Int. J. Electrochem. Sci., **(2019)** 10121 – 10129, doi: 10.20964/2019.11.09

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

6-dibutylamino-1,3,5-triazine-2,4-dithiolmonosodium as an inhibitor of brass corrosion in 0.5 M sodium chloride solution

Qian Zhao[1,*], *Fang Wang*[2,*], *Peilin Dang*[3]

[1] Shaanxi Key Laboratory of Disaster Monitoring and Mechanism Simulation, College of Geography and Environment, Baoji University of Arts and Sciences, Baoji, Shaanxi 721013, P.R. China;
[2] College of Chemistry & Pharmacy, Northwest A&F University, Yangling, Shaanxi 712100, China;
[3]AVIC Xi'an Aircraft Industry (Group) Company Ltd., Xi'an, Shaanxi 710089, China;
[*]E-mail: qianzhao@bjwlxy.cn; wangfang4070@nwsuaf.edu.cn

Received: 9 July 2019 / *Accepted:* 18 August 2019 / *Published:* 7 October 2019

The inhibition action of 6-dibutylamino-1,3,5-triazine-2,4-dithiolmonosodium (DBN) on the corrosion of brass in a 0.5 M sodium chloride solution has been investigated using weight loss methods, potentiodynamic polarization curves, contact angle measurements and scanning electron microscopy (SEM) techniques. Results indicated that the inhibition efficiency increases with increasing concentration of DBN. The potentiodynamic polarization results showed that the corrosion inhibition efficiency reaches 98% when the concentration of DBN is 1.2 mM. Adsorption of DBN inhibitors on the brass/chloride surface is found to follow the Langmuir's adsorption isotherm. The calculated ΔG_{ads} value of -17.56kJ/mol demonstrates that the adsorption of DBN on brass surface is a spontaneous and exothermic process at 30 °C. Further, morphology observation results reveal that the DBN acts as a good inhibitor for brass in chloride solution.

Keywords: Triazinedithiols, Brass, inhibition action, adsorption behavior

1. INTRODUCTION

Copper and alloys have a wide variety of applications in technology and industrial production fields because their good mechanical workability, excellent thermal and electrical conductivity[1-4]. The Cu-Zn alloys are known as brass, which are often used for the construction of cooled heat exchangers, piping and tubes in fresh or sea water[4, 5]. However, copper alloys are unstable in humid atmosphere or corrosive medium, especially brass is susceptible to a corrosion process namely dezincification, which may bring severe problems to its functionality. Thus, numerous studies have been devoted to the inhibition of copper and brass corrosion by organic inhibitors which happened via

adsorption on the metal surface. The adsorption process results in an effective blocking of the active corrosion spots of copper dissolution, in this way, the corrosion rate is reduced[5-8].

The employment of heterocyclic derivatives containing S, N or O as corrosion inhibitors is one of the most efficient approaches to protect the completeness of copper and brass surface. The presence of multiple active centers, heteroatom as well as the existence of a free electron pair in the inhibitors favors the adsorption of these heterocyclic molecules on metallic surface[9-11]. However, the application of some heterocyclic compounds can be limited for their toxicity and higher cost. Triazinedithiol and its monosodium salt, has the special tautomer of thiol–thione (Figure 1), are considered as eco-friendly inhibitors because their excellent qualities including cost-effective, high solubility, high reactive and without unfavorable mercaptan smell[12-15]. Based on the available literature, data on the reaction mechanism of triazinedithiol as a corrosion inhibitor for brass in sodium chloride solution is insufficient.

The aim of this paper is to explore the influence of 6-dibutylamino-1,3,5-triazine-2,4-dithiolmonosodium (DBN, Figure 1) on the corrosion of brass in 0.5 M NaCl, and its inhibition action and adsorption behavior has been investigated by different techniques, such as weight loss methods, potentiodynamic polarization measurements, contact angle and scanning electron microscopic studies. Results are reported and discussed.

