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Research on thiazole corrosion inhibitor with lubricating properties

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Corrosion and wear caused the failure of the metal materials in the drilling process. A new type of corrosion inhibition – thiazole corrosion inhibitor with lubricating properties (ZD) prolonging the service life of metal equipment was synthesized and characterized by infrared spectroscopy. The corrosion inhibition and lubrication performance of ZD in 25 wt% KCl solution were investigated by the weight loss method, extreme-pressure lubrication tests, electrochemical measurements and molecular dynamics simulation; the effect of ZD on the corrosion and lubrication properties of drilling fluid was also evaluated via scanning electron microscopy (SEM), four-ball friction tests and so on. Experimental results showed that addition of 3.0 wt% ZD can significantly reduce the corrosion rate of N80 steel in 25 wt% KCl solution and greatly improve lubricating properties. In addition, ZD had little effect on rheological properties and filtration of the saltwater drilling fluid, improved the lubrication properties of drilling fluid and reduced the corrosion reaction of metals, which indicated that ZD was well compatible with drilling fluid. According to theoretical calculations, ZD molecules can spontaneously squeeze away the water molecules adsorbed on the surface of Fe(001), forming a dense organic film to protect the metal.
Keywords: thiazole; corrosion inhibition; lubricating properties; adsorption energy; water-based drilling fluid; filtration measurements

Дослідження тіазольного інгібітора корозії зі змащувальними властивостями. *Zhi-wei An, Qiang Zhou, Qian Wang*

Корозія та знос сталі є причиною руйнування металевих матеріалів у процесі буріння. Синтезовано і досліджено властивості тіазольнового інгібітора корозії зі змащувальними властивостями, що продовжує термін служби металевого обладнання. Інгібування корозії та змащувальні характеристики були досліджені методом інфрачервоної спектроскопії, втрати ваги, випробуванням на змащення при екстремальному тиску, електрохімічними вимірюваннями та моделюванням молекулярної динаміки. Експериментальні результати показали, що додавання 3,0 мас.% тіазольного інгібітора може значно знизити швидкість корозії сталі N80 в 25 мас.% розчині KCl і значно покращити змащувальні властивості. Крім того, він мало впливав на реологічні властивості та фільтрацію морського бурового розчину. Згідно з теоретичним розрахунком, молекули тіазольного інгібітора можуть мимовільно віджимати молекули води, адсорбовані на поверхні Fe(001), утворюючи щільну органічну плівку для захисту металу.

1 Introduction

The saltwater drilling fluid system constructed with potassium chloride and polymer has strong inhibition, good capability of stabilizing borehole and rheological properties, and also meets the requirements of environmental friendliness and low cost, which makes it widely used in various drilling platforms [1-3]. The high content of potassium chloride in the saltwater drilling fluid system can effectively inhibit cuttings dispersion and borehole expansion. However, the transport of electrons on metal surfaces is enhanced by chloride ions with strong penetration ability, resulting in small pitting of drilling tools and casing [4]. In addition, the high content of potassium chloride can cause poor lubrication performance of the saltwater drilling fluid, increasing the friction between drilling tools and the hole to shorten the service life of the metal [5]. The actual problem is to prevent corrosion and wear of the metal. At present, corrosion and wear belong to different research fields, and the control of corrosion and wear is usually treated as two separate research topics. In order to solve the corrosion problem, one of the most economical and efficient methods is to add corrosion inhibitor [6]. At the same time, the solution to the wear problem is to add lubricants [7]. Adding lubricants can not only reduce the wear of metal equipment, but also improve drilling torque and drilling safety. Corrosion inhibitor and lubricant were usually added into the saltwater drilling fluid simultaneously, which can lead to problems with the addition of many types of additives, increasing the costs of the drilling fluid. Hence, it is of great significance to study additives with both resistance to corrosion and wear. At present, the mechanism of action of a corrosion inhibitor with lubricating properties cannot be clearly demonstrated in the existing studies. It has been reported that thiazole corrosion inhibitor and lubricant can form coordination bond with metal to efficiently adsorb on the metal surface due to the high electron cloud density of nitrogen and sulfur on the thiazole ring, preventing the metal from contacting the corrosive medium and forming an oil film to reduce the wear of metal equipment [8-9]. Such molecules can play a role in corrosion inhibition and lubrication. There are few relevant literature reports on thiazole corrosion inhibitor with lubricating properties.

