

Simple N Compounds Electrochemical Behavior of Steel in Aqueous Solutions

A. Abraham¹ S. Abd El Wanees^{2,3*} S.M. Abd El Haleem² A. Taha²

1.Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt

2.Chemistry Department, ¹Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt

3.Chemistry Department, Faculty of Science, Tabuk University, Tabuk, Saudi Arabia

Abstract

Chemical polishing or electropolishing, instead of mechanical polishing, are recommended for the attainment of metallic surface polishes without the introduction of contaminates or tensions in the surface layers of the metal. The fundamental difference between the chemical and electropolishing processes is that in the latter anodic currents/potentials are used to help in the dissolution and passivation of the metal. The electropolishing process inhibited with different ratio by addition of amide derivatives with concentration range 1×10^{-6} to $5 \times 10^{-3} \text{M}$. The results reveal that amides have strongest inhibitive effect ranging from 4 to 38 %. Thermodynamic parameters as well as adsorption isotherms were driven.

Keywords: Electropolishing, amide derivatives Thermodynamic parameters, adsorption

1. INTRODUCTION

Steel is an essential metal used in the construction and engineering industry all over the world. It is used in every field of our life, from construction products up to automotive industry. There are many thousands steel types published, registered, or standardized worldwide, all of them take different chemical construction. In addition, all the different possible heat treatments, cold-forming conditions, microstructures, shapes, and surface finishes mean that there are a different number of options available for the steel user. Also, steels can be considered into a few major groups according to their chemical compositions, applications, shapes, and surface conditions.

Corrosion inhibitors can be used to prevent steel dissolution. Amines are known to be very effective inhibitors for metal and alloys in different corrosion media. Benzotriazole for instances, was studied and found to have excellent inhibition properties in several corrosion environments [1,2]. The molecule contains nitrogen atoms and it is also useful in preventing copper staining and tarnishing [3].

The inhibiting action of these organic compounds is usually attributed to their interactions with the steel surface via their adsorption. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process, in general, the adsorption of an inhibitor on a metal surface depends on the nature and the surface charge of the metal, the adsorption mode, its chemical structure and the type of electrolyte solution [4].

Mechanical polish or grind is a good polishing method, but it has the disadvantage of hardening the surface inducing a degree of residual tension and oxide incorporation, introducing scratch marks and damaged layers [5]. On the other hand, chemical polishing does not induce surface tensions and removes the surface by chemical dissolution, promoting the preferential removal of surface roughness, but at relatively slow rates. In electrochemical polishing, or electropolishing the dissolution rate of the metallic surface is significantly increased by the application of anodic currents [6, 7].

Actually, electropolishing is defined as the improvement of the surface finish of a metal effected by making it anodic in an appropriate solution. The prepared materials can be used for different purposes. Among of which are: (i) removal of deformations in metallic surfaces, e.g., non-metallic inclusions being an important tool in the fabrication of nuclear equipment, high-pressure vessels and fan blades for jet engines; (ii) electropolishing of reactors, tubes, installations, valves, heat exchangers, making these materials more corrosion resistant and with a smooth, easily cleaned surface, and (iii) removal of burrs from metallic machines after blanking or milling processes, sharpening of tools, control of the dimensions of measurement instruments, smoothing of machine parts subjected to friction [6-9].

The characterization of an electropolishing process is carried out through its polarization curve (current density versus potential [7,10] obtained under stationary state conditions. Processes that work adequately are associated to a wide potential range at constant current (polishing plateau), but the value of the constant current can be fairly critical [7,8,10]- if it is too small the metal is passivated, if excessively large the metal dissolves under solution diffusion control but heating may cause surface deterioration, in neither case leading of effective electropolishing

The objective of this study is to investigate the effect of some organic amides (methanamide, ethanamide, butanamide, and urea) on the inhibition of the electropolishing of steel in phosphoric acid at different conditions. The rate of anodic corrosion is determined by measuring the limiting current.

2. EXPERIMENTAL PROCEDURE

2.1. Chemicals

Analar grade H_3PO_4 (98% w/w) and double distilled water used to prepare the electrolyte. The organic amides were used in this work are formamide, acetamide, butanamide, and urea.

2.2. Apparatus and Procedure:

Fig (1) shows the cell and electrical circuit used in this study. The cell consists of a rectangular plastic container having the dimensions 5.1x5x10 cm with electrodes filling the whole cross section. The electrodes were rectangular steel sheets of 10 cm height and 5 cm width. Electrodes separation was 5 cm. A porous PVC diaphragm was used to prevent the effect of H_2 bubbles. The electrical circuit consists of 6V D.C. power supply, while a voltmeter is connected in parallel with the cell to measure the voltage and multi range ammeter connected in series with cell to measure the current.

