

New study of passivation as an isotherm on metals surface: theoretical and experimental approach

Most of the studies on metals surfaces paid attention to adsorption isotherm. The present study focuses on passivation as an isotherm and its relation to Gibbs free energy and other thermodynamic parameters. Based on the equilibrium and dynamics of the processes that occur at the interface between the solid (surface) and reaction products, passivation isotherm model was created. The mode of relationship among the reaction products, metals surfaces and the inhibitor was also obtained. New expressions for passivation processes were introduced and new mathematical models for passivation as an isotherm were created.

Key words: Passivity, Oxidation, Weigh loss, Passive film

1. INTRODUCTION

The study of inorganic compounds as corrosion inhibitor on the metal surface is of tremendous practical importance. When the product of a reaction occurs on the surface, it encounters a net attractive potential similar to the potential between the two molecules [1]. In both non-oxidizing and oxidizing agents, oxygen plays an important role for passivation on the metal surface. Oxidizing agents can act in the absence of oxygen as the compound itself contains oxygen.

The formation of passive films on the metal surface has been explained by two theories [2]. The first theory states the formation of a metal oxide or other reacting compounds on the metal surface at room temperature called "oxide film theory". The second theory states the adsorption of oxygen on the surface forming a chemisorbed film. Therefore, all chemisorbed film reacts over a period of time with the underlying metal to form metal oxides. Metal oxides can be classified as network formers, intermediates or modifiers. The metals that fall into network forming or intermediates tend to grow protective oxides which support anion or mixed anion-cation movement. The network formers are neocrystalline, while the intermediates tend to be microcrystalline at low temperatures.

Many researchers reported on metals and alloys surface based on the mechanism of adsorption and adsorption isotherm. The present study establishes a new scope on the study of surfaces dynamics by introducing passivation as passivation isotherm. New expressions, definitions and mathematical model related to passivation and passivation isotherm have been created.

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2. THEORETICAL APPROACH

2.1. Definition

Passivity is the result of formation of a highly protective, but very thin (about 0.0004 mm thick) and quite invisible film on the surface of the metals or alloys, which makes it nobler [3]. The surface which is passivated is called passivite. The product which causes passivity is called passivate. The latter is different from passivator. The ability of metals to resist its dissolution because of passivate is called degree of passivity (θ).

2.2. Assumptions for passivity

The passivation process may be a physipassivation or chemipassivation which depends on the surface coverage with temperature. Chemipassivation involves the formation of chemical bonds. However, physipassivation is the formation of van der Waal's forces between molecules and the metal surface. It is usually not possible to make a sharp distinction between these two kinds of passivation except to say that, the Gibbs free energy change is much larger for physipassivation. Physical passivation is likely to be reversed by raising the temperature or lowering the force of external factors on the surface. Passivity involves the following assumptions:

- a) Diffusion of passivate to the metal surface.
- b) Passivity is usually chemipassivation or physipassivation on the surface.
- c) The process is controlled by oxidation.
- d) Depletion of products.
- e) Diffusion of products away from the surface.
- f) The products are non-porous.

2.3. Theoretical calculations

The degree of passivity (θ) on the metal surface is increased with increasing concentration of original inhibitor. The study of inhibition efficiency and its

relation with temperature on the metal surface indicated that, the passivate is strongly or weakly adsorbed on the metal surface. Based on a strong or weak oxidizing agents / non-oxidizing agents in presence of oxygen, quick / slow formation of passivate may occur on the metal surface. Passivity is a crucial factor in determining the ability of the metal to resist the corrosion.

As in the case of adsorption process, the efficiency of the inhibitor for passivation process is given by the following relation:

$$IE(\%) = \frac{(X_a - X_p)}{X_a} \times 100 \tag{1}$$

where X may be corrosion rate (CR), or corrosion current density (I_{corr}) or charge transfer resistance (R_{ct}), and subscripts a and p indicate the absence and presence of the inhibitor. According to Eq.(1), the degree of passivity (θ) can be calculated by following equation:

$$\theta = \frac{IE(\%)}{100} \tag{2}$$

Here θ is the active site covered by the passivate and $(1 - \theta)$ is the uncovered active site (Fig. 1). In general, the strength of the passive film increases with increasing concentration of original inhibitor.

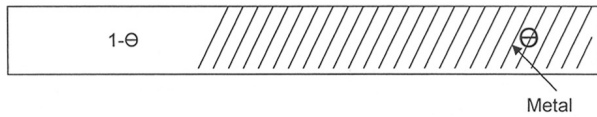
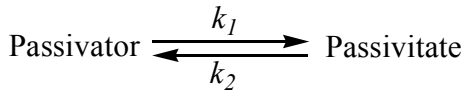


Fig.1: Degree of surface coverage on the metal

Suppose a metal is in contact with passivator, the molecules of passivator form a protective metal oxide film called passivate. A state of equilibrium is attained between passivator and passivate.



