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Corrosion Inhibition and Adsorption Properties of Soy Polymer Extract of Glycine Mac-L On Mild Steel in Acidic Medium

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ABSTRACT

Soy polymer was extracted from soybean [Glycine Mac-L] and used in studying the corrosion inhibition of mild steel in 2 molar mass solution of hydrochloric acid and compared with the corrosion inhibition properties of poly [vinyl pyrrolidone] in the same acidic medium, using hydrogen evolution method at temperature range of 25-60^{O}C and inhibitor concentration range of 0.01-0.2g/mol. The result of the study shows that soy polymer has higher inhibition efficiency than poly [vinyl pyrrolidone] PVP. The corrosion rate decreased with increasing concentration of soy polymer and PVP while the inhibition efficiency [%1] of both decreased with increased in temperature. The highest value of activation energy obtained with the inhibitors was 62.8kj/mol which supports the mechanism of physical adsorption since it is less than 80.0kj/mol. The negative values of free energy of adsorption ∆Gasd which ranged from – 8.1 to - 3.6 at 60^{O}C and – 17.5 to – 8.7 kj/mol at 25^{O}C suggest spontaneous adsorption. The inhibitors were found to obey Freundlich adsorption isotherm. The soy polymer is more environmentally friendly and more corrosion inhibitive than poly [vinyl pyrrolidone].

Keywords: Soy polymer, Biodegradable, Corrosion, Inhibition, Adsorption

INTRODUCTION

Synthetic and non-degradable polymers have been in use for the control or inhibition of corrosion since the past decades and have posed a serious problem due to their toxicity hence, the need for biodegradable or environmentally friendly polymers or green polymers [1]. These toxic effects not only affect organisms but also poison the earth. As a result, products with high efficiency of function and high environmental friendliness are desired. Therefore, green chemistry or method of corrosion control is not an absolute goal or destination but a dedication to a process for continual improvement, in which the environment is considered alongside the chemistry. Metals exposed to acid pickling and other activities in the industry are attacked by the acid which can be prevented or controlled using inhibitors. Though these inhibitors perform effectively, they impart toxic substance to the environment, which create another hazard even worse than the protection of the metals [1]. Adsorption process is influenced by the nature and surface charge of the metal, by the type of aggressive electrolyte and by the chemical structure of the inhibitor. Adsorption isotherms therefore, are very important in understanding the mechanism of corrosion reactions [4].

LITERATURE REVIEW

The term corrosion is a natural phenomenon, greatly understood as rusting of iron and has since been defined differently by various authors but all definitions led to the degeneration and destruction of metals due to the reaction between the metal and its environment. In 2012, Bill and Hinds defined corrosion as a chemical attack on solid materials particularly metals resulting in reaction between the material and its environment that produces a deterioration of the material and its properties, the environment being acidic, alkali etc [3]. Metals corrode therefore, because the lowest free energy state in many metals in an oxygenated and hydrated environment is that of oxides and when metal atoms ionize and go into solution or combine with oxygen to form a compound that flakes off or dissolves. The surface dissolves when this metal is exposed to different concentrations of acids. Bared metal surface sites become exposed leading to a sequence of electro chemical reactions as the metal dissolves. Hydrochloric acid and sulphuric acid solutions are often used in the industry for cleaning, decaling and pickling of steel structures processes which are normally accompanied by considerable dissolution of the metal and substantial loss of the steel [2]. Since the past many years, the study of the corrosion behaviour of mild steel in different aggressive environments has been attracting considerable attention because of the many important applications of the metal.