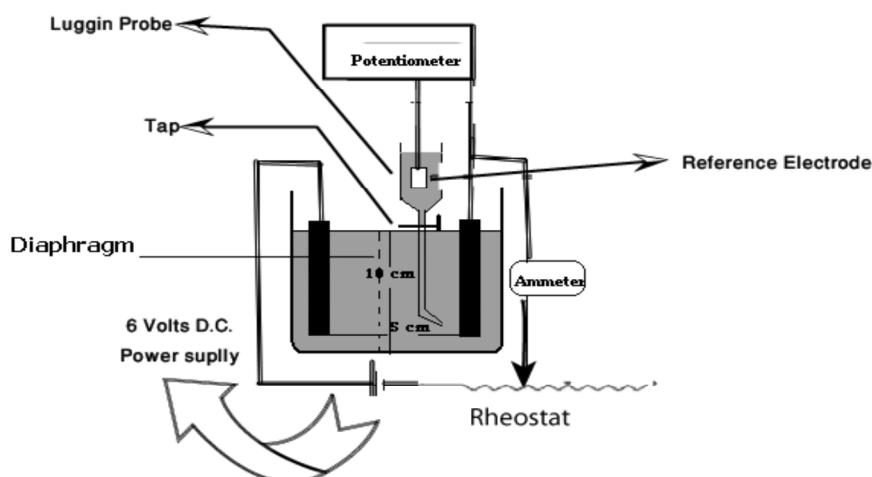


Figure 1. The electrolytic cell and electrical circuit,

2.3. Measurements of the Limiting Current:

Polarization curves were obtained by increasing the cell current stepwise and the steady state anode potential against a reference electrode consisted of a wire immersed in a cup of Luggin tube filled with phosphoric acid concentration similar to that in the cell, the tip of the Luggin tube was placed 0.5-cm from the anode. The potential difference between the anode and the reference electrode was measured by high impedance potentiometer. Phosphoric acid of concentration 8 M were prepared from Analar grade phosphoric acid and distilled water. The anode height varied from 1-5 cm. Before each run, the back part of the anode was insulated with polystyrene lacquers and the active surface of the anode was polished with fine emery paper, degreased with trichloroethylene, washed with alcohol and finally rinsed in distilled water. Electrode treatment was similar to that used by Wilke [11]. Organic amide concentration were $10^{-6} - 10^{-3}$ mol. l^{-1} . The rate of electropolishing of steel was determined at 25°C.

3. RESULTS AND DISCUSSIONS

3.1. Relation between current and voltage

The first step in this study is to determine the limiting current (or relation between the current and voltage) for steel electrode in phosphoric acid solution at 25°C. The observed limiting current is indicated in Table 1 this relation is plotted in figure 2.

Table 1. Variation of the current and voltage for steel electrode in phosphoric acid solution at different temperature.

Current at different Reaction temperature, °C				V
40	35	30	25	
320	280	250	200	100
420	330	320	300	200
500	400	380	350	300
650	500	480	450	400
700	600	600	550	500
800	720	660	620	600
810	730	665	630	1200
830	750	690	640	1300
900	780	700	650	1400

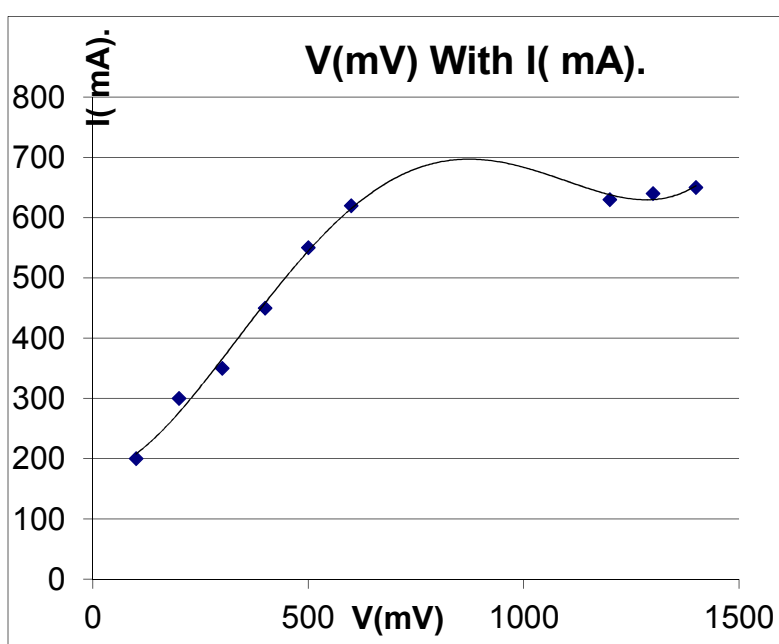


Figure 2. Current and voltage relation for steel electrode in phosphoric acid solution at 25 C

3.2. Effect of amide concentration on the limiting current:

The observed limiting current density, which represents the rate of steel metal corrosion in phosphoric acid, at 25 °C, decrease with increasing the concentration of the organic amides under study.

From the practical point of view and on the basis of results obtained the uses of amides studied in the concentration range between (1×10^{-6} to 1×10^{-3} mole/L) affects the corrosion of steel metal in 8 M H_3PO_4 acid [12, 13].

From the values of the limiting current in absence of organic amides, I and in presence of organic amides, I_L , the percentage inhibition can be calculated from the following equation:

$$\% \text{ inhibition} = \left(\frac{I - I_L}{I} \right) 100 \quad \rightarrow (2)$$

Table (2) is showing that the percentage inhibition caused by organic amides range from 5 – 42 % depending on the amide type, concentration and temperature. The limiting current decreases with increasing the concentration of amides, which agree with other previous work [14, 15]. The decreasing in the limiting current densities with increasing the concentration of amides may be due to the increase in the diffusion layer thickness, which relates the resistance of electrolyte to the rate of mass transfer of steel ion from anode surface to the bulk solution.

Table 2. The values of the limiting current at different concentrations of amides, at different temperatures.

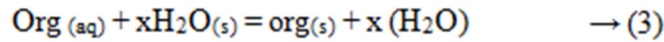
Amide	Concentration (mol/l) x10 ⁶	298 K	303 K	308 K	313 K
Formamide	0	630	665	730	810
	1	380	410	450	500
	5	360	380	410	460
	10	330	350	380	420
	50	300	320	350	390
	100	270	290	320	360
	500	230	260	290	330
Acetamide	0	630	665	730	810
	1	360	390	410	450
	5	350	350	380	410
	10	330	320	350	380
	50	330	290	320	350
	100	250	260	290	330
	500	200	230	260	300
Butanamide	0	630	665	730	810
	1	420	450	490	500
	5	390	410	460	470
	10	360	380	430	440
	50	330	350	400	410
	100	300	320	370	380
	500	270	300	330	350
Urea	0	630	665	730	810
	1	350	380	420	450
	5	320	350	390	410
	10	280	320	360	380
	50	250	280	330	350
	100	200	240	300	320
	500	170	200	270	300

