抑制 Q235 钢 CO₂ 腐蚀的气液双相咪唑啉衍生物缓蚀剂的缓蚀行为

王 彬 杜 敏* 张 静

(中国海洋大学化学化工学院, 海洋化学理论与工程技术教育部重点实验室, 山东 青岛 266100)

摘要: 采用失重法、电化学交流阻抗谱(EIS)及傅里叶变换红外(FT-IR)光谱、原子力显微镜(AFM)、X射线光电子能谱(XPS)等分析测试方法研究了硫脲基咪唑啉衍生物(TAI)作为抑制 CO₂ 腐蚀的气液双相缓蚀剂的缓蚀行为。结果表明, 该硫脲基咪唑啉缓蚀剂能有效地抑制 Q235 钢在气液双相中的 CO₂ 腐蚀。AFM 测试结果表明该缓蚀剂能显著地降低碳钢表面的腐蚀破坏, 并且由于碳钢表面形成的缓蚀剂吸附膜的疏水作用, 可在 AFM 探头和碳钢表面之间检测到更大的粘附力, 而探针与试样表面之间的长程静电斥力在气相中增加, 在液相中由于表面电荷的屏蔽效应而减小。XPS 和 FT-IR 光谱测试表明液相中和气相中在碳钢表面形成吸附膜的缓蚀剂成分分别是硫脲基咪唑啉衍生物和其酸水解产物——酰胺。以上结果也进一步证实了咪唑啉衍生物在酸性溶液中的水解机理。

关键词: CO₂ 腐蚀; 咪唑啉衍生物; 酸水解; 傅立叶变换红外光谱; 原子力显微镜; X射线光电子能谱
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Inhibition Performance of an Imidazoline Derivative as a Gas-Liquid Two-Phase Inhibitor for Q235 Steel against CO₂ Corrosion

WANG Bin DU Min* ZHANG Jing

(Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education,
College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, Shandong Province, P. R. China)

Abstract: We investigated the inhibition performance of a new imidazoline derivative inhibitor, TAI, which can be used as a gas-liquid two-phase inhibitor against CO₂ corrosion by weight-loss method, electrochemical impedance spectroscopy (EIS), Fourier transform-infrared (FT-IR) spectroscopy, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). Results revealed that the thioureido imidazoline inhibitor was an effective inhibitor against CO₂ corrosion in gas and liquid two phases. Surface analysis by AFM showed that damage to the metallic surface was considerably reduced in the presence of the TAI inhibitor. A bigger adhesive force between the AFM probe and the steel surface was detected owing to hydrophobic interaction from the inhibitors in the two phases. The long range repulsive force between the AFM probe and the steel surface increased in gas phase but decreased in liquid phase by the screening effect of surface charges. XPS and FT-IR spectra proved that the adsorption films on the metal surfaces with protective properties of TAI and acid hydrolysis products (amides) of the TAI were present in liquid phase and in gas phase, respectively. The above results further confirmed the hydrolysis mechanism of imidazoline derivatives in acid solution.

Key Words: CO₂ corrosion; Imidazoline derivative; Acid hydrolysis; Fourier transform-infrared spectroscopy; Atomic force microscopy; X-ray photoelectron spectroscopy

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*Corresponding author. Email: sdm06@126.com; Tel: +86-532-66781637.

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CO₂ corrosion, usually called sweet corrosion, is one of the most serious forms of corrosion in the oil, gas production, and transportation industry^[1-2]. The enhanced corrosion by CO₂ in the solution is greater than that by solution acidification^[3]. Until now, most work has been carried out on the influence factors and mechanism of CO₂ corrosion and various methods for CO₂ corrosion control in liquid phase^[4-9], however, with the rapid development of oil and gas industry, there are more and more natural gas wells and gas transmission lines of oilfield leading to CO₂ corrosion in gas and liquid two phases, which is a research hot spot in recent years. Using chemical treatment to prevent steel from CO₂ corrosion is one of the most cost-effective ways^[10]. Imidazoline, as a type of corrosion inhibitor, is most commonly used for protecting oil wells, gas wells or pipelines from CO₂ corrosion due to its good adsorption character and the formation of a chemical film on the surface of iron and steel^[11-16]. Despite their extensive use in liquid phase against CO₂ corrosion, there are few studies on the inhibition performance of imidazoline derivative as a gas-liquid two-phase inhibitor for CO₂ corrosion.

