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# The effect of initiator concentrations on corrosion inhibition activity of polymeric derivatives of 2-vinylpyridin

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**Abstract.** This study aims to investigate the effect of initiator concentrations of polymeric derivatives of 2-vinylpyridine, P(2VP) as corrosion inhibitors of mild steel in CO<sub>2</sub>-saturated brine solution. Polymerization of the monomer was conducted using hydrogen peroxide initiator with four different concentrations of 0.25; 0.33; 0.50; and 0.80 mole, to produce four oligomers referred to as P(2VP)A, P(2VP)B, P(2VP)C, and P(2VP)D, respectively. A series of corrosion experiments was conducted to determine the corrosion rate of the mild steel using weight loss and linear polarization resistance (LPR) methods. The effect of inhibitor concentration, and temperature, on the corrosion rate was also investigated. The oligomers synthesized were found to have different physical appearance. Two oligomers, the P(2VP)A and P(2VP)B, were found as yellow viscous liquids, with O(2VP)B is more viscous than P(2VP)A, while the other two oligomers, P(2VP)C and P(2VP)D exist as yellow solids. The experimental results reveal that the use of monomer led to higher corrosion rate compared to that of blank experiment, but reduced corrosion rate was achieved with the use of the oligomers. P(2VP)A as an oligomer synthesized with the lowest concentration of H<sub>2</sub>O<sub>2</sub> initiator inhibited the corrosion more effective than the higher concentrations. It was also found that the higher the concentration of the oligomer, the better the protection. For temperature, the opposite is true, indicating that the oligomer was physically adsorbed onto the surface of mild steel.

**Keyword:** 2-vinylpyridine monomer, oligomer, corrosion inhibitor, mild steel, brine solution.

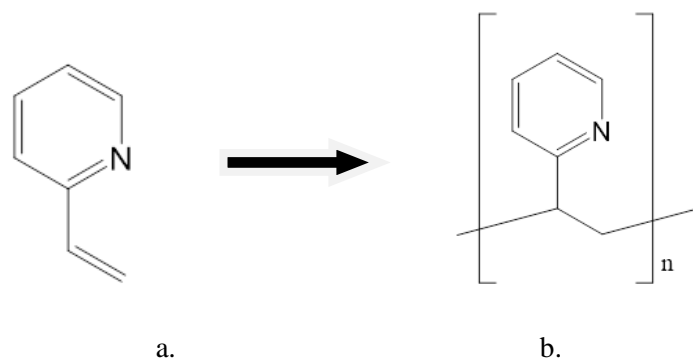
## 1. Introduction

Polymeric compounds containing heteroatoms, such as sulphur [1] phosphor [2], and nitrogen [3-5], have been reported as reliable corrosion inhibitor to protect metallic materials in various corrosive environments. This efficiency is attributed to higher basicity and electron density of the heteroatoms which play as active sites for adsorption of inhibitor on the metal surface. Of particular interest are oligomers, consist of between 3 and 8 units of monomers, since they were adsorbed effectively on the surface of the metal to form a protective layer against corrosion attack [1,5,6]. In previous study [3-



5,7], the use of several derivatives of pyridine as corrosion inhibitor for carbon steel in acidic medium has been reported.

In this study, the efficacy of 2-vinylpyridine (Figure 1) as a monomer was compared to that the low molecular weight polymer known as oligomers synthesized using hydrogen peroxide as an initiator. To obtain the oligomers with different molecular weight, the synthesis was carried-out using the initiator with different amounts. Although the exact molecular weight cannot be obtained, however, based on previous study with 4VP [5] it was found that varying initiator concentrations led to production of oligomers with different molecular weights. In this regard, it presumably that the same is true for 2VP. The monomer and the synthesized oligomers were than tested as corrosion inhibitor for mild steel in brine solution saturated with CO<sub>2</sub> gas, by using the wheel test and linear polarization resistance (LPR) methods. For simplicity, the monomer 2-vinylpyridine is abbreviated as 2VP, whilst the oligomers as P(2VP)s.



