Palm Olein Corrosion Inhibitor For Aluminium In Hcl Solution

Junaidah Jai[1] and Wan Shabuddin Wan Ali

Faculty of Chemical Engineering,
Universiti Teknologi MARA,
60340450 Shah Alam, Malaysia
[1]Email: junejai@salam.uitm.edu.my

ABSTRACT

Aluminium (Al) is a low cost, lightweight and corrosion resistant material, which corrodes when exposed to pitting agents. Palm olein exhibits characteristics, which indicate its suitability as a corrosion inhibitor. Tween 20, hexane and diethyl triamine were used as additives to Palm olein to form the inhibitor formulation POT20HA. The inhibition efficiency (IE) and behaviour of the POT20HA were determined using potentiodynamic polarization in which Al 6061 samples were immersed in a 1 M HCl solution at 26, 50 and 70 ^{o}C in the presence of different POT20HA concentrations: 0, 0.03, 0.07, 0.10, 0.13 and 0.17 M. The IE increased with increasing POT20HA concentration, but decreased with increasing temperature. The work presented indicates that POT20HA is a mixed-type inhibitor capable of inhibiting both corrosive anodic and cathodic reactions. According to the Langmuir isotherm results POT20HA adsorbs on the Al 6061 surface through semi-physiosorption and/or semi-chemisorption. The POT20HA adsorption mechanism on Al 6061 takes through the protonation of micelles by the HCl solution, whereby protonated micelles in the presence of chloride ions adsorb on both cathodic and anodic surface corrosion sites.

Keywords: Aluminium; Polarization; Acid corrosion; Adsorption mechanism; Adsorption isotherm relationship

Introduction

Oil and water are immiscible, but in the presence of suitable additives in appropriate concentrations oil in water produces an emulsion. Emulsions are widely used as lubricants, cutting oils, coatings, textile finishing, detergents, cosmetics, agrochemicals, food, pharmaceuticals and, more importantly, corrosion inhibitors [1].

There has been increasing interest in the use of natural products as corrosion inhibitors, such as organic compounds synthesized and extracted from aromatic herbs, spices or medical plants. Raja and Sethuraman [2] stated that natural compounds have the potential to be highly effective corrosion inhibitors since they are biodegradable, readily available and are non-toxic. Extensive research has been performed on natural extracts including *vanillin* [3], *opuntia* [4], *khillah* [5], *sansevieria trifasciata* [6], *lawsonia* [7], *azadirachta indica leaves* [8], *olive leaves* [9], *phyllanthus amarus* [10], *occimum viridis* [11], *nypa fruticans wurmb* [12], *fenugreek leaves* [13], berberine extracted from *coptis chinensis* [14] and *musa sapientum peel* [15]. The presence of certain functional groups within the molecular structure of these natural extracts contributes to their ability to inhibit corrosion. For instance the carbonyl, methoxy and hydroxyl groups arranged around the aromatic rings in *vanillin* inhibit the corrosion of metal surfaces [3]. *Opuntia* extract comprises mainly of polysaccharides; a mixture of mucilage and pectin, which act as a barrier to mass and charge transfer and consequently protects the metal surface from aggressive anions [4]. The use of natural dyes as corrosion inhibitors; congo red [16], bismark brown [17], methylene blue dye [18], mangrove tannin [19], vegetal tannin [20], chestnut tannin [21] and mimosa tannin [22], is well-documented.

Natural oil is another promising corrosion inhibitor and pennyroyal oil from *mentha pulegium* [23] has been successfully used as a corrosion inhibitor for steel in HCl solutions. Adsorption of pennyroyal oil on the steel surface was achieved using *R*-(+)-*Pulegone* as the principal constituent of the essential oil. Artemisia oil extracted from *artemisis herba alba* contains β-*thujone* and has also been found to inhibit steel corrosion [24]. Yaakob reported that palm olein from Crude Palm Oil (CPO) exhibited potential as a mild steel corrosion protector in acidic solutions [25]. CPO contains equal amounts of saturated and unsaturated fatty acids; palm stearin and palm olein, respectively. The main component of palm olein is oleic acid $(C_{18}H_{34}O_2)$ which contains a carboxylic acid group and single double bond.

The presence of the two π-bond systems is believed to enable adsorption on the metal surface, which is in accordance with the work of El-Etre who reported that large molecular structures with double bonds, reactive centres or groups are able to adsorb and cover large metal surface areas [9].

Palm olein itself exhibits significant potential as a corrosion inhibitor, however it needs to be soluble and stable in the selected medium. In order for an oil based inhibitor to effective in an aqueous medium requires the natural immiscibility to be overcome through the application of suitable surfactants or emulsifiers.

Emulsifiers consist of two parts, namely, a polar hydrophilic head and a polar lipophilic tail, where the head can be cationic, anionic, amphoteric or non-ionic and the tail is a hydrocarbon chain [26]. Emulsifiers placed in a mixture of water and oil arrange with respect to preferred solubility, so that the head is in the water and the tail is in the oil [27].

Popular emulsifiers for oil in water are poly(oxyethylene) x-sobitane-monolaurate (Tween 20), sorbitan monooleate (Span 80), polyoxyethyleneglycol dodecyl ether (Brig35) and polyoxyethylene (20) sorbitan monooleate (Tween 80) [28]. Saturated emulsifier water-oil mixtures spontaneously produce thermodynamically stable micelles at the immiscible-phase boundary, Figure. 1 [27].