The aim of this work was to study the inhibition performance of imidazoline derivative synthesized in our lab against CO₂ corrosion in gas and liquid two phases. It was confirmed that the imidazoline derivative performed excellently as a gas-liquid two-phase inhibitor for CO₂ corrosion. Furthermore, we interpreted the inhibition mechanism of the inhibitor in the two phases using XPS, FT-IR, and AFM.

1 Experimental

1.1 Material preparation

The test material selected for study was Q235 steel, its composition (w, %) was 0.16 C, 0.53 Mn, 0.30 Si, <0.045 P, <0.055 S, Fe balance. The sample surfaces were abraded with a series of silicon carbide papers, and then they were washed with distilled water and degreased in acetone, then dried at room temperature.

The structure of TAI (1-(2-thioureidoethyl)-2-alkyl imidazoline) inhibitor used for this work is shown as follow:

An aqueous solution of 2% (w) NaCl saturated with CO₂ was used as a blank solution. The pH of the solution was 4.53. The saltwater was prepared from analytical grade reagents using double distilled water in accordance with the procedure described in the standard ASTM E 200-97^[17].

1.2 Corrosion weight loss measurement

Three specimens (50 mm×10 mm×3 mm) were immersed in and placed upon 500 mL CO₂-saturated solution with and without TAI inhibitors in a closed vessel for 72 h immersion at 333 K, respectively. The coupons were then taken out of the closed

vessel, removed rust in the descaling liquid, rinsed with distilled water, dried and weighted. Preparation and evaluation of the metallic compounds were carried out according to ASTM G 1-88^[18] and ASTM G 31-72^[19].

1.3 Zero charge potential measurement

For EIS measurement, the cell assembly consisted of Q235 steel as working electrode, a platinum foil as counter electrode, and a saturated calomel electrode (SCE) as a reference electrode with a Luggin capillary bridge. The metal samples of the working electrode were embedded in epoxy resin, leaving a geometrical surface area of 1 cm² exposed to the electrolyte. EIS measurements were carried out using IM6e (ZAHNER, Germany) electrochemistry workstation with perturbation amplitude of 5 mV at the corrosion potential and the frequency range was from 100 kHz to 10 mHz. For the zero charge potential test, EIS measurements were performed at the following potentials with respect to SCE: -450, -500, -550, -600, -620, -650, -680, -700, -750, -800, and -900 mV. Zview 2 software was used to obtain differential capacities (C_d) through fitting the measured data. Curves of C_d versus E (i.e., C_d - E) were plotted. The potential corresponding to the minimum value of C_d was just the zero charge potential of the working electrode in the electrolyte in the absence and presence of TAI inhibitor.

1.4 XPS, FT-IR, and AFM analyses

The samples with dimensions 10 mm×10 mm×1 mm were exposed to the TAI solution in a closed vessel to form adsorption films on the sample surfaces in gas and liquid two phases at 333 K. XPS spectra were performed with a PHI 5300 spectrometer (Perkin-Elmer, USA) using Al K_α radiation as excitation sources. A take-off angle of 45° from the surface was employed. All the analyses were performed at a pressure below 1×10⁻⁶ Pa.

Infrared spectra of the inhibitor films formed on the sample surfaces were measured by a VERTEX 70 FT-IR spectrometer (Bruker Optics, Germany) with ATR accessory using a liquid nitrogen cooled mercury-cadmium-tellurium (MCT-A) detector. The infrared reflection spectra were obtained with 64 scans. The resolution was 4.0 cm⁻¹ and the spectral region was from 4000 to 400 cm⁻¹. The OPUS software was used to analyze these spectra. In order to eliminate the strong disturbances of IR absorbance arising from carbon dioxide and water absorbed on the surface of the samples, the absorbance background of carbon dioxide and water were taken out during the data recording in all experiments.

AFM measurements were carried out using a commercial SPA400 AFM (SEIKO, Japan). The force curves were measured in contact mode using Si₃N₄ tips with spring constant of 0.02 N·m⁻¹ and the imaging process was performed in tapping mode using Si tips with spring constant of 3 N·m⁻¹.

