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1. Introduction

Indolizine quaternary ammonium salt inhibitors, part III:† insights into the highly effective lowtoxicity acid corrosion inhibitor – synthesis and protection performance

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Three indolizine derivatives (Di-BQC, QM-DiBQC, and PyM-DiBQC), which were prepared facilely in high yield via a 1,3-dipolar cycloaddition reaction, were found to exhibit good corrosion inhibition for steel in concentrated acid without the synergism of propargyl alcohol (PA). The inhibitive derivatives exhibit high protection efficiency and have eco-friendly advantages over the highly toxic PA. The accurate formulas and structures of the three compounds are characterized by high resolution mass spectrometry (HRMS) and nuclear magnetic resonance (NMR) spectroscopy. The corrosion inhibition performance of the indolizine derivatives toward N80 steel was investigated in 15 wt% HCl and 20 wt% HCl by weight loss measurements, electrochemical tests (Tafel and EIS), SEM/EDX analysis and theoretical calculations. The biological toxicity was investigated by using the Microtox toxicity test. At 90 °C, a dosage of 0.1 wt% indolizine derivatives in 15 wt% HCl would decrease the corrosion rate of N80 steel dramatically to less than 10 g m⁻² h⁻¹. While for PA, a much higher corrosion rate was observed under the same conditions, indicating that the indolizine derivatives are more effective inhibitors in contrast with PA. Results from gravimetric analysis as well as the electrochemical studies and DFT methods are in good agreement, verifying the fine corrosion prevention of the three compounds. The results of biotoxicity tests confirmed the relatively low-toxicity properties of the indolizing derivatives and the suggested inhibition mechanism was also discussed. All the conclusions above indicate that the new indolizine derivatives could be presented as highly effective acidizing inhibitors and the derivatives may offer a new enlightening strategy for corrosion protection under acidizing conditions.

Considering that acid corrosion problems represent a significant cost burden in petroleum engineering, the prevention of mild corrosion in acid media is worth investigating. The choice of an appropriate corrosion control method can help to avoid the problems of concentrated acid corrosion.¹⁻⁴ For this reason, corrosion inhibitors are generally used in acid blends to reduce corrosion on metallic surfaces when concentrated acid is pumped downhole for damage removal, stimulation treatment, and other clean-up operations.^{5,6}

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As a result, new effective corrosion inhibitors in strong acid media (especially during acidizing) are in great demand in the crude oil and gas industry. A variety of organic corrosion inhibitors that contain heteroatoms (N, O, P, and S) or aromatic unsaturated functional moieties have been developed to retard the corrosion of tubulars, casing, and downhole metal components. Among numerous corrosion inhibitors, quaternary ammonium salts have been investigated and used for decades.7-9 Quaternary heterocyclic ammonium compounds such as N-alkyl quinolinium salts,¹⁰ N-alkyl pyridinium salts,¹¹ and polymeric quinolinium compounds¹² have been studied for their protective efficacy.^{13,14} It has been widely accepted that benzyl quinolinium chloride (BQC) shows good inhibitive performance toward N80 steel under acidizing conditions.^{2,15,16} Many other nitrogen or heteroatomcontaining heterocyclics such as Mannich bases, furfuryl alcohol, fatty acid triazoles, and benzimidazole have been used to protect steel from severe corrosion.² Propargyl alcohol (PA), although producing toxic vapours during the acidizing process, is widely used as a highly effective synergistic corrosion inhibitor.

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Since PA is relatively expensive and of high toxicity, this excellent inhibitor usually acts as a key synergistic component in inhibitors and is not recommended to be used in prohibited areas.^{8,17} All these characteristics of PA and the other high-toxicity inhibitors call for the constant exploration of novel highly efficient, environmentally friendly inhibitive compounds that might replace the currently used poisonous components.

The objective of this work is to introduce a new method and mechanism for synthesizing the highly effective corrosion inhibitor that has been reported previously.¹⁵ The other two inhibitive indolizine derivatives were also obtained through a similar reaction at a relatively high yield. All the indolizine derivatives in this paper were prepared from BQC (the commonly used quaternary heterocyclic ammonium salt inhibitor for acidizing) and chemical structures of the derivatives were characterized. Compared with PA, the effectiveness and low-toxic property of the indolizine derivatives as fine corrosion inhibitors for N80 steel in HCl are discussed and confirmed by the experimental results.

2. Experimental section

2.1 Materials

The fundamental raw materials used in the synthesis of the indolizine derivatives in this study are listed as follows: quinoline, pyridine, benzyl chloride, chloroacetic acid and Na_2CO_3 . These chemical reagents, solvent and PA were obtained from Adamas-beta[®] and used without further purification. API N80 steel was used as the test material: the elemental composition of the N80 steel is given in Table 1.

N80 steel coupons measuring 50 mm \times 10 mm \times 3 mm were used for weight loss analysis. While under electrochemical test conditions, similar coupons with 1 cm² exposed surface patches were used as working electrodes. The exposed area of the coupons was abraded with increasing grades of silicon carbide abrasive papers and then cleaned with anhydrous ethanol. Before testing, all coupons were kept and dried at room temperature for at least 24 h.

Hydrochloric acid, at concentrations of 4.407 M (approx. 15 wt%) and 6.016 M (approx. 20 wt%), was prepared from stock concentrated HCl (12.08 M) obtained from Sigma Aldrich[®] by diluting with double-distilled water.

2.2 Synthesis and characterization

Fig. 1 shows the chemical structure of the conventional indolizine. The preparation of the three indolizine derivatives through 1,3-dipolar cycloaddition reaction is illustrated in Fig. 2. BQC was prepared easily according to the literature¹⁵ and the synthesis of DiBQC, QM-DiBQC, and PyM-DiBQC was performed by reference to published methods.^{18,19}

Table 1	Chemi	cal con	npositio	on of the	e N80	steel o	coupor	ı	
Element	С	Р	Si	S	Mn	Cr	V	Al	Fe
In wt%	0.34	0.02	0.25	0.015	1.6	0.15	0.11	0.02	Balance



The highlighted nitrogen containing heterocyclic parts in Fig. 1 and 2 should be assigned to the indolizine structure.^{19,20} Considering that the chemical structures of the three compounds contain an indolizine derived functional group, they can be classified as indolizine derivatives, or more specifically, defined as 'indolizine quaternary ammonium salts'.¹

The chemical structure, molecular weight, and abbreviated nomenclature of the compounds of interest in this study are listed in Table 2. HRMS (electrospray ionization, positive ion mode) and NMR (Agilent NMR-400 MHz) were used to determine the mass of the molecular ion of the synthesized compounds.

Quaternary quinoline salt BQC was obtained easily by the method shown in Fig. 2. Quinoline and 1.0 equiv. benzyl chloride were mixed with distilled water in a flask. The reaction mixture was stirred and heated to 90 °C for 6 hours. After cooling, the solid product was washed in acetone and recrystallized three times from ethanol. The purified benzyl quinolinium chloride (BQC) was obtained as a white crystalline solid. Yield: 89%. ¹H NMR (400 MHz, D₂O): δ 9.18 (d, *J* = 7.5 Hz, 1H), 8.97 (d, *J* = 8.8 Hz, 1H), 8.15 (dd, *J* = 5.6, 4.5 Hz, 2H), 7.92 (m, 2H), 7.72 (t, *J* = 9.6 Hz, 1H), 7.24 (m, 3H), 7.16 (m, 2H), 6.06 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 148.88, 148.32, 137.98, 135.88 132.68, 130.69, 130.18, 129.94, 129.28, 129.17, 127.27, 121.58, 118.51, 60.75. HRMS: calcd for [C₁₆H₁₄N]⁺: 220.2891; found: 220.2890.