Table 3. Variation of the percentage inhibition of different amides of steel electrode at different temperature.

mide	Concentration (mol / l) x10 ⁶	at 298 K	at 303 K	at 308 K	at 313 K
Formamide	1	39.68	38.35	38.36	38.27
	5	42.86	42.86	43.84	43.21
	10	47.62	47.37	47.95	48.15
	50	52.38	51.88	52.05	51.85
	100	57.14	56.39	56.16	55.56
	500	63.49	60.90	60.27	59.26
Acetamide	1	42.86	41.35	43.84	44.44
	5	44.44	47.37	47.95	49.38
	10	47.62	51.88	52.05	53.09
	50	47.62	56.39	56.16	56.79
	100	60.32	60.90	60.27	59.26
	500	68.25	65.41	64.38	62.96
Butanamide	1	33.33	32.33	32.88	38.27
	5	38.10	38.35	36.99	41.98
	10	42.86	42.86	41.10	45.68
	50	47.62	47.37	45.21	49.38
	100	52.38	51.88	49.32	53.09
	500	57.14	54.89	54.79	56.79
Urea	1	44.44	42.86	42.47	44.44
	5	49.21	47.37	46.58	49.38
	10	55.56	51.88	50.68	53.09
	50	60.32	57.89	54.79	56.79
	100	68.25	63.91	58.90	60.49
	500	73.02	69.92	63.01	62.96

3.3 Adsorption Isotherm

The adsorption of the inhibitor molecules from aqueous solutions can be regarded as substitution adsorption process between the amide compounds in the aqueous phase and water molecules adsorbed on the electrode surface (H₂O).



where x (the size ratio) is the number of water molecules displaced by one molecule of inhibitor. The above process reaches equilibrium when the chemical potential on the left hand equal to that of the right hand side.

Adsorption isotherms are very important in determining the mechanism of electrochemical reactions. The most frequently used isotherms are those of Langmuir, Frumkin, Parsons, Temkin, Flory-Huggins, and Bockris-Swinkels [16].

These entire isotherms are of the general form:

$$f(\Theta, x)\exp(-s\Theta) = KC \quad \rightarrow (4)$$

where f(Θ, x) is the configuration factor which depends essentially on the physical model and assumption underlying the derivation of the isotherm. The mechanism of inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface [17,18].

3.4. Application of Isotherm:

The degree of surface coverage (Θ) at constant temperature was determined from the following equation[19,20].

$$\Theta = \frac{I - I_L}{I} \quad \rightarrow (5)$$

Figs (2.a – 2.d) show the Flory-Huggins adsorption isotherm for steel electrode in H₃PO₄ plotted as log Θ /C against log (1- Θ) at 25°C. A straight line is obtained with a slope X and intercept log x K. The experimental data fits the Flory-Huggins adsorption isotherm which represented by:

$$\log \Theta /C = \log xk + x \log (1- \Theta) \quad \rightarrow (6)$$

where x is the number of water molecules replaced by one molecule of the inhibitor. It is clear that, the surface coverage data are useful for discussing adsorption characteristics. The adsorption of inhibitors at metal-solution interface may be due to the formation of electrostatic or covalent bonding between the adsorbates and the metal surface [21].

The kinetic adsorption isotherm for steel electrode in H₃PO₄, at 25°C, may be written in the form [22]:

$$\log \Theta /1- \Theta = \log k' + y \log C \quad \rightarrow (7)$$

From equation (7) a plot of log Θ /1- Θ against log C should yields a straight line with intercept of log K' and slop = y , where y is the number of inhibitor molecules occupy one active site. The binding constant of adsorption K= k'/y, where 1/y is the number of the active surface sites occupied by one molecule of the inhibitor, and k is the binding constant. Figs (3.a– 3.d) show linear relationships between log Θ/1-Θ and log C, at 25°C, and the calculated values of 1/y and K are given in Table (2). It is obvious that the value of 1/y for all compounds are higher than one indicating that, the given inhibitors molecules are attached to more than one active site. The free energy of adsorption (ΔG_{ads}). At different concentrations of the amides as calculated from the following equation:

$$\Delta G_{ads} = -RT \ln (55.5 K) \quad \rightarrow (8)$$

The value 55.5 is the concentration of water in the solution mol/l.

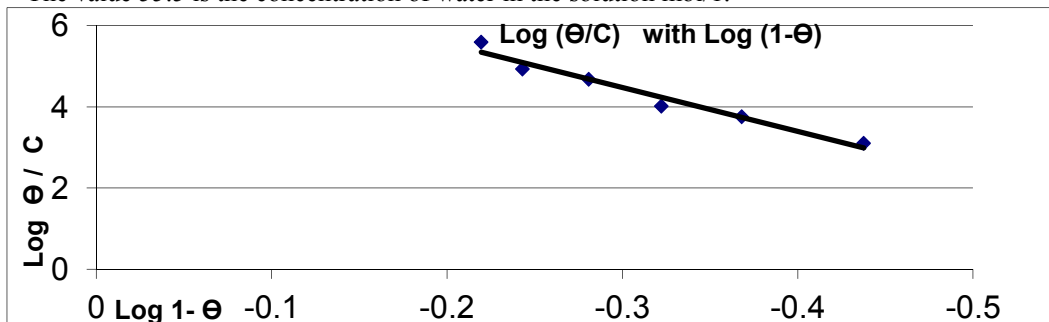


Figure 3.a Flory Huggins adsorption isotherm at 25° C at different concentrations of formamide in a steel divided cell with 8 M H₃PO₄

