

Electrochemical behavior of steel in citric acid solutions devoid of and containing some organic compounds

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Abstract - The electrochemical behavior of steel electrode immersed in citric acid solutions has been followed and discussed using potential measurements under open-circuit conditions. The effect of increasing concentrations, temperature of solution and addition of some organic compounds are also investigated. It is found that, the steel electrode can be passivated in naturally aerated solutions of citric acid and the rate of oxide film growth follows a direct logarithm law, as evident from the linear relationship between the open-circuit potential and the logarithm of immersion time. The rate of oxide film growth decreases by raising the solution temperature. The addition of some organic compounds as urea, phenylhydrazine and 1,2-phenylenediamine decrease the destruction of the passive film and thus increase the inhibition process.

Key words: steel, citric acid, corrosion, Oxide film thickening, inhibition.

I. INTRODUCTION

Steel is the most widely used as constructional material in many industries due to its excellent mechanical and low cost. It is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment. Acid solutions are widely used in industry, e.g., chemical cleaning, descaling, pickling, and oil-well acidizing. Organic acid belong to the group of the most important chemicals used in several industries such as textile, leather, chemical and food, pulp and paper, drugs and pharmaceutical, plastics and fibers. These acids are used as reagents for the manufacture of various chemicals ranging from drugs and pharmaceutical to plastics and fibers [1-5].

The study of the corrosion behavior of steel in different environments is very important to achieve the most suitable passivators and inhibitors to increase the live period of steel equipment. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [6]. The progress of this field has been phenomenal in recent years and is borne out by the output of literature [7]. Because of the general aggressivity of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials.

Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. The influence of organic compounds containing nitrogen, such as amines and heterocyclic compounds, on the corrosion of steel in acidic solutions has been investigated by several works [6 - 9]. Compounds with π -electrons and functional groups containing heteroatoms which can donate lone pair electrons are found to be particularly used as inhibitors for corrosion of metals. The existing data show that most organic inhibitors act by adsorption on the metal surface. The most important prerequisites for compounds to be efficient inhibitors are: substances should form a compact barrier film, they should chemisorb on the metal surface, have a high adsorption energy on the metal surface, and the barrier layer thus formed should increase the inner layer thickness [10].

Citric acid is the natural organic acid produced in oranges and other citric fruits. It is generally regarded as safe for use in food products. It is a common material used in many food and beverages sold on the market. This means that citric acid is compatible with the environment and can usually be blended into sanitary sewage systems with environmental agency approval. Morris and Bryan [11] attributed the corrosion of steel in citric acid solutions to the diffusion process of hydrogen through

the steel. They found that accelerators and inhibitors affect the rate of deposition of hydrogen rather than the formation of bubbles. Urea used as corrosion inhibition of steel in concrete immersed in simulated concrete pore (SCP) solution [12]. Potentiodynamic polarization measurements showed a shifting in Corrosion potential (E_{cor}) toward positive direction and a decreased in corrosion current density (I_{cor}), corrosion rate (CR) of steel samples immersed in SCP solutions containing urea inhibitor compared with control sample which is an indication of formation of protective passive film on steel surface and also indicate that urea fertilizer maintained stable passivity even in presence of aggressive chloride ions. Phenyl hydrazine derivatives used as corrosion inhibitors of mild steel in solutions of phosphoric acid. Potentiodynamic polarization and ac impedance (eis) measurements revealed that these compounds are a good mixed-type inhibitors [13]. The inhibition effect of phenylenediamine towards the corrosion of steel in different media was investigated [14-15]. The polarization measurements indicated that the inhibitors are of mixed type and inhibit corrosion by adsorption on the surface of steel due to the presence of more than one active center in the inhibitor molecule.

The aim of the present work is to shed more light on the electrochemical behavior of the steel electrode in citric acid solutions. The effect of the some factors, e.g., solution concentration (5×10^{-4} – 0.5 M), and temperature changes (25-55°C) on the initial rate of oxide film growth are examined. The addition of increasing concentrations of urea, phenylhydrazine and 1,2-phenylenediamine was also investigated.

II. EXPERIMENTAL

The steel electrodes were made from steel samples produced by the Egyptian Mill steel Company (Helwan- Cairo) and having the following chemical composition:

C	Si	Mn	P	S	Fe
0.32	0.24	0.89	0.024	0.019	98.507

mass %

The steel electrodes were fixed to borosilicate glass tubes with epoxy resin so that the total exposed surface area was 1.33 cm². Electrical contacts were achieved through thick copper wires soldered to the ends of the steel rods not exposed to the solution. Before being used, the steel electrodes were abraded into uniform surfaces by a grinding machine (model Jean Wirtz TG 200, Germany) using successive 0-, 00- and 000-grades emery papers, rinsed with acetone and finally washed with triply distilled water before immersing in the test solution.

The potential of the steel electrode was measured in naturally aerated 5×10^{-4} M and 0.5 M citric acid solutions to the nearest mV on a Wenking potentiometer Type PPT 70 relative to the saturated calomel electrode (SCE). The steady- state potentials were considered as those values which did not change by more than 1 mV in 10 minutes. Furthermore, the effect of some organic inhibitors including urea, phenyl hydrazine and 1,2-phenylenediamine on the behavior of steel in citric acid was also investigated.