**Figure 1.** Molecular structure of monomer 2-vinylpyridine, 2VP (a) and oligomer 2-vinylpyridine, P(2VP).

## 2. Materials and methods

### 2.1. Instruments

Instrumentations used were rotary evaporator, Heidolph rotator, balance/weighting, wheel oven manufactured by Detailed Design, Texas., Pine Model MSRX electrode rotator, digital hot plate, EG&G Princeton Applied Research Model 273A Potentiostat and EG&G Model 314 Multiplexer.

### 2.2. Preparation of solutions

The corrosion electrolyte used was a brine solution prepared by dissolving sodium chloride, NaCl, at 3 % (w/v) and sodium bicarbonate, NaHCO<sub>3</sub>, analytical reagent (AR), at 100 mg L<sup>-1</sup> in milli-Q water. The electrolyte was saturated with food grade CO<sub>2</sub> gas at atmospheric pressure by purging the solution with the gas at a rate of approximately 150–200 mL min<sup>-1</sup>. Inhibitor solution with the concentration of 10,000 mg L<sup>-1</sup> was prepared by dissolving the inhibitor in methanol.

### 2.3. Preparation of materials

Mild steels (coupon and cylindrical electrode) used in this experiment were SAE/AISI Grade 1022 according to AS 1443 with the spectrographic analysis of the steel provided the chemical composition; 0.22 % C, 0.74 % Mn, 0.02 % Si, 0.014 % S, 0.02 % P, 0.05 % Ni, 0.04 % Cr, <0.01 % Mo, <0.01 % Cu, <0.01 % Al, and the remainder Fe. Coupons (2 x 1 x 0.1) cm used for weight loss measurements were prepared by sand blasting a sheet of mild steel with garnet (size 0.89 mm) and cut to size using a guillotine. The coupons were degreased by placing them in a beaker filled with ethanol and sonicated for two minutes. The coupons were dried and the dimensions and weights were accurately recorded. A mild steel cylinder electrode (working electrode of linear polarization measurements) which has surface area of 3.02 cm<sup>2</sup> was prepared by polishing the surface with silicon carbide paper (grade 360, 400, 600 and 800) on a Heidolph rotator (rotated at 750 rpm), using ethanol as a lubricant.

#### 2.4. Polymerization of 2-vinylpyridine

The synthesis of oligomers was conducted with the reaction composition as shown in Table 1. The monomer (2-vinylpyridine), methanol and water as solvent, and H<sub>2</sub>O<sub>2</sub> as an initiator were mixed, and then heated to reflux for 2 – 10 hours. After reaction was completed, the solvent was removed by using a rotary evaporator, and the product was isolated using high vacuum distillation. This method was used in previous research [4].

**Table 1.** Reaction composition for synthesis of 2VP oligomers.

| Monomer<br>2VP(g) | Methanol (mL) | Milli-Q Water<br>(mL) | Hydrogen<br>Peroxide (mol) | Oligomers<br>produced |
|-------------------|---------------|-----------------------|----------------------------|-----------------------|
| 30                | 75            | 75                    | 0.25                       | P(2VP)A               |
| 30                | 75            | 75                    | 0.33                       | P(2VP)B               |
| 30                | 75            | 75                    | 0.50                       | P(2VP)C               |
| 30                | 75            | 75                    | 0.80                       | P(2VP)D               |

As can be seen in Table 1, the concentration of initiator (hydrogen peroxide) was varied while the rest three reactants were kept at constant quantity. This approach was taken since it is generally known that the extent of polymerization is influenced by the initiator concentration. It is then expected that the oligomers with different molecular weights will be produced from the reaction compositions applied, as shown in Table 1.