Where k_1 is the rate constant of formation and k_2 is that of depletion for passivate. If r_1 and r_2 are the rate of formation and depletion of passivate respectively, then

$$r_1 = k_1(1 - \theta)C \tag{3}$$

$$r_2 = k_2\theta \tag{4}$$

At equilibrium, the rate of formation is equal to the rate of depletion.

$$k_1(1 - \theta)C = k_2\theta \tag{5}$$

From Eq.(5), the degree of passivity (θ) and the equilibrium passivation constant (K_{pass}) are related as follows:

$$\frac{\theta}{(1 - \theta)} = K_{pass} C \tag{6}$$

where $K_{pass} = \frac{k_1}{k_2}$

After many attempts using excel software to find the best expression for passivation isotherm, the following equation was found to be the best description for most of the passivation isotherms:

$$\frac{1}{(1 - \theta)^{1/x}} = K \frac{1}{C^{n/x}} C^n \tag{7}$$

Where C is the concentration of inhibitor and n is a number which reflects the ability of passivate to protect the metal surface against corrosion. Eq.(7) is given a name “**Badiea-Mohana passivation isotherm model**”. Here $x = 3$ and $0 < n \leq 1.4$ for passivation and $x = 1$ and $0 < n < 2$ for adsorption. If $n < 1.4$, the passivate on the metal surface is more stable and easily occurs to protect the metal surface. If $n \geq 1.4$, it is very difficult for passivate to protect the metal surface and also, the passivate molecules are less stable (Fig. 2). Note that, if $x = 1$ and $n = 1$, Eq.(7) becomes Langmuir adsorption isotherm.

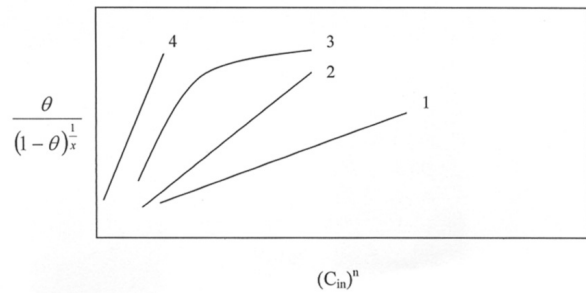


Fig.2: Relationship between degree of passivity and concentration of inhibitors. Passivate stability 4 > Passivate stability 2 > Passivate stability 1

In Eq.(7), $\frac{1}{x}$ is taken as a power for $(1 - \theta)$ in order to give more fit (R^2 close to 1) and also to enlarge the intercept. Also $\frac{1}{x}$ is taken as a power for K_{pass} to obtain a large K_{pass} ($K \gg K^{1/3}$). This is because the

concentration of oxygen is so small in solution compared to concentration of water in solution (55.5 mol/L). The formation of passivate on the metal surface is slow and the depletion is assumed to be slower, so K_{pass} will be large. From Eq.(7), a large equilibrium can be obtained as the passivation process must be spontaneous. Therefore, linear fit depends on x and n . In our assumption, $n < 1$ for better fit.

The process is controlled by oxygen in air or any oxidizing/non-oxidizing agents as transition metals content. Therefore, the required concentration of oxygen as an adsorbed layer for passivation must be determined. Using van der Waal's equation $[(p + a/v^2)(v - b) = RT]$ and QUICK BASIC version 3.22-XP software, the molar volume of oxygen in the standard conditions has been computed (see appendix A). The density (mol/L) or concentration of oxygen required as an adsorbed layer for passivation can be calculated using the equation $\rho = \frac{I}{v}$. The concentration of oxygen required as an adsorbed layer for passivation was found to be 41.325×10^{-3} (mol/L). Using this value, the Gibbs free energy of passivation (ΔG_{pass}) and the equilibrium passivation constant (K_{pass}) are related by the following equation:

$$K_{pass} = \frac{I}{41.33 \times 10^{-3}} \exp\left(\frac{-\Delta G_{pass}}{RT}\right) \quad (8)$$

Where R is universal gas constant and T is absolute temperature. From Eq.(8), the enthalpy and entropy of passivation can also be calculated.

The effect of x and n on the formation of passivate on the metal surface can be explained by Fig. 2. Line 4 reflects that, the passivate is more stable than that in line 1, this means that, n has ability to form a protective layer (oxide film or other reacting compound) in line 4 more than in lines 1 or 2.

3. TESTING THE MODEL

In order to verify the performance of the model, experimental testing with gravimetric and spectrophotometric methods were employed.