Chamnamai *et al.,* [29] reported that non-ionic emulsifiers, such as Tween 20 (Figure. 2), can be used to stabilize emulsions by controlling micelle growth of micelles size.
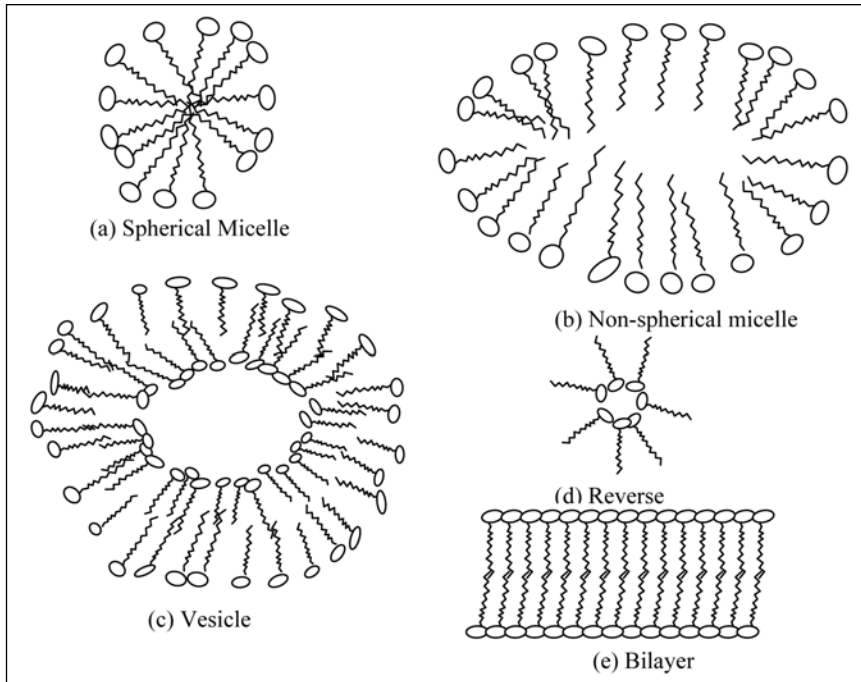
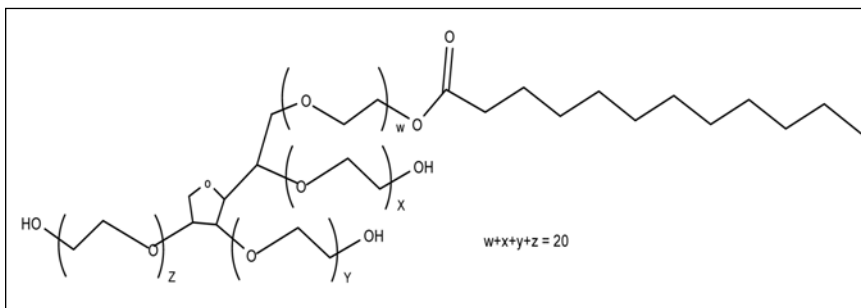Figure 1: Different Types of Micelle Structures [27]

Figure 2: Molecular Structure of Poly(oxyethylene)x-sobitane-monolaurate (Tween 20)

Goyal reported that the intermolecular forces between the emulsifier molecules in the presence of water are weak and can be easily modified by manipulating them through the addition of salts or changing the

temperature [30]. Heating mixtures beyond the cloud point; the point at which wax crystals first precipitate in oils, causes micellar solutions to separate into two phases; one rich and the other dilute in micelles. Non-ionic micellar interactions are dominated by van der Waal's forces, but are limited by hydration and the water molecules attached to the hydrophilic micellar heads. As the temperature of micellar solutions increases hydration decreases, and hence van der Waal's interactions become stronger and interaction between non-ionic micelles becomes more desirable leading to phase separation and the formation of two phases.

There are four thermodynamically stable types of emulsion [31]:

1.   Winsor I; oil is emulsified in the water phase and the water phase appears turbid and contains solubilized oil. The upper excess oil phase is clear.
2.   Winsor II; water is emulsified in the oil phase and this phase appears turbid and contains solubilized water. The lower excess water phase is clear.
3.   Winsor III; a turbid middle phase, in which both oil and water solubilize. Excess water and oil phases exist. The middle phase presented is a bi-continuous system, but different structures are possible.
4.   Winsor IV; an extension of Winsor III. In the Winsor IV system, there is no excess oil and water present; they are fully solubilized by the large volume of surfactant.
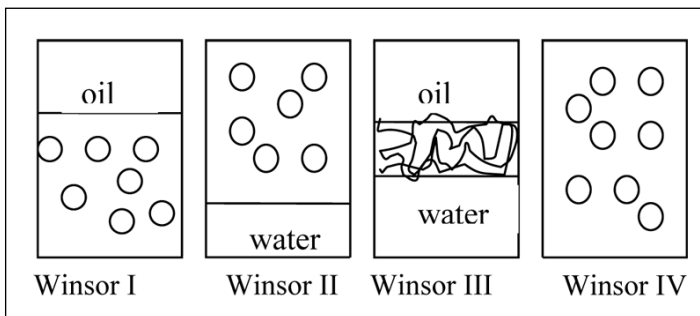

Figure 3: Winsor Emulsions

53

The identification of an emulsion system for a specific application requires the determination of specific quantities of oil and emulsifier. Stuwold *et al.* determined that the weight to weight ratios of oil and emulsifier required to effectively protect aluminium against staining lie in the range 5:1 to 1:2 [32].

