volume of the solution to be electrolysed. For this purpose, a long thin platinum wire being coiled helically was used in order to gain a large surface area (*ca.* 3 cm²). The solution volume to be electrolysed was in the order of several ml. In order to ensure the homogeneity of the solution composition the electrode was rotated at a rate of 1000 rpm.

The removal of oxygen from the cell system was particularly important in studying the current transient during the controlled potential electrolysis. In this case, helium gas was bubbled into the cell system and the whole assembly was put into a grove box filled with streaming nitrogen.

Measurements have been done in two different ways. First, the working electrode immersed in the solution containing organic compound was first equilibrated at +0.25 volt sce where no hydrogenation takes place and then stepped to a desired potential, -0.25 volt mainly, and the current was recorded. This method, which was applied to phenol in the previous paper,²⁾ was however erroneous because the difficulty in the correction of background current due to trace amount of dissolved oxygen. When this method was applied to maleic acid, the electricity passed often exceeded the theoretical value within one hour or less, indicating the contribution of background current enormous. Because of this reason, the measurements in this paper were made by keeping the potential at -0.25 volt sce, where hydrogenation could occur, from the first. After a prolonged electrolysis for several hours, the background current became minimum and then maleic acid was added to the solution and the measurement started. This method is advantageous in the sense of making the background correction unnecessary. On the other hand, however, because of the slow attainment of the "steady" state of reaction, the initial stage of the reaction was not suitable for analysis.

2. Results and Discussion

2.1 Analysis of transient current

We consider a surface reaction occurring between two adsorbed reactants, A and B. Suppose that the adsorption steps of both reactants are in quasi equilibrium and the rate determining step is located in the succeeding steps.

If the rate is first order with respect to the surface concentration of each reactant, it can be formalized as

$$\text{rate} = k' {}_s\Gamma_A \theta_A \cdot {}_s\Gamma_B \theta_B \quad (5)$$

where ${}_s\Gamma_A$ is the surface excess at saturation and θ the fractional coverage. If charge transfer step is involved in the sequence of the reaction, the rate

can be expressed by electric current

$$i = nFk'_s \Gamma_A \theta_A s \Gamma_B \theta_B \quad (6)$$

Eq. (6) can safely be simplified as

$$i = nF(k'/m) (s \Gamma_A)^2 \theta_B (1 - \theta_B) \quad (7)$$

if we assume the relationships generally accepted

$$s \Gamma_A = m s \Gamma_B$$

$$\theta_A = (1 - \theta_B)$$

where m is a constant showing the relative number of the surface sites covered by the molecules of A and B.

Note that the variation of $(1 - \theta_B)$ due to the concentration change during the course of electrolysis is small enough and can be assumed constant except the final stage of electrolysis. For example, at the 50% conversion of maleic acid to succinic acid, the change in $(1 - \theta_B)$ is less than 5% (see Fig. 1).

Eq. (7) is then simplified to

$$i \doteq nF(k/m) (s \Gamma_A)^2 \theta_B \quad (8)$$

A. Temkin isotherm.

We first consider the case where the surface coverage is described by the Temkin isotherm. Introducing eq. (1) into (8), we obtain a differential equation

$$i = nF \frac{dM}{dt} = nFV \frac{dC_B}{dt} = \text{const} \cdot \log C_B \quad (9)$$

where V is the volume of the solution to be electrolysed.

The integration of eq. (9) leads to an equation of the form

$$F(C) - F(C_0) = Bt \quad (10)$$

$$\text{where } F(C) = \log |\log C| + \sum \frac{(\log C)^r}{r \cdot r!} \quad (11)$$

$$B = k k_a (s \Gamma_A)^2 (1/mV) \quad (12)$$

and C_0 means the initial concentration of reactant B, maleic acid in the present case.

It is worth noting that although the function in the second term of eq. (11) is a converging function, the manner of the conversion depends on the magnitude of C . When the value of C expressed in mole per litre is used

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directly, the conversion is very slow and the summation should be done over 17 to 18 terms. When, C is expressed in the unit of mM scale, the function converges quickly and the summation over the first four terms is sufficient for the practical purposes.

The concentration change during the course of electrolysis can easily be evaluated by recording the quantity of electricity passed until a given time to examine the reality of eq. (10).

