Chitosan and Polyvinyl Propenenitrile: Synergistic Anti-Corrosive Activity on Mild Steel in Acidic Medium using Weight Loss Method

Ugomma C. Onyeije[1]
Department of Pure and Industrial Chemistry,
Nnamdi Azikiwe University, Awka,
Nigeria

Stevens A. Odoemelam[2]
Department of Chemistry, Michael Okpara University
of Agriculture, Umudike, Abia State,
Nigeria.

Melford C. Egbujor[3]* Chigbundu N. Emeruwa[4]
Department of Chemical Sciences,
Rhema University Nigeria,
Aba, Abia State, Nigeria,

Kalu D. Ogwo[5]
College of Basic and Applied Sciences,
Rhema University Nigeria, Aba,
Abia State, Nigeria,

Ugochukwu B. Amadi[6]
Chemistry Unit, Akanu Ibiam Federal
Polytechnic Unwana,
Ebonyi State, Nigeria

Abstract:- Corrosion is an electrochemical process that has constituted serious environmental problems to industries, homes and other environment. Metals of various types and grades are widely used in industrial installations and are often exposed to some aggressive media including acid, base and salt. Due to the fact that various industrial installations made of metals such mild steel, aluminum, and zinc are susceptible to corrosion attack during acid wash, etching, scale removal, etc., acid corrosion of these metals has garnered greater consideration and research. Numerous inhibitors have apparently been researched and used to reduce the rate of corrosion of important metals in light of these and other impacts, with positive results. The majority of the typical corrosion inhibitors, however, are poisonous, expensive, non-biodegradable, and difficult to get, according to environmental and other issues. The combination of inhibitors to improve anti-corrosive activity through synergistic actions remains a very important strategy for combating corrosion of mild steel. In this work, we combinedchitosan (CT) and polyvinyl propenenitrile (PVP), and explored their anti-corrosive action on mild steel in acidic medium via weight loss method. Results obtained from the weight loss experiment indicated that, the instantaneous inhibition efficiencies of the mixture of CT and PVP were higher than their individual inhibition efficiencies. Results showed that the corrosion inhibition efficiencies of a mixture of CT and PVP (77.49469 %) was higher than the individual components of CT (64.25 %) and PVP (52.02 %) at 303K.

Keywords:- Chitosan, polyvinyl propenenitrile, corrosion, mild steel, synergism

I. INTRODUCTION

The majority of organic corrosion inhibitors are biodegradable and free of heavy metals or other harmful substances. Some research teams have reported using naturally occurring compounds to successfully prevent metal corrosion in both acidic and alkaline environments (Onyeije et al., 2023; Abiola et al., 2007). Synergism is the combined activity of a compound that has a higher overall impact than the sum of its parts. It now ranks among the most crucial elements in inhibition procedures and forms the cornerstone of all current corrosion inhibitor formulations. Corrosion inhibitor synergism might result from interactions between inhibitor components or from interactions between an inhibitor and an ion in aqueous solution (Kokalj et al., 2023).

The synergism parameter (S) can be calculated using the relationship expressed by equation 1 (Ehteshanmzade *et al*., 2006)

$$S = \frac{1 - \eta_A - \eta_B - \eta_A \eta_B}{1 - \eta_A \eta_B}$$

1

where A and B are the separate inhibition efficiencies of compounds A and B; AB is the combined inhibition effectiveness of two inhibitors. When S <1, it can be claimed that one compound's adsorption opposes the other's adsorption. If S is equal to 1, A and B are individually absorbed at the metal/surface interface with no interaction between them; however, if S > 1, a synergistic effect will be seen (Babi-Samardzija et al., 2005). All current formulations of corrosion inhibitors are built on the principle of synergism, one of the most significant phenomena in corrosion inhibition process (Kalman et al., 2000). Utilizing this opportunity will allow you to lower the amount of chemicals used and apply more ecologically friendly but less potent ingredients.