#### 2.5. Weight loss measurement

To commence the experiments, a series of clean glass bottles (220 mL) were prepared to be used in the experiment. Five brine solutions with the same volume of 175 mL were prepared. One solution was used without addition of oligomer, while the other four samples were used for the experiments with oligomer, in which each of the solutions was added with specified one specified oligomer. Each of the samples was then purged for 45 minutes with CO<sub>2</sub> gas (at about 250 mL min<sup>-1</sup>). A mild steel coupon prepared was placed into the bottles and the bottles were capped with crown seals and placed in a wheel oven at 50°C for 24 hours. After the completion of the experiment, the bottles were removed from the oven, and the coupons were removed and immediately placed in Clarke's solution (a solution composed of 2% of Sb<sub>2</sub>O<sub>3</sub> and 5% SnCl<sub>2</sub>, dissolved in concentrated HCl) for 45 seconds in order to remove the corrosion product from the surface. The coupon was dipped into water for about 5 seconds, and into ethanol for another 5 seconds, and then dried and accurately weighed. This method was used for investigation of oligomer 4-vinylpyridine as a corrosion inhibitor [4].

For calculation of the weight loss (W), the corrosion rate (CR) and the inhibition efficiency (%P), the following Equations (1, 2 and 3) were used.

$$W = W(i) - W(t) \quad (1)$$

$$CR = \frac{1}{A} \frac{W}{2.54t} \quad (2)$$

$$\% P = \frac{(CR_0 - CR_i)}{CR_0} \times 100\% \quad (3)$$

Where W = weight loss (gram), W(i) = initial weight of coupon, W(t) = final weight of coupon, CR = corrosion rate (mm<sup>-1</sup> = millimeter per year), A = area of coupon (cm<sup>2</sup>), D = density (gcm<sup>-3</sup>) of coupon, which is equal to 7.86 g cm<sup>-3</sup> for carbon steel, t = time of exposure (days), %P = percentage of protection, CR<sub>0</sub> = corrosion rate without inhibitor and CR<sub>i</sub> = corrosion rate with inhibitor.

### 2.6. Linear polarization resistance (LPR) measurements

The experimental setup used is the same with the previous study [4-5]. The working electrode prepared was fitted to the end of the threaded shaft that was connected to a Pine rotator. The electrochemical cell (reaction vessel) was filled with 500 mL of brine solution and sparged with CO<sub>2</sub> until it was saturated (approximately 45 minutes). The sparging with CO<sub>2</sub> (100 mL min<sup>-1</sup>) was maintained during all experiments. A platinum gauze auxiliary electrode, Ag/AgCl reference electrode and thermocouple were placed in the cell. The cell was heated and regulated by a thermocouple on a digital hot plate at 30, 50, and 70°C. The working electrode was inserted and operated at a speed of 1000 rpm through connection to a Pine Model MSR-X electrode rotator. The rotating electrode with speed of 1000 rpm was prepared for simulating turbulent flow conditions related to data obtained in real life system [8,9]. The electrochemical cell was connected for LPR measurement.

LPR measurements were carried out using an EG&G Princeton Applied Research Model 273A Potentiostat and EG&G Model 314 Multiplexer. The instrument was controlled using EG&G Model 352 Corrosion Software, version 2.10. The working electrode was polarized from +10 to -10 with respect to the corrosion potential using an anodic scan of 0.1 mV s<sup>-1</sup>. The polarization resistance was determined from the ensuing potential current plot, and converted to a corrosion rate by using assumed Tafel slope of  $\beta_{a,c} = 100$  mV/decade. A blank measurement, with no inhibitor, was completed before inhibitor was added using a micro-pipette (0.1-0.2 mL). Eight LP measurements were completed for the blank and each inhibitor concentration, and last three readings were averaged to give a steady state corrosion rate. The experimental work was done at various temperatures.

## 3. Results and discussion

### 3.1. Synthesis of oligomers

The oligomers synthesized were found to have different physical appearance. Two oligomers, the P(2VP)A and P(2VP)B, were found as yellow viscous liquids, with P(2VP)B is more viscous than P(2VP)A, while the other two oligomers, P(2VP)C and P(2VP)D exist as yellow solids. These different phases of the products signify that the oligomers have different molecular weights, which also demonstrated that the concentration of initiator plays an important role in governing the extent of polymerization reaction. This finding is in accordance with the reports by Scriven et al [10] and Ilim et al [4], in which it is suggested that hydrogen peroxide acts as both initiator and as chain transfer agent in a polymerization reaction. Based on the different physical states of the oligomers, it can be inferred that corrosion inhibition by the oligomers could be related to molecular weight of the oligomer.