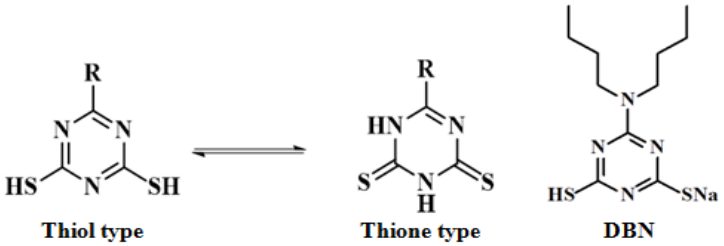

Figure 1. Triazindithiols tautomer of thiol-thione type and the molecular structure of DBN

2. EXPERIMENTAL

2.1. Materials and sample preparation

The samples employed in present study are commercial brass with the following elemental composition (wt. %): 60.61% Cu, 39.19% Zn, 0.12% Al and 0.08% Si. Prior to each measurement, rectangular specimen of brass (with dimension of 30 × 50 × 0.3 mm) was polished successively with 2.5 μm, 1.5 μm and 0.5 μm diamond spray polish does, then the polished samples were rinsed, dried and degreased according to the standard methods. All solutions used in this study were prepared with AR (analytical reagent) grade chemicals. DBN is prepared by the chemical reaction between NaSH and 6-N,N-dibutylamino-1,3,5-triazine-2,4-dichloride[16], and the inhibitor concentrations varied from 0.05 to 1.5 mM. The standard aggressive medium was 0.5 M NaCl solution.

2.2. Characterization

Weight loss test was performed as described elsewhere[17]. The brass samples in triplicate were submerged in a 0.5 M NaCl solution contained inhibitor with concentration of inhibitor varies from 0

mM to 1.5 mM. The temperature was maintained at 30 °C controlled by a thermostat aqueous bath. The corrosion rates (v g·m^{-2}·h^{-1}) and inhibition efficiency (η_w %) were obtained according to the following equations[18]:

$$v = \frac{\Delta W}{s \cdot t} \quad (1)$$

$$\eta_w = \frac{v - v'}{v} \times 100\% \quad (2)$$

where s is the area of aluminum alloy specimen (m^2); t is the exposure time (h); ΔW is the weight loss value (g); v and v' are the corrosion rate (g·m^{-2}·h^{-1}) in the absence and presence of DBN inhibitor, respectively.

Potentiodynamic polarization measurements were carried out using the Electrochemical Workstation (Model: Chenhua Instru-ments Co., Ltd., Shanghai). The traditional three-electrode system was employed. The brass specimens with 1 cm^2 area exposed was the working electrode, the platinum sheet was counter electrode and the reference one was a saturated calomel electrode (SCE). The polarization curves for brass samples in the test solution with and without various concentrations of inhibitors were recorded from -250 to +250 mV versus OCP. Prior to each measurement, all electrodes were immersed in solution for 1 h to obtain a constant potential, then the polarization tests were performed at a scan rate of 0.5 mV/s.

The surface wetability of brass samples after immersing in 0.5 M NaCl with different concentration of DBN inhibitor for 2 h were studied by contact angles (CAs) with a telescopic goniometer (HARKE-SPCAX1). The CA values obtained were the average values by measuring five different positions on each brass sample. The surfaces morphologies of brass samples immersed in 0.5 M NaCl with different concentration of DBN inhibitors for 15 days were observed by SEM (JSM-6360LV, JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV, respectively.

3. RESULTS AND DISCUSSION

3.1. Weight Loss Study

The inhibition efficiency (η_w) and corrosion rates (v) of brass samples obtained from the weight loss method in a 0.5 M NaCl solution with different concentrations of DBN inhibitors (0.05–1.5 mM) at 30 °C are showed in Figure 2. From figure 2, we can find that the inhibition efficiency increases and the corrosion rate decrease when increase the concentration of studied inhibitors. When DBN concentration varies from 0.05 mM to 1.2 mM, there is a decrease in corrosion rate from 29.8 g·m^{-2}·h^{-1} to 2.52 g·m^{-2}·h^{-1} and an increase in efficiency from 59% to 97% (Figure 1). This indicates that the addition of DBN inhibitor retarding the corrosion of brass in a sodium chloride solution. When DBN concentration is low, more molecules are needed to adequately cover the brass surface. In addition, we find that further enhancement in DBN concentration did not cause any significant changes in the function of inhibitor, suggesting that the existence of a limiting value. The results are attributed to the amassing of DBN molecules onto the positively charged brass surface causing a decrease in

direct contact with brass and corrosive environment. Similar results were observed in other studies, for example, Sherlock and Selim studied the corrosion inhibition efficiency of stannous tin and resins for mild steel, they both found that the inhibition reached a limiting value when inhibitors attained a certain concentration [19, 20].

