Australian Journal of Basic and Applied Sciences, 8(15) Special 2014, Pages: 174-179

AENSI Journals

Australian Journal of Basic and Applied Sciences

ISSN:1991-8178

Journal home page: www.ajbasweb.com

Efficiency of Benzyl Dimethyl (2-Hydroxyethyl) Ammonium Chloride as Corrosion Inhibitor in Acetic Acid

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ARTICLE INFO

Article history:
Received 15 September 2014
Accepted 5 October 2014
Available online 25 October 2014

Keywords:
Inhibition efficiency,
Carbon steel,
Corrosion inhibitor,
Adsorption

ABSTRACT

The inhibition performance of benzyl dimethyl (2-hydroxyethyl) ammonium chloride (BDC) as corrosion inhibitor for carbon steel in 1 M acetic acid has been investigated by weight loss measurements**.** The aim of this study is to identify the inhibition efficiency of BDC by varies the concentration and temperature.In order to investigate the BDC performance, further study on thermodynamic and adsorption mechanism has been implied. Weight loss analysis revealed that the corrosion rate of carbon steel decreased with the increasing of BDC concentration and the achievement of inhibition efficiencyreached up to 60%. Meanwhile, this performance is inversely proportional with the increasing of temperature. The result from activation parameters indicated that dissolution process of carbon steel can be restrained by formation of BDC thin film on the carbon steel surface throughan adsorption process. The process of adsorption is seen to follow Langmuir adsorption isotherm and the adsorption mechanism of BDC occurred by both physisorption and chemisorption processes. The performance of this inhibitor was also supported by morphology analysis on the carbon steel surface**.** This study revealed that BDC has showed good inhibition properties to protect the carbon steel in acetic acid medium.

ToCite ThisArticle: Mohd Nazri Idris, Abdul Razak Daud and Norinsan Kamil Othman., Efficiency of Benzyl Dimethyl (2-Hydroxyethyl) Ammonium Chloride as Corrosion Inhibitor in Acetic Acid. ***Aust. J. Basic & Appl. Sci.,*** *8(15): 174-179, 2014*

INTRODUCTION

Application of inhibitor to prevent corrosion on carbon steel was widely used in petroleum industries, water cooler system, storage tank and so on (Dkhireche *et al*., 2013; Hassanzadeh, 2007; Sawada *et al*., 2007; Keny *et al*., 2008). Most inhibitors are able to adsorb on the metallic compound by physisorption or chemisorption to create a thin film on the metal/solution interface. This formation became a barrier to control the dissolution process of metallic ions and suppress the corrosion activities and active reaction between the water molecules or any corrosive medium with the metal surface. In general practice, organic inhibitors containing hetero-atoms such as N, S, O and P together with unsaturated bond like double and triple bond were commonly selected especially when the acid solution is been applied (Musa *et al*., 2012; Tourabi *et al*., 2013).

Application of quaternary ammonium compound as corrosion inhibitor in acidic medium such as HCl and H_2SO_4 on various metallic compounds has been extensively studied. The existing of strong electrostatic force contributed by cationic charges and accompanied by the co-adsorption of halide ions provides sufficient tendency for adsorption process, due to charges neutralization (Vasudevan *et al*., 1995). Additionally, the chemical composition, chemical structure and their affinity to interact with the metallic ion were also affecting their effectiveness (Popova *et al*., 2011). Substitution of aromatic group such as phenyl or benzyl on the quaternary ammonium structure provides excellent contribution to increase the inhibition efficiency and surface coverage (Behpour *et al*., 2009; Kokalj, 2013).

The use of BDC, which is one of the quaternary ammonium compounds in acidic medium, has been rarely investigated on the metallic compound. Present study, the efficiency of BDC as corrosion inhibitor in 1 M acetic acid has been investigated for carbon steel, which is usually used in petroleum pipeline system. The focus was by varying the temperature and BDC concentration, and the study was carried out by weight loss measurement and surface analysis.