The weight loss approach has been extensively utilized in monitoring the corrosion of metals and their inhibition (Nkuzinna et al 2014). The method is cheap and can be easily applied and is therefore a preferred method in corrosion monitoring. It has been found that due to the absence of surface perturbation, weight loss simulates the real situation better than electrochemical methods (Tavassoli-Salardini, 2004). Mercer (1990) also stated that the method is usually used as the first step in corrosion studies but may not provide all the information about local corrosion attack such as pitting corrosion (Tavassoli-Salardini, 2004). ASTMGI-90 (Siebert, 1985) is the standard protocol for weight loss. Thus, the corrosion rate is represented by equation 2:

$$\text{Corrosion rate: } \frac{K \times W}{ATD} \qquad 2$$

where K is a constant equal to 6.67×10^7 and 8.76×10^4 when units of g/m^2day^{-1} and mm/y are respectively used. W stands for weight loss (in grams), A for area (in cm^3), T for immersion time (in hours), and D for density (in g/cm^3). Alternately, the corrosion rate can be determined from the slope of a plot of weight loss over time (Abdallah 2004). based on the metrics of weight loss,the inhibition efficiency of an inhibitor can be calculated using Equation 3 (Emregul and Hayvali 2006).

$$IE\% = \left[\frac{w_0 - w_1}{w_0} \right] \qquad 3$$

where W_0 and W_1 are the weight losses without inhibitor and in the presence of inhibitor respectively. From equation 3, the percentage increment in efficiency (I%) in the temperature range $T_R(k)$ is defined by a chemical adsorption process (equation 4)

$$I\% = [(IE (T_2) - IE (T_1)] / IE(T_2) \times 100 \qquad 4$$

where $IE(T_2)$ and $IE(T_1)$ are inhibition efficiencies at temperatures, T_2 and T_1 respectively. According to Oguzie et al (2004a, 2004b), in most cases, inhibition becomes less stabilized in the system as the temperature is suddenly increased above 323K such that the stabilization factor (SF) can be expressed as shown by equation 5

$$SF = S_1 + S_2 \qquad 5$$

where S_1 and S_2 are percentage increments in efficiency at lower and at higher temperatures respectively. Data obtained from weight loss measurements are often used in the calculation of numerous thermodynamic and kinetic parameters, For example, the activation energy between temperature, T_1 and T_2 can be calculated from the Arrhenius equation (equation 6):

$$log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad 6$$

The anti-corrosive activity of chitosan (CT) as an individual corrosion inhibitor against mild steel was recently determined by our research group (Onyeije et al 2023). Thus, in this work we combinedchitosan (CT) and polyvinyl propenenitrile (PVP) together and explored their synergistic anti-corrosive activity on mild steel in acidic medium.

II. MATERIALS AND METHODS

A. Materials

The mild steel sample used for the study was purchased from Ken Johnson Nigeria Limited, located in Uyo in AkwaIbom State of Nigeria. Chemically, the mild steel is composed of Mn (0.46 %), C (0.17 %), Si (0.26 %), P (0.0047 %), Fe (98.935) and S (0.017 %) (% wt). In order to obtained coupons for weight loss method, the mild steel sheet was mechanically sliced into coupons that were each 5 cm by 4 cm in size. The mild steel sheet was sliced into 2 x 1.5 cm coupons for the electrochemical studies. Each coupon was polished using a progression of emery papers with varying grits, working from coarsest to finest (600). They were washed with ethanol, cleansed with acetone and stored in a dessicator after drying in the air. The chitosan used for the study was supplied by Prof. Lee. D. Wilson of the Department of Chemistry, University of Saskatchewan, Saskatoon, Canada. The PVP was purchased from Sigma Chemical store. All reagents used were of analar grade. This included HCl, zinc dust, NaOH, ethanol and acetone

B. Weight loss experiment

For the weight loss experiment, a mild steel coupon that had previously been weighed was completely immersed in 250 ml of the test solution (i.e., various concentrations of acid, inhibitors) in a beaker. The beaker was placed in a bath of water that was held at a temperature of 30 ºC. The same experiments were repeated at ages 40, 50, and 60 ºC. Each sample's weight prior to immersion was determined using a Scaltec high precision balance (Model SPB31). Every 24 hours, a sample was removed from the test solution, cleaned in an aluminum dust-infused NaOH solution, dried in acetone, and then reweighed. The overall amount of weight reduction was determined by the weight difference over a 168-hour period.. The inhibition efficiency (%η) for each inhibitor was calculated using the formula,

$$\%I = \left(1 - \frac{W_1}{W_2} \right) \times 100 \qquad 7$$

where W1 and W2 are the weight losses (g/dm3) for mild steel in the presence and absence of inhibitor in HCl solution, respectively. The degree of surface coverage θ is given by the equation 8:

$$\theta = \left(1 - \frac{W_1}{W_2} \right) \qquad 8$$

The rates of corrosion of mild steel observed with different concentrations of HCl were determined via immersion period of 168h from weight loss using equation 9 (Yurt et al., 2004)

$$Corrosion\ rate\ (mpy)\ = \frac{W}{At}$$

9

where W = weight loss (mg); A = area of specimen (square inches) and t = period of immersion (hour).