2 Results and discussion

2.1 Weight loss measurement

Table 1 presents the values of the corrosion rates (v) and the

Table 1 Corrosion rate and inhibition efficiency values obtained from weight loss method at various TAI concentrations at 333 K in gas and liquid two phases

$c(\text{TAI})/(\text{mg} \cdot \text{L}^{-1})$	$v_{\text{liquid}}/(\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1})$	$\eta_{\text{liquid}}(\%)$	$v_{\text{gas}}/(\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1})$	$\eta_{\text{gas}}(\%)$
0	0.3371	—	0.6372	—
25	0.0861	74.5	0.3164	50.3
50	0.0708	79.0	0.1892	70.3
75	0.0893	73.5	0.1084	83.0
100	0.0854	74.7	0.1480	76.8

inhibition efficiencies (η), which are calculated using the following equations^[20]:

$$\nu = \frac{8.76 \times 10^7 \Delta m}{\rho A t} \quad (1)$$

$$\eta = \frac{\nu_0 - \nu_{\text{inh}}}{\nu_0} \times 100\% \quad (2)$$

where A is electrode area (cm^2), t represents the immersion time (h), Δm is the mass loss (g), ρ corresponds to the steel density ($\text{kg} \cdot \text{m}^{-3}$), ν_{inh} and ν_0 are the corrosion rates ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) of Q235 steel with and without TAI, respectively. It is evident from Table 1 that the TAI inhibitor can protect Q235 steel from CO_2 corrosion efficiently in gas and liquid two phases at 333 K. The inhibition efficiencies in liquid phase are all above 73% and change slightly with the increase in TAI concentration and the highest η was 79.0% in the presence of $50 \text{ mg} \cdot \text{L}^{-1}$ TAI. However, the change in inhibition efficiency in gas phase is significantly greater with TAI concentration and the highest η was 83.0% in the presence of $75 \text{ mg} \cdot \text{L}^{-1}$ TAI.

2.2 Zero charge potential measurement

The measured typical Nyquist diagrams of electrochemical impedance spectra of Q235 steel in the test solution in the absence and presence of $50 \text{ mg} \cdot \text{L}^{-1}$ TAI are shown in Fig.1.

As shown in Fig.1, the typical Nyquist plot for Q235 steel in blank solution contains a depressed semicircular shape in the complex impedance plane, with the center under the real axis, which is a typical behavior for solid metal electrodes that show frequency dispersion of the impedance data^[21]. Dispersion has been attributed to roughness and other inhomogeneities of the solid surface^[22–23]. The typical Nyquist plot of Q235 steel with the addition of $50 \text{ mg} \cdot \text{L}^{-1}$ TAI presents one depressed semicir-

Fig.1 Measured typical Nyquist plots for Q235 steel in the test solution in the absence and presence of $50 \text{ mg} \cdot \text{L}^{-1}$ TAI

Fig.2 Differential capacity curves for Q235 steel in the test solution with and without $50 \text{ mg} \cdot \text{L}^{-1}$ TAI

cle with a long tail at the low frequency region. The tail is inclined at an angle close to 45° to the real-axis at very low frequency. This behavior indicates that the diffusion process of ions takes place on the electrode after the addition of TAI inhibitor.

The values of differential capacity of the test electrode at selected potentials can be gotten by Zview software using corresponding equivalent circuit, and the C_d - E diagram is plotted in Fig.2. It can be seen from Fig.2 that the potentials of zero charge (PZC) of Q235 steel in the blank solution and solution containing $50 \text{ mg} \cdot \text{L}^{-1}$ TAI are -680 and -620 mV, respectively. Since the corrosion potentials in the uninhibited and inhibited solutions are -700 mV and in the range of -620 to -650 mV (vs SCE), separately, so at natural corrosion potential, the surface of electrode has always extra negative charges in the solution with and without inhibitor. The addition of TAI in the solution affects both the shape and the capacitance values of the electrode. The decrease of the capacitance is an indication that the TAI inhibitor adsorbs on the metal surface. This effect can be correlated with decrease in the dielectric constant and / or an increase in the thickness of the electrical double layer^[24–25].

2.3 FT-IR measurement

Imidazoline and its derivatives in acid solution can hydrolyze generating amides (AMI) as shown in Scheme 1^[26].

