IOP Conf. Series: Materials Science and Engineering **334** (2018) 012048 doi:10.1088/1757-899X/334/1/012048

Inhibition effect of fatty amides with secondary compound on carbon steel corrosion in hydrodynamic condition

I M Ibrahim[1,3], J Jai[1], M Daud[2] and Md A Hashim[1]

[1] Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, MALAYSIA.
[2] Industrial Technology Division, Malaysian Nuclear Agency (Nuclear Malaysia) Bangi, 43000 Kajang Selangor, MALAYSIA

E-mail: iznimariah@yahoo.com

Abstract. The inhibition effect demonstrates an increase in the inhibition performance in presence of a secondary compound in the inhibited solution. This study introduces fatty amides as corrosion inhibitor and oxygen scavenger, namely, sodium sulphite as a secondary compound. The main objective is to determine the synergistic inhibition effect of a system by using fatty amides together with sodium sulphite in hydrodynamic condition. The synergistic inhibition of fatty amides and sodium sulphite on corrosion of carbon steel in 3.5 wt% sodium chloride solution had been studied using linear polarization resistance method and scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX). Electrochemical measurement was carried out using rotating cylinder electrode at different flow regimes (static, laminar, transition and turbulent). Linear polarization resistance experiments showed the changes in polarization resistance when the rotation speed increased. It found that, by addition of fatty amides together with sodium sulphite in test solution, the inhibition efficiency increased when rotation speed increased. The results collected from LPR experiment correlated with results from SEM-EDX. The results showed inhibition efficiency of system was enhanced when fatty amides and oxygen scavengers were present together.

1. Introduction

Presently, the use of organic inhibitor has become a known practice for protection of internal surface made of carbon steel that are in contact with aggressive environment [1]. Amide-based organic compounds have an extensive utilization in industry especially as corrosion inhibitor [2]. An oxygen scavenger, namely, sodium sulphite was introduced as a secondary substance in a test solution containing fatty amides to increase the inhibition efficiency. In flow velocities (hydrodynamic), one would expect that the corrosion mechanism to be more aggressive compared to static condition. For example in oil and gas pipeline system, the transportation of fluid in the pipeline involved the hydrodynamic factor. The fluid flow causes an increase in the transportation rate of chemical species to/from the metal surface, thus resulting in an increase of the internal corrosion rate. Some literature reported on pipeline leaking in Tioga, North Dakota in September 2013 was due to severe internal

[3] To whom any correspondence should be addressed.

corrosion [3]. Such corrosion problems have cost billions of dollars every year and in the middle of 2013 this cost has reached about 3-5% of Gross Domestic Product (GDP) in the United States [4].

According to previous studies, the addition of a secondary substance has increased the inhibition efficiencies due to synergistic effect [5], [6]. Most of the investigations on synergistic effect were under static condition. There are a few studies in the literature on the hydrodynamic effects due to synergism. Some authors have investigated the synergistic effect on inhibition efficiencies in hydrodynamic using different chemicals. For example, Carrillo, et al (2012) [7] evaluates the effectiveness of sodium molybdate with nitrite, phosphate and silicate. Another authors used silicate and phosphonate combination to control corrosion in transmission pipeline [8] and a previous study used ternary inhibitor formulation containing folic acid, a phosphonate and zinc ions [9]. Thus, the main objective of this study is to determine the inhibiton efficiencies when fatty amides are used together with sodium sulphite in different rotation speeds at room temperature (25^{o}C).

2. Experimental

The test solution used 3.5 wt% sodium chloride (NaCl) solution. The fatty amide was synthesized by following the reaction path as reported previously [10]. The working electrode (cylinder electrode) used is made of carbon steel with chemical composition C 0.04 %, Al 0.23 %, Mn 0.74 %, Ni 0.056 %, Cu 0.059 %, Cr 0.060 %, Zn 0.54 %, Pb 0.02 % and the remaining iron analysed by using Inductively Coupled Plasma (ICP) with Optical Emission Spectrometer (OES). The details dimension of the cylinder electrode was reported in our previous study [11]. The cylinder electrode was first mechanically grind and polished using sand paper in grades from 220 to 1000. Then it washed with distilled water and rinsed with acetone. Similar preparation for cylinder electrode was reported by the previous study [12]. Another two electrodes used are saturated calomel and graphite rod as reference and graphite electrode. The electrochemical tests carried out in a rotating cylinder electrode, RCE (Model 636) connected to a Gamry potentiostat. The experiments were performed with rotation speed at 1, 10 and 100 rotation per minute (RPM) which classified as laminar, transition and turbulent respectively at room temperature (25^{o}C). The rotation speed was calculated from Reynolds number (Re) as the following Equation (1) [13]:

$$\mathrm{Re} = \frac{\rho \times u_{cyl} \times d_{cyl}}{\mu} \tag{1}$$

Where ρ, u, dcyl and μ are solution density (1.023 g/cm3), linear velocity (cm/s) of cylinder electrode, diameter of cylinder electrode and solution viscosity (0.00959 g/cm.s) respectively. The measurement of linear polarization resistance test was performed in one hour at a scan rate of 0.166 mV/s for a range of voltage ±20 mV. Constant concentration of fatty amides (20 ppm) with addition of different concentrations of sodium sulphite (500, 1000, and 2000 ppm) were tested in the 3.5 wt. %, NaCl solution. The effect of different concentrations of sodium sulphite was studied. The selection of concentration is based on the preliminary result obtained previously. Then, the inhibition efficiency, IE (%) was calculated using corrosion rate (C.R) as shown in the following Equation (2):

$$I.E(\%) = \frac{C.R_{blank} - C.R_{inh}}{C.R_{blank}} \times 100\% \tag{2}$$

Where $C.R_{blank}$ and $C.R_{inh}$ are the corrosion rate in the absence and presence of the inhibitors respectively. The surface morphologies of the polarized samples were investigated using scanning electron microscope equipped with an Energy dispersive X-ray spectrometer for chemical analysis.

3. Result and discussion

3.1 Electrochemical measurements

In general, the flow is considered under laminar in using RCE provided that Re is less than 50. When Re is greater than 200, the flow is considered under turbulent flow. The transition regime from laminar to turbulent flow occurs when Re between 50 and 200 [14]. The calculated Reynolds number values presented in Table 1 shows three different flow regimes were investigated namely laminar, transition and turbulent flow. The linear polarization resistance (LPR) test was conducted to obtain corrosion rate, C.R (mm/yr). LPR measurement was used because it is an accurate and a rapid method to measure the corrosion rate [15].

Table 2 shows the formulations and the indicators used in this study. The rotation speed at different flow regimes influenced the corrosion rate. The corrosion rate against rotation speeds showed in Figure 1 while its numerical value was tabulated in Table 3. The solutions with addition of 20 ppm fatty amides together with different concentrations of sodium sulphite were tested in different flow regimes. The individual substance of fatty amides or sodium sulphite was also tested to illustrate the comparison. From Figure 1, two patterns were observed describing the trend of corrosion rate. Firstly; for combination system of fatty amides with sodium sulphite, the corrosion rate decreased from laminar (1 RPM) to transition (10 RPM) and increased in turbulent (100 RPM). Secondly; for most of the individual substance (individual fatty amides and individual sodium sulphite), the corrosion rate increased when the rotation speed is increased.

Table 1. Variation in Reynolds number for different rotational speeds in NaCl solution at room temperature (25^{o}C) with laminar, transition and turbulent.

Rotation speed (Revolution per minute, RPM)	1	10	100
Reynolds number (Re)	8	80	804
Anticipated flow regimes	Laminar	Transition	Turbulent

Table 2. The formulation and indicator of chemicals added into the test solution.