### 3.2. Weight loss measurement

In this study, weight loss or wheel test was used as a screening method to evaluate potential of the oligomers as corrosion inhibitors, and the results are shown in Table 2.

**Table 2.** Wheel test results using monomer and oligomers, carried out at 50°C.

| No | Compound Name  | Amount Added (ppm) | Coupon Area (cm <sup>2</sup> ) | Weight Loss (g) | Corrosion Rate Average (mmpy) | Protection (%) |
|----|----------------|--------------------|--------------------------------|-----------------|-------------------------------|----------------|
| 1  | Brine solution | -                  | 4.8899                         | 0.0352          | 3.3468                        | -              |
| 2  | 2VP            | 50                 | 4.8677                         | 0.0477          | 4.5500                        | -44.26         |
| 3  | P(2VP)A        | 50                 | 4.8105                         | 0.0183          | 1.1768                        | 64.83          |
| 4  | P(2VP)B        | 50                 | 4.8825                         | 0.0199          | 1.2608                        | 62.32          |
| 5  | P(2VP)C        | 50                 | 4.8854                         | 0.0214          | 1.3611                        | 59.33          |
| 6  | P(2VP)D        | 50                 | 4.8172                         | 0.0198          | 1.9049                        | 43.08          |

The results presented in Table 2 clearly demonstrate that the four oligomers tested display the ability to inhibit the corrosion, while the monomer the opposite is observed. Comparing the percentage of protection provided by the oligomers, it can be seen that the protection ability of the oligomers steadily decreases from P(2VP)A to P(2VP)D. If this trend is related to molecular weight, it can be inferred that the oligomers with lower molecular weight are more effective than those with higher molecular weights. Experiment with NaCl 3 % solution brine resulted in corrosion rate of 3.35 mmpy. This result is in agreement with the results reported by others [11-13].

3.3. Linear polarization results (LPR)

LPR has also been used to study the 2VP monomer and four synthesized products as corrosion inhibitors of mild steel in 3% NaCl solution saturated with CO<sub>2</sub> gas at various temperatures and concentrations. The experimental data obtained from linear polarization measurement was corrosion rate (CR) of each measurement.

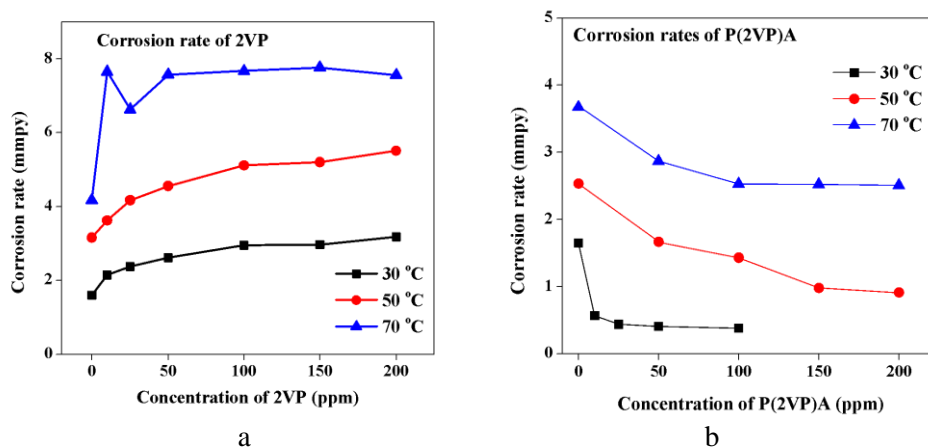


Figure 2. Corrosion rate of 2VP (a) and P(2VP) (b) at various of concentrations and temperatures.

