

## Synthesis and Application of a Benzotriazole Mannich Base as Effective Corrosion Inhibitor for N80 Steel in High Concentrated HCl

Ya Wu, Hongjiang Yu, Shijun Chen, Jiao Yan and Xuefan Gu\*, Yan Li and Gang Chen\*  
College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an Shaanxi 710065, China.

[gangchen@xsyu.edu.cn](mailto:gangchen@xsyu.edu.cn)\*

(Received on 21<sup>st</sup> January 2016, accepted in revised form 16<sup>th</sup> May 2016)

**Summary:** A benzotriazole Mannich base, *N*-(*N*-diethylethanamine)-methyl benzotriazole (DEAMB), was synthesized and analyzed by NMR and MS. The corrosion inhibition of DEAMB and the inhibition mechanism in 2M and 3M HCl solution were investigated and discussed. The research results showed that DEAMB can inhibit the acidic corrosion with moderate to high inhibition efficiency in kinds of conditions, and the inhibition mechanism should be mainly contributed to the molecules adsorption on the steel surface, which is further confirmed by potentiodynamic polarization studies.

**Keywords:** Benzotriazole; Mannich base; Synthesis; Corrosion inhibition

### Introduction

In the oilfield, acidification is used to enhance the oil recovery. During the acidification operation, high concentrated HCl solution (10-30%) is pumped into wells to create highly conductive channels by etching the fracture walls irregularly [1]. Although some steel has resistance properties against corrosion using in the oil field, however, it is a great challenge for the instruments involved in acidification operation, especially in high concentration of HCl under high temperature [2, 3]. To improve its corrosion resistance, some work has been focusing on heat treatment and/or changing chemical composition. But, in such aggressiveness of acidic media, the most effective method for the protection of many metals against such acid attack is the use of corrosion inhibitors [2-4]. The inhibition of the corrosion has been proved to be the formation of donor-acceptor surface complexes between a vacant *d*-orbital of a metal and non-bonding electron pairs or *p*-electrons of an organic inhibitor, and nitrogenous compound is widely used. Among the different kinds of nitrogenous compound, triazoles are regarded as environmentally acceptable as acidic corrosion inhibitors [5, 6]. Besides, some polydentate Mannich base compounds (PMCs) have been found to be effective corrosion inhibitors for various metals in high concentrated acid media [7, 8]. Several azotriazole derivatives have been studied as inhibitors in HCl solutions [9, 10], but the inhibition of such compounds under high concentration of HCl has not been investigated. In this work, a Mannich base, *N*-(*N*-diethylethanamine)-methyl benzotriazole (DEAMB), is synthesized for the use of corrosion inhibition for mild steel in high concentrated HCl

solution, and the using conditions and the inhibition mechanism will also be studied systematically.

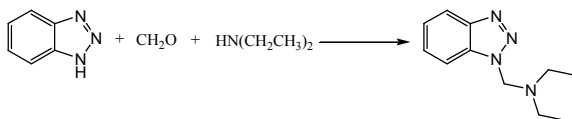
### Experimental

All starting materials and solvents (A.R. grade) were commercially available and were used without further purification. NMR spectra were recorded using a Bruker Drx-400 spectrometer operating at 400 MHz for <sup>1</sup>H. Mass spectra were recorded on a Micromass Platform spectrometer using a direct-inlet system operating in the electron impact (EI) mode at 75 eV. Elemental analyses were obtained using a Carlo Erba 1106 elemental analyzer.

### Synthesis

*N*-(*N*-diethylethanamine)-methyl benzotriazole (DEAMB) was synthesized according to published methods (as shown in Scheme 1). Benzotriazole, formaldehyde and diethylamine were dissolved in methanol (30 ml). The mixture was refluxed until the disappearance of benzotriazole, as evidenced by thin-layer chromatography. The solvent was removed in vacuo and the residue was separated by column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1), giving the title compound. <sup>1</sup>H-NMR (D<sub>6</sub>-DMSO, 400 MHz): δ 7.98 (d, J=8.2Hz, 1H, Ar-H), 7.78(d, J=8.5Hz, 1H, Ar-H), 7.59 (t, J=7.7Hz, 1H, Ar-H), 7.45(d, J=6.2Hz, 1H, Ar-H), 4.76(s, 2H, -CH<sub>2</sub>-), 3.29 (q, J=8.2Hz, 4H, -CH<sub>2</sub>CH<sub>3</sub>), 1.88(q, J=8.2Hz, 6H, -CH<sub>2</sub>CH<sub>3</sub>); MS (EI) *m/z*: 204 (M<sup>+</sup>).

\*To whom all correspondence should be addressed.