3.1. Experimental work for the application of passivation isotherm

Materials and methods

Commercial grade low carbon steel specimens with a composition (wt %) of 0.15- C; 0.37- Si; 0.04- P; 0.01- Al; 0.05- Mn; 0.05- S and the remainder iron and dimensions of 19 mm diameter, 5 mm length and 1 mm thickness were used for mass loss measu-

rements. The specimens were polished with emery paper grade of 320-600, degreased and washed with distilled water, rinsed with benzene for 5 seconds, dried with tissue paper, rinsed with acetone for 5 seconds and dried with tissue paper, then kept in a dissector until use. The ferric ions content in the test solution was determined by spectrophotometric method [4] using uv-visible spectrophotometer (Elico Co. India). The initial weight of the specimen was recorded using an analytical balance (precision ± 0.1 mg) before immersion in the industrial water. Temperatures of solution (30 - 80 °C) were controlled using a thermostatically controlled water bath with mechanical stirrer (± 0.1 °C, Weibr Ltd. Mumbai, India). The fluid velocities through the specimens (1.44 - 2.02 m/s) were set at desired velocity using speed regulator motor (Eltek Ltd. Mumbai, India). Analar grade sodium nitrite and borax were used as inhibitors. The corrosion rate (CR) was computed using the following equation:

$$CR = \frac{24 \times 10^6 W}{t A} \quad (9)$$

Where W is mass loss (g), t is immersion time (h) and A is the surface area of the specimen (mm^2).

4. RESULTS AND DISCUSSION

Passivation isotherm

Inhibition efficiency (IE %) and degree of passivity (θ) have been calculated using Eqs. (1) and (2) at optimal rotational speed. The corrosion rate (CR), inhibition efficiency (IE %) and degree of passivity (θ) were obtained at various individual and synergistic combination of sodium nitrite and borax under different conditions of temperatures and fluid velocities. The results are compiled in Table 1. Individual sodium nitrite exhibited higher values of CR when compared to sodium nitrite-borax blend. At the lowest concentration of sodium nitrite, the CR was higher than those in its absence. This is attributed to the pitting corrosion, which takes place when inhibitor is not present in sufficient quantity at a corroding surface. This is due to inability to rectify every fault in the passive oxide film [5]. K_{pass} was calculated from the intercept of the plots of

$\log\left(\frac{\theta}{(1-\theta)^{0.33}}\right)$ versus $\log C$ (Fig. 3) at different

temperature. Slopes of the plots lie between 0 and 1, and the linear regression is around 0.980 confirming the applicability of Badiea-Mohana passivation isotherm. K_{pass} , ΔG_{pass} and regression were depicted in Table 2. The low negative values of ΔG_{pass} obtained

demonstrate that, the process is not strong physipassivation. Using equation, $\Delta G_{pass} = \Delta H_{pass} - T\Delta S_{pass}$, the entropy of passivation (ΔS_{pass}) and enthalpy of

passivation (ΔH_{pass}) can be obtained from the slope and intercept of a plot ΔG_{pass} versus T .

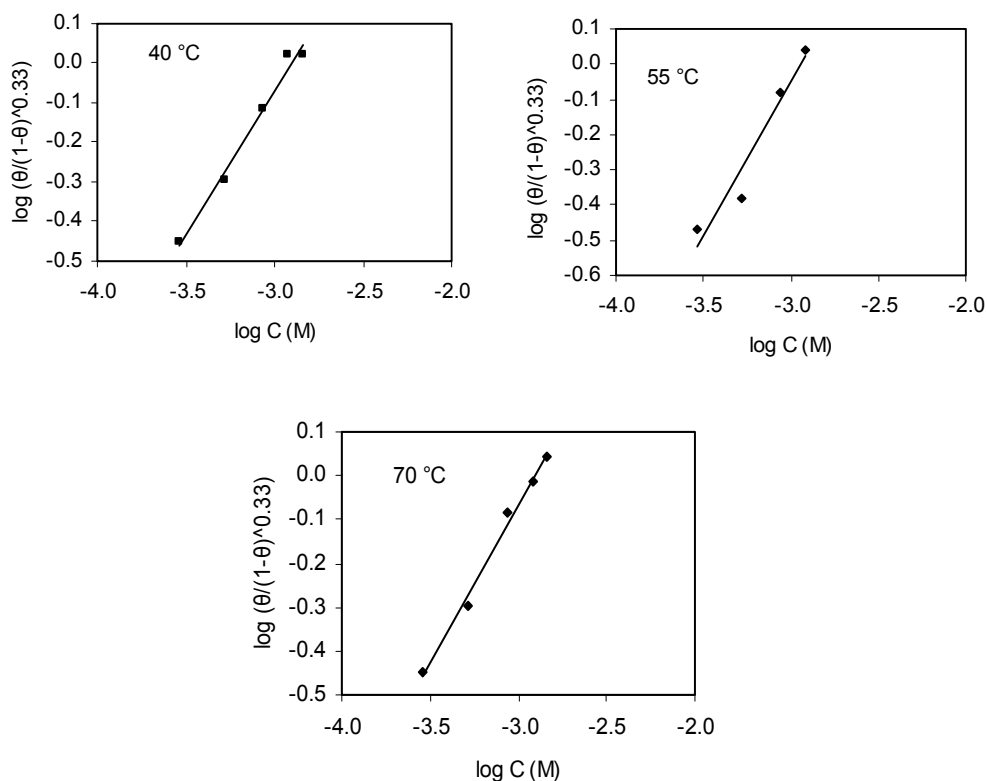


Fig.3: Badiea-Mohana passivation isotherm for low carbon steel surface in industrial water.