Electrolytic solutions were prepared from analytical grade reagents and triply-distilled water. Solutions of citric acid with different concentrations were prepared by dissolving the corresponding quantitative weights of solid citric acid in the appropriate volumes of distilled water. The addition of increasing concentrations of urea, phenyl hydrazine and 1,2-phenylenediamine were prepared with a tested concentration of citric acid. The cell has a double wall jacket through which water, at the adjusted temperature, was circulated. Measurements were carried out at a constant temperature $25 \pm 0.1^\circ\text{C}$, except those related to the effect of temperature. The cell temperature was controlled using an ultra-thermostat type polyscience (USA). The main joint of the cell contains openings for both the steel electrode and the reference electrode (SCE). No trails were made to measure the oxygen content of the solution.

III. RESULTS AND DISCUSSION

3.1. Effect of citric acid concentration

The behavior of steel in citric acid solutions of different concentrations is followed by measuring the open-circuit potential of steel electrode as function of time until steady-state potentials are reached. The curves of Fig.1. A, represent such behavior in citric acid solutions of concentrations varying between $5 \times 10^{-4} \text{M}$ and 0.5M . Inspection of the curves of this figure reveals that, the steady-state potentials, E_{st} , in all solutions concentrations are invariably approached from more negative values following the immersion of the electrode in solution and attain constancy after a period of ~ 2 h. Also, in all solutions of different concentrations of citric acid, E_{st} tends towards less negative values as the concentration of citric acid increased. The steady state potential, E_{st} , varies with the logarithm of the molar concentration of citric acid, Fig.1. B, according to a straight line relation [16-18]:

$$E_{st} = a_1 + b_1 \log C_{\text{citric}} \quad (1)$$

where a_1 and b_1 are constants which depend on the solution concentration and the metal under test. The value of the constant $a_1 = -590 \text{ mV (SCE)}$ represents the steady state potential of steel electrode, E_{st} , in 1 M citric acid solution and b_1 amounts to 48 mV/min . The literature showed similar behavior for other metals, e.g., Zn [18], Ni [16], Zn alloy [19], Fe [20] and steel [17]. At relatively high concentrations of citric acid the potential moves in the noble direction with increasing the acid concentration according to equation (1) and the corrosion process is dependent on the breakdown of the pre-immersion oxide film. Thus, the destruction of the film leads to an increase in the anodic areas at the expense of the cathodic areas. At higher concentrations of citric acid solutions, the potential shifts toward less negative direction indicating that the corrosion process becomes controlled by the cathodic reaction [21]. The open-circuit potential of the electrode reaches steady values after a time ranging from ~ 100 to 120 min. Under these conditions, it is concluded that the cathodic reactions predominate over the anodic ones [16, 20].

The way by which the oxide develops on the steel is best understood by presenting the results of potential–time on semi-logarithmic plots. As can be seen from the curves of Fig. 2 A, the open circuit potential of the steel electrode was found to vary with the logarithm of the immersion time, t , in all citric acid solution concentrations, according to [16-18, 20, 22-24]:

$$E = a_2 + b_2 \log t \quad (2)$$

where a_2 and b_2 are constants. The value of the constant b_2 which is the rate of potential rise (expressed as $\partial E / \partial \log t$) has actually increased slightly with increasing the citric acid concentration. Such behavior indicates that the oxide film thickening on the steel electrode, under the prevailing experimental conditions, follows a direct logarithmic law. The more interesting feature of the curves of Fig 2 A is the fact that the E - $\log t$ curves are composed of two distinguished segments before reaching the final steady-state potentials. The first segment of these curves represents the first 20 minutes of immersion of the metal in the test solution; the rate of potential build-up is low. The slopes of these parts of the curves are dependent on the concentration. After definite, fairly-reproducible times, the rate of potential change (second segment) increases appreciably. The slope of both segments increases with increasing the concentration indicating increased rate of oxide film formation. The break in the E - $\log t$ relation may be related to the duplex nature of the formed oxide film on the steel surface [18]. Similar behavior is recorded before with zinc [18], titanium [25] and iron-chromium-nickel alloy [26].

However, it has been suggested before [18] that the driving force of the surface oxide film formation on metal is the free energy change of the reaction between metal and the test solution. This reaction is assumed to proceed by migration of metal cation and/or oxygen ion vacancies from metal towards the electrolyte or possibly by migration of negative oxygen ion in opposite direction [18, 27]. The

field in oxide film is assumed to decrease as the oxide thickness on the metal increases until a steady film thickness is reached, where a steady-state potentials is attained. The relation governing the influence of electric field, H , and ion transport is expected to follow the familiar Gunthereschulzeand Betz relationship [28]:

$$i_a = k_a \exp (BH) \quad (3)$$

where i_a is the imposed anodic current density, k_a and B are constants, and H is the effective field strength. The idea was presented that under open circuit conditions, i_a can originate from the specific adsorption of anions on the oxide covered- metal [26]. This creates image charges of the same magnitude but of opposite sign at the oxide/metal interface, sufficient to promote ion transfer through the oxide to the film/solution interface.