Scheme-1: Synthesis of *N*-((1H-benzo[d][1,2,3]triazol-1-yl)methyl)-*N*-ethylethanamine

#### Weight Loss Determination

The corrosion tests were performed on N80 steel with a composition (in wt.%) C: 0.20, P: 0.015, Si: 1.45, S: 0.15, Mn: 0.020, and Fe balance. The corrosive medium for the study was hydrochloric acid solution of concentrations of 2M or 3M HCl. It was prepared from analytical grade 35% HCl and double-distilled water. In each experiment, 250 mL acid solution was used and all corrosion experiments were performed under normal atmospheric pressure.

Gravimetric measurements are carried out in a glass bottle. Each test was done with two specimens at the same time to guarantee the reliability of the results. In the weight loss experiment, Inhibitor efficiency was determined by hanging 2 pieces of the steel coupons into 250 mL 2M or 3M HCl with and without the addition of different concentrations (from 100 to 2000 ppm) of the synthesized inhibitors. After 2 h of immersion, the coupons were removed, scrubbed with bristle brush under running water in order to remove the corrosion product, washed with acetone, degreased by ethanol, dried and reweighed. Then the tests were repeated with different concentrations of inhibitors at varying temperatures (30–60°C). From the initial and final weights of the specimens, the loss of weights was calculated, and the percentage inhibition efficiency (IE (%)) was calculated using the relationship below[9]:

$$IE(\%) = \left( \frac{W_{\text{corr}} - W_{\text{corr(inh)}}}{W_{\text{corr}}} \right) \times 100 \quad (1)$$

where  $W_{\text{corr}}$  and  $W_{\text{corr(inh)}}$  are the corrosion rates of mild steel in the absence and presence of inhibition, respectively.

#### Electrochemical Measurements

The electrodes were mechanically abraded with a series of emery papers (800 and 1200 grades), then rinsed in acetone and double-distilled water before their immersion in the experimental solution.

Electrochemical measurements were conducted in a conventional three-electrode thermo stated cell. The electrode was inserted into a Teflon tube and isolated with polyester so that only its section (0.5cm<sup>2</sup>) was allowed to contact the aggressive solutions. A platinum disk as counter electrode and standard calomel electrode (SCE) as the reference electrode have been used in the electrochemical studies.

The potentiodynamic curves were recorded using a CS350 system connected to a personal computer. The working electrode was first immersed in the test solution for 60 min to establish a steady state open circuit potential. After measuring the open circuit, potential dynamic polarization curves were obtained with a scan rate of 0.5 mV/s. Corrosion rates (corrosion current densities) were obtained from the polarization curves by linear extrapolation of the anodic and cathodic branches of the Tafel plots at points 100 mV more positive and more negative than the  $E_{\text{corr}}$ .

#### CS350 Electrochemical Workstation Hardware Parameters

Potentiostat potential control:  $\pm 10V$ ; Current Control Range:  $\pm 2.0A$ ; Potential control precision:  $0.1\% \times \text{full scale reading} \pm 1mV$ ; Current control accuracy:  $0.1\% \times \text{full scale reading}$ ; Potential resolution:  $10\mu V$  ( $>100Hz$ ),  $2\mu V$  ( $<10Hz$ ); Current resolution:  $<10pA$ ; Potential rise time:  $<1\mu S$  ( $<10mA$ ),  $<10\mu S$  ( $<2A$ ); Auxiliary 24-bit data acquisition-10KHz, 20bit-1KHz; Reference electrode input impedance:  $1012 \text{ ohms} \parallel 20pF$ ; Current range 2A-100nA, a total of 8 files; Tank pressure: 21V; CV and LSV scan rate: 0.01-20000mV/s; CA and CC pulse width: 0.0001-1000s; Potential scan potential incremental: 0.1mV-1V/mS; SWV frequency: 0.001-100KHz; DPV and NPV pulse width: 0.0001-1000s; AD data acquisition: 16 bits-1MHz, 24bit-100Hz; Minimum potential increment CV: 0.075mV.

## Results and Discussion

### Inhibition

Steel has been treated by changing chemical composition and heat to improve the corrosion resistance. But for the aggressiveness of acidic media in oil field, there is a great challenge in high concentrated HCl solution under high temperature. As reported, the most effective method for the protection against such acid attack is use of corrosion

inhibitors. Schiff base, Mannich base and imidazoline and some other heterocyclic compounds have been used as acidic corrosion inhibitors, but the dosage or the price is too high to be acceptable. In this work, the performance of *N*-(*N*-diethylethanamine)-methyl benzotriazole (DEAMB) was investigated as a corrosion inhibitor with the concentration from 10 to 200 ppm in 2M and 3M HCl, and the results were shown in Table 1. From the results, it can be found that almost all the inhibition efficiencies (IE) increase along with the concentration of inhibitor, but there are some differences in the two concentrations and under different temperatures. When the concentration is up to 100ppm, the IEs are all in high level, and it reaches to 93.93% with the concentration of 100 ppm in 2M HCl solution at 45 °C.