B. Langmuir isotherm.

When the preceding adsorption step is described by the Langmuir isotherm instead of Temkin, eq. (8) should be rewritten in the form

$$i = \frac{n}{m} Fk(s\Gamma_A)^2 \frac{bC}{1+bC} \quad (13)$$

in place of eq. (9). This equation leads to another relationship

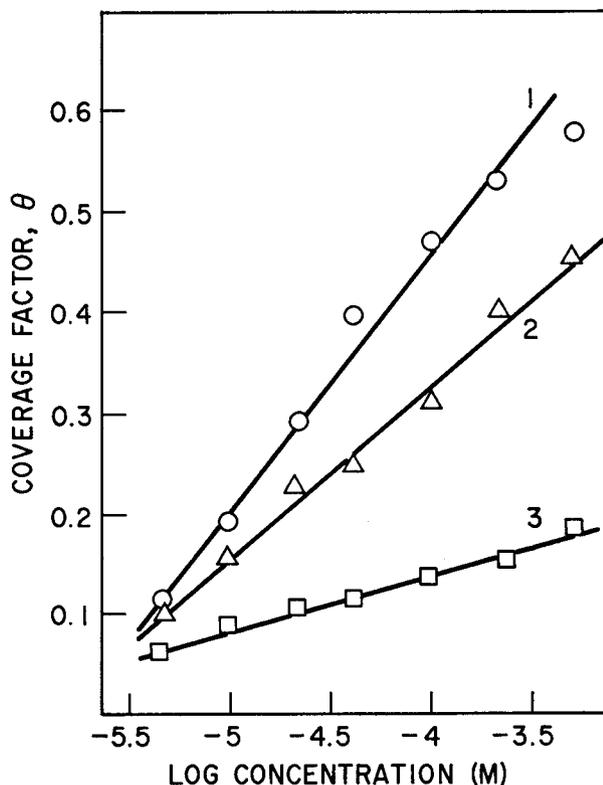


Fig. 1. Surface coverage of phenol (1), maleic acid (2) and acetone (3) against the logarithmic concentration.

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$$\frac{2.3}{b} \log C + C = At + \text{const.} \quad (14)$$

where $A = \frac{k}{mV_s} \Gamma_A$

2.2 Comparison with experiments

We have already reported that the electrocatalytic hydrogenation of phenol takes place on platinum electrodes to accord with the assumptions used in deriving equations following to eq. (9). A similar mechanism was also proposed by Kita³⁾ and Vasiliev⁴⁾ for several olefinic compounds. Kita and his coworkers³⁾ elucidated the detailed mechanism of the reaction using techniques of isotope tracer experiments besides various electrochemical methods. Vasiliev and his coworkers⁴⁾ studied extensively the adsorption behavior of maleic acid utilizing potentiodynamic methods. We thus at-

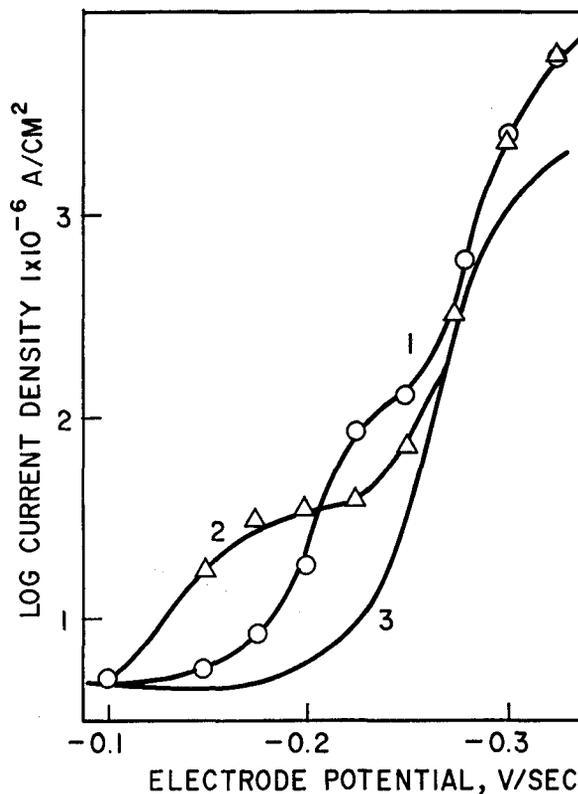


Fig. 2. Steady state polarization curves of phenol (1), maleic acid (2) and acetone (3). The curve for acetone merges into the background.

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tempted to extend our study to maleic acid which is one of the best example of the electrocatalytic hydrogenation.

Fig. 1 shows the change in surface coverage against the logarithmic concentration of both maleic acid and acetone. Data for phenol are also shown for comparison. The surface coverage was determined by measuring the depression of the adsorbed hydrogen wave which appears in cyclic voltammetry. All the compounds are seen to obey the empirical formula, $\theta = k_a \log C$. The proportionality constants, k_a , are 0.16, 0.12 and 0.05 for phenol, maleic acid and acetone, respectively.