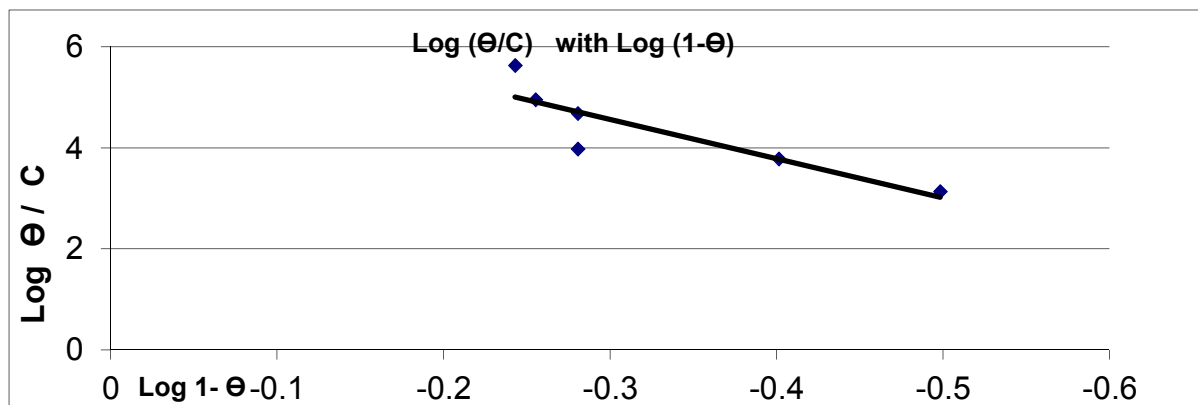


Figure 3.b Flory Huggins adsorption isotherm at 25 C at different concentrations of acetamide in a steel divided cell with 8 M H₃PO₄

The values of ΔG_{ads} are given in Table (4). In all cases, the (ΔG_{ads}) values are negative and lie in the range of 30.0–33.0 KJ/mol. The most efficient inhibitor shows the most negative (ΔG_{ads}) value. This suggests that, they are strongly adsorbed on metal surface. The negative values of (ΔG_{ads}) indicates that the spontaneous ion of the inhibitors. It's found that (ΔG_{ads}) values are more positive than (- 40) indicating that the inhibitors are physically adsorbed on the metal surface. Talati [22] has also reported similar results.

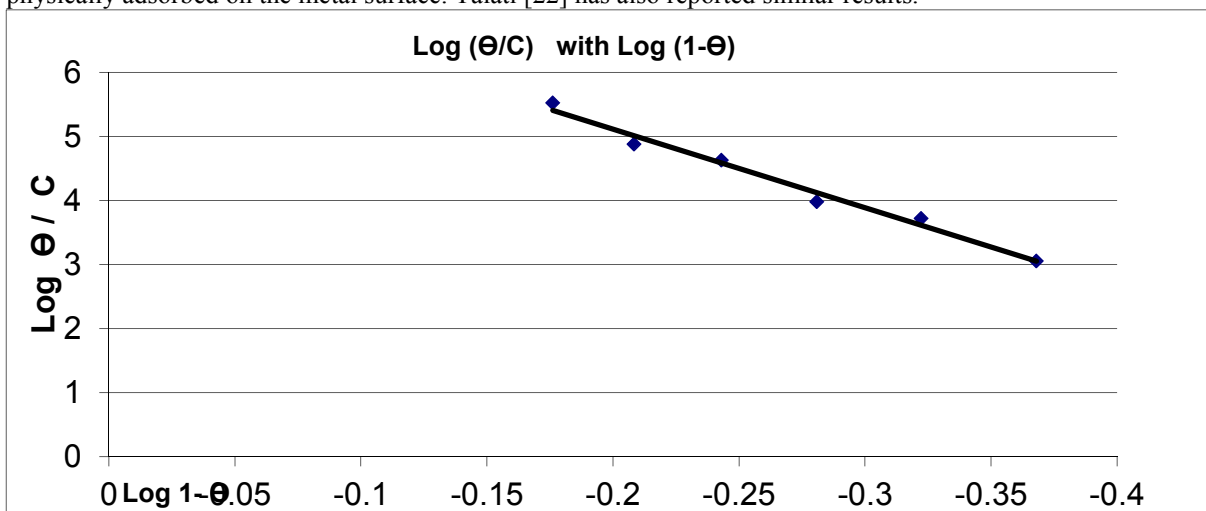


Figure 3.c Flory Huggins adsorption Isotherm at 25 C at different concentrations of butanamide in a steel divided cell with 8 M H₃PO₄

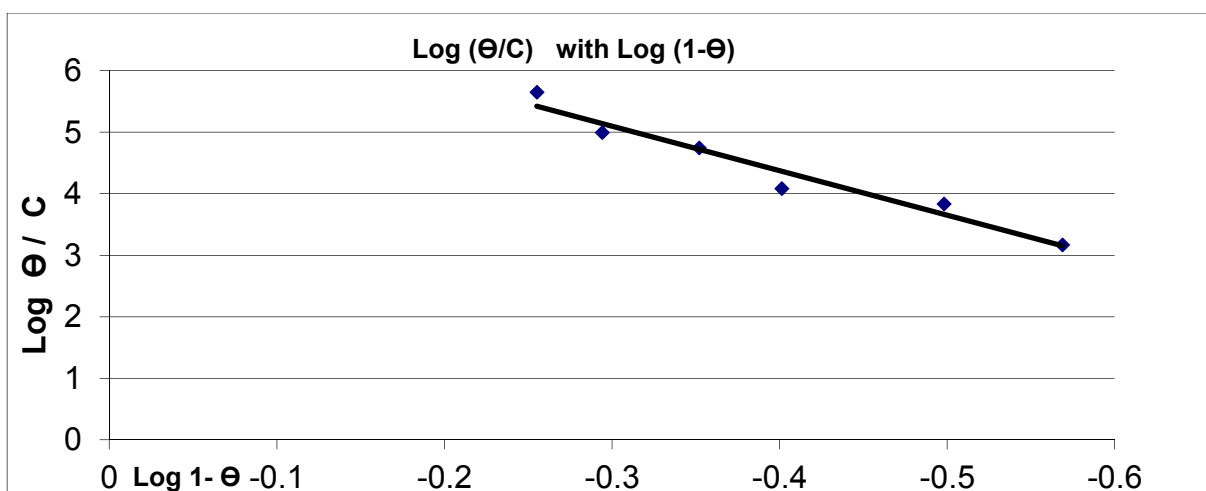


Figure 3.d Flory Huggins Adsorption Isotherm at 25 C at different concentrations of Urea in a steel Divided cell with 8 M H₃PO₄