As illustrated in Fig. 2, for the synthesis of Di-BQC: firstly, BQC and 1.0 equiv. Na₂CO₃ were dissolved in ethanol as the solvent and heated at 60 °C for 10 hours, then the pigment-like mixture containing Di-BQC was obtained. The mixture was recrystallised in acetone/chloroform (1:3, v/v) twice and Di-BQC was purified as a yellow solid. Yield: 33%. ¹H NMR (400 MHz, CDCl₃): δ 12.26 (s, 1H), 9.38 (d, *J* = 13.7 Hz, 1H), 8.00 (m, 2H), 7.90 (d, *J* = 8.6 Hz, 1H), 7.77 (m, 2H), 7.65 (m, 2H), 7.60–7.20 (m, 12H), 6.35 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 149.93, 135.53, 134.31, 133.82, 133.59, 133.38, 131.46, 130.98, 130.79, 130.06, 129.31, 129.24, 129.10, 129.05, 128.43, 127.91, 127.48, 126.97, 126.78, 125.12, 124.81, 122.67, 119.82, 119.38, 118.24, 118.03, 109.76, 59.58. HRMS: calcd for [C₃₂H₂₃N₂]⁺: 435.1854; found: 435.1854.

For the synthesis of QM-DiBQC: BQC and 1.0 equiv. acetoxyl quinolinium chloride (AcQC, obtained by quaternization of quinoline and chloroacetic acid in advance) were combined and heated to 80 °C in acetonitrile as the solvent for 5 hours. The indolizine derivative QM-DiBQC was formed through an intermolecular 1,3-dipolar cycloaddition reaction. The product was recrystallised in ethanol/acetone (1:1, v/v) twice and finally QM-DiBQC was purified as a bright yellow powder. Yield: 49%. ¹H NMR (400 MHz, DMSO-d₆): δ 10.57 (s, 1H), 9.85 (s, 1H), 8.84



Fig. 2 Synthesis of the indolizine derivatives Di-BQC, QM-DiBQC, and PyM-DiBQC from quaternary quinolinium BQC salts

Table 2 Name, structure, and molecular weight of the corrosion inhibitors

Name (Abbr.)	Structure	Molecular weight
Propargyl alcohol (PA)	но∕──≡сн	56.05
Benzyl quinoline chloride (BQC)	NCI NCI	255.5
Dimer indolizine derivative of benzyl quinoline chloride (Di-BQC)		470.6
Quinolyl-3-methene-dimer indolizine derivative of BQC (QM-DiBQC)	N CI N N CI	394.7
Pyridyl-3-methene-dimer indolizine derivative of BQC (PyM-DiBQC)		344.7

(d, J = 8.6 Hz, 1H), 8.71–8.56 (m, 2H), 8.32 (t, J = 10.6, 8.4 Hz, 2H), 8.20 (d, J = 8.6 Hz, 1H), 8.08 (t, J = 7.7 Hz, 1H), 7.94–7.83 (m, 2H), 7.80 (td, J = 7.8, 7.2, 1.6 Hz, 1H), 7.45 (d, J = 7.1 Hz, 2H), 7.36 (dt, J = 21.7, 7.1 Hz, 3H), 6.14 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 148.71, 135.33, 133.77, 133.17, 132.33, 131.62, 130.34, 130.27, 129.50, 129.31, 128.88, 128.71, 128.23, 127.30, 126.04, 126.00, 122.91, 122.03, 120.33, 117.71, 116.51, 110.17, 109.79, 59.42. HRMS: calcd for $[C_{26}H_{19}N_2]^+$: 359.1543; found: 359.1545.

PyM-DiBQC was synthesised from BQC and acetoxyl pyridinium chloride (AcPyC) and the preparation process is similar to that of the preparation of QM-DiBQC. Yield: 41%. ¹H NMR (400 MHz, DMSO-d₆): δ 10.22 (s, 1H), 9.67 (s, 1H), 8.58 (d, *J* = 8.7 Hz, 1H), 8.70–8.44 (m, 2H), 8.21 (d, *J* = 8.9 Hz, 1H), 8.15 (t, *J* = 7.6 Hz, 1H), 7.85–7.97 (m, 2H), 7.26 (dt, *J* = 20.5, 7.3 Hz, 3H),

6.11 (s, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 148.87, 135.39, 132.98, 132.11, 131.60, 130.58, 130.30, 129.27, 128.77, 128.24, 128.15, 125.88, 125.73, 122.84, 120.16, 117.35, 116.04, 109.94, 109.86, 59.66. HRMS: calcd for $[C_{22}H_{17}N_2]^+$: 309.3831; found: 309.3830.

2.3 Weight loss test

Weight loss measurements at 90 °C and 120 °C were all conducted in a high-temperature, high-pressure apparatus at 1000-psi. The coupon was immersed in 15 wt% or 20 wt% HCl solutions in the absence or presence of a series of concentrations of the five inhibitors listed in Table 2 for 4 h at 90 °C or 120 °C, respectively. In comparison with the inhibition of the synthesized indolizine derivatives, the synergistic protection performance of the PA mixtures with BQC was also investigated in 15 wt% HCl solution at 90 °C with a dosage ranging from 0.01 wt% to 0.20 wt%. The ratio of volume (mL) of corrosive solutions to surface area (cm²) of each coupon (V/A) was 20:1. Before each test, the masses of the coupons were determined to ± 0.1 mg. Two identical coupons were used in each test, and the average corrosion rate thereof was calculated. After the test, the coupons were removed, cooled to room temperature, washed using ethanol, dried, and weighed.

The corrosion rate of each coupon was calculated as follows:

$$R = \frac{m_1 - m_2}{S \times t} \tag{1}$$

where R (g m⁻² h⁻¹) is the corrosion rate and m_1 (g) and m_2 (g) are the masses of each coupon before and after 4 h immersion. S (m²) is the exposed surface area, and t (h) is the immersion time. The corrosion inhibition efficiency (IE) of N80 steel can be calculated by the following equation:²¹

IE (%) =
$$\frac{R_0 - R_{\rm corr}}{R_0} \times 100$$
 (2)

where R_0 (g m⁻² h⁻¹) and R_{corr} (g m⁻² h⁻¹) are the corrosion rates without and with inhibitor, respectively. The mean corrosion rate (R_{corr}) and the mean inhibition efficiency (IE) are obtained from weight loss measurements of N80 steel in HCl with and without various concentrations of the five inhibitors. The coupons were examined visually for localized corrosion, observed as pits or edge attack, and the pitting corrosion can be qualitatively described by assigning a visual pitting index (PI).^{16,22} The maximum allowable pitting index during the test period is PI ≤ 2 (preferably zero), as recommended by internal procedures. The visual pitting indices ranging from PI = 0 (no pitting) to PI = 9 (severe and extensive pitting) are given in Table 3.

2.4 Electrochemical analysis

A Gamry Reference 600 electrochemical workstation was used to perform the electrochemical test. Both the potentiodynamic polarization (Tafel curves) and electrochemical impedance spectroscopy (EIS) tests were carried out in 15 wt% HCl at 25 °C under non-stirred conditions.^{23,24}

To conduct the electrochemical test, N80 steel with a 1×1 cm exposed surface area was used as the working electrode (WE); a saturated calomel electrode (SCE, coupled to a fine Luggin capillary) and a platinum electrode were used as the reference electrode and counter electrode (CE), respectively. The Luggin capillary was kept close to the working electrode to decrease the

Index	Description of pitting
0	None
1	Minor cut edge corrosion
2	No pits on major surfaces. Small shallow pits on cut edges
3	Pin point pits on surface <25
4	Pin point pits on surface > 25
5	<10 pits 16–31 mils diameter, 8–16 mils deep
6	11–25 pits with P.I. of 5
7	>25 pits with P.I. of 5
8	Large pits 63–126 mils diameter, >31 mils deep

iR drop. The corrosive medium was kept under quiescent conditions throughout the experiment. In each test solution, the three-electrode cell was fixed in the corrosive medium for 3600 s in order to ensure a stable open circuit potential. Both the potentiodynamic polarization and the EIS measurements were performed at the open circuit potential.

The data obtained from the electrochemical test were analysed using the Gamry Instrument Framework version 1.5 software and all the electrochemical data are presented without iR correction. The electrochemical experiments were done in the presence and absence of the five inhibitors at the same concentrations as those in the weight loss tests.