Micelle size contributes significantly to emulsion stability for which smaller micelles are more desirable and can be achieved with respect to manipulation of the emulsion pH and temperature. Liu et al. reported that nano-emulsions of paraffin oil in water with micelle size below 200 ηm could be obtained at 50 °C due to a decrease in cohesion forces between the oil molecules [28]. Guzey *et al.* investigated aqueous corn oil micelles and determined that at pH 7 small micelles 0.35-6 μm in diameter were produced [33].

Additives can also be used to stabilize emulsions. Akzo Nobel Surfactants reported the use of iso-propanol as a stabilizer in an aqueous oil-based inhibitor [34], other physical stabilizers that have been used include waxes, cellulose derivatives and resins [35]. Diethylenetriamine (DETA), a wax, has been successfully used as an additive in conjunction with palm olein to protect mild steel [25]. In the presence of a suitable emulsifier and stabilizing agents natural oils can be formulated into an effective water soluble corrosion inhibitor.

Corrosion inhibitors adsorb to metal surfaces through physical and chemical adsorption. Physical adsorption or physisorption occurs when the Gibbs free energy (ΔG^o_{ads}) is less than zero yet greater than -20 kJ/mol and bonding between the inhibitor and metal surface can be attributed to van der Waals forces. Chemical adsorption or chemisorption is the formation of a chemical bond between the inhibitor molecules and the metal surface when the ΔG^o_{ads} is more negative than -40 kJ/mol [36]. If the ΔG^o_{ads} value lies in the range -20 to -40 kJ/mol adsorption is considered to be semi-physiosorption and/or semi-chemisorption [37]. The negative Gibbs free energy corresponds to inhibitor adsorption on the metal surface being a spontaneous process.

An isotherm is a curve, described by an equation, which corresponds to the molecules attached to a surface at various concentrations at a fixed temperature. There are several adsorption models that have been used to interpret the inhibition mechanism of corrosion inhibitors; the most common of which are Langmuir, Temkin and Frumkin [38,13]. The Frumkin adsorption isotherm is as follows [39,40]:

$$\ln\left(\frac{\theta}{C(1-\theta)}\right) = \ln K + 2a\theta \tag{1}$$

where θ is the surface coverage (θ = IE/100), C is the inhibitor concentration, K is the binding constant for the adsorption reaction and 'a' is the lateral interaction term, which describes the molecular interactions in the adsorption layer and the heterogeneity of the surface. A plot of $\ln[\theta/C(1-\theta)]$ versus θ yields values for both 'a' and 'K', where 'a' may take both positive and negative values for which positive values indicate an increase in adsorption energy. Small binding constant values, K, indicate weak interaction between the adsorbed molecules and the metal surface, which inherently implies that the inhibitor can be easily removed.

The Temkin adsorption isotherm is as follows [41,42]:

$$\theta = \left(\frac{1}{f}\right)\ln(KC) \tag{2}$$

where f is a molecular interaction parameter related to interactions in the adsorption layer and the heterogeneous surface, and K is the adsorption equilibrium constant. Plotting θ versus ln C yields values for 'K' and 'f'.

Corrosion inhibitors derived from natural compounds, which tend to form monolayers, are generally well-described by the Langmuir adsorption isotherm [15,5,7,13,12]. The Langmuir adsorption isotherm may be expressed as follows:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{3}$$

where K (M^{-1}) is the equilibrium adsorption constant and can be determined by plotting C/θ versus C.

The work presented focuses on palm olein as a corrosion inhibitor for Al 6061 exposed to a 1 M HCl solution and is evaluated with respect to polarization, adsorption isotherms and a proposed adsorption mechanism.

Materials and experimental procedure

The material studied was an aluminium alloy (Al 6061) suitable for automotive application. A stock emulsion solution was prepared by blending palm olein (PO), obtained from crude palm oil supplied by Jugra Palm Oil, Banting, Selangor, Malaysia, and the emulsifier poly(oxyethylene) x-sobitane-monolaurate (T20) in the ratio 5:1 (w/w) (PO:T20). The PO was obtained from crude palm oil supplied by Jugra Palm Oil, Banting, Selangor, Malaysia. The inhibitor formulation was prepared by blending 25 vol.% of the stock (POT20) solution with 0.5 vol.% hexane (H) and distilled water at pH 7 and 50 °C for 1 hour. The blended emulsion solution was then allowed to settle in a separating funnel for 1 day before the bottom layer (the dilute emulsion) was collected. DETA was added to the dilute emulsion (POT20H) in the volume ratio 50:2 (POT20H:DETA) before stirring for 30 min at room temperature. The resultant formulation was labeled as POT20HA and analysed with respect to pH, micelle shape and size. The concentration of the POT20HA formulation was determined by performing acid-base titrations using POT20HA aqueous solutions run with a 0.1 M HCl solution. For the purposes of POT20HA concentration calculations it was assumed that neutralization occurred according to the following equation [43]:

$$POT20HA: + H\text{-}Cl \rightarrow Cl^- + POT20HA\text{-}H \qquad (4)$$
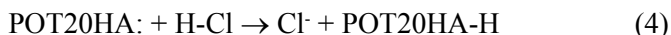
The results of the titration calibrations are presented in Table 1 below:

Table 1: POT20HA Calibration

% (v/v)	Molarity (M)
10	0.03
20	0.07
30	0.10
40	0.13
50	0.17
100	0.33

Polarization tests were performed on Al 6061 samples of size 1 cm × 1 cm × 0.03 cm, which had been degreased in an acetone solution for 30

minutes, rinsed using distilled water and dried. Samples were mounted in a blend of EpoFix resin and hardener from Stuers so that only 1 cm² surface area was left exposed to the corrosive media. The exposed surface was mechanically polished with 180 and 600 grade sandpaper, cleaned with distilled water and acetone, and dried.