In 2012, Rani and Basu defined green inhibitors as naturally occurring substances which are biodegradable and do not contain toxic compounds but contains corrosion inhibitive properties [1]. In 2014, Eashiel portrayed that soybean is a class of the bean family having protein as its predominant part and has variety of compositions including carbohydrates, oil, vitamins, minerals which are in small proportion compared to the protein content [6]. The main make-up of the protein is the amino acid, having both basic amino group [NH_2] and the acidic carboxyl group [COOH]. The soybean [soy protein] exists as a colloidal solution in water called Sol. Sols consist of aggregates of several protein molecules or micelles and are tightly wrapped on an envelope of water and carry an electric change. In solution [in water], amino acid becomes ionized to form dipolar ions called Zwitteronic form meaning harmaphorite in German language [6]. Variation in pH determines whether the ammonium group or the negative carboxylate ion will predominate. Thus, in solution there is deprotonation of carboxylic acid and protonation of the amino group leading to the formation of carboxylate ion [negative] and positive ammonium ion respectively. The successful use of naturally-occurring substances to inhibit corrosion of metals in acid and alkaline environments had been reported by some research groups. Umoren and Ekanem in 2010 studied inhibition of mild steel corrosion in H_2SO_4 using exudates gum from pachylobus edulis and synergistic potassium halide additives and reported that corrosion rate increased with increase in acid concentration [5]. Other researchers had studied inhibition of mild steel corrosion using pineapple leaves extract [2]. Some researchers had carried out studies on corrosion inhibition of mild steel by Amygdalina and polyvinyl pyrolidone in acidic medium using weight loss and hydrogen evolution methods and reported that corrosion rates of mild steel decreased and the inhibition efficiency increased with the increasing concentration of inhibitors while the inhibition efficiency decreased with rise in temperature [4]. The values of activation energy Ea should be less than 80.0kj/mol for a physical adsorption mechanism and the negative values of free energy of adsorption ΔGads up to -20KJ/mol are consistent with electrostatic interaction between the charged metal and charged molecules with signified physical adsorption [4]. Apart from the deleterious effects of hydrogen uptake by a corroding metal, the hydrogen gas evolution agitates the interface dispersing the corrosion product.

PROCESSING PROCEDURE

Collection of Samples

The materials used in this study were Soybean seeds obtained from a local farm in Nigeria, Poly [vinyl pyrolidone][PVP], H polymers, Mild steel, Hydrochloric acid, Ethanol, Acetone, Abrasives and Apparatus; Electronic weighing balance, Standard Gasometrical equipment, Oven, Hand drier were obtained from Nigeria.

Preparation of Mild Steel

Mild steel sheet used was mechanically cut to form different coupons, each of dimension 3 x 3 x 3cm. each coupon was roughed using an abrasive before been degreased with ethanol, dried in acetone and by the use of an electrical hand drier.

Extraction and Modification of Soy Polymer

Soybean seeds were weighed and sorted to remove extraneous material. The seeds were washed with clean water and then cooked in clean boiling water for 30mins. The water was drained off and the seeds dehulled and dried in an oven at temperature of 80^{O}C. the seeds were toasted for 20mins at a temperature between 80^{O} – 100^{O}C. The dehulled and toasted seeds were milled into powdered form using grinding mill. The soybean powder was sieved to obtain a very fine powder.

Preparation of the Corrosion Inhibitor Sample

The soybean fine powder obtained was used in preparing different concentrations of the inhibitor [soy polymer] by dissolving 10g and 50g of the soybean powder in 250ml of distilled water respectively and stirred mechanically to obtain a homogenous solution. The samples are marked in this paper as; SP–1 for the 0.04g/ml concentration of Soy Polymer, SP–2 for the 0.2g/ml concentration of Soy Polymer, PVP–1 for the 0.04g/ml concentration of poly [vinyl pyrolidone], PVP-2 for the 0.2g/ml concentration of poly [vinyl pyrolidone]

EXPERIMENTAL METHOD

Hydrogen Evolution Method

The hydrogen evolution [gasometric] method was carried out as seen in figure 1 and the progress of corrosion reaction was monitored by careful measurement of the volume of hydrogen gas evolved at fixed time intervals.