The Tafel polarization was carried out from a cathodic potential of -250 mV to an anodic potential of +250 mV by changing the electrode potential *versus* OCP at a sweep rate of $0.2 \text{ mV s}^{-1.25}$ The corrosion current density (I_{corr}) and E_{corr} were measured by the Tafel linear extrapolation procedure. The linear Tafel segments of anodic and cathodic areas were extrapolated to E_{corr} to obtain the value of I_{corr} . The IE calculated from the Tafel curves was measured using the following relationship:

$$IE (\%) = \frac{I_{corr} - I_{corr'}}{I_{corr}} \times 100$$
(3)

where I_{corr} and I_{corr}' are the mean values of the uninhibited and inhibited corrosion current densities, respectively.

The EIS measurements were made at the corrosion potential $(E_{\rm corr})$ over a frequency range from 100 000 Hz to 0.01 Hz, using an amplitude signal of 5 mV peak-to-peak and a scan rate of 10 points per decade of frequency.²⁶ The EIS results were collected and analyzed by ZSimpWin software. The inhibition efficiencies (IEs) can be calculated from the Nyquist plots by means of the following equation:

IE (%) =
$$\frac{R_{\rm p}' - R_{\rm p}}{R_{\rm p}'} \times 100$$
 (4)

where R_p and R_p' are the polarization resistance of the steel in the absence and presence of the inhibitors, respectively. The value of R_p or R_p' was obtained through the equivalent circuit model, which was employed to simulate the experimental EIS results by ZSimpWin software.

2.5 Surface characterization

For surface morphological investigations of the N80 samples in the acid solutions with and without the synthesized inhibitors, scanning electron microscopy and energy dispersive X-ray spectroscopy analyses (SEM/EDX) were performed by using a HITACHI S-4800 scanning electron microscope at an accelerating voltage of 30 kV. The change in steel surface composition before and after the immersion was investigated by using an energy dispersive X-ray analyzer (EDAX XM2-60S, HITACHI) equipped with a scanning electron microscope. The coupons were pre-treated and immersed in the corrosive medium as per the same procedure in the weight loss tests. Before the SEM/EDX test, the coupons were taken out of the corrosive solutions, cleaned with distilled water and ethanol, and dried with cool air. The micrographs of the corroded N80 samples and the EDX spectra of the coupons in the presence and absence of the inhibitor were obtained.

2.6 Computational details

2.6.1 Quantum chemical calculations. In this work, density functional theory (DFT)-based quantum chemical calculations were performed by the DMol³ module in BOVIA Materials Studio software (version 8.0, Accelrys, Inc.). Geometrical optimizations and frequency calculations were conducted with the employed generalized gradient approximation functional (GGA) with a double numerical basis set with polarization (DNP). The following quantum chemical indices were taken into consideration: energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LOMO}), energy gap: $\Delta E = E_{\text{LOMO}} - E_{\text{HOMO}}$ and dipole moment (μ). The HOMO and LUMO, which reveal the active sites of the studied inhibitive molecules, were illustrated and discussed.

2.6.2 Molecular dynamics (MD) simulations. The strength of the interaction between corrosion inhibitors and the Fe(110) surface was studied by using the Forcite module implemented in the MS software from BIOVIA Company, USA. The Monte Carlo simulation methodology used the adsorption locator module in the MS 8.0 version to model the adsorption process of the inhibitor molecules onto the Fe(110) surface. The molecular dynamics processes were performed in a three-dimensional simulation box (22.34 Å \times 22.34 Å \times 38.11 Å) with periodic boundary conditions. Fe(110) was next enlarged to a (9 \times 9) supercell to provide enough surface for the interaction of the inhibitors and a vacuum of 30 Å thickness was built on the Fe(110) model surface to model a representative part of the interface devoid of any arbitrary boundary effects. The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field was used to optimize the structures for the systems within the whole simulation procedures.

During the simulations, the Fe atoms were kept 'frozen' in advance so that the inhibitor molecule would be allowed to reach the metal surface freely. The molecular dynamics stimulations were conducted in the *NVT* canonical ensemble at 298 K with a time step of 0.1 fs and a total simulation time of 1000 ps using the Anderson thermostat. The trajectory was recorded every 2000 fs. Adsorption energy ($E_{adsorption}$) between the inhibitor molecule and Fe(110) surface was calculated as follows:

$$E_{\text{adsorption}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhinitor}}) \tag{5}$$

where E_{total} is the total energy of the simulation system, and E_{surface} and $E_{\text{inhinitor}}$ are the energies of Fe crystal and the free state inhibitor molecule, respectively. The binding energy (E_{binding}) equals the negative value of the adsorption energy:

$$E_{\text{binding}} = -E_{\text{adsorption}} \tag{6}$$

2.7 Microtox toxicity test

The toxicity test was performed using the Microtox method by exposing a suspension of active marine luminescent bacterium

Photobacterium phosphoreum to different concentrations of the five inhibitors at 25 °C.²⁷ The light output of the bacterial suspension before and after its exposure to the sample (lasting for 15 minutes) is measured by a photomultiplier tube.^{28,29} The light emitted by the luminescent bacteria is a product of their metabolic processes. The light output is proportional to the toxicity of the sample because the exposure to toxic chemicals interferes with their metabolic processes and results in a reduction of the light output. At the endpoint of the test, an effective concentration for a 50% reduction in light output, that is, the EC₅₀, is calculated.

Results and discussion

3.1 Formation mechanism of the indolizine derivatives

The concept of 'indolizine quaternary ammonium salts' was proposed because the conventional indolizine *N*-containing heterocycle (see Fig. 1) and the quaternary N^+ ion exist within the fused molecules.¹ Therefore, similar compounds could also be classified as indolizine derivatives. As shown in Fig. 2, the homogenous indolizine derivative Di-BQC was prepared from BQC through 1,3-dipolar cycloaddition.^{18,30} Actually, Di-BQC could be considered as a dimer of BQC and, as a result, Di-BQC was obtained by combining two molecules of BQC.

The other two derivatives QM-DiBQC and PyM-DiBQC were synthesized from BQC and AcQC as well as AcPyC, respectively (Fig. 2). The quaternary salts were combined and heated in solvent, and the dimer derivatives QM-DiBQC and PyM-DiBQC were formed through an intermolecular 1,3-dipolar cyclo-addition reaction. The cycloaddition reaction was followed by the initial decarboxylation step, which produces the active *N*-ylide intermediate.^{1,31-34} Since the 3-position of QM-DiBQC and PyM-DiBQC is a hydrogen atom, these two compounds could be named as '3-unsubstituted' indolizine derivatives.^{32,34} The accurate structures of these indolizine derivatives were characterized through HRMS and NMR analyses and the detailed results are shown in Section 2.2.

In the related previous research,¹⁵ the formation mechanism of a similar compound was ambiguous (Michael reaction) and the structure of the compound was not classified accurately. The highly effective inhibitive compound was merely separated from the by-product mixture of the quaternization process for BQC several years ago. Owing to a new understanding of the 1,3-dipolar cycloaddition route, the same derivative could now be targeted and synthesized and the yield of the derivatives was increased dramatically in this work. Furthermore, a facile synthesis process of the similar 3-unsubstituted inhibitive indolizine derivatives was also provided according to the new mechanism.

3.2 Gravimetric measurements

The relationship between the dosage and the corrosion rate of N80 coupons in hydrochloric acid in the absence and presence of the five inhibitors at 90 $^{\circ}$ C and 120 $^{\circ}$ C is shown in Fig. 3(a) and (b), respectively. The pitting index of each point in the weight loss test is also provided in Table 3.

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Fig. 3 (a) The corrosion rate and the pitting index (numbers) for N80 steel in HCl at 90 °C in the absence and presence of the five inhibitors for 4 h obtained by the weight loss test. (b) The corrosion rate and the pitting index (numbers) for N80 steel in HCl at 120 °C in the absence and presence of the five inhibitors for 4 h obtained by the weight loss test.