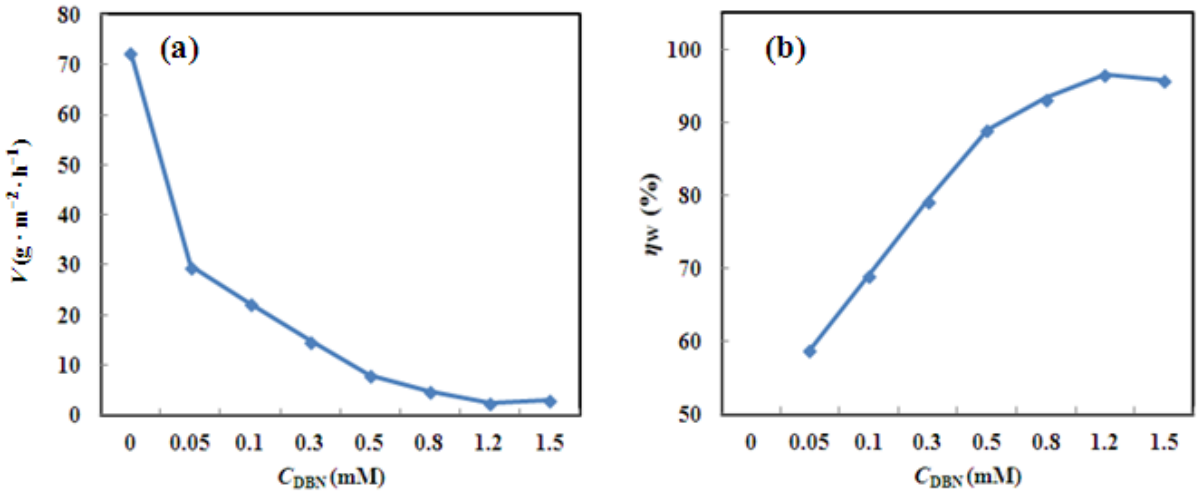

Figure 2. Corrosion rates (a) and inhibition efficiency (b) of brass in 0.5 M NaCl with different concentrations of DBN (30 °C).

3.2. Potentiodynamic Polarization Measurements.

Figure 3 presented the potentiodynamic polarization profiles of brass in 0.5 M NaCl solution with different concentration of DBN (0.05–1.5 mM) inhibitor at 30 °C. The corrosion kinetics parameters including corrosion potential (E_{corr}), anodic Tafel slopes (β_a, β_c) and corrosion current density (I_{corr}) were exhibited in Table 1, where the inhibition efficiency η_p (%) was calculated by[21]:

$$\eta_p(\%) = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100 \qquad (3)$$

Where I_{corr}^0 and I_{corr}^i are the corrosion current densities of brass 0.5 M NaCl with different concentration of inhibitor.

From Figure 3, we find that the cathodic currents are significantly decreased with the presence of DBN inhibitor, which indicating a reduction of the hydrogen evolution reaction attributed to the adsorption of DBN molecules on the active sites. Table 1 shows the I_{corr} value of blank brass is 0.52 μA·cm^{-2} and E_{corr} is -270 mV. When DBN inhibitor is contained in the corrosive solution, the I_{corr} decreased significantly and E_{corr} shifted to negative direction. This result suggested that DBN molecules adsorbed on brass surface to form a protective namofilm to inhibit the corrosion reaction of brass and show good anticorrosion performance in 0.5 M NaCl solution. As the DBN concentration increased from 0.05 mM to 1.2 mM, the I_{corr} value decreased and the η_p value increased gradually. The lowest I_{corr} values (0.012 μA·cm^{-2}) and highest inhibition efficiency (98%) are obtained (Table 1) when the adding amount of DBN reached 1.2 mM, which indicating that the adsorption of the inhibitor molecules on brass surface appears an equilibrium state of saturation when DBN concentration is

around 1.2 mM. If the DBN concentration be further increased, the saturated adsorption DBN polymer film will be influenced by the molecular interaction. Therefore the adsorption stability and inhibition ability of DBN molecules would be affected.

