Adsorption Behaviour and Thermodynamic Study of Triazine as A Corrosion Inhibitor for Mild Steel in Oilfield Produced Water

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Abstract. In recent years, the corrosion problem of equipment and pipeline caused by oilfield produced water is becoming increasingly serious. In this work, corrosion inhibitor of triazine, synthesized from formaldehyde and ethanolamine, was evaluated using weight-loss techniques. The triazine was found to inhibit the corrosion of mild steel in simulated oilfield produced water. The adsorption of inhibitor was studied, which was consistent with the assumption of Langmuir adsorption model. Thermodynamic parameters of corrosion inhibition process were further calculated and analyzed, which indicated that adsorption of triazine inhibitor was exothermic, spontaneous and physical process.

Keywords: Triazine; oilfield produced water; adsorption; corrosion inhibition.

1 Introduction

In the extraction process of crude oil, a lot of water resources are needed to attain displacement of reservoir oil [1, 2]. Subsequently, injected water and formation water will be produced with crude oil. Large amount of oilfield produced water will be produced after demulsification, which is characterized by high oil content, high organic matter content, high salinity and complex and variable composition [3-7]. Produced water is generally re-injected and recycled for oil displacement after treatment [8]. Oilfield produced water will cause different degrees of corrosion in the process of production and injection [9], which will affect the working efficiency and service life, and even reduce the production efficiency. Recently, novel corrosion inhibitors, such as polymers, N-heterocyclic compounds and plant extracts [10-12], play an indispensable role in the development and application of corrosion inhibition industry. Many non-heterocyclic organic compounds have certain corrosion inhibition activities, but some of them can cause damage to the human and the environment with higher toxicity. Consequently, more researchers dedicated to development of eco-friendly, cheap, non-toxic corrosion inhibitors. In recent years, eco-friendly compounds such as cefixime [13], erythromycin [14] and ciprofloxacin [15] have been widely studied in corrosion inhibition. It was reported that inhibitor can be adsorbed on the material through the action of chemical bonds to achieve the purpose of protection [16-18]. Triazine is N-heterocyclic compounds with lone pair electrons and have potential as corrosion inhibitor. In this study, triazine compound synthesized from formaldehyde and ethanolamine with the ratio of 1：1 can be used as corrosion inhibitor for mild steel. Adsorption properties as well as thermodynamic parameters were further investigated to explain adsorption behavior.

2 Experimental

2.1 Materials

Ethanolamine, formaldehyde, anhydrous calcium chloride, magnesium chloride hexahydrate, sodium bicarbonate and anhydrous sodium sulfate were supplied from Tianjin Tianli Chemical Reagent Co., Ltd with analytically pure. Sodium chloride and Potassium chlorid was supplied from Tianjin Shengao Chemical Reagent Co., Ltd with analytically pure. The tested material is A30 steel plates with the chemical composition (wt pct) C: 1.30, Cr: 4.20, Mo: 5.00, V: 3.10, W: 6.40, Co: 8.30 and Fe balance.

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2.2 Synthesis of triazine

The corrosion inhibitor of triazine is synthesized by condensation of formaldehyde and ethanolamine, the chemical reaction equation is shown in Fig. 1. The three-necked flask was used as a reaction vessel, which was placed in the water bath thermostat at 60°C. After adding a certain amount of ethanolamine, quantitative amount of formaldehyde was slowly added within 0.5h and stirred evenly. Under the condition of reflux condensation, formaldehyde and ethanolamine reacted for 3h. After that, the synthesized compound was obtained. Subsequently, it was cooled to room temperature.

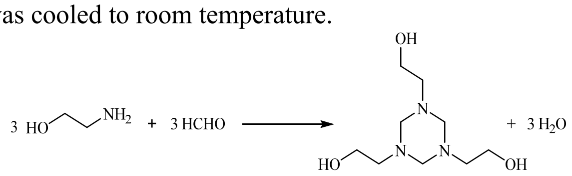

Fig. 1 The reaction equation for the synthesis of triazine.

2.3 Preparation of corrosive solution

The simulated oilfield produced water samples were prepared, which contains a certain amount of corrosive ions. Quantitative ionic compounds including 21.65g $CaCl_2$, 1.4g $MgCl_2{\cdot}6H_2O$, 0.09g $NaHCO_3$, 1.12g Na_2SO_4, 0.9g KCl and 8.24g NaCl were weighed and dissolved in distilled water successively. Then volumetric flask was used to determined volume to 1L, the simulated oilfield produced water was obtained. Subsequently, each 100mL of simulated oilfield produced water was added in several glass bottles as corrosion solution. Then, different amounts of synthesized triazine corrosion inhibitors were added so that their concentrations in the water samples were 0, 0.1%, 0.2%, 0.5%, 1.0% and 2.0%, respectively.