Thiazole corrosion inhibitors are investigated via experiments and theoretical calculations. Yüce et al. [10] investigated the application of 2-amino-4-methyl-thiazole as a corrosion inhibitor for mild steel in 0.5 M HCl solution. The experimental analysis showed that the high corrosion inhibition efficiency of 2-amino-4-methyl-thiazole was associated with its strong adsorption as a barrier film on the mild steel surface. Döner et al. [11] studied 2-amino-5-mercapto–1,3,4-thiadiazole (2A5MT) and 2-mercapto-thiazoline (2MT) for protecting mild steel in a corrosive medium. It was concluded that 2A5MT showed higher corrosion resistance than 2MT, which was verified by the theoretical calculations. In recent years, thiazole compounds as lubricants were studied. Hakala et al. [12] synthesized thiazole derivative used as water-soluble lubricating additive, which can effectively improve the tribological properties of water-glycol in a proper concentration. The experimental analysis showed that benzothiazole group can greatly improve the friction-reducing and anti-wear capacities of the base fluid. Sulek et al. [13] synthesized a new type of lubricant containing benzothiazole. Results showed that the lubricant possessed excellent extreme pressure and good anti-wear performances.

In order to prolong the service life of metal equipment, thiazole corrosion inhibitor with lubricating properties (code ZD) was synthesized in this paper. The stable complexes and chelates were generated by adsorption of thiazole heterocyclic compounds on Fe atoms. Such adsorption can reduce corrosion and friction, which can protect metal equipment and improve drilling safety. The structure of thiazole corrosion inhibitor with lubricating properties was analyzed by the FT-IR spectra. The corrosion inhibition and lubrication performance of ZD were investigated by the weight loss method, extreme-pressure lubrication tests, electrochemical measurements and molecular dynamics simulation. The effect of ZD on the corrosion and lubrication properties of drilling fluid was also evaluated via the weight loss method, scanning electron microscopy (SEM), four-ball friction tests and so on.

2 Materials and Methods

2.1 Materials

Analytical grade NaOH, Na_2CO_3, KCl, 2-aminobenzothiazole, acetophenone, formaldehyde, benzene, anhydrous ethanol, sodium chloroacetic acid and hydrochloric acid were provided by Sinopharm Chemical Reagent Co., Ltd., wherein NaOH and Na_2CO_3 were used to adjust the pH of the saltwater drilling fluid system; hydrochloric acid was deployed as catalyst to synthesize corrosion inhibitor with lubricating properties, and KCl worked as liquid weighted agent and inhibitor of the fluid. Filtrate reducer (code STARCH), viscosifier (code XC), high temperature stabilizer (code WZ-HT) and plugging agent (code BISEAL) were supplied by Wuxi Jingke Fine Chemical Co as the main components of the saltwater drilling fluid system.

2.2 Methods

2.2.1 Synthesis and characterization of ZD

Based on the Mannich reaction and the quaternization reaction, a new type of thiazole corrosion inhibitor with lubricating properties was synthesized using 2-aminobenzothiazole, acetophenone, formaldehyde and sodium chloroacetic acid as raw materials. An amount of 10g 2-aminobenzothiazole, 6g acetophenone, 4g formaldehyde and 80g anhydrous ethanol were firstly added into a three-mouth flask equipped with a stirrer, a reflux condenser and a thermometer, and the solution was stirred for 1.0 h at 50°C to make raw materials fully dissolved in anhydrous ethanol. After that, a certain amount of hydrochloric acid was added to bring the pH value of the reaction system to 5. The reaction system was heated to 80 °C and maintained for 5 h with stirring, followed by adding 5g sodium chloroacetic acid. Then, quaternization reaction was performed for 8h with stirring. Finally, the product was obtained by washing with benzene and drying in an oven at 70 °C. The resulting product was prepared with KBr to get the samples. The infrared spectra were obtained on the Nicolet750 size Fourier Transform Infrared Spectrometer to analyze the functional groups of the samples.