Polarization measurements were performed in a three-electrode electrochemical cell with a 2 cm² platinum mesh counter electrode and a Saturated Calomel Electrode (SCE) reference using a Voltalab (PGP201) connected to a personal computer to provide the potential for the tests. Prior to measurement, electrodes were immersed in a test solution for 60 minutes under open circuit conditions to attain steady state. The potentiodynamic polarization measurements were performed at a scanning rate of 1 mV/s, starting from a potential of -1200 and increasing to +200 mV with respect to the SCE. Tafel curves were constructed and used to determine the corrosion behaviour of the samples with respect to the corrosion potential (E_{corr}), corrosion current density (i_{corr}), polarization resistance (R_p), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and Corrosion Rate (*CR*). The inhibition efficiency (IE) for the potentiodynamic polarization tests was calculated according to the following equation:

$$IE\% = \left(\frac{CR^0 - CR}{CR^0} \right) \times 100 \tag{5}$$

where CR and CR⁰ are the corrosion rates of Al 6061 in the presence and absence of the inhibitor, respectively. All tests were performed multiple times at 299, 323 and 343 K using POT20HA concentrations of 0.00, 0.03, 0.07, 0.10, 0.13 and 0.17 M in 1 M HCl solutions to ensure reproducibility.

Results and Discussions

Table 2 presents the electrochemical parameter results for the Al 6061 samples immersed in 1 M HCl. It is evident that the corrosion potential (E_{corr}), corrosion current (i_{corr}) and the CR exhibit a general decrease in magnitude with increasing POT20HA concentration, whereas the converse is true for the polarization resistance (R_p). The R_p increased significantly as the POT20HA increased to 0.17 M and may be attributed to improved

surface coverage, which also corresponds to an increase in IE. It is of note that there is greater disparity in the IE values with increasing temperature and concentration, which may be attributed to increased corrosion activity at higher temperatures. The anodic and cathodic Tafel slope values, β_a and β_c, respectively, change with concentration and indicates that the inhibitor's presence may affect the cathodic and anodic corrosion reactions. The Tafel curves have been used to evaluate this hypothesis.

Table 2: Polarization Test Results with Respect to Concentration and Temperature

| Parameter	E_{corr} (mV)	i_{corr} (mA/ cm²)	R_p (ohm. cm²)	β_a (mV)	β_c (mV)	Corrosion rate (mm/y)	IE (%)
Concentration of POT20HA				299 K			
Blank	-759	33.504	5.65	922.9	-1209	375.20	-
0.03 M	-779	0.639	14.56	131.4	-197	7.16	98
0.07 M	-784	0.417	15.79	84.8	-170	4.67	99
0.10 M	-750	0.394	31.20	159.8	-303	4.41	99
0.13 M	-756	0.158	38.56	90.4	-272	1.77	100
0.17 M	-722	0.020	792.44	37.0	-554	0.219	100
				323 K			
Blank	-806	37.823	2.54	571.7	-715	423.600	-
0.03 M	-809	5.000	5.33	110	-287	61.280	86
0.07 M	-775	4.464	40.03	336.4	-405	14.760	97
0.10 M	-761	0.673	43.69	229.9	-287	6.781	98
0.13 M	-754	0.775	129.89	308.1	-369	7.812	98
0.17 M	-736	0.006	1530	74.8	-959	0.006	100
				343 K			
Blank	-831	30.957	1.98	347.2	-453	346.700	-
0.03 M	-849	3.945	14.64	193.2	-342	44.180	87
0.07 M	-809	2.733	29.21	553.8	-475	30.600	91
0.10 M	-803	1.245	20.53	101.3	-262	13.940	96
0.13 M	-800	1.270	64.68	4.3	-452	14.220	96
0.17 M	-740	0.493	774.20	321.7	-31	4.966	99
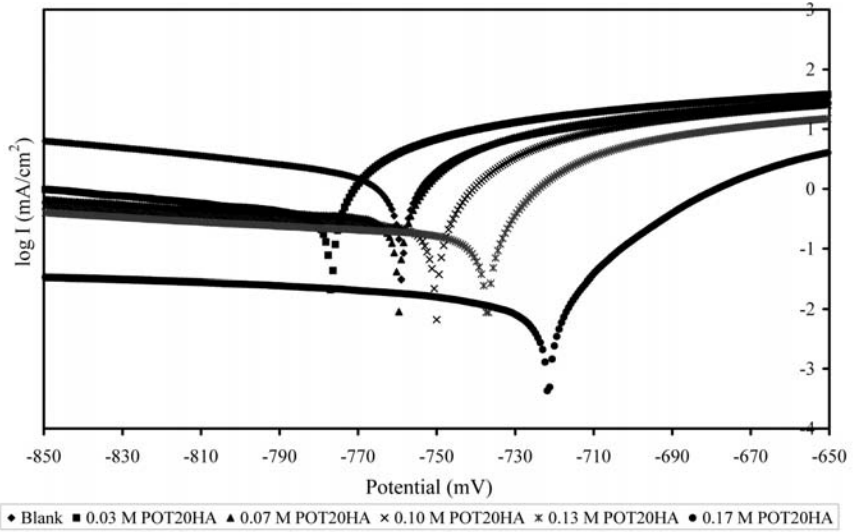
Figure 4: Polarization Curve for Al 6061 Samples Immersed
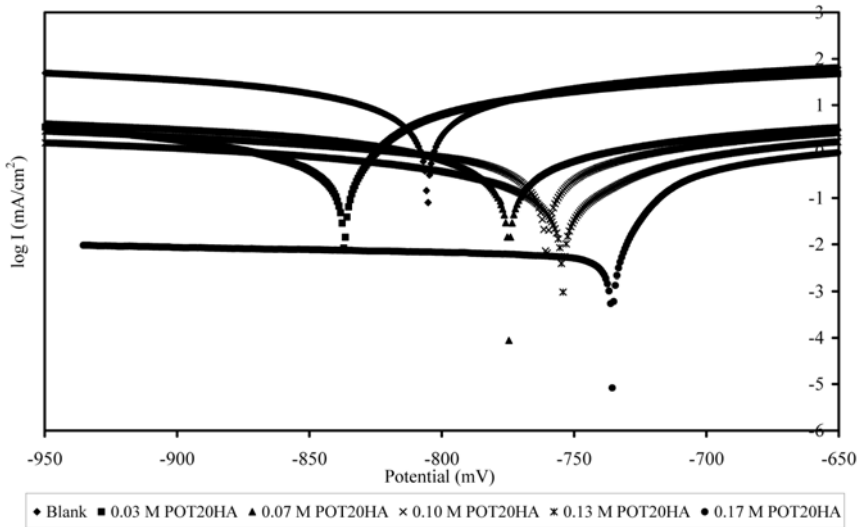in 1 M HCl at 299K