2.4 Treatment of steel sheets

The corrosion inhibition test of mild steel was carried out by hanging method. Mild steel sheets were abraded with emery papers and their surface area was recorded as S. Then the initial mass of each mild steel plate was weighed by an analytical balance and recorded as m_1.
Each group of two mild steel sheets was suspended in glass bottles containing corrosive solutions of different corrosion inhibitors with ropes, then these bottles were placed in a constant temperature water bath at a specific temperature. After maintaining at a specific temperature for 48 hours, each steel sheet was taken out and dried by qualitative filter paper. Continue to immerse the mild steel sheets in dilute hydrochloric acid to remove the rust on its surface, then the liquid on the surface was dried with filter paper. After that, they were washed with petroleum ether and ethanol respectively. Finally, the mass of each treated mild steel sheet was weighed with an analytical balance and recorded as m2.

2.5 Corrosion inhibition performance evaluation

The corrosion inhibition performance of prepared triazine was evaluated by weight-loss techniques, which mainly depend on general corrosion rate and inhibition efficiency. The general corrosion rates (*W*) were obtained from equation (1):

$$W = \frac{\Delta m}{St} \tag{1}$$

$$\Delta m = m_1 - m_2 \tag{2}$$

Δm—the weight loss, which was obtained from equation (2), g; *S*—the area of mild steel sheet, cm^2; *t*—the time of immersion, h.
The inhibition efficiency *(E%)* was obtained as suggestd in equation (3):

$$E\% = \frac{\Delta m_0 - \Delta m_t}{\Delta m_0} \times 100\% \tag{3}$$

Δm_0—the weight loss without triazine, g; Δm_t—the weight loss with triazine, g.

3 Result and Discussion

3.1 Adsorption isotherm

According to related literature, inhibition mechanism of inhibitor is due to its adsorption on the surface of metal [19, 20]. With increase of concentration, the surface coverage (θ) of corrosion inhibitor on the mild steel is gradually increasing until the molecular adsorption reaches saturation (the coverage tend to 1). The weight loss rate of mild steel dropped to the lowest, corrosion rate up to peak. According to equation(4), the surface coverage of triazine inhibitors at varying temperatures and concentrations was obtained from equation (4):

$$\theta = \frac{W_0 - W_t}{W_0} \tag{4}$$

W_0—the corrosion rates in the absence of triazine, $g{\cdot}cm^{-2}{\cdot}h^{-1}$; W_t—the corrosion rates in the presence of triazine, $g{\cdot}cm^{-2}{\cdot}h^{-1}$.
The adsorption of organic molecules generally as a monolayer on the metal, which was assumed by the Langmuir adsorption model [21]. The surface coverage (θ) was obtained from equation (5):

$$\frac{c}{\theta} = fc + \frac{f}{K} \tag{5}$$

K—the equilibrium adsorption constant; *f*—the slope of curve.
The ratio of concentration and surface coverage (c/θ) was as the vertical coordinate, while the concentration (c) was as the horizontal coordinate, four well-correlated straight lines were obtained, as shown in Fig. 2. And the linear regression coefficients (R^2) are close to 1, which indicate that the adsorption of triazine on the mild steel in this salt solution conforms to the Langmuir adsorption model. Obviously, triazine molecules can inhibit the corrosion of active sites by adsorbing on metal surfaces, contributing to the decrease of corrosion rate and the protection of materials [22].

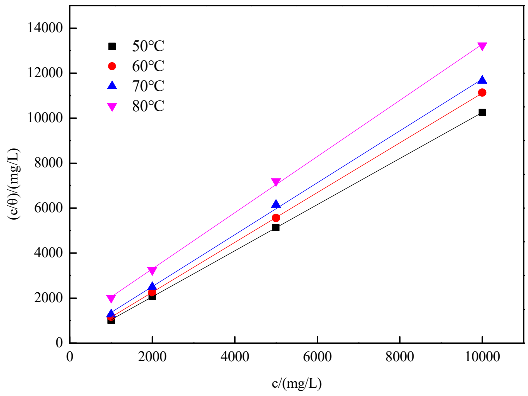

Fig. 2 The adsorption isotherm of the corrosion inhibitor of triazine at different concentrations at different temperatures.

3.2 Thermodynamic study

Thermodynamic parameters were further studied. The value of the equilibrium adsorption constant (K) of triazine for steel in simulated oilfield produced water at different temperature were calculated by using the equation (5). As shown in Table 1, the values of K decrease along with increase of temperature, and the K is a function of temperature. It shows that the adsorption capacity is larger and corrosion inhibition effect is better under lower temperature.

Table 1 The equilibrium adsorption constant (K) of triazine at different temperature.