2.2.2 Weight Loss Measurement and Surface Examination with SEM

Weight loss measurements were conducted on N80 steel samples of dimensions 4 cm × 1cm× 0.14 cm. These steels were polished with silicon carbide abrasive paper, rinsed with distilled water, dried in anhydrous ethanol and warm air. According to the SY/ T5273-2000 standard (Chinese standard), the corrosion rate of the pretreated N80 steel in 25 wt% KCl solution and the saltwater drilling fluid system was measured by the weight loss method. The test steps were as follows: N80 steel samples were put into a wide jar containing 25 wt% KCl solution and into the saltwater drilling fluid system with a certain concentration of ZD, and soaked for 168 h at 80℃. The corrosion inhibition effect of ZD on N80 steel was evaluated, and the calculation formulas are (1) – (2).

The composition of the saltwater drilling fluid was: water + 0.20 wt% NaOH + 0.20 wt % Na_2CO_3 + 3.0 wt% STARCH +3.0 wt% BISEAL + 0.6 wt% XC +1.0 wt % WZ-HT + 25 wt% KCl (ρ = 1.2 g/cm^3).

$$r_{corr}=\frac{8.76\times10^4\times\left(m\text{-}m_t\right)}{S\times t\times\rho} \quad (1)$$

In this relation, r_{corr} refers to corrosion rate of N80 steels (mm/a), S is the total area of N80 steel samples (cm^2), ρ is the density of N80 steel (g/cm^3), t is soaking time of N80 steels in corrosive medium (h), m and m_t indicate the mass of N80 steels before and after experimental test (g), respectively.

$$\eta = (\triangle m_0\text{-}\triangle m_1)/\triangle m_0\times100\% \quad (2)$$

In this relation, η indicates corrosion inhibition efficiency of ZD, $\triangle m_0$ is the loss of N80 steels in corrosion medium without ZD (g), $\triangle m_1$ is the loss of N80 steels in corrosion medium with ZD (g).

N80 steel samples were immersed in the saltwater drilling fluid system with and without ZD. At the end of the experiment, N80 steel samples were then washed with distilled water, dried in warm air. Finally, morphological studies of N80 steels were undertaken by the JSM-5610 model scanning electron microscope (JEOL, Japan).

2.2.3 Electrochemical measurements

The corrosion inhibition mechanism of ZD on N80 steel was studied by the CHI660 model electrochemical analyzer. The saltwater drilling fluid system containing different concentrations of ZD was used as a corrosive medium. The experimental temperature was 40 ℃, the polarization curve scanning range was -300 ~ -600 mV and the potential scanning rate was 5 mV/s.

2.2.4 Lubrication test

Extreme-pressure lubrication tests were performed on 25 wt% KCl solution and the saltwater drilling fluid system. A FANN 212 model extreme-pressure lubrication meter (FANN Instrument Company, USA) was used to determine the extreme pressure coefficients of the two systems mentioned above with different concentrations of ZD. Four-ball friction tests were performed to measure the lubrication effect of ZD on the saltwater drilling fluid system using a MS–10A four-ball friction test machine (Xiamen Tianji Automation Co., Ltd., China), at a load of 150 N, speed of 150r·min^{-1}, and friction applied over 30 min. The scratches on the surfaces of the steel balls were subsequently examined.