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MATERIALS AND METHODS

The chemical compositions of carbon steel in weight percentage were 0.258 C, 0.466 Mn, 0.427 Si, 0.013 P, 0.015 Ni, 0.019 Cu, 0.132 Al and balance is Fe. Carbon steel was cut to the size of 12 x 10 x 5 mm and wet abraded with emery paper up to 1200 grade, rinsed with distilled water and cleaned with acetone. BDC was purchased from Sigma Aldrich Co. Ltd and prepared in concentration range of 2.5 to 15.0 mM in 1 M acetic acid solution. Figure 1 shows the chemical structure of BDC compound.

Weight loss test was conducted at temperatures 25 to 55 ± 1^{o}C using a thermostat controlled water bath. All samples were weighted and immediately immersed for 6 hours into different solution medium. After immersion, all samples were cleaned according to ASTM G1-03 standard and dried by blowing cold air. Analytical balance was used to determine the weight loss. The samples were reproduced in triplicate and the average was calculated. The corrosion rate, C_r(mg/cm^{2}h) of carbon steel in the absence and presence of different BDC concentration was calculated by equation (1);

$$C_r = \Delta W/At \quad (1)$$

where ΔW is the average weight loss (mg), A is the total surface area (cm^2) and t is the immersion time (h). Surface coverage, θ and inhibition efficiency, *IE%* of BDC were calculated by using equation (2) and equation (3), respectively;

$$\theta = 1-C_r'/C_r \quad (2)$$

$$IE\ \% = 100(1-C_r'/C_r) \quad (3)$$

where C_r and C_r' are the corrosion rate of carbon steel in the absence and presence of BDC, respectively. Morphology of carbon steel surface was analyzed by scanning electron microscope model Hitachi TM3000.

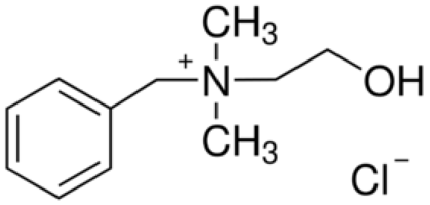


Fig. 1: Chemical structure of benzyl dimethyl (2-hydroxyethyl) ammonium chloride.

RESULTS AND DISCUSSION

Figure 2 shows the corrosion rate obtained from weight loss analysis. In this figure, the corrosion rate values decreased with the increasing of BDC concentration at all temperature. As can be seen, the lowest corrosion rate droppedwas about 0.4 mg/cm^{2}hwhen applying 15 mM BDC at 55 ^{o}C as compared to 1 M acetic acid at same temperature. At 25 and 40 ^{o}C, the corrosion rate decreased in almost 0.5 to 0.2 mg/cm^2.h as compared with the control medium, respectively. This result indicated that BDC has a potential to be applied as a corrosion inhibitor for carbon steel in acetic acid. By increasing the concentration, BDC molecules had more tendency to adsorb onto the carbon steel surface, thus increased the surface coverage. The adsorption of these molecules may create a barrier to protect the steel surface from reacting with water molecules and acetic acid medium. The same behavior had seen to be occurred for many organic inhibitors (Solomon *et al*., 2010; Tourabi *et al*., 2013; Sahin *et al*., 2002). Meanwhile, the increment of IE% was also obtained by increasing the BDC concentration as shown in figure 3. It is important to note here that, the interaction between BDC molecules and the steel surface occurred due to electrostatic attraction and the surface coverage increased with the increasing of BDC concentration. This performance indicated that strong interaction bonding existed between the carbon steel surface and BDC cationic, N^+. Additionally, this interaction was alsocontributed by π-electron bonding from the benzyl group, thus blocking the active corrosion part and decreasing the corrosion rate (Tourabi *et al*., 2013).

On the other hand, the rise of temperature is found to increase the corrosion rate of carbon steel in acetic acid. This result revealed that BDC molecules obtained enough energy to desorb from the steel surface into the bulk solution at higher temperature. As presented in Figure 3, the inhibition efficiency (IE%) of all BDC concentrations increased from 25 to 40 ^{o}C, but at 55 ^{o}C, it reduced the IE% at all concentration studied. In this study, the maximum IE% value has reached to 60% at 40 ^{o}C. Thus, the adsorption process of BDC in acetic acid can be considered as temperature depending.