Formulation	Indicator
Blank solution	F_o
Individual 20 ppm fatty amides	F_1
Individual 500 ppm sodium sulphite	F_2
Individual 2000 ppm sodium sulphite	F_3
20 fatty amides with 500 ppm sodium sulphite	F_4
20 fatty amides with 2000 ppm sodium sulphite	F_5

Table 3 shows that, the highest inhibition efficicency is F_5 in each rotation which are 94, 51, 61 and 74% in 0, 1, 10 and 100 RPM respectively. They provided dual protection to the carbon steel surface. The fatty amides consist of mixture of amides molecules including stearamide, linoleamide, erucamide, palmitamide and oleamide. The difference in chain lengths of amides provided significant advantages to play a role as an effective corrosion inhibitor to protect the surface of carbon steel. More various chain-lengths of fatty amides compounds formed more protection layers on the surface. In fact, the long chains of carbons can lead to difficulties and prolong the diffusion path for aggressive molecule in solution especially oxygen and water molecule to penetrate onto steel surface. Besides, fatty amides molecules contain nitrogen element (N) that is known to have a pair of electron (lone pair) from sp^2 electron configuration that promotes surface adsorption. The lone pair can adsorb onto carbon steel surface then, forming a protective layer. This finding was also supported by previous studies [16], [17]. In addition, the presence of sodium sulphite in the inhibited solution containing fatty amides reduced the culprit molecule in the aqueous solution namely dissolved oxygen. Sodium sulphite reacted with the dissolved oxygen and then reduced the concentration of dissolved oxygen in the solution. The reaction between sodium sulphite and dissolved oxygen is as following the Equation (3):

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \tag{3}$$

The corrosion rates are greatly decreased in all tested rotation speeds when fatty amides and sodium sulphite (F_4 and F_5) were used together as shown in Table 3. It could be that, the combination of fatty amides with sodium sulphite that contribute to synergistic effect to enhance the inhibition efficiency compared to merely individual fatty amides or sodium sulphite. The presence of sodium sulphite in the inhibited solution suppressed the cathodic reaction in corrosion mechanism and indirectly helped the film formation of fatty amides. The sodium sulphite indirectly supported film formation by scavenging the dissolved oxygen in the solution and then reduced the chances of dissolved oxygen to attack the metal surface. The reaction of sodium sulphite and dissolved oxygen produced sodium sulfate, Na_2SO_4. However, the sodium sulfate do not contribute any consequences to the corrosion process and was proven in the previous study [18]. When concentration of sodium sulphite increased (500, 1000 and 2000 ppm) in the inhibited solution, more dissolved oxygen molecules in the solution reacted and depleted in the solution which results in more protected film formation of fatty amides. Another highlight is the corrosin rate and inhibition efficiency achieved by both individual fatty amide and sodium sulphite (F_1, F_2 and F_3). The corrosion rate of specimens increased in addition of individual substances when tested in the different rotation speeds. Thus, the calculated inhibition efficiency of individual substance (F_1, F_2 and F_3) in Table 3 shows much lower values compared to the inhibition by combination of both in all tested flow velocities. In fact, there are some negative values in the inhibition efficiency of individual fatty amides and individual sodium sulphite when tested in moving condition. It suggested that both individual fatty amide and sodium sulphite able to promote the corrosion reaction instead of inhibited the corrosion process. When facing different flow velocities (laminar, transition and turbulent) the individual substance increased the corrosion rate due to insufficient protection. Thus, the corrosion inhibition provided by formulation of F_1, F_2 and F_3 unable work properly, particularly in the rotation speeds. It also indicated that the presence of both fatty amides and sodium sulphite are needed to maintain the inhibition effeciency even in turbulent condition.

The influence of rotation speeds on the corrosion performance is an important factor to be considered in this study. According to Jiang et al (2005) [19], the rotation speeds have two opposite effects on the inhibition performances. First, it increased the mass transport of inhibitor molecules to the specimen surface and it was beneficial to improve the inhibition efficiency. On the other hand, the rotation speeds results in high shear stress that will remove the inhibitor layers from the specimen surface. This second effect of rotation speed had an adverse effect to inhibition performance. In this current study, the formulation of combination substances (F_4 and F_5) decreased the corrosion rate from 1 RPM (laminar) to 100 RPM (turbulent) as illustrated in the Figure 1 and numerical values as tabulated in Table 3. The increase in mass transfer of fatty amides onto specimen surface at higher rotation speeds provided the maximum protection in this study. Larger amount of fatty amides were either physically or chemically adsorb, then forming protection layers. At the same time, large amount of sodium sulphite in the inhibited solution reacted with dissolved oxygen in the solution making the specimen surface indirectly well protected. In the combination system (F_4 and F_5), the formulations can perform better in the following order $F_5 > F_4$ in most of flow velocities tested. The corrosion rate increased when tested in the different rotation speeds for formulation of individual substances (F_1, F_2 and F_3). It showed the inhibition process of individual substances during rotation speeds was not working properly. In fact, as shown in the Table 3, the inhibition efficiency of individual substance reached negative values. It indicates that, the addition of individual substance in difference rotation speeds promoted corrosion reaction instead of inhibited the corrosion process.