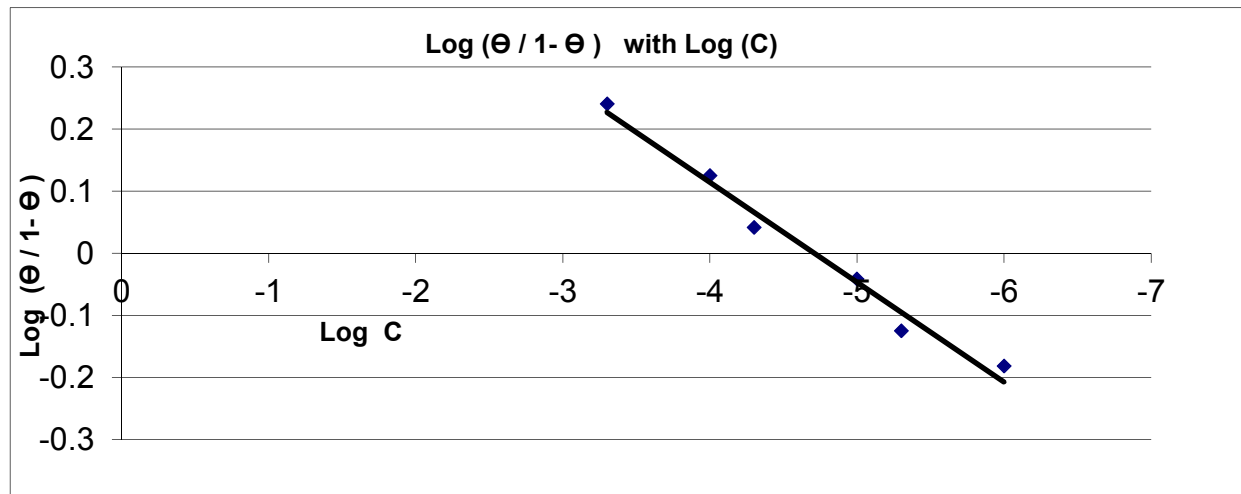


Figure 4.a Kinetic adsorption isotherm at 25 C at different concentrations of formamide in a steel divided cell with 8 M H₃PO₄

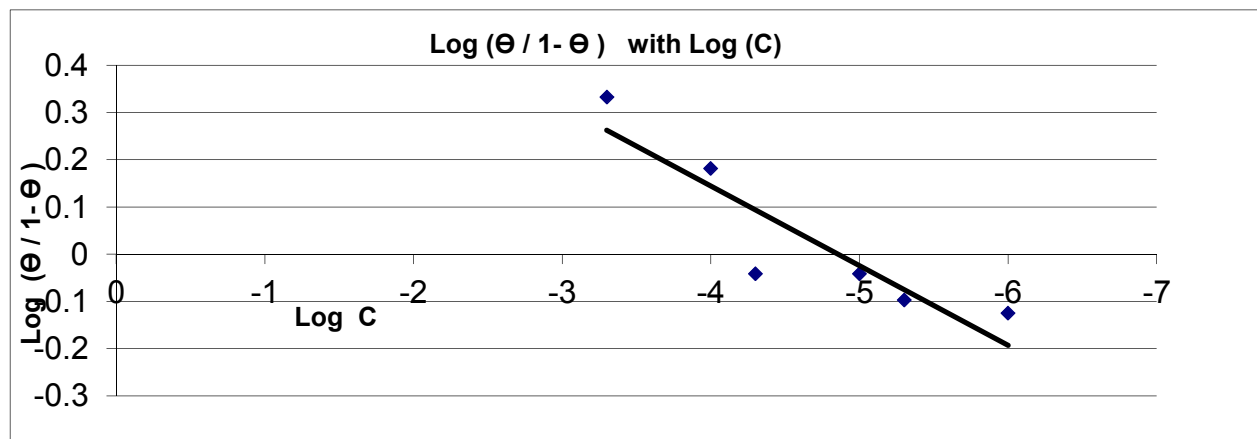


Figure 4.b Kinetic Adsorption Isotherm at 25 C at different concentrations of acetamide in a steel divided cell with 8 M H₃PO₄

