The effect of concentration and temperature on the activities of Polyethylene Oxide (PEO) as iron corrosion inhibitor in electrolyte solution of NaCl

T Sudiarti*, A Y Silviyanadewi and A Supriadin
Chemistry Department, Universitas Islam Negeri Sunan Gunung Djati Bandung, Bandung, Indonesia
*tety.sudiarti@uinsgd.ac.id

Abstract. Internal corrosion in the piping system is a serious problem. The use of corrosion inhibitors for corrosion control in piping systems is a practical and cost-effective method. Many polymers have been reported to be used as an inhibitor corrosion. However, there was little attention to the research of Polyethylene Oxide (PEO) as a corrosion inhibitor in NaCl medium. The purpose of this study was to determine the corrosion inhibition activity of polymeric compounds of polyethylene oxide against ferrous metals in 1% NaCl electrolyte solution. The study of Polyethylene Oxide (PEO) activity as a corrosion inhibitor in 1% NaCl electrolyte solution was carried out by the Wheel Test method with variations in concentration and temperature. The surface analysis of iron by SEM (Scanning Electron Microscopy). The results showed that polyethylene oxide (PEO) had the optimum inhibitory activity at a concentration of 16 ppm, with inhibition efficiency of 80.15% at 25˚C. Polyethylene Oxide has adsorption properties which are in accordance with the Langmuir adsorption isotherm with free adsorption energy of -21.385 kJ / mol. The results of the surface analysis by Scanning Electron Microscopy (SEM) showed that polyethylene oxide could inhibit corrosion rates with iron surfaces that had fewer pores than without inhibitors.

1. Introduction
In the petroleum mining industry, pipes made of carbon steel (90% iron) are used for the distribution of crude oil from drilling fields to processing refineries. The crude oil produced is usually still mixed with salts (chloride, sulfate, and carbonate salts), low molecular mass organic acids (formic acid), and acidic gases (CO₂ and H₂S gases). The presence of particulates such as salt, organic acids, and acidic gases can be a very corrosive medium to the inside of the pipe if it reacts with water. The most common type of corrosion in the petroleum industry is general and local corrosion [1]. The occurrence of internal corrosion in the operation of the pipeline flow line is a major problem [2], because the internal corrosion of the piping system is a process of metal degradation that is serious and costly, besides engineering efforts and maintenance phases are also very burdensome [3].

The use of corrosion inhibitors is one of the most common and suitable ways to overcome internal corrosion problems without modifying the corrosive environment [4] because corrosion inhibitors are a practical and cost-effective method of corrosion control in monitoring piping systems, depending on the selection of good inhibitors [3]. Polymer compounds that cover heteroatoms (N, O, S), π-electrons and phenyl rings provide the ability to adsorb onto the metal surface through adsorption. Polymer
compounds are excellent candidates for corrosion inhibition, because they have a high molecular weight that helps them protect the additional surface area of metal [4]. Many polymers have been reported to be used as an inhibitor corrosion, such as polysaccharides [5], polyamine derivatives, polycarboxylates/polycarboxylicacids, phosphate ester, polysulfides, polyaspartates [6], polyvinylamide derivatives [7], polyamines [8], octylphenol polyethylene oxide [9], cationic surfactants based on polyethylene glycol and [10].

However, there was little attention to the research of Polyethylene Oxide (PEO) as a corrosion inhibitor in NaCl medium. Polyethylene oxide is a synthetic polymer compound that is water-soluble or hydrophilic, semi-crystalline and non-toxic [11,12,13]. Polyethylene oxide has a free electron oxygen group which allows it to have the ability to form complexes with iron ions so that it can be adsorbed strongly on metal surfaces.

The purpose of this study was to determine the corrosion inhibition activity of polymeric compounds of polyethylene oxide against ferrous metals in 1% NaCl electrolyte solution which is in accordance with one of the conditions in the petroleum mining industry. This study included determining the corrosion rate of iron with a wheel test method with variations in inhibitor concentration and temperature variation. Then the adsorption mechanism analysis and analysis of metal surface with SEM were carried out on conditions before and after the use of inhibitors.

2. Experimental

2.1. Materials
The materials used in this study are polyethylene oxide (PEO) (Sigma Aldrich), sodium chloride (NaCl) pa, ethanol (C₂H₅OH) 96%, iron metal, technical acetone, carbide silicon sandpaper.