Table-1: The corrosion inhibition efficiency of DEAMB.

Concentration (ppm)	HCl Concentration (M)	Temperature (°C)	Inhibition Efficiency (%)
10	2	30	32.23
10	2	45	22.49
10	2	60	37.40
10	3	30	12.74
10	3	45	10.77
10	3	60	19.30
20	2	30	46.18
20	2	45	58.01
20	2	60	56.81
20	3	30	66.51
20	3	45	55.09
20	3	60	48.91
50	2	30	84.82
50	2	45	77.63
50	2	60	82.93
50	3	30	80.15
50	3	45	77.20
50	3	60	67.65
100	2	30	93.93
100	2	45	87.28
100	2	60	93.60
100	3	30	88.61
100	3	45	93.93
100	3	60	90.85

#### Mechanism

It has been disclosed that organic inhibitors inhibit the corrosion by adsorption onto the metal surface forming a film. There are two main types of interaction: physical adsorption and chemisorption, which are effected by the chemical structure of the inhibitor, the charge of the metal and the type of electrolyte. The conjugated double bonds and N, O, S atoms in the organic molecules help to form *p-d* bonds between the inhibitor and metal resulting from overlap of *p*-electrons to the 3*d* vacant orbital of metal atoms, which can enhance the adsorption of the inhibitors on the metal surface [10]. The steady conformation of DEAMB was expressed in Figure 1, which has been simulated by a minimize energy of

MM2 in Chem3D, and the *p*-electrons of the hydroxyl groups was colored in pink. From the simulation, it can be found that the inhibition efficiency afforded by DEAMB may be due to the its electron rich N atoms, imidazole and phenyl group, and the possible coordination points are unshared electron pair of heteroatoms and *p*-electrons of imidazole and phenyl group.

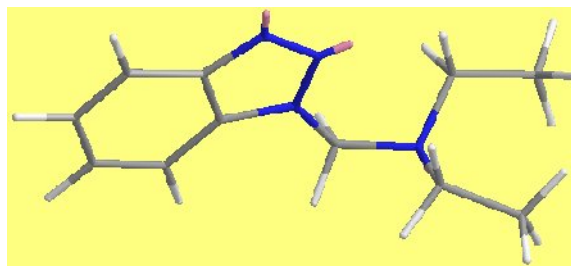


Fig. 1: The steady conformation of DEAMB.

#### Tafel Polarization Measurements

To study the inhibition mechanism further, the anodic and cathodic polarization were screened, and the curves of a mild steel electrode in 2 M HCl in absence and presence of different concentrations of DEAMB at 298 K are shown in Figure 2. And the electrochemical corrosion kinetic parameters, such as corrosion potential ( $E_{corr}$ ), cathodic and anodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ) and corrosion current density  $I_{corr}$  obtained by extrapolation of the Tafel lines are shown in Table 2. The calculated IE (%) is obtained from the following equation.

$$IE(\%) = \left( \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \right) \times 100 \quad (2)$$

where  $I_{corr}$  and  $I_{corr(i)}$  are current corrosion densities obtained in the absence and presence of inhibitors, respectively. It was found that both cathodic and anodic reactions of the steel electrode corrosion were inhibited by adding DEAMB. The result indicates that the present of the DEAMB retards the hydrogen evolution reaction and also reduces anodic dissolution [11]. It can be found that the corrosion rate measured by potentiodynamic polarization is decreased and the IE increases along with the increasing of inhibitor concentration, which indicates that the inhibition is due to its adsorption on the steel surface [12]. Under the concentration of 100 ppm, DEAMB exhibits maximum IE of 69.0%. However, it can be found that the IEs obtained from

potentiodynamic polarization experiments were quite different from those calculated from weight-loss measurements, which can be attributable to the fact that the weight-loss method gives average corrosion rate within a relative long time, whereas potentiodynamic polarization experiment gives corrosion rates instantaneously. These differences may arise obviously because the time required to form an adsorbed layer of inhibitors on metal surface is different for different inhibitors [12].

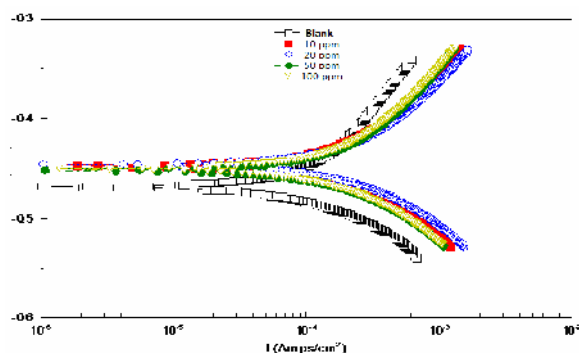


Fig. 2: The polarization curve of A3 steel in the HCl solution containing DEAMB.