It was further suggested that H in equation (3) could be replaced is by the quantity E/δ , where E is the measured potential relative to the suitable reference half cell, and δ is the thickness of the oxide film. The change of electrode potential to more positive values would necessitate a corresponding equivalent increase in the thickness of the oxide film, so as to keep the field strength E/δ , constant. Following this reasoning an equation was derived which describes the variation of the open-circuit potential of metal carrying very thin oxide film, E , with time, t [16] viz,

$$E = \text{const.} + 2.303\delta/B \log t \quad (4)$$

where δ represents the rate of oxide film thickening per unit decade of time, and B is a constant which is identified as [29]:

$$B = (nF/RT)\alpha\delta' \quad (5)$$

where α is the transfer coefficient similar to that encountered in normal electrochemical reactions [29], ($0 < \alpha < 1$) and δ' is the width of the energy barrier surmounted by the ion during transfer. From the values of the slopes of the straight lines of Fig.2 A, relating the variation of E with $\log t$, one readily calculate the values of the rate of oxide thickening, δ , in citric acid solutions of different concentrations. By analogy with the case of iron-chrome [26] and aluminium [30] we assume that trivalent cations diffuse through the film to oxide film interface. The constant n in equation (5) is set equal to 3, and B acquires the value 58.9 nmV^{-1} . In Fig.2 B, the values of the rate of oxide thickening, δ , (nm per unit decade of time) are plotted as function of the logarithm of citric acid concentration. A straight line is obtained having a slope of $0.47 \text{ nm/ unit decade of time}$.

Inspection of the curves of Figs. 2 A and B reveals that the initial rate of oxide film thickening of the steel electrode, under examination, in naturally aerated solutions of citric increases with increasing the concentration of solution until reaching the steady state value. From the slopes of the straight line relationship of Fig. 2 A, a tenfold increase in the concentration of citric acid causes an increase in the initial rate of oxide film thickening by only 0.47 of oxide film thickening.

3.2 Effect of temperature

The curves of Fig.3. A, represent the variation of the open-circuit potential of the steel electrode, E , with time in naturally aerated 0.5 M citric acid at temperatures varying between 25 and 55°C. Inspection of the curves of this figure reveals that raising the solution temperature is accompanied by a marked effect on the value of the steady state potential, E_{st} . The latter varies with temperature in according with the straight line of Fig.3. B, It is quite clear that raising the temperature decreases the initial rate of oxide film growth or enhances the corrosion of the steel and the extent of corrosion promotion increases with raising the temperature, as reflected by the shifting of the final steady potential in the negative direction. This could be attributed to the decrease of solution viscosity and the consequent increase in the mobility of ions with raising the solution temperature[31].The straight

lines present in Fig. 4 A relate the variation of the open-circuit potential of the steel-electrode with the logarithm of the immersion time, t , in aerated 0.5 M citric acid solutions, at temperatures ranging from 25 to 55 °C. The slopes of these straight lines decrease with raising the temperature. The calculated values of the initial rate of oxide film thickening on the steel electrode, at varying temperatures, are plotted as function of $1/T$ (K^{-1}) in Fig.4 B. From the Arrhenius plots of this figure; the free activation energy of oxide film thickening on steel surface is computed to be 17.8 kJ/mole. This low value of activation energy (<40 kJ/mole) indicates that the process of oxide film thickening on the steel electrode is under diffusion control [32, 33, 34].

3.3 Effect of addition of some organic inhibitors

The effect of addition of increasing concentrations of urea, phenylhydrazine and 1,2-phenylenediamine on the behavior of steel in 5×10^{-4} M citric acid solution was examined. Fig 5 A, represent the variation of the open-circuit potential of the steel electrode, E , with time in naturally aerated 5×10^{-4} M citric acid solutions devoid of and containing increasing concentrations of 1,2-phenylenediamine, as an example of the inhibitors used at 25 °C. Inspection of the curves in Fig 5 B reveals that, in presence of these compounds, the steady-state potentials, $E_{st.}$, are approached from negative values and shift to the more noble direction as the higher the concentrations of these inhibitors. The inhibition action of these inhibitors depends on the amine groups (NH_2), the molecular structure effect, rigidity of π -delocalized system and inhibitor concentration [35-36]. Junter suggested that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is suppose also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of steel, leading to the formation of a corrosion protecting film [37]. It is apparent that the adsorption of P-phenylenediamine (PPD) on the steel surface could occur directly on the basis of donor acceptor between the lone pairs of the heteroatoms, the extensively delocalized electrons over the C6 ring of benzene, the PPD molecule and the vacant d-orbitals of iron surface atoms [38]. The functional group responsible for PPD adsorption on metal surface is the lone pair of the nitrogen atom: iron ions on metal surface which act as a Lewis acid because they accept electrons from a donor group [39]. Phenylhydrazine, on the other hand, is assumed to inhibit the corrosion by the formation of phenylhydrazine-complex which is precipitated on the metal surface. However, its lower inhibition efficiency could be attributed to its lower tendency to form its corresponding salt or to the presence of the benzene ring which lying parallel to the electrode surface affecting thus the p electrons interaction with the metal surface[40]. Urea has ability to be a good corrosion inhibitor for the corrosion of steel and the inhibitive power of urea may be due to the presence of the nitrogen and the oxygen atoms in its structure which give it the ability to enhance the inner protective layer of γFe_3O_4 and/or forming a protective outer layer of urea – Fe^{+2} complex [41, 42].