2.2.5 Molecular dynamics simulation

The adsorption configuration of a ZD molecule on the iron surface was simulated using the Forcite model with Material Studio. We choose the Fe 1001) crystal surface to simulate the adsorption process of a ZD molecule on the copper surface. The entire simulation process was performed in the COMPASS force field with the NVT specification set. Cyclical frontier was 298K, the time step was 1fs, and the total

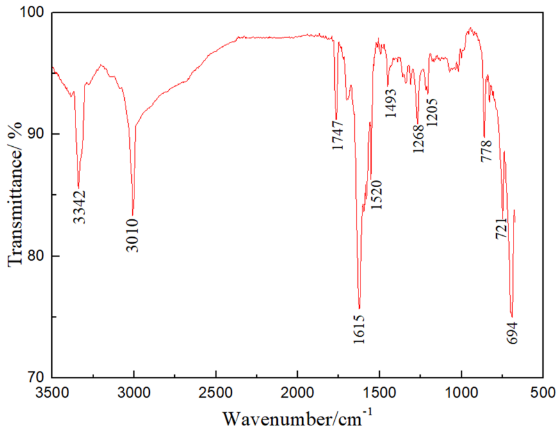

Fig.1 FTIR spectrum of ZD

calculation time was 300 ps. The adsorption energy of a ZD molecule on the metal surface was calculated theoretically, and the adsorption energy can be obtained via formula (3) as following

$$E_{absorption} = -(E_{surface} + E_{molecule}) + E_{total} \quad (3)$$

where E_{total} is the total energy. $E_{surface}$ represents the metal surface energy without adsorbed ZD molecules. $E_{molecule}$ is the energy of ZD molecules. $E_{absorption}$ represents the adsorption energy of ZD molecules on metal surface.

2.2.6 Rheological properties and filtration measurements

The saltwater drilling fluid system with ZD was aged at 80°C for 16 h. Rheological properties of the system after the aging process were measured at six specific shear rates, i.e., 600, 300, 200, 100, 6, and 3 rpm using a ZNN-D6 rotational viscometer to calculate apparent viscosity (AV), plastic viscosity (PV) and yield point (YP). The calculation formulas are as follows:

$$AV = \theta_{600}/2 \ (mPa \cdot s) \quad (4)$$

$$PV = \theta_{600} - \theta_{300} \ (mPa \cdot s) \quad (5)$$

$$YP = 0.511(\theta_{300} - PV) \ (Pa) \quad (6)$$

According to the American Petroleum Institute (API) standards, the API filtration loss (FL_{API}) of the system was evaluated with the use of a mud-absorbing apparatus ZNS.

3. Results and discussion

3.1 FTIR analysis

The structure of ZD was determined by FTIR spectroscopy, as shown in Fig.1. As indicated, the absorption peak of ZD at 1520 cm^{-1} corresponds to the C=N stretching vibration of the five-membered thiazole ring. The absorption peak at 1747 cm^{-1} is characteristic of the absorption of a carboxylic acid. The absorption peak at 694 cm^{-1} is the stretching vibration peak of C-S, and the strong absorption peak at 3010 cm^{-1} is due to the stretching vibration of =C-H. The peaks at 778 cm^{-1} and 721 cm^{-1} correspond to the bimodal flexural vibration of the benzene ring, and the peak at 1615 cm^{-1} corresponds to the skeleton vibration of the benzene ring. The absorption peaks at 3342 cm^{-1} and 1493 cm^{-1} correspond to the stretching vibration and the bending vibration of secondary amine. The above analysis indicates that the designed molecule has been successfully synthesized.

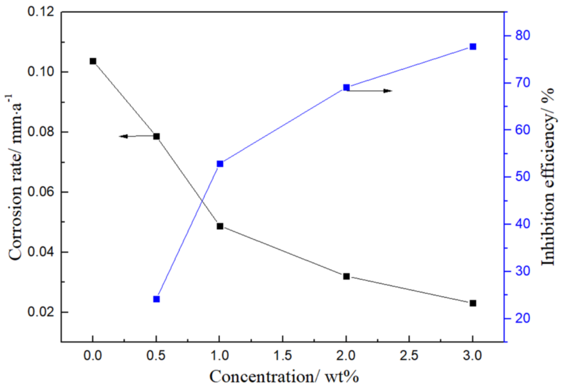

Fig.2 Effect of ZD on corrosion rate of N80 steel

3.2 Analysis on corrosion inhibition of ZD

The corrosion rate of N80 steel in 25 wt% KCl solution with different concentrations of ZD is presented in Fig.2. As indicated, the corrosion rate of N80 steel in 25 wt% KCl solution gradually decreased with an increase in the concentration of ZD, indicating that ZD can obviously inhibit the corrosion reaction on the N80 steel surface. When the ZD concentration was of 3.0 wt%, the corrosion rate of N80 steel can reduce to 0.0223 mm/a, and its corrosion inhibition efficiency was 77%. It is clear that ZD molecules can be stably adsorbed on the surface of N80 to prevent the corrosive medium from breaking the metal.