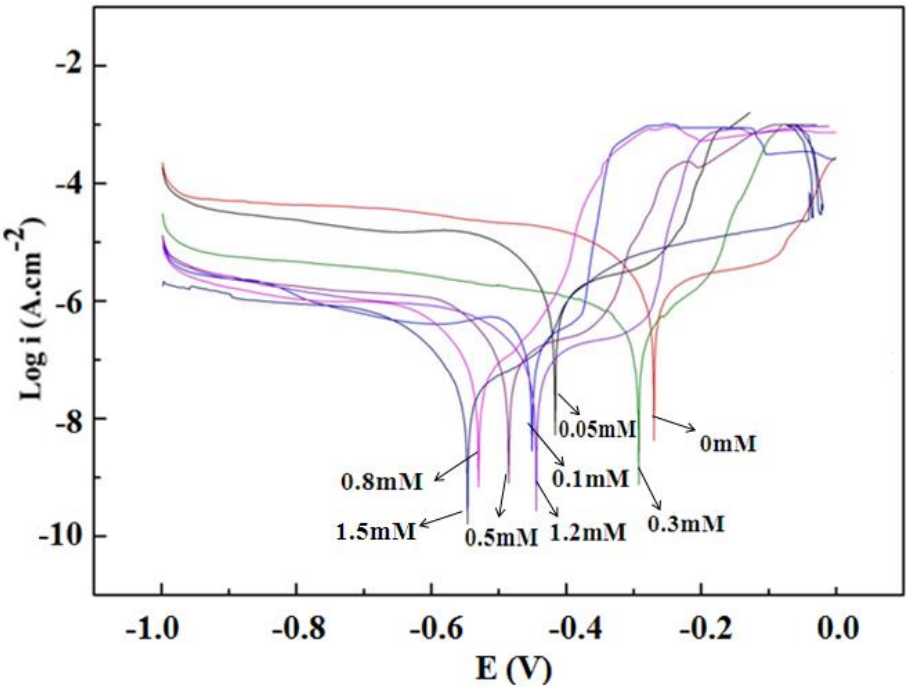

Figure 3. Potentiodymanic polarization curves for brass in 0.5 M NaCl in absence and presence of different concentrations of DBN.

Table 1. Tafel polarization parameters of the corrosion for brass in 0.5 M NaCl in absence and presence of different concentrations of DBN.

$C_{inhibitor}$ (mM)	β_a (mV dec^{-1})	$-\beta_c$ (mV dec^{-1})	I_{corr} (A cm^{-2})	$-E_{corr}$ (mV/SCE)	η_p (%)
0	74	70	5.23×10^{-7}	270	—
0.05	78	73	2.05×10^{-7}	416	61
0.1	82	91	1.68×10^{-7}	446	68
0.3	81	70	1.14×10^{-7}	292	78
0.5	78	73	4.74×10^{-7}	485	91
0.8	80	92	1.72×10^{-8}	530	96
1.2	66	73	1.21×10^{-8}	441	98
1.5	68	69	1.26×10^{-8}	546	97

3.3. Adsorption isotherm

Adsorption isotherm could provide fundamental information about the adsorption of inhibitor on metal surface[22]. To confirm the adsorption mode, the values of surface coverage (θ) corresponding to variant DBN concentrations at have been used to find the best adsorption isotherm among the most used isotherms (Frumkin, DeBoer, Langmuir, Parsons, Temkin, Freundlich and Flory-

Huggins). Figure 4 confirm that the adsorption of DBN molecules on brass surface obeys the Langmuir adsorption model. A straight line is obtained when C/θ is plotted against C and the linear regression coefficient (R^2) of the fitted data is quite close to 1 (Figure 4). This indicates that DBN molecules formed a single molecule adsorbed layer on brass surface, and there was almost no interaction between absorbed molecules. Adsorption equation can be written in the following[23] :

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \qquad (4)$$

where c is the concentration of inhibitor, K_{ads} is the adsorptive equilibrium constant and θ is the surface coverage equal to inhibition efficiency $\eta_w/100$.

Gibbs free energy (ΔG_{ads}) is calculated using the following equation[24]:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \qquad (5)$$

where R ($J \cdot mol^{-1} \cdot K^{-1}$) is the gas equilibrium constant, T (K) is the temperature, and the value 55.5 ($mol \cdot L^{-1}$) is the molecular concentration of water in solution.

In Figure 4, the intercept on the vertical axis is the value of 1/ K_{ads}, which is 19.23. Then according to Eq. (3), we calculated the ΔG_{ads} = -17.56 kJ/mol at 30 °C. The negative value of ΔG_{ads} demonstrates that the adsorption of DBN molecules on brass surface is a spontaneous process. Generally, values of ΔG_{ads} up to -20 kJ/mol, are regarded as physisorption, the inhibition acts due to the electrostatic interactions between the charged molecules and the charged metal, while values of ΔG_{ads} around -40 kJ/mol or higher are associated with chemisorption because of sharing or transfer of electrons from extract organic molecules to metal surface to form a coordinate type of bond[25, 26]. For the investigated DBN inhibitor, the calculated ΔG_{ads} value less than -20 kJ/mol, indicating that the process of DBN molecules adsorbed on brass surface in 0.5 M NaCl solution at 30 °C was a typical physical absorption.