According to the literature,^{35,36} the ratio between the acid volume and the coupon surface area (V/A) can affect the coupon weight loss results, and usually a V/A ratio of 21 mL in⁻² (3.4 mL cm^{-2}) would stimulate acidizing through a 5.5-in diameter pipe. In this paper, the V/A ratio of 20 mL cm⁻² is sufficient and reasonable to stimulate acidizing through a 23-in diameter pipe.³⁷ From Fig. 3, it can be observed that the corrosion rate decreased with increasing dosage of the five inhibitors. For all the concentrations, both PA and the three novel indolizine derivatives can protect the raw metal more effectively than BQC and this result is in accordance with the previous report.¹⁵ It is even more exciting to notice in Fig. 3 that, in general, the inhibition of the three heterocyclic derivatives is much better than that of propargyl alcohol.

Another important result from the gravimetric tests should not be overlooked: although the quinolinium salt BQC has been utilized as the key component of many commercially available inhibitor products for decades, the primary salts could not retard the corrosion speed effectively in contrast with the three dimer derivatives. The result of gravimetric experiments reported here is more exciting than those of the corrosion inhibitors in the literature.^{38–41} The inhibition of the three indolizine derivative in Fig. 3 is in good agreement with previous work,^{1,15} revealing that compared with the original quinolinium salts, the indolizine derivatives could exhibit a much stronger anti-corrosion ability in strong acid media. Also, from Fig. 3, it can be seen clearly that there is a systematic decrease in the visual pitting index with increasing concentration for each of the inhibitors.

As reported in the literature,^{2,17} PA is best used in practice in synergy with many quaternary ammonium salts (including BQC). The synergistic inhibition performance of PA mixtures with BQC in different molar ratios from PA:BQC = 1:20 to $5:1 \pmod{100}$ is shown in Fig. 4. The experiment was conducted at four different total corrosion inhibitor (CI) dosages from 0.01 wt% to 0.2 wt%.

It is obvious from Fig. 4 that when PA or BQC was added solely into the corrosive solution, PA would invariably decrease the corrosion rate much more significantly than BQC, showing that the protection of PA far outweigh that of BQC. When the



Fig. 4 The corrosion rate and the pitting index (numbers) for N80 steel in 15 wt% HCl at 90 °C in the presence of mixtures of PA with BQC.

total CI is lower than 0.1 wt%, the inhibition of any mixture is inferior to that of pure PA. However, when the total CI dosage reaches 0.1 wt% or 0.2 wt%, the presence of the mixed inhibitor $(PA: BQC \pmod{mol^{-1}} = 1:1, 2:1 \text{ and } 5:1)$ could slow down the corrosion rate more effectively than PA. From the above descriptions, no one can deny the fact that PA could show a fine synergistic effect with BQC.

Conclusions can be made by comparing Fig. 3(a) and 4 that when the inhibitor dosage is below 0.1 wt% (the black and red lines in Fig. 4), the inhibition of any PA/BQC mixture is worse than those of the indolizine derivatives (see Fig. 3(a)). It is only when the total CI dosage is beyond 0.1 wt% (the blue and violet lines in Fig. 4) that the protection performance of the mixture $(PA: BQC \pmod{mol^{-1}} = 5:1)$ might possibly be the same as that of the indolizine derivatives, as shown in Fig. 3(a). It could be summarized from the above description that all the derivatives of BQC (DiBQC, QM-DiBQC, and PyM-DiBQC) could exhibit a superior inhibition to that of propargyl alcohol.

From Fig. 4, it could be noted that there is an overall decrease in the corrosion rate and pitting index with increasing dosage of each inhibitor. For these groups, the assigned pitting indices lie in the range from 1 to 7. Severe pitting is observed when BQC is present as the only additive, while the use of PA would produce a much smoother surface with a relatively low corrosion rate and pitting indices.

3.3 Tafel plots

The fundamental expression for describing the over potential/ current relationship of the corrosion system, which consisted of a cathodic reaction and an anodic reaction, is the following Butler-Volmer equation:^{42,43}

$$i = i_0 \left\{ \exp\left[\frac{2.303(E - E_{eq})}{b_a}\right] - \exp\left[\frac{2.303(E - E_{eq})}{b_c}\right] \right\}$$
(7)

where E is the electrode potential; E_{eq} is the equilibrium potential; i_0 is the exchange current density; b_c and b_a are the cathodic and anodic Tafel slopes, respectively. When E is far away from E_{eq} , eqn (7) gives Tafel's law:

$$E = a \pm b \log|i| \tag{8}$$

where a is a constant, and b equals b_c or b_a . Eqn (8) indicates that the logarithm of the external current density varies linearly with the potential at high overpotential. The corrosion current density can be determined by extrapolating the straight line of $E \sim \log |i|$ back to the equilibrium potential. The cathodic Tafel slope of the linear behaviour is:

$$b_{\rm c} = \frac{2.303RT}{\alpha_{\rm c} nF}$$

and the anodic Tafel slope of the linear behaviour is:

$$b_{\rm a} = \frac{2.303RT}{\alpha_{\rm a} nF}$$

where α_c and α_a are, respectively, the cathodic and anodic charge transfer coefficients; n is the number of electrons involved in the electrode reaction; F is the Faraday constant and R is the universal gas constant. The Tafel parameters including corrosion current density (I_{corr}) , corrosion potential (E_{corr}) , cathodic Tafel slope (b_c) , anodic Tafel slope (b_a) and the inhibition efficiency (IE) calculated from the Tafel plots according to formula (4) are given in Table 4.

The results in Table 4 show that the corrosion current density decreases dramatically while the inhibition efficiency increases in the presence of the inhibitors, particularly for the three indolizine derivatives. Obviously, as the indolizine derivatives were added, the corrosion current density (I_{corr}) in Table 4 declined much faster and could reach a much lower value compared with the other two inhibitors BOC and PA, indicating that the protection performance of the three indolizine derivatives Di-BQC, QM-DiBQC, and PyM-DiBQC is far better than that of the others, especially at lower dosages from 0.01 wt% to 0.1 wt%. Compared with their precursor quaternary ammonium salts, the active adsorption sites are doubled and reinforced in the planar indolizine derived dimers, and it is not difficult to explain their good protection effect.

After a detailed inspection of Table 4, for the indolizine derivatives, it seems that the inhibition efficiencies hardly grow further once the dosages are over 0.10 wt% (this may be due to the relatively restricted solubility at room temperature). As a result, 0.1 wt% is chosen to be a reasonable dosage for the comparison of the inhibitors and Tafel plots (polarization curves) of N80 steel in 15 wt% HCl with or without 0.1 wt% inhibitors are given in Fig. 5.

As shown in Fig. 5, a decrease in both cathodic and anodic currents $(\log I)$ was observed when the inhibitor was added to the solution, suggesting that the inhibitor could either reduce the dissolution speed in the anodic areas or retard the cathodic hydrogen evolution process at the same time.⁴¹ Also, as shown in both Table 4 and Fig. 5, compared with those of the control group, the polarization curves and corrosion potential (E_{corr}) show minor shifts towards the more anodic regions for all the inhibitors. The changes in E_{corr} value were 28 mV for BQC,

Table 4 Potentiodynamic parameters and inhibition efficiency (IE) of N80 steel in 15 wt% HCl in the absence and presence of inhibitor

Inhibitor	Dosage (in wt%)	$b_{\rm a}~({\rm mV~dec^{-1}})$	$-b_{\rm c}~({\rm mV~dec^{-1}})$	$I_{\rm corr}$ (µA cm ⁻²)	$-E_{\rm corr}$ (mV vs. SCE)	IE (%)
No inhibitor	0	87.6	110.8	897.7	428	_
BQC	0.01	96.5	106.9	376.6	417	58.0
	0.05	107.8	121.7	209.3	408	76.7
	0.10	108.2	123.3	111.0	400	87.6
	0.20	113.7	129.8	65.4	396	92.7
PA	0.01	100.3	110.5	168.1	429	81.3
	0.05	111.4	120.6	106.9	410	88.1
	0.10	113.5	140.7	90.8	403	89.9
	0.20	112.9	138.8	42.4	388	95.3
Di-BQC	0.01	99.8	107.2	46.5	394	94.8
	0.05	114.3	129.5	34.9	432	96.1
	0.10	120.1	138.1	28.7	414	96.8
	0.20	123.4	140.8	26.9	409	97.0
QM-DiBQC	0.01	98.8	113.2	49.6	425	94.5
	0.05	109.1	118.7	37.0	412	95.9
	0.10	118.9	130.0	34.1	398	96.2
	0.20	116.8	131.4	32.8	389	96.3
PyM-DiBQC	0.01	101.0	109.9	51.0	420	94.3
	0.05	109.4	118.1	44.4	409	95.0
	0.10	105.6	129.3	41.2	402	95.4
	0.20	111.7	134.8	40.9	385	95.4



Fig. 5 The Tafel curves for N80 steel in 15 wt% HCl without and with inhibitors.