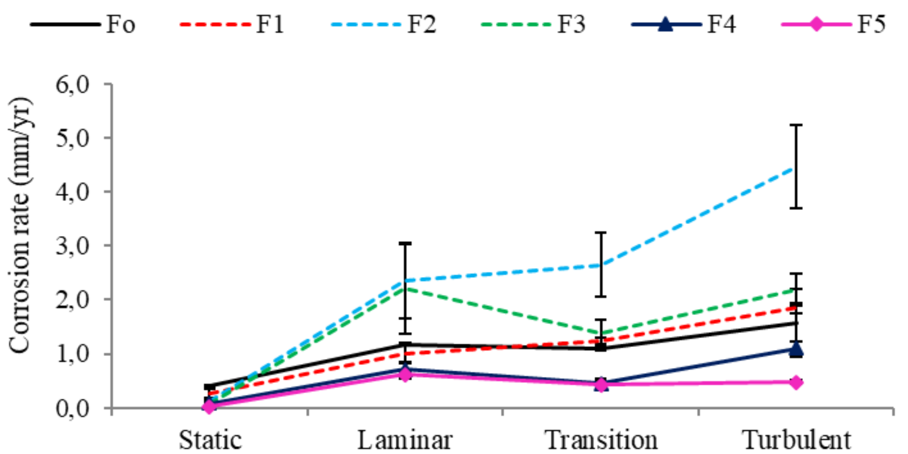


Figure 1. Influence of rotation speed on corrosion rate values of steel at different flow regimes; static, laminar (1 RPM), transition (10 RPM) and turbulent (100 RPM) using linear polarization resistance (LPR) test.

Table 3. The values of corrosion rate, C.R (ohm.cm^2) and inhibition efficiency, IE (%) of systems in different rotation speeds (0, 1, 10 and 100 RPM).

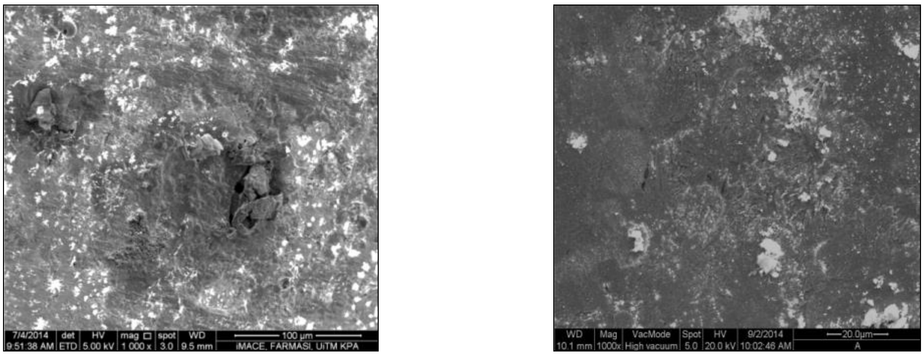
Solutions	0 RPM (Static)		1 RPM (Laminar)		10 RPM (Transition)		100 RPM (Turbulent)	
	C.R (mm/yr)	I.E (%)	C.R (mm/yr)	IE (%)	C.R (mm/yr)	IE (%)	C.R (mm/yr)	IE (%)
F_0	0.396	-	1.178	-	1.095	-	1.572	-
F_1	0.257	35	1.003	2	1.234	-3	1.844	-16
F_2	0.119	70	2.355	-108	2.652	-121	4.466	-131
F_3	0.066	83	2.202	-55	1.388	-11	2.190	-28
F_4	0.080	80	0.709	33	0.443	59	1.097	45
F_5	0.025	94	0.613	51	0.426	61	0.468	74