The curves in Fig. 6 A, represent the variation of the open-circuit potential, E , of the steel electrode with the logarithm of the immersion time, t , in naturally aerated 5×10^{-4} M citric acid solution containing increasing concentrations of 1,2- phenylenediamine, Similar curves are also obtained in presence of phenyl hydrazine and urea. Inspection of the curves present in Fig. 6 A and the like reveals that, in all solution concentrations studied, E varies with $\log t$ until reaching the steady-state potentials according to the relation:

$$E = a_3 + b_3 \log t \quad (6)$$

where a_3 and b_3 are constants. Following the attainment of the steady potentials, the open-circuit potentials drop into the negative direction to reach new steady-state values which become less active the higher the concentration of the present inhibitors. With increasing the concentration of the

additives, the potentials move into the positive direction to reach steady-state values which are also more noble the higher the additives concentration. The slope b_3 of the straight line portion of the E - $\log t$ curves is slightly increased with increasing the inhibitor concentration indicating oxide film growth rather than film destruction. From the slopes of the E - $\log t$ curves in Fig. 6 A and the like, the rate of oxide film thickening is calculated. In Fig. 6 B, the variation of the rate of oxide film thickening with the logarithm of the molar concentration of the added inhibitors is depicted. As can be seen, the rate of the oxide film thickening changes linearly with the logarithm of the molar concentration of the inhibitors, C_{inh} , according to:

$$\text{Rate of oxide film thickening} = k + n \log C_{inh} \quad (7)$$

where k and n are constants given in Table 1. The constant k represents the rate of oxide film thickening (nm/unit decade of time) in presence of 1 M inhibitors. The slope n increases only slightly with increasing the concentration of inhibitors. From the values of the constants k and n of Equation (7), Table 1, the efficiency of the studied compounds, 1,2- phenylenediamine, phenylhydrazine and urea, as corrosion inhibitors of steel decreases in the order: (strong) 1,2-phenylenediamine > phenyl hydrazine > urea (weak).

The curves of Fig. 7 A represent the variation of the open-circuit potential of the steel electrode, E , with time in naturally aerated 5×10^{-4} M citric acid and 1M 1,2-phenylenediamine at temperatures varying between 25 and 55°C (as an example of the inhibitors used). Inspection of the curves of this figure reveals that raising the solution temperature is accompanied by a marked effect on the value of the steady state potential, E_{st} . The latter varies with temperature in according with the straight line of Fig. 7 B. It is quite clear that raising the temperature decreases the adsorption of organic compounds on the surface of steel electrode which accompanied by shifting of potentials toward more negative values and thus the extent of destruction of the passive film increases with raising the temperature. This could be attributed to the decrease of solution viscosity and the consequent increase in the mobility of ions with raising the solution temperature[31]. The straight lines present in Fig. 8 A relate the variation of the open-circuit potential of the steel-electrode with the logarithm of the immersion time, t , in naturally aerated 5×10^{-4} M citric acid solutions containing a 1M 1,2-phenylenediamine (as an example of the inhibitors used), at temperatures ranging from 25 to 55 °C. The slopes of these straight lines decrease with raising the temperature. The calculated values of the initial rate of oxide film thickening on the steel electrode, at varying temperatures, are plotted as function of $1/T$ (°K) in Fig. 8 B. From the Arrhenius plots of this figure; the free activation energies, ΔE_a , of oxide film thickening on steel surface are computed to be 16.33, 28.37 and 30.77 kJ/mole for urea, phenyl hydrazine and 1,2-phenylenediamine, respectively. The higher the value of ΔE_a , indicating the greater tendency of such compounds to inhibit the destruction of the passive film formed on steel electrode and thus the inhibition action of these organic compounds decreased in the order: (the highest) 1,2-phenylenediamine > phenylhydrazine > urea (the lowest).

IV. CONCLUSIONS

From the measurements of the open-circuit potential of the steel electrode in naturally aerated citric acid solutions in absence and presence of some organic compounds, the following conclusions could be drawn:

- (1) The steel electrode can be passivated in naturally aerated solutions of citric acid in spite of the previous data represented different behaviors in deaerated conditions.
- (2) The steady potentials, E_{st} , are approached from negative values and with increasing concentrations of citric acid solutions, E_{st} , shifts to less negative values indicating that the thickening and the stability of the passive film increased.

(3) E_{st} varies with citric acid concentration according to:

$E_{st} = a_1 + b_1 \log C_{\text{citric}}$, where a_1 and b_1 are constants.

(4) The initial rate of oxide film thickening follows a direct logarithm law, as evident from the variation of the open-circuit potential, E , with $\log t$; where $E = a_2 + b_2 \log t$.

(5) The initial rate of oxide film thickening decreases with raising the temperature due to the partial dissolution of the oxide film.

(6) The free activation energy of oxide film thickening is calculated and found to be 17.8 kJ/mole, indicating that the process of oxide film growth is under diffusion control.

(7) The addition of increasing concentrations of some organic compounds such as 1,2-phenylenediamine, phenyl hydrazine and urea inhibit the destruction of the passive film on steel electrode and the inhibition effect of these compounds decreases in the order: (the highest) 1,2-phenylenediamine > phenylhydrazine > urea (the lowest).