Figure 5: Polarization Curve for Al 6061 Samples Immersed
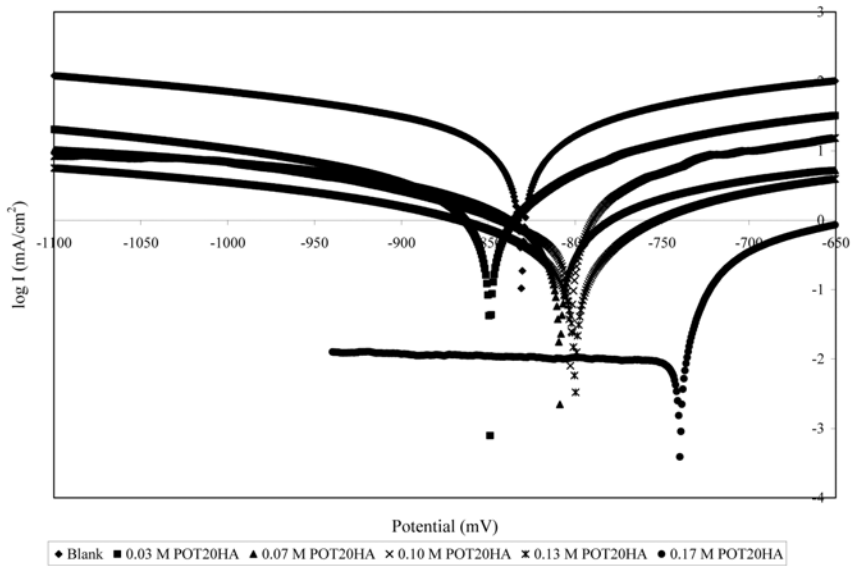in 1 M HCl at 323K

Figure 6: Polarization Curve for Al 6061 Samples Immersed
in 1 M HCl at 343K

The Tafel curves presented in Figures 4, 5 and 6 indicate that increasing the POT20HA concentration suppresses and above 0.07 M consistently shifts the anodic (right) and cathodic (left) branches of the Tafel curves to the right. The E_{corr} difference between the POT20HA and the blank was less than 85 mV, which means that POT20HA can be classified as a mixed type inhibitor with predominantly anodic action if concentrations of 0.07 M and above are used or cathodic action in the case of 0.03 M [44,45]. These results indicate that POT20HA inhibits both anodic and cathodic corrosion reactions.

Adsorption isotherm

Analysis of the adsorption isotherms was performed using the Frumkin, Temkin and Langmuir models. Table 3 presents the results of the coefficient of determination (R^2) analysis with respect to the three considered models from which it is evident that only the Langmuir isotherm model, which assumes no interaction between adsorbed species and thus enables surface

saturation to occur, describes the experimental data sufficiently well. It is therefore likely that monolayer inhibitor adsorption occurs on the Al surface [46].

Table 3: Evaluation of the Adsorption Isotherm Models

Temperature, K	Frumkin	Temkin	Langmuir
299	0.4089	0.9129	1.0000
323	0.3967	0.8901	0.9997
343	0.3491	0.9545	0.9991

The standard free energy of adsorption, ΔG^o_{ads} (kJ/mol), with respect to temperature have been determined according to the van't Hoff equation [36]:

$$\ln K = \ln \frac{1}{55.5} - \frac{\Delta G^0_{ads}}{RT} \tag{6}$$

where (1/55.5) is the relative molar density with respect to pure water, R is the universal gas constant 8.314 J/(mol.K) and T(K) is the temperature. Table 4 presents the K and ΔG^o_{ads} values with temperature for the evaluated Langmuir curves for which it should be noted that all ΔG^o_{ads} values lie in the range -20 to -40 kJ/mol, thus indicating semi-physiosorption and/or semi-chemisorption of inhibitor molecules onto the metal surface [37].