Infrared spectroscopy is a powerful tool for investigating adsorption films on metal surfaces. At the simplest level, infrared spectroscopy can confirm the presence of molecules adsorbed on a surface^[27]. In order to characterize the formation of inhibitor films on steel surfaces in gas and liquid two phases, FT-IR spectroscopy test was performed, as shown in Fig.3. The strong peaks at 3289 and 3265 cm^{-1} correspond to N-H stretching vibration. There are peaks at 2920 , 2922 cm^{-1} and 2853 , 2876 cm^{-1} due to the asymmetric stretching vibration and symmetric stretching vibration of $-\text{CH}_2-$ in the molecule, respectively. The peaks at 1025 , 1018 cm^{-1} and 2053 , 2054 cm^{-1} can be assigned to the C=S stretching vibration and the decomposition product of thiourea $-\text{S}-\text{C}\equiv\text{N}$ stretching vibration, separately. The peaks at 1602 and 1282 cm^{-1} in Fig.3(b) are the stretching frequencies of C-N and C=N, respectively, which

Scheme 1 Process of hydrolysis of imidazoline and its derivatives

are the very typical characteristic of imidazoline ring^[28]. The peaks at 1630 and 1562 cm^{-1} in Fig.3(a) are the stretching frequencies of $-\text{CONH}$, which indicate the existence of amide^[29-30]. So the above results prove that the TAI inhibitor and its acid hydrolysis product (amides) form adsorption films on sample surfaces in liquid phase and in gas phase, respectively.

2.4 AFM observation

Fig.4 shows the three-dimensional AFM images of Q235 steel surface. The initial surface morphology (a) indicates that there are a few scratches from mechanical polishing treatment, and the roughness is 100.75 nm. Figs.4 (b) and (d) show that the specimens after exposure to the uninhibited solution are badly damaged, especially the sample in gas phase, whose surface roughness is up to 1029.29 nm. However, Figs.4 (c) and (e) show that the samples after exposure to the solution containing 50 $\text{mg} \cdot \text{L}^{-1}$ TAI are still flat and uniform relatively, and the surface roughnesses in gas phase and in liquid phase decrease to 310.13 and 111.40 nm, respectively, which is the result of the protective formation of an inhibitor layer in the two phases^[31].

2.5 AFM force curves

The force-distance curves measured on the sample surfaces after immersion for 2 h in the test solution with and without 50

$\text{mg} \cdot \text{L}^{-1}$ TAI at 333 K are depicted in Fig.5. In order to minimize error brought by uncertain factors, 10 force curves were measured in every selective region and the average adhesive forces were calculated.

The force-distance curves recorded in uninhibited solution in the two phases both exhibit adhesive force characteristics, which is mainly due to the capillary force produced by water condensation between the tip and the sample to form liquid^[32], and the average adhesive force is calculated to be 3.78 nN in liquid phase and 2.66 nN in gas phase, respectively. However, the average adhesive force increases to 6.16 nN in gas phase and 5.10 nN in liquid phase after the samples exposure to the inhibited solution as a result of adhesive function between the sample and the tip of the probe when the surfaces are covered by organic films^[33].

It can also be seen from Fig.5(b) that, in liquid phase, repulsive forces in blank solution is detected at bigger Z displacement than in solution containing 50 $\text{mg} \cdot \text{L}^{-1}$ TAI and the repulsive force in the former solution is greater at the same Z displacement, which is contrary to the results in gas phase as shown in Fig.5(a). In an aqueous solution, Si_3N_4 tip became negatively charged^[34], and the Q235 steel surface in the test so-

Fig.3 FT-IR spectra of inhibitor adsorption films on the sample surfaces

(a) in gas phase; (b) in liquid phase

Fig.4 Three-dimensional AFM images of Q235 steel

(a) initial surface; (b) and (d) the samples exposure to the uninhibited solution for 2 h at 333 K in gas phase and in liquid phase, respectively; (c) and (e) the samples exposure to the solution containing $50 \text{ mg} \cdot \text{L}^{-1}$ TAI at 333 K for 2 h in gas phase and in liquid phase, separately

lution was also negatively charged as discussed above, so when the tip moved close to sample surface, a long-range electrostatic repulsive force would appear at a certain displacement. In acid solution containing TAI inhibitor, the positive charged TAI ammonium ion adsorbed onto the sample surface so that the negative charges on the sample and the tip surfaces were partly shielded. So the long-range electrostatic repulsive force between the tip and the sample surface decreased and the repulsive force was detected at smaller Z displacement. However, as been discussed above from FT-IR result, the inhibitor adsorbed on the sample surface forming film in gas phase was AMI, the atoms N, O, and S in AMI carried excess negative charge and adsorbed chemically on the sample surface. So the long-range electrostatic repulsive force between the tip and sample surface increased and the repulsive force detected at bigger Z displacement