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Ligands of Tables

Table 1. The values of k and n in equation (7)

Organic compound	K	n
Urea	1	0.12
Phenylhydrazine	1.15	0.14
1,2-phenylenediamine	2.06	0.27

Ligands of Figures

Fig. no.	Title
1. A	Variation of the open-circuit potential, E, of the steel electrode with time, in naturally aerated citric acid solutions of different concentrations.
1. B	Variation of the steady-state potential, E _{st.} , of the steel electrode with the logarithm concentrations of naturally aerated citric acid solutions.
2. A	Variation of the open-circuit potential, E, of the steel electrode, in naturally aerated citric acid solutions of different concentrations, with the logarithm of immersion time, t.
2. B	Variation of the initial rate of oxide thickening, δ ⁻ , with the different concentration of naturally aerated citric acid solutions.
3. A	Variation of the open-circuit potential, E, of the steel electrode with time, in naturally aerated 0.5 M citric acid solutions, at different temperatures.
3. B	Variation in the steady-state potential, E _{st.} , of the steel electrode in naturally aerated 0.5 M citric acid solutions, with the temperatures.
4. A	Variation of the open-circuit potential, E, of the steel electrode in naturally aerated 0.5 M citric acid solutions at different temperatures, with the logarithm of time, t.
4. B	Variation in the initial rate of oxide thickening, δ ⁻ , of the steel electrode in, naturally aerated 0.5M citric acid solutions, with the 1/T, K ⁻¹ .
5. A	Variation of the open-circuit potential, E, of the steel electrode with time, in naturally aerated 5x10 ⁻⁴ M citric acid solutions, devoid of and containing different concentrations of 1,2-phenylenediamine.
5. B	Variation in the steady-state potential, E _{st.} , of the steel electrode in naturally aerated 5x10 ⁻⁴ M citric acid solutions, with the logarithm concentration of 1,2-phenylenediamine .
6. A	Variation of the open-circuit potential, E, of the steel electrode with the logarithm of time, t, in naturally aerated 5x10 ⁻⁴ M citric acid solutions, devoid of and containing different concentrations of 1,2-phenylenediamine.
6. B	Variation of the initial rate of oxide thickening, δ ⁻ , with the logarithm of concentrations of 1,2-phenylenediamine in 5x10 ⁻⁴ M naturally aerated citric acid solutions.
7. A	Variation of the open-circuit potential, E, of the steel electrode with time, in naturally aerated 5x10 ⁻⁴ M citric acid + 1M 1,2-phenylenediamine at different temperatures.
7. B	Variation in the steady-state potential, E _{st.} , of the steel electrode in naturally aerated 5x10 ⁻⁴ M citric acid + 1M 1,2-phenylenediamine solutions, with the logarithm temperatures.
8. A	Variation of the open-circuit potential, E, of the steel electrode with the logarithm of time, in naturally aerated 5x10 ⁻⁴ M citric acid + 1M 1,2-phenylenediamine solutions.
8. B	Variation in the initial rate of oxide thickening, δ ⁻ , of the steel electrode, in naturally aerated 5x10 ⁻⁴ M citric acid + 1M 1,2-phenylenediamine with 1/T, K ⁻¹ .

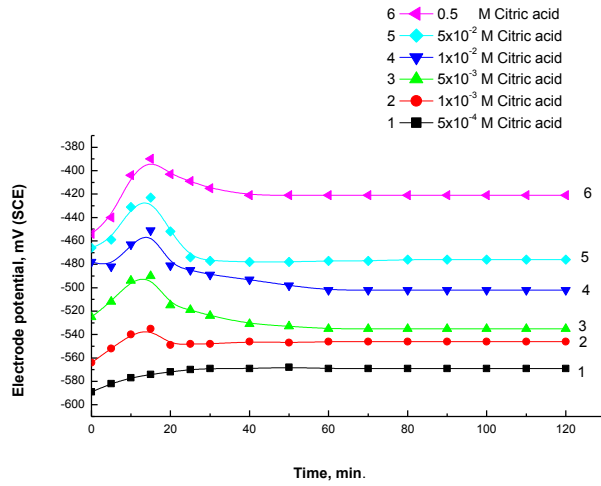


Fig. 1(A)

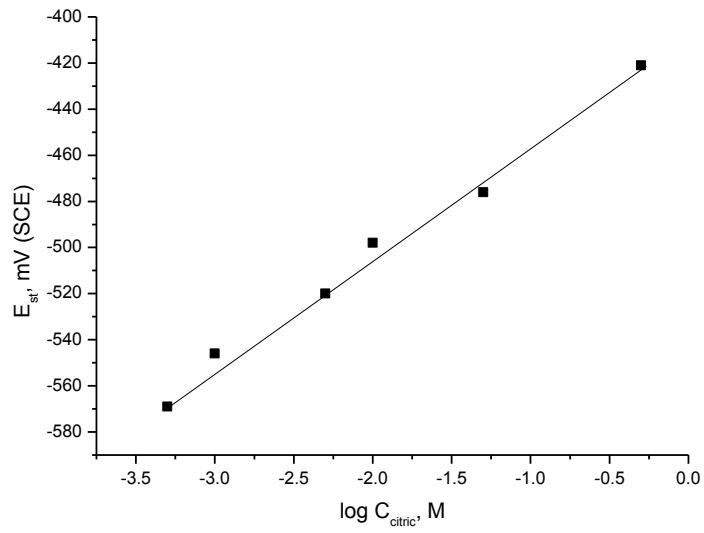


Fig. 1(B)