Table 1. Performance of individual and synergistic combination of sodium nitrite and borax at different temperatures and at 1.56 m s^{-1}

Temperature [°C]	c (ppm)		CR ($\text{g m}^{-2} \text{ d}^{-1}$)		IE (%)	θ
	Sodium nitrite	Borax	Mass loss	Spectrophotometric		
	blank	blank	–	8.923		
	20	–	–	8.938	-0.17	-0.002
	36	–	–	8.127	8.92	0.089
30	60	–	–	7.539	15.51	0.155
	83	–	–	7.022	21.30	0.213
	100	–	–	6.021	32.52	0.325
	blank	blank	8.81	8.923		
	20	400	6.45	6.583	26.22	0.262
	36	720	6.09	6.237	30.10	0.301
30	60	1200	3.42	3.840	56.97	0.570
	83	1660	2.13	2.208	75.25	0.753
	100	2000	3.20	2.310	74.11	0.741
	blank	blank	9.12	9.482		
	20	400	5.86	6.117	35.49	0.355
	36	720	6.00	6.058	36.11	0.361

40	60	1200		3.65	4.001	57.80	0.578
	83	1660		2.60	2.539	73.22	0.732
	100	2000		3.05	2.582	72.77	0.728
	blank	blank		12.06	12.864		
	20	400		8.21	8.992	30.10	0.301
	36	720		7.99	8.257	35.81	0.358
55	60	1200		4.49	5.007	61.08	0.611
	83	1660		3.12	3.586	72.12	0.721
	100	2000		3.14	3.585	72.13	0.721
	blank	blank		16.87	16.823		
	20	400		11.05	11.552	31.33	0.313
	36	720		9.46	10.328	38.61	0.386
70	60	1200		6.38	6.597	60.79	0.608
	83	1660		5.00	5.508	67.26	0.673
	100	2000		5.58	5.519	67.19	0.672
	blank	blank		14.49	15.883		
	20	400		10.18	11.257	29.13	0.291
	36	720		8.76	9.154	42.37	0.424
80	60	1200		5.51	6.493	59.12	0.591
	83	1660		4.33	4.837	69.55	0.696
	100	2000		4.96	4.888	69.22	0.692

Table 2. Thermodynamic parameters of passivation process on low carbon steel surface in industrial water at different temperature and at 1.56 m/s

Temperature (K)	K_{pass} (L mol ⁻¹)	Regression	ΔG_{pass} (kJ mol ⁻¹)	ΔH_{pass} (kJ mol ⁻¹)	ΔS_{pass} (J mol ⁻¹ K ⁻¹)
303	1,918.32	0.962	-11.02		
313	378.00	0.987	-7.15	-12.04	-8.40
328	1,105.15	0.948	-10.42		
343	386.50	0.990	-7.90		
353	730.00	0.986	-10.00		

The negative value of ΔH_{pass} obtained (Table 2) indicated that, the exothermic behavior of passivation process occurred on the metal surface. Moreover, the negative value of ΔS_{pass} revealed that, the passive film is thermodynamically unstable.

5. CONCLUSION

Mathematical models for passivation isotherm were created as a new approach based on the mechanism of inorganic inhibitors on the metals and alloys surfaces. There are two types of passivation occur on the metal surface, chemipassivity and physipassivity. Further studies should be focused on the types of passivation isotherm.

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Appendix A

REM Program for calculation of concentration of oxygen required as an adsorbed layer for passivation using van der Wall's equation

V=10E+50

FOR I=1 TO 10E+50

B=0.03183: A=1.378: P=1.0235: R=0.08315: T=298.15

P % is atmospheric pressure (bar); R % is universal gas constant (L bar K⁻¹ mol⁻¹); T % is temperature in K and A (L² bar mol⁻²) and B (L mol⁻¹) are constant.

V1=B+((R*T)/(P+(A/V^2)))

C=V1

RO=1/C

IF (C-V=0) then 110

V=C

NEXT I

110 PRINT "Molar Volume of Oxygen (L/mol)=";C, "Density(mol/L)=";RO

END

RUN

Molar Volume of Oxygen (L/mol) = 24.19822 Density (mol/L) = 4.132535E