3.2 Surface morphology and surface analysis by SEM-EDX

Figure 2 shows the Scanning Electron Microscope, SEM images of the selected carbon steel specimen under critical condition of turbulent flow. Figure 2(a) shows a selected area of specimen tested in the presence of 20 ppm fatty amides individually and Figure 2(b) shows specimen in the presence of 20 ppm fatty amides with 2000 ppm sodium sulphite (F_5). It is observed that the specimen surface tested in solution containing individual 20 ppm fatty amides in turbulent condition was severely damaged with the emerging of cracks and pores as observed in Figure 2(a). It was suggested that the dissolution of metal and penetration of aggressive species in the test solution such as chloride ions (Cl^-) onto the metal surface was occurred. The steel surface was not well protected by individual fatty amides during turbulent flow. The adsorption of fatty amides molecule were detached from the surface due to high shear stress applied. It was supported by analysis of chemical composition which indicated the absence of nitrogen element from the surface. Meanwhile, figure 2(b) shows a better surface morphology with the presence of both fatty amides and sodium sulphite, F_5. In addition, the EDX evaluations show a higher percentage of elemental oxygen can be observed in Figure 3(a) compared to Figure 3(b) due to the higher formation of oxide products in specimen tested in individual fatty amide during turbulent condition.

4. Conclusion

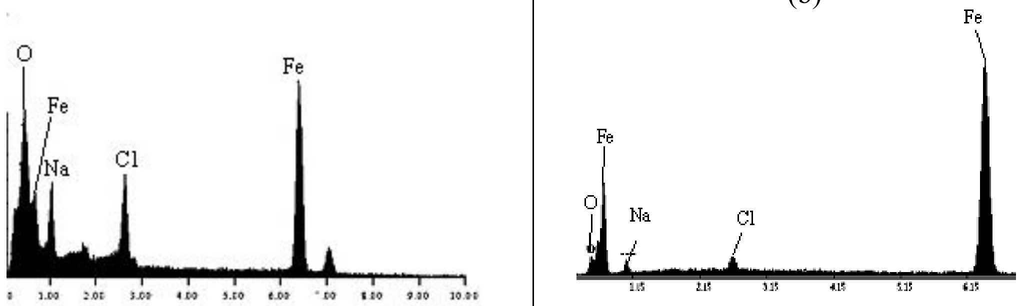
The inhibition property can be enhanced with the presence of both fatty amides and sodium sulphite at different flow velocities. The enhancement of inhibition actions are due to binary protections provided by surface adsorption of fatty amide and reaction of sodium sulphite with dissolved oxygen molecules. This shows a synergistic effect between fatty amides with sodium sulphite present in the inhibition system even when facing different flow velocities.



(a) (b)

Figure 2. SEM images for specimens surface immersed in test solution in turbulent condition containing (a) only 20 ppm fatty amides (b) 20 ppm fatty amides with 2000 ppm sodium sulphite.

(a) (b)



Elements	Wt (%)	Elements	Wt (%)
Oxygen, O	21.34	Oxygen, O	2.92
Sodium, Na	5.96	Sodium, Na	4.76
Chloride, Cl	4.86	Chloride, Cl	1.84
Iron, Fe	67.84	Iron, Fe	90.48
Total	100	Total	100

Figure 3. EDX analysis of polarized samples in turbulent condition containing (a) 20 ppm fatty amides (b) 20 ppm fatty amides with 2000 ppm sodium sulphite.

Acknowledgement
The authors would like to thank and gratefully acknowledged use of services and research facilities available at the Faculty of Chemical Engineering, Universiti Teknologi MARA, Malaysia and MTeG, Malaysian Nuclear Agency (Nuclear Malaysia).