Figure 2 shows the corrosion rates of 2VP (a) and P(2VP)A (b) at various concentrations of 0-200 ppm and temperature varies (30, 50 and 70 °C). It can be seen in Figure 2 that the 2VP monomer promotes corrosion, the higher the 2-VP concentration, the higher the corrosion rate and the promotion decreases at 50 °C. Whereas the presence of P(2VP)A in Figures 2 (b) shows that the corrosion rates are inversely proportional to the concentrations of P(2VP)A, which means that the higher the concentration, the smaller the corrosion rate.

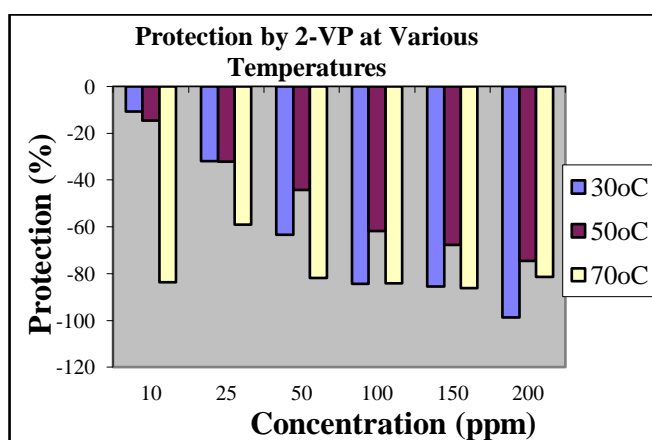
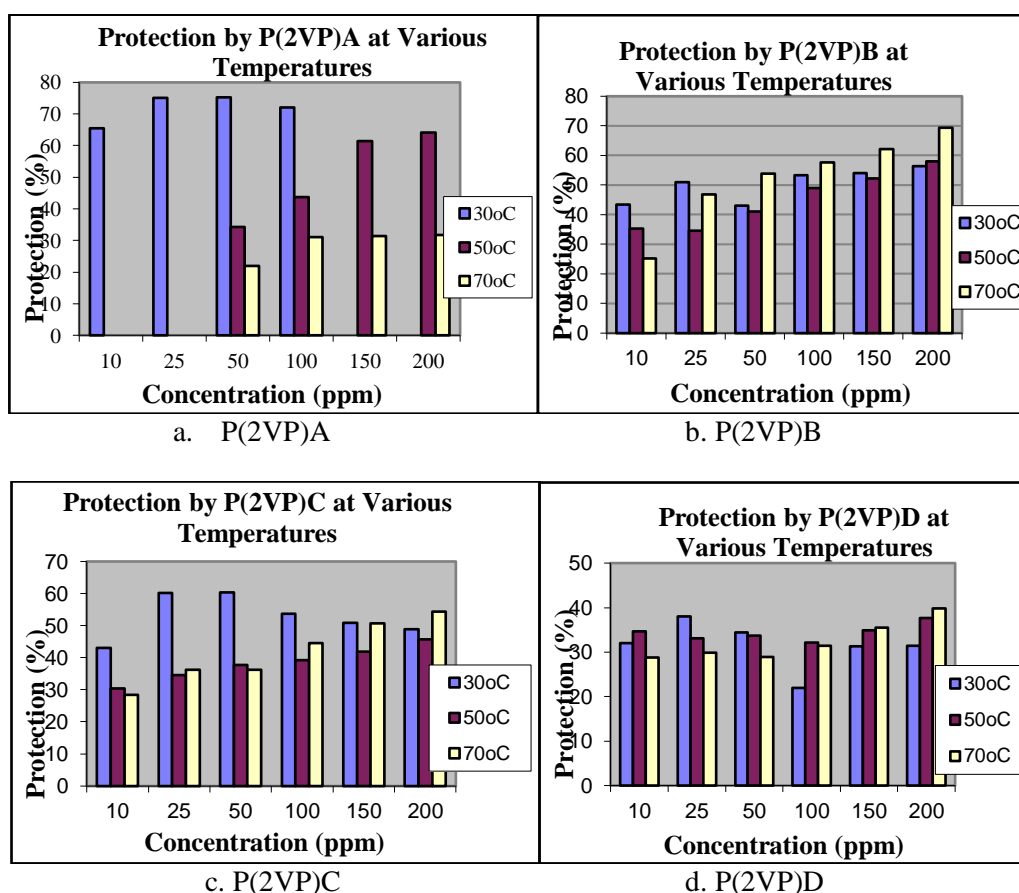


Figure 3. Protections of 2VP at various of concentrations and temperatures.