Table-2: Potentiodynamic polarization parameters for the corrosion of the A3 steel in the HCl solution containing DEAMB

Concentration (ppm)	E <sub>o</sub> (V)	I <sub>o</sub> (A/cm <sup>2</sup> )	β <sub>a</sub> (mV)	β <sub>c</sub> (mV)	Corrosion rate (mm/a)	IE (%)
0	-0.4544	2.9238×10 <sup>-4</sup>	203.05	130.75	3.4390	
10	-0.4469	1.9194×10 <sup>-4</sup>	179.61	109.45	2.8576	16.9
20	-0.4907	1.8549×10 <sup>-4</sup>	253.97	130.67	1.9817	42.2
50	-0.4818	1.6709×10 <sup>-4</sup>	257.34	132.33	1.4359	58.2
100	-0.4798	1.0401×10 <sup>-4</sup>	236.79	109.47	1.0644	69.0

## Conclusions

*N*-(*N*-diethylethanamine)-methyl benzotriazole (DEAMB) was prepared, characterized and used as acidic corrosion inhibitor in HCl solution. The inhibition and the mechanism on the corrosion of A3 steel in 2M and 3M HCl solution were screened and discussed. DEAMB can inhibit the acidic corrosion with moderate inhibition efficiency in different concentrations and temperatures, and the highest reaches to 93.93%. A Tafel polarization measurement was employed to study the instant corrosion rate and discuss the corrosion mechanism, which indicates the extracts behave as mixed type inhibitor.

## Acknowledgment

This work was supported by National Science Foundation of China (21376189) and Scientific and Scientific Research Program Funded

by Shaanxi Provincial Education Department (15JS089).

## References

1. J. K. Borchardt, T. F. Yen, Oil Field Chemistry—Enhanced Recovery and Production Stimulation, *YTO ON CAN.*, 608 (1988).
2. Y. R. Liu, Z. M. Gao, Z. Zhang, D. F. Shi, Electrochemically Aided Deposition of TiO<sub>2</sub> Films on Ni-P Pre-Plated A3 Carbon Steel, *Energ. Environ. Sci.*, **19**, 323 (2007).
3. K. Stanly Jacob, G. Parameswaran, Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution by Schiff Base Furoin Thiosemicarbazone, *Corros. Sci.*, **52**, 224 (2010).
4. G. Chen, M. Zhang, J. R. Zhao, R. Zhou, Z. C. Meng, J. Zhang, Investigation of Ginkgo Biloba Leave Extracts as Corrosion and Oil Field Microorganism Inhibitors, *Chem. Cent. J.*, **7**, 83 (2013).
5. H. Gu, C. Li, Y. Xu, W. Hu, M. Chen, Q. Wan, Structural Features and Antioxidant Activity of Tannin from Persimmon Pulp, *Food. Res. Int.*, **41**, 208 (2008).
6. U. V. Mallavadhani, A. K. Panda, Y. R. Rao, Review Article Number 134 Pharmacology and Chemotaxonomy of *Diospyros*, *Photochem. Photobiol.*, **49**, 901 (1998).
7. G. Chen, H. Su, Y. Song, Y. Gao, J. Zhang, X. Hao and J. R. Zhao, Synthesis and Evaluation of Isatin Derivatives as High Concentrated Hydrochloric Acid Corrosion Inhibitors for Q235A Steel in Oil Field, *Res. Chem. Intermed.*, **39**, 3669 (2013).
8. N. Soltani, M. Behpour, S. M. Ghoreishi and H. Naeim, Synthesis and Evaluation of Isatin Derivatives as Corrosion Inhibitors for Q235A Steel in Highly Concentrated HCl, *Corros. Sci.*, **52**, 1351 (2010).
9. K. F. Khaled, N. Hackenman, Ortho-Substituted Anilines to Inhibit Copper Corrosion in Aerated 0.5 M Hydrochloric Acid, *Electrochim. Acta* **49**, 485 (2004).
10. S. Issaadi, T. Douadi, A. Zouaoui, S. Chafa, M. A. Khan and G. Bouet, Novel Thiophene Symmetrical Schiff Base Compounds as Corrosion Inhibitor for Mild Steel in Acidic Media, *Corros. Sci.*, **53**, 1484 (2011).
11. E. Bayol, K. Kayakirilmaz and M. Erbil, The Inhibitive Effect of Hexa- Methylene tetramine on the Acid Corrosion of Steel, *Mater. Chem. Phys.*, **104**, 74 (2007).
12. E. E. Sherbini El Foad, Effect of Some Ethoxylated Fatty Acids on the Corrosion Behaviour of Mild Steel in Sulphuric Acid Solution, *Mater. Chem. Phys.*, **60**, 286 (1999).