Fig. 6 Nyquist plots for N80 steel in 15 wt% HCl without and with the same concentration (at 0.1 wt%) of the five inhibitors at 25 °C. (The plot for blank has been shown in inset.)

25 mV for PA, 14 mV for Di-BQC, 30 mV for QM-DiBQC, and 26 mV for PyM-DiBQC towards the anodic region. According to the literature, the displacement of $E_{\rm corr}$ in Table 3 between blank and any inhibitor groups lies within ±85 mV per SCE, indicating that the five inhibitors studied here could be characterised as mixed-type inhibitors.^{17,44}

3.4 Electrochemical impedance spectroscopy (EIS)

As 0.1 wt% was chosen as the moderate dosage for the five inhibitors in the Tafel plots (Fig. 5), the corresponding EIS Nyquist plots, and Bode and phase angle curves are also displayed at the same dosage (0.1 wt%) in Fig. 6 and 7. It is well known that in Nyquist plots, the diameter of the capacitive loop represents the charge transfer resistance of the electrode, and a higher diameter of the impedance semicircle indicates better protection.^{17,38} Therefore, it is a convenient and direct way to use the capacitive loop diameter to identify a better corrosion inhibitor. Naturally, the Nyquist plots of the steel are

semi-circular in uninhibited corrosive medium, while in the presence of the inhibitors, the shape of the semicircle is depressed. This phenomenon can generally be attributed to different factors like the frequency dispersion and surface roughness of the electrode.⁴² Fig. 6 shows that the imperfect diameters of the depressed capacitive loops in the inhibited solutions are increased sharply compared with those in the uninhibited group for all five inhibitors (especially the three indolizine derivatives). This implies that all the inhibitors could exhibit anti-corrosion ability in the corrosive solution. More importantly, it can be summarized from Fig. 6 that after being transformed into the indolizine derivative, the inhibition performance of BQC in hydrochloric acid shows a marked increase; the novel indolizine derivatives show a highly efficient protection performance.²¹⁻²³ It is apparent from Fig. 3 and 6 that the results obtained from weight loss measurements and EIS tests are in good agreement; the dimer indolizine derivatives



Fig. 7 The Bode plots (a) and phase plots (b) for N80 steel in 15 wt% HCl without and with the same concentration (at 0.1 wt%) of the five inhibitors at 25 °C.

are more likely to be used as the key inhibitive component than their precursor BQC and propargyl alcohol.

The Nyquist plots for N80 steel in the blank group as well as that in the inhibited solutions have a similar appearance, which means that these inhibitors are retarding the corrosion process without changing the corrosive mechanism.²² Evidently, the inhibited and uninhibited Nyquist plots both exhibit a single semicircular capacitive loop, indicating that the corrosion process is under charge-transfer control.^{5,6}

Fig. 7(a) and (b) shows the Bode impedance and phase angle plots for N80 steel corrosion immersed in 15 wt% HCl solution. It can be noticed that only one narrow phase peak is present in the studied frequency range with and without the five inhibitors, suggesting that there is only one time constant, which can be ascribed to the charge transfer resistance and electric double layer capacitance. Compared with that of BQC and PA, the presence of the three dimer indolizine derivatives leads to an apparent increase in the impedance modulus at low frequency. Meanwhile, the phase angle shifted to a more negative direction, which demonstrated the formation of a more effective protection layer at the steel surface and a decreased corrosion speed upon adding indolizine derivatives into the acid solution.

Fig. 8 shows the equivalent circuit model employed to simulate the results of the EIS test. The equivalent circuit consists of a constant phase element (CPE), a polarization resistance (R_p), and a solution resistance (R_s). The value of R_p is considered to represent a combination of the charge transfer



Fig. 8 Equivalent circuit model used to fit the EIS Nyquist plots.

resistance (R_{ct}) , the accumulation resistance (R_a) , the diffuse layer resistance (R_d) and the film resistance (R_f) , since the presence of inhibitors leads to depressed semi-circles in the Nyquist plots in Fig. 6.²⁴

The fitted spectra obtained by using the equivalent circuit to fit the experimental data for N80 steel in 15 wt% HCl with 0.1 wt% concentrations of the five inhibitors are shown in Fig. 9. The calculated EIS parameters are displayed in Table 5 according to the model circuit and calculated by the ZSimpWin software and they could be employed to study the protective performance of the inhibitors.

In Table 5, generally, as the dosages increases, the polarization resistance (R_p) increases, while the values of electric double layer capacitance ($C_{\rm dl}$, which is related to the charge storage ability of the double layer) keep on decreasing. With the adsorption of the inhibitive molecules, the reduction of accumulated charges and the increase in the thickness of the electrical double layer lead to the reduction of C_{dl} . This could be due to the possible replacement of water molecules by the adsorbed inhibitive compounds on the steel surface.^{38,44} With the increase in inhibitor concentration, the gradual increase of R_p implies a greater blocking effect of the active metal surface, and meanwhile, the transfer of charges from the metal surface to the corrosive medium becomes more and more difficult.^{42,43} Upon inspection of the data in Table 5, it can be stated significantly that the inhibitors functioned by adsorption at the steel/solution surface. The difference of $R_{\rm p}$ between the inhibitors in Table 5 is well consistent with the imperfect diameter of the impedance semicircles shown in Fig. 6. All the discussions above implied that the indolizine derivative could form a strongly adsorbed protective layer on the metal surface.

3.5 Surface investigation

The rough N80 steel surface with big cracks after the weight loss measurement without inhibitor is shown in Fig. 10(a). A large amount of corrosion particles could be observed when the coupon was immersed in the uninhibited acid directly. Fig. 10(c) shows the micrograph of the metal surface in the



presence of Di-BQC at a dosage of 0.1 wt%. It is obvious that the surface of the specimen was smoother when the indolizine derivative was added. This phenomenon reveals that similar inhibitive dimer indolizine derivatives would perform well as a strong acid inhibitor and suggests the formation of a protective film on the steel surface. The results of the related EDX spectra are shown in Fig. 10(b and d). The EDX spectra of steel after corrosion in blank the HCl aqueous solution (Fig. 10b) exhibited the characteristic signals of Fe, C and O elements, which originally existed in the raw material. The EDX spectra recorded in the presence of the novel inhibitive derivatives (using Di-BQC as an example) showed the characteristic peaks for N and Cl, which confirmed the presence and formation of the protective film of indolizine derivative mole

3.6 Quantum chemistry calculations

inhibitor on the steel surface in concentrated HCl.

The frontier molecular orbitals provide information about the inhibitor molecules involved in the donor-acceptor relationship between the inhibitor and the metal atoms. Quantum chemical parameters such as E_{HOMO} , E_{LOMO} , the energy gap $\Delta E (E_{\text{LOMO}} - E_{\text{HOMO}})$ and dipole moment (μ) were obtained in order to predict the inhibitors' protection activity toward the metal surface.