When hydrogenation takes place steadily, a finite value of current corresponding to the rate of hydrogenation should flow at a fixed electrode potential. This was confirmed by measuring the steady state polarization curves (Fig. 2). Fig. 3 shows the effect of concentration of organic reactants

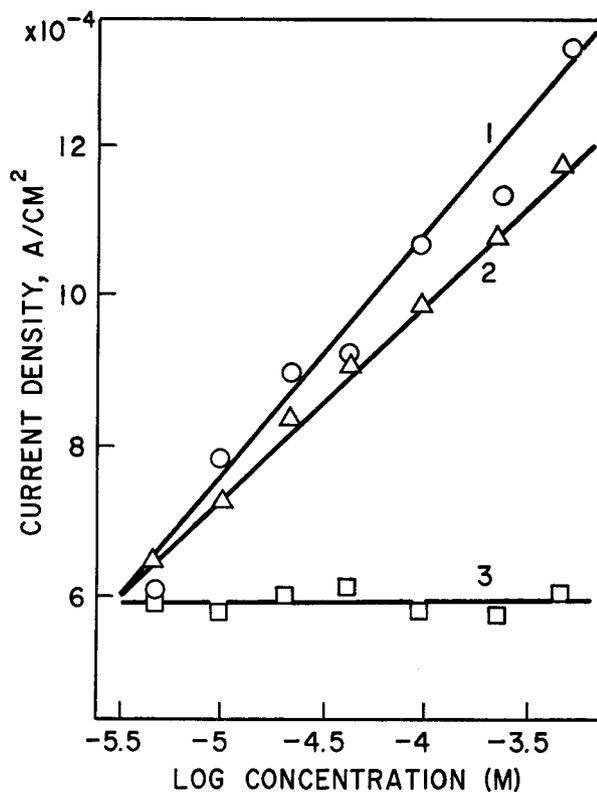


Fig. 3. Relationship between the logarithmic concentration and initial current. The initial current was determined at 0.5 seconds after stepping the electrode potential to -0.25 volt from the base potential, $+0.25$ volt sce.

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on the current, which was determined at 0.5 seconds after stepping the electrode potential to -0.25 volt from the base potential $+0.25$ volt sce. It is clearly seen that the current increases with the logarithmic concentration of phenol and maleic acid. In contrast to these compounds, acetone is not hydrogenated at an appreciable rate.

These observations provide bases for assuming the reaction mechanism to be expressed by eqs. (2) through (4). Obviously, eq. (10), which was derived for the Temkin isotherm, should be applied for the present case. Fig. 4 indicates the transient current analysis on the base of eq. (10). Two curves in the figure correspond to two different solution volumes, 5 and 7.5 ml, respectively. It is clearly seen that a linear relationship exists between the chronocoulometric function $F(C)$ and the time elapsed. The linear portion of the curves covers the conversion of maleic acid to succinic acid from 34% to 82% for curve 1 and 18% to 48% for the curve 2, respectively. The deviation appearing in the initial part of the curve may be correlated to the slow attainment of the "steady" state of the reaction. In fact, according to the data of Vasiliev⁴⁾ the rate of maleic acid adsorption is rather slow and necessitates several to some ten minutes of time depending on the concentration for attaining the saturation coverage.

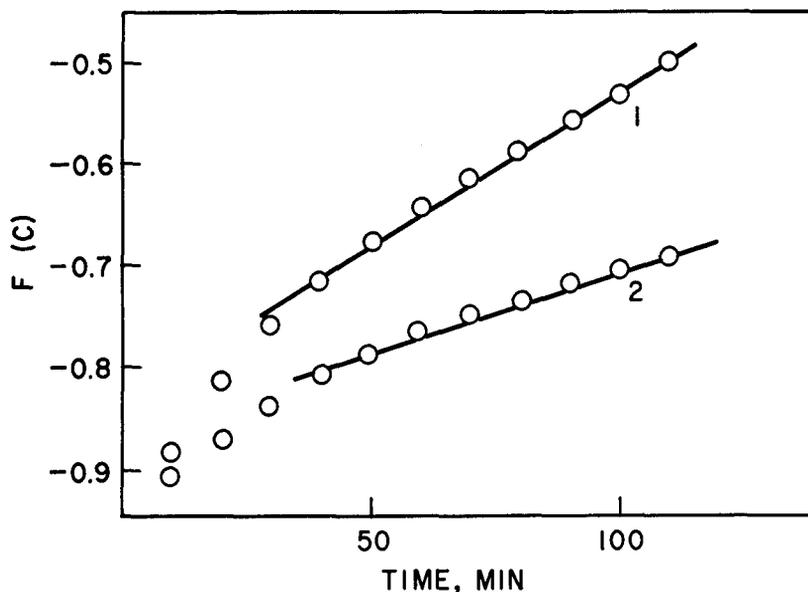


Fig. 4. Transient current analysis based on eq. (10). The solution volumes were 5 ml (curve 1) and 7.5 ml (curve 2).

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According to the prediction of eq. (12), the slope of the straight line should be proportional to the inverse solution volume. The values were 4.97 and 2.58×10^{-5} for $V=5$ and 7.5 ml , respectively. The ratio 1.93 can be compared with the expected value 1.50.

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