3.3 Analysis of electrochemical properties of ZS

The polarization curves of N80 steel in 25 wt% KCl solution containing different concentrations of ZD are shown in Fig.3, and the electrochemical parameters obtained by Cview software are shown in Table 1. As indicated, with increasing ZD concentration, the corrosion current density (I_{corr}) of N80 steel gradually decreased, indicating that the corrosion reaction on the surface of N80 steel was effectively inhibited. It has been observed that the addi-

Table 1. Polarization Parameters for N80 steel in 25 wt% KCl solution

ZD (wt%)	E_{corr}/V	I_{corr}/(A·cm^{-2})	η(%)
0	–0.421	4.549×10^{-4}	–
0.5	–0.468	3.115×10^{-4}	31.10
1.0	–0.459	2.281×10^{-4}	49.86
2.0	–0.445	1.506×10^{-4}	66.90
3.0	–0.431	1.223×10^{-5}	73.12

tion of ZD affects both the anodic and cathodic partial reactions, clearly shifting the corrosion potential (E_{corr}) towards more negative (cathodic) values. The negative shift was greater than 30mV, indicating that ZD belonged to cathode controlled corrosion inhibitors [14]. ZD molecules with N atom, S atom and benzene ring can form the ligand bond on the metal surface, and then the adsorption film was formed to achieve the purpose of protecting metal. In addition, the corrosion inhibition efficiency of ZD tested by the polarization curve was consistent with the weight loss method.

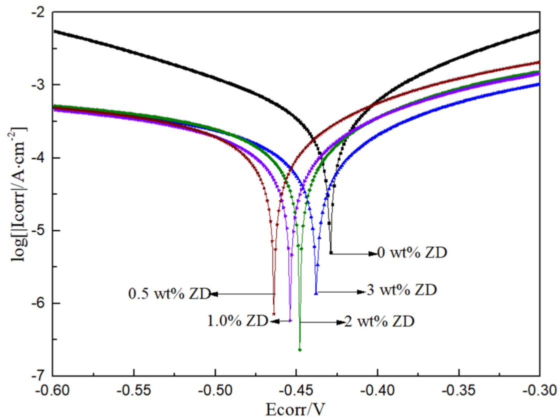

Fig.3. Polarization curves of N80 steel in 25 wt% KCl solution without and with ZD

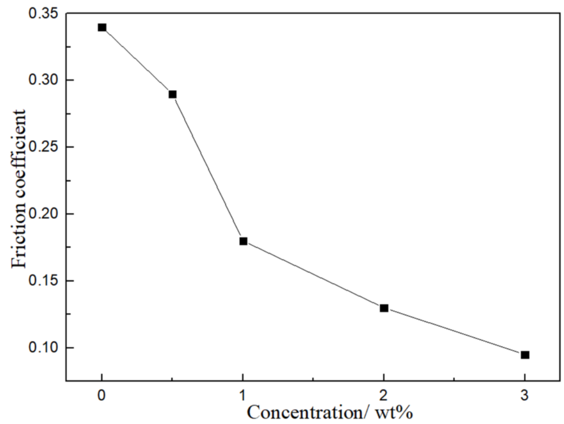

Fig.4. Extreme-pressure lubrication test results of 25 wt% KCl solution containing different concentrations of ZD

3.4 Analysis on lubricating properties of ZS

Extreme-pressure lubrication test results of 25 wt% KCl solution containing different concentrations of ZD are shown in Fig.4. The lower the friction coefficient, the better the lubricity. In Fig. 4, with increasing concentration of ZD, the friction coefficient of the KCl solution system gradually decreases, indicating that addition of ZD improves lubricating properties of KCl solution system. The friction coefficient of the KCl solution system with 3.0 wt% ZD was reduced to 0.095. ZD molecules with thiazole and benzene rings can stably adhere to metal surfaces to form an oil film, reducing the contact area between metals, and the ester group in ZD molecules can also play an important role in improving lubricating properties of the KCl solution system.