The above quantum chemistry parameters were determined after geometric optimization with respect to all nuclear coordinates and are listed in Table 6. Fig. 11 shows the optimized structures of the inhibitors and Fig. 12 illustrates the diagrams of the frontier molecular orbital density distributions: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which generally represent the regions of a molecule that can donate or accept electrons, respectively.⁴⁵

As can be observed from Fig. 12, for the indolizine derivative molecules, the HOMO and LUMO are mostly delocalized throughout the conjugated plane over the whole molecule, whereas the frontier orbital of BQC is mainly distributed on the substituted benzene ring. For this reason, the relatively poor inhibition performance of BQC in strong hydrochloric acid in our former research work could be explained reasonably and a parallel adsorption orientation of the indolizine derivatives onto the metal surface is expected.¹⁵ The distributions of

Table 5 EIS parameters and inhibition efficiency (IE) of N80 steel in 15 wt% HCl in the absence and presence of inhibitor

Inhibitor	Dosage (in wt%)	$\frac{R_{ m s}}{(\Omega \ m cm^2)}$	${R_{ m p} \over (\Omega \ { m cm}^2)}$	$C_{ m dl} \ (\mu { m F} \ { m cm}^{-2})$	IE (%)
No inhibitor	0	1.21	20.7	157.8	_
BQC	0.01	1.08	141.4	143.1	85.4
	0.05	1.13	168.0	130.5	87.7
	0.10	0.97	198.3	106.4	84.2
	0.20	1.01	249.7	88.7	89.6
PA	0.01	0.99	306.6	130.1	93.2
	0.05	1.13	334.7	108.9	93.8
	0.10	1.05	364.5	95.3	94.3
	0.20	1.04	443.8	83.8	95.3
Di-BQC	0.01	1.16	338.0	117.1	93.9
	0.05	0.98	479.8	105.6	95.7
	0.10	1.10	558.5	90.4	96.3
	0.20	0.99	600.3	73.8	96.5
QM-DiBQC	0.01	1.11	345.8	120.0	94.0
	0.05	1.13	457.9	103.8	95.5
	0.10	0.96	543.0	93.1	96.3
	0.20	1.21	582.3	75.5	96.4
PyM-DiBQC	0.01	1.08	350.7	122.5	94.1
•	0.05	1.13	433.6	104.3	95.2
	0.10	0.97	550.4	92.9	96.4
	0.20	1.01	569.1	77.7	96.2

 Table 6
 Calculated quantum chemical parameters of BQC and its indolizine derivatives

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (D)
BQC	-9.304	-5.896	3.408	5.45
Di-BQC	-7.872	-5.804	2.068	1.28
QM-DiBQC	-8.143	-5.994	2.149	1.32
PyM-DiBQC	-8.462	-6.137	2.325	5.20

the frontier molecular orbital density also indicate that the newly formed five-membered indolizine fused group would play an important role as an active site for the interaction between these aromatic plane derivatives and the metallic surface.

The adsorption of inhibitive molecules onto the steel surface results from 'donor-acceptor' interactions between the compounds and the metal surface. The $E_{\rm HOMO}$ is usually associated with the capacity of a molecule to donate electrons and the $E_{\rm LUMO}$ represents the ability of the molecule to accept electrons. High values of $E_{\rm HOMO}$ indicate the tendency of inhibitor molecules to donate electrons to the acceptor species with empty molecular orbitals. Conversely, the lower value of $E_{\rm LUMO}$ suggests the easier acceptance of electrons from the Fe surface and results in a higher inhibition efficiency.⁴⁶ The energy gap



Fig. 10 SEM micrograph (a) and EDX spectrum (b) of N80 steel after being immersed in 15 wt% HCl solution for 4 hours; SEM micrograph (c) and EDX spectrum (d) of N80 steel after immersion in 15% HCl with 0.1 wt% Di-BQC.

NJC



Fig. 11 Optimized molecular structures of the inhibitors: (a) BQC, (b) Di-BQC, (c) QM-DiBQC, and (d) PyM-DiBQC.



Fig. 12 Frontier molecular orbital density distributions of the inhibitors: BQC, Di-BQC, QM-DiBQC and PyM-DiBQC (left, HOMO; right, LUMO).

 ΔE between the LUMO and HOMO energy levels is another important factor as a function of reactivity of the inhibitor molecule towards adsorption onto the metal surface. A molecule with a small value of ΔE is easily polarized, which facilitates adsorption and enhances the efficiency of the inhibitor. In Table 6, compared with the ΔE value of BQC, the highly effective potential protection of the three indolizine derivatives is apparent. The increasing tendency of ΔE from Di-BQC (2.068 eV) to PyM-DiBQC (2.325 eV) in Table 6 shows that Di-BQC has a higher adsorptive ability on the metal surface compared to the other two derivatives, which correlates well with the experimental findings in gravimetric tests and electrochemical studies.

3.7 Molecular dynamics simulations

In order to better understand the adsorption behaviour of the indolizine derivatives on the steel surface, Metropolis Monte Carlo simulation was carried out to quantify the adsorption of a single inhibitor molecule on the Fe surface. Fig. 13 shows the snapshots of the stable equilibrium configuration of BQC and its related indolizine derivatives on the Fe(110) surface. It is easy to notice in Fig. 13 that the dimer inhibitive molecules adsorbed in a nearly parallel orientation to the model metal surface, which effectively maximized the contact and improved the surface coverage on N80 steel. It is documented in the literature that the higher the binding energy (E_{binding}) , the stronger the interaction of inhibitor molecules with metal surfaces.47 The order of Ebinding is Di-BQC $(227.30 \text{ kcal mol}^{-1}) > \text{QM-DiBQC} (198.44 \text{ kcal mol}^{-1}) >$ PyM-DiBQC (173.62 kcal mol⁻¹) > BQC (110.28 kcal mol⁻¹). Therefore, it could be concluded that the indolizine derivatives are expected to inhibit the metal corrosion more effectively than their precursor BQC. The theoretical results from molecular dynamics simulation speculation are in good agreement with the results from the experimental measurements discussed in Sections 3.2 to 3.4 as well as the conclusions from the quantum chemistry calculations.



Fig. 13 Equilibrium adsorption configurations recorded for the inhibitors on the Fe(110) surface: BQC, Di-BQC, QM-DiBQC and PyM-DiBQC (left, side view; right, top view).

 Table 7
 EC₅₀ values of the inhibitors

Inhibitor	$\mathrm{EC}_{50} \ \mathrm{(mg \ L^{-1})}$
PA BQC	$3.3 imes 10^2 \ 1.2 imes 10^6$
Di-BQC OM-DiBOC	$egin{array}{c} 2.3 imes10^{5}\ 1.4 imes10^{5} \end{array}$
PyM-DiBQC	$9.7 imes10^4$

3.8 Ecological (toxicity) aspects

The results of the Microtox toxicity test are shown in Table 7. Usually, when the value of EC_{50} is higher than 2.0×10^4 mg L⁻¹, the sample could be classified as 'practically nontoxic' or 'low toxicity'.²⁷ According to Table 7, it is apparent that the newly synthesized indolizine derivatives have much better eco-friendly advantages than the widely used high-toxicity propargyl alcohol.

3.9 Possible mechanism of inhibition

Electron-rich heteroatoms (nitrogen, sulphur, oxygen, *etc.*) and the aromatic conjugated functional groups (usually containing delocalized π -electrons) are the key inhibitive structures among most of the organic corrosion inhibitors. The interaction of organic inhibitors with metallic surfaces involves donor–acceptor interactions.² The π electrons and unshared electron pairs in the organic inhibitors would coordinate with the empty d-orbitals of the crude metal atoms to form coordination bonds (usually known as chemical adsorption), and eventually, the inhibitive molecular groups would become firmly adsorbed onto the steel surface.⁵ The adsorbed inhibitors would thereby protect the steel from the contact of the corrosive H⁺ ions. It is clear that the quaternary ammonium cation and the five or six membered aromatic rings, which are rich in unshared π -electrons, are the two major inhibitive groups in BQC and its indolizine derivatives.^{2,15}

By comparison of these indolizine derivatives and their precursor BQC, the condensed dimer derivative of the quaternary salt could provide much more active adsorption sites.^{48,49} As a result, after the protonation of the electron-rich tertiary N atom, the newly formed adsorption sites and delocalized π -electrons will fasten the inhibitor to the crude surface and thus prevent the corrosive ions from approaching the metal, leading to a significant increase in the inhibition.^{50–52} In addition, the unsaturated planar hydrophobic groups among the indolizine derivatives would also prohibit the corrosive H⁺ ions from approaching the metallic surface and become firmly adsorbed on the bare metalic material to form a protective film.^{45,53–55} These are possibly the main reasons why the condensed indolizine derivatives would behave as such good corrosion inhibitors compared to the simple quinolinium salt and PA.