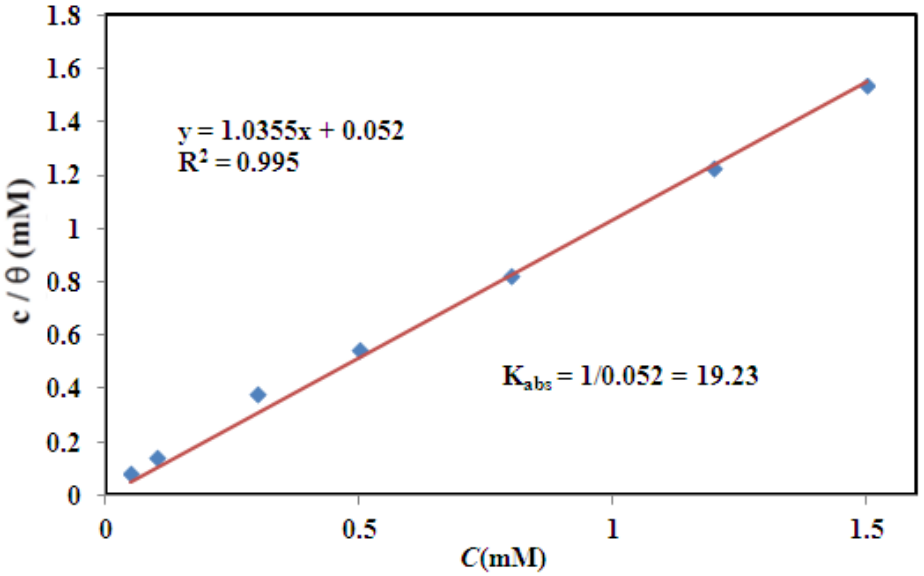

Figure 4. Langmuir isotherm adsorption isotherm of DBN in 0.5 M NaCl solution 30 °C.

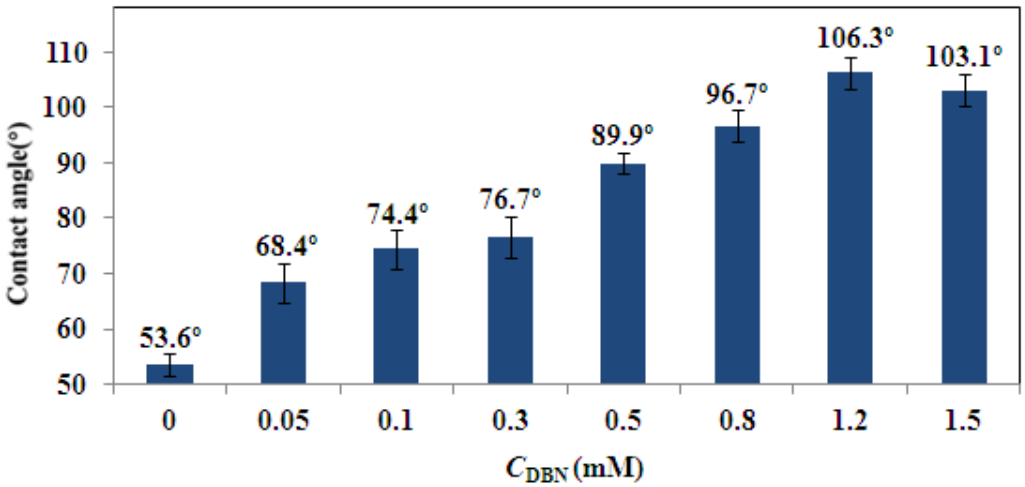

Figure 5. Contact angles of brass samples surfaces in 0.5 M NaCl in absence and presence of different concentrations of DBN.