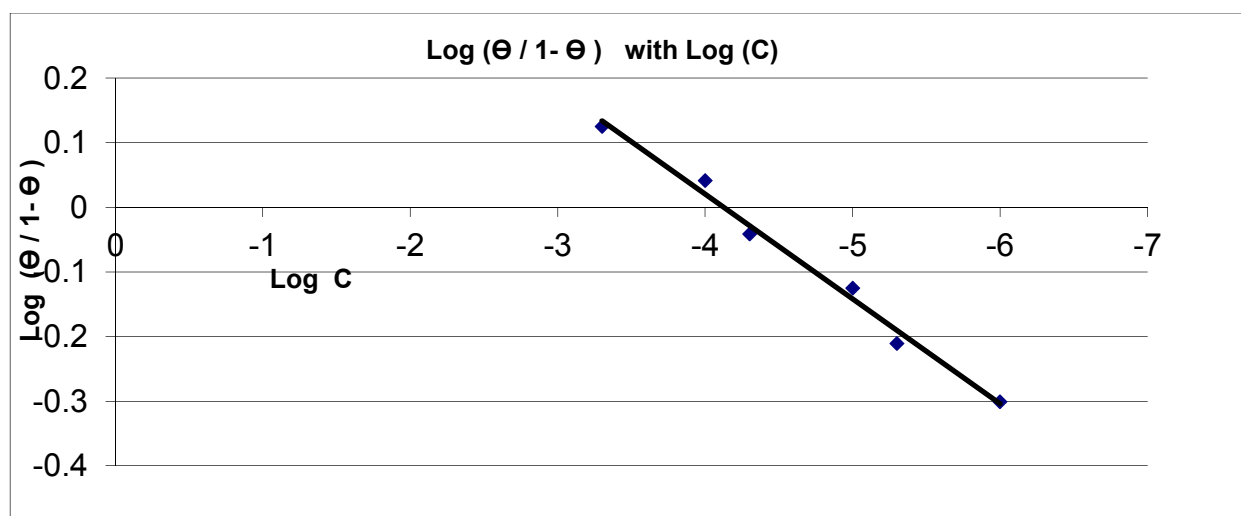


Figure 4.c Kinetic adsorption isotherm at 25 C at different concentrations of butanamide in a steel divided cell with 8 M H₃PO₄

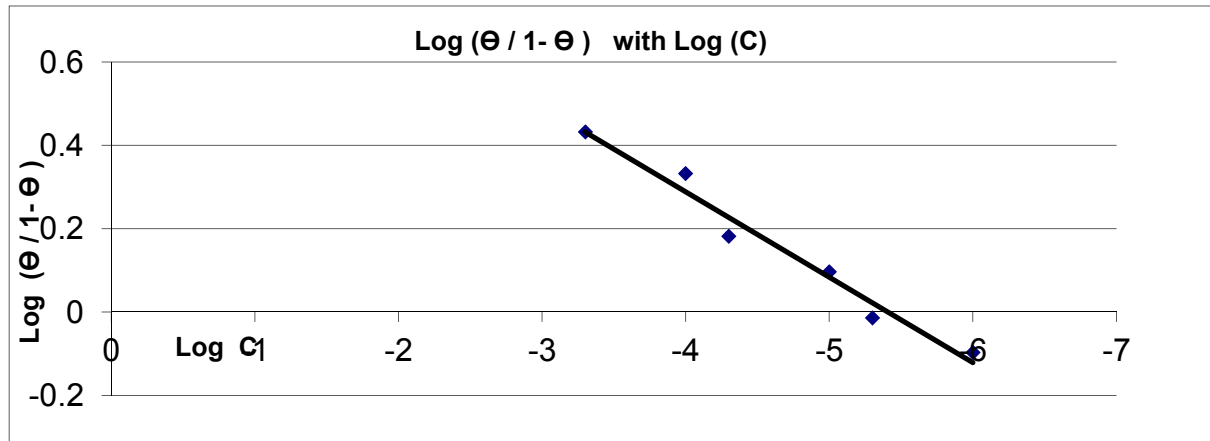


Figure 4.d Kinetic Adsorption Isotherm at 25 C at different concentrations of Urea in a steel Divided cell with 8 M H₃PO₄

Table 4. Thermodynamic parameters, K, X and 1/Y of H₃PO₄ of the used amides, at 25 °. C

Compound	Flory - Huggins		Kinetic Adsorption Isotherm		
	X	K	K'	1/Y	K
Formamide	10.78308	4770740	5.724	6.218	51419.1
Acetamide	7.772863	1016194.4	6.601	5.927	72044.9
Butanamide	12.25545	2987964	4.671	6.162	13330.6
Urea	7.233889	2565986.4	12.81	4.884	256916

Table 5. The calculated values of free energy of adsorption (K.J. mol⁻¹) in the presence of the amides

Compound	Flory - Huggins	Kinetic Adsorption Isotherm
	-ΔG _{ads} (Kj mol ⁻¹)	-ΔG _{ads} (Kj mol ⁻¹)
Formamide	48.09	36.86
Acetamide	44.26	37.69
Butanamide	46.93	33.51
Urea	46.56	40.85

3.5.Effect of temperature and thermodynamic treatment of the reaction

The effect of temperature on the rate of steel electropolishing with and without organic additives was determined in the temperature ranges (25-40°C). It observed that the electropolishing rate increases with temperature for different concentrations of organic additives [23].

It is obviously seen that, the E_a values with and without organic additives are less than < 40 k J mol⁻¹, also indicating that the diffusion processes are controlling the electropolishing reaction[24]. The thermodynamic parameters such as change in free energy ΔG*, enthalpy ΔH* and entropy ΔS* were calculated in same way as the related researches did in literature [25–28]. From transition state equation [34] a straight line was obtained, from which ΔH* and ΔS* can be calculated from the slope and intercept, respectively. The free energy change, ΔG*, can be represented as follows:

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \rightarrow (9)$$

The results indicated that the tested compounds acted as inhibitors through adsorption on steel surface, which resulted in formation of a barrier to mass and charge transfer. The values of ΔH* reflect the strong adsorption of these compounds on steel surface. The negative values of ΔS* pointed to a greater order produced during the process of activation.

This can be achieved by the formation of activated complex representing the association or fixation with consequent loss in the degree of freedom of the system during the process. ΔG* values showed limited increase with rise in the concentration of organic additives revealing that weak dependence of ΔG* on the composition of the organic additives can be attributed largely to the general linear composition between ΔH* and ΔS* for the given temperature [23,30].