III. RESULTS AND DISCUSSION

Figure 1 revealed that the corrosion of mild steel in solutions of HCl is dependent on the following factors: period of immersion, temperature and concentration of CT and PVP. It was observed that the corrosion rate of mild steel in the absence of CT and PVP was higher than the corrosion rate of mild steel in their presence. It is also seen from figure 1 that the plots are arranged downward with increasing concentrations of CT and PVP which also indicate that the inhibition of corrosion by CT and PVP was concentration-dependent and increased when the concentration of the inhibitor increased. This suggests that the mechanism of inhibition of corrosion by CT and PVP was by physical adsorption on the surface of mild steel. For a physiosorption mechanism, the extent of adsorption (as measured by inhibition efficiency) decreases with increase in temperature, whereas for chemical adsorption, the extent of adsorption decreases with increase in temperature. The directly proportional increase in inhibition efficiency with concentration indicated that the extent of adsorption increased as the concentration of the inhibitor was increased. This is possible because with increasing inhibitor concentration, the fraction of the inhibitor transported to the surface of the mild steel would normally increase correspondingly.

Figure 1 shows plots for the variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing mixtures of CT and PVP in various ratios. However, the mixture that gave the highest inhibition efficiency was 1:3 ratio of CT and PVP while 1:1 ratio gave the least inhibition efficiency. Generally, the decreasing inhibition efficiency for the various mixtures of CT and PVP examined followed the order: 1:3> 1:2> 2:1>3:1>1:1. This shows that although CT was found to be a better inhibitor than PVP, its inhibition efficiency when blended with PVP did not depend significantly on the concentration of the CT or the PVP but on their ratio in the mixture. In this study the ratio of CT to PVP required for optimum efficiency was found to be 1:3. This observation may be attributed to structural and functional changes in the polymer as a result of blending. Polymer-polymer blend can lead to changes in functional group, chemical structure and other physicochemical parameters of the polymer. Since the adsorption properties of polymers can be affected by changes in physicochemical and functional properties of the polymers, then it justified why the inhibition efficiency of polymers was affected by blending.

Values of inhibition efficiencies obtained for the various blends are presented in Table 1. Synergistic parameters for the various CT and PVP blends were calculated using the following formula.