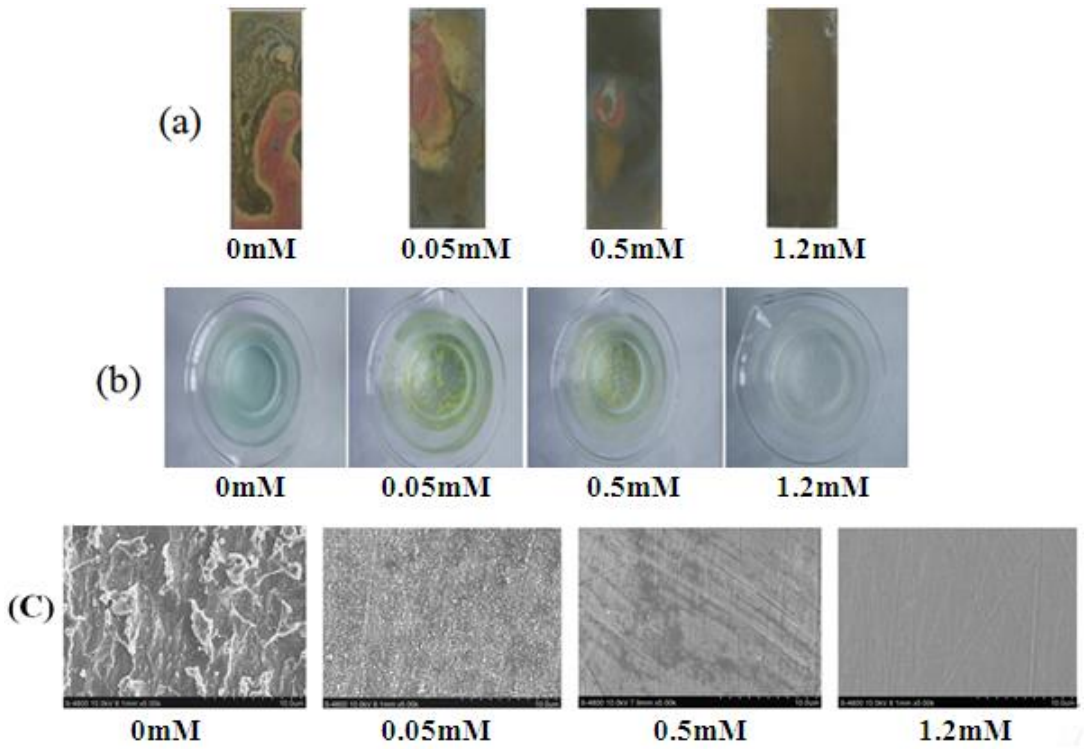

Figure 6. Photographs of saline immersion test after 15 days of immersion in 0.5 M NaCl solution. (a) Blank and treated grass (b) Solution after the saline immersion test (c) SEM images of treated grass

3.4 Surface morphology observation

Contact angles were measured to elucidate the wetability of the obtained brass samples, and Figure 5 showed the water contact angles of samples surfaces after immersing in 0.5 M NaCl with different concentration of DBN inhibitor for 2 h. It can be seen that the wetability was improved after adding DBN inhibitor compared with the bare brass sample. The water contact angles increased with

the increasing of DBN concentration, indicating that the coverage of hydrophobic adsorbed film is getting larger with the increase of DBN molecules. The contact angle reached 106.3° when the concentration of DBN was 1.2 mM, which implied that a compact hydrophobic film has been formed and covered the whole brass surface. Moreover, a slight decline of contact angle (103.1°) was found when the DBN concentration increased to 1.5 mM. This may attributed to a reduction of in the stabilty of adsorption film caused by the enhancement of inter action of molecular and when the concentration of DBN continue to increase.

To further study the performance of DBN protective films, SEM technique was carried out to observe the surface morphology of brass samples after a saline immersion test. Brass samples were immersing in 0.5 M NaCl solution for 15 days without and with the presence of DBN inhibitor. Three concentrations (0.05 mM, 0.5 mM and 1.2 mM) of DBN were arranged respectively. Photographs and SEM images of saline immersion test after 15 days of immersion in 0.5 M NaCl solution are exhibited in Figure 6. In the blank test, the brass plate exhibited a relative rough surface with deep cracksb and the pale blue solution was due to the presence of copper ions (Figure 6), which indicates that the the brass has suffered a serious damage and dissolution. In contrast, damage to the brasss was reduced when DBN added in the NaCl solution. A relative smooth surface and a nearly transparent solution is observed when the presence of 1.2 M DBN inhibitor (Figure 6), which revealed that a compact protective DBN obserbed layer formed and the brass dissolution rate was effectively inhibited.