T (K)	R^2	f	K ($\times10^2$ L·mol^{-1})
323	0.9996	1.0250	317.46
333	0.9986	1.1069	48.90
343	0.9807	1.1536	12.25
353	0.9964	1.2491	3.42

The ΔG can be calculated from equation (6), which was shown in Table 2.

$$\Delta G = -RT\ln K \quad (6)$$

K—the equilibrium adsorption constant; *R*—the universal gas constant; *T*—the absolute temperature, K.

Table 2 Thermodynamic parameters of adsorption process.

T (K)	ΔH (kJ·mol^{-1})	ΔG (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
323	-143.23	-15.31	-395.83
333		-10.77	-397.60
343		-7.08	-396.77
353		-3.55	-395.53

It can be seen in Table 2 that the values of ΔG are negative, indicating that adsorption of triazine is irreversible and spontaneous process. And the values increase gradually with the increase of temperature, which confirms that the adsorption capacity of triazine on the mental is weakened. Therefore, its corrosion inhibition performance becomes worse. According to relevant reports in the literature, when the value of ΔG no more than 20 kJ·mol^{-1}, it is shared that process is physical adsorption [23]. Consequently, the corrosion inhibition of triazine is closer to physical adsorption. As shown in Table 2, the absolute value of ΔG decreased along with increase of temperature, which explain that the high temperature condition is not conducive to spontaneous adsorption.

According to the Van´ t Hoff equation (7), the heat of adsorption (ΔH) was calculated:

$$\ln K = -\frac{\Delta H}{RT} + B \quad (7)$$

K—the equilibrium adsorption constant; *R*—the universal gas constant; *T*—the absolute temperature, K; *B*—Constant.

The relation of ln *K* versus 1/*T* yield a straight line in the Fig. 3. The slope of the line is equal to −ΔH/R. And ΔH value calculated as listed in Table 2. It is shown that the value is negative, which explain the adsorption of triazine is exothermic process.

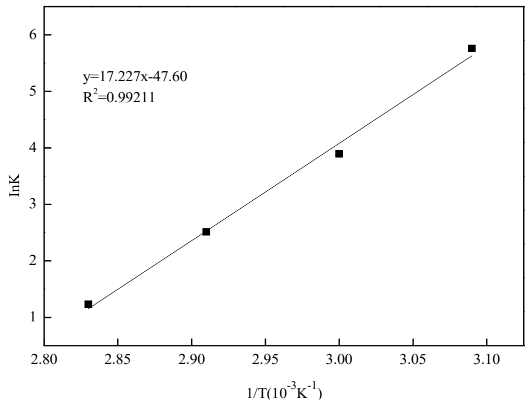

Fig. 3 Curve of adsorption coefficient of triazine on steel sheet with temperature.

The standard entropy of adsorption (ΔS) was obtained using equation (8):

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (8)$$

In the adsorption of inhibitor, water molecules desorbed from the metal firstly [24], system disorder degree increases (ΔS > 0). Orderly arrangement of the corrosion inhibitor on the mental reduces system disorder degree (ΔS < 0). The results in Table 2 show that ΔS values are negative, indicating the orderly arrangement of corrosion inhibitors dominates in the adsorption, leading to increasing corrosion inhibition effect.

4 Conclusion

The corrosion inhibitor of triazine showed well corrosion inhibition for mild steel in oilfield produced water. With the increase of concentration, the general corrosion rate decreased, while the inhibition efficiency increased. It was unfavorable for corrosion inhibition under relatively high temperature. Adsorption capacity of triazine on mild steel became weaker and the corrosion inhibition effect became worse with increase of temperature. Adsorption of triazine on mild steel conformed to the Langmuir adsorption isotherm. Thermodynamic analysis showed that the adsorption was spontaneous, physical and exothermic process.