Table 4: Langmuir Isotherm Model Analysis Results

Temperature (K)	K (M^{-1})	ΔG^o_{ads} (kJ/mol)
299	982.12	-27.11
323	193.45	-24.92
343	151.52	-25.77

Adsorption Mechanism

The adsorption mechanism of the inhibitor on the Al surface has been evaluated with respect to emulsion analysis. The POT20HA emulsion contains spherical micelles of diameter 0.04-300 μm, Figure. 7 and 8, and are negatively charged according to the work of Liu and Guo [47], since the emulsion is alkaline. If the micelles are negatively charged they are capable of forming electrostatic bonds or being physically adsorbed on the positively charged Al 6061 surface.
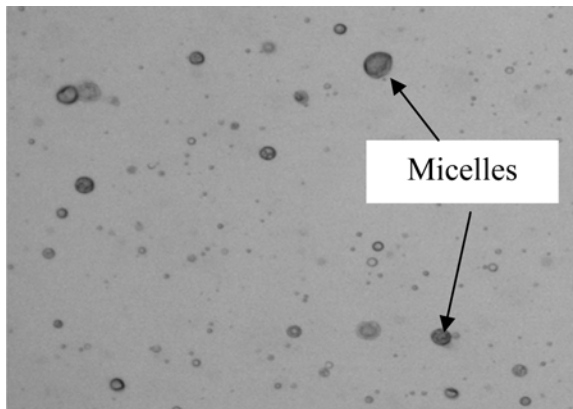

Figure 7: Micelles in the POT20HA Emulsion

The Langmuir and potentiodynamic polarization results indicate that POT20HA physiadsorbs on the Al surface through weak van der Waal forces and acts as a mixed type inhibitor able to inhibit both anodic and cathodic corrosion reactions. Under corrosion conditions, through exposure to a 1 M HCl solution, the micellar POT20HA is expected to be fully protonated [48].
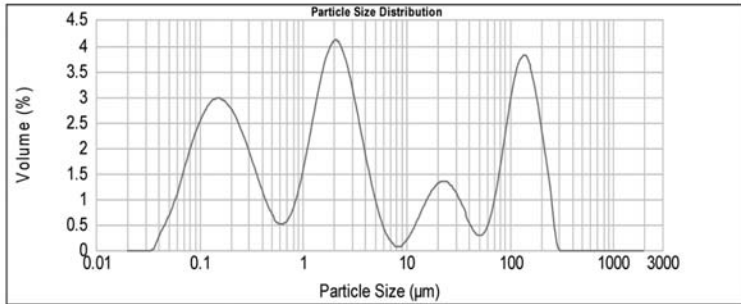
Figure 8: POT20HA Micelle Size Analysis

If the micelles are cationic species they will adsorb on the cathodic corrosion surface sites and block H_2 evolution. Figure. 9(a) and (b) present a schematic illustration of a spherical micelle and a schematic of the attachment of protonated micelles on the cathodic sites of the Al surface, respectively.
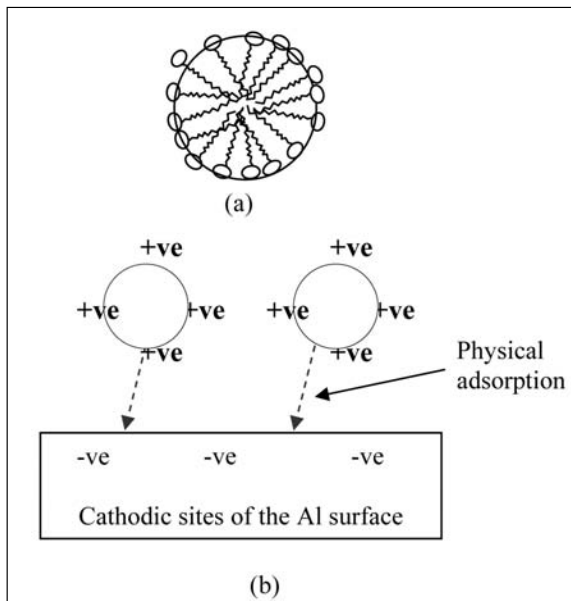

Figure 9: Schematic Representation of (a) a Spherical Micelle and (b) the Attachment Mechanism of Protonated Micelles on the Al Surface

Protonated micelles can also be expected to adsorb on the anodic Al surface through electrostatic interactions with chloride ions (Cl⁻) from the 1 M HCl solution which adsorbed on the anodic corrosion sites on the Al surface thus forming a negatively charged layer, Figure 10. The presence of POT20HA as a corrosion inhibitor in a 1 M HCl solution can control the dissolution of Al as well as the evolution of H_2.
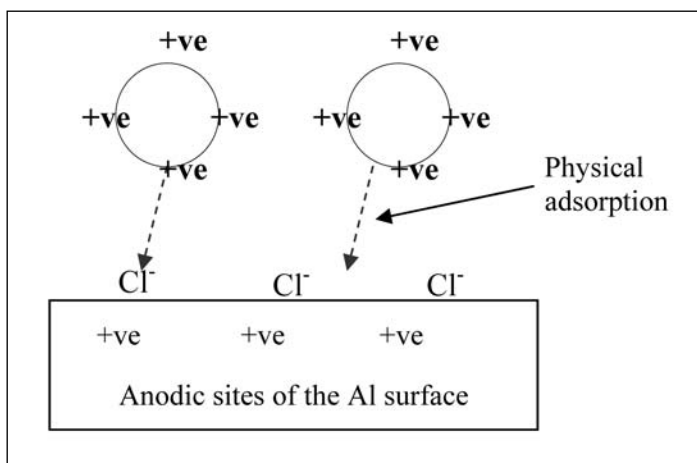

Figure 10: Schematic Representation of the Attachment Mechanism of Protonated Micelles on the Anodic Al Surface

Conclusion

POT20HA exhibits significant potential as a corrosion inhibitor, particularly at high HCl concentrations (0.17 M). The results of the potentiodynamic polarization and Langmuir isotherm analyses indicate that it is a mixed type corrosion inhibitor with the potential to inhibit both anodic and cathodic corrosion reactions, and that POY20HA adsorbs on the Al 6061 surface through semi- physiosorption and/or semi-chemisorption. It is proposed based upon the results of this work that in the presence of a 1 M HCl solution the POT20HA is fully protonated and is capable of physiadsorbtion to both cathodic and anodic sites on the Al surface through weak van der Waal forces and electrostatic interactions, respectively.