References

[1] G. Khan, K. M. S. Newaz, W. J. Basirun, H. Mohd Ali, F. Faraj Lafta, and G. M. Khan, "Application of Natural Product Extracts as Green Corrosion Inhibitors for Metals and Alloys in Acid Pickling Processes- A review," *Int. J. Electrochem. Sci.*, vol. 10, pp. 6120–6134, 2015.
[2] A. Yildirim, S. Öztürk, and M. Çetin, "Novel amide-based cationic surfactants as efficient corrosion inhibitors for carbon steel in HCl and H2SO4 media," *J. Surfactants Deterg.*, vol. 16, no. 1, pp. 13–23, 2013.
[3] P. Hoffman and W. Bryan, "Year-in-Review : 2013," 2014.
[4] M. P. H. Gerhardus H. Koch and and N. G. T. Y. P. V. J. H. P. Brongers, "Corrosion costs and preventive strategies in the United States," 2002.
[5] S. A. Umoren and U. F. Ekanem, "Inhibition of mild steel corrosion in H2SO4 using exudate gum from pahylobus edulis and synergistic potassium halide additives," *Chem. Eng. Commun.*, vol. 197, no. 10, pp. 1339–1356, 2010.
[6] A. Y. Musa, A. B. Mohamad, A. A. H. Kadhum, M. S. Takriff, and L. T. Tien, "Synergistic effect of potassium iodide with phthalazone on the corrosion," *J. Corros. Sci.*, vol. 53, 2011.
[7] I. Carrillo, B. Valdez, R. Zlatev, M. Stoytcheva, M. Carrillo, and R. Bäßler, "Electrochemical study of oxyanions effect on galvanic corrosion inhibition," *Int. J. Electrochem. Sci.*, vol. 7, pp. 8688–8701, 2012.
[8] M. Salasi, T. Shahrabi, and E. Roayaei, "Effect of inhibitor concentration and hydrodynamic conditions on the inhibitive behaviour of combinations of sodium silicate and HEDP for corrosion control in carbon steel water transmission pipes," *Anti-Corrosion Methods Mater.*, vol. 54, no. 2, pp. 82–92, 2007.
[9] D. S. Kalyani, S. R. S, S. B. M, and B. Sreedhar, "Synergistic effect of folic acid on corrosion inhibition of carbon steel in presence of a phosphanet and zinc ions," *Int. J. Recent Sci. Res.*, vol. 6, pp. 4361–4365, 2015.
[10] I. M. Ibrahim, J. Jai, and M. A. Hashim, "Comparative inhibition effect of synthesized fatty amides mixture, pyridine and pyrrole on carbon steel in saline environment," *Appl. Mech. Mater.*, vol. 575, pp. 206–209, 2014.
[11] I. M. Ibrahim, M. Daud, J. Jai, and A. Hashim, "Effect of secondary species on inhibition efficiency of fatty amide mixtures in dynamic environment," *Int. J. Eng. Technol.*, vol. 7, no. 3, pp. 844–851, 2015.
[12] I. M. Ibrahim, S. Yunus, and M. A. Hashim, "Relative performance of isoproopylamine, pyrrole and pyridine as corrosion inhibitors for carbon steels in saline water at mildly elevated temperatures," *Int. J. Sci. Eng. Res.*, vol. 4, no. 2, 2013.
[13] Pine Research Instrumentation, "Study of mass-transport limited corrosion using pine rotating cylinder electrodes-An overview of theory and practise," pp. 1–6, 2006.
[14] A. Y. Musa, A. H. Kadhum, and A. B. Muhamad, "Corrosion inhibitor film forming in aerated and deaerated solutions," *Int. J. Electrochem. Sci.*, vol. 5, pp. 1911–1921, 2010.
[15] ASTM G59-97 (Reapproved), *Standard test methods for conducting potentiodynamic polarization resistance measurement*. 2009, pp. 1–4.
[16] B. E. A. Rani and B. B. J. Basu, "Green inhibitors for corrosion protection of metals and alloys: An overview," *Int. J. Corros.*, vol. 2012, no. i, 2012.
[17] I. M. Ibrahim, J. Jai, and M. A. Hashim, "Inhibitive effect of fatty amide and secondary species on the corrosion of carbon steel," *Adv. Mater. Res.*, vol. 1133, pp. 366–370, 2016.

[18] T. I. Wu and J. K. Wu, "Effect of sulfate ions on corrosion inhibition of AA 7075 aluminum alloy in sodium chloride solutions," *Corrosion*, vol. 51, no. 3, pp. 185–190, 1995.
[19] X. Jiang, Y. G. Zheng, and W. Ke, "Effect of flow velocity and entrained sand on inhibition performances of two inhibitors for CO2 corrosion of N80 steel in 3% NaCl solution," *Corros. Sci.*, vol. 47, no. 11, pp. 2636–2658, 2005.