3.5.1. The isokinetic relationship

Variation in the change in the rate within series may be caused by changes in either, or both, the enthalpy or the entropy of activation the correlation of ΔH* with ΔS* is linear relationship may be stated as:

$$\Delta H^* = \beta \Delta S^* + \text{constant} \quad \rightarrow (10)$$

$$\delta \Delta H^* = \beta \Delta S^* \quad \rightarrow (11)$$

The operator, δ , concerns difference between any two reactions in the series. Substituting from the equation (10) into the familiar relationship:

$$\delta \Delta H^* = \delta \Delta G^* + T \delta \Delta S^* \quad \rightarrow (12)$$

We obtain

$$\beta \delta \Delta S^* = \delta \Delta G^* + T \delta \Delta S^* \quad \rightarrow (13)$$

where $\delta \Delta G^* = \text{zero}$, $\beta = T$. In other words, the slop in a linear plot of ΔH^* versus ΔS^* is the temperature at which all reactions that conform to the line occur at the same rate. β therefor known as the isokienetic temperature. The isokienetic plot of ΔH^* and ΔS^* for different concentrations of the organic amides, Fig (4.a – 4.d) and was found to be linear and the isokienetic temperature (β) was computed from the slop of the plot as 335K, 308K, and 337K, for formamide, acetamide, and urea these values are much higher than that of the experimental temperature 298 K indicating that the rate of the reaction is enthalpy controlled, but for butanamide the reaction is entropy controlled as the value of isokienetic temperature is lower than 298 K.

Table 6. The values of E^* and all thermodynamic parameters for all different concentrations of the amides.

Amide	Concentration (mol / l) x10 ⁶	E	ΔH	ΔS	ΔG
		KJmol ⁻¹	KJmol ⁻¹	Jmol ⁻¹ K ⁻¹	KJmol ⁻¹
Formamide	0	13.11	10.57	-155.96	58.22
	1	14.20	11.66	-156.47	59.46
	5	12.55	10.01	-162.50	59.66
	10	12.47	9.93	-163.45	59.87
	50	13.57	11.03	-160.56	60.09
	100	14.89	12.35	-157.04	60.32
	500	18.48	15.95	-146.20	60.61
Acetamide	0	13.11	10.57	-155.96	58.22
	1	11.15	8.61	-167.08	59.65
	5	8.60	6.06	-176.07	59.85
	10	7.90	5.36	-179.01	60.04
	50	4.15	1.61	-191.82	60.22
	100	14.56	12.02	-158.87	60.56
	500	20.76	18.22	-139.71	60.91
Butanamide	0	13.11	10.57	-155.96	58.22
	1	9.46	6.92	-171.42	59.28
	5	10.48	7.94	-168.68	59.47
	10	11.27	8.73	-166.69	59.65
	50	12.19	9.65	-164.34	59.85
	100	13.27	10.73	-161.50	60.07
	500	13.57	11.04	-161.26	60.30
Urea	0	13.11	10.57	-155.96	58.22
	1	13.25	10.71	-160.26	59.67
	5	13.23	10.69	-161.04	59.89
	10	16.07	13.53	-152.51	60.13
	50	18.23	15.69	-146.32	60.39
	100	25.38	22.85	-124.05	60.74
	500	31.11	28.57	-106.39	61.07

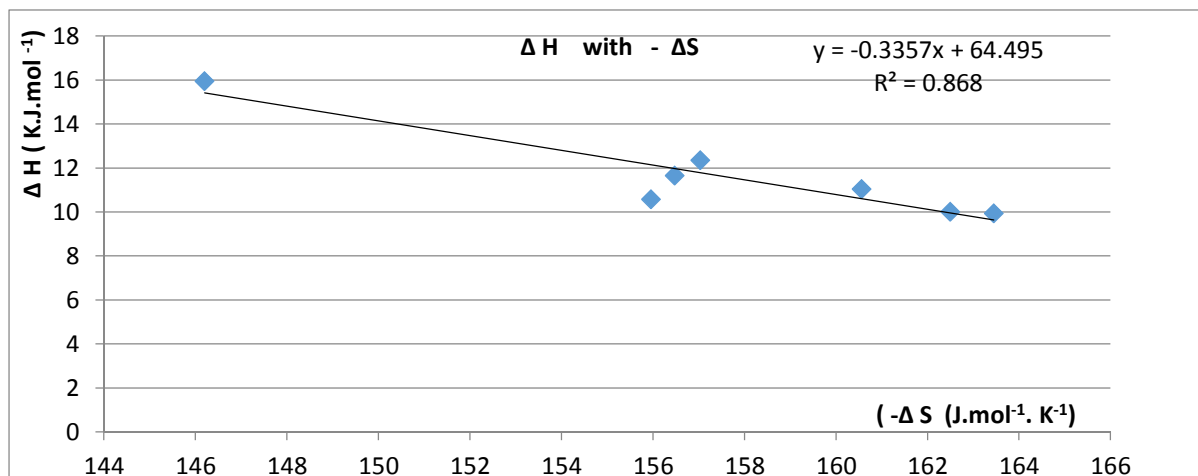


Figure 5.a Relation between ΔH and $-\Delta S$ at 25°C at different concentrations of formamide in a steel divided cell with 8 M H_3PO_4

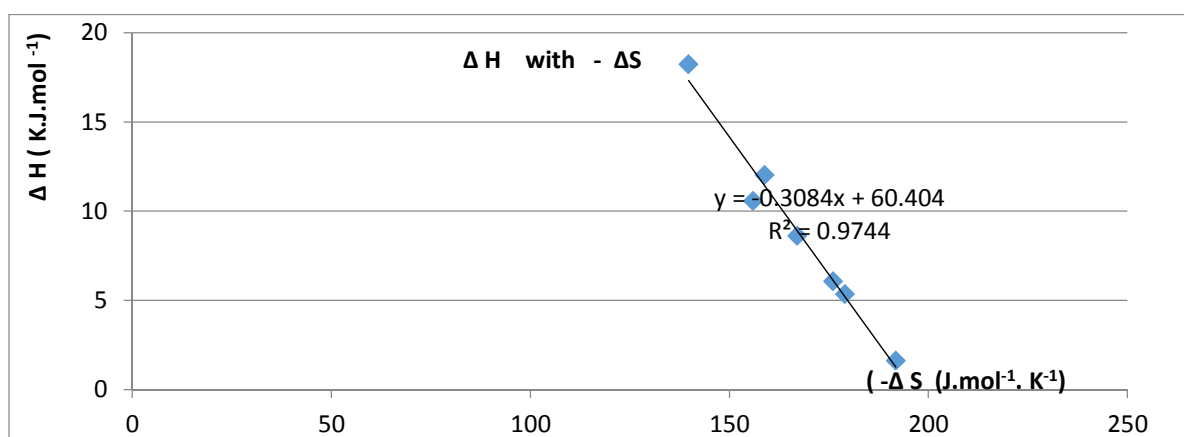


Figure 5.b Relation between ΔH and $-\Delta S$ at 25 °C at different concentrations of acetamide in a steel divided cell with 8 M H_3PO_4