Acknowledgements

References

[1] B.K. Paul, S.P. Moulik, 2001. 'Uses and applications of microemulsions', *Current Sci.,* 80(8), pp. 990 – 1001.

[2] P.B. Raja, M.G. Sethuraman, 2008. 'Natural products as corrosion inhibitor for metals in corrosive media - A review', *Mat. Lett.,* 62(1), pp. 113 – 116.

[3] A.Y. El-Etre, 2001. 'Inhibition of acid corrosion of aluminium using vanillin', *Corros. Sci.,* 43, pp. 1031 – 1039.

[4] A.Y. El-Etre, 2003. 'Inhibition of aluminium corrosion using opuntia extract', *Corros. Sci.,* 45, pp. 2485 – 2495.

[5] A.Y. El-Etre, 2006. 'Khillah extract as inhibitor for acid corrosion of SX 316 steel', *Applied Surface Sci.,* 252(24), pp. 8521 – 8525.

[6] E. E. Oguzie, 2007. 'Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract', *Corros. Sci.,* 49, pp. 1527 – 1539.

[7] A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, 2005. 'Corrosion inhibition of some metals using lawsonia extract', *Corros. Sci.,* 47, pp. 385 – 395.

[8] L. Valek, S. Martinez, 2007. 'Copper corrosion inhibition by Azadirachta indica leaves extract in 0.5 M sulphuric acid', *Mat. Lett.,* 61, pp. 148 – 151.

[9] A.Y. El-Etre, 2007. 'Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves', *J. of Colloid and Interface Sci.,* 314, pp. 578 – 583.

[10] P.C. Okafor, *et al.,* 2008. 'Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media', *Corros. Sci.,* 50(8), pp. 2310 – 2317.

[11] E.E. Oguzie, 2006. 'Studied on the inhibitive effect of Occimum viridis extract on the acid corrosion of mild steel', *Material Chem. and Phy.,* 99, pp. 441 – 446.

[12] K. O. Orubite, N.C. Oforka,. 2004. 'Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of *Nypa fruticans Wurmb'*, *Mat. Lett.,* 58, pp. 1768 – 1772.

[13] E.A. Noor, 2007. 'Temperature effects on the corrosion inhibition of mild steel in acidic solutions by aqueous extract of Fenugreek leaves', *Inter. J. of Electrochem. Sci., 2,* pp. 996 – 1017.

[14] Y. Li, P. Zhao, Q. Liang, B. Hou, 2005. 'Berberine as a natural source inhibitor for mild steel in 1 M H_2SO_4', *Applied Surface Sci.,* 252(5), pp. 1245-1253.

[15] N.O. Eddy, E.E. Ebenso, 2008. 'Adsorption and inhibitive properties of ethanol extracts of Musa sapientum peels as a green corrosion inhibitor for mild steel in H_2SO_4, *African J. of Pure and Applied Chem.,* 2(6), pp. 046 – 054.

[16] E.E. Oguzie, E.E. Ebenso, 2006. 'Studies on the corrosion inhibiting effect of Congo red dye-halide mixtures', *Pigment and Resin Tech.,* 35(1), pp. 30 – 35.

[17] E.E. Oguzie, *et al.,* 2006. 'Corrosion inhibition and adsorption behaviour of bismark brown dye on aluminium in sodium hydroxide solution', *Mat. Lett.,* 60(28), pp. 3376 – 3378.

[18] E.E. Oguzie, *et al.,* 2004. 'Evaluation of the inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid', *Mat. Chem. and Phy.,* 87, pp. 394 – 401.

[19] A.A. Rahim, *et al.,* 2007. 'Mangrove tannins and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium, *Corros. Sci.,* 49, pp. 402 – 417.

[20] J. Mabrour, *et al.,* 2004. 'Effect of vegetal tannin on anodic copper dissolution in chloride solutions', *Corros. Sci.,* 46, pp. 1833 –1847.

[21] S.Martinez, I. Štagljar, 2003. 'Correlation between the molecular structure and the corrosion inhibition efficiency of chestnut tannin in acidic solutions', *J. of Molecular Structure (Theochem).,* 640, pp. 167 – 174.

[22] S. Martinez, 2006. 'Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms', *Mat. Chem. and Phy.,* 77, pp. 97 – 102.

[23] A. Bouyanzer, B. Hammouti, L. Majidi, 2006. 'Pennyroyal oil from Mentha pulegium as corrosion inhibitor for steel in 1M HCl', *Materials Letters.,* 60(23), pp. 2840 – 2843.

[24] M. Benabdelah, M. Benkaddour, B. Hammouti, 2006. 'Inhibition of steel corrosion in 2 M H_3PO_4 by artemisia oil', *Applied Surface Sci.,* 252, pp. 6212-6217.