3.5 Molecular dynamics simulation analysis

Molecular dynamics simulation has a crucial significance for microscopic understanding of the adsorption of ZD molecules on the iron surface [15]. The adsorption configuration of a ZD molecule on the Fe(001) crystal plane was shown in Fig.5, and the adsorption energy of a ZD molecule on metal surface was shown in Table 2. As indicated, a ZD molecule changed from the original three-dimensional configuration to a plane configuration, which can improve the ability of ZD molecules to cover metal surface. Obviously, a dense organic film was formed on the metal surface, which can effectively isolate the corrosive environment from metal destruction. In addition, according to theoretical calculation, the adsorption energy of ZD molecules on the surface of Fe(001) was greater than that of water molecules on the surface of Fe(001), indicating that ZD molecules can squeeze out the water molecules adsorbed on the surface of Fe(001) to protect the metal.

Table 2. Analysis of the adsorption energy of a ZD molecule on Fe(001) crystal plane

Molecule	E_{total}	$E_{surface}$	$E_{molecule}$	$E_{absorption}$
ZD	–771206.10	–770938.05	–54.67	–213.38
H_2O	–770776.72	–770758.32	7.23	–25.63

Table 3. Test results of the saltwater drilling fluid after the aging process

Sample	PV/(mPa·s)	YP/Pa	Friction coefficient	API/mL	Corrosion rate/ mm·a^{-1}
drilling fluid	24	9	0.13	5.4	0.098
drilling fluid with 3.0 wt% ZD	25	9	0.081	5.2	0.042

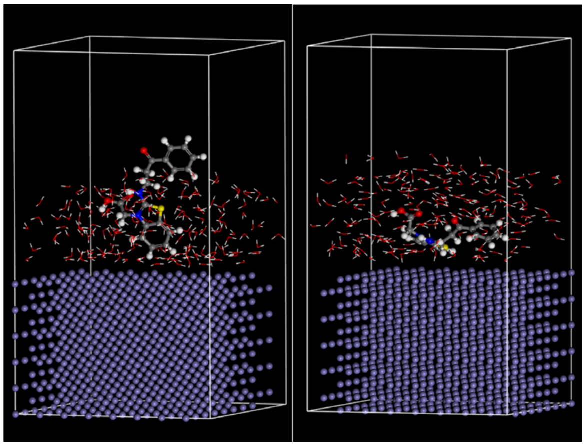

Fig.5. The adsorption configuration of ZD molecule on the Fe(001) crystal plane (Initial adsorption (left), and equilibrium configuration (right))

3.6 The effect of ZD on drilling fluid

The filtration, lubrication, corrosion rate and rheological properties of the saltwater drilling fluid system with 3.0 wt% ZD after the aging process were measured, and the test results are shown in Table 3. According to Table 3, ZD had little effect on rheological properties and filtration of the saltwater drilling fluid, which indicated that ZD was well compatible with drilling fluid. The addition of 3 wt% ZD significantly reduced the corrosion rate of N80 steel soaked in the saltwater drilling fluid. Thus, ZD can greatly improve lubricating properties of the saltwater drilling fluid; this clearly shows that thiazole corrosion inhibitor with lubricating properties (ZD) makes the drilling fluid more suitable for field drilling.

SEM images of the surfaces of N80 steels soaked in the saltwater drilling fluid are shown in Fig.6. Fig. 6 shows rough corrosion marks appeared on the surface of N80 steel soaked in the saltwater drilling fluid without ZD; these indicate the destruction of metal surfaces by corrosive media. At the same time, the surface of N80 steel soaked in the saltwater drilling fluid with 3.0 wt% ZD was relatively flat, and its mechanical grinding is very clear. It was shown that ZD molecules can be adsorbed on the metal surface to form a dense organic film, which can isolate the corrosive medium and prevent corrosion.