Theoretical Models

The Freundlich Isotherm model was found to follow the general formula;

$$F[\theta, x]\exp[2a\theta] = Kc \tag{1}$$

Where F [θ, x] is the configuration factor which depends on the physical on the model and assumption underlying the derivative of the isotherm, θ is the surface coverage, C is the inhibitor concentration, X is the size ration, A is the molecular interaction parameter, K is the equilibrium constant of adsorption

Inhibition efficiency [%1] $= \left(1 - \frac{W_i}{W_o}\right) \times 100$ (2)

Where Wi, and Wo are the corrosion rates for mild steel in the presence and absence of the inhibitors respectively.

Corrosion rate [mpy] $= \frac{435w}{eAt}$ (3)

Where w is the weight loss[g], e is the density of the specimen [gcm^{-3}], A is the area of the specimen [cm^2] and the exposure time [h].

Inhibition efficiency $= \left(1 - \frac{V^1_{Ht}}{V^0_{Ht}}\right) \times 100$ (4)

Where V^1_{Ht} and V^o_{Ht} are the volumes of hydrogen evolved at time t for inhibited and uninhibited solutions respectively.

The values of activation energy Ea for mud steel corrosion can be calculated from

$$LogCR = LogA - \frac{E_a}{2.303RT} \quad (5)$$

Where CR = corrosion rate, A is the Arrhenius constant or pre-exponential factor, Ea is the activation energy of the reaction, R is the gas constant and T is the temperature.

The equation below can still be obtained by substituting the corresponding values of corrosion rates [$e_!$ And e_2] at $25^{O}C$ [T_1] and 60^oC [T_2] respectively.

$$Log\frac{e_2}{e_1} = \frac{E_a}{2.303R} \quad (6)$$

The free energy of adsorption ΔGads values are obtained from

$$LogC = Log\left(\frac{\theta}{1-\theta}\right) - LogB \quad (7)$$

Where $LogB = -1.74 - \left[\Delta Gads / 2.303RT\right]$

C is the concentration of the inhibitor and θ is the surface coverage.

$$\theta = 1 - \frac{W_1}{W_0} \quad (8)$$

where w_o and $w_{1\ are}$ the corrosion rates for mild steel in absence and presence of inhibitor respectively.

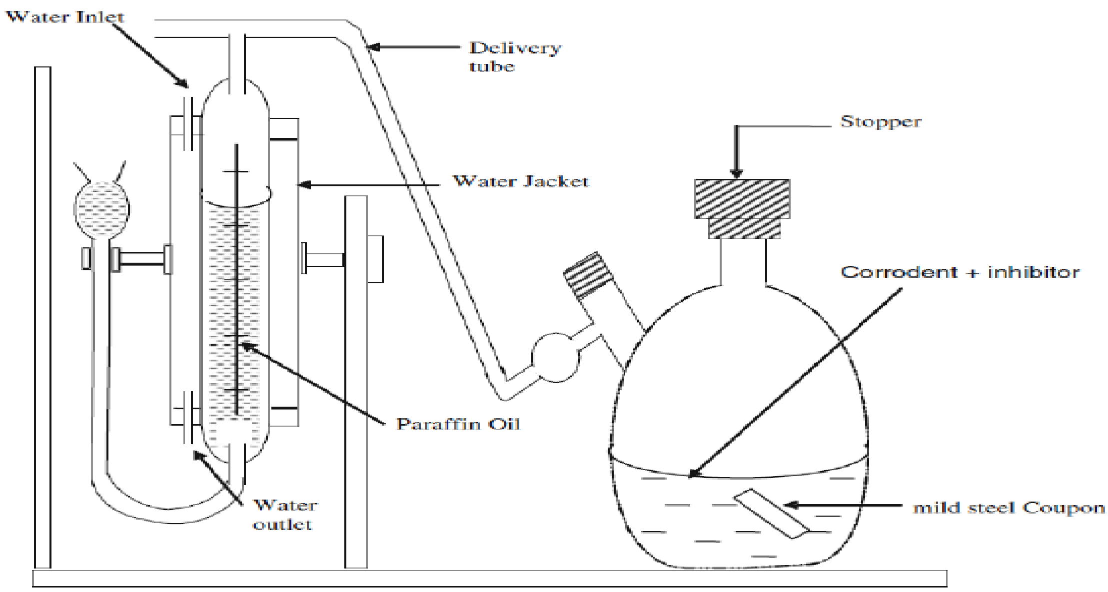

Fig. 1A Diagram of the Gasometric Apparatus used for Hydrogen Gas Evolution Method