4. CONCLUSIONS

DBN acts as an excellent inhibitor for corrosion of brass in 0.5 M NaCl solution. Resutlts from weight lost test, potentiodynamic polarization measurements and surface morphology observation all showed that 1.2 mM is the optimal concentration of inhibitor with the best corrosion inhibition performance. Adsorption of DBN on brass surface obeys the Langmuir isotherm at 30°C, and the process of DBN molecules adsorped on brass surface is spontaneous and a typically physical process.

ACKNOWLEDGEMENTS
This research was supported by the Natural Science Basic Research Plan in Shaanxi Province of China (No. 2018JQ5191), the Young Talent fund of University Association for Science and Technology in Shaanxi，China (No. 20180419) and the Doctoral Scientific Research Foundation of Baoji University of Arts and Sciences (No. ZK2018044).

References

1. F. Vasilyev, S. Virolainen and T. Sainio, Chemical Engineering Science, *Corros. Sci.*, 171 (2017) 88.
2. M. Walkowicz, P. Osuch, B. Smyrak, T. Knych, E. Rudnik, Ł. Cieniek, A. Różańska, A. Chmielarczyk, D. Romaniszyn and M. Bulanda, *Corros. Sci.*, 140 (2018) 321.
3. B.N. Bennett, M.Z. Martin, D.N. Leonard and E. Garlea, *Appl. Phys. B*, 124 (2018) 42.
4. M.C. Gorovei, L. Benea , *IOP Conference Series:Mater. Sci. Eng.*, 374 (2018) 1.
5. A.S. Fouda, F.I. El-Dossoki and I.A. Shady, *Green Chem. Lett. Rev.*, 11 (2018) 67.
6. M.M. Nandi, R. Banerjee, *Cheminform*, 45 (2015) 48.
7. A.G.G. Allah, H. Moustafa, *J. Appl. Electrochem.*, 22 (1992) 644.
8. D.Q. Zhang, L.X. Gao, and G.D. Zhou, *Corros. Sci.*, 46 (2004) 3031.

9. R.S. Abdel Hameed, M. Alfakeer and M. Abdallah, *Surf. Eng. Appl. Electrochem.,* 54 (2018) 599.
10. M.A. Elmorsi, A.M. Hassanein, *Corros. Sci.,* 41 (1999) 2337.
11. T. Shahrabi, H. Tavakholi and M.G. Hosseini, *Anti-Corros. Meth. Mater.,* 54 (2007) 308.
12. H. Baba, T. Kodama, *Corros. Sci.*, 41 (1999) 1987.
13. M.M. Hu, D.M. Zhang, *Mater. Sci. Forum*, 809 (2014) 554.
14. F.Wang, J. Liu, Y. Li and R. Fan, Int. J. Electrochem. Sci. 7(2012)3672.
15. A.M. Al-Sabagh, N.G. Kandile, N.M. Nasser, M.R. Mishrif and A.E. El-Tabey, *Egyptian J. Petroleum,* 22 (2013) 351.
16. F. Zhang, Y. Ge, W. Wang, X. Yu, X. Shen, J. Liu, X. Liu, D. Tian, F. Shen and Y. Yu, *Int, J. Mol.. Sci.*, 13 (2012) 6040.
17. M.A. Amin, *J. Appl. Electrochem.*, 36 (2006) 215.
18. A.A.A. Shikshak, A.A. Mansour and A. Taher, *Appl. Mech. Mater.,* 799 (2015) 232.
19. M.I. Selim, A.A. Yassin and B.G. Ateya, *Chemischer Informationsdienst,* 17 (1978) 923.
20. Sherlock, J. C., *British Corros. J.*, 10 (2013) 144.
21. C.B.P. Kumar, K.N. Mohana, *J. Taiwan Inst. Chem. Eng.*, 45 (2014) 1031.
22. A.Y. MUSA, *J. Cent. South Univ.,* 17 (2010) 34.
23. D.C. Jones, E.W. Birks, *J. Chem., Soc*, 145 (1951) 1127.
24. A. Dabrowski, *Adv. Colloid Interface Sci.,* 93 (2001) 135.
25. H.S. Gadow, M.M. Motawea and H.M. Elabbasy, *RSC Adv.,* 7 (2017) 29883.
26. A.R. Hoseinzadeh, I. Danaee, M.H. Maddahy and M.R. Avei, *Chem. Eng. Commun.*, 201 (2014) 380.