2.6 XPS analysis

Fig.6 shows the XPS spectra measured on the sample surfaces after 10 h of AMI and TAI film-forming periods in gas and liquid two phases. It can be seen from Fig.6 that the elements Fe, C, N, and O are detected. The peaks of C and N, produced by inhibitors TAI and AMI, are present because these elements

Fig.5 Typical force–distance curves recorded between the probe and the sample

(a) in gas phase; (b) in liquid phase

are the basis of the compound structure, which may also be the reason why the S element has not been detected. The binding energies are corrected for charge effects by referencing the C 1s to the peak at 284.6 eV. The XPS envelope spectrum of Fe 2p (Fig.6(d)) depicts a double peak profile in the two phases, which could be attributed to the oxidation state of Fe, which means that a certain degree of oxidation of Fe happened^[35]. The O 1s peaks at 531.5 and 531.9 eV in the two phases are attributed to the oxide on the electrode surface. The N 1s curves in gas and liquid two phases contain complex forms, which are assigned to the corresponding species through a deconvolution fitting procedure, in this way peak identification of characteristic elements is in agreement with suitable databases^[36–38]. The XPS spectra for N 1s display five peaks in liquid phase (Fig.6 (e)). The binding energy of the peak at 399.9 eV can be assigned to the $-\text{CSNH}-$ group, while the characteristic peaks at 399.2 and 400.5 eV may be ascribed to the presence of $\text{C}=\text{N}$ and $\text{C}-\text{N}$ bonds, respectively. The peak detected at 401.6 eV is attributed to positively charged nitrogen $-\text{N}^+$ and the peak at 402.6 eV to the N atom in the TAI interacting with the Fe surface, which agrees well with the information reported in the pertinent literature^[37,39]. Three kinds of N 1s peaks are present in the XPS spectra in gas phase. The N 1s peak at 399.1 eV corresponds to the $\text{C}-\text{N}$ bond, the binding energy of the peak at 399.9 eV can be assigned to the $-\text{CSNH}-$ and $-\text{CONH}-$

Fig.6 XPS spectra of Q235 steel after exposure to TAI solution for 10 h in gas and liquid two phases

(a) survey; (b) C 1s; (c) O 1s; (d) Fe 2p; (e) N 1s in liquid phase; (f) N 1s in gas phase

group and the peak at 401.2 eV to the N atom in the AMI interacting with the Fe surface^[40–41]. The shift of binding energy can be explained by the interaction of Fe and N atoms. The N 1s peaks of the XPS spectra in the two phases further indicate that the adsorption films of AMI and ATI are present on the sample surfaces in gas phase and in liquid phase, separately.

3 Conclusions

In summary, the imidazoline derivative inhibitor TAI could protect Q235 steel from CO₂ corrosion effectively in gas and liquid two phases. TAI formed adsorption film on steel surface

in liquid phase while AMI in gas phase, which generated from TAI acid hydrolysis. The chemical adsorption of the inhibitors occurred by the formation of coordination bonds between the heteroatom atoms of the inhibitors and Fe on the metallic surface, as it was demonstrated by the FT-IR and XPS surface analysis. AFM results showed that AMI and TAI inhibitors could considerably reduce the damage on the metallic surface and decrease the surface roughness. After the sample exposure to the TAI solution in the two phases, a bigger adhesive force was detected owing to hydrophobic interaction from the inhibitors of TAI and AMI and the long range-repulsive force be-

tween the AFM probe and the steel surface increased in gas phase but decreased in liquid phase by screening effect of surface charges. The above results further confirmed the hydrolysis mechanism of imidazoline derivatives in acid solution.

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