2.2. Preparation of PEO solution
0.1 gram of PEO powder is weighed in a watch glass, dissolved with distilled water up to 100 mL to get a solution with a concentration of 1000 ppm, then stir until homogeneous.

2.3. Preparation of NaCl 1% solution
NaCl 1% electrolyte solution is made by weighing 10 grams of NaCl which is then dissolved in a beaker and diluted into a 1 liter measuring flask with distilled water to the boundary mark.

2.4. Preparation of iron sample
Preparation of iron metal samples was carried out by cutting iron specimens with a size of 10x10x3 mm and then slightly perforated. Before being used for testing, the iron surface is smoothed with silicon carbide sandpaper and then cleaned with acetone and put the mattress thread on the hole, then weighed.

2.5. Measurement of corrosion rate by wheel test method and determination of inhibition efficiency (EI)
The wheel test method is a method of measuring the corrosion rate based on a weight loss measurement method from metal specimens tested during the exposure time in the corrosion medium [14].

Test solutions with varying concentrations that have been made are inserted into vial bottles. Then the iron metal is immersed in the test solution, closed and allowed to stand for 45 hours. Then the metal is removed, cleaned, dried, and weighed. The treatment was repeated with the effect of temperature variations namely 25 °C, 35 °C, 45 °C and 55 °C. Then the corrosion rate value is calculated using the following formula [15]:

\[ R = \frac{k \times \Delta w}{D \times A \times t} \]  

Where respectively R, \( \Delta w \), D, A, t, k were corrosion rate (mm / year), lost weight (gram), density (g / mm³), section area (mm²), Immersion time (year), and constant (8.76 x 10⁴).

Then the efficiency of inhibitors can be determined using the following formula [16]:
\[
\% EI = \left( \frac{CR_o - CR_i}{CR_o} \right) \times 100
\]  

(2)

Where respectively \( % EI \), \( CR_o \), \( CR_i \) were inhibition efficiency, corrosion rate without inhibitor and corrosion rate with inhibitor.

2.6. Surface analysis by SEM

Surface analysis was carried out on ferrous metals without immersion in the test solution, ferrous metals with immersion in test solutions without inhibitors in the most corrosive conditions, namely at 55 °C and ferrous metals soaked in the test solution with inhibitors. Soaking is carried out for 45 hours, then the metal is removed, cleaned, dried. Then surface analysis was carried out with SEM.

3. Results and discussion

3.1. Effect of inhibitor concentration (PEO) to corrosion rate and inhibition efficiency

Figure 1 showed that addition of inhibitors decreases the corrosion rate, and the reduction in corrosion rate increases with increasing inhibitor concentration, due to an increase in adsorption inhibitors on the metal surface. The decrease in corrosion rate occurs to the optimum limit, then the corrosion rate increases again even though it is relatively small due to the desorption of inhibitors from the metal surface.

![Figure 1. Effect of inhibitor concentration (PEO).](image)

Corrosion rates in the presence of PEO in electrolyte solutions decreased when compared with the addition of PEO. This is due to the presence of an epoxy group. This epoxy can form complex compounds with Fe (III) on the metal surface, so that the corrosion rate will decrease. This complex compound will block the attack of corrosive ions on the metal surface, so the corrosion rate will decrease. Figure 2 showed interaction mechanism between iron ions and PEO that was proposed.

![Figure 2. Proposed of interaction mechanism between iron ions and PEO.](image)
Figure 3. Effect of inhibitor concentration (PEO) to inhibition efficiency ($EI$).

Figure 3 showed the optimum inhibitor efficiency value was produced at 16 ppm inhibitor concentration, with the highest efficiency value of 80.15% compared to other concentrations, this is because the condition of Fe-epoxy complexes formed perfectly and covered the entire iron surface. While the lowest efficiency is obtained at a concentration of 24 ppm, this is due to desorption.

3.2. Effect of temperature to inhibition efficiency

The increase in temperature can cause the energy level of molecules on the metal surface to experience competition between the adsorption force and the desorption style of the metal. The higher the temperature, the lower the value of corrosion inhibition efficiency due to the increased speed of oxidation of Fe on the metal surface so that the adsorbate of the PEO will be easily separated from the iron surface. High temperatures cause high oxygen diffusion in the solution so that the corrosion rate is high, and cause low efficiency. The value of inhibition efficiency with temperature variations decreases and reaches the lowest limit at a temperature of 55 °C at 8.25% (Figure 4).

Figure 4. Effect of Temperature to inhibition efficiency.