Acknowledgments

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References

1. Wang L., He Y., Chen H., Meng Z., Wang, Z., Experimental investigation of the live oil-water relative permeability and displacement efficiency on Kingfisher waxy oil reservoir. Journal of Petroleum Science and Engineering, 178 (2019) 1029-1043.
2. Cao W., Xie K., Lu X., Liu Y., Zhang Y., Effect of profile-control oil-displacement agent on increasing oil recovery and its mechanism. Fuel, 237 (2019) 1151-1160.
3. Cristóvão R.O., Pinto V.M., Martins R.J., Loureiro J M., Boaventura R.A., Assessing the influence of oil and grease and salt content on fish canning wastewater biodegradation through respirometric tests. Journal of cleaner production, 127 (2016) 343-351.
4. Riley S.M., Ahoor D.C., Regnery J., Cath T.Y., Tracking oil and gas wastewater-derived organic matter in a hybrid biofilter membrane treatment system: A multi-analytical approach. Science of the Total Environment, 613 (2016) 208-217.
5. Frank V.B., Regnery J., Chan K.E., Ramey D.F., Spear J.R., Cath T.Y., Co-treatment of residential and oil and gas production wastewater with a hybrid sequencing batch reactor-membrane bioreactor process. Journal of water process engineering, 17 (2017) 82-94.
6. Frank V.B., Co-treatment of domestic and oil & gas wastewater with a hybrid sequencing batch reactor-membrane bioreactor (Doctoral dissertation, Colorado School of Mines. Arthur Lakes Library), (2016).
7. Nur M.M.A., Buma A.G., Opportunities and challenges of microalgal cultivation on wastewater, with special focus on palm oil mill effluent and the production of high value compounds. Waste and Biomass Valorization (2018) 1-19.
8. Hwang J., Sharma M.M., Generation and filtration of O/W emulsions under near-wellbore flow conditions during produced water re-injection. Journal of Petroleum Science and Engineering, 165 (2018) 798-810.
9. Liu H., Gu T., Lv Y., Asif M., Xiong F., Zhang G., Liu H., Corrosion inhibition and anti-bacterial efficacy of benzalkonium chloride in artificial CO2-saturated oilfield produced water. Corrosion Science, 117 (2017) 24-34.
10. Umoren S.A., Solomon M.M., Madhankumar A., Obot I.B., Exploration of natural polymers for use as green corrosion inhibitors for AZ31 magnesium alloy in saline environment. Carbohydrate Polymers, 230 (2020) 115466.
11. Singh A., Ansari K.R., Quraishi M.A., Kaya S., Banerjee P., The effect of an N-heterocyclic compound on corrosion inhibition of J55 steel in sweet corrosive medium. New Journal of Chemistry, 43(16) (2019) 6303-6313.
12. Verma C., Ebenso E.E., Bahadur I., Quraishi M.A., An overview on plant extracts as environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media. Journal of molecular liquids, 266 (2018) 577-590.
13. Gbassi G.K., Ouedraogo A., Berte M., Trokourey A., Aluminum corrosion inhibition by cefixime drug: experimental and DFT studies. Journal of Electrochemical Science and Engineering, 8(4) (2018) 303-320.
14. Brigitta V.A., Thangavelu C., Rajendran S., Al-Hashem A., Corrosion resistance of SS18/8 alloy, SS316L alloy, Gold18 carat and Gold 22 carat in artificial saliva in the absence and presence of erythromycin tablet 500mg. Zaštita materijala, 59(2) (2018) 182-188.
15. Thanapackiam P., Rameshkumar S., Subramanian S.S., Mallaiya K., Electrochemical evaluation of inhibition efficiency of ciprofloxacin on the corrosion of copper in acid media. Materials Chemistry and Physics, 174 (2016) 129-137.
16. Verma C., Olasunkanmi L.O., Ebenso E.E., Quraishi M.A., Substituents effect on corrosion inhibition performance of organic compounds in aggressive ionic solutions: a review. Journal of Molecular Liquids, 251 (2018) 100-118.
17. Kadhim A., Al-Okbi A.K., Jamil D.M., Qussay A., Al-Amiery A.A., Gaaz T.S., Nassir M.H., Experimental and theoretical studies of benzoxazines corrosion inhibitors. Results in physics, 7 (2017) 4013-4019.
18. Mendonça G.L., Costa S.N., Freire V.N., Casciano P.N., Correia A.N., Lima-Neto P., Understanding the corrosion inhibition of carbon steel and copper in sulphuric acid medium by amino acids using electrochemical techniques allied to molecular modelling methods. Corrosion Science, 115 (2017) 41-55.
19. Guo L., Qi C., Zheng X., Zhang R., Shen X., Kaya S., Toward understanding the adsorption mechanism of large size organic corrosion inhibitors on an Fe (110) surface using the DFTB method. RSC advances, 7(46) (2017) 29042-29050.
20. Alaneme K.K., Olusegun S.J., Adelowo O.T., Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel immersed in acidic solutions. Alexandria Engineering Journal, 55(1) (2016) 673-681.

21. Onuchukwu A.I., Chemistry of Surface and Colloid, Ambix Printers, Lagos, 2006.
22. Hong M.S., Park Y., Kim J.G., Kim K., Effect of incorporating MoS2 in organic coatings on the corrosion resistance of 316L stainless steel in a 3.5% NaCl solution. Coatings, 9(1) (2019) 45.
23. Bekçi Z., Seki Y., Yurdakoç M.K., Equilibrium studies for trimethoprim adsorption on montmorillonite KSF. Journal of hazardous materials, 133(1-3) (2006) 233-242.
24. Singh A.K., Quraishi M.A., Effect of 2, 2′ benzothiazolyl disulfide on the corrosion of mild steel in acid media. Corrosion science, 51(11) (2009) 2752-2760.