The efficiency of BDC to inhibit the dissolution process in corrosion activity can be deliberated by thermodynamic function. One of the most important parameter is activation energy, E_a (kJ/mol). This value has been determined by applying Arrhenius equation as shown in equation (4) (Obot *et al*., 2012);

$$\ln C_r = \ln A - E_a/RT \qquad (4)$$

where C_r is the corrosion rate (mg/cm^{2}h), A is the Arrhenius frequency factor (mg/cm^{2}h), R is the gas constant (8.314 J/molK) and T (K) is the absolute temperature. E_a was easily determined from the slope of linear regression between ln C_r and $1/T$. The A value was determined by this intercept plot. Figure 4 shows the Arrhenius plots of different BDC concentration used and the analysis is elucidated in table 1.

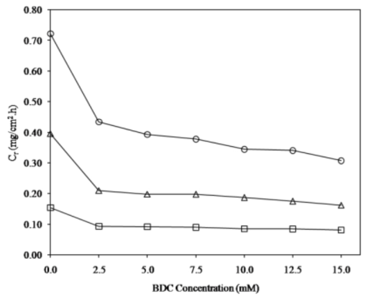


Fig. 2: Corrosion rate of different BDC concentration in 1M acetic acid solution at (□) 25°C, (Δ) 40°C and (○) 60°C.

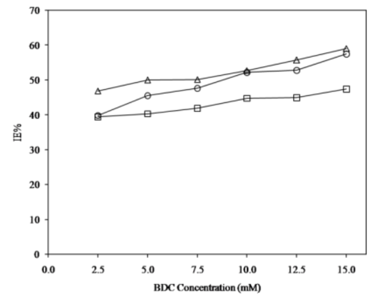


Fig. 3: IE% of BDC in 1M acetic acid solution at (□) 25°C, (Δ) 40°C and (○) 60°C.

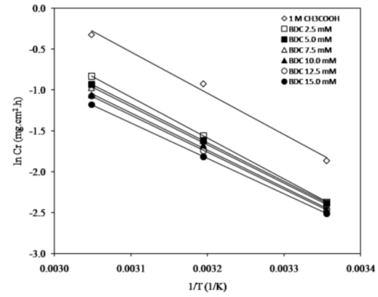


Fig. 4: Arrhenius plot of carbon steel in 1 M acetic acid with and without BDC.

Table 1: Activation parameters for carbon steel in 1 M acetic acid with different BDC concentration.

BDC Con. (mM)	E_a (kJ/mol)	ΔH (kJ/mol)	ΔS (J/molK)
0.0	41.95	39.36	-128.0
2.5	41.64	39.05	-133.6
5.0	39.35	36.75	-141.4
7.5	39.05	36.45	-142.5
10.0	37.95	35.35	-146.6
12.5	37.66	35.07	-147.7
15.0	36.08	33.48	-153.4

Data in table 1 indicated thatE_a values of carbon steel immersed in different BDC concentration had slightly decreasedas compared with 1 M acetic acid solution. Decreasing in E_a values in the presence of BDC suggested that the mechanism of chemisorptions process occurredon the active surfaceby BDC molecules. The same results were also determined by using others organic inhibitor(Behpour *et al*., 2010; Desimone *et al*., 2011). This result also indicated that the thickness of double layer has not been facilitated by BDC molecules at steel/solutioninterface. Decreasing in E_a values can also be elaborated in term of higher achievement in surface coverage, which is contributed by higher BDC concentration and additionally provided more efficiency to adsorb on the carbon steel active surface. Increasing on the surface coverage will reflect to changing the rate determining step of metal dissolution to the second step of metal ions diffusion through the film of corrosion product and inhibitor (Behpour *et al*., 2010). It is generally known that the rate of metal dissolution was the sum of corrosion rate of the metal surface and the rate of part covered surface by adsorbed inhibitor. In the case of higher degree of surface coverage, the corrosive mechanism was directly considered from the reaction of metal surface with the inhibitor molecules and the first step of bare metal surface reaction is considering no substantial contribution (Riggs & Hurd, 1967). Thus, the E_a of carbon steel in the presence of BDC can be smaller than absence of BDC compound.