Four-ball friction experiments were performed to further study the lubrication effects of the ZD on the saltwater drilling fluid, and experimental results are shown in Fig. 7. The results show that the diameter of scratches was 1.004mm in the saltwater drilling fluid test. After the addition of 3 wt% ZD, the spot diameter was 0.645mm, indicating that ZD can improve the lubricating properties of the saltwater drilling fluid. Based on the above experimental analysis, it was very clear that thiazole corrosion inhibitor with lubricating properties (ZD) reduced corrosion and wear of metal.

4. Conclusions

Based on the Mannich reaction and the quaternization reaction, thiazole corrosion inhibitor with lubricating properties (ZD) was synthesized by using 2-aminobenzothiazole, acetophenone, formaldehyde and sodium chlo-

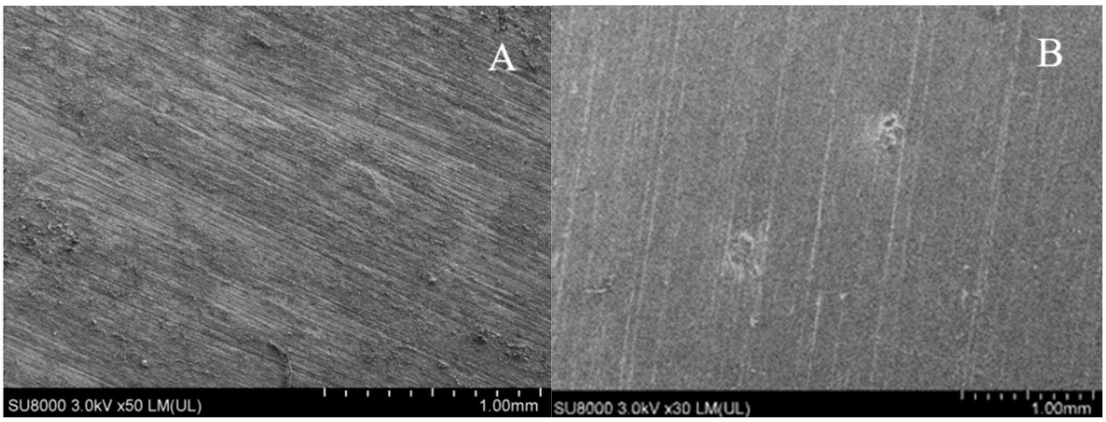

Fig.6. SEM images of N80 steels soaked in the saltwater drilling fluid (A, without ZD; B, with 3.0 wt%)

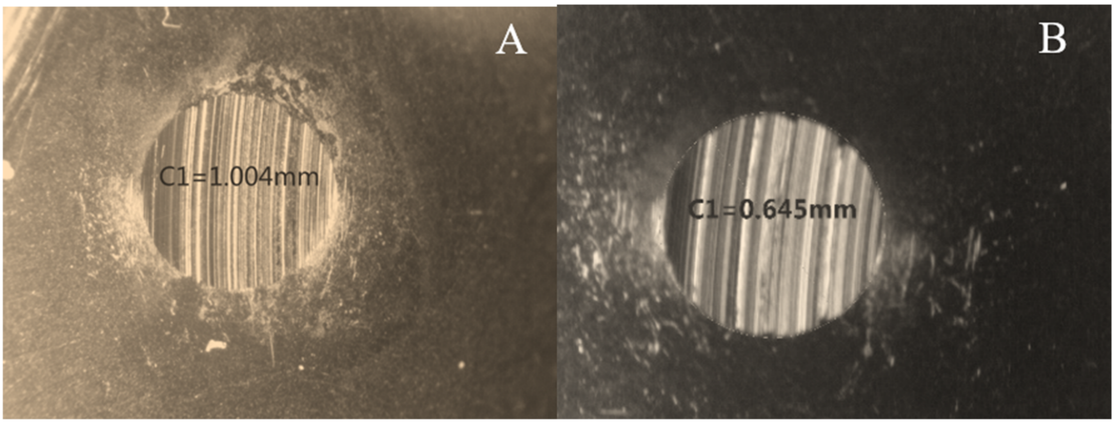

Fig.7. Comparison of the scratches after treatment with the saltwater drilling fluid (A, without ZD; B, with 3.0 wt%)