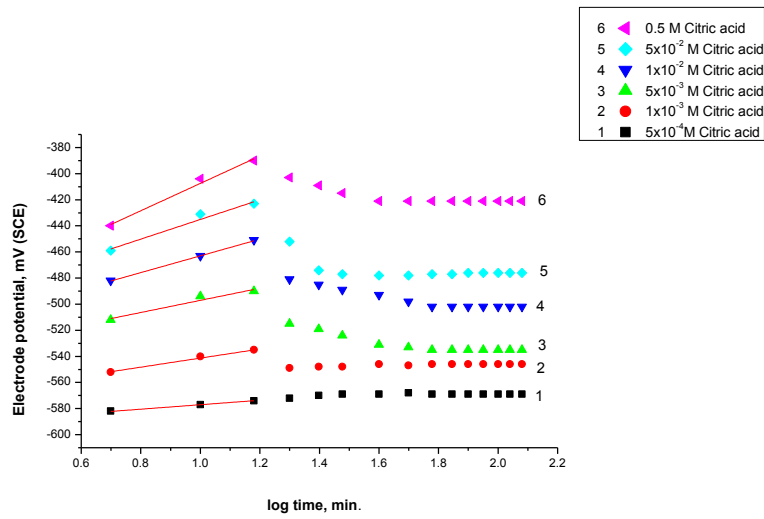


Fig. 2(A)

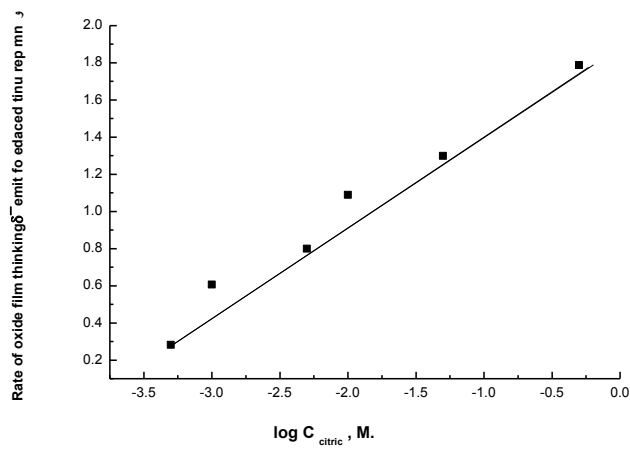


Fig. 2(B)

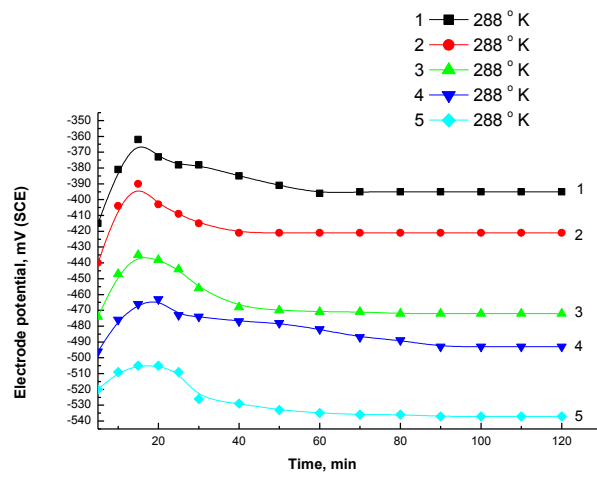


Fig. 3(A)

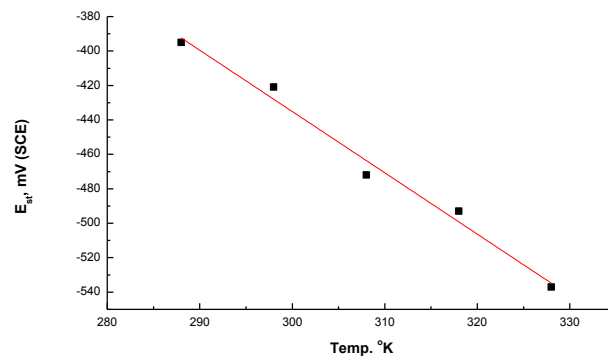


Fig. 3(B)