On top of that, activation enthalpy, ΔH and entropy, ΔS were also being analyzed to specify the energy contribution in this corrosion process. These values can be determined by using transition state equation (5) (Behpour *et al*., 2009);

$$C_r = (RT/Nh)exp(\Delta S/R)exp(-\Delta H/RT) \tag{5}$$

where C_r is the corrosion rate, R is the gas constant, T is absolute temperature, A is the Avogadro number (6.022×10^{23}) and h is the Plank's constant (6.626×10^{-34}). The values of both ΔH and ΔS can be measured from the slope and intercept of linear regression plot between ln (C_r/T) and$1/T$.The plot of transition state equation is shown in figure 5 and the variations of ΔH and ΔS for different BDC concentrations are elucidated in table 1. As presented in this table, all ΔH are positive in values, indicating that dissolution process is an endothermic in nature. The values of ΔS obtained are relatively low and negative for all BDC concentrations. This result indicated that active movement of dissolution ions has been minimized due to adsorption of BDC molecules on the steel surface. These conditions proved that BDC has a potential to inhibit the carbon steel in this acetic acid medium.

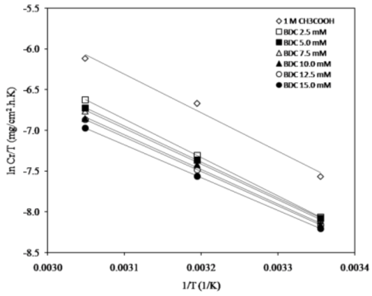


Fig. 5: Carbon steel transition state in 1M acetic acid with and without BDC.

The adsorption process of BDC molecules onto carbon steel surface wasanalyzed by series of adsorption isotherm model i.e. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The degree of surface coverage was evaluated from the result of weight loss method. The best fitted isotherm was determined by the highest correlation coefficient, R^2 value. The analysis proved that the adsorption process obeyed Langmuir adsorption isotherm and the R^2 values are 0.995, 0.991 and 0.991 for adsorption process at temperature 25, 40 and 55 °C, respectively. According to Langmuir adsorption isotherm, the relationship between surface coverage and BDC concentrations can be calculated by equation (6) (Musa *et al*., 2012);

$$C/\theta = 1/K_{ads} + C \tag{6}$$

where θ is the surface coverage, C is the BDC concentration (mM) and K_{ads} is the equilibrium constant (mM^{-1})of Langmuir adsorption process. The K_{ads} is well known, related to free adsorption energy, ΔG^o_{ads} by using equation (7) (Benbouya *et al*., 2012);

$$\Delta G^o_{ads} = -RTln(55.5\ K_{ads}) \tag{7}$$

where 55.5 is the water concentration in solution, R is the molar gas constant (J/molK) and T is the absolute temperature (K).

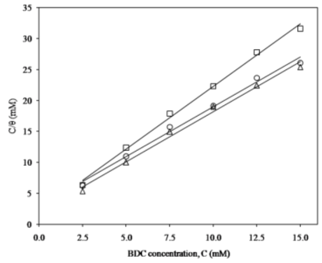


Fig. 6: Langmuir adsorption isotherm for BDC on carbon steel at (□) 25°C , (Δ) 40°C and (○) 60°C.

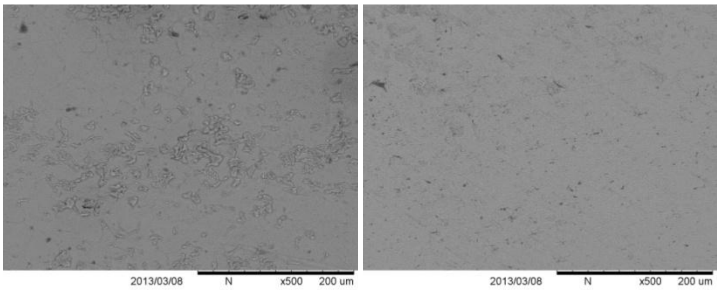
Figure 6 shows the plots of C/θ versus C at different temperatures. The K_{ads} was determined from the intercept of linear regression plot and the values are 0.495, 0.494 and 0.343 mM^{-1}at temperature 25, 40 and 55 ^oC, respectively. Thus, the analyses of ΔG^o_{ads} at these temperatures are -25.323, -26.598 and -26.872 kJ/mol, respectively. These results revealed that the ΔG^o_{ads} values are negative at all temperature studied and indicated spontaneous adsorption processes. It is agreed that,ΔG^o_{ads} value at -20 kJ/mol or lower (more positive) signifies the adsorption with electrostatic interaction occurs between adsorbate and adsorbent interface namely, physisorption, while the values of more negative than -40 kJ/mol indicating that charge sharing between the molecules and metal surface has taken place namely, chemisorption(Seifzadeh *et al*., 2013). As obtained in this study, the values of ΔG^o_{ads} are in the range of -20 kJ/mol and -40 kJ/mol, signifying both physisorption and chemisorptions processes are potentially take place. The adsorption model in this analysis was in good agreement with the above thermodynamics analysis.