roacetic acid as raw materials. The corrosion rate of N80 steel in 25 wt% KCl solution with 3.0 wt% ZD was 0.0223 mm/a, and its corrosion inhibition efficiency was 77%. Addition of 3.0 wt% ZD was seen to affect the anodic as well as the cathodic partial reactions. ZD belongs to the cathode controlled corrosion inhibitor, and the addition of 3 wt% ZD significantly reduced the corrosion rate of N80 steel soaked in the saltwater drilling fluid.

The friction coefficient of the KCl solution system with 3.0 wt% ZD was reduced to 0.095. Thus, ZD can greatly improve lubricating properties of the saltwater drilling fluid. It was clearly exhibited that thiazole corrosion inhibitor with lubricating properties (ZD) made the drilling fluid more suitable for field drilling. In addition, ZD had little effect on rheological properties and filtration of the saltwater drilling fluid, which indicated that ZD was well compatible with the drilling fluid.

ZD molecules change from the original three-dimensional configuration to a plane configuration, which promotes the ability of ZD molecules to cover metal surface; at the same time, the adsorption energy of ZD molecules on the surface of Fe(001) was higher than that of water molecules, indicating that ZD molecules can squeeze out the water molecules adsorbed on the surface of Fe(001) and protect the metal.

References

1. Suri, A.; Sharma, M.M, *SPE J.* **9**, 13, (2004).
2. Hossain M. E.; Wajheeuddin M, *Pet. Sci.* **13**(2), 292, (2016).
3. Mainier,F.B.; Figueiredo, A.A.M.; Freitas,A. E.R.; Perassolli, V. *J Environ Prot.,* **7**(13), **2025**, (2016).
4. Chaudhry, A.U.; Mittal,V.; Mishra, B, *Dyes and Pigments*, **118**, 18, (2015).
5. Sönmez,A.; Kok,M.V.; Ozel,R, *J Pet Sci Eng.* **108**, 64, (2013).
6. Oguzie, E. E.; Adindu, C. B.; Enenebeaku, C. K.; Ogukwe, C. E.; Oguzie, K. L, *J. Physical Chemistry C*, **116**(25), 13603, (2012).
[7. Nunes,D.G.;daSilva,A.P.M.;Cajaiba,J.;Perez-Gramatges, A.; Lachter,E.R, *J Appl Polym Sci*, **131**(22), 214 (2012).
8. Mohan, P. G.; Kalaignan, P, *J. Mater. Sci. Technol.* **29**, 1096, (2013).
9. El-Haddad, M.N.; Fouda, A.S., *J. Dispersion Sci. Technol.* **34**: 1471, (2013).
10. Yüce, A. O.; Mert, B. D.; Karda, G.; Yazc,B, *Corrosion Science*, **83**(6), 310, (2014).
11. Doener, A. H.; Solmaz, R.; Oezcan, M.; Kardas,G. L, *Corrosion Science*, **53**(9), 2902 (2011).
12. Hakala, T. J.; Metsajoki, J.; Granqvist, N.; Milani, R.; Szilvay, G. R.; Elomaa, O, *Tribology International*, **90**, 60, (2015).
13. Sulek, M.W.; Wasilewski, T, *Lubrication Science*, **26**(2), 81, (2014).
14. Moradighadi, N.; Lewis, S.; Olivo, J. D,; Young, D.;Nesic.S,. *Corrosion Houston Tx*, **77**(3),:266, (2021).
15. Danaee, I.; Khomami, M.N.; Attar, A.A., *Mater. Chem. Phys.* **135**,658,(2012).