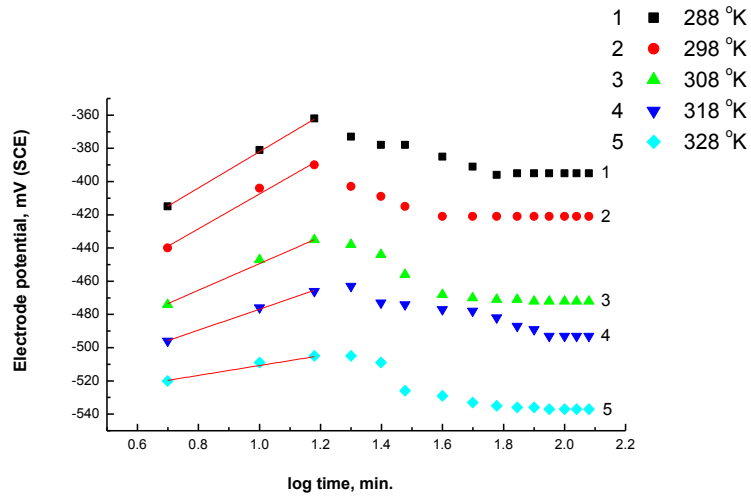


Fig. 4(A)

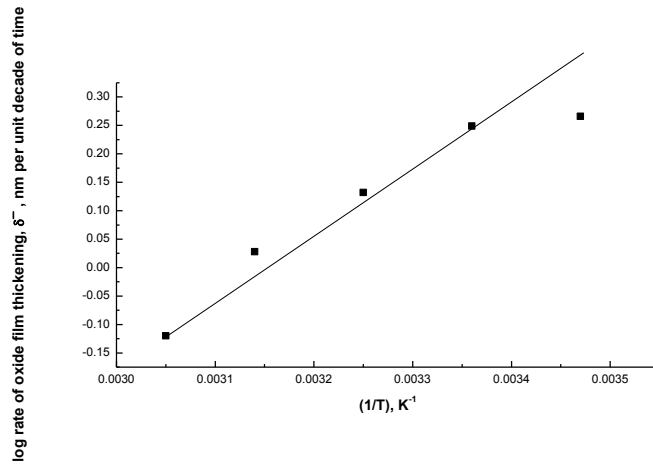


Fig. 4(B)

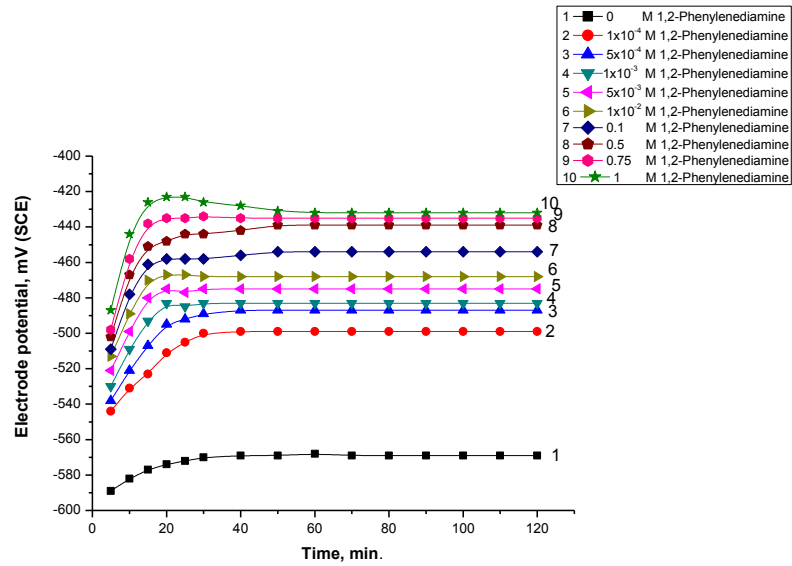


Fig. 5(A)

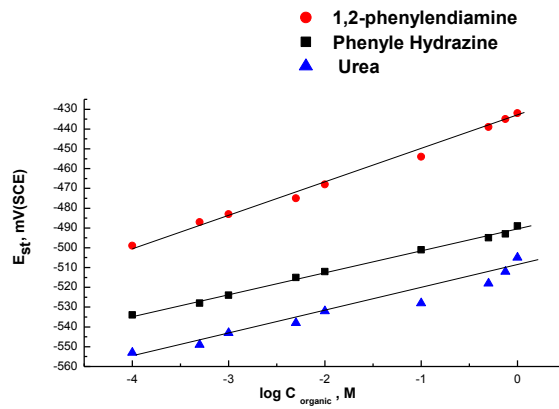


Fig. 5(B)

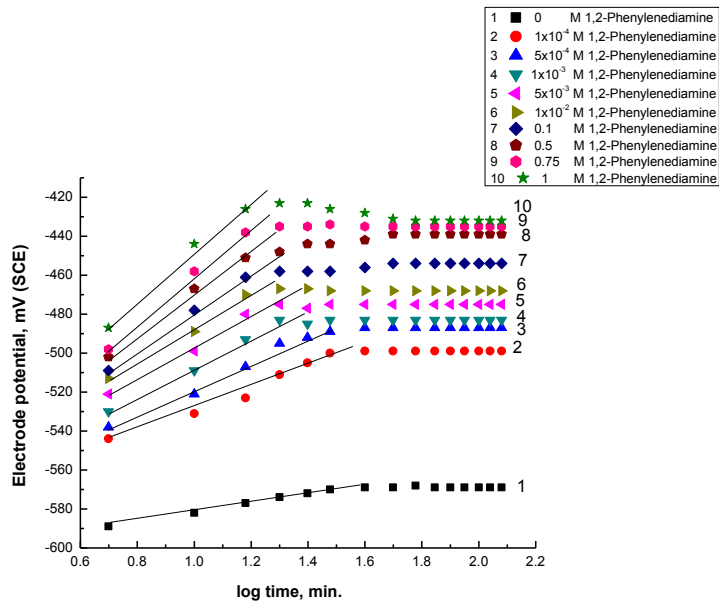


Fig. 6(A)