RESULTS

The results in Table 1, figures 2 and 3 show that amount of hydrogen gas evolved was reduced in the presence of soy polymer and PVP with respect to time, concentration and temperature. Table 2 shows that increase in concentration of inhibitor decreases corrosion rate and increases inhibition efficiency while rise in temperature increases corrosion rate and decreases inhibition efficiency. The values of activation energy Ea in Table 2 which is 26.1kj/mol in the absence of the inhibitor and range from 48.2 to 62.8kj/mol in the presence of inhibitor support the mechanism of physical adsorption. Also in Table 2, the negative values of free energy of adsorption ΔGasd which ranged from – 8.1 to - 3.6 kj/mol at 60^{O}C and from – 17.5 to – 8.7 kj/mol at 25^{O}C show spontaneous physical adsorption. The free energy of adsorption obtained increased with temperature and concentration indicating more interaction between the metal and the inhibitors. The results in Table 3 and linear plot in figure 4 show that Freundlich isotherm was obeyed and adsorption of the inhibitor onto the mild steel surface is by physical adsorption. The soy polymer which is usually protonated at the N atom in the acidic solution can interact with the metal surface through electrostatic interaction [physical adsorption] and can be adsorbed at the cathodic sites and then, hinders the hydrogen evolution reaction with possible contribution from the lone pair of electrons on the oxygen atom.

Table -1 Values of Hydrogen Gas Evolved for Mild Steel Corrosion in 2M Hcl in the Absence and Presence of the Inhibitors for Different Concentration [0.04g/ml - 0.2g/ml] at 25^0C and 60^0C

Temp.	Time[Hour]	Blank	PVP -10.04g/ml	PVP -20.2g/ml	SP -10.04g/ml	SP -20.2g/ml
25^0C	5	0.47	0.83	0.30	0.15	0.04
	10	0.85	0.83	0.75	0.24	0.12
	15	1.42	0.89	0.80	0.33	0.20
	20	1.99	0.93	0.83	0.42	0.28
	25	2.50	0.97	0.88	0.51	0.38
	30	3.01	0.98	0.90	0.60	0.44
	35	3.54	1.50	0.95	0.66	0.52
	40	3.94	1.51	0.97	0.76	0.59
	45	4.33	1.60	1.01	0.88	0.66
	50	4.67	1.66	1.37	1.00	0.69
60^0C	5	0.90	0.66	0.42	0.14	0.45
	10	1.82	0.83	0.49	0.35	0.50
	15	2.75	1.08	0.50	0.48	0.53
	20	3.66	1.32	0.54	0.56	0.55
	25	4.56	1.45	0.55	0.61	0.56
	30	5.49	1.50	0.72	0.71	0.74
	35	6.38	1.59	0.85	0.72	0.86
	40	7.26	1.69	0.90	0.85	0.93
	45	8.10	1.82	0.99	0.82	1.02
	50	8.83	1.99	1.00	0.99	1.75