4. Conclusions

Novel indolizine derivatives of benzyl quinoline chloride were characterised and investigated for their potential use as highefficiency low-toxicity corrosion inhibitors in strong acid media. Based on the results in this study, the following conclusions can be drawn: 1. The indolizine derivatives Di-BQC, QM-DiBQC, and PyM-DiBQC, with highly effective corrosion inhibition efficiencies and eco-friendly properties, were synthesised facilely from the conventional corrosion inhibitor benzyl quinoline chloride (BQC). The formation mechanism of the derivatives was proposed reasonably as the 1,3-dipolar cycloaddition and the three indolizine derivatives are prepared in relatively high yields.

2. The excellent anti-corrosion performance of the indolizine derivatives for N80 steel was confirmed and evaluated in concentrated hydrochloric acid. The results obtained from gravimetric tests, electrochemical methods, surface analysis and theoretical calculations were in good agreement and confirmed the exciting inhibition of the newly synthesized indolizine derivatives. The inhibition of the indolizine derivatives is even better than that of propargyl alcohol.

3. The biological toxicity assessment showed a considerable eco-friendly advantage of the indolizine derivatives. The use of inhibitive indolizine derivatives as acidizing inhibitors may offer a new strategy for effective corrosion protection in strong acid media.

Conflicts of interest

The authors declare no competing financial interest.

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References

- 1 Y. F. Wang, Z. Yang, F. T. Zhan, Z. F. LYu, C. Y. Han, X. N. Wang, W. H. Chen, M. C. Ding, R. Z. Wang and Y. N. Jiang, Indolizine quaternary ammonium salt inhibitors part II: a reinvestigation of an old-fashioned strong acid corrosion inhibitor phenacyl quinolinium bromide and its indolizine derivative, *New J. Chem.*, 2018, **42**, 12977–12989.
- 2 M. Finšgar and J. Jackson, Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review, *Corros. Sci.*, 2014, **86**, 17–41.
- 3 Ali A. Al-Taq, A. Ali Shaikh and A. A. Alrustum, Performance Variation of Quaternary Amine Corrosion Inhibitors as a Function of Hydrocarbon Chain Length with Respect to

Temperature, SPE 190900. Society of Petroleum Engineers International Oilfield Corrosion Conference and Exhibition, Aberdeen, UK, June 18-19, 2018.

- 4 J. J. Wylde, N. Turner, M. Austill, C. Okocha and N. Obeyesekere, Development, Testing and Field Application of a Novel Combination Foamer-Iron Sulfide Scale Inhibitor-Corrosion Inhibitor in East Texa, SPE 184584. Society of Petroleum Engineers International Conference on Oilfield Chemistry, Montgomery, USA, April 3-5, 2017.
- 5 E. Barmatov, T. Hughes and M. Nagl, Efficiency of filmforming corrosion inhibitors in strong hydrochloric acid under laminar and turbulent flow conditions, *Corros. Sci.*, 2015, **92**, 85–94.
- 6 S. Kumar, D. Sharma, P. Yadav and M. Yadav, Experimental and quantum chemical studies on corrosion inhibition effect of synthesized organic compounds on N80 steel in hydrochloric acid, *Ind. Eng. Chem. Res.*, 2013, **52**, 14019–14029.
- 7 M. I. Al-Katheeri and H. A. Nasr-El-Din, Application of CE and CE-MS to Assay Corrosion Inhibitors Used in Well Stimulation Treatments, SPE 95112. Society of Petroleum Engineers International Symposium on Oilfield Corrosion, Aberdeen, UK, May 13-14, 2005.
- 8 C. Sitz, W. Frenier and C. Vallejo, Acid Corrosion Inhibitors with Improved Environmental Profiles, SPE 155966. Society of Petroleum Engineers International Conference and Exhibition on Oilfield Corrosion, Aberdeen, UK, May 28-29, 2012.
- 9 J. J. Wylde, C. Okocha, M. Bluth, A. Savin and B. Adamson, Iron Sulfide Inhibition: Field Application of an Innovative Polymeric Chemical, SPE 173730. Society of Petroleum Engineers International Symposium on Oilfield Chemistry, The Woodlands, USA, April 13-15, 2015.
- M. L. Walker, *Metal corrosion inhibiting compositions*, European Patent 0593230 A1, April 20, 1994.
- 11 M. M. Brezinski, *Corrosion inhibited organic acid compositions and methods*, US Patent 5976416 A, United State, November 2, 1999.
- 12 Y. C. Long, *Quaternary quinolinium compounds*, European Patent 0328319 B1, September 28, 1994.
- 13 M. A. Hegazy, M. Abdallah, M. K. Awad and M. Rezk, Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution. Part I: Experimental results, *Corros. Sci.*, 2014, **81**, 54–64.
- 14 A. Popova, M. Christov, A. Vasilev and A. Zwetanova, Mono-and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part I: Gravimetric and voltammetric results, *Corros. Sci.*, 2011, 53, 679–686.
- 15 Z. Yang, F. T. Zhan, Y. Pan, Z. F. LYu, C. Y. Han, Y. P. Hu, P. P. Ding, T. G. Gao, X. Y. Zhou and Y. N. Jiang, Structure of a novel Benzyl Quinolinium Chloride derivative and its effective corrosion inhibition in 15 wt% hydrochloric acid, *Corros. Sci.*, 2015, **99**, 281–294.
- 16 X. Y. Zhang, Y. X. Zheng, X. P. Wang, Y. F. Yan and W. Wu, Corrosion inhibition of N80 steel using novel diquaternary ammonium salts in 15% hydrochloric acid, *Ind. Eng. Chem. Res.*, 2014, 53, 14199–14207.

- 17 E. Barmatov, T. Hughes and M. Nagl, Performance of organic corrosion inhibitors on carbon steels and high alloys in 4M hydrochloric acid, NACE-2015-5893. National Association of Corrosion Engineers (NACE) CORROSION Conference & Expo, Dallas, USA, March 15-19, 2015.
- 18 Y. Liu, H. Y. Hu, J. Zhou, W. Wang, Y. He and C. Wang, Application of primary halogenated hydrocarbons for the synthesis of 3-aryl and 3-alkyl indolizines, *Org. Biomol. Chem.*, 2017, **15**, 5016–5025.
- 19 J. F. Xu, H. Y. Hu, Y. Liu, X. Wang, Y. H. Kan and C. Wang, Four-component reaction for the synthesis of indolizines by copper-catalyzed aerobic oxidative dehydrogenative aromatization, *Eur. J. Org. Chem.*, 2017, 257–261.
- 20 J. Jacobs, E. V. Hende, S. Claessens and N. D. Kimpe, Pyridinium ylids in heterocyclic synthesis, *Curr. Org. Chem.*, 2015, **15**, 1340–1362.
- 21 I. Obot, New benzimidazole derivatives as corrosion inhibitors for carbon steel in HCl solution, NACE-2015-5941. National Association of Corrosion Engineers (NACE) CORROSION Conference & Expo, Dallas, USA, March 15-19, 2015.
- 22 T. L. Hughes, J. Duboue, E. Barmatov, J. Geddes and L. Li, Contact & Optical Profilometry for Quantitative Characterization of Pitting Corrosion, NACE-2014-4249. National Association of Corrosion Engineers (NACE) CORROSION Conference & Expo, San Antonio, USA, March 9-13, 2014.
- 23 H. H. Huang, Q. Yao, B. L. Liu, N. Shan and H. L. Chen, Synthesis and characterization of scale and corrosion inhibitors with hyper-branched structure and the mechanism, *New J. Chem.*, 2017, **41**, 12205–12217.
- 24 M. Das, A. Biswas, B. K. Kundu, S. M. Mobin, G. Udayabhanu and S. Mukhopadhyay, Targeted synthesis of cadmium(II) Schiff base complexes towards corrosion inhibition on mild steel, *RSC Adv.*, 2017, 7, 48569–48585.
- 25 M. A. Hegazy, A. Y. El-Etre, M. El-Shafaie and K. M. Berry, Novel cationic surfactants for corrosion inhibition of carbon steel pipelines in oil and gas wells applications, *J. Mol. Liq.*, 2016, **214**, 347–356.
- 26 X. H. Li, X. G. Xie, S. D. Deng and G. B. Du, Inhibition effect of two mercaptopyrimidine derivatives on cold rolled steel in HCl solution, *Corros. Sci.*, 2015, **92**, 136–147.
- 27 G. F. Whale, Potential Applications of the Microtox Toxicity Test Within the Offshore Oil and Gas Industry, SPE 27176. Society of Petroleum Engineers Second International Conference on Heanh, Safety & Environment in Oil & Gas Exploration, & Production, Jakarta, Indonesia, January, 25-27, 1994.
- 28 R. G. Bland, C. Y. Chang and G. W. Bettge, Toxicity of Drilling Fluids Using Photobacteria and Mysid Shrimp Bioassays, SPE 16689. Society of Petroleum Engineers 62nd Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Dallas, USA, September, 27–30, 1987.
- 29 S. J. Hoskin and A. W. Strohl, On-Site Monitoring of Drilling Fluids Toxicity, SPE 26005. SPE/EPA Exploration & Production Environmental Conference, San Antonio, Texas, USA, March, 7–10, 1993.