According to these analyses, it is suggested that the adsorption mechanism of BDC molecules is able to take place by quasi-substitution process between the BDC molecules in solution and water molecules at the steel surface (Sahin *et al*., 2002; Tao *et al*., 2009). Since the adsorbed water dissolved into the solution, the amount of BDC ions begin to replace the active sites by electrostatic force between N^+ group and pi electrons bonds in the benzyl group with the negative charges on the carbon steel surface. Substitution process between BDC molecules and adsorbed water can be represented by using equation (8) (Idris *et al*., 2013; Sahin *et al*., 2002):

$$BDC_{sol} + xH_2O_{ads} ==> BDC_{ads} + xH_2O_{sol} \quad (8)$$

where BDC_{sol} and BDC_{ads} represent the BDC molecules in the solution and as adsorbed position, respectively. H_2O_{ads} represents the initial water molecules adsorbed on carbon steel and x is the number of water molecules replaced from this process. At low concentration, it was believed that BDC molecules will occupy less surface area of the steel and dissolution process takes place on the surface active site. By increasing the concentration, more compact of BDC thin film formed and acted as a barrier to prevent the steel from corrodes.

Scanning electron microscopy has been used to analyze the effect of BDC on the carbon steel surface. Figure 7a shows the micrograph of carbon steel immersed in 1 M acetic acid for six hours in the absence of BDC. The micrograph indicated that a strong damage occurred in the steel surface due to corrosion effect. However, micrograph in Figure 7b with the presence of 5 mM BDC in 1 M acetic acid was remarkably improved and less damage in comparison to uninhibited carbon steel. This morphology proved that BDC molecules were successfully adsorbed and created a thin film to suppress the dissolution process of metallic ions.



(a) (b)

Fig. 7: Morphology analysis of carbon steel surface (a) without BDC and (b) with 5 mM BDC in 1M acetic acid for six hours.

Conclusion:

This study revealed that BDC is able to inhibit the corrosion of carbon steel in 1M acetic acid by forming a thin film barrier. The inhibition efficiency of this inhibitor is depending on the temperature and concentration used. The adsorption process of BDC onto the carbon steel followed Langmuir adsorption isotherm model and the adsorption mechanism occurred due to physisorption and chemisorption process.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the Ministry of Education Malaysia and Universiti Kebangsaan Malaysia for financial support via research grants, ERGS/1/2012/STGS05/ UKM/02/2 and DPP-2013-035.

REFERENCES

Behpour, M., S.M. Ghoreishi, N. Mohammadi, N. Soltani and M. Salavati-Niasari, 2010. Investigation of some Schiff base compounds containing disulfide bond as HCl corrosion inhibitors for mild steel. Corrosion Science, 52(12): 4046-4057.

Behpour, M., S.M. Ghoreishi, N. Soltani and M. Salavati-Niasari, 2009. The inhibitive effect of some bis-N,S-bidentate Schiff bases on corrosion behaviour of 304 stainless steel in hydrochloric acid solution. Corrosion Science, 51(5): 1073-1082.

Benbouya, K., B. Zerga, M. Sfaira, M. Taleb, M.E. Touhami, B. Hammouti, H. Benzeid and E. Essassi, 2012. WL, IE and EIS Studies on the Corrosion Behaviour of Mild Steel by 7-substituted 3-methylquinoxalin-2 (1H)-ones and thiones in Hydrochloric Acid Medium. Int. J. Electrochem. Sci, 7(7): 6313-6330.

Desimone, M.P., G. Grundmeier, G. Gordillo and S.N. Simison, 2011. Amphiphilic amido-amine as an effective corrosion inhibitor for mild steel exposed to CO2 saturated solution: Polarization, EIS and PM-IRRAS studies. Electrochimica Acta, 56(8): 2990-2998.