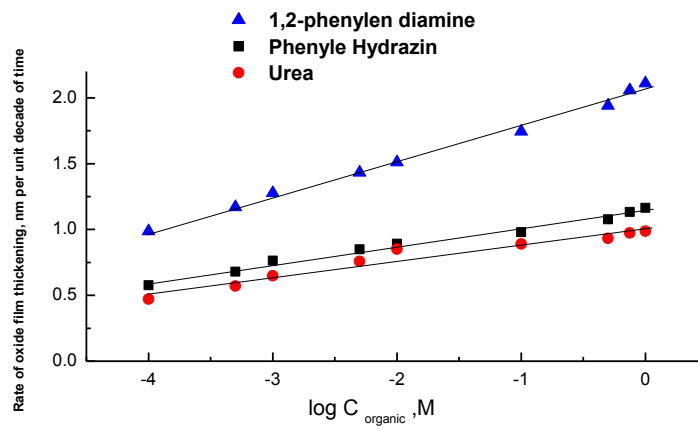


Fig. 6(B)

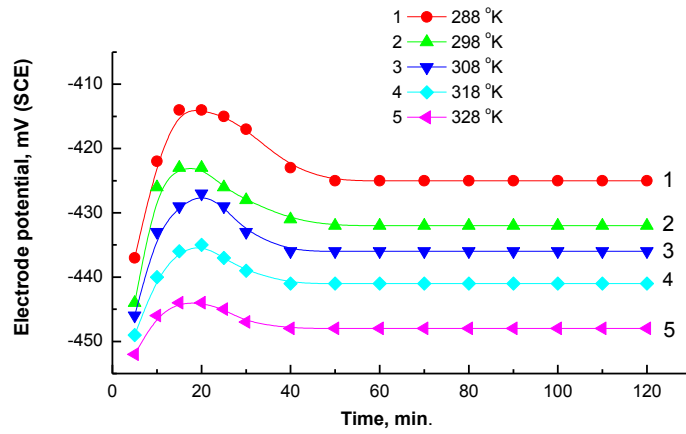


Fig. 7(A)

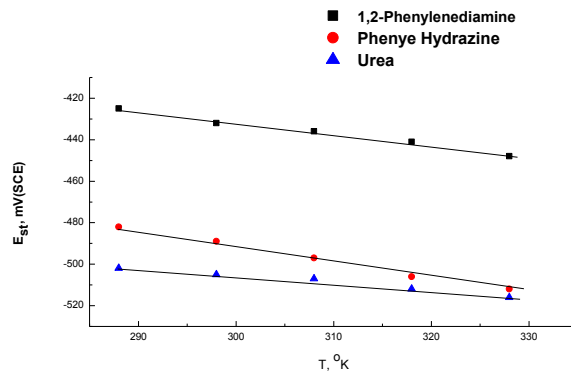


Fig. 7(B)

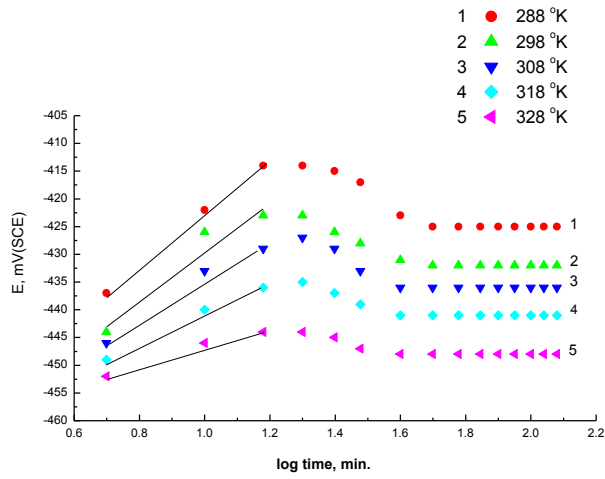


Fig. 8(A)

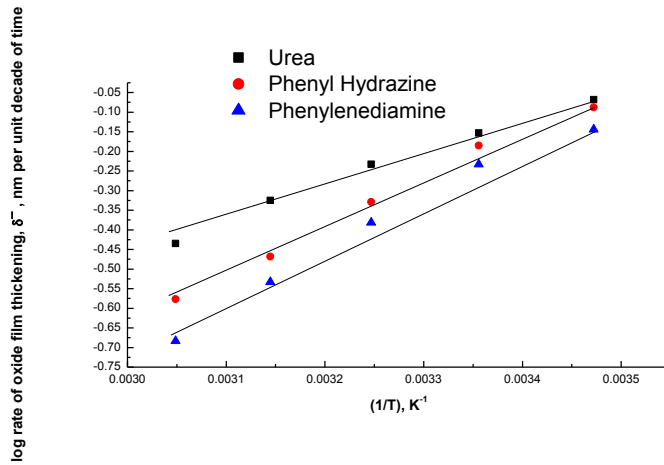


Fig. 8(B)