- 30 D. S. Allgäuer, P. Mayer and H. Mayr, Nucleophilicity parameters of pyridinium ylides and their use in mechanistic analyses, *J. Am. Chem. Soc.*, 2013, **135**, 15216–15223.
- 31 K. W. Ratts, R. K. Howe and W. G. Phillips, Formation of pyridinium ylides and condensation with aldehydes, *J. Am. Chem. Soc.*, 1969, **91**, 6115–6121.
- 32 L. D. Zhang, F. Liang, L. Z. Sun, Y. F. Hu and H. W. Hu, A novel and practical synthesis of 3-unsubstituted indolizines, *Synthesis*, 2000, 1733–1737.
- 33 H. Quast and A. Gelléri, Heterocyclische Ylide, V. Cycloaddition von N-Chinoliniummethylid an N-methylchinoliniumkationen, *Liebigs Ann. Chem.*, 1975, 5, 939–945.
- 34 H. Y. Hu, G. D. Li, N. Gu and M. Ji, Synthesis of 3-Unsubstituted Indolizines from Electron Deficient Alkenes under Transition Metal Free Conditions, *Chin. J. Org. Chem.*, 2016, **36**, 330–335, in Chinese.
- 35 E. Barmatov, J. Geddes, T. Hughes and M. Nagl, Research on corrosion inhibitors for acid stimulation, NACE-2012-1573. National Association of Corrosion Engineers (NACE) COR-ROSION Conference & Expo, Salt Lake City, USA, March 11-15, 2012.
- 36 W. E. Billing and D. Morris, Effect of acid colume and inhibitor quantity on corrosion of steel oil field tubing in hydrochloric acid, *Corrosion*, 1960, **17**, 208–214.
- 37 C. F. Smith, F. E. Dollarhide and N. J. Byth, Acid corrosion inhibitors are we getting what we need?, *J. Pet. Technol.*, 1978, 30, 737–746.
- 38 J. T. Zhang, J. Zhao, N. S. Zhang, C. T. Qu and X. Zhang, Synergized action of CuCl on recycled cigarette butts as corrosion inhibitor for N80 steel at 90 °C in 15% HCl, *Ind. Eng. Chem. Res.*, 2011, **50**, 7264–7272.
- 39 M. C. Sun, W. Z. Wang, Y. E. Tao and Z. M. Chen, Oil well acidification corrosion inhibitor and its preparation and application, CN Patent 103589413 A, November 2, 2016.
- 40 Y. B. Lu, S. Q. Zhang and F. L. Bai, *A method of preparing new* efficient acidification corrosion inhibitor and its application, CN Patent 103468238 A, December 12, 2013.
- 41 M. M. Brezinski, *Metal corrosion inhibitor with oligomerized aromatic amines for use in aqueous acid solutions*, US Patent 5792420 A, August 11, 1998.
- 42 O. Yepez, N. Obeyesekere and J. J. Wylde, Can critical pitting temperature be used on carbon steel? and finding the localized corrosion behavior in the impedance spectra of the CO₂ corrosion process, NACE-2018-11389. National Association of Corrosion Engineers (NACE) CORROSION Conference & Expo, Phoenix, USA, April 15-19, 2018.
- 43 X. L. Zhang, Z. H. Jiang, Z. P. Yao, Y. Song and Z. D. Wu, Effects of scan rate on the potentiodynamic polarization curve obtained to determine the Tafel slopes and corrosion current density, *Corros. Sci.*, 2009, **51**, 581–587.

- 44 X. Zhao, H. Yu, C. Chen and Q. Chen, Evaluation and mechanism of corrosion inhibition performance of new corrosion inhibitor, NACE-2018-11029. National Association of Corrosion Engineers (NACE) CORROSION Conference & Expo, Phoenix, USA, April 15–19, 2018.
- 45 C. B. Verma, M. A. Quraishi and A. Singh, 2-Aminobenzene-1,3-dicarbonitriles as green corrosion inhibitor for mild steel in 1 M HCl: Electrochemical, thermodynamic, surface and quantum chemical investigation, *J. Taiwan Inst. Chem. Eng.*, 2015, **49**, 229–239.
- 46 H. M. Abd El-Lateef, M. A. Abo-Riya and A. H. Tantawy, Empirical and quantum chemical studies on the corrosion inhibitionperformance of some novel synthesized cationic gemini surfactantson carbon steel pipelines in acid pickling processes, *Corros. Sci.*, 2016, **108**, 94–110.
- 47 S. D. Deng, X. H. Li and X. G. Xie, Hydroxymethyl urea and 1,3-bis(hydroxymethyl) urea as corrosion inhibitors for steel in HCl solution, *Corros. Sci.*, 2014, **80**, 276–289.
- 48 M. Goyal, S. Kumar, I. Bahadur, C. Verma and E. E. Ebenso, Organic corrosion inhibitors for industrial cleaning of ferrous and nonferrous metals in acidic solutions: A review, *J. Mol. Liq.*, 2018, 256, 565–573.
- 49 A. Kumar, M. Trivedi, Bhaskaran, R. K. Sharma and G. Singh, Synthetic, spectral and structural studies of a Schiff base and its anticorrosive activity on mild steel in H₂SO₄, *New J. Chem.*, 2017, **41**, 8459–8468.
- 50 I. Ahamad, R. Prasad and M. A. Quraishi, Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steel in acidic media, *Corros. Sci.*, 2010, **52**, 1427–1481.
- 51 G. Sığırcık, D. Yildirim and T. Tüken, Synthesis and inhibitory effect of *N*,*N'*-bis(1-phenylethanol)ethylenediamine against steel corrosion in HCl Media, *Corros. Sci.*, 2017, **120**, 184–193.
- 52 J. M. Roque, T. Pandiyan, J. Cruz and E. García-Ochoa, DFT and electrochemical studies of tris(benzimidazole-2-ylmethyl)amine as an efficient corrosion inhibitor for carbon steel surface, *Corros. Sci.*, 2008, **50**, 614–624.
- 53 Y. G. Avdeev, Y. I. Kuznetsov and A. K. Buryak, Inhibition of steel corrosion by unsaturated aldehydes in solutions of mineral acids, *Corros. Sci.*, 2013, 69, 50–60.
- 54 R. Baskar, M. Gopiraman, D. Kesavan, I. S. Kim and K. Subramanian, Synthesis, Characterization, and Electrochemical Studies of Novel Biphenyl Based Compounds, *Ind. Eng. Chem. Res.*, 2012, **51**, 3966–3974.
- 55 J. Haque, V. Srivastava, C. Verma, H. Lgaz, R. Salghi and M. A. Quraishi, *N*-Methyl-*N*,*N*,*N*-trioctylammonium chloride as a novel and green corrosion inhibitor for mild steel in an acid chloride medium: electrochemical, DFT and MD studies, *New J. Chem.*, 2017, **41**, 13647–13662.