3.3. Adsorption isotherm

The adsorption isotherm can be determined if the effect of the inhibitor is caused mainly because of the adsorption on the metal surface. Adsorption isotherms can provide additional information about the properties of inhibitors. The surface fraction covered by an inhibitor $\theta$ is determined by a ratio of $EI$ (%) / 100. There are several adsorption isotherms that can be used to explain the behavior of inhibitors in a medium. In this experiment it was found that the Langmuir adsorption isotherm provided the best picture to describe the behavior of PEO inhibitors in NaCl 1% solution.

From the Langmuir adsorption isotherm (Figure 5) it can be determined that the price of $\Delta G_{ads}$ is -21.385 KJ / mol. The negative $\Delta G_{ads}$ value indicates that the adsorption process is a spontaneous process and has strong interaction characteristics and stability between the layers absorbed with the steel surface. The free energy value of adsorption which is <-40 kJ / mol, indicates physical adsorption [17].
3.4. **Surface analysis by SEM**

The results of Scanning Electron Microscopy (SEM) analysis on the surface of iron in electrolyte solutions without inhibitors (PEO), with inhibitors (PEO) that are oven-heated for 45 hours can be seen in Figure 6. The picture shows that holes in the electrolyte without PEO formed holes (corrosion), but with PEO a thin layer is formed on the surface. This proves that PEO can be said as an inhibitor of the occurrence of corrosion (inhibitors), because it appears that a thin layer can reduce the corrosion rate.

![Figure 6](image)

**Figure 6.** The Surface analysis by SEM: (a) before being corroded (b) without inhibitor (c) with inhibitor.

4. **Conclusion**

Polyethylene oxide (PEO) had the optimum inhibitory activity at a concentration of 16 ppm, with inhibition efficiency of 80.15% at 25°C. Polyethylene Oxide has adsorption properties which are in accordance with the Langmuir adsorption isotherm with free adsorption energy of $-21.385 \text{ kJ/mol}$. The results of surface analysis by Scanning Electron Microscopy (SEM) showed that polyethylene oxide could inhibit corrosion rates with iron surfaces that had fewer pores than without inhibitors.

References

[1] Finšgar M and Jackson J 2014 *Corros Sci.* **86** 17-41.
[2] Ghareba S, and Omanovic S 2010 *Corros.Science.** **52** 2104-2113.
[3] Yahya S, Othman N, and Ismail M C 2019 *Engineering Failure Analysis.* **100** 365-380.
[4] Singh A, Sonia N, Deyuana Y, and Kumarc A 2019 *Result in Physics.* **13** 102116.
[5] EL-Haddad M N 2014 *Carbohydr. Polym.* **112** 595–602.
[6] Tiu B D B and Advincula R C 2015 *Reactive and Functional Polym.* **95** 25–45
[7] Lin Y, Singh A, Ebenso E E, Wu Y, Zhu C and Zhu H, 2015 *J. Taiwan Inst. Chem. Eng.* **46** 214–222.
[8] Jeyaprabha C, Sathiyaranayanan S and Venkatachari G 2006 *J. Appl. Polym. Sci.* **101** 2144–2153.
[9] Algaber A S, El-Nemma E M and Saleh M M 2004 *Materials Chem. and Phys.* **86** 26–32
[10] Abd-Elaal A A, Shaban S M and Tawfik S M 2017 *J. of the Assoc. of Arab Univers. for Basic and Appl. Sci.* **24**, 54–65
[11] Pang P and Englezos P 2001 Physicochem. and Eng. 204, 23-29
[12] Koduru H K, Iliev M T, Kondamarreddy K K, Karashanova D, Vlakhov T, Zhao X Z and Scaramuzza N 2016 J. of Phys. 764, 1-9.
[13] Sajid M, Akash H and Kanwal 2015 Polym. Rev. 30, 1-36
[14] NACE International Task Group T-1D-34 1996 Laboratory Test Method for Evaluating Oil field Corrosion Inhibitors, in NACE International Publication (Texas) 1-13
[15] Khatak H S and Raj B Corrosion of Austenitic Stainless Steels: Mechanism, Mitigation, and Monitoring 2002 (Kalpakam, India: Alpha Science International Ltd).
[16] Hasan K H, Khadom A A and Kursheed N H 2016 South African J. of Chem. Eng. 22 1-5.
[17] Fuchs R 2007 Electrochim. Acta. 52, 4974-4981