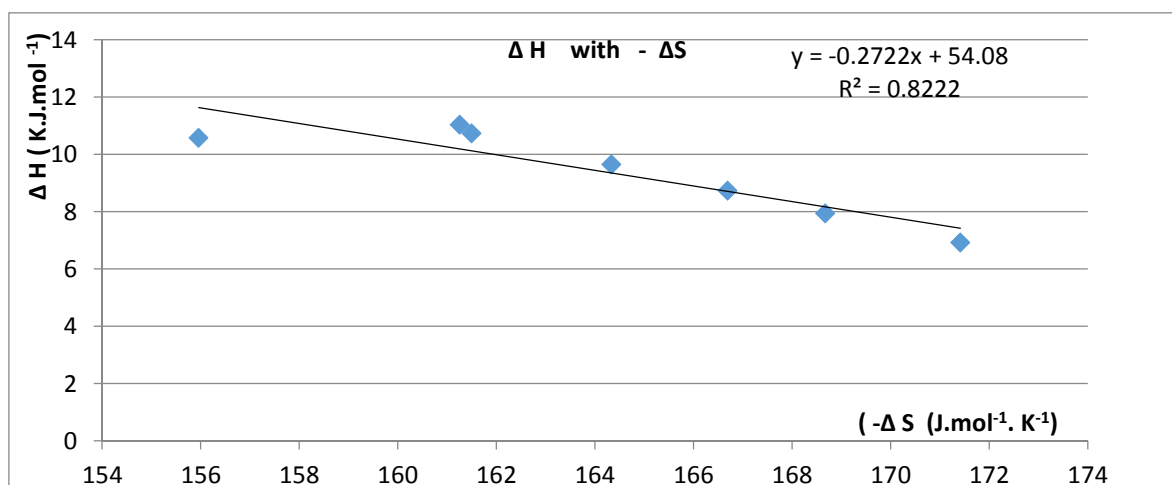


Figure 5.c Relation between ΔH and $-\Delta S$ at 25 °C at different concentrations of butanamide in a steel divided cell with 8 M H_3PO_4

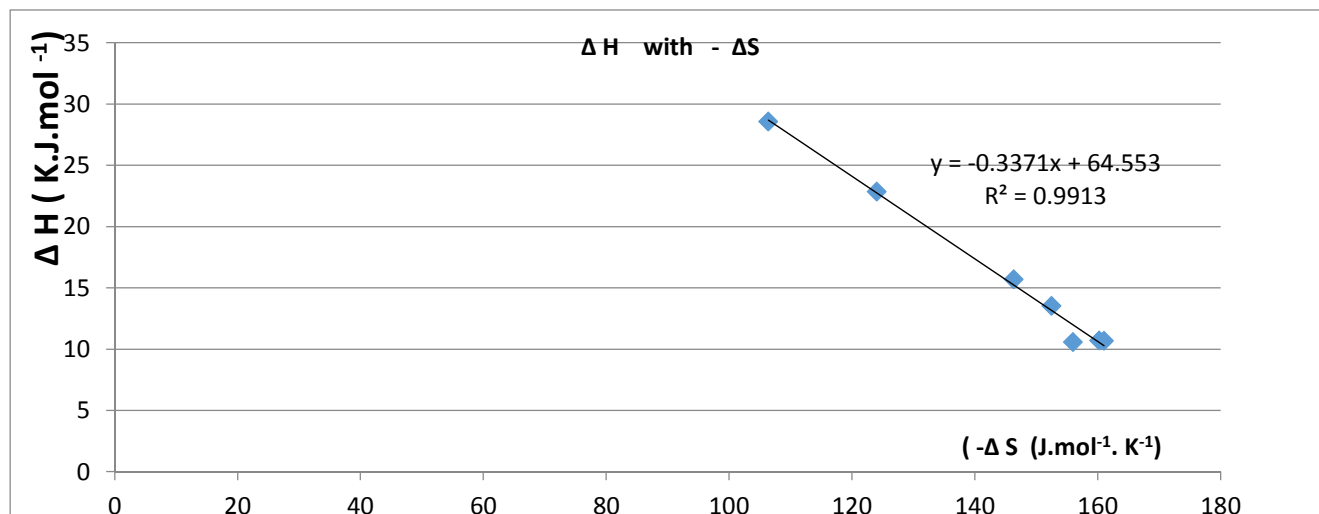


Figure 5.d Relation between ΔH and $-\Delta S$ at 25°C at different concentrations of urea in a steel divided cell with 8 M H_3PO_4

Figure (5). *The isokinetic relationship* for (a) Formamide, (b) Acetamide, (c) Butanamide, and (d) Urea.

4. CONCLUSION

Electropolishing of steel in phosphoric acid is considered as corrosion rate of steel. It is measured by measuring the limiting current. The rate of corrosion decreases by adding of organic amides (formamide, acetamide, butanamide, and urea). The following conclusion are:

- The rate of inhibition ranged from 33-73 % depending on the type of the amide and its concentration.
- The corrosion rate increases by increasing the temperature and the activation energy of the reaction is less than 40 k. j. i.e. the reaction is diffusion controlled. All amides verify Flory – Huggins and Kinetic Adsorption Isotherm.
- Dimensionless group were calculated which indicated that the corrosion process takes place by forced convection.

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