Dkhireche, N., A. Dahami, A. Rochdi, J. Hmimou, R. Touir, M. Ebn Touhami, M. El Bakri, A. El Hallaoui, A. Anouar and H. Takenouti, 2013. Corrosion and scale inhibition of low carbon steel in cooling water system by 2-propargyl-5-o-hydroxyphenyltetrazole. Journal of Industrial and Engineering Chemistry, 19(6): 1996-2003.

Hassanzadeh, A., 2007. Validity of dynamic electrochemical impedance spectra of some amine corrosion inhibitors in petroleum/water corrosive mixtures by Kramers–Kronig transformation. Corrosion Science, 49(4): 1895-1906.

Idris, M.N., A.R. Daud, N.K. Othman and A. Jalar, 2013. Corrosion control by benzyl triethylammonium chloride: Effects of temperture and its concentration. International Journal of Engineering & Technolgy, 13(03): 47-51.

Keny, S.J., A.G. Kumbhar, C. Thinaharan and G. Venkateswaran, 2008. Gallic acid as a corrosion inhibitor of carbon steel in chemical decontamination formulation. Corrosion Science, 50(2): 411-419.

Kokalj, A., 2013. Formation and structure of inhibitive molecular film of imidazole on iron surface. Corrosion Science, 68(1): 195-203.

Musa, A.Y., A.B. Mohamad, A.A.H. Kadhum, M.S. Takriff and W. Ahmoda, 2012. Quantum chemical studies on corrosion inhibition for series of thio compounds on mild steel in hydrochloric acid. Journal of Industrial and Engineering Chemistry, 18(1): 551-555.

Obot, I.B., E.E. Ebenso, N.O. Obi-Egbedi, A. Afolabi and Z. Gasem, 2012. Experimental and theoretical investigations of adsorption characteristics of itraconazole as green corrosion inhibitor at a mild steel/hydrochloric acid interface. Research on Chemical Intermediates, 38(8): 1761-1779.

Popova, A., M. Christov and A. Vasilev, 2011. Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part II: Electrochemical impedance and polarisation resistance results. Corrosion Science, 53(1): 1770-1777.

Riggs, O.L. and R.M. Hurd, 1967. Temperature coefficient of corrosion inhibitor. Corrosion Science, 23(252-258.

Sahin, M., S. Bilgic and H. Yilmaz, 2002. The inhibition effects of some cyclic nitrogen compounds on the corrosion of the steel in NaCl mediums. Applied Surface Science, 195(14): 1-7.

Sawada, S., J. Kubo, C.L. Page and M.M. Page, 2007. Electrochemical injection of organic corrosion inhibitors into carbonated cementitious materials: Part 1. Effects on pore solution chemistry. Corrosion Science, 49(3): 1186-1204.

Seifzadeh, D., H. Basharnavaz and A. Bezaatpour, 2013. A Schiff base compound as effective corrosion inhibitor for magnesium in acidic media. Materials Chemistry and Physics, 138(23): 794-802.

Solomon, M.M., S.A. Umoren, I.I. Udosoro and A.P. Udoh, 2010. Inhibitive and adsorption behaviour of carboxymethyl cellulose on mild steel corrosion in sulphuric acid solution. Corrosion Science, 52(4): 1317-1325.

Tao, Z., S. Zhang, W. Li and B. Hou, 2009. Corrosion inhibition of mild steel in acidic solution by some oxo-triazole derivatives. Corrosion Science, 51(11): 2588-2595.

Tourabi, M., K. Nohair, M. Traisnel, C. Jama and F. Bentiss, 2013. Electrochemical and XPS studies of the corrosion inhibition of carbon steel in hydrochloric acid pickling solutions by 3,5-bis(2-thienylmethyl)-4-amino-1,2,4-triazole. Corrosion Science, 75(1): 123-133.

Vasudevan, T., S. Muralidharan, S. Alwarappan and S.V.K. Iyer, 1995. The influence of N-hexadecyl benzyl dimethyl ammonium chloride on the corrosion of mild steel in acids. Corrosion Science, 37(8): 1235-1244.