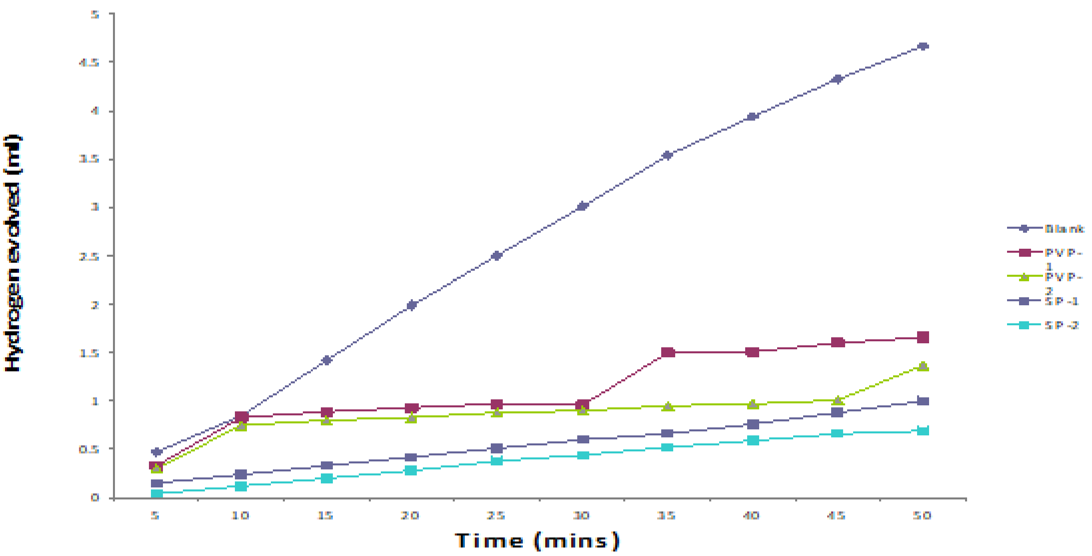

Fig 2 Hydrogen evolved-time curves for mild steel corrosion on 2M Hcl in the absence and presence of the different concentrations of the inhibitors at 25^{O}C

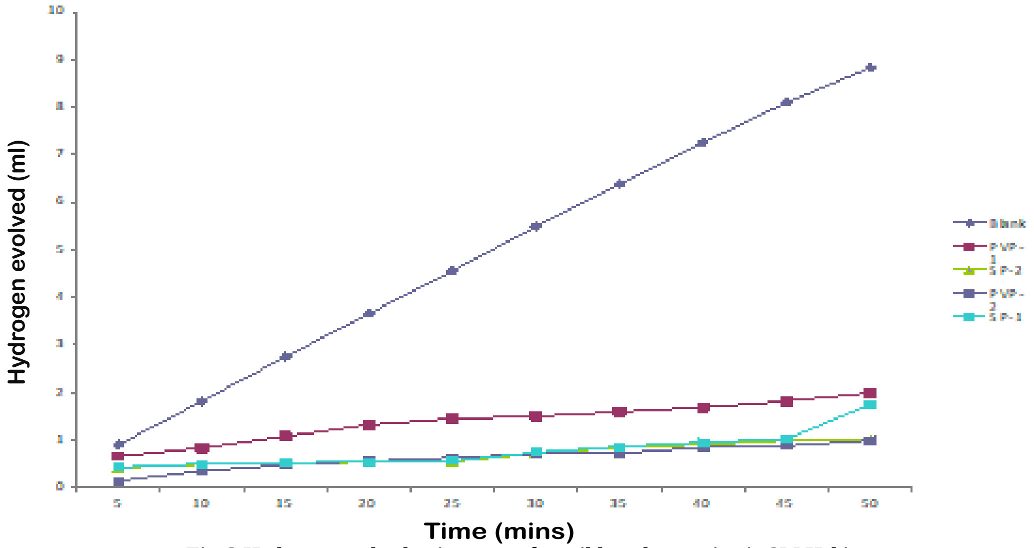

Fig. 3 Hydrogen evolved – time cures for mild steel corrosion in 2M Hcl in the absence and presence of the different concentrations of the inhibitors at 60^{O}C

Thermodynamics and Adsorption Consideration

Table -2 Calculated values of Activation Energy, Corrosion Rate [mpy], Inhibition Efficiency [%1] and Free Energy of Adsorption for Mild Steel Corrosion in 2M Hcl for Different Concentrations [[0.04g/ml - 0.2g/ml] at 25 and 60^{O}C

			PVP -1[0.04g/ml]		PVP -2 [0.2g/ml]		SP -1 [0.04g/ml]		SP -2 [0.2g/ml]	
Activation Energy Ea [kj/mol]	26.50		48.20		51.90		55.80		62.80	
Temperature	25^{O}C	60^{O}C	25^{O}C	60^{O}C	25^{O}C	60^{O}C	25^{O}C	60^{O}C	25^{O}C	60^{O}C
CorrosionRate	9.30	17.66	1.28	2.20	1.10	2.02	2.00	3.68	1.48	3.80
InhibitionEfficiency	-	-	53.21	39.23	64.92	44.81	78.59	42.43	84.15	38.91
Free Energy of Adsorption	-	-	- 17.5	- 8.1	-10.2	- 7.8	-15.0	- 6.2	- 8.7	- 3.6

Table -3 Values for Freundlich Adsorption Isotherm for Mild Steel Corrosion in 2m Hcl in the Presence of Inhibitor at 25^{O}C and 60^{O}C

Temperatures		PVP -1[0.04g/ml]	PVP -2 [0.2g/ml]	SP -1 [0.04g/ml]	SP -2 [0.2g/ml]
25^{O}C	Log [%1]	1.896	1.924	1.621	1.792
	Log Conc	1	1.699	1	1.699
60^{O}C	Log [%1]	1.583	1.602	1.342	1.491
	Log Conc	1	1.699	1	1.699

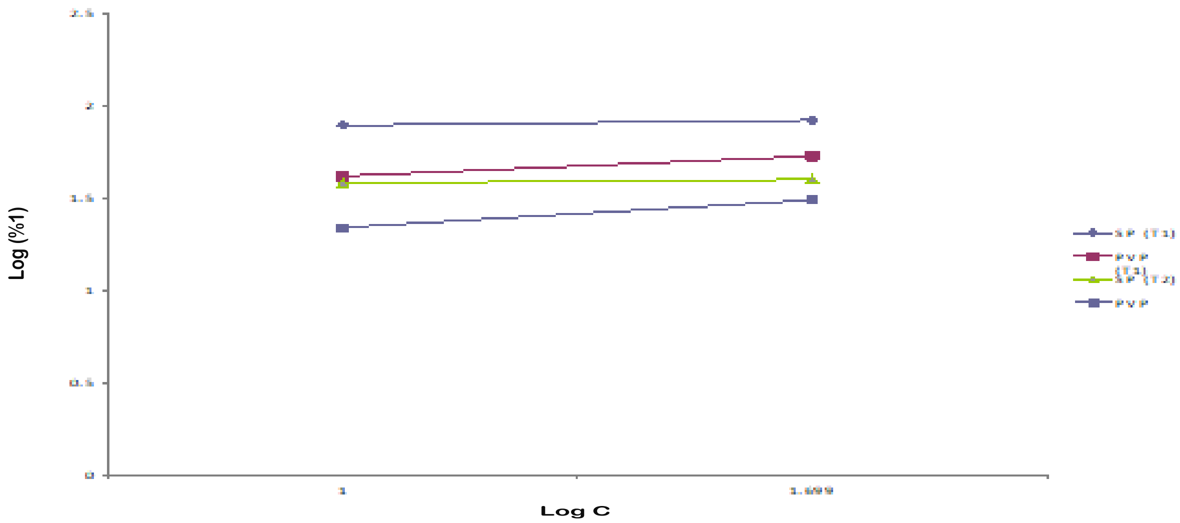

Fig. 4 Friendrich adsorption isotherm curves for mild steel corrosion in 2m Hcl in the presence of inhibitors at 25^{O}C - 60^{O}C

CONCLUSION

It can be concluded based on this study that soy polymer obtained from soybean [Glycine Mac-L] is suitable to be used as a corrosion inhibitor for mild steel in an acidic medium and it has better inhibitive properties than poly [vinyl pyrrolidone] with respect to temperature, time and concentration. The interaction between the inhibitor and mild steel is by physical adsorption. The soy polymer is an environmentally friendly inhibitor since its source soybean is obtained naturally from plant.

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