The obtained corrosion rates were used to calculate percentage of protection (% P) by using Equation (3) and the results are shown in Figure 3 for monomer 2VP and Figure 4 for P(2VP) in which percent protection as a function of temperatures and concentrations for each of the inhibitors tested was plotted. Figure 3 shows the plot of percent protection as a function of concentrations at various temperatures demonstrated that 2VP monomer gives a negative protection that can be concluded promotes carbon dioxide corrosion more significantly at higher temperature.

For the experiments with the use of oligomers, the results presented in Figure 4a-d, showing percent protection as a function of concentrations at various temperatures, it was found that the corrosion protection increases with decreasing temperature.



**Figure 4.** Protections of (a) P(2VP)A. (b) P(2VP)B. (c) P(2VP)C. and (d) P(2VP)D.

Monomer 2VP provides negative protection which means that monomer 2VP cannot protect against corrosion but on the other hand monomer 2VP promotes carbon dioxide corrosion with a lower promotion rate at 50 °C. The percentage of protection P(2VP)A is higher with increasing concentration, and the protection increases with decreasing temperature. Meanwhile, the protective ability of P(2VP)B was almost the same at the three treatment temperatures. The protective ability of oligomers in the form of viscous liquid, namely P(2VP)A and P(2VP)B (having a lower molecular weight) is better than P(2VP)C and P(2VP)D which are solid. The protection of P(2VP)A increases with decreasing temperature and the interaction with surface of mild steel indicated as physisorption. This result is different from the oligomers of 4VP [4] and oligomer of 4VPP [5] observed in previous study, in which the protection increases with increasing temperature.

In accordance with the mechanism of inhibition by nitrogen-containing inhibitors, Lopez et al [14] suggested that the main character for the formation of the most common metal-inhibitor bonds is

nitrogen from pyridine which functions as a strong base. In this study it can be concluded that the most important role in forming bonds between the surface of mild steel and the inhibitors is played by nitrogen atom in pyridine. The interactions between organic inhibitors (or filming inhibitors) results into the adsorption and formation of surface film over the interfaces of metal and environments (or electrolytes) that isolates the metals from corrosive surrounding and protect from corrosion [15]. Based on temperature effect of the protection, the interactions between oligomer P(2VP) and surface of mild steel were predicted as physisorption [5,13,16-18].

#### 4. Conclusion

The nitrogen containing oligomers of poly 2-vinylpyridine (2VP) have been synthesized from monomer 2-VP using hydrogen peroxide as the initiator at various concentrations. Four oligomers synthesized were found to have different physical appearance. Two oligomers, the P(2VP)A and P(2VP)B, were found as yellow viscous liquids, with P(2VP)B is more viscous than P(2VP)A, while the other two oligomers, P(2VP)C and P(2VP)D exist as yellow solids. Wheel test results as screening tests showed that all of the oligomeric products protected the mild steel from carbon dioxide corrosion at various levels of concentration whilst the monomer promoted the corrosion. LPR also gave similar results with the degree of protection depends on the temperature and the concentration of the oligomer. The protection afforded by the P(2VP) oligomer was better at lower temperature. The oligomer synthesized using the lowest initiator concentration of H<sub>2</sub>O<sub>2</sub> referred to as P(2VP)A protected more effective than other products. The monomer of 2VP cannot inhibit the corrosion rates, and on the contrary it was found to promote the carbon dioxide corrosion. Based on the temperature effect, the oligomers derived from 2VP were physisorbed on the surface of mild steels.

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