$$S = \frac{1 - I_{1+2}}{1 - I_{12}}$$

10

where I_{1+2} is the sum of the inhibition efficiency of CT and PVP without blending while I_{12} is the combined inhibition efficiency. Calculated values of S for the various ratios of CT:PVP blends are also presented in Table 1.
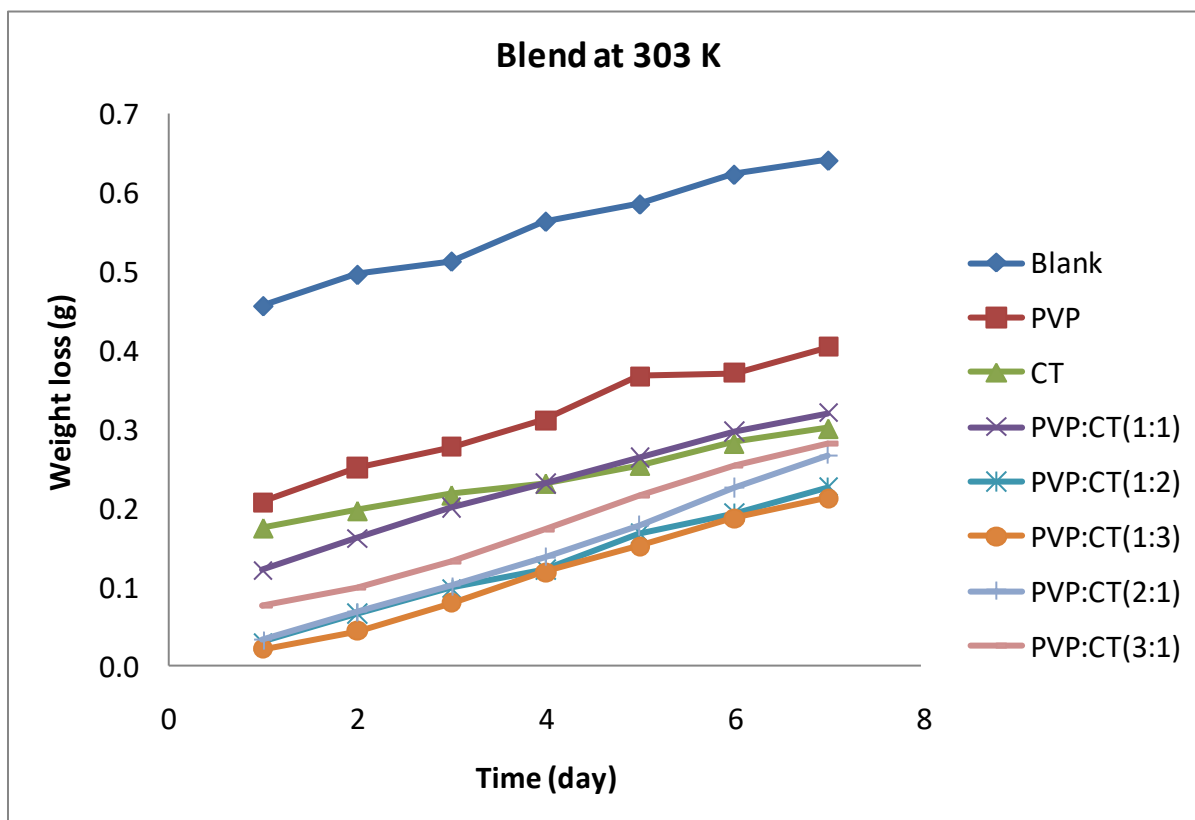
Fig. 1: Variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl in the absence and presence of various concentrations of CT and PVP at 303k

Table 1: Inhibition efficiency and synergistic parameters for the inhibition of various mixtures of CT and PVP

CT:PVP	%IE	S
01:01	65.92357	2.927805
01:02	75.90234	2.670976
01:03	77.49469	2.636192
02:01	71.65605	2.771398
03:01	70.06369	2.81224

Table 2: Inhibition efficiency of CT for the corrosion of mild steel in 0.1 M HCl at 303K

C (mg/L)	%IE
10	47.62
30	53.92
50	57.36
70	59.86
100	64.25

Table 3: Inhibition efficiency of PVP for the corrosion of mild steel in 0.1 M HCl at 303K

C (mg/L)	%IE
10	36.82
30	38.60
50	40.86
70	46.67
100	52.02

The comparative analysis of table 1-3 showed that the combination of CT and PVP produced the highest inhibition efficiency (77.49469 %) followed by CT (64.25 %) and PVP (52.02 %) at 303K. This suggests that the higher corrosion inhibition efficiency of the mixture of CT and PVP could be attributed to synergism arising from the combination of the two inhibitors. The results shows that the synergistic parameters were greater than unity for all the blend, which indicate that the adsorption of CT was enhanced by the adsorption of PVP. This co-administration of CT and PVP significantly enhanced the inhibition efficiency of the inhibitor.

IV. CONCLUSION

The use of mixture CT and PVP as a corrosion inhibitors is economic, eco friendly and efficient. The results gotten from weight loss experiment revealed that the mixture of CT and PVP resulted in significant inhibition of the corrosion of mild steel in solutions of HCl and that the inhibition efficiency of the mixture increased when there was an increase in their concentrations but decreased with increasing temperature.

The distinguishing properties of CT and PVP such as unique bonding, strong adsorption, and superb surface coverage have expanded their utility as corrosion inhibitors. Experimental analysis displayed excellent corrosion inhibitory efficiency and the inhibitory activity of the mixture of CT and PVP against the corrosion of mild steel was very significant. Furthermore, the combination of CT and PVP resulted in higher corrosion inhibition efficiency than the individual components of the mixture.

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