[25] N. Yaakob, 2007. *Development of palm oil based anti-corrosion material for underwater protection,* Master dissertation, Universiti Teknologi MARA, Shah Alam , Malaysia.

[26] T. Hargreaves, 2003. *Chemical formulation an overview of surfactant-based preparations used in everyday life,* The Royal Society of Chemistry, Cambridge, United Kingdom.

[27] D.J. McClement, 2000. *Food emulsions principles, practice, and techniques.* CRC Press LLC, Florida, United State of America.

[28] W. Liu, *et al.,* 2006. 'Formation and stability of paraffin oil-in-water nano-emulsions prepared by the emulsion inversion point method', J. of *Colloid and Interface Sci.,* 303, pp. 557 – 563.

[29] R. Chanamai, G. Horn, D.J. McClements, 2002. 'Influence of oil polarity on droplet growth in oil-in-water emulsions stabilized by a weakly adsorbing biopolymer or a nonionic surfactant', *J. of Colloid and Interface Sci.,* 247, pp. 167 – 176.

[30] P.S. Goyal, V.K. Aswal, 2001. 'Micellar structure and inter-micelle interactions in micellar solutions: results of small angle neutron scattering studies', *Current Sci.,* 80(8), pp. 972 – 979.

[31] B.P. Binks, *et al.*, 2000. 'Stability of oil-in-water emulsions in a low interfacial tension system', *Langmuir.,* 16, pp. 1025 – 1034.

[32] R.J. Sturwold, W.E. Utz. N. Christ, W.R. Ford, G.P. Koch, 1979. Preventing of water staining of aluminium, *United States Patent* 4153464.

[33] D. Guzey, H.J. Kim, D.J. McClement, 2004. 'Factor influencing B-lactoglobulin-pectin membranes', *Food Hydrocolloids.* 18, pp. 967 – 975.

[34] Akzo Nobel Surfactants. Corrosion inhibitions for oilfield production. Retrieved July 25, 2007 from http://surface.akzonobelus.com/bulletins/ Corrosion%20Inhibitors%20for%20Oilfield%20Productions.pdf

[35] World Intellectual Property Organization. Fuel comprising an emulsion between water and a liquid hydrocarbon. Retrieved August 2005 from http://www.wipo.int/ipdl/

[36]   S. Cheng, *et al.,* 2007. 'Carboxymenthylchitosan as an ecofriendly inhibitor for mild steel in 1 M HCl', *Mat. Lett.,* 61(14 – 15), pp. 3276 – 3280.

[37] D. Wahyuningrum, S. Achmad, Y.M. Syah, Buchari, B. Bundjali, B. Ariwahjoedi, 2008. 'The correlation between structure and corrosion

inhibition activity of 4,5-diphenyl-1-vinylimidazole derivative compounds towards mild steel in 1% NaCl solution'. *International Journal of Electrochemical Science,* 3, pp. 154 – 166.

[38] S. Martinez, I. Stern, 2002. 'Thermodynamic characterization of metal dissolution and inhibition adsorption processes in the low carbon steel/mimosa tannin/sulfuric acid system'. *Applied Surface Science,* 199, pp. 83 – 89.

[39] S. Abd El Rehim, H. H. Hassan, M.A. Amin, 2001. 'Corrosion inhibition of aluminium by 1,1(lauryl amido)propyl ammonium chloride in HCl solution'. *Materials Chemistry and Physics,* 70, pp. 64 – 72.

[40] H. Ashassi-Sorkhabi, Z. Ghasemi, D. Seifzadeh, 2005. 'The inhibition effect of some amino acids towards the corrosion of aliminium in 1 M HCl + 1M H_2SO_4 solution'. *Applied Surface Science,* 249, pp. 408 – 418.

[41] A.K. Maayata, A.A.F. Al-Rawashdeh, 2004. 'Inhibition of acid corrosion of pure aluminium by some organic compounds', *Corros. Sci.,* 46, pp. 1129 – 1140.

[42] M.S. Morad, 2008. 'Inhibition of iron corrosion in acid solutions by Cefatrexyl: behaviour near and at the corrosion potential', *Corros. Sci.,* 50, pp. 436 – 448.

[43] J. McMurry, 2004. *Organic Chemistry,* (6th Ed.) United State of America:Thomson Learning Inc.

[44] Y. Yan, *et al.,* 2008. 'Electrochemical and quantum chemical study of pureness as corrosion inhibitors for mild steel in 1M HCl solution', *Electrochimica Acta.,* 53(20). pp. 5953 – 5960.

[45] E. S. Ferreira, *et al.,* 2004. Evaluation of the inhibitor effect of -ascorbic acid on the corrosion of mild steel, *Mat. Chem. and Phy.*, 83(1), pp. 129 – 134.

[46] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, 2007. '2,3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1 M HCl'. *Materials Chemistry and Physics,* 105(1), pp. 1 – 5.

[47] Y. Liu, R. Guo, 2008. 'pH-dependent structures and properties of casein micelles', *Biophysical Chem.,* 136(2-3), pp. 67 – 73.

[48] P. Singh, K. Bhrara, G. Singh, 2008. 'Adsorption and kinetic studies of L-leucine as an inhibitor on mild steel in acidic media', *Applied Surface Sci.,* 254(18), pp. 5927-5935.

[38]. H. Ashassi-Sorkhabi, Z. Ghasemi, D. Seifzadeh, 2005. 'The inhibition effect of some amino acids towards the corrosion of aluminium in 1 M HCl + 1M H_2SO_4 solution'. *Applied Surface Sci.